

coatings

Special Issue Reprint

Effects of Laser Treatment on Surface Characterization and Mechanical Properties of Alloys

Edited by
Avik Samanta

mdpi.com/journal/coatings



Effects of Laser Treatment on Surface Characterization and Mechanical Properties of Alloys

Effects of Laser Treatment on Surface Characterization and Mechanical Properties of Alloys

Guest Editor

Avik Samanta



Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

Guest Editor

Avik Samanta
Department of Mechanical
Engineering
University of South Florida
Tampa, FL
USA

Editorial Office

MDPI AG
Grosspeteranlage 5
4052 Basel, Switzerland

This is a reprint of the Special Issue, published open access by the journal *Coatings* (ISSN 2079-6412), freely accessible at: https://www.mdpi.com/journal/coatings/special-issues/laser_mechanical_alloys.

For citation purposes, cite each article independently as indicated on the article page online and as indicated below:

Lastname, A.A.; Lastname, B.B. Article Title. <i>Journal Name</i> Year , Volume Number, Page Range.
--

ISBN 978-3-7258-4303-9 (Hbk)

ISBN 978-3-7258-4304-6 (PDF)

<https://doi.org/10.3390/books978-3-7258-4304-6>

© 2025 by the authors. Articles in this book are Open Access and distributed under the Creative Commons Attribution (CC BY) license. The book as a whole is distributed by MDPI under the terms and conditions of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

Contents

About the Editor	vii
Preface	ix
Avik Samanta	
Special Issue: "Effects of Laser Treatment on Surface Characterization and Mechanical Properties of Alloys"	
Reprinted from: <i>Coatings</i> 2025 , <i>15</i> , 544, https://doi.org/10.3390/coatings15050544	1
Xinlin Wang, Jinkun Jiang, Chengui Xia and Yang Yu	
Macroscopic and Microstructural Features of Metal Thin-Wall Fabricated by Laser Material Deposition: A Review	
Reprinted from: <i>Coatings</i> 2022 , <i>12</i> , 1104, https://doi.org/10.3390/coatings12081104	4
Haoran Zhang, Yaowei Yong, Fuwei Wang, Yuan Liang, Lin Liu, Hong Liu and Yang Gao	
Progress on the Properties of Ceramic Phase-Reinforced High-Entropy Alloy Composite Coatings Produced via Laser Cladding	
Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 127, https://doi.org/10.3390/coatings14010127	27
Lipei Liu, Yinghua Lin, Longsheng Peng, Xin Kang and Xinlin Wang	
Progress in Microstructure Design and Control of High-Hardness Fe-Based Alloy Coatings via Laser Cladding	
Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 1351, https://doi.org/10.3390/coatings14111351	47
Zhaomei Xu, Zhengye Zhang, Qi Sun, Jiale Xu, Zhao Meng, Yizhi Liu and Xiankai Meng	
Effects of Nanosecond-Pulsed Laser Milling on the Surface Properties of Al ₂ O ₃ Ceramics	
Reprinted from: <i>Coatings</i> 2022 , <i>12</i> , 1687, https://doi.org/10.3390/coatings12111687	71
Yujie Fan, Kang Zhao, Mengjie Hao, Jing Xia, Xiaoyan Guan and Fanghua Liu	
An Analysis of the Morphology Evolution of YG8 Cemented Carbide by Laser Ablation in the Liquid Phase	
Reprinted from: <i>Coatings</i> 2023 , <i>13</i> , 2061, https://doi.org/10.3390/coatings13122061	81
Changfeng Fan, Xue Wang, Xiaoli Yin, Wei Huang, Yujie Da, Hao Jiang, et al.	
Adhesion Strength and Anti-Corrosion Performance of Ceramic Coating on Laser-Textured Aluminum Alloy	
Reprinted from: <i>Coatings</i> 2023 , <i>13</i> , 2098, https://doi.org/10.3390/coatings13122098	92
Maaz Akhtar, Muhammad Muzamil, Muhammad Samiuddin, Naser Alsaleh, Rashid Khan, Mahad Ali Khan, et al.	
Post-Wear Surface Morphology Assessment of Selective Laser Melting (SLM) AlSi10Mg Specimens after Heat Exposure to Different Gas Flames	
Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 252, https://doi.org/10.3390/coatings14030252	104
Peng Luo, Wanxi Feng, Gang Zu, Linyin Luo and Jun Xiao	
Microstructure and Impact Toughness of Laser-Arc Hybrid Welded Joint of Medium-Thick TC4 Titanium Alloy	
Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 395, https://doi.org/10.3390/coatings14040395	125
Bin Zhang, Hua Yan, Zhisheng Xia, Peilei Zhang, Haichuan Shi and Qinghua Lu	
Influence of Scanning Strategy and Post-Treatment on Cracks and Mechanical Properties of Selective-Laser-Melted K438 Superalloy	
Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 414, https://doi.org/10.3390/coatings14040414	142

Xinlin Wang, Jing Zhu, Yongchang Tian, Jinkun Jiang and Tianmin Guan Macroscopic Characteristic and Properties of Inconel 625 Cladding Layers on a Cylinder Liner Based on Laser Cladding Assisted by a Steady-State Magnetic Field Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 438, https://doi.org/10.3390/coatings14040438	164
Qiming Sun and Dayu Zheng Experimental Analysis and Wear Prediction Model Based on Friction Heat for Dry Sliding Contact Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 742, https://doi.org/10.3390/coatings14060742	185
Yanbo Song, Ying Liang, Hongbing Liu, Luchan Lin, Yanfeng Gao, Hua Zhang and Jin Yang Influence of Scanning Paths on the Weld Pool Behavior, Microstructure, and Mechanical Property of AA2060 Al-Li Alloy Joints by Laser Beam Oscillation Welding Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 1065, https://doi.org/10.3390/coatings14081065	201
Chang Li, Jiabo Liu, Shuchao Li, Fanhong Kong, Xuan Wang, Han Sun and Yichang Sun Evolutionary Mechanism of Solidification Behavior in the Melt Pool During Disk Laser Cladding with 316L Alloy Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 1337, https://doi.org/10.3390/coatings14101337	219
Xing Han, Chang Li, Hao Zhan, Shuchao Li, Jiabo Liu, Fanhong Kong and Xuan Wang Simulation of Dendrite Remelting via the Phase-Field Method Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 1364, https://doi.org/10.3390/coatings14111364	240
Xing Han, Hao Zhan, Chang Li, Xuan Wang, Jiabo Liu, Shuchao Li, et al. A Simulation Study on the Effect of Supersonic Ultrasonic Acoustic Streaming on Solidification Dendrite Growth Behavior During Laser Cladding Based on Boundary Coupling Reprinted from: <i>Coatings</i> 2024 , <i>14</i> , 1381, https://doi.org/10.3390/coatings14111381	251

About the Editor

Avik Samanta

Avik Samanta is an Assistant Professor in the Department of Mechanical Engineering at the University of South Florida (USF), Tampa, Florida. His research interests encompass advanced manufacturing, laser-based material processing, surface engineering, wettability modification, and stimuli-responsive materials. He is spearheading the Laser-Aided Materials, Manufacturing, and Processing (LAM2P) research group in advancing laser engineering techniques for innovative functional materials and pioneering new manufacturing processes employing advanced manufacturing technologies. He is the author of many papers in leading journals, including ACS Applied Materials and Interfaces, Applied Surface Science, Materials and Design, and the Journal of Manufacturing Processes. He has served as a Guest Editor for the journals “Coatings”, “Lubricants”, and “JOM”. Previously, he was a Postdoctoral Researcher at the Pacific Northwest National Laboratory (PNNL), USA. He received his doctoral degree in Mechanical Engineering from the University of Iowa, Iowa City, Iowa. He was also associated with Taiwan Semiconductor Manufacturing Company (TSMC) in Hsinchu, Taiwan, as a product engineer before his doctoral study.

Preface

Across all the efforts in this Special Issue, a recurring theme is evident, namely that laser processing is not a stand-alone technique but rather a platform that integrates process physics, material science, computational modeling, and application-specific design. The advancements presented in this Special Issue affirm the capacity to precisely shape the structural, mechanical, and chemical profile of alloy surfaces, whether for durability, biocompatibility, or energy-efficient performance. As the editor of this Special Issue, I extend sincere thanks to the authors for their excellent contributions and to the reviewers for their careful and constructive evaluations. This wide range of studies shows how laser-based surface treatment is gaining global interest and becoming more critical in developing the materials of the future.

Avik Samanta

Guest Editor

Editorial

Special Issue: “Effects of Laser Treatment on Surface Characterization and Mechanical Properties of Alloys”

Avik Samanta

Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA;
aviksamanta@usf.edu; Tel.: +1-(813)-974-5623

Laser-based material processing methods have emerged as an innovative approach in advanced manufacturing, enabling significant control over microstructural evolution and surface functionality in metallic systems. Modern industrial sectors, such as the aerospace, automotive, biomedical, energy, and marine sectors, require materials that possess superior bulk properties and exhibit engineered surface characteristics tailored to specific performance criteria, such as wear resistance, corrosion protection, thermal stability, or biocompatibility. This Special Issue brings together a diverse and comprehensive selection of recent advancements that reflect the potential of laser technologies across different classes of alloys, coating strategies, and hybrid processing techniques. A total of fifteen articles featured in this Special Issue collectively showcase the strategic deployment of laser in a variety of contexts: laser cladding, laser welding, laser surface texturing, laser milling, and hybrid treatments incorporating ultrasonic vibrations, magnetic fields, or micro-arc oxidation. A key unifying theme across these contributions is the emphasis on process–structure–property relationships, and how specific processing parameters (e.g., laser power, scan strategy, pulse duration, or beam oscillation) directly influence solidification dynamics, microstructural morphology, and, ultimately, mechanical or tribological behavior.

Laser cladding, in particular, remains a focal point of interest due to its capabilities in repairing high-value components and fabricating wear- and corrosion-resistant coatings. The research contributions demonstrate the microstructure modification and mechanical property enhancement of alloy systems, such as ceramic phase-reinforced high-entropy alloy [1], high-hardness Fe-based alloy coatings [2], and Inconel superalloys [3]. The introduction of hard ceramic phases during cladding has shown considerable promise in improving hardness, toughness, and service life under extreme conditions [1]. Incorporating alloying elements (B, Si, Mo, Nb, V, Mn, Cr) can introduce dislocation strengthening, grain refinement strengthening, and solid solution strengthening in Fe alloys, resulting in enhanced hardness [2]. The addition of ceramic and rare-earth oxide particles, and the in-situ synthesis of ceramic particles, can also enhance hardness and mitigate crack formation. Steady-state magnetic fields applied during laser cladding of Inconel 625 can stabilize the crystal structure and refine the grains [3]. The introduction of a low-intensity magnetic field significantly improves the uniformity, surface hardness, tribological performance, and corrosion resistance of the clad layer. Assistance from several other physical fields, such as ultrasonics and thermals, can control porosity and crack formation within the clad layer [2]. Complementing the experimental works, a simulation-driven study explores the solidification dynamics in 316L stainless steel during laser cladding [4]. The melt pool characteristics were simulated by numerical calculation, and the phase field model predicted dendrite formation. This work elucidates the formation of dendritic morphologies and highlights the dominant influence of convective flow within the melt

pool, pointing to the importance of precise control over processing parameters in achieving desirable microstructural outcomes. Numerical simulations revealed that ultrasonic acoustic streaming significantly influences dendritic structure formation during the laser cladding process [5]. This multi-scale simulation highlights how ultrasound-assisted flow fields influence dendrite tilt, solute redistribution, and solidification uniformity, leading to defect suppression and structural refinement.

Several studies examine the interplay between laser parameters, scanning strategies, and alloy compositions in shaping the mechanical response of treated surfaces using selective laser melting (SLM) [6,7] and laser material deposition (LMD) [8]. Different laser scanning strategies for SLM-printed K438 superalloys affect crack suppression and mechanical strength [6]. Experimental results demonstrate that strategic scanning paths and post-heat treatment protocols can markedly improve tensile strength and minimize residual stresses, factors vital for high-temperature aerospace applications. The wear performance and morphology of SLM-printed AlSi10Mg can be significantly influenced by exposure to different flames, such as carburizing, oxidizing, and neutral [7]. A broader perspective of macroscopic and microstructural behavior is explained for laser material deposition for thin-wall structures. It emphasizes how process parameters like z-increment and deposition height affect grain growth directionality, hardness profiles, and residual stress distribution, factors crucial to the stability of additively manufactured metallic structures [8]. A key highlight of the issue is the application of advanced simulation tools to gain mechanistic insights into microstructural evolution during laser–material interaction. A phase-field model is developed to simulate dendrite remelting under thermal loads, which provides fundamental insight into how temperature-induced remelting sequences govern solid–liquid interface dynamics [9]. This study highlights how lateral dendrites remelt ahead of primary arms, and how remelting evolves in multiple stages, particularly under inhomogeneous heating, an important factor in layered manufacturing and laser repair operations.

Laser hybrid processes also feature prominently in this issue. The impact of hybrid laser-arc welding on the microstructure and toughness of TC4 titanium alloy joints is discussed in the context of the integration of mechanical enhancements with structural integrity, noting improved impact resistance due to acicular martensite refinement and grain boundary modifications [10]. Their multi-layer, multi-pass welding approach highlights the trade-offs between porosity control, grain refinement, and crack resistance, key concerns for components exposed to cyclic mechanical and thermal loads. The pattern of laser scanning plays a crucial role in shaping the weld pool dynamics, refining the microstructure, and enhancing the mechanical behavior of AA2060 Al-Li alloy joints during oscillating laser beam welding [11].

Improving surface adhesion and corrosion resistance is also addressed through combined laser texturing and ceramic coating by micro-arc oxidation for aluminum alloy [12]. The hybrid laser surface treatment led to a 58% enhancement in adhesive joint strength and shifted the failure mode to cohesive fracture. Laser ablation, performed in a liquid-phase environment, was found to systematically modify the surface morphology of YG8 cemented carbide, with pit shape and taper evolving consistently with increasing ablation cycles [13]. This study shows that the number of ablation cycles governs the transition from convex to cratered morphologies, offering precise control over texture formation for tribo-functional coatings. Another promising direction shown in this issue is the use of laser-induced surface modification to improve tribological performance. The effect of nanosecond-pulsed laser milling on Al₂O₃ ceramics is explored, revealing a strong dependence of surface roughness and milling depth on laser power and scanning frequency [14]. These findings open avenues for tailoring ceramic surfaces for wear-critical applications. Lastly, an

improved Archard wear model is developed, incorporating frictional heating effects [15]. The model achieved improved wear prediction accuracy across multiple metallic systems, including stainless steel, aluminum alloys, and titanium. The model better captured wear dynamics under varying loads and sliding velocities, contributing to a better predictive tool for tribological analysis.

This Special Issue showcases a vibrant landscape of research at the intersection of laser-material interaction, alloy design, and mechanical performance. These studies collectively highlight how precise control of laser parameters, supported by robust modeling and experimental validation, can dramatically enhance the functionality of metallic systems across aerospace, automotive, biomedical, and energy sectors.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Zhang, H.; Yong, Y.; Wang, F.; Liang, Y.; Liu, L.; Liu, H.; Gao, Y. Progress on the Properties of Ceramic Phase-Reinforced High-Entropy Alloy Composite Coatings Produced via Laser Cladding. *Coatings* **2024**, *14*, 127. [CrossRef]
2. Liu, L.; Lin, Y.; Peng, L.; Kang, X.; Wang, X. Progress in Microstructure Design and Control of High-Hardness Fe-Based Alloy Coatings via Laser Cladding. *Coatings* **2024**, *14*, 1351. [CrossRef]
3. Wang, X.; Zhu, J.; Tian, Y.; Jiang, J.; Guan, T. Macroscopic Characteristic and Properties of Inconel 625 Cladding Layers on a Cylinder Liner Based on Laser Cladding Assisted by a Steady-State Magnetic Field. *Coatings* **2024**, *14*, 438. [CrossRef]
4. Li, C.; Liu, J.; Li, S.; Kong, F.; Wang, X.; Sun, H.; Sun, Y. Evolutionary Mechanism of Solidification Behavior in the Melt Pool During Disk Laser Cladding with 316L Alloy. *Coatings* **2024**, *14*, 1337. [CrossRef]
5. Han, X.; Zhan, H.; Li, C.; Wang, X.; Liu, J.; Li, S.; Sun, Q.; Kong, F. A Simulation Study on the Effect of Supersonic Ultrasonic Acoustic Streaming on Solidification Dendrite Growth Behavior During Laser Cladding Based on Boundary Coupling. *Coatings* **2024**, *14*, 1381. [CrossRef]
6. Zhang, B.; Yan, H.; Xia, Z.; Zhang, P.; Shi, H.; Lu, Q. Influence of Scanning Strategy and Post-Treatment on Cracks and Mechanical Properties of Selective-Laser-Melted K438 Superalloy. *Coatings* **2024**, *14*, 414. [CrossRef]
7. Akhtar, M.; Muzamil, M.; Samiuddin, M.; Alsaleh, N.; Khan, R.; Khan, M.A.; Djuansjah, J.; Siddiqui, A.K.; Majeed, A. Post-Wear Surface Morphology Assessment of Selective Laser Melting (SLM) AlSi10Mg Specimens after Heat Exposure to Different Gas Flames. *Coatings* **2024**, *14*, 252. [CrossRef]
8. Wang, X.; Jiang, J.; Xia, C.; Yu, Y. Macroscopic and Microstructural Features of Metal Thin-Wall Fabricated by Laser Material Deposition: A Review. *Coatings* **2022**, *12*, 1104. [CrossRef]
9. Han, X.; Li, C.; Zhan, H.; Li, S.; Liu, J.; Kong, F.; Wang, X. Simulation of Dendrite Remelting via the Phase-Field Method. *Coatings* **2024**, *14*, 1364. [CrossRef]
10. Luo, P.; Feng, W.; Zu, G.; Luo, L.; Xiao, J. Microstructure and Impact Toughness of Laser-Arc Hybrid Welded Joint of Medium-Thick TC4 Titanium Alloy. *Coatings* **2024**, *14*, 395. [CrossRef]
11. Song, Y.; Liang, Y.; Liu, H.; Lin, L.; Gao, Y.; Zhang, H.; Yang, J. Influence of Scanning Paths on the Weld Pool Behavior, Microstructure, and Mechanical Property of AA2060 Al-Li Alloy Joints by Laser Beam Oscillation Welding. *Coatings* **2024**, *14*, 1065. [CrossRef]
12. Fan, C.; Wang, X.; Yin, X.; Huang, W.; Da, Y.; Jiang, H.; Cao, J.; Gai, Y.; Zhang, W. Adhesion Strength and Anti-Corrosion Performance of Ceramic Coating on Laser-Textured Aluminum Alloy. *Coatings* **2023**, *13*, 2098. [CrossRef]
13. Fan, Y.; Zhao, K.; Hao, M.; Xia, J.; Guan, X.; Liu, F. An Analysis of the Morphology Evolution of YG8 Cemented Carbide by Laser Ablation in the Liquid Phase. *Coatings* **2023**, *13*, 2061. [CrossRef]
14. Xu, Z.; Zhang, Z.; Sun, Q.; Xu, J.; Meng, Z.; Liu, Y.; Meng, X. Effects of Nanosecond-Pulsed Laser Milling on the Surface Properties of Al₂O₃ Ceramics. *Coatings* **2022**, *12*, 1687. [CrossRef]
15. Sun, Q.; Zheng, D. Experimental Analysis and Wear Prediction Model Based on Friction Heat for Dry Sliding Contact. *Coatings* **2024**, *14*, 742. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Macroscopic and Microstructural Features of Metal Thin-Wall Fabricated by Laser Material Deposition: A Review

Xinlin Wang *, Jinkun Jiang, Chengui Xia and Yang Yu

School of Mechanical Engineering, Dalian Jiaotong University, Dalian 116028, China;
jiangjinkundybala@163.com (J.J.); xcg17866537247@163.com (C.X.); 18241113599@163.com (Y.Y.)

* Correspondence: wxl_me@djtu.edu.cn

Abstract: Owing to the versatility without expanding the machine's size, thin-wall has been widely used in high-value parts. The investigation of laser additive manufacturing (LAM), which has advantages such as high powder density, easy controllability, and excellent stability, on the fabrication of thin-wall has drawn much attention. In this paper, the research status of macroscopic and microstructural features of metal thin-wall fabricated by LAM has been reviewed. The deposition quality was mainly focused on the effect of process parameters and especially the matching of z-increment and single deposition height. Based on the grain size and growth of columnar, the characteristics of microstructures were analyzed. Considering the structural feature of thin-wall, the effect of grain size and phases on the hardness and distribution of hardness were discussed. The effect of grain size, phases and loading direction on the tensile properties were reviewed. The distribution and modification of thermal stress were presented.

Keywords: thin-wall; laser material deposition; deposition quality; microstructure; microhardness; tensile properties; thermal stress

1. Introduction

Thin-wall, which always possesses small thickness and complex structure, can allow machine to have more functions without expanding the machine's size and to assemble small machines [1,2]. So, it is widely used in high-value parts, such as aircraft engine cowling, space airborne equipment, key auto components and so forth [3,4]. The thin-wall parts can be made by the conventional processes, such as casting, welding, assembling and so on, in which the disadvantages such as long process cycle, cumbersome, low material utilization, and low bonding strength. Owing to the incremental layer-by-layer manufacturing by adding material, laser additive manufacturing (LAM), which has many advantages such as high powder density, easy controllability, and excellent stability, can cover the mentioned above disadvantages in fabrication of thin-wall by conventional processes and directly create the final mental thin-wall parts [5–10].

LAM mainly includes powder bed fusion (PBF) mode, such as selective laser melting/selective laser sintering [11–13], and direct laser deposition (DLD) mode, such as laser material deposition (LMD) [14–16]. In PBF process, the powder is preset in powder bed and fed by the scraper layer-by-layer. Due to the existing of powder bed, the fabricated part is surrounded and supported by the un-melted powder during the fabricating process. In addition, the used workbench and powder in PBF are smaller than that of in DLD process. Therefore, the PBF process is suitable for the fabrication of part with small size and complex structure [17,18]. However, in the LMD process, the powder is delivered by inert gas such as argon gas into the molten pool that contributes to the improvement of controllability of fabrication process [19]. Due to the bigger power particle size and diameters of laser spot, the parts created by LMD usually possesses larger thickness and surface roughness that can be improved by the post-treatment process such as milling [20–22]. Thus, the LMD

process is more suitable for the fabrication of parts with bigger size. In particular, the LMD has incomparable advantages in fabrication of functionally graded material, repairing of high value-add component with big size and cladding the enhancement coating on the substrate [3,23,24]. Therefore, the LMD process has a promising application prospect in the fabrication and repairing of thin-wall parts in the areas of aerospace, aviation, die and mold, etc. [25]. In LMD process, laser beam acts as the heating source to create a molten pool on the substrate and the powder, which is delivered by the flowing inert gas, is injected into the molten pool simultaneously. The delivered powder would be captured by the molten pool and melt. After the laser beam goes away, the molten pool solidifies and increases the volume. Based on the scanning path designed by the computer, the laser beam and powder feed nozzle move above the substrate and create the first expected clad layer. Then, the laser cladding head moves up z-increment to the new position for the preparing of deposition of second layer. Based on the first layer, the new layer can be deposited through creating metallurgical bonding with the first layer along the scanning path. Similar process, in which the latter layers are sequentially created on the former layer, repeats again and again that makes the three-dimensional (3D) part to be built layer-by-layer [26–30].

The LMD process of thin-wall, in which single-track and multi-layers are deposited, is unfavorable for the heat conduction that results in the heat accumulation [31]. The thickness of thin-wall is closely related to the width of the single deposited layer, which is significantly affected to the diameter of laser spot, laser power, powder feed rate, scanning speed and so on. Owing to the small thickness and heat accumulation, the thin-wall created by LMD is easy to deform if the fabrication process cannot be precisely controlled. Therefore, based on the different structure feature of targeted thin-wall, the optimization of LMD process of thin-wall should be conducted to modify the heat history during the fabrication process and then obtain a high-quality thin-wall with superior mechanical properties. The capability and challenges of LMD on fabrication and repairing of thin-wall parts has drawn researchers' much attention. Therefore, based on the simulation of temperature field, law of energy conservation, law of mass conservation, and process experiments, some investigation about the effect of fabrication process on the surface quality, microstructures, microhardness, tensile properties, and residual stress have been conducted. The deposited material refers to Fe-based alloy, Ni-based alloy, titanium and so on. Table 1 provides a summary of some common materials that have been investigated for the fabrication and repairing of thin-wall by LMD. In addition, the used parameters including laser power, powder feed rate, scanning speed, and z-increment, which are the most influential factors for the deposition of LMD, also are presented in Table 1. This article provides an overview of the macroscopic and microstructural features of metal thin-wall deposited by LMD.

Table 1. Summary of materials used in metal thin-wall by laser material deposition.

Substrate	Powder (Particle Size)	Z-Increment (mm)	Laser Power (W)	Scanning Speed (mm/s)	Powder Feed Rate (g/s)	Ref.
steel C1045, 20#45# steel, 304, 304L, 316L, 42CrMo4 steel	316L, 410, 304L, 313	0.05–0.3	250, 300, 350, 800, 1000, 1600	1~14, 5.5, 6, 8.3, 13	0.13, 0.194, 0.04, 0.078	[2,26,32–45]
	Fe-16Al (wt%)	0.25	-	9	0.2	[46]
	24# steel, Pure iron	-	220, 250, 300	2.5~3.5	0.012, 0.58, 0.77	[1,47]
	M4, Fe 105 steel	-	260, 440, 500	5.5, 8.3	0.1	[48,49]
45# steel, 316L, Q235	Ni60, Ni60A	-	800, 2500	3.3, 5	0.067, 0.083, 0.117	[50,51]
	IN 718, IN625	0.3	175~275, 650, 1000	6~10	0.033, 0.198, 0.333	[52–54]

Table 1. Cont.

Substrate	Powder (Particle Size)		Z-Increment (mm)	Laser Power (W)	Scanning Speed (mm/s)	Powder Feed Rate (g/s)	Ref.
γ -TiAl, Ti-6Al-4V	Ti-based (45~150)	γ -TiAl	-	200, 250, 300	8, 10, 12	0.048~0.733	[55]
		Ti-6Al-4V	-	800, 1000	5	0.033~0.135	[56,57]
316L	-	CrCoNi	0.4	800	9.5	0.228	[58]
EN AW-5083	-	Al-Mg-Mn	-	500, 550, 600	9.167	-	[59]

2. Surface Quality and Dimension Precision

Owing to the existing of multitudinous parameters during the LMD process, the successfully optimization of parameters is different to accomplish. The interactional relationships between the input parameters, such as laser power, scanning speed, powder feed rate, defocusing, and z-increment, as well as the deposition results, such as size, precision, and shape of deposited parts still lack for a comprehensive experimental and theoretical outstanding [60,61]. In particular, the laser power, scanning speed, and powder feed rate were regarded as the three-main parameters to affecting the LMD process. Lu indicated that increasing the laser power without over-burning could reduce the adhesion of powder, surface waviness, surface roughness, and then improve the surface quality. It can be explained by the increase of temperature of the molten pool, which was beneficial to increase the flow rate of the molten pool and melt the powder. Moreover, the increased of laser power contributed to the remelting of the former layer and reduced the surface waviness. In addition, the increase of scanning speed and decrease of powder feed rate contributed to the declination of surface waviness and surface roughness because the small deposition thickness and contact angle could be obtained [45].

In the deposition process of thin-wall, which possesses the features of single-track and multi-layers, the effect of geometrical feature of the former layer on the deposition of latter layer is easier to show up than the deposition of multi-track. The unsuitable parameters would result in corrugated surface and even shutoff of thin-wall deposition process [62]. Finally, the fact, that whether the parameter is suitable or not, can be reflected by the matching relation between the single deposition height and z-increment of laser cladding head. In the ideal case, the z-increment should be equal to the single deposition height to assure the constant defocusing and single deposition height. However, owing the existing the fluctuation and instantaneous defects, the matching relation cannot be ideally assured that has been proved extremely detrimental to the surface quality and precision of thin-wall parts [63,64]. The effect of matching of z-increment and single deposition height on the fabrication of thin-wall is analyzed in the follow section.

2.1. Matching of Z-Increment and Single Deposition Height

In addition to the laser power, powder feed rate, and scanning speed, the z-increment is also an important parameter for the deposition of thin-wall parts, and it has significant influence on the surface roughness, dimension precision, and surface oxidation that was proved by researchers [32,65]. With the different z-increment, the thin-wall presents various contours during another parameter is same. The contours of thin-wall are mainly related to the matching relationship between the z-increment and single deposition height.

As shown in Figure 1a, both the powder convergence point and laser focus point overlap. During the focus points exactly are seated on the deposition surface, the powder utilization, the power density, and the deposition efficiency are biggest. During the focus points are below or above the deposition surface, the decrease of powder utilization and power density result in the reduction of deposition height. As shown in Figure 1b, during the z-increment is smaller than the single deposition height, at the beginning of deposition process, the thin-wall is deposited rapidly with a single deposition height, which is bigger than the z-increment, because the sufficient powder can be captured by the molten pool.

However, the deposited surface, in which the molten pool exists, would shift to the position which is above the focus points of laser and powder. The minus defocusing appeared in the subsequent deposition process. Owing to the passive defocusing, powder captured by the molten pool decreases that leads to the reduction of the deposition height of latter layer. With the reduction of single deposition height, the minus defocusing, f_1 , decreases in the deposition process of latter layer that contributes to the increase of single deposition height. Similar process repeated during the deposition process. Thus, so-called self-regulation-effect presents. During the z -increment is smaller than the single deposition height, the self-regulation-effect can ensure the molten pool to capture sufficient powder and create a deposition layer. However, during the z -increment is extremely smaller than the single deposition height, the minus defocus is big that results in the significantly decreased powder utilization and depositing efficiency. As shown in Figure 1c, during the z -increment is bigger than the single deposition height, the positive defocusing, f_2 , presents that results in the decrease of captured powder by molten pool and then the deposition height. The decreased deposition height leads to the increase of positive defocusing that makes the further decrease of deposition height. Similar interactional effect repeats that would result in gradually increase of positive defocusing, insufficient powder captured by molten pool and failure in deposition of thin-wall finally. As reported in the research work by Bi et al., in which the 316L thin-wall parts were fabricated with 120 layers and different z -increment, the height of fabricated thin-wall with the z -increment of 0.05 mm was obvious lower than that by z -increment of 0.15 mm which was much closer to the single deposition height. However, the surface of deposited thin-wall still showed flat and smooth as shown in Figure 2a. During the z -increment was 0.25 mm, the surface of deposited thin-wall showed strong fluctuation and pool surface quality as shown in Figure 2b [32].

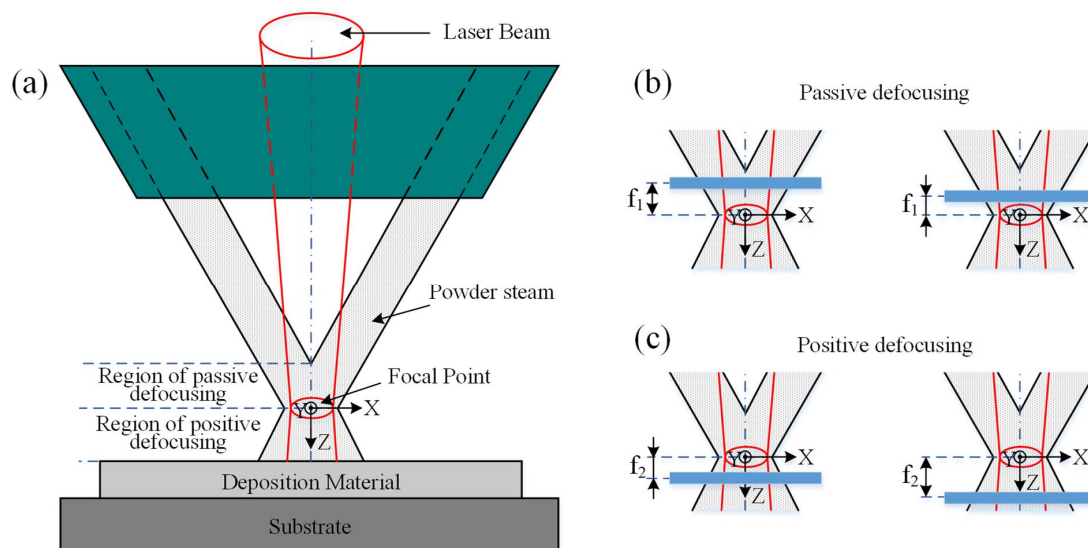


Figure 1. Schematic diagram of (a) relative position between the deposition surface and laser focus point, (b) passive defocusing, and (c) positive defocusing.

However, during the laser focus point and powder convergence point present noncoincidence, the condition would change. For example, Zhu et al. fabricated 316L thin-wall parts used LMD and investigated the relative position between the laser focus point, powder convergence point, and substrate. Table 2 shows the maximum values of 316L thin-walled parts' top surface unevenness measured with different laser and powder defocusing distances. The results shown that the maximum surface unevenness was 0.325 mm and 0.702 mm during the powder defocusing distance was -1 mm and laser focus distance was -3 mm, respectively. The fact indicated that a high surface quality was obtained during the powder converged below the substrate and laser focused above the substrate. In addition,

compared to the influence of laser focus position, the variation of distance between the powder convergence point and substrate played a leading role in the influence on the surface quality. Finally, with the powder and laser defocusing distance of -1 and $+3$ mm, respectively, a thin-walled blade sample with the maximum surface unevenness of 0.242 mm were deposited. The high quality surface of thin-walled sample indicated the compensated mechanism by the self-regulation effect [33].

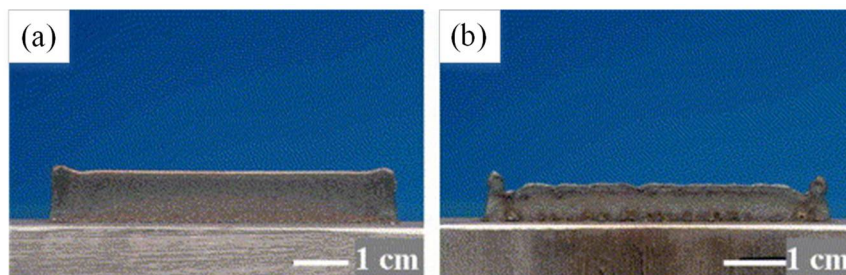


Figure 2. The 316L thin-wall fabricated by LMD with z-increment of (a) 0.15 mm and (b) 0.25 mm (Reprinted from ref. [32], copyright (2006), with permission from Elsevier).

Table 2. Maximum values of 316L thin-walled parts' top surface unevenness measured with different laser defocusing distances (D_l) and powder defocusing distances (D_p) [33].

D_p (mm)	D_l (mm)	Total Layer Numbers	Surface Unevenness (mm)
-1	$+$	90	0.325
0	(Above the substrate)		1.098
1			2.886
$+$	-3		2.403
(Above the substrate)	0		1.098
	3		0.702

2.2. Thin-Wall with Complex Structures

In addition to the rectangular thin-wall which was common in most studies, the thin-wall parts with more complex structures were also investigated. As shown in Figure 3a, Zhang optimized the process parameters of 316L deposition by LMD and fabricated the complex polygon, rotary blade, and acronymic emblem thin-wall [14]. Aiming at the circumferentially inclined thin-walled cylinders, Sun et al. obtained the relationship between inclination angle and circumferential offset by developing the model. They also pointed out that the 316L inclined thin-wall can be fabricated with high quality during the z-increment is 0.224 mm, the offset angle is 0.75° and the inclination angle is 25.95° [35]. Li proposed a method of fractal stratification and fabricated flat-top 316L thin-wall on a special-shaped substrate as shown in Figure 3b. Based on the segmented variable speed and segmented deposited height, the flat-top thin-wall parts with the size error of 8% were created. Based on the relationship between z-increment and deposition height as well as the self-regulation effect [66]. Wang et al. proposed three-dimensional deposition way, in which the z-increment was different at the different point in single deposition layer, and analyzed the effect of parallel and three-dimensional deposition way on the mechanical properties [26]. Carrol et al. deposited Ti-6Al-4V cruciform thin-wall to investigate the anisotropic tensile behavior [67]. Tian et al. fabricated 316L hollow thin-walled cylinder with high forming quality and shape accuracy by using the optimized z-increment of 0.224 mm [38]. In order to solving the problem of variable width forming, Zhang et al. proposed a variable width method and obtained the Inconel 718 thin-wall with variable width and same height through changing the overlapping rate and the scanning speed as shown in Figure 3d [52]. Li et al. investigated the scanning strategy for the fabrication of ring-shaped thin-wall and confirmed the laser changing-point as the better scanning strategy. As shown in Figure 3e, Wang fabricated the 316L thin-walled overhang structure

with the reciprocating deposition way in which the collapsed ends can be prevented owing to the compensation of height caused by the periodical change between the start and end side. Finally, they obtained the maximum angle of inclination (θ) was 32.9° based on the optimization of z-increment [68].

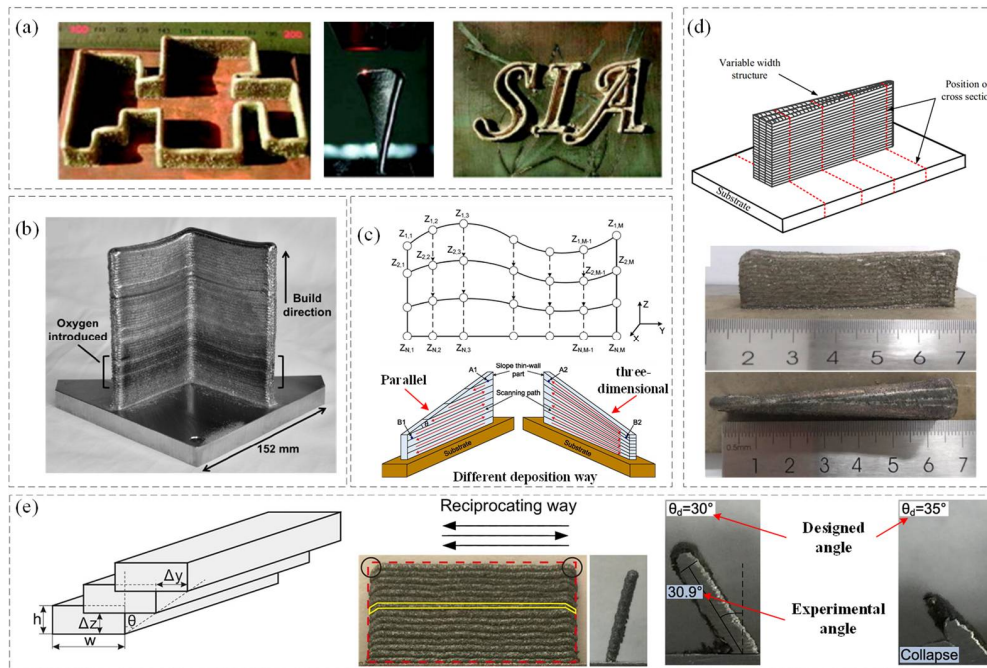


Figure 3. (a) Images of 316L thin-wall parts with complex structures (Reprinted from ref. [14], copyright (2013), with permission from Elsevier); (b) Image of deposited cruciform thin-wall (Reprinted from ref. [67], copyright (2015), with permission from Elsevier); (c) 316L slope thin-wall part fabricated using parallel and three-dimensional deposition way (Reprinted from ref. [26], copyright (2020), with permission from Elsevier); (d) Schematic and samples of typical variable width thin-walled structures [52]; (e) Schematic and 316L thin-walled overhang structures (Reprinted from ref. [68] copyright (2018), with permission from Elsevier).

3. Microstructures

3.1. Grain Size

As shown in Figure 4a, the microstructures of thin-wall created by LMD are affected by the solidification rate of molten pool, the ratio of cooling rate to thermal gradient (R), and the temperature gradient at the solid liquid interface (G). The solid-liquid interface shape is determined by the G/R and the grain size is affected by the cooling rate which is represent by $G \times R$ [8,9,69,70]. Based on the microstructures' characteristics, thin-wall can be divided into three regions which names the upper, middle, and bottom region. In the bottom region which is near the interface zone between the deposition layer and substrate, the amount of G/R is very high that contributes to the growth of solid-liquid interface at a low-speed flat interface and the occurrence of cellular and even the planar crystal [46,71]. With the continuous of LMD process, the decrease of G/R contributes to the occurrence of columnar dendritic crystals which present in the middle region of thin-wall. In addition, the orientation of heat transfer is from the upper to the bottom of the thin-wall that results in the columnar grains growth along the perpendicular direction to the substrate. With the progression of LMD process, which is accompanied with the heat accumulation, the decreased G/R results in the formation of equiaxed crystal in the upper region of thin-wall [72,73].

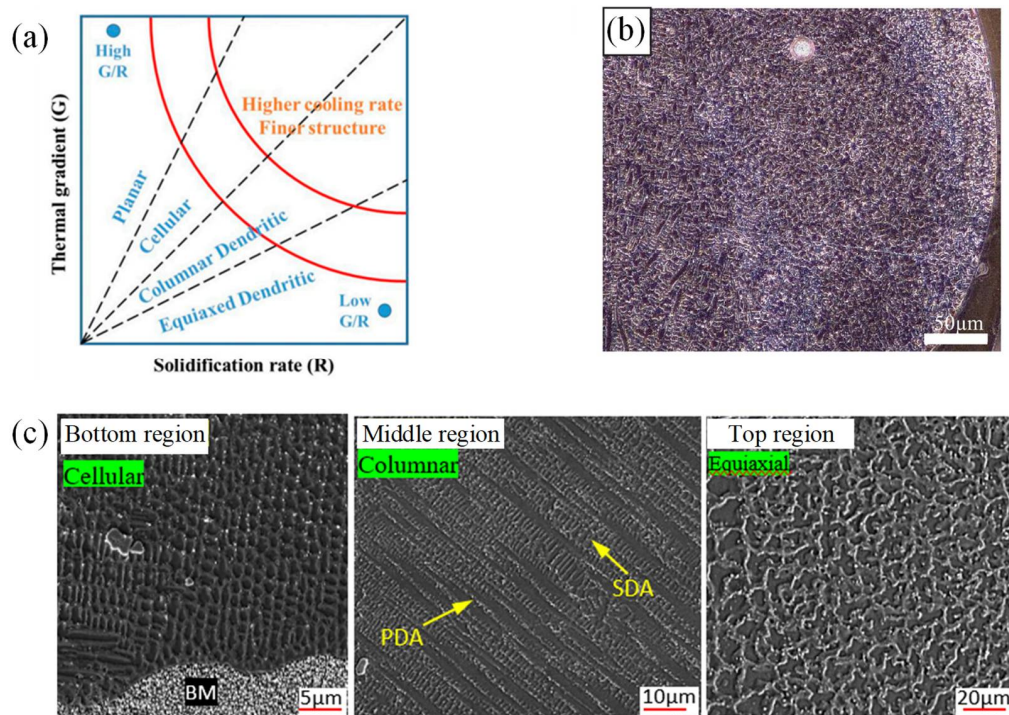


Figure 4. (a) Solidification map established by solidification parameters (Reprinted from ref. [72], copyright (2021), with permission from Elsevier); (b) Evolution of grain structure of IN625 thin-wall from columnar (core/interfacial), large equiaxed grains (transition), to small equiaxed grains (surface) (Reprinted from ref. [74], copyright (2020), with permission from Elsevier); (c) Evolution of grain structure of IN625 thin-wall from cellular (bottom region), columnar (middle region), to equiaxed grains (top region) (Reprinted from ref. [73], copyright (2020), with permission from Elsevier).

For example, Xue et al. pointed out that the sub-grain size of the bottom, middle, and upper region of the CrCoNi medium-entropy alloy thin-wall was gradually increased owing to the decreased temperature gradient and then the cooling rate [58]. Bi et al. fabricated 316L thin-wall with a 0.15 mm z-increment and 120 layers. The microstructure of deposited thin-wall presented a mixture of cellular and dendrite structures. The bottom region, which had bigger cooling rate and better cooling conditions, showed smaller grain size and the microstructure near the edge was coarser because of the higher temperature and lower cooling rate [32]. Yu et al. fabricated Fe 105 steel thin-wall on the 45# steel and observed the epitaxial growth of columnar crystal inverting the heat flow direction. With the height increased, the crystal gradually changed from a single thick columnar crystal to a small cross-dendrite and tiny equiaxed crystals in the middle of deposition layers. The microstructure of the top region presented the denser and smaller equiaxed [49]. Zhao et al. processed Al-4.55Mg-0.51Mn-0.65Sc-0.30Zr alloy thin-wall and observed the equiaxed 3~5 and 8~10 μm sized grains near the bottom as well as the columnar 15~20 μm sized grains in the middle of deposition [59]. As shown in Figure 4b, the images of microstructure of IN625 thin-wall provided by Kim et al. showed that the column grain near the bottom region, where possessed the high thermal gradient in heat transfer, transformed to large equiaxed grain with the grain size of 5 μm in the middle region and then small equiaxed grain with the grain size of 2 μm in the upper region of thin-wall, where most of the heat was transferred by conduction [74]. The similar results were reported by Cao et al. in their study where the microstructure of IN625 deposition present the cellular grains near the bottom region, columnar grains near the middle region, and equiaxed grains near the top region [73]. Liu fabricated IN718 thin-wall, whose microstructure mainly consisted of γ columnar dendrites and small amount of (γ + Laves) eutectics in the interdendritic areas, and measured the primary dendrite arm space which can reflected the grain size.

The results showed the primary dendrite arm space increased from 11.5 to 38 μm with the measured region changed from bottom to upper region of thin-wall [53].

In addition, there are some other factors, such as different region along the parallel direction, thickness of thin-wall, and particle size, affecting the grain size of the thin-wall. Owing to the edge effect, which means the higher temperature gradient near the edge region and lower temperature gradient in the middle region of thin-wall part [75]. That was also verified by the research of Wang et al. in which 316L thin-wall parts with the height of 60 mm were fabricated. The microstructure showed smaller grain size near the edge regions compared to that in the middle region [37]. Karczewski et al. deposited box-like Fe-16Al (wt%) thin-wall with different thickness. The average grain size of thin-wall was about 200, 200~300, 200~800 μm during the thickness was 0.5, 1, 2, and 5 mm, respectively, that also was verified by other researcher [76]. In addition, the thicker thin-wall possessed B2-type structure owing to the higher cooling rate. However, the thin-wall with the thickness of 0.5 mm presented DO3-type structure because of the low cooling rate [46]. By observation of transverse and longitudinal cross-section of WC/Ni thin-wall with the height of 5.7 mm and thickness of 1.7 mm, Huang pointed out that the uniform thickness demonstrate that the interface remelted and created metallurgical bonding between adjacent layers in the multi-layer LMD process. They also emphasized that modulation of particle size was significant for sake of controlling and designing the ideal microstructures [77]. Furthermore, in order to obtain the refined microstructure of thin-wall, auxiliary methods, such as ultrasonic vibration (UV), magnetic field, and electric -magnetic coupled field, were chosen to modify the microstructure [78–81]. Liu et al. deposited the Fe 60 on the Q 235 steel with the auxiliary of rotating magnetic field and obtained smaller grain size compared to that without the magnetic field owing to the existing of electromagnetic stirring which contributed to the breaking of columnar crystal and creating of crystal nucleus [79]. Gatzen et al. conducted the deposition of AlSi18 with the auxiliary of electric -magnetic coupled field and pointed out that the increase of current can intensify the convection of molten pool and promote the peritectic reaction [80]. Ning deposited 17-4PH Fe-Cr stainless steel on the low carbon steel by ultrasonic vibration-assisted LMD. The columnar grain structure with an average size of about 7~11 μm was observed inside the deposition fabricated without UV. However, the deposition fabricated with UV presented equiaxed grain with smaller size of about 1.5~3 μm that attributed to the actions of acoustic streaming and cavitation induced by UV [81].

3.2. Growth of Columnar

The long columnar sub-grains of the thin-wall grew along the height direction and passed through multiple deposition layers that attributed to the epitaxial mechanism. During the LMD process of thin-wall, the partial melting of substrate grains, the melting of molten pool, and the semi-melted grains averted the nucleation barrier and directly nucleate on the bonding surface that induced the sub-grains to grow along the original direction of the semi-melted grains. However, the inclined angle of long columnar sub-grains to the vertical direction was affected by the scanning direction because the scanning strategy can provide a certain temperature gradient in the parallel direction [39,82,83]. As shown in Figure 5a where CrCoNi medium-entropy alloy thin-wall was fabricated, the angle of growth direction of sub-grains and vertical direction kept constant owing to the same scanning direction which caused the maximum heat dissipation direction and temperature gradient direction to be along the same direction [58]. As shown in Figure 5b where the IN718 thin-wall was fabricated by continuous wave laser, during the bidirectional scanning direction was used, the angle of growth direction of columnar grains and vertical direction, which was about 60°~80°, presented periodical variation. However, as shown in Figure 5c, during the quasi-continuous-wave laser with the pulse frequency of 100 Hz was used, the normal of growth direction of columnar grains in each layer is about 45° to the scanning direction that resulted in the almost vertical angle of growth direction between two adjacent layers. Therefore, the highly oriented “zigzag” columnar grains were obtained [54].

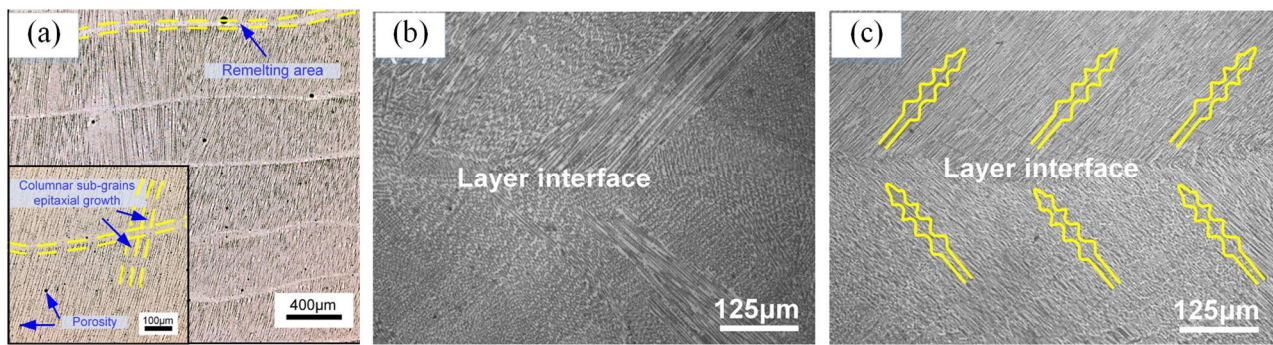


Figure 5. (a) Microstructure of CrCoNi medium-entropy alloy thin-wall (Reprinted from ref. [58], copyright (2021), with permission from Elsevier); microstructure of the IN718 thin-wall with the (b) continuous wave laser and (c) quasi-continuous-wave laser (Reprinted from ref. [54], copyright (2021), with permission from Elsevier).

In the molten pool created during the LMD process, the crystal growth and microstructure formation are determined by the solidification conditions of the advancing solidification interface. The sufficient extent of constitutional supercooling (CS) contributes to the growth of equiaxed grains ahead of the solidification interface. The ratio of G/V , where G is the thermal gradient and V is solidification velocity, can describe the extent of CS. A lower G/V conduces to the increased extent of CS that results in greater capability of equiaxed grains formation. When the G_n/V , where n is a material-dependent constant, exceeds a critical value which is represented by K_{CET} , the columnar structure can be obtained. As shown in Figure 6, along the solidification interface in the longitudinal section of Rene N5 deposition created by Liu, the ratio of $|G_{001}|^{3.4}/|V_{001}|$ decreased from the bottom to the top of the molten pool trailing edge. However, the ratio of $|G_{100}|^{3.4}/|V_{100}|$ presented an opposite trend. As shown in Figure 6c, at the top of solidification interface, the $|G_{100}|^{3.4}/|V_{100}|$ had a maximum value and $|G_{001}|^{3.4}/|V_{001}|$ presented the minimum value, while at the bottom of solidification interface, $|G_{001}|^{3.4}/|V_{001}|$ achieved the maximum value and $|G_{100}|^{3.4}/|V_{100}|$ had a minimum value. In addition, the ratio of $|G_{001}|^{3.4}/|V_{001}|$ is much bigger than the ratio of $|G_{100}|^{3.4}/|V_{100}|$. This indicated that in the longitudinal direction, the (100)/[100] crystallographic orientation is less competitive than the (001)/[100] crystallographic orientation which naturally acted as the epitaxial growth direction of the columnar dendrite trunk. The results of $|G_{001}|^{3.4}/|V_{001}|$ and $|G_{010}|^{3.4}/|V_{010}|$ in the transverse section presented the similar relationships which implied that the (010)/[100] crystallographic orientation is less competitive than the (001)/[100] crystallographic orientation which naturally acted as the epitaxial growth direction of the columnar dendrite [84]. Then observed the increased amount of stray grains during the angle between the dendrite growth direction and thermal gradient direction (β) was close to 45° because of the similar solidification condition in the [001] and [100] direction that contributed to the dendrites grow along both direction. The competitive growth of these two preferred orientations also conduced to the occurrence of columnar-to-equiaxed transition in the dendrite intersection area. However, when the angle β was less than 30° or more than 60° , no obvious stray grain was observed [85]. Fu et al. pointed out that in the deposition of Ti-6Al-4V thin-wall, columnar β -grains possessed the preferential growth in the direction of [100] which was paralleled with the maximum G direction. Compared to the initial two layers, the competitive growth reduced the number of columnar β -grains and increased the sizes in the low regions of thin-wall. With the progress of deposition process, the decrease of dissipation rate and increase of heat accumulation resulted in the reduction of G gradually. In the middle region of thin-wall, the length of columnar β -grains decreased, and the nucleation events increased before the solid/liquid interface that also conduced to the occurrence of a small amount of equiaxed grains. Finally, the equiaxed grains were observed in the upper regions because of the further decreased of G [86].

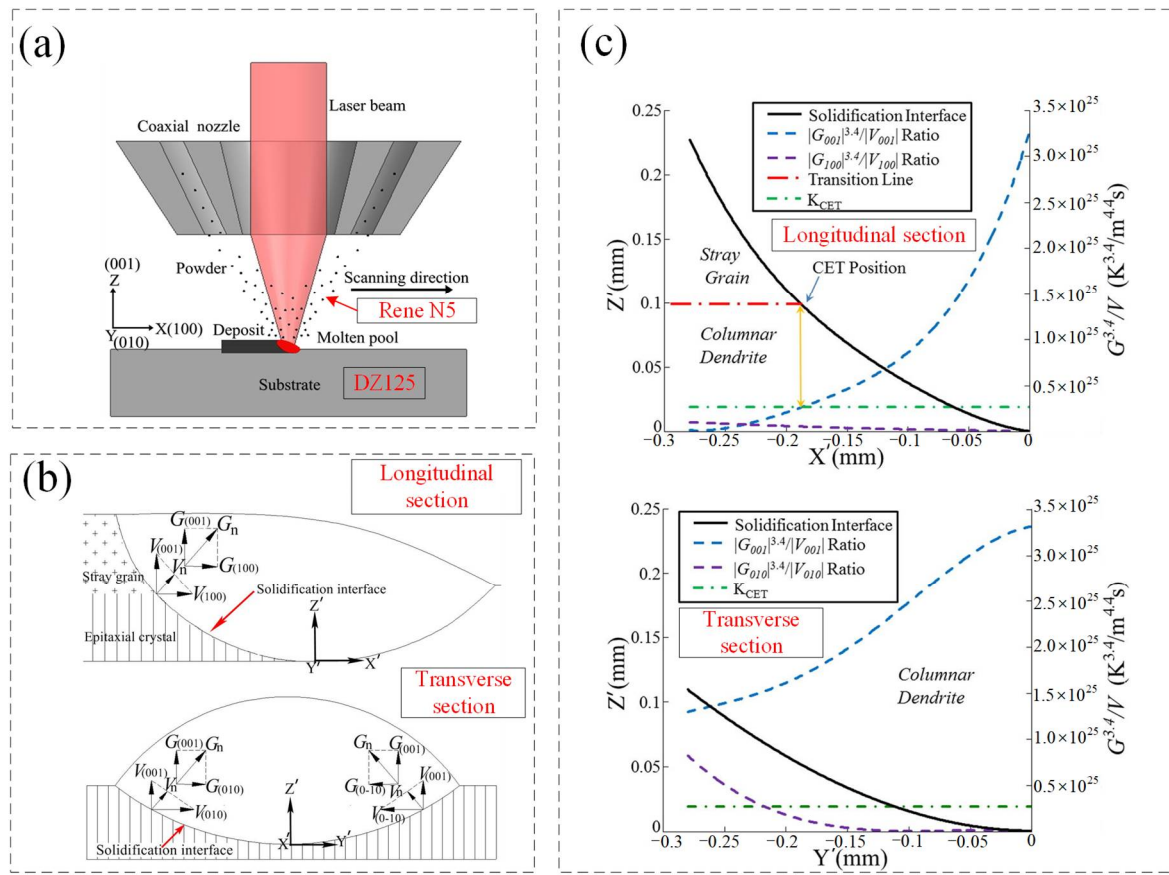


Figure 6. (a) Schematic of the LMD process, (b) The geometrical relationship of the magnitudes of G_{hkl} and V_{hkl} along the preferred growth directions relative to those normal to the solidification interface in the different section, and (c) The solidification conditions ahead of the solidification interface in the different section of a simulation deposition. (Reprinted from ref. [84], copyright (2015), with permission from Elsevier).

4. Microhardness

4.1. Effect of Grain Size and Phases

Microhardness, which is recognized as an important indicator to evaluate the mechanical properties, is determined by the microstructure and composition. The decrease of grain size conduces to the improvement of microhardness. The small grain size contributes to the increase of microhardness that also can be indicated by the Hall-Petch formula which is as follows [46,87]:

$$H_v = H_0 + k_H d^{-1/2} \quad (1)$$

where H_v represents the hardness, H_0 and k_H represents the constants which are related to the hardness, and d represents the average grain size. The grain size is closely related to the cooling rate of molten pool during the LMD process. The cooling rate is affected by the process parameters, the different region of thin-wall, and the dimensions of thin-wall part. Liu also pointed that the microhardness in the upper region was slightly lower than that in the middle region of thin-wall because the upper region formed oxide affected by the air and the middle region formed a denser and fine crystal structure [47]. The microhardness of CrCoNi medium-entropy alloy thin-wall fabricated by Xue et al. presented gradually decrease from the bottom region with the value of 245.6 HV to the upper region with the value of 179.6 HV [58]. Karczewski et al. pointed out that the microhardness of deposited box-like Fe-16Al (wt%) thin-wall was affected by the thickness of thin-wall. The results shown that the microhardness was about 337 ± 13 , 333 ± 15 , 371 ± 18 , 381 ± 17 HV during

the thickness was 0.5, 1, 2, and 5 mm, respectively. The increase of thickness increase the cooling rate, the grain size, and then the microhardness [46].

The formation of strengthening structure and hardening phase also contribute to the improvement of hardness. Li deposited the IN718 superslloy and indicated that the hardness in the bottom, middle, and top region were 385, 381, and 298 HV, respectively. The improvement of hardness in the bottom and middle region attributed to the precipitation of γ'' and γ' phase [88]. The IN718 thin-wall deposited by Xu et al. also presented higher hardness in the bottom region compared on the middle and top region that was ascribed to the enhanced precipitation hardening caused by reiterated thermal cycles. In the bottom region, the partial dissolution of Laves phases provided free Nb atoms which can diffuse into the matrix and accelerate γ'' precipitation in the inter-dendritic region [89]. Xiang et al. used the pulsed LMD to deposited the CoNiTi medium-entropy alloy and obtained the high hardness with the value of 571 ± 46 HV which was about five times of the hardness in the substrate (114 ± 4 HV) that contributed to the formation of solid-solution hardening BCC phase and second-phase hardening from the Ti_2Ti and Ti_2Co type intermetallic compounds [90].

4.2. Distribution of Microhardness

With the increase of the height of thin-wall, the heat accumulation aggravates and the influence of thermal history on the microhardness become complex that result in the various of microhardness in the different region of thin-wall part. In the vertical direction of the thin-wall, the microhardness distribution can be explained as follows. In the deposition process of thin-wall where the scanning path is single-track and multi-layer, the top surface of former deposited layer is remelted and the whole former layers is reheated that results in the occurrence of different regions in the former layer. Huang et al. divided the former layers into four regions including remelted region, semisolid region, secondary quenching region and tempering region. The remelted and semisolid region were accompanied with the repaid melting and solidification process. The solidification of semisolid region contributed to the crystallization of coarse grains. The remelted region, which was integrated with the latter layer, provided platform for the coarse grain to grow that resulted in the appearance of coarse grain zone at the interface between the adjacent layers. As shown in Figure 7a, the troughs in the curve represented the coarse regions of the interface as a result of remelting and reheating. The secondary quenching region, which is the quenching region in the former layer deposition process, underwent secondary quenching that led to the increase of microhardness. Owing to the long distance to the top surface, the bottom region of the former layer suffered low reheating temperature and underwent tempering that attributed to the insufficient quantity of heat which is transmitted from new deposited layer. The results indicated that the microhardness distribution across the longitudinal section of WC/Ni thin-wall with the height of 6 mm presented a periodical fluctuation, as shown in Figure 7a, that attributed to the remelting and reheating during the deposition of latter layer and then the variation of the grain size [77]. The periodical fluctuation of the hardness with the increase of height also was indicated in the work reported by Wang et al. as shown in Figure 7d. In addition, the hardness near the edge region presented higher than that in the middle region because of the finer grains near the edge region [37]. Zhang et al. observed the similar rules of hardness in the SS410 thin-wall part with the height of 20 mm. They indicated that the interface between the substrate and deposition presented the maximum hardness with the value of 350 HV because of the existing of ferrite and retained austenite. During the height was above 2 mm, the hardness decreased suddenly to 200 HV and then kept consistent in the deposition where the microstructure mainly consisted of ferrite [40].

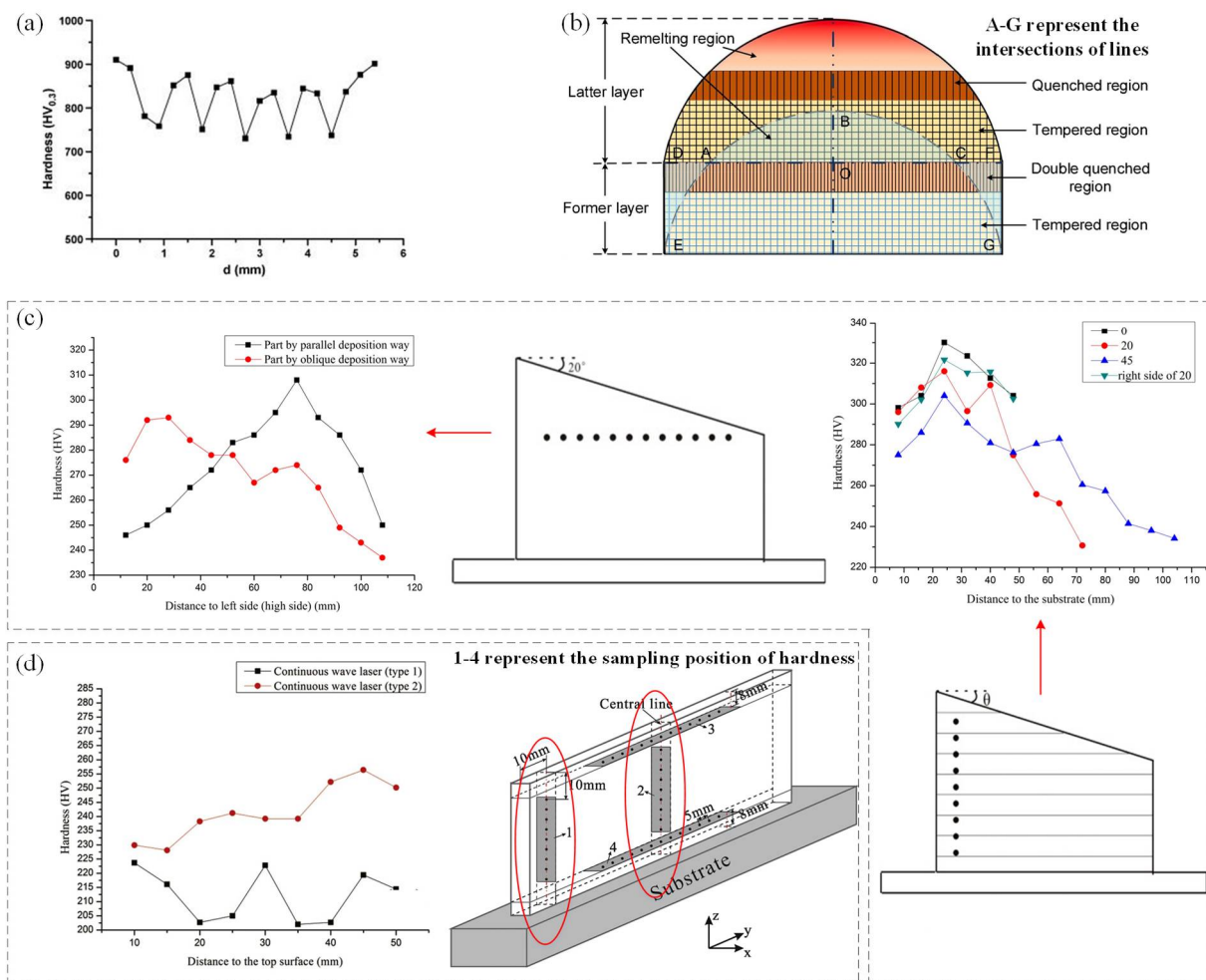


Figure 7. (a) Hardness distribution in height-direction of the WC/Ni thin wall sample, (Reprinted from ref. [77], copyright (2009), with permission from Elsevier); (b) Schematic illustration of thermal history in laser material deposition process (Reprinted from ref. [26], copyright (2020), with permission from Elsevier); (c) Hardness distribution in parallel and vertical direction of the 316L slope thin-wall (Reprinted from ref. [2], copyright (2016), with permission from Elsevier); (d) Hardness distribution in the vertical direction of 316L thin wall (Reprinted from ref. [37], copyright (2016), with permission from Elsevier).

However, the microhardness distribution of thin-wall with great height in the perpendicular direction would present different rules. Wang fabricated 316L slope thin-wall part with three-dimensional and parallel deposition way. The height of deposited thin-wall part exceeded 50 mm. It was worth noting that the microhardness increased initially and then decreased with the increase of distance to the interface between the deposition and substrate. The maximum value of hardness presented at the distance of about 25 mm to the interface. Wang pointed out that the tempering, which was harmful for the hardness, played a dominant role in affecting the hardness distribution in the perpendicular direction as shown in Figure 7b. During the height was lower than 25 mm, the heat was effectively transferred by the substrate and the inputted heat was insufficient to warm the former layers that resulted in the highlight of the tempering effect of latter deposition process on the former layer high. Thus, the hardness increased with the distance to the interface increased during the distance was lower than 25 mm. However, during the height exceeded 25 mm, the temperature of former layer became high owing to the heat accumulation that led to the tempering of former layers on the latter layers dominated the process. Thus, the hardness decreased with the increase of distance to the interface during the height exceeded 25 mm [26].

In addition, the hardness distribution along the parallel direction was relatively uniform because of the similar conditions and grain size. However, the hardness of edge and middle of the thin-wall always presented slight different owing to the slight different temperature gradient. It was worthy to notice that the hardness distribution of slope thin-wall along the parallel direction was significantly different as shown in Figure 7c. Owing to the more inputted heat and longer heating time, the high side of slope thin-wall with parallel deposition way suffered from obvious temping effect that resulted in the maximum hardness near the low side. In the case of three-dimensional deposition way as shown in Figure 3c, the maximum hardness presented near the high side that attributed to the identical inputted heat along the surface of slope thin-wall and higher cooling rate caused by the bigger height and deposition volume near the high side [26].

5. Tensile Properties

5.1. Effect of Grain Size

The indicator of tensile properties always consists of the yield strength, ultimate tensile strength, and elongation. The grain size is a factor to affect the yield strength that can be expressed by the Hall-Petch relation [91]:

$$\sigma_y = \sigma_0 + k/d^{1/2} \quad (2)$$

where σ_y is the yield strength, d is the grain size, σ_0 and k are the constants related to the materials. The decrease of the grain size can increase the yield strength. The finer grains can bring higher grain boundaries and dislocation density that contributes to the strengthening of the materials by hindering the movement of the dislocations. Owing to the generation of refined dendrites in the thin-wall fabricated by the LMD process in which the cooling rate of molten pool was high, the LMD-ed thin-wall possessed higher tensile strength compared to the conventional machining ones. However, the elongation presented contrary law. The one reason for the lower elongation was the occurrence of atmospheric oxidation caused by the LMD process without the vacuum environment of glove box [14]. For instance, the yield strength, ultimate tensile strength, and elongation of the CrCoNi medium-entropy alloy thin-wall in the vertical direction showed higher than that in the parallel direction because of the smaller grain size [58]. Compared to the cast samples as shown in Table 3, the yield strength and ultimate tensile strength of the thin-wall fabricated by LMD increased about 39.5%~100%. However, the elongation showed approximately with that by the casting process [58,92,93].

Table 3. Tensile properties of CrCoNi medium-entropy alloy and 316 samples of thin-wall fabricated by LMD and casting process in the vertical and parallel direction.

Powder	Process Route	Loading Direction	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Ref.
CrCoNi	LAM	vertical	360.793	584.584	53.690	[58]
		parallel	364.941	574.558	36.943	
	Casting	-	257.713	547.935	82.650	[93]
		-	~170	~480	~55	
316	LAM	vertical	352	536	46	[14]
		parallel	558	639	21	
	Anneal	-	241	586	50	

5.2. Effect of Phases

In the deposition process of thin-wall, the average temperature inside of deposition and the duration time of the high temperature range will be increased compared to the single-track deposition process. Therefore, the intense thermal cycling effects may conduce

the temperature to rise to the phase transition point or even induce solid phase transition that will eventually affects the tensile properties of thin-wall. In the investigation of anisotropic tensile behavior of deposited Ti-6Al-4V cruciform thin-wall reported by Carroll et al., the prior- β grains have long axes of about 1.5~10 mm along with the vertical direction. The boundaries of prior- β grains were decorated with the grain boundary α phase which conduced to the decrease of elongation by furnishing a preferential path for damage accumulation aligned with the prior- β grain boundaries. Compared to the previous results, the yield and tensile strength of the cruciform thin-wall reduced but still were well above the requirement for cast and wrought of Ti-6Al-4V, as shown in Table 4. They observed little α' (hcp martensite) in the microstructures. This observation indicated that the cooling rate during the deposition of cruciform thin-wall was above the β transfer of $\sim 1000^\circ\text{C}$, while rapid was not sufficient fast to allow the formation of martensite which was generally stronger than α - β microstructures owing to the presence of lattice strains [94]. Thus, the absence of martensite was account for the reduction of yield and tensile strength of cruciform thin-wall [67]. Li pointed out that although the grain size is coarser compared to the SLM process where the improvement of yield strength was mainly determined by the fine grains, the interaction between the precipitation and dislocation induced the IN718 to act as a precipitation strengthened superalloy. They deposited IN718 superalloy and the results of tensile test showed that the yield strength at the bottom, middle, and top region were 745.1 ± 5.2 , 752.2 ± 12.1 , and 464.7 ± 44.2 MPa, respectively. The results can be explained by the precipitation of strengthening phases (γ'' and γ') in the bottom and middle region [88]. The ductility of IN718 during the tensile process was investigated by Xu et al. from the angle of Laves phases. They indicated that the granular laves phases had strong coordination and can be retained or directly separated from the γ matrix, while the failure of long-chain Laves phases were mainly in forms of debonding and fragmentation during the tensile process that implied the granular Laves phases presented higher ability of plastic deformation compared to the long-chain Laves phases [89].

Table 4. Summary of relevant Ti-6Al-4V mechanical properties by LMD process during the tensile axis was along longitudinal orientation [67].

Built Part Geometry	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)
Test coupon	1105 ± 19	1163 ± 22	4 ± 1
Tall wall	1052 ± 27	1153 ± 13	5.3 ± 2.1
Flat plate	984 ± 25	1069 ± 19	5.4 ± 1
Cruciform thin-wall	959 ± 22	1064 ± 23 MPa	11
Wrought	973 ± 8	1050 ± 8	17

5.3. Effect of Loading Direction

The ductile deformation is also related to the grain sliding which is caused by shearing force. Due to the existing of molten pool boundaries (MPBs) caused by overlapping between the molten pools, the fracture preferentially occurs along the boundaries where the bonding force is weaker [13]. In the fabrication of thin-wall where the single-track and multi-layer are deposited, the laser spot is continuous during the scanning of single-track that contributes to the disappearing of MPBs. However, the MPBs caused by the layer-by-layer deposition process are obvious and present perpendicular to the epitaxial growth direction of grains as shown in Figure 8a. Figure 8b illustrates the different relationship between the shearing force and tensile loading direction. The shearing force along the direction of grain sliding (τ) can be expressed as:

$$\tau = \frac{F \cos \theta_F}{A / \cos \lambda} = \frac{F}{A} \cos \theta_F \times \cos \lambda \quad (3)$$

where F represents the tensile force, θ_F represents the angle between the direction of grain sliding and tensile force, λ is the angle between the sliding surface and tensile force, A represents the cross-section area acted by tensile stress. The tensile stress (F/A) increases until reaches the yield strength of the material with the increase of tensile force (F). Furthermore, the slide would happen after the shearing force exceeds the ultimate value which the sliding surface can sustain that means the occurrence of deformation. Therefore, as shown in Figure 8b, during tensile force is along the vertical direction, the thin-wall present the low tensile strength because the tensile force is approximately parallel to the sliding surface that contributes to the high shearing force and pool ability for hindering the tensile force. However, in the case of tensile test along the parallel direction of thin-wall, the angle between the sliding surface and tensile force is big that results in the small shearing force and high tensile strength [13,26].

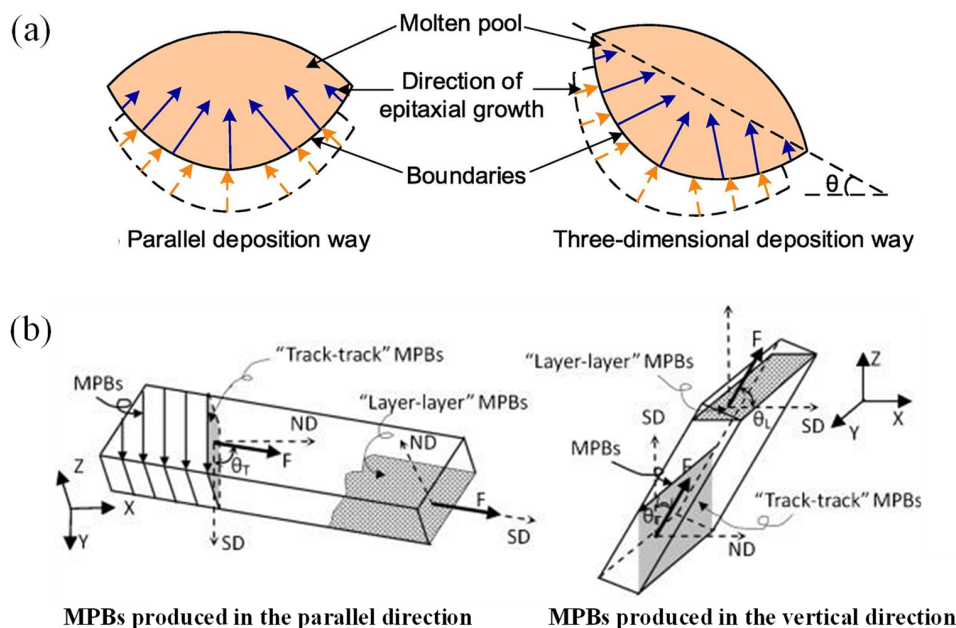


Figure 8. (a) Schematic of direction of grain growth in different deposition way (Reprinted from ref. [26], copyright (2020), with permission from Elsevier); (b) The force analysis diagram of molten pool boundaries produced in horizontal and vertical direction (Reprinted from ref. [13], copyright (2014), with permission from Elsevier).

Wang et al. fabricated 316L thin-wall with the height of 60 mm as shown in Figure 9a and investigated the ultimate tensile strength and elongation along different loading direction. The results showed that the UTS of the sample 1, 2, and 3, whose loading direction was horizontal, were higher than that of sample 4, 5, and 6, whose loading direction was vertical. The dendritic boundaries of the thin-wall were primarily perpendicular to the scanning path that contributes to the higher UTS during the loading force was parallel to the scanning path because of the effective hindering for the dislocation movement of samples. However, the results of elongation presented contrasting rules [37,95]. Zhang conducted the tensile test of 316 thin-wall along the vertical and parallel directions as shown in Figure 9b and the experimental results were summarized in Table 3. It can be seen that the tensile performance appeared anisotropic with the tensile direction. Compared to the samples tested along the vertical direction where the interlayer bonding places easily become the fracture source, the tensile strengths along the parallel direction with the yield strength of 558 MPa and ultimate tensile strength of 639 MPa were higher. Owing to the dendrites can hold better ductility along the growth orientation, the higher elongation was presented during the vertical loading direction was used that also can be verified by the features of dimples as shown in Figure 9b. The dimples in fracture surface of vertical

tensile samples were much deeper and denser that indicated the vertical tensile direction possesses better ductility [14]. As shown in Figures 7c and 9c, the results of tensile test in the investigation of 316L slope thin-wall with the angle θ of 20° reported by X. Wang et al. revealed that the biggest UTS was presented due to the smallest shearing force during the angle between tensile loading direction and horizontal direction (β) was 45° . During the angle β was 90° , the small angle between the direction of tensile loading and sliding surface as well as the high shearing force led to the low UTS [26].

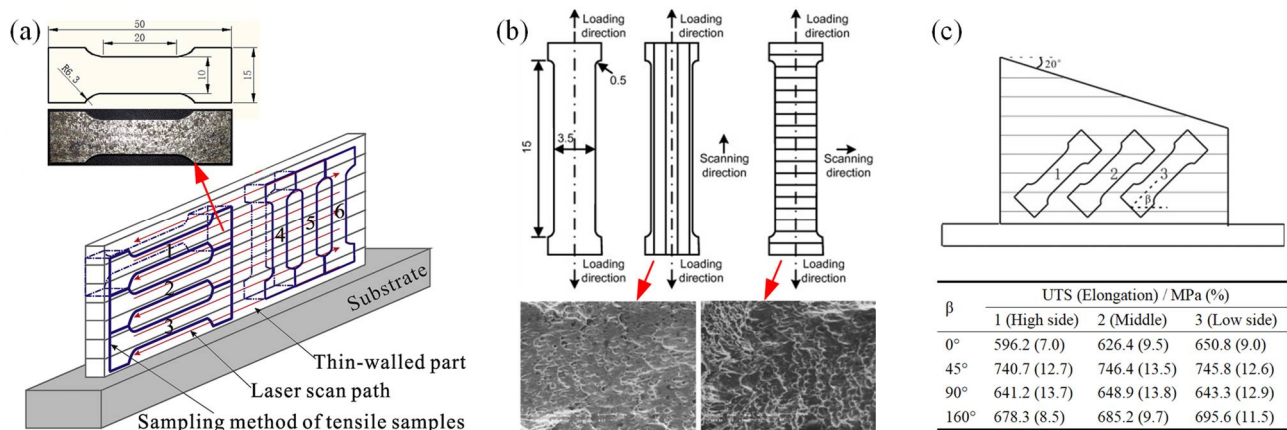


Figure 9. (a) Schematic for tensile test specimens of 316L thin-wall. (Reprinted from ref. [37], copyright (2016), with permission from Elsevier); (b) Schematic for tensile test specimens SEM morphology of tensile fracture surface of 316 thin-wall (Reprinted from ref. [14], copyright (2013), with permission from Elsevier). (c) Schematic for tensile test specimens of 316L slope thin-wall (Reprinted from ref. [2], copyright (2016), with permission from Elsevier).

6. Thermal Stress

6.1. Distribution of Thermal Stress

LMD, which is a process accompanied with non-uniform heating and melting, induces extremely uneven temperature distribution around the molten pool that leads to uneven contraction and expansion in different region of the deposition layer and ultimately leads to residual stress and deformation [96]. When the deposition stress exceeds the yield limit, the deformation, which is mainly caused by deposition stress, occurs. During the LMD process, the region acted by the laser beam is rapidly heated and melted, but the temperature of the region, which is far from the laser beam, is low that results in uneven thermal expansion. The metal of laser-active region experiences thermally expanded which is constrained by the surrounding cold material that contributes to the causing of compressive stress in thermal material and tensile stress in cold material. The increase of temperature decreases the yield limit of metal in the laser-active region. As shown in Figure 10b, during the thermal expansion of the deposition is larger than that of substrate, the arch deformation occurs. However, after the laser beam goes away as shown in Figure 10c, the material in the laser-active region shrinks and undergoes tensile stress, but the material in the cold region undergoes compressive stress that results in the occurrence of warping deformation under the influence of shrinkage force [46].

The plastic deformation of the crystalline material was assumed to obey the Von Mises yield criterion and the associated flow rule. The following equation can express the equivalent von Mises stress (EVMS):

$$\sigma_e = \frac{\left[(\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{yy} - \sigma_{zz})^2 + (\sigma_{zz} - \sigma_{xx})^2 \right]^{\frac{1}{2}}}{\sqrt{2}(1 + \nu')} \quad (4)$$

where ν' represents the equivalent Poisson's ratio. The EVMS is a uniaxial random stress that is characterized in frequency domain by a power spectral density, which is calculated as a linear combination of the auto- and cross-spectra of multiaxial random stress. The EVMS can be used to quickly estimate the fatigue damage in frequency domain [97]. It can be seen from the Equation (4) that the EVMS is composed of three principal stresses including the X-directional stress, Y-directional stress, and Z-directional stress [51]. Therefore, in order to estimate the properties of thin-wall by LMD, the different directional stresses of thin-wall have been tested and simulated by many researchers.

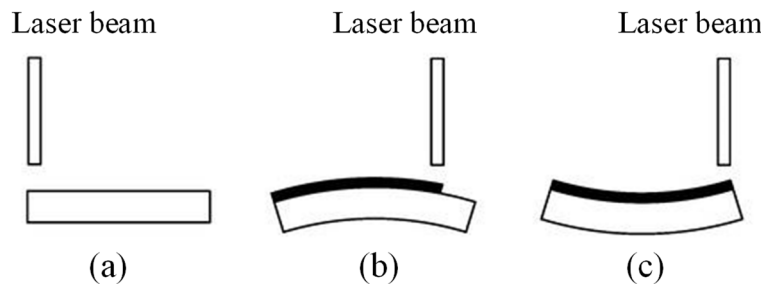


Figure 10. Schematic of the deformation process of thin-walled parts. (a) Before the LAM; (b) During the LAM; (c) After the LAM (Reprinted from ref. [46]. copyright (2020), with permission from MDPI).

The time-dependent temperature distribution plays a significant role in the stress pattern of the thin-wall with four layers fabricated by the LMD process. Owing to the unhandy monitoring of time-dependent temperature, the numerical analysis is a powerful tool. M. Alimardani et al. obtained 3D temperature distribution and stress pattern for any elapsed time during the LMD process of 304L thin-wall by numerical simulation. As shown in Figure 11a,b, the stress concentration presented around the molten pool during the laser beam moved to the middle region. However, as the laser beam arrived at the edge region, the growth of stress concentration can be observed and two regions of concentration, including the region around molten pool and the corner of thin-wall. In addition, with the increase of deposition height, the heat loss by convection/radiation gradually became dominant compared to the heat loss by conduction that contributed to the increase of temperature, volume of molten pool, and then the powder catchment [98]. It was worth to noticed that the thermal stains and stress decreased with the increase of deposition height and the decrease of the temperature gradient. Although the decreased trend of stress presented along the height direction, the maximum stresses still occurred at the edge region of the layers 2~4 [43].

As reported by Wang et al. [37] and Rangaswamy et al. [99], for the Z-directional stress, the tensile stress played the dominant role at the edge region and compress stress was presented at the central region of thin-wall part. For the Y-directional stress, the tensile stress and compress stress were observed at the central and edge region, respectively. The occurrence of tensile stress can be justified that the scanning speed gave less time to material stretched in the Y-direction owing to different cooling rate to recover its position [37,100]. Balichakra investigated the residuals tress of γ -TiAl thin-wall and pointed out that the encountered transient thermal gradients significantly affected the state and magnitude of residual stress. In addition, the compressive stress decreased with the increase of height of deposition in the vertical direction [55].

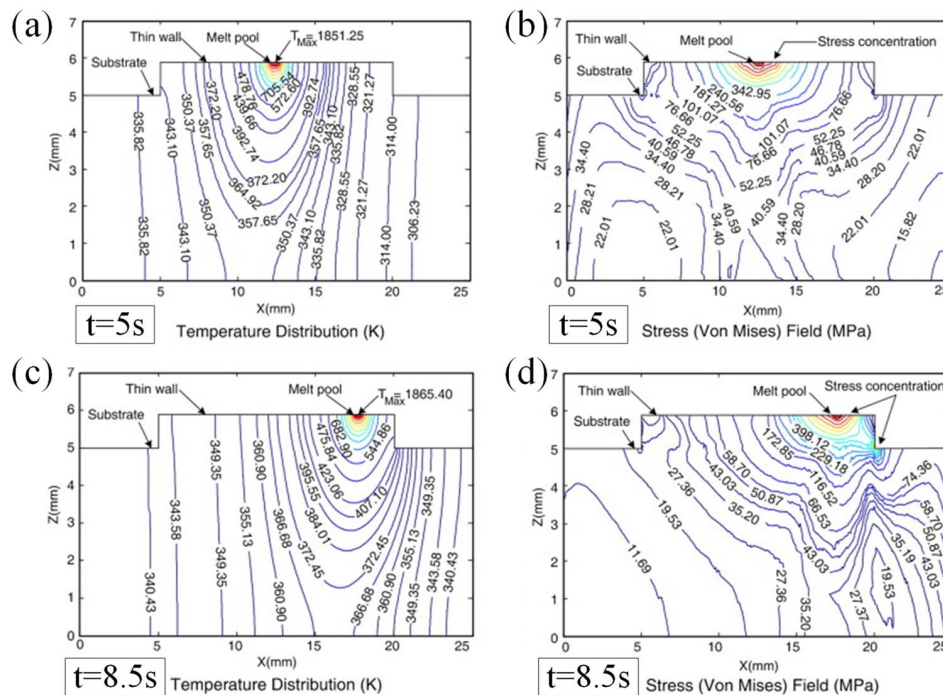


Figure 11. (a,c) Thermal field (isothermal contours), (b,d) stress field (Von Mises) for the second-layer deposition at different times on the surface normal to $y = 0$ (Reprinted from ref. [43], copyright (2009), with permission from Elsevier).

6.2. Modification of Thermal Stress

Preheating of the substrate is an effective treatment to improve the status of stress distribution and alleviate the deformation. Zhang built Ni 60A thin-wall on the Q235 substrate with the preheating temperature of 200, 300, 400, 500 and 600 °C. They pointed out that the tensile stress along the horizontal direction decreased with the increase of preheating temperature because of the alleviation of the temperature gradient. The preheating of substrate contributed to the volume increasing of deposition owing to the more powder melted into the molten pool. The increase of the preheating temperature caused the increase of volume of deposition, the increase of tensile stress, and more significant contraction of depositions during cooling [50]. However, Alimardani et al. pointed that the thermal stress of 304 thin-wall showed inconspicuous decrease after preheating the substrate to 500 K during the laser power kept constant. However, the maximum thermal stress significantly reduced by preheating the substrate and decreasing the laser power. For instance, compared to the thermal stress induced by the laser power of 300 W and non-preheat treatment of substrate, the maximum stress decreased by 16.7% during the laser power was 250 W and the preheating temperature was 700 K. The maximum stress only presented 3.6% reduction with the same preheating temperature and laser power of 300 W. These results demonstrated that preheating the substrate accompanied with optimizing the laser power can significantly reduce the thermal stress [43].

Using of pulsed laser is another method to modifying the stress pattern of the thin-wall. Wang fabricated the 316L thin-wall with pulsed wave laser (PW) and continuous wave laser (CW). Compared to the CW laser, the pattern of Z-directional stress of thin-wall by PW laser presented opposite trend that the tensile stress was induced in the central region. In addition, the decrease of inputted energy by reducing the pulse time can relieve the tensile stress and even drew forth the compress stress. For the Y-directional stress, the stress showed a periodic variation between the tensile and compress stress that was explained as the effect of duty cycle which is the special feature in pulse laser [37].

7. Conclusions

This review addresses the research status of deposition quality, microstructures, micro-hardness, tensile properties, and thermal stress of metal thin-wall created by laser material deposition. The main conclusions can be drawn as follows:

- (1) Except for the process parameters, such as laser power, scanning speed, powder feed rate, the matching of z-increment and single deposition height played a significant role in affecting the surface quality and dimension precision. During the z-increment was bigger than the single deposition height, the positive de-focusing could result in gradually insufficient powder captured by molten pool, decrease of single deposition height, and then the failure in deposition of thin-wall finally because of the interactional effect. However, during the z-increment was smaller than the deposition height, the self-regulation-effect could assure the molten pool to capture sufficient powder and create a deposition layer. Based on the optimizing of the fabrication process, some thin-wall parts with complex structures, such as inclined thin-walled cylinder, special-shaped bottom thin-wall, slope thin-wall, thin-walled overhang structures and so on, were fabricated with high quality.
- (2) Based on the microstructures' characteristics, the thin-wall could be divided into three regions which names the upper, middle, and bottom region. Plane, columnar, and cellular crystal presented in the bottom, middle, and upper region of thin-wall, respectively. Owing to the decrease of temperature gradient with the increase of deposition height, the grain size gradually decreases because of the reduction of cooling rate. The long columnar grains of the thin-wall grew almost along the height direction and passed through multiple deposition layers that attributed to the epitaxial mechanism. The growth direction of columnar grains could be affected by the changing of heat dissipation direction.
- (3) Microhardness had a negative correlation with the grain size. During the deposition height is small, the hardness decreased slightly from the bottom to upper region because of the decrease of grain size. Owing to the remelting and reheating which could lead to the coarse regions, the hardness was periodic variation. During the deposition height is great, the hardness increased initially and then decreased with the increase of height that attributed to the temping effect between the former layers and latter layers. The formation of strengthening structure and hardening phase also contribute to the improvement of hardness. In addition, the hardness distribution along the parallel direction was relatively uniform because of the similar conditions and grain size.
- (4) The finer grains can improve the tensile strength because of the higher grain boundaries and dislocation density which can hindering the movement of the dislocations. The UTS of thin-wall fabricated by LMD process was bigger than that by conventional process such as casting. However, the elongation presented adverse rules. During the tensile loading was along the parallel direction, the small shearing force contributes to the big tensile strength. In the case of vertical direction of tensile loading, owing to the small angle between the sliding surface and tensile force, the low tensile strength was present because of the high shearing force during the tensile test. The intense thermal cycling effects may induce solid phase transition and eventually affects the tensile properties of thin-wall. In addition, with the changing of shape of thin-wall, the tensile strength could be changed owing to the different direction of MPBs.
- (5) The encountered transient thermal gradients significantly affected the state and magnitude of residual stress. By pre-heating of the substrate and utilization of pulsed laser, the pattern of thermal stress could be modified.

Author Contributions: Investigation, X.W. and J.J.; writing—original draft preparation, X.W.; writing—review and editing, X.W., J.J., C.X. and Y.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Liaoning Province, grant number 2020-BS-206, Liaoning Department of Education Scientific Research Foundation, grant number JDL2020022, and Scientific and technological research program of China National Railway Group Limited, grant number N2021T010.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, J.; Li, L. Direct fabrication of thin-wall parts by laser cladding. *J. Manuf. Process.* **2006**, *8*, 1–7. [CrossRef]
2. Wang, X.; Deng, D.; Qi, M.; Zhang, H. Influences of deposition strategies and oblique angle on properties of AISI316L stainless steel oblique thin-walled part by direct laser fabrication. *Opt. Laser Technol.* **2016**, *80*, 138–144. [CrossRef]
3. Liu, Y.; Liu, C.; Liu, W.; Ma, Y.; Zhang, C.; Cai, Q.; Liu, B. Microstructure and properties of Ti/Al lightweight graded material by direct laser deposition. *Mater. Sci. Technol.* **2018**, *34*, 945–951. [CrossRef]
4. Ouyang, H.; Yu, Z.; Chen, T.; Fu, X.-J. Sub-Regional Process Planning for Large Nuclear Power Head. *Mach. Des. Manuf.* **2014**, *5*, 253–255.
5. Herzog, D.; Seyda, V.; Wycisk, E.; Emmelmann, C. Additive manufacturing of metals. *Acta Mater.* **2016**, *117*, 371–392. [CrossRef]
6. Huang, S.H.; Liu, P.; Mokasdar, A.; Hou, L. Additive manufacturing and its societal impact: A literature review. *Int. J. Adv. Manuf. Technol.* **2012**, *67*, 1191–1203. [CrossRef]
7. Shim, D.-S.; Baek, G.-Y.; Seo, J.-S.; Shin, G.-Y.; Kim, K.-P.; Lee, K.-Y. Effect of layer thickness setting on deposition characteristics in direct energy deposition (DED) process. *Opt. Laser Technol.* **2016**, *86*, 69–78. [CrossRef]
8. Thompson, S.M.; Bian, L.; Shamsaei, N.; Yadollahi, A. An overview of Direct Laser Deposition for additive manufacturing; Part I: Transport phenomena, modeling and diagnostics. *Addit. Manuf.* **2015**, *8*, 36–62. [CrossRef]
9. Shamsaei, N.; Yadollahi, A.; Bian, L.; Thompson, S.M. An overview of Direct Laser Deposition for additive manufacturing; Part II: Mechanical behavior, process parameter optimization and control. *Addit. Manuf.* **2015**, *8*, 12–35. [CrossRef]
10. Das, S.; Beama, J.J.; Wohler, M.; Bourell, D.L. Direct laser freeform fabrication of high performance metal components. *Rapid Prototyp. J.* **1998**, *4*, 112–117. [CrossRef]
11. Zhang, B.; Dembinski, L.; Coddet, C. The study of the laser parameters and environment variables effect on mechanical properties of high compact parts elaborated by selective laser melting 316L powder. *Mater. Sci. Eng. A* **2013**, *584*, 21–31. [CrossRef]
12. Mumtaz, K.; Hopkinson, N. Selective laser melting of thin wall parts using pulse shaping. *J. Mater. Process. Technol.* **2010**, *210*, 279–287. [CrossRef]
13. Shifeng, W.; Shuai, L.; Qingsong, W.; Yan, C.; Sheng, Z.; Yusheng, S. Effect of molten pool boundaries on the mechanical properties of selective laser melting parts. *J. Mater. Process. Technol.* **2014**, *214*, 2660–2667. [CrossRef]
14. Zhang, K.; Wang, S.; Liu, W.; Shang, X. Characterization of stainless steel parts by Laser Metal Deposition Shaping. *Mater. Des.* **2014**, *55*, 104–119. [CrossRef]
15. El Cheikh, H.; Courant, B.; Branchu, S.; Huang, X.; Hascoët, J.-Y.; Guillén, R. Direct Laser Fabrication process with coaxial powder projection of 316L steel. Geometrical characteristics and microstructure characterization of wall structures. *Opt. Lasers Eng.* **2012**, *50*, 1779–1784. [CrossRef]
16. Sun, W. Application Status and Development Trend of Additive Manufacturing Technology for Metal Materials. *Guangdong Sci. Ence Technol.* **2021**, *30*, 99–102.
17. Yap, C.Y.; Chua, C.K.; Dong, Z.L.; Liu, Z.H.; Zhang, D.Q.; Loh, L.E.; Sing, S.L. Review of selective laser melting: Materials and applications. *Appl. Phys. Rev.* **2015**, *2*, 041101. [CrossRef]
18. Lu, L.; Guo, K.; Sun, J.; Zhang, G.; Sun, C. Investigation on hot sizing process based on creep mechanism for laser clad thin-walled titanium alloy components. *J. Laser Appl.* **2019**, *31*, 042002. [CrossRef]
19. Yu, J.; Lin, X.; Ma, L.; Wang, J.; Fu, X.; Chen, J.; Huang, W. Influence of laser deposition patterns on part distortion, interior quality and mechanical properties by laser solid forming (LSF). *Mater. Sci. Eng. A* **2011**, *528*, 1094–1104. [CrossRef]
20. Zhang, H.; Chong, K.; Zhao, W.; Sun, Z. Effects of pulse parameters on in-situ Ti-V carbides size and properties of Fe-based laser cladding layers. *Surf. Coat. Technol.* **2018**, *344*, 163–169. [CrossRef]
21. Zhan, M.; Sun, G.; Wang, Z.; Shen, X.; Yan, Y.; Ni, Z. Numerical and experimental investigation on laser metal deposition as repair technology for 316L stainless steel. *Opt. Laser Technol.* **2019**, *118*, 84–92. [CrossRef]
22. Yu, J.; Rombouts, M.; Maes, G. Cracking behavior and mechanical properties of austenitic stainless steel parts produced by laser metal deposition. *Mater. Des.* **2013**, *45*, 228–235. [CrossRef]
23. Ocylok, S.; Weisheit, A.; Kelbassa, I. Functionally graded multi-layers by laser cladding for increased wear and corrosion protection. *Phys. Procedia* **2010**, *5*, 359–367. [CrossRef]
24. Abioye, T.E.; Farayibi, P.K.; Kinnel, P.; Clare, A.T. Functionally graded Ni-Ti microstructures synthesised in process by direct laser metal deposition. *Int. J. Adv. Manuf. Technol.* **2015**, *79*, 843–850. [CrossRef]

25. Corbin, D.; Nassar, A.; Reutzel, E.; Allison, M.; Nathan, A. Effect of directed energy deposition processing parameters on laser deposited Inconel®718: External morphology. *J. Laser Appl.* **2017**, *29*, 022001. [CrossRef]
26. Wang, X.; Liu, Z.; Guo, Z.; Hu, Y. A fundamental investigation on three-dimensional laser material deposition of AISI316L stainless steel. *Opt. Laser Technol.* **2020**, *126*, 106107. [CrossRef]
27. Zhang, K.; Liu, W.; Shang, X. Research on the processing experiments of laser metal deposition shaping. *Opt. Laser Technol.* **2007**, *39*, 549–557. [CrossRef]
28. D'Oliveira, A.S.C.M.; da Silva, P.S.C.P.; Vilar, R.M.C. Microstructural features of consecutive layers of Stellite 6 deposited by laser cladding. *Surf. Coat. Tech.* **2002**, *153*, 203–209. [CrossRef]
29. Wang, X.; Lei, L.; Yu, H. A Review on Microstructural Features and Mechanical Properties of Wheels/Rails Cladded by Laser Cladding. *Micromachines* **2021**, *12*, 152. [CrossRef] [PubMed]
30. Wang, X.; Yu, H.; Jiang, J.; Xia, C.; Zhang, Z. Influences of Pulse Shaping on Single-Track Clad of AISI316L Stainless Steel by Laser Material Deposition. *Coatings* **2022**, *12*, 248. [CrossRef]
31. Lepski, D.; Brückner, F. *Laser Cladding*; Springer: Berlin/Heidelberg, Germany, 2009; pp. 235–279.
32. Bi, G.; Gasser, A.; Wissenbach, K.; Drenker, A.; Poprawe, R. Investigation on the direct laser metallic powder deposition process via temperature measurement. *Appl. Surf. Sci.* **2006**, *253*, 1411–1416. [CrossRef]
33. Zhu, G.; Li, D.; Zhang, A.; Pi, G.; Tang, Y. The influence of laser and powder defocusing characteristics on the surface quality in laser direct metal deposition. *Opt. Laser Technol.* **2012**, *44*, 349–356. [CrossRef]
34. Gangxian, Z.; Anfeng, Z.; Dichen, L.; Gang, P. Model of layer thickness of thin-walled parts in laser metal direct manufacturing. *Trans. China Weld. Inst.* **2010**, *8*, 57–60.
35. Jiayu, S.; Tianbiao, Y.; Yu, Z.; Lin, Y.; Chuang, G. Research on laser cladding forming process of circumferentially inclined thin-walled cylinders. *Chin. J. Lasers* **2018**, *45*, 0802004. [CrossRef]
36. Mahmood, K.; Pinkerton, A.J. Direct laser deposition with different types of 316L steel particle: A comparative study of final part properties. *Proc. Inst. Mech. Eng. Part B J. Eng. Manuf.* **2013**, *227*, 520–531. [CrossRef]
37. Wang, X.; Deng, D.; Yi, H.; Xu, H.; Yang, S.; Zhang, H. Influences of pulse laser parameters on properties of AISI316L stainless steel thin-walled part by laser material deposition. *Opt. Laser Technol.* **2017**, *92*, 5–14. [CrossRef]
38. Yu, T.; Sun, J.; Qu, W.; Zhao, Y.; Yang, L. Influences of z-axis increment and analyses of defects of AISI 316L stainless steel hollow thin-walled cylinder. *Int. J. Adv. Manuf. Technol.* **2018**, *97*, 2203–2220. [CrossRef]
39. Xin, B.; Zhou, X.; Cheng, G.; Yao, J.; Gong, Y. Microstructure and mechanical properties of thin-wall structure by hybrid laser metal deposition and laser remelting process. *Opt. Laser Technol.* **2020**, *127*, 106087. [CrossRef]
40. Zhang, Y.; Yu, G.; He, X.; Ning, W.; Zheng, C. Numerical and experimental investigation of multilayer SS410 thin wall built by laser direct metal deposition. *J. Mater. Process. Technol.* **2012**, *212*, 106–112. [CrossRef]
41. Tan, H.; Chen, J.; Zhang, F.; Lin, X.; Huang, W. Process analysis for laser solid forming of thin-wall structure. *Int. J. Mach. Tools Manuf.* **2010**, *50*, 1–8. [CrossRef]
42. Zhu, G.; Zhang, A.; Li, D.; Tang, Y.; Tong, Z.; Lu, Q. Numerical simulation of thermal behavior during laser direct metal deposition. *Int. J. Adv. Manuf. Technol.* **2011**, *55*, 945–954. [CrossRef]
43. Alimardani, M.; Toyserkani, E.; Huissoon, J.P.; Paul, C.P. On the delamination and crack formation in a thin wall fabricated using laser solid freeform fabrication process: An experimental–numerical investigation. *Opt. Lasers Eng.* **2009**, *47*, 1160–1168. [CrossRef]
44. Pinkerton, A.J.; Li, L. An experimental and numerical study of the influence of diode laser beam shape on thin wall direct metal deposition. *J. Laser Appl.* **2005**, *17*, 47–56. [CrossRef]
45. Lu, L.; Shi, T.; Zhang, J.; Mei, Y.; Cheng, D.; Fu, G.; Yu, S. Research on surface finish of thin-wall parts by laser with coaxial inside-beam powder feeding. *J. Laser Appl.* **2021**, *33*, 022003. [CrossRef]
46. Yu, J.; Sun, W.; Huang, H.; Huang, Y. Study on the deformation control and microstructures of thin-walled parts repaired by laser cladding. *Coatings* **2020**, *10*, 369. [CrossRef]
47. Liu, J.; Li, L. Effects of powder concentration distribution on fabrication of thin-wall parts in coaxial laser cladding. *Opt. Laser Technol.* **2005**, *37*, 287–292. [CrossRef]
48. Jardin, R.T.; Tuninetti, V.; Tchuindjang, J.T.; Hashemi, N.; Carrus, R.; Mertens, A.; Duchêne, L.; Tran, H.S.; Habraken, A.M. Sensitivity Analysis in the Modelling of a High Speed Steel Thin-Wall Produced by Directed Energy Deposition. *Metals* **2020**, *10*, 1554. [CrossRef]
49. Yu, T.; Bao, Y. Research on manufacturing technology of thin-walled parts of Fe105 metal based on laser cladding. *J. Phys. Conf. Ser.* **2019**, *1187*, 032043. [CrossRef]
50. Zhang, K.; Wang, S.; Liu, W.; Long, R. Effects of substrate preheating on the thin-wall part built by laser metal deposition shaping. *Appl. Surf. Sci.* **2014**, *317*, 839–855. [CrossRef]
51. Long, R.; Sun, S.; Lian, Z. The influence of scanning methods on the cracking failure of thin-wall metal parts fabricated by laser direct deposition shaping. *Eng. Fail. Anal.* **2016**, *59*, 269–278. [CrossRef]
52. Zhang, H.; Zhu, L.; Xue, P. Laser direct metal deposition of variable width thin-walled structures in Inconel 718 alloy by coaxial powder feeding. *Int. J. Adv. Manuf. Technol.* **2020**, *108*, 821–840. [CrossRef]
53. Liu, F.; Lin, X.; Leng, H.; Cao, J.; Liu, Q.; Huang, C.; Huang, W. Microstructural changes in a laser solid forming Inconel 718 superalloy thin wall in the deposition direction. *Opt. Laser Technol.* **2013**, *45*, 330–335. [CrossRef]

54. Xiao, H.; Cheng, M.; Song, L. Direct fabrication of single-crystal-like structure using quasi-continuous-wave laser additive manufacturing. *J. Mater. Sci. Technol.* **2021**, *60*, 216–221. [CrossRef]
55. Balichakra, M.; Bontha, S.; Krishna, P.; Balla, V.K. Prediction and validation of residual stresses generated during laser metal deposition of γ titanium aluminide thin wall structures. *Mater. Res. Express* **2019**, *6*, 106550. [CrossRef]
56. Ahsan, M.N.; Pinkerton, A.J.; Moat, R.J.; Shackleton, J. A comparative study of laser direct metal deposition characteristics using gas and plasma-atomized Ti–6Al–4V powders. *Mater. Sci. Eng. A* **2011**, *528*, 7648–7657. [CrossRef]
57. Ahsan, M.N.; Bradley, R.; Pinkerton, A.J. Microcomputed tomography analysis of intralayer porosity generation in laser direct metal deposition and its causes. *J. Laser Appl.* **2011**, *23*, 022009. [CrossRef]
58. Xue, P.; Zhu, L.; Xu, P.; Ren, Y.; Xin, B.; Wang, S.; Yang, Z.; Ning, J.; Meng, G.; Liu, Z. CrCoNi medium-entropy alloy thin-walled parts manufactured by laser metal deposition: Microstructure evolution and mechanical anisotropy. *Mater. Sci. Eng. A* **2021**, *817*, 141306. [CrossRef]
59. Zhao, T.; Cai, W.; Dahmen, M.; Schaible, J.; Hong, C.; Gasser, A.; Weisheit, A.; Biermann, T.; Kelbassa, I.; Zhang, H. Ageing response of an Al–Mg–Mn–Sc–Zr alloy processed by laser metal deposition in thin-wall structures. *Vacuum* **2018**, *158*, 121–125. [CrossRef]
60. Huang, Y.-L.; Liu, J.; Ma, N.-H.; Li, J.-G. Three-dimensional analytical model on laser-powder interaction during laser cladding. *J. Laser Appl.* **2006**, *18*, 42–46. [CrossRef]
61. Cong, W.; Ning, F. A fundamental investigation on ultrasonic vibration-assisted laser engineered net shaping of stainless steel. *Int. J. Mach. Tools Manuf.* **2017**, *121*, 61–69. [CrossRef]
62. Huang, W.; Chen, J.; Li, Y.; Lin, X. Laser rapid forming technology of high-performance dense metal components with complex structure. In *Proceedings of Lasers in Material Processing and Manufacturing II*; SPIE: Bellingham, WA, USA; pp. 67–75.
63. Wang, J.-H.; Han, F.-Z.; Ying, W.-S. Surface evenness control of laser solid formed thin-walled parts based on the mathematical model of the single cladding layer thickness. *J. Laser Appl.* **2019**, *31*, 022009.
64. Gu, D.D.; Meiners, W.; Wissenbach, K.; Poprawe, R. Laser additive manufacturing of metallic components: Materials, processes and mechanisms. *Int. Mater. Rev.* **2012**, *57*, 133–164.
65. Devesse, W.; De Baere, D.; Guillaume, P. Modeling of laser beam and powder flow interaction in laser cladding using ray-tracing. *J. Laser Appl.* **2015**, *27*, S29208. [CrossRef]
66. Dongsheng, L.; Tuo, S.; Shihong, S.; Weiwei, J.; Shuguang, W. Laser Cladding Forming Technology of Flat-Top Thin-Walled Part Based on Special-Shaped Base Surface. *Chin. J. Lasers* **2019**, *46*, 1102002. [CrossRef]
67. Carroll, B.E.; Palmer, T.A.; Beese, A.M. Anisotropic tensile behavior of Ti–6Al–4V components fabricated with directed energy deposition additive manufacturing. *Acta Mater.* **2015**, *87*, 309–320. [CrossRef]
68. Wang, X.; Deng, D.; Hu, Y.; Ning, F.; Wang, H.; Cong, W.; Zhang, H. Overhang structure and accuracy in laser engineered net shaping of Fe–Cr steel. *Opt. Laser Technol.* **2018**, *106*, 357–365.
69. Selcuk, C. Laser metal deposition for powder metallurgy parts. *Powder Metall.* **2011**, *54*, 94–99. [CrossRef]
70. Wang, X.; Jiang, J.; Tian, Y. A Review on Macroscopic and Microstructural Features of Metallic Coating Created by Pulsed Laser Material Deposition. *Micromachines* **2022**, *13*, 659. [CrossRef]
71. Bontha, S.; Klingbeil, N.W.; Kobryn, P.A.; Fraser, H.L. Thermal process maps for predicting solidification microstructure in laser fabrication of thin-wall structures. *J. Mater. Process. Technol.* **2006**, *178*, 135–142. [CrossRef]
72. Yang, K.; Wang, Z.D.; Chen, M.Z.; Lan, H.F.; Sun, G.F.; Ni, Z.H. Effect of pulse frequency on the morphology, microstructure, and corrosion resistance of high-nitrogen steel prepared by laser directed energy deposition. *Surf. Coat. Technol.* **2021**, *421*, 127450. [CrossRef]
73. Cao, Y.; Farouk, N.; Taheri, M.; Yumashev, A.V.; Bozorg, S.F.K.; Ojo, O.O. Evolution of solidification and microstructure in laser-clad IN625 superalloy powder on GTD-111 superalloy. *Surf. Coat. Technol.* **2021**, *412*, 127010. [CrossRef]
74. Kim, M.J.; Saldana, C. Thin wall deposition of IN625 using directed energy deposition. *J. Manuf. Process.* **2020**, *56*, 1366–1373. [CrossRef]
75. Tabernero, I.; Lamikiz, A.; Martínez, S.; Ukar, E.; Figueras, J. Evaluation of the mechanical properties of Inconel 718 components built by laser cladding. *Int. J. Mach. Tools Manuf.* **2011**, *51*, 465–470. [CrossRef]
76. Atwood, C.; Ensz, M.; Greene, D.; Griffith, M.; Harwell, L.; Reckaway, D.; Romero, T.; Schlienger, E.; Smugeresky, J. Laser engineered net shaping (LENS (TM)): A tool for direct fabrication of metal parts. In *International Congress on Applications of Lasers & Electro-Optics*; Laser Institute of America: Orlando, FL, USA, 1998.
77. Huang, F.; Jiang, Z.; Liu, X.; Lian, J.; Chen, L. Microstructure and properties of thin wall by laser cladding forming. *J. Mater. Process. Technol.* **2009**, *209*, 4970–4976. [CrossRef]
78. Hu, Y.; Wang, L.; Yao, J.; Xia, H.; Li, J.; Liu, R. Effects of electromagnetic compound field on the escape behavior of pores in molten pool during laser cladding. *Surf. Coat. Technol.* **2020**, *383*, 125198. [CrossRef]
79. Liu, H.; Ji, S.; Jiang, Y.; Zhang, X.; Wang, C. Microstructure and Property of Fe60 Composite Coatings by Rotating Magnetic Field Auxiliary Laser Cladding. *Chin. J. Lasers* **2013**, *40*, 0103007.
80. Gatzen, M.; Tang, Z.; Vollertsen, F. Effect of electromagnetic stirring on the Element Distribution in Laser Beam Welding of Aluminium with Filler Wire. *Phys. Procedia* **2011**, *12*, 56–65. [CrossRef]
81. Ning, F.; Cong, W. Microstructures and mechanical properties of Fe–Cr stainless steel parts fabricated by ultrasonic vibration-assisted laser engineered net shaping process. *Mater. Lett.* **2016**, *179*, 61–64. [CrossRef]

82. Sun, S.-H.; Hagihara, K.; Nakano, T. Effect of scanning strategy on texture formation in Ni-25 at.% Mo alloys fabricated by selective laser melting. *Mater. Des.* **2018**, *140*, 307–316. [CrossRef]
83. Xiang, S.; Li, J.; Luan, H.; Amar, A.; Lu, S.; Li, K.; Zhang, L.; Liu, X.; Le, G.; Wang, X. Effects of process parameters on microstructures and tensile properties of laser melting deposited CrMnFeCoNi high entropy alloys. *Mater. Sci. Eng. A* **2019**, *743*, 412–417. [CrossRef]
84. Liu, Z.; Qi, H. Effects of substrate crystallographic orientations on crystal growth and microstructure formation in laser powder deposition of nickel-based superalloy. *Acta Mater.* **2015**, *87*, 248–258. [CrossRef]
85. Chen, H.; Lu, Y.; Luo, D.; Lai, J.; Liu, D. Epitaxial laser deposition of single crystal Ni-based superalloys: Repair of complex geometry. *J. Mater. Process. Technol.* **2020**, *285*, 116782. [CrossRef]
86. Fu, Y.; Guo, N.; Wang, G.; Yu, M.; Cheng, Q.; Zhang, D. Underwater additive manufacturing of Ti-6Al-4V alloy by laser metal deposition: Formability, grain growth and microstructure evolution. *Mater. Des.* **2021**, *197*, 109196. [CrossRef]
87. Wang, K.; Du, D.; Liu, G.; Chang, B.; Ju, J.; Sun, S.; Fu, H. Microstructure and property of laser clad Fe-based composite layer containing Nb and B4C powders. *J. Alloys Compd.* **2019**, *802*, 373–384. [CrossRef]
88. Li, Z.; Chen, J.; Sui, S.; Zhong, C.; Lu, X.; Lin, X. The microstructure evolution and tensile properties of Inconel 718 fabricated by high-deposition-rate laser directed energy deposition. *Addit. Manuf.* **2020**, *31*, 100941. [CrossRef]
89. Xu, L.; Chai, Z.; Chen, H.; Zhang, X.; Xie, J.; Chen, X. Tailoring Laves phase and mechanical properties of directed energy deposited Inconel 718 thin-wall via a gradient laser power method. *Mater. Sci. Eng. A* **2021**, *824*, 141822. [CrossRef]
90. Xiang, K.; Chai, L.; Wang, Y.; Wang, H.; Guo, N.; Ma, Y.; Murty, K.L. Microstructural characteristics and hardness of CoNiTi medium-entropy alloy coating on pure Ti substrate prepared by pulsed laser cladding. *J. Alloys Compd.* **2020**, *849*, 156704. [CrossRef]
91. Hansen, N. Hall–Petch relation and boundary strengthening. *Scr. Mater.* **2004**, *51*, 801–806. [CrossRef]
92. Shi, Y.; Wang, Y.-D.; Li, S.; Li, R.; Wang, Y. Mechanical behavior in boron-microalloyed CoCrNi medium-entropy alloy studied by in situ high-energy X-ray diffraction. *Mater. Sci. Eng. A* **2020**, *788*, 139600. [CrossRef]
93. Liu, X.; Laplanche, G.; Kostka, A.; Fries, S.; Pfetzinger-Micklich, J.; Liu, G.; George, E. Columnar to equiaxed transition and grain refinement of cast CrCoNi medium-entropy alloy by microalloying with titanium and carbon. *J. Alloys Compd.* **2019**, *775*, 1068–1076. [CrossRef]
94. Peters, M.; Hemptnermacher, J.; Kumpf, J.; Leyens, C. Structure and properties of titanium and titanium alloys. In *Titanium and Titanium Alloys: Fundamentals and Applications*; Wiley-VCH: Hoboken, NJ, USA, 2003; pp. 1–36.
95. Qiu, C.; Ravi, G.A.; Dance, C.; Ranson, A.; Dilworth, S.; Attallah, M.M. Fabrication of large Ti-6Al-4V structures by direct laser deposition. *J. Alloys Compd.* **2015**, *629*, 351–361. [CrossRef]
96. Balla, V.K.; Das, M.; Mohammad, A.; Al-Ahmari, A.M. Additive Manufacturing of γ -TiAl: Processing, Microstructure, and Properties. *Adv. Eng. Mater.* **2016**, *18*, 1208–1215. [CrossRef]
97. Long, R.-S.; Liu, W.-J.; Xing, F.; Wang, H.-B. Numerical simulation of thermal behavior during laser metal deposition shaping. *Trans. Nonferrous Met. Soc. China* **2008**, *18*, 691–699. [CrossRef]
98. Bergman, T.L.; Lavine, A.S.; Incropera, F.P.; DeWitt, D.P. *Introduction to Heat Transfer*; John Wiley & Sons: Hoboken, NJ, USA, 2011.
99. Rangaswamy, P.; Griffith, M.L.; Prime, M.B.; Holden, T.M.; Rogge, R.B.; Edwards, J.M.; Sebring, R.J. Residual stresses in LENS[®] components using neutron diffraction and contour method. *Mater. Sci. Eng. A* **2005**, *399*, 72–83. [CrossRef]
100. Wang, L.; Felicelli, S.D.; Pratt, P. Residual stresses in LENS-deposited AISI 410 stainless steel plates. *Mater. Sci. Eng. A* **2008**, *496*, 234–241. [CrossRef]

Review

Progress on the Properties of Ceramic Phase-Reinforced High-Entropy Alloy Composite Coatings Produced via Laser Cladding

Haoran Zhang ^{1,2,3}, Yaowei Yong ^{2,*}, Fuwei Wang ^{1,3}, Yuan Liang ^{1,3}, Lin Liu ⁴, Hong Liu ^{1,3} and Yang Gao ^{1,3,*}

¹ College of Mechatronic Engineering, North Minzu University, Yinchuan 750021, China; 18738712334@163.com (H.Z.); wang_fuwei@nmu.edu.cn (F.W.); ly18895087502@163.com (Y.L.); hlongiu@163.com (H.L.)

² School of Mechanical Engineering, Ningxia University, Yinchuan 750021, China

³ Ningxia Engineering Research Center for Hybrid Manufacturing System, Yinchuan 750021, China

⁴ Department of Mechanical Engineering, University of Kansas, Lawrence, KS 66045, USA; linliu@ku.edu

* Correspondence: yywnxu@163.com (Y.Y.); 2008034@nmu.edu.cn (Y.G.)

Abstract: The production of ceramic phase-reinforced high-entropy alloy composite coatings with excellent mechanical properties, high-temperature oxidation resistance, and corrosion resistance via laser cladding is a new hotspot in the field of surface engineering. However, as high-entropy alloys have a wide range of constituent systems and different kinds of ceramic particles are introduced in different ways that give the coatings unique microscopic organization, structure, and synthesized performance, it is necessary to review the methods of preparing ceramic phase-reinforced high-entropy alloys composite coatings via laser cladding. In this paper, the latest research progress on laser cladding technology in the preparation of ceramic phase-reinforced high-entropy alloy composite coatings is first reviewed. On this basis, the effects of ceramic particles, alloying elements, process parameters, and the microstructure and properties of the coatings are analyzed with the examples of the in situ generation method and the externally added method. Finally, research gaps and future trends are pointed out, serving as a reference for the subsequent research, application, and development of the preparation of ceramic phase-reinforced high-entropy alloy composite coatings.

Keywords: laser cladding; surface modification; ceramic reinforcement; protective coatings; high-entropy alloy; fabrication methods

1. Introduction

High-entropy alloys (HEAs) are a category of alloys constituted by five or more elemental components combined in equiatomic or near-equiatomic proportions. These alloys are characterized by a mixing entropy that exceeds the melting entropy of the alloy, enabling the formation of a high-entropy solid-solution phase [1]. High-entropy alloys, also known as multiprincipal element alloys, were discovered in 2004 by Ye et al. [2] from Taiwan, and Cantor et al. [3] from Britain published the research results of preparing HEAs; since then, a research upsurge of HEAs was set off. High-entropy alloys have four main effects: a high entropy effect in thermodynamics, a lattice distortion effect in structure, a hysteresis diffusion effect in dynamics, and a cocktail effect in properties [4,5]. These four effects allow it to exhibit many excellent properties that are superior to traditional alloys, such as high fatigue resistance [6], hardness [5], high wear resistance [7], excellent corrosion resistance [8], and good thermal stability [9]. Bulk amorphous alloys have become a new research area and represent an important direction of the future development of materials. Because of the highly mixed entropies of these alloys, they form solid solutions with simple crystalline structures in which CoCrCuFeNi acts as a representative of a face-centered cubic solid solution (FCC), body-centered cubic solid solution (BCC) supported by AlCoCrFeNi,

and hexagonal close packing (HPC). The orthorhombic structure or a combination of these phases can be achieved by altering the high-entropy alloying elements. The combination of high-entropy alloy coatings and new surface treatment technologies provides new research ideas to enhance the comprehensive performance of the base material, such as hardness, wear resistance, and corrosion resistance. In the last decade, researchers have been investigating the mechanisms of laser-cladded coatings to improve the overall performance of coatings for industrial applications. Studies have indicated that adding ceramic particles to high-entropy alloys can significantly improve the mechanical properties of coatings, wear resistance, and other comprehensive properties [10,11]. Ceramic particles have superior properties, such as high-temperature resistance and wear resistance. Usually, the addition of ceramic particles in composites can significantly improve the hardness and wear resistance of the composites so as to obtain composites with excellent performance. Liu et al. [12] added solid lubricant (MoS_2) and hard ceramic-reinforcing particles (B_4C) in an Al 7075 aluminum alloy matrix alloy, which is used for automotive hybrid aluminum composites so that the abrasion resistance and the coefficient of friction of aluminum hybrid composites can be significantly improved. Ceramic particles are often introduced into high-entropy alloys (Figure 1), which are mainly divided into metal ceramics and non-metal ceramics and their selection, which is based on suitable ceramic content and the matching between ceramics and high entropy. Selecting the appropriate ceramic content and matching ceramic and high-entropy alloy coatings is the key to ensuring the strong synergistic performance of the molten cladding layer. High-entropy alloy composite coating materials integrate the superior strength, toughness, and processability of metals with the outstanding wear resistance and corrosion resistance of ceramics, thus amalgamating the merits of both material categories, expanding the prospects for combining materials science and metallurgy, and providing a potential new research direction for the manufacture of materials with high abrasion resistance, corrosion resistance, and other high-end needs [13,14].

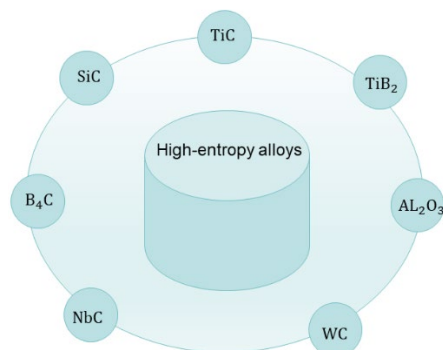


Figure 1. Types of ceramic particles often involved in high-entropy alloys.

The manufacturing processes for high-entropy alloy coatings include a variety of main processes, including magnetron sputtering [15], laser cladding [16], electrodeposition [17], plasma spraying [18], etc. Laser cladding is the preparation of a selected powder system on the surface of the substrate. It uses a high-energy density laser as a heat source to melt the material on the surface of the workpiece substrate, form a coating with special physicochemical properties, and achieve the connection of the coating. The substrate material is a large amount of protective gas required to prevent oxidation of the melting process during the laser cladding process. Ultrasound assistance and monitoring systems are usually added. The laser coating equipment and the heat-affected zone of the coating process are illustrated in Figure 2. To date, laser cladding and thermal spraying are the more popular methods to prepare high-entropy alloy coatings. The combination of thermal spraying coating and the substrate is mainly mechanical inlay, while the combination of laser cladding coating and the substrate is a metallurgical combination, which has better performance under heavy load impact. Mu et al. [19] used thermal spraying technology to prepare AlCoCrFeNi high-entropy alloy coatings compared with Cai et al. [20], who

used the laser cladding method to prepare FeCoCrNiAl; it can be clearly seen that the laser cladding method of high-entropy alloy coatings has the characteristics of small deformation, high density, low dilution, a wide range of powder selection, good metallurgical bonding, etc. It is obvious that the high-entropy alloy coatings prepared via laser cladding have the characteristics of small deformation, high density, low dilution rate, a wide range of powder selection, and good metallurgical bonding [21,22]. In the current manufacturing field, the production of high-performance coatings via laser deposition welding is a key solution for achieving complex, extreme, highly sensitive, and efficient application environments, which offers wide developmental potential in repairing defective parts and improving the mechanical properties of workpiece surfaces and is usually applied in the fields of aerospace, machinery, and medical equipment [23,24].

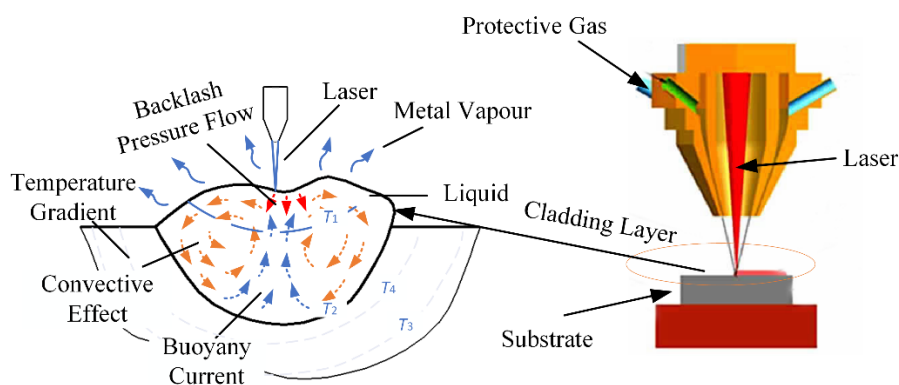


Figure 2. Heat-affected zone (HAZ) with melt pool and device schematic.

The frictional wear of mechanical components during operation leads to a shortening of the service life of components and the failure of machinery and equipment, resulting in a large waste of energy and materials. More than 30% of the world's available energy is lost due to friction and wear, and more than 70% of industrial components are scrapped due to friction and wear [25]. In aviation, navigation, and related fields, materials are subjected to stringent demands for corrosion resistance, high-temperature wear resistance, and oxidation resistance. For example, 304 stainless steels are popularly utilized in vehicles, marine, and other fields, which have superior corrosion prevention and mechanical properties but poor hardness and wear resistance. TC4 alloy is usually applied in the aerospace field, with higher requirements for hardness and wear properties. The use of high-entropy alloy composite coatings reinforced with a ceramic phase on the surface of critical parts is therefore considered to be an effective way to enhance the comprehensive performance of the parts. Therefore, numerous researchers have used surface modification techniques such as CMT to increase mechanical properties such as wear resistance and hardness of mechanical parts [26]. The preparation of ceramic phase-reinforced high-entropy alloy composite coatings on the surface of critical parts is an effective method to enhance the comprehensive performance of the parts. Laser coating preparation is used for ceramic phase-reinforced high-entropy alloy composite coatings with excellent corrosion resistance, wear resistance, and high hardness. Most researchers focus on the alloying element ratio of the high-entropy alloy coating, the parameters of the coating process, and the heat treatment process on the coating properties of the research. The production method of high-entropy alloy composite coatings and the correlation between the microstructure and the performance of the high-entropy alloy composite coatings summarized are still insufficient. The present paper reviews the research progress of ceramic phase-reinforced high-entropy alloy composite coatings in recent years. It focuses on the analysis and summary of the method of producing composite coatings in terms of the microstructure and properties of high-entropy alloy composite coatings. The purpose of this analysis is for the future use of laser cladding for the production of composite coatings from high-entropic alloys and to conduct in-depth research to bring enlightenment.

2. Preparation of Ceramic Phase-Reinforced High-Entropic Alloy Composite Coatings

Different composition systems of high-entropic alloys determine the clad layer's mechanical, physical, and electrochemical properties and the workpiece's application range after cladding. The production of high-entropy alloy composite coatings on the surface of the substrate using laser cladding is divided into two main categories: the in situ generation method and the additive method, as depicted in Figure 3. Using the above two methods, the high-entropy alloy composite coating used to introduce the ceramic phase can be caused by the transformation of the internal phase structure of the coating. Changes in grain size or the formation of new phases contribute to enhancements in the hardness, wear resistance, corrosion resistance, high-temperature oxidation resistance, and other properties of the high-entropy composite coating.

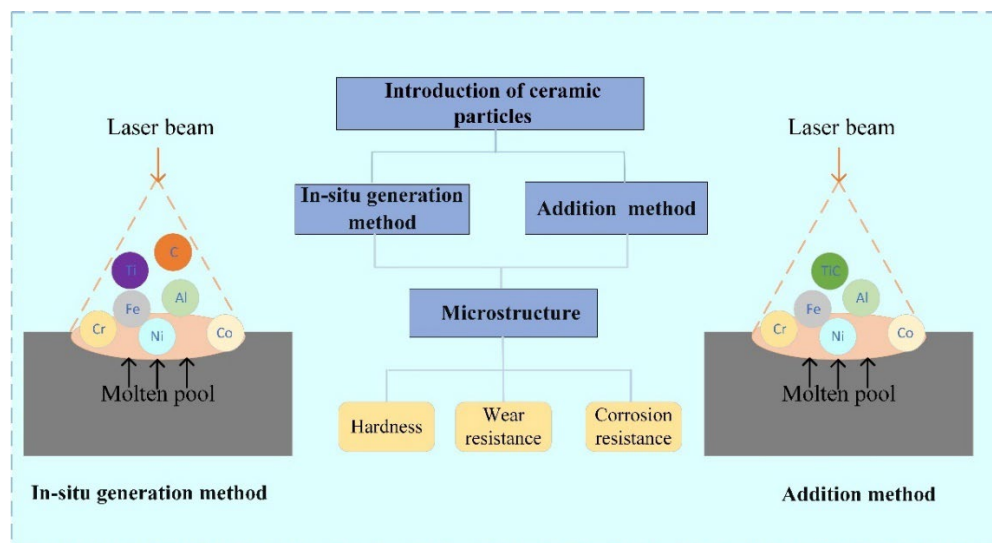


Figure 3. Schematic diagram of the introduction method of ceramic particles.

2.1. In Situ Generation Method

The in situ generation method refers to the in situ generation of the ceramic phase during the preparation of composite coatings and is based on the reaction between the raw materials or between the raw materials and the surrounding gases in the plasma. It is based on the original method of the in situ generation of metal/ceramic composite coatings, high-entropic alloy as a metal base, in situ generation of ceramic phase to improve the mechanics of high-entropic alloy composite coatings, and other comprehensive achievements. Preparing in situ-generated ceramic phase high-entropy alloy-based composite coatings using laser cladding is an effective method to solve the problem of poor interfacial bonding between ceramic particles and the metal matrix [27]. This method prepares the composite coatings with a simple process and a high deposition rate, and the matrix and composite ceramic phase possess good bonding properties and wettability. The ceramic particles generated in situ by the chemical reaction are disposed uniformly in the metal matrix, which reduces the influence between the interfaces and improves the overall performance and service life of the coating. Some researchers, including Feng et al. [28], Yang et al. [29], and Lin et al. [30], used the in situ generation of ceramic particles such as borides and carbides to significantly elevate the properties of entropy alloy coatings in terms of hardness, wear resistance, and corrosion resistance.

Guo et al. [31] successfully fabricated in situ-generated TiC ceramic-reinforced CoCrCuFeNiSi_{0.2} coatings on 304 stainless steel via laser cladding. The experimental results show that with the increase of Ti and C, the composite coating CoCrCuFeNiSi_{0.2} (Ti, C)_x change from a single FCC solid-solution structure to an FCC Solid-solution structure. With the addition of Ti and C, the in situ TiC ceramics are mainly distributed at the grain boundaries. It can be observed that the coating has a typical dendritic structure at (Ti,

C)₀, and as the (Ti, C)_x content increases, white particles gradually appear in the grain boundaries, and the size of the white particles gradually increases. The white particles are in situ-generated TiC particles. The in situ-generated TiC particles perform solid-solution strengthening and diffusion strengthening on the high-entropy coating, which significantly increases the hardness and wear resistance of the coating. With a maximum hardness of 517.2 HV_{0.2} and an average microhardness of 498.5 HV_{0.2}, the (Ti, C)_{1.0} coating has the highest hardness, nearly 2 points higher than the HEA coatings without Ti and C. The hardness of the (Ti, C)_{1.5} coating is lower than that of the (Ti, C)_{1.0} coating, but as the content of Ti and C increases, the size of the TiC particles generated in situ in the coating increases as well, weakening the reinforcing effect. (Ti, C)_{1.0} has the best wear performance; the gradual increase in TiC ceramic produced in situ lowers the coefficient of friction of the CoCrCuFeNiSi_{0.2} HEA coatings and significantly improves the coating's resistance to abrasion. During the wear process, (Ti, C)_{1.5} large ceramic particles exert a plowing effect on the coating, making wear grooves on the surface more noticeable.

The performance of high-entropic alloy composite coatings is strongly influenced by the size of in situ-generated ceramic particles. Liu et al. [32] produced AlCoCrFeNiTi_x reinforced with TiC particles in situ that were authigenic using laser cladding on the surface of AISI 1045 steel. In contrast to that, Guo et al. [31] used the laser thinning effect to extract the high-entropic Fe and C elements in the coatings from the AISI 1045 steel matrix. Two BCC phases, Fe-Cr and Al-Ni, along with a trace amount of in situ TiC phase in the form of micro- and nanoparticle-sized particles, made up the coatings. The composite coatings of CoCrCuFeNiTi_{1.0} HEA with the highest average microhardness (860.1 HV_{0.3}) exhibited a direct correlation with the increased volume fraction of the TiC particle phase (2.6%). The three-dimensional morphological characteristics and height analysis curves of the wear of the CTi₀ coating and the CTi_{1.0} coating at high-temperature conditions are provided. The wear mechanism of this coating at high-temperature coating is mainly oxidative and adhesive wear. Compared with the wear characteristics under ambient conditions, the wear under high-temperature conditions exhibits bumps caused by plastic deformation rather than obvious furrows. According to the results of the height analysis, the height variation in the wear region of the CTi_{1.0} coating is significantly smaller than that of the CTi₀ coating. These results suggest the existence of oxidative wear during the wear process, especially at high temperatures, which is usually associated with frictional heat. The micro- and nano-sized TiC particles improve the coating hardness and high-temperature friction resistance via solid-solution strengthening, diffusion strengthening, and grain refinement, demonstrating that oxidative and adhesive wear are the primary mechanisms of the coating's wear at high temperatures. Compared to high-entropy alloy coatings, different ceramics have different mechanisms and reinforcing effects. Zhou et al. [33] examined the effects of two ceramic particles, B₄C and SiC, on the mechanical properties and microstructure of CoCrMoNbTi high-entropy alloy coatings. The findings indicated that B₄C had the strongest strengthening effect on the high-entropy alloy coating's properties. The coating's microhardness increased from 666.2 HV_{0.5} to 886.9 HV_{0.5}, which was attributed to the in situ generation of TiC during the melting process from C and Ti elements in the TC₄ substrate, which served as a role in precipitation reinforcement and grain refining on the coating. Additionally, the alloy's room temperature abrasion resistance was improved, and the coefficient of friction and wear rate were significantly decreased.

Refractory alloying components (e.g., G., Nb, Ta, W, Mo, and V) cause HEA coatings to exhibit lattice distortion, obstruct dislocation motion, and encourage the development of BCC phases, thereby fortifying the coatings with the solid solution. Additionally, their larger atomic radius typically results in an increase in the solid solution's lattice constant [34], enhancing the coatings' mechanical qualities and wear resistance. Recent studies by Chang et al. [35], Xiang et al. [36], Liu et al. [37], and Li et al. [38] examined the effects of refractory alloying elements on the characteristics of high-entropy alloy coatings. Based on how well strength, plasticity, and density match, refractory alloy elements can be broadly categorized into three groups. The first group is made up of high-density W and Mo alloys

as well as other elements from the fifth and sixth subgroups. The second group is made up of low-density, high-plasticity, and high-entropy refractory alloys that contain elements from the fourth subgroup with lower density, like B, Ti, Zr, and Hf. The third category consists of elements from the third period that are added to the previously listed elements, like Al and Si. The third category combines refractory alloys with high entropy, modified strength, and toughness with third-cycle elements like Al and Si. The coordinated action of ceramic phases and refractory alloy elements is studied in high-entropy alloy composite coatings to generate new research ideas for coatings with high abrasion resistance and excellent mechanical properties. In their study, Zhao et al. [39] investigated the synergistic effect of Mo and in situ TiC on AlCoCrFeNi HEA coatings. They found that the grain size of the coating was only 1/24 of that of the AlCoCrFeNi coatings. Additionally, the hardness of the coating increased by 69.3%, and the wear resistance improved by 5.77 times due to the synergistic effect of Mo and in situ TiC.

TiB and TiC are ceramic-reinforced particles known for their excellent performance. TiB exhibits exceptional physical and thermomechanical properties [40], boasting a remarkable hardness of up to 27 GPa. On the other hand, TiC possesses a high modulus of elasticity, high hardness, low coefficient of friction, excellent chemical stability, and good wettability with the metal substrate. Additionally, coatings containing an excess of elemental Ti in solid-solution form not only significantly enhance the base material's mechanical properties and wear resistance [41] but also act as a solid lubricant, thereby reducing the coating wear rate. These properties make it a promising candidate for improving high-entropy alloy coatings. However, the in situ generation of single TiB₂ ceramic particles for high-entropy alloy coatings exhibits poor high-temperature oxidation properties and low fracture toughness. To overcome these limitations, incorporating two or more ceramic-reinforcing phases has been explored to enhance the thermal stability of high-entropy alloy coatings and achieve coating grain refinement. The resulting high-entropy alloy composite coatings exhibit high hardness, high wear resistance, and high-temperature oxidation resistance [42–44]. He et al. [45] conducted a study on the preparation of CoCrMoNbTi high-entropy alloy coatings by adding B₄C on a titanium alloy substrate using a laser melting technique. The researchers observed that as the B₄C content increased, the solid phase in the coating underwent three stages: $BCC_1 + BCC_2 \rightarrow BCC_1 + BCC_2 + TiC \rightarrow BCC_1 + BCC_2 + TiC + TiB$. In addition, two ceramic-reinforced phases, TiC and TiB, were generated in situ. These ceramic particles were found to be diffusely distributed in the coating and exhibited different morphologies. The presence of these particles inhibited grain growth and resulted in grain refinement, leading to a submicron grain size. The hardness of the coating increased from 666.26 HV_{0.5} to 954.11 HV_{0.5}, and Young's modulus increased from 168.88 GPa to 240.35 GPa. These enhancements significantly improved the hardness and tensile strength of the coating. Yan et al. [46] successfully prepared in situ Ti (C, N)-reinforced AlCoCrFeNiSi high-entropy alloy coatings with a functional gradient bilayer structure on an H13 steel substrate. This study aimed to address the poor toughness and brittleness issues of the coatings. Unlike previous studies by He et al. [45] and others, Yan et al. [46] utilized Ti and C powders as precursor reactants for Ti (C, N) ceramic particles and high-purity nitrogen as the protective gas. The involvement of nitrogen in the coating reaction resulted in the in situ generation of Ti (C, N) ceramic particles. The microhardness of the coatings and the results of the EBSD and EDS analyses are depicted in Figures 4 and 5. This study indicates that the coatings prepared via this method possess a double gradient. The first layer is an FCC solid solution, and the second layer is a mixture of disordered BCC phase (Fe-Cr) and ordered B₂ phase (Al-Ni-Ti). It has a high content of Ti (C, N) ceramic particles and TiSi₂ speckled between grain boundaries in the microstructure. The high hardness of the second layer is attributed to the diffuse reinforcement induced by the ceramic particles. The in situ-generated Ti (C, N) ceramic particles, as non-deformable particles, effectively enhance the surface hardness of the HEA gradient coating. Additionally, the reticular TiSi₂ distribution along the body-centered cubic grain boundaries impedes grain boundary migration and contributes to the microstructure refinement, further enhancing the high hardness of the

second layer. The main wear mechanisms of the coating are oxidative wear and a small amount of abrasive wear. The strong interfacial bonding between the in situ-generated Ti (C, N) particles and the HEA substrate provides the coating with high surface hardness and resistance to plastic deformation. Similar to Yan et al., Liu et al. [47] utilized high-purity nitrogen as a protective gas to melt-coat FeCoNiCrMnTix (atomic ratio $x = 0, 0.5, 1.0$, and 1.5) HEA-coated high-entropy alloy coatings onto the surface of 304 stainless steel in order to produce high-quality, defect-free coatings. This process resulted in the in situ formation of TiN particles. The coating is composed of the FCC phase, TiN phase, and Laves phase. As the Ti content ($x = 0, 0.5, 1.0$, and 1.5) increases, a stepped crystalline morphology gradually forms, and the amount of TiN particles in the coating increases, thereby enhancing the wear resistance of the coating. However, when the Ti content exceeds 1.0 reduced defects in coatings.

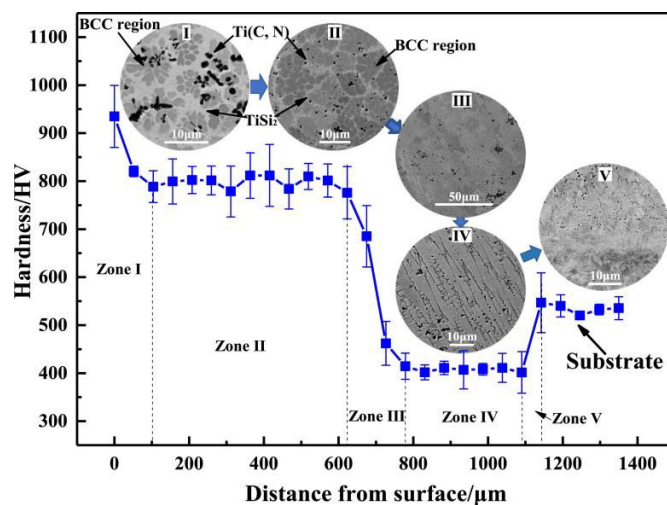


Figure 4. The hardness profile and corresponding microstructures of the HEA gradient coating [46].

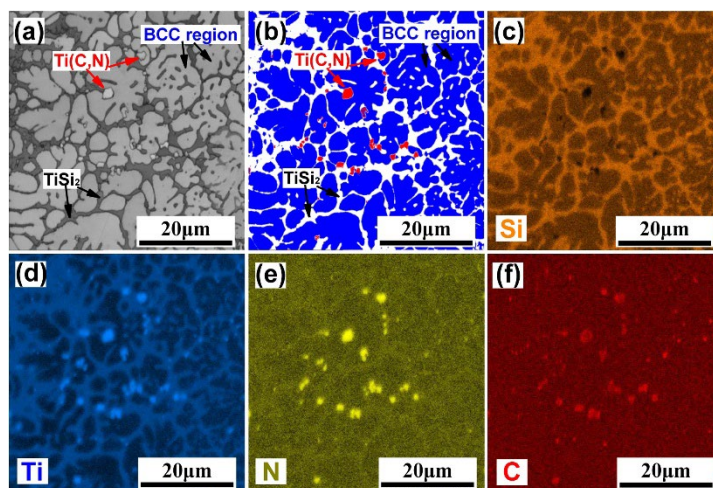


Figure 5. The EBSD and EDS results of microstructures in zone I: (a) EBSD band contrast (BC) map, (b) EBSD phase map, (c–f) EDS element distribution maps for Si, Ti, N, and C [46].

Currently, laser cladding primarily utilizes various in situ generation methods to enhance the ceramic phase. These methods include in situ single generation, in situ single generation with high melting point element doping, in situ double generation, in situ multi-gradient generation, and others. These methods are illustrated in Figure 6. Research has shown that ceramic particles generated in situ from some elements in the matrix are concentrated in the submicron or micro-nanometer level and exhibit uniform distribution.

Increasing the ceramic particle content effectively enhances the composite coating's hardness, wear resistance, and high-temperature abrasion resistance. However, the overall content of ceramic particles in the composite coatings is relatively low. Alternatively, content generated in situ are added to the elements to obtain a relatively high ceramic content in the entropy alloy composite coatings. In that case, the size of the ceramic particles will gradually increase with the increase in element content. Once the ceramic particles reach a certain size, the comprehensive performance of the composite coatings will decrease. Therefore, it is necessary to investigate the optimal content ratio of the elements to obtain excellent performance of the coatings when using this method to obtain ceramic particles. The in situ generation of single-phase ceramic phases is a straightforward process, allowing for the easy prediction and analysis of the phase composition of the composite coating after fusion coating. The combined action of high melting point elements and ceramic phases can further refine the grains and enhance composite coatings' wear resistance and mechanical properties compared to the generation of single ceramic phases. However, the high melting point elements come at a higher cost. The in situ generation of dual ceramic phases compensates for the single ceramic phase's limitations in terms of high-temperature oxidation and other properties. Building on this, in situ multi-ceramic phase gradient generation solves the issue of poor toughness in the coating. It can yield composite coatings with good hardness and plastic properties by increasing the ceramic content. Nevertheless, the method of coating preparation becomes more complex, and controlling the composition of the coating phase in each layer and the overall ceramic content is challenging. Each method has its advantages and disadvantages. However, different in situ generation methods can yield different phases and unique microstructures, further enhancing the hardness, abrasion resistance, high-temperature oxidation resistance, and corrosion resistance of high-entropy alloy coatings. These methods provide new design ideas for obtaining high-quality, high-entropy alloy coatings.

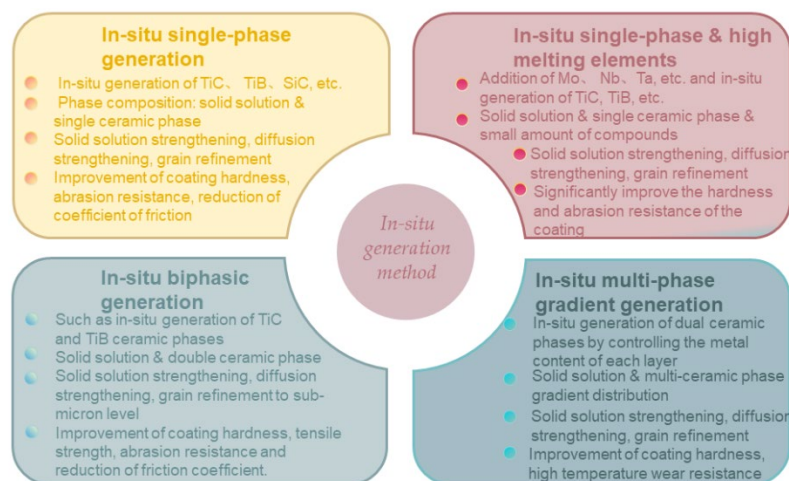


Figure 6. Summary of in situ generation method.

2.2. Addition Method

The additive method involves mixing ceramic powder and high-entropy alloy powder according to a certain proportion, ball milling the mixture, and pre-positioning it on the surface of the substrate. Alternatively, synchronous powder delivery can be used under the protection of inert gas or in a vacuum environment using a laser heat source to melt the pre-positioned coatings or spray powder, so that the powder into the metal substrate surface to form a ceramic phase reinforced by the high-entropy alloy coatings. The pre-positioning method is commonly used in experimental protocols where the powder particles are on the nano-scale, and the simultaneous powder feeding is mostly used for mixed powders of tens of microns or more.

The external addition method allows for the accurate control of the size and content of ceramic particles in high-entropy alloy composite coatings compared to the in situ generation method. Wang et al. [48], Li et al. [49], and Xi et al. [50] discovered that a small number of small-sized ceramic particles can greatly refine the grain size of the target material and effectively enhance its mechanical properties. Cai et al. [51] conducted an investigation on the laser fusion coating of FeMnCrNiCo + x(TiC) (x = 0, 5, 10, 15 wt%) coatings. The experiments involved adding a mixture of TiC ceramic particles with particle sizes ranging from 10 μm to 20 μm . This study shows that the joint action of TiC ceramic particles with small-size particles (SSP), large-size particles (LSP), and precipitation phase at the grain boundary can refine the metal grains of the coating. The average grain size in the CoCrNiMn fusion cladding layer is 75.881 μm . However, with the addition of x = 0, 5, 10, 15 wt% TiC ceramic particles, the average grain size decreases to 36.061 μm , 29.714 μm , and 25.706 μm , respectively. This grain refinement significantly improves the resistance to plastic deformation of the fusion cladding layer. It is important to note that the plastic deformation resistance of the fusion-coated layer is significantly improved. However, as the ceramic content increases, coating cracks tend to extend along the grain direction. Additionally, excessive ceramic content during the friction process can accelerate the detachment of ceramic particles from the surface of the coating. Li et al. [52], in order to further improve the hardness and abrasion resistance of the AlCoCrFeNi high-entropy alloy, investigated the effect of different ceramic contents on the performance of the high-entropy coatings. Experiments in the AlCoCrFeNi high-entropy alloy with different mass fractions (10%, 20%, 30%) of NbC ceramic particles were added, and the coatings were prepared using the laser cladding method to study the organizational evolution and mechanical behaviors of the composite coatings with different contents of NbC particles. NbC particles are mainly distributed in the grain boundaries of the high-entropy alloys, and the NbC particles have a strong pinch effect, which has unique advantages in inhibiting the growth of high-entropy alloys' grains. NbC particles have a strong pinch effect, which has a unique advantage in inhibiting the grain growth of high-entropy alloys, and the FCC phase in the coating decreases as the content of NbC particles increases. When the mass fraction of NbC particles is 20%, the alloy has the highest hardness (525 HV), the best wear resistance with an average coefficient of friction value of 1.023, and a mass loss of 1.05 mg. The additive method allows for a flexible selection of ceramic particles, overcoming the limitations of the in situ generation method. SiC is an excellent ceramic reinforcement because of its high hardness, excellent wear resistance, superior thermal conductivity, and high-temperature oxidation resistance; it is often selected as the reinforcing phase for metallic materials. Xu et al. [53] prepared SiC particle-reinforced CoCrFeNiCu composite coatings on the surface of 316 L stainless steel using the laser melting technique. The CoCrFeNiCu (SiC)_x HEA coating is a face-centered cubic structure, and a second phase consisting of Cr₇C₃ is formed at the grain boundaries. Grain boundary strengthening improves the hardness, wear resistance, and corrosion resistance. For the CoCrFeNiCu (SiC)₁₅ HEA coating, the microhardness, wear, and friction coefficients were 568.4 HV, 0.9 mg, and 0.35, respectively. With the increase of SiC content, the corrosion resistance of CoCrFeNiCu (SiC)_x HEA coatings in 3.5% NaCl solution increases. The corrosion performance of the CoCrFeNiCu (SiC)_{1.0} coatings is better than the other coatings, and the wear resistance, tribological properties, and corrosion resistance of CoCrFeNiCu high-entropy alloy with the addition of SiC ceramic phase are significant. The wear resistance, tribological properties, and corrosion resistance of CoCrFeNiCu high-entropy alloy with SiC ceramic phase are significantly improved. In the high-entropy alloy composite coatings with added ceramics, changes in the atomic ratio of certain constituent elements in the high-entropy alloy base will cause a phase change in the coating and thus improve the coating properties and the effect of changes in the atomic ratio in the high-entropy coatings on the properties of the composite coatings can be conveniently realized by the additive method. Xu et al. [54] investigated the effect of the content of Al and Ti on the properties of the AlCoCrFeNiTi HEA coatings reinforced by SiC particles under laser melting conditions. The influence of

Al and Ti element content on the characteristics of AlCoCrFeNiTi coatings reinforced with SiC particles under laser melting conditions was examined. The microstructures, phase compositions, mechanical properties, and corrosion resistance of the coatings with and without SiC particles were analyzed and compared, offering novel research to elucidate the advancement of high-strength and high-wear-resistant high-entropy alloy coatings. The results show that SiC particles decompose into Si and C during liquid phase deposition. The cubic phase L_{21} in the $Al_{0.5}$ alloy coatings precipitates out of the disordered BCC matrix and transforms into the coarse lath-like organization composed of the L_{21} and FCC matrix in the $Al_{0.5}/SiC$ coatings. Meanwhile, the braided network structure in the $Al_{0.8}/SiC$ alloy coatings was more refined with the increase of the volume fraction of the B2 phase. The hardness of the $Al_{0.8}/SiC$ alloy coatings increased from 637 $HV_{0.2}$ to 718 $HV_{0.2}$, and the coefficient of friction was reduced from 0.40 to 0.31. The presence of SiC particles exerted a detrimental impact on the microhardness of the $Al_{0.5}/SiC$ alloy coating, leading to a decrease from 743 $HV_{0.2}$ to 679 $HV_{0.2}$. This was attributed to the coarsening of the microstructure and an increased fraction of the supple FCC solid solution. The formation of a fine cubic L_{21} phase in the disordered BCC matrix in the $Al_{0.5}$ alloy coatings was replaced by a lath-like coupled organization consisting of FCC and L_{21} phases. As a result, the coating microhardness shows a decreasing trend.

High-content ceramic particles reinforced laser fusion composite coatings are brittle and generate huge thermal stresses during the laser fusion process, which often leads to the presence of cracks. The selection and design of metal matrix materials is an effective way to solve the cracking problem of metal–ceramic composite coatings. Due to the special composition design, high-entropy alloys (HEAs) have excellent wear resistance, corrosion resistance, and high-temperature softening resistance. In particular, HEAs with face-centered cubic (FCC) single solid-phase structures exhibit good toughness and corrosion resistance but low hardness and strength. Combining FCC HEAs with ceramic particles can obtain composite coatings with high strength and toughness. Ma et al. [55] successfully prepared a crack-free 60 wt% WC particle-reinforced FeCoNiCr high-entropy alloy composite coating. The composite coating consists of a face-centered cubic (FCC) solid-solution phase, WC, W_2C , and Co_4W_2C . The composite coating consists of dendrites, massive precipitated phases, and herringbone-like precipitated phases distributed around the WC particles. The composite coating has no obvious weaving structure. The average microhardness of the composite coatings was 506 $HV_{0.05}$. The average coefficient of friction and wear volume loss were 0.474 and 0.041 mm^3 , respectively, significantly improving the coatings' hardness and wear resistance.

When the physical properties of the ceramic particles and the alloy matrix are different, increasing residual stresses within the coating as the ceramic addition increases can lead to cracks within the coating. According to studies [56–60], the best option to reduce residual stresses and enhance wear and corrosion performance is to use gradient coatings with continuous compositional content variations. Functional gradient coatings on ceramic and metallic materials lead to coatings with continuous gradient behavior in terms of organization and properties. These coatings meet the specific performance requirements at different locations of the part and address the defects associated with poor bond strength and rapid changes in properties at the metal/ceramic interface. Wang et al. [61] and Chen et al. [62] showed that gradient coatings improve the performance of ceramic composite coatings to a large extent and provide new ideas for surface modification and repair of parts. Zhang et al. [63] explored a new method of ceramic-reinforced CoCrFeNiMo_{0.2} high-entropy alloy composite gradient coating in order to strengthen the high-entropy alloy with a face-centered cubic structure, and the design of the coating on the substrate surface. SiC was not added to the first layer of material to improve the bonding strength between the coating and the matrix, and the SiC content was increased layer by layer. Process optimization parameters were used, and each layer was cooled for three minutes after fusion coating to reduce heat accumulation. The cross-sectional SEM images of the gradient coatings are shown in Figure 7, with good bonding between the coating and

the substrate and between the coating and the interlayer, no cracks within the coating, and obvious porosity in the fourth layer, and the morphology of the coatings is directly correlated with the increase in SiC content. When a high-power laser melts, silicon carbide mainly decomposes into graphite and silicon vapor. Some carbon atoms dissolve in the solid solution, while others combine with other alloying elements to form carbides. Excessive decomposition of silicon carbide leads to an excess of elemental carbon. In a high-temperature melt pool, the carbon adsorbs to each other and covers the gaseous material, slowing down the release of the gas. The melt pool solidifies rapidly, and the gases have no time to escape. As a result of the pressure, a structure with large pores on the coating and small pores underneath is eventually formed. The gradient coatings prepared using this method possessed good frictional and mechanical properties, with the second, third, and fourth layers exhibiting significantly higher average hardnesses, measured at 594 HV, 722 HV, and 788 HV, respectively, which can be attributed to the presence of a body-centered cubic structure, carbides, and grain-boundary strengthening effects. The hardness of these layers is three to four times higher than that of the first layer. The wear mechanism changes from adhesive wear to abrasive wear as the number of coating layers increases. The wear rates of the second, third, and fourth layers were all reduced by at least 87% compared to the first layer. However, different forms of abrasive wear were observed between these layers. The results of this study have important engineering implications.

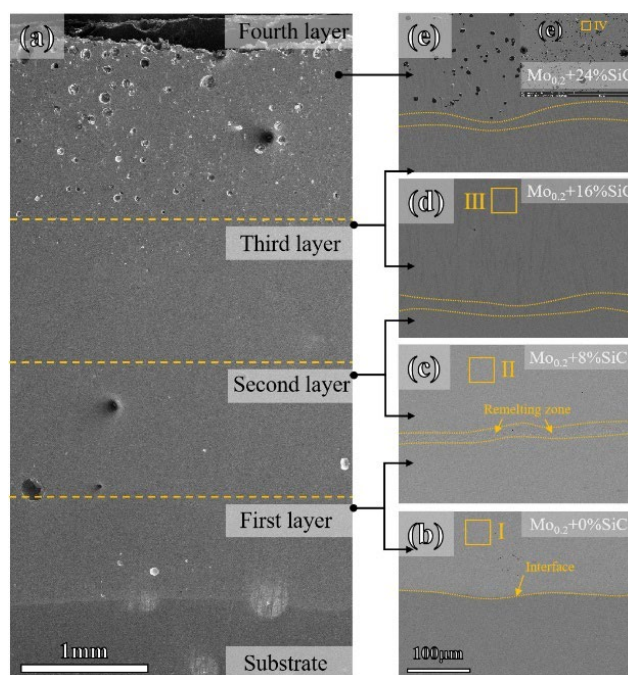


Figure 7. (a) full view of the cross section of the gradient coating; (b) the bonding area between the substrate and the coating; (c) combined area of the first and second layers; (d) combined area of the second and third floors; (e) combined area of the third and fourth floors [63].

The additive method is currently focused on the high-entropy alloy to add a ceramic phase, high-entropy alloy of certain elements in the change on the addition of ceramic phase after the coating performance, gradient composite coatings, and other research methods as shown in Figure 8, each method of ceramic particles added to the content and size of the different will have an impact on the coating organization and thus affecting the performance of the coating. Compared to the in situ generation method, the additive method can flexibly control the size and content of ceramic particles in the coating. Although the coating obtained via the additive method is easy to produce micro-cracks along the direction of the ceramic particles, via the control of the ceramic content, particle size, and

process parameters, it can effectively control the cracks produced by the coating to obtain excellent performance.

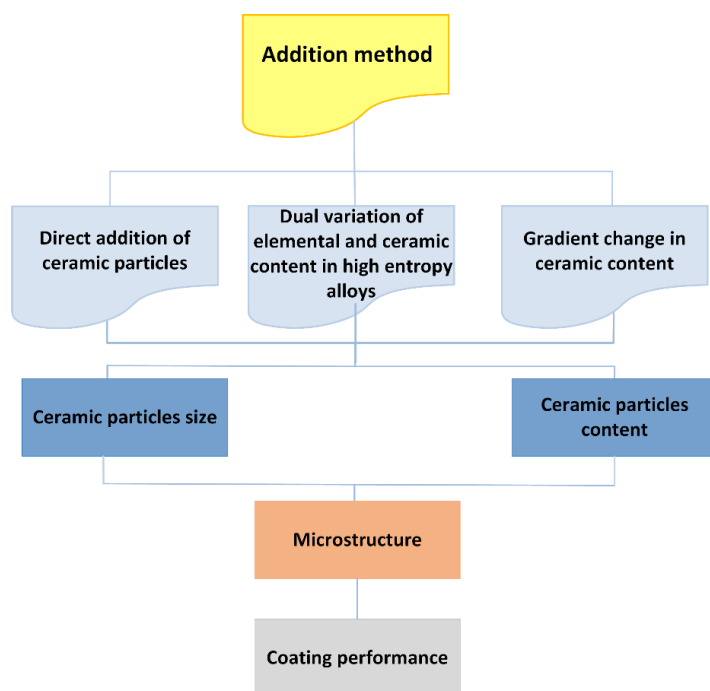


Figure 8. Summary chart of additive method studies.

3. Discussion

There are many factors affecting the surface quality and coating properties of high-entropy alloy composite coatings, which can be mainly classified into three categories. As shown in Figure 9, the first category is the laser process parameters and laser characteristics, such as laser power, spot size, focal length and laser wavelength, beam profile, polarization, and so on. The second category is the substrate surface parameters such as protective gas, scanning path, scanning speed, lap rate, and preheating and heat treatment of the substrate. The third category is the properties of high-entropy alloy composite coatings. The method of introducing ceramic particles, the size of ceramic particles, the content of ceramic particles in the high-entropy coating, and the uniformity of ceramic particles within the coating all have a non-negligible effect on the properties of high-entropy alloy composite coatings. This paper focuses on the collation and in-depth discussion of the influence of the third category of influencing factors on the microstructure and macroscopic properties of ceramic phase-reinforced high-entropy alloy composite coatings. The main approaches for preparing ceramic phase-reinforced high-entropy alloy composite coatings using the laser melting method are the in situ generation method and additive method. The in situ generation method utilizes laser thermal energy to generate the ceramic phase by chemical reaction in situ. The ceramic phase obtained is uniformly distributed, and the coating forms a good metallurgical bond with the substrate, which can reduce the stress concentration on the coating, thus effectively reducing the phenomena of coating cracking and ceramic particle detachment. The ceramic particles synthesized by this method are much finer, which can effectively prevent the growth of grain branching and thus refine the grains. However, it is difficult to control the content of ceramic particles in the coating by the in situ generation method, making it challenging to obtain high-entropy alloy coatings with high ceramic content. Compared with the in situ generation method, the addition method shows a more controllable coating composition, which enables to obtain high-entropy alloy coatings with high ceramic content, and the size of ceramic particles in the coatings can be precisely controlled. However, it is prone to phenomena such as cracks and micropores inside the coating, which makes it difficult to obtain uniformly distributed

ceramic particles. In general, selecting the appropriate preparation method based on the properties of the desired coating can effectively minimize coating defects and result in a high-quality coating. Overall, the specific choice of preparation method needs to be rationally selected according to the performance of the desired coating so as to obtain a high-quality coating. Based on the above discussion, we further summarized the data in the reported literature on the effect of coating preparation methods on the microstructure and properties of coatings, as shown in Table 1.

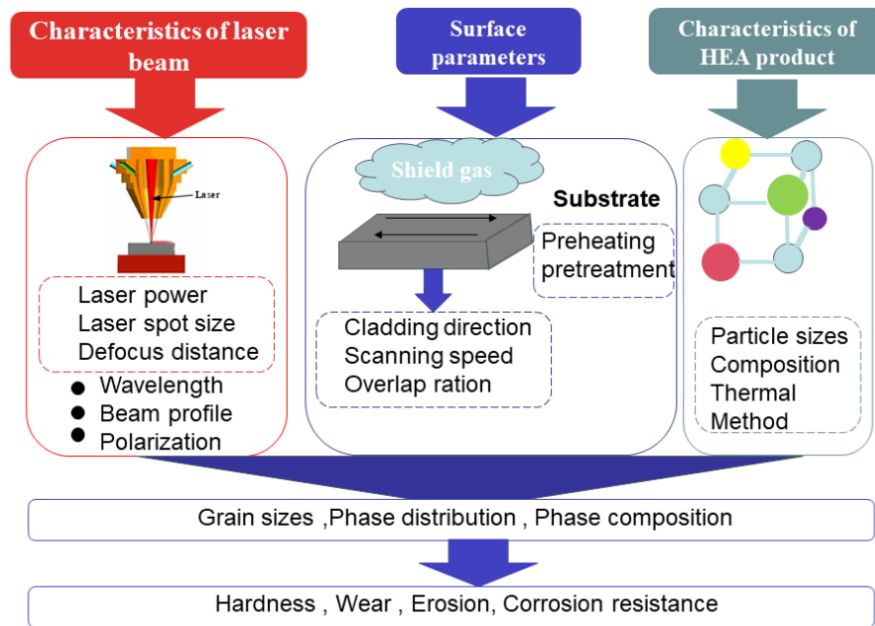


Figure 9. Factors affecting ceramic phase-reinforced high-entropy alloy composite coatings.

Table 1. Overview of process parameters, HEA compositions, ceramic particles, microstructures, and major properties.

Preparation Method	Process Parameters	Substrate Materials	HEAs	Ceramic Particles	Phase (Minor–Major)	Optimal Performance	Ref.
In situ	LP 1500 W SR 7.5 mm/s SD 3 mm OR 40%	304 stainless steel	CoCrCuFeNiSi _{0.2}	TiC	FCC, TiC	H = 498.5 HV WV = 0.42 mm ³	[31]
	LP 2400 W SR 5 mm/s SD 4.6 mm OR 40%	AISI 1045 steel	AlCoCrFeNiTi _x (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0)	TiC	Two BCC, TiC	H = 860.1 HV HWR = 5.8×10^{-8} mm ³ N ⁻¹ m ⁻¹	[32]
	LP 1500 W SR 5 mm/s SD 3 mm OR 35%	Ti-6Al-4 V titanium alloy	CoCrMoNbTi	TiC	BCC ₁ and BCC ₂ , TiC	H = 886.9 HV WR = 3.83×10^{-4} mm ³ N ⁻¹ m ⁻¹	[34]
	LP 1000 W SR 18 mm/s SD 35 mm OR 30%	Q235 steel	AlCoCrFeNi	Mo, TiC	BCC, TiC,	H = 1006.3 HV E _r = 243.3 Gpa	[39]
	LP 1500 W SR 5 mm/s SD 3 mm OR 35%	Ti-6Al-4V titanium alloy	CoCrMoNbTi	TiC, TiB	BCC, TiC, TiB	H = 954.11 HV E _r = 240.35 Gpa	[45]
	LP 600 W SR 8 mm/s SD 1 mm	H13 steel	AlCoCrFeNiSi	Ti(C, N)	FCC, BCC, B ₂	H = 934 HV WL = 12 mg	[46]
	LP 1500 W SR 800 mm/min SD 2 mm	Ti-6Al-4V titanium alloy	MoNbTaW	TiN/(Nb, Ti) ₅ Si ₃	TiN/(Nb, Ti) ₅ Si ₃ , BCC	H = 628.07 HV WV = 0.95×10^{-7} um ³	[64]

Table 1. Cont.

Preparation Method	Process Parameters	Substrate Materials	HEAs	Ceramic Particles	Phase (Minor–Major)	Optimal Performance	Ref.
Addition	LP 1300 W SR 5 mm/s SD 3 mm OR 30%	4Cr5MoSiV1 die steel	FeMnCrNiCo	TiC	FCC,TiC	H = 288.3 HV	[51]
	LP 2500 W SR 4 mm/s SD 3 mm OR 30%	Q235 steel	AlCoCrFeNi	NbC	FCC,BCC,NbC	H = 525 HV WL = 12 mg FC = 1.023	[52]
	LP 2000 W SR 180 mm/min SD 20.4 mm	316 L stainless steel	CoCrFeNiCu	SiC	FCC,SiC,Cr ₇ C ₃	H = 563.4 HV Ba = 471.6 mv CR = 0.040087 mm/a	[53]
	LP 2000 W SR 11 mm/s SD 4 mm	AISI1045 steel	AlxCoCrFeNiTi1-x	SiC	FCC,BCC,L2 ₁ -Ni ₂ AlTi	H = 743 HV FC = 0.31	[54]
	LP 1600 W SR 10 mm/s SD 4 mm OR 50%	316 L stainless steel	FeCoNiCr	WC	FCC,WC,W ₂ C,Co ₄ W ₂ C	H = 506 HV WV = 0.041	[55]
	LP 2100 W SR 800 mm/s SD 3 × 3 mm	45 steel	CoCrFeNiMo _{0.2}	SiC	FCC,BCC,M ₂₃ C ₆ ,M ₇ C ₃	H = 788 HV	[63]
	LP 1300 W SR 6 mm/s SD 3 mm OR 30%	304 stainless steel	CrMnFeCoNiM (M = TiC, NbC, B ₄ C)	TiC, NbC, B ₄ C	TiC:FCC,TiC NbC:FCC,NbC B ₄ C:M ₂ B, M ₂₃ C ₆ ,FCC	COF = 0.15–0.25	[65]

The elements Co, Cr, Fe, and Ni have similar atomic radii, which make it easy to form a single FCC or BCC phase. The BCC phase shows high strength and hardness but poor toughness; and the FCC phase presents high plasticity but low hardness. Many scholars introduced the elements Al, Ti, Mo, and V with large atomic radii into this alloy system to enhance the lattice distortion of high-entropy alloys, thus promoting the generation of the BCC phase. On the basis of this high-entropy alloy system, the introduction of ceramic particles using different preparation methods may effectively improve the properties of high-entropy alloys, such as hardness and wear resistance. It is clear from Table 1 that in the use of in situ generation method to obtain ceramic particles, most scholars adopt the introduction of non-metallic elements such as C, N, B, etc., which form trace intermetallic compounds with Ti elements in situ and are uniformly distributed in the coatings with the effect of dispersion strengthening, solid-solution strengthening, and grain refining, and thus significantly improve the hardness, abrasion resistance, and plastic deformation resistance of the coatings. As for the addition method, it mostly focuses on the introduction of ceramic particles such as SiC, TiC, NbC, B₄C, and WC. Since the addition method is flexible in controlling the content of ceramic particles in the coating, the ceramic content in the coating is usually higher than that of the in situ generation method, thus obtaining coatings with higher hardness and better abrasion resistance.

Regarding the preparation of high-entropy alloy composite coatings using the laser cladding method, although it has the characteristics of small deformation, high densification, low dilution rate, and good metallurgical bonding, there are still some minor deficiencies at present. The coatings prepared using the laser cladding method usually have four kinds of defects: cracks, porosity, residual stress, and rough casting organization with high chemical inhomogeneity. These phenomena have a non-negligible impact on the coating's quality and properties, and we need to adopt certain methods to reduce the defects in the preparation of high-entropy alloy composite coatings. Therefore, on the basis of choosing a suitable method of introducing ceramic particles, laser cladding defects can be reduced or eliminated in four ways. As shown in Figure 10, the main cause of cracks in the coating is the high-temperature gradient between the cladding and the substrate. Most authors have investigated the effect of heating the substrate prior to laser cladding on the quality of the coating, and positive results have been observed [66]. Liu et al. [32] obtained good quality high-entropy alloy composite coatings by preheating the substrate

at 200 degrees Celsius when preparing TiC-reinforced AlCoCrFeNi high-entropy alloy composite coatings. Therefore, the preheating treatment of the substrate before fusion coating can effectively alleviate the phenomenon of cracking of the coating with high thermal stress after fusion coating. Then, in order to improve the metallurgical bonding between the coating and the substrate, many scholars have tried to introduce an intermediate layer between the substrate and the coating to reduce the residual stress and improve the cracking phenomenon. This provides new design ideas to enhance the quality of the prepared composite coatings and reduce coating defects. At the same time, the selection of appropriate laser cladding parameters via experiments has an important reference value for improving the defects on the inner surface of the coating.

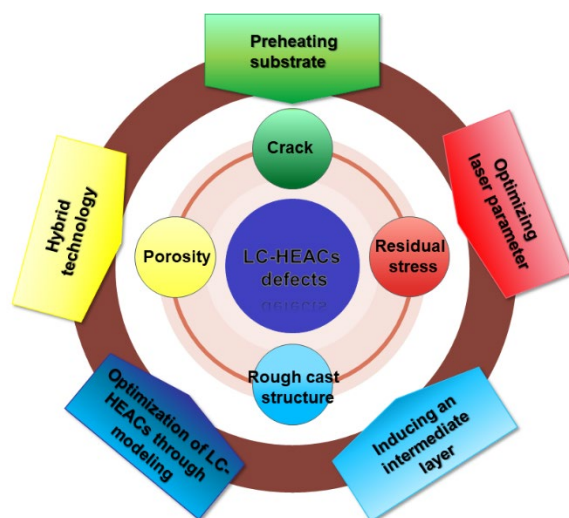


Figure 10. LC-HEAs defects and eliminates the problems of laser cladding methods.

An appropriate scanning strategy and suitable process parameters are crucial for obtaining crack-free microstructures. The laser process parameters mainly include laser power, laser scanning speed, spot diameter, powder delivery, lap rate, preset coating thickness, etc., among which the laser power and scanning speed are the main factors affecting the coating quality. The majority of research has concentrated on investigating the impact of laser process parameters on the coating properties of high-entropy alloys, with limited attention given to the exploration of laser process parameters on the coating properties of high-entropy alloys reinforced with ceramic phases. The optimal scanning power and scanning speed based on different systems in the existing literature are summarized as shown in Figure 11, which shows that the optimal laser power concentrates between 1300 and 2000 W and the optimal scanning speed lies in the range of 5–14 mm/s [31,32,34,39,45,46,51–55,64]. Therefore, this range may provide a reference for the selection of process parameters for the subsequent laser cladding process. With the development of simulation software, laser cladding process parameters can be optimized by cladding process simulation, which provides a reference for selecting the best process parameters. To improve the phenomena of elemental segregation, rough cast structure with high chemical heterogeneity, and porosity inclusions in the coating, hybrid technology is needed in the cladding process. Wen et al. [67] used a combination of substrate preheating and ultrasonic-assisted technology to obtain FeCrCoAlMn0.5Mo0.1-based HEACs with no defects and good wear and corrosion resistance. At the same time, the heat treatment technology for the high-entropy alloy composite coating after cladding can effectively diminish the grain boundary anti-cracking sensitivity and improve the wear resistance of the coating. Meanwhile, the heat treatment process of ceramic phase-reinforced high-entropy alloy coating is less studied, and the organizational evolution of ceramic phase-reinforced high-entropy alloy composite coatings via the heat treatment process is still uncertain; these directions are the focus of future research on composite high-entropy alloy coatings.

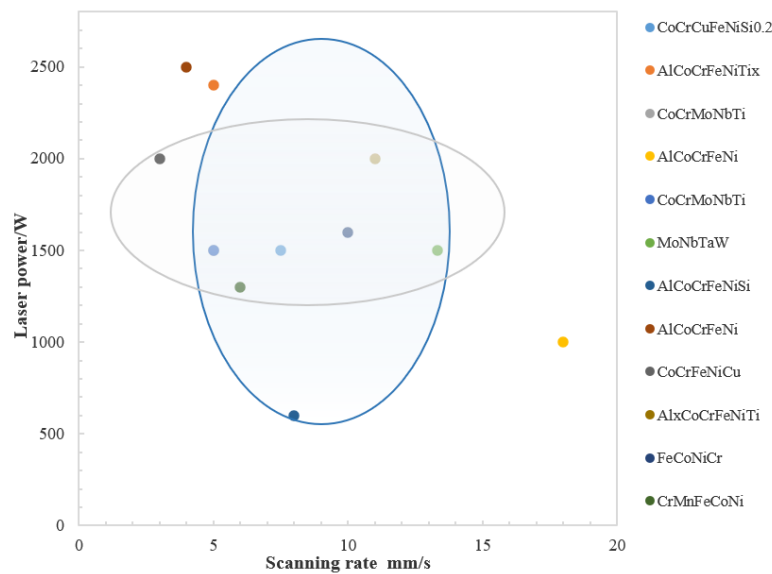


Figure 11. Power and scanning speed of ceramic phase-reinforced high-entropy alloy composite coatings.

4. Conclusions

Ceramic phase-reinforced high-entropy alloy composite coatings show excellent hardness, abrasion resistance, corrosion resistance, and high-temperature oxidation resistance, which may improve the service life of mechanical equipment and has broad industrial application prospects. In recent years, more and more researchers have committed to the study of high-entropy alloy composite coatings, but high-entropy alloy composite coatings are still in the primary stage of development. This paper reviewed the current research results, and the future developments of high-entropy alloy composite coatings are summarized as follows:

- (1) Simulation research of high-entropy alloy composite coating. The current simulation of high-entropy alloy coating is primarily based on first principle calculation, molecular dynamics simulation, and phase diagram calculation. These methods aim to predict the formation behavior of high-entropy alloy and simulate the melting process of the coating. However, the existing simulation software lacks accuracy in simulating the coupling of multiple physical fields (such as temperature, fluid, and stress) during the laser melting and cladding of high-entropy alloy composite coatings. Additionally, it does not have a comprehensive selection of coating materials, including powder particle size and preparation process. As a result, most research on high-entropy alloy composite coatings still relies on repeated experiments. To overcome these limitations, it is necessary to enhance the simulation software by introducing new options for material parameters and preparation processes. This will enable a flexible, efficient, and cost-effective research and development process.
- (2) High-entropy alloy composite coatings in extreme conditions. Existing research on the performance of ceramic phase-reinforced high-entropy alloy composite coatings mostly focuses on mechanical properties, friction properties, and electrochemical corrosion properties at room temperature. Research on extreme conditions such as thermal fatigue performance, ultra-low temperature performance, irradiation resistance, and other properties is less. Via the study of its performance under extreme conditions, it is expected to be applied to the surface protection of key components under special conditions, such as aerospace turbine blades, oil drilling parts, biomedical fields, superconducting materials, etc.
- (3) New process research. Ceramic phase-reinforced high-entropy alloy composite coatings are prone to defects such as porosity and cracks in the coating during laser melting and cladding. The development of new processes such as laser-ultrasonic

vibration composite, electric field–magnetic field synergism, and other multi-physical field composite processing processes can effectively mitigate the generation of coating defects. Obtaining high-quality coatings via new processes may facilitate industrialized production applications.

- (4) The study of different kinds of ceramic contents and self-lubricating phases in high-entropy alloy composite coatings. With the increase of ceramic content in high-entropy alloys or the mismatch between the selected ceramic phase and the high-entropy alloy system, will lead to defects such as porosity and cracks in the fusion coating process. This is due to differences in chemical potentials, thermal coefficients of linear expansion, etc. A self-lubricating phase is usually introduced to improve coating defects. Thus, it is of great interest to further investigate the different types of ceramic contents and suitable self-lubricating phases in composite coatings to improve coating defects.

Author Contributions: Conceptualization, H.Z. and Y.Y.; methodology, H.L., Y.G., H.Z. and F.W.; investigation, Y.L., L.L. and H.Z.; writing, review, and editing, H.Z. and L.L.; visualization, H.L. and Y.G.; supervision, Y.Y.; funding acquisition, H.L. and Y.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [the Ningxia Natural Science Foundation] grant number [No. 2023AAC02047], [the National Science Foundation of China] grant number [No. 51165019], [the Ningxia Engineering Research Center for Hybrid Manufacturing System Foundation] grant number [No. 2023GCJS008] And [Ningxia Key Research and Development Program (Special Talents)] grant number [2020BEB04030].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Zhang, Y.; Zhou, Y.J.; Lin, J.P.; Chen, G.L.; Liaw, P.K. Solid-Solution Phase Formation Rules for Multi-component Alloys. *Adv. Eng. Mater.* **2008**, *10*, 534–538. [CrossRef]
- Yeh, J.-W.; Chen, S.-K.; Lin, S.-J. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303. [CrossRef]
- Cantor, B.; Chang, I.T.H.; Knight, P.; Vincent, A.J.B. Microstructural development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* **2004**, *375–377*, 213–218. [CrossRef]
- Yeh, J.W.; Chen, Y.L.; Lin, S.J.; Chen, S.K. High-Entropy Alloys—A New Era of Exploitation. *Mater. Sci. Forum* **2007**, *560*, 1–9. [CrossRef]
- Zhang, Y.; Zuo, T.T.; Tang, Z.; Gao, M.C.; Dahmen, K.A.; Liaw, P.K.; Lu, Z.P. Microstructures and properties of high-entropy alloys. *Prog. Mater. Sci.* **2014**, *61*, 1–93. [CrossRef]
- Liu, K.; Komarasamy, M.; Gwalani, B.; Shukla, S.; Mishra, R.S. Fatigue behavior of ultrafine grained triplex Al_{0.3}CoCrFeNi high entropy alloy. *Scr. Mater.* **2019**, *158*, 116–120. [CrossRef]
- Wang, W.; Wang, J.; Sun, Z.; Li, J.; Li, L.; Song, X.; Wen, X.; Xie, L.; Yang, X. Effect of Mo and aging temperature on corrosion behavior of (CoCrFeNi)_{100-x}Mo_x high-entropy alloys. *J. Alloys Compd.* **2020**, *812*, 152139. [CrossRef]
- Chuang, M.-H.; Tsai, M.-H.; Wang, W.-R.; Lin, S.-J.; Yeh, J.-W. Microstructure and wear behavior of Al_xCo_{1.5}CrFeNi_{1.5}Ti_y high-entropy alloys. *Acta Mater.* **2011**, *59*, 6308–6317. [CrossRef]
- Li, Y.; Shi, Y. Microhardness, wear resistance, and corrosion resistance of Al_xCrFeCoNiCu high-entropy alloy coatings on aluminum by laser cladding. *Opt. Laser Technol.* **2021**, *134*, 106632. [CrossRef]
- Rogal, Ł.; Kalita, D.; Tarasek, A.; Bobrowski, P.; Czerwinski, F. Effect of SiC nano-particles on microstructure and mechanical properties of the CoCrFeMnNi high entropy alloy. *J. Alloys Compd.* **2017**, *708*, 344–352. [CrossRef]
- Yang, J.; Liu, W.; Fu, M.; Wen, J.; Li, K.; Lin, P.; Wang, C.; He, P.; Lin, T.; Mei, H.; et al. Joining SiCf/SiC composites to Al_{0.3}CoCrFeNi high-entropy alloys with a Cu–Ti filler alloy: Interfacial reactions, high-entropy effects, and mechanical properties. *Mater. Sci. Eng. A* **2023**, *881*, 145390. [CrossRef]
- Liu, S.; Wang, Y.; Muthuramalingam, T.; Anbuezhayan, G. Effect of B₄C and MOS₂ reinforcement on micro structure and wear properties of aluminum hybrid composite for automotive applications. *Compos. Part B Eng.* **2019**, *176*, 107329. [CrossRef]

13. Arif, Z.U.; Khalid, M.Y.; ur Rehman, E.; Ullah, S.; Atif, M.; Tariq, A. A review on laser cladding of high-entropy alloys, their recent trends and potential applications. *J. Manuf. Process.* **2021**, *68*, 225–273. [CrossRef]
14. Yang, S.; Yan, X.; Yang, K.; Fu, Z. Effect of the addition of nano- Al_2O_3 on the microstructure and mechanical properties of twinned $\text{Al}_{0.4}\text{FeCrCoNi}_{1.2}\text{Ti}_{0.3}$ alloys. *Vacuum* **2016**, *131*, 69–72. [CrossRef]
15. Braic, M.; Braic, V.; Vladescu, A.; Zoita, C.N.; Balaceanu, M. Solid solution or amorphous phase formation in TiZr-based ternary to quinary multi-principal-element films. *Prog. Nat. Sci. Mater. Int.* **2014**, *24*, 305–312. [CrossRef]
16. Ji, X.; Duan, H.; Zhang, H.; Ma, J. Slurry Erosion Resistance of Laser Clad NiCoCrFeAl₃ High-Entropy Alloy Coatings. *Tribol. Trans.* **2015**, *58*, 1119–1123. [CrossRef]
17. Yao, C.-Z.; Zhang, P.; Liu, M.; Li, G.-R.; Ye, J.-Q.; Liu, P.; Tong, Y.-X. Electrochemical preparation and magnetic study of Bi-Fe-Co-Ni-Mn high entropy alloy. *Electrochim. Acta* **2008**, *53*, 8359–8365. [CrossRef]
18. Yue, T.; Xie, H.; Lin, X.; Yang, H.; Meng, G. Microstructure of Laser Re-Melted AlCoCrCuFeNi High Entropy Alloy Coatings Produced by Plasma Spraying. *Entropy* **2013**, *15*, 2833–2845. [CrossRef]
19. Mu, Y.; Zhang, L.; Xu, L.; Prashanth, K.; Zhang, N.; Ma, X.; Jia, Y.; Xu, Y.; Jia, Y.; Wang, G. Frictional Wear and Corrosion Behavior of AlCoCrFeNi High-Entropy Alloy Coatings Synthesized by Atmospheric Plasma Spraying. *Entropy* **2020**, *22*, 740. [CrossRef]
20. Cai, Y.; Zhu, L.; Cui, Y.; Geng, K.; Manladan, S.M.; Luo, Z.; Han, J. Strengthening mechanisms in multi-phase FeCoCrNiAl_{1.0} high-entropy alloy cladding layer. *Mater. Charact.* **2020**, *159*, 110037. [CrossRef]
21. Sun, S.; Durand, Y.; Brandt, M. Parametric investigation of pulsed Nd: YAG laser cladding of stellite 6 on stainless steel. *Surf. Coat. Technol.* **2005**, *194*, 225–231. [CrossRef]
22. Menghani, J.; Vyas, A.; Patel, P.; Natsu, H.; More, S. Wear, erosion and corrosion behavior of laser clad high entropy alloy coatings—A review. *Mater. Today Proc.* **2021**, *38*, 2824–2829. [CrossRef]
23. Liu, Y.; Xiang, D.; Wang, K.; Yu, T. Corrosion of Laser Cladding High-Entropy Alloy Coatings: A Review. *Coatings* **2022**, *12*, 1669. [CrossRef]
24. Cheng, W.; Ji, L.; Zhang, L.; Wang, H.; Sun, W. Refractory high-entropy alloys fabricated using laser technologies: A concrete review. *J. Mater. Res. Technol.* **2023**, *24*, 7497–7524. [CrossRef]
25. Xie, H.; Tong, Y.; Bai, Y.; Li, X.; Han, Y.; Hua, K.; Wang, H. Wear-Resistance of High-Entropy Alloy Coatings and High-Entropy Alloy-Based Composite Coatings Prepared by the Laser Cladding Technology: A Review. *Adv. Eng. Mater.* **2023**, *25*, 2300426. [CrossRef]
26. Kołodziejczak, P.; Bober, M.; Chmielewski, T. Wear Resistance Comparison Research of High-Alloy Protective Coatings for Power Industry Prepared by Means of CMT Cladding. *Appl. Sci.* **2022**, *12*, 4568. [CrossRef]
27. Liang, J.; Yin, X.; Lin, Z.; Chen, S.; Liu, C.; Wang, C. Microstructure and wear behaviors of laser cladding in-situ synthetic (TiBx+TiC)/(Ti₂Ni+TiNi) gradient composite coatings. *Vacuum* **2020**, *176*, 109305. [CrossRef]
28. Feng, Y.; Feng, K.; Yao, C.; Li, Z.; Sun, J. Microstructure and properties of in-situ synthesized (Ti₃Al + TiB)/Ti composites by laser cladding. *Mater. Des.* **2018**, *157*, 258–272. [CrossRef]
29. Yang, L.; Yu, T.; Li, M.; Zhao, Y.; Sun, J. Microstructure and wear resistance of in-situ synthesized Ti(C, N) ceramic reinforced Fe-based coating by laser cladding. *Ceram. Int.* **2018**, *44*, 22538–22548. [CrossRef]
30. Lin, Y.; Jiang, C.; Lin, Z.; Chen, Q.; Lei, Y.; Fu, H. Laser in-situ synthesis of high aspect ratio TiB fiber bundle reinforced titanium matrix composite coating. *Opt. Laser Technol.* **2019**, *115*, 364–373. [CrossRef]
31. Guo, Y.; Li, C.; Zeng, M.; Wang, J.; Deng, P.; Wang, Y. In-situ TiC reinforced CoCrCuFeNiSi_{0.2} high-entropy alloy coatings designed for enhanced wear performance by laser cladding. *Mater. Chem. Phys.* **2020**, *242*, 122522. [CrossRef]
32. Liu, H.; Liu, J.; Chen, P.; Yang, H. Microstructure and high temperature wear behaviour of in-situ TiC reinforced AlCoCrFeNi-based high-entropy alloy composite coatings fabricated by laser cladding. *Opt. Laser Technol.* **2019**, *118*, 140–150. [CrossRef]
33. Zhou, X.; He, L.; Zhang, M.; Wang, P. Effect of ceramic particles on microstructure and properties of CoCrMoNbTi high-entropy alloy coating fabricated by laser cladding. *Optik* **2023**, *285*, 170987. [CrossRef]
34. Zhu, J.M.; Fu, H.M.; Zhang, H.F.; Wang, A.M.; Li, H.; Hu, Z.Q. Microstructures and compressive properties of multicomponent AlCoCrFeNiMox alloys. *Mater. Sci. Eng. A* **2010**, *527*, 6975–6979. [CrossRef]
35. Chang, R.; Fang, W.; Bai, X.; Xia, C.; Zhang, X.; Yu, H.; Liu, B.; Yin, F. Effects of tungsten additions on the microstructure and mechanical properties of CoCrNi medium entropy alloys. *J. Alloys Compd.* **2019**, *790*, 732–743. [CrossRef]
36. Xiang, K.; Chen, L.-Y.; Chai, L.; Guo, N.; Wang, H. Microstructural characteristics and properties of CoCrFeNiNb_x high-entropy alloy coatings on pure titanium substrate by pulsed laser cladding. *Appl. Surf. Sci.* **2020**, *517*, 146214. [CrossRef]
37. Liu, H.; Gao, Q.; Dai, J.; Chen, P.; Gao, W.; Hao, J.; Yang, H. Microstructure and high-temperature wear behavior of CoCrFeNiW_x high-entropy alloy coatings fabricated by laser cladding. *Tribol. Int.* **2022**, *172*, 107574. [CrossRef]
38. Li, Z.; Jing, C.; Feng, Y.; Wu, Z.; Lin, T.; Zhao, J. Microstructure evolution and properties of laser cladding Nb containing eutectic high entropy alloys. *Int. J. Refract. Met. Hard Mater.* **2023**, *110*, 105992. [CrossRef]
39. Zhao, W.; Yu, K.; Ma, Q.; Song, C.; Xiao, G.; Zhang, H.; Lv, Y.; Guo, N.; Li, Z. Synergistic effects of Mo and in-situ TiC on the microstructure and wear resistance of AlCoCrFeNi high entropy alloy fabricated by laser cladding. *Tribol. Int.* **2023**, *188*, 108827. [CrossRef]
40. Zhao, Y.; Yu, T.; Chen, L.; Chen, Y.; Guan, C.; Sun, J. Microstructure and wear resistance behavior of Ti–C–B₄C-reinforced composite coating. *Ceram. Int.* **2020**, *46*, 25136–25148. [CrossRef]

41. Ye, F.; Yang, Y.; Lou, Z.; Feng, L.; Guo, L.; Yu, J. Microstructure and wear resistance of TiC reinforced AlCoCrFeNi_{2.1} eutectic high entropy alloy layer fabricated by micro-plasma cladding. *Mater. Lett.* **2021**, *284*, 128859. [CrossRef]
42. Patil, A.S.; Hiwarkar, V.D.; Verma, P.K.; Khatirkar, R.K. Effect of TiB₂ addition on the microstructure and wear resistance of Ti-6Al-4V alloy fabricated through direct metal laser sintering (DMLS). *J. Alloys Compd.* **2019**, *777*, 165–173. [CrossRef]
43. Geng, L.; Ni, D.R.; Zhang, J.; Zheng, Z.Z. Hybrid effect of TiB_w and TiC_p on tensile properties of in situ titanium matrix composites. *J. Alloys Compd.* **2008**, *463*, 488–492. [CrossRef]
44. Song, R.; Li, J.; Shao, J.Z.; Bai, L.L.; Chen, J.L.; Qu, C.C. Microstructural evolution and wear behaviors of laser cladding Ti₂Ni/ α (Ti) dual-phase coating reinforced by TiB and TiC. *Appl. Surf. Sci.* **2015**, *355*, 298–309. [CrossRef]
45. He, L.; Zhang, M.; Wang, D.; Ye, X.; Zhou, Y.; Ruan, D.; Zhang, W. Microstructure and mechanical properties of in-situ dual ceramic phase synergistic strengthened CoCrMoNbTi(B₄C)_x high entropy alloy coating. *Opt. Laser Technol.* **2023**, *161*, 109172. [CrossRef]
46. Yan, G.; Zheng, M.; Ye, Z.; Gu, J.; Li, C.; Wu, C.; Wang, B. In-situ Ti(C, N) reinforced AlCoCrFeNiSi-based high entropy alloy coating with functional gradient double-layer structure fabricated by laser cladding. *J. Alloys Compd.* **2021**, *886*, 161252. [CrossRef]
47. Liu, S.S.; Zhang, M.; Zhao, G.L.; Wang, X.H.; Wang, J.F. Microstructure and properties of ceramic particle reinforced FeCoNiCrMnTi high entropy alloy laser cladding coating. *Intermetallics* **2022**, *140*, 107402. [CrossRef]
48. Wang, J.; Yang, H.; Huang, H.; Ruan, J.; Ji, S. Microstructure and mechanical properties of SiC whisker reinforced CoCrNi medium entropy alloys. *Mater. Lett.* **2019**, *254*, 77–80. [CrossRef]
49. Li, B.; Zhang, L.; Yang, B. Grain refinement and localized amorphization of additively manufactured high-entropy alloy matrix composites reinforced by nano ceramic particles via selective-laser-melting/remelting. *Compos. Commun.* **2020**, *19*, 56–60. [CrossRef]
50. Xi, L.; Gu, D.; Guo, S.; Wang, R.; Ding, K.; Prashanth, K.G. Grain refinement in laser manufactured Al-based composites with TiB₂ ceramic. *J. Mater. Res. Technol.* **2020**, *9*, 2611–2622. [CrossRef]
51. Cai, Y.; Zhu, L.; Cui, Y.; Shan, M.; Li, H.; Xin, Y.; Han, J. Fracture and wear mechanisms of FeMnCrNiCo + x(TiC) composite high-entropy alloy cladding layers. *Appl. Surf. Sci.* **2021**, *543*, 148794. [CrossRef]
52. Li, X.; Feng, Y.; Liu, B.; Yi, D.; Yang, X.; Zhang, W.; Chen, G.; Liu, Y.; Bai, P. Influence of NbC particles on microstructure and mechanical properties of AlCoCrFeNi high-entropy alloy coatings prepared by laser cladding. *J. Alloys Compd.* **2019**, *788*, 485–494. [CrossRef]
53. Xu, L.; Du, H.; Liu, J.; Feng, D.; Xia, S. Microstructure, Mechanical, and Electrochemical Properties of SiC Particle Reinforced CoCrFeNiCu High-Entropy Alloy Coatings. *Coatings* **2022**, *12*, 519. [CrossRef]
54. Xu, Y.; Wang, G.; Song, Q.; Lu, X.; Li, Z.; Zhao, Q.; Chen, Y. Microstructure, mechanical properties, and corrosion resistance of SiC reinforced Al_xCoCrFeNiTi_{1-x} high-entropy alloy coatings prepared by laser cladding. *Surf. Coat. Technol.* **2022**, *437*, 128349. [CrossRef]
55. Ma, Q.; Lu, B.; Zhang, Y.; Wang, Y.; Yan, X.; Liu, M.; Zhao, G. Crack-free 60 wt% WC reinforced FeCoNiCr high-entropy alloy composite coating fabricated by laser cladding. *Mater. Lett.* **2022**, *324*, 132667. [CrossRef]
56. Taleghani, P.R.; Valefi, Z.; Ehsani, N. Evaluation of oxidation and thermal insulation capability of nanostructured La₂(Zr_{0.7}Ce_{0.3})₂O₇/YSZ functionally graded coatings. *Ceram. Int.* **2021**, *47*, 8915–8929. [CrossRef]
57. Sopronyi, M.; Nita, C.; Le Meins, J.-M.; Vidal, L.; Jipa, F.; Axente, E.; Matei Ghimbeu, C.; Sima, F. Laser-assisted synthesis of carbon coatings with cobalt oxide nanoparticles embedded in gradient of composition and sizes. *Surf. Coat. Technol.* **2021**, *419*, 127301. [CrossRef]
58. Li, L.; Wang, J.; Lin, P.; Liu, H. Microstructure and mechanical properties of functionally graded TiC_p/Ti₆Al₄V composite fabricated by laser melting deposition. *Ceram. Int.* **2017**, *43*, 16638–16651. [CrossRef]
59. Guévenoux, C.; Hallais, S.; Balit, Y.; Charles, A.; Charkaluk, E.; Constantinescu, A. Plastic strain localization induced by microstructural gradient in laser cladding repaired structures. *Theor. Appl. Fract. Mech.* **2020**, *107*, 102520. [CrossRef]
60. Cui, Y.; Shen, J.; Geng, K.; Hu, S. Fabrication of FeCoCrNiMnAl_{0.5}-FeCoCrNiMnAl gradient HEA coating by laser cladding technique. *Surf. Coat. Technol.* **2021**, *412*, 127077. [CrossRef]
61. Wang, Q.; Li, Q.; Zhang, L.; Chen, D.X.; Jin, H.; Li, J.D.; Zhang, J.W.; Ban, C.Y. Microstructure and properties of Ni-WC gradient composite coating prepared by laser cladding. *Ceram. Int.* **2022**, *48*, 7905–7917. [CrossRef]
62. Chen, L.; Chen, Y.; Chen, X.; Yu, T.; Wang, Z. Microstructure and properties of in situ TiC/Ni functionally gradient coatings by powder-fed laser cladding. *Ceram. Int.* **2022**, *48*, 36789–36801. [CrossRef]
63. Zhang, S.; Sun, Y.; Cheng, W.; Chen, Y.; Gu, J.; Chen, G. Microstructure and tribological behavior of CoCrFeNiMo_{0.2}/SiC high-entropy alloy gradient composite coating prepared by laser cladding. *Surf. Coat. Technol.* **2023**, *467*, 129681. [CrossRef]
64. Hao, X.; Liu, H.; Zhang, X.; Tao, J.; Wang, Y.; Yang, C.; Liu, Y. Microstructure and wear resistance of in-situ TiN/(Nb, Ti)₅Si₃ reinforced MoNbTaWTi-based refractory high entropy alloy composite coatings by laser cladding. *Appl. Surf. Sci.* **2023**, *626*, 157240. [CrossRef]
65. Sun, D.; Zhu, L.; Cai, Y.; Yan, Y.; Ge, F.; Shan, M.; Tian, Y.; Han, J.; Jiang, Z. Tribology comparison of laser-cladded CrMnFeCoNi coatings reinforced by three types of ceramic (TiC/NbC/B₄C). *Surf. Coat. Technol.* **2022**, *450*, 129013. [CrossRef]

66. Huang, C.; Zhang, Y.; Vilar, R.; Shen, J. Dry sliding wear behavior of laser clad TiVCrAlSi high entropy alloy coatings on Ti-6Al-4V substrate. *Mater. Des.* **2012**, *41*, 338–343. [CrossRef]
67. Wen, X.; Cui, X.; Jin, G.; Zhang, X.; Zhang, Y.; Zhang, D.; Fang, Y. Design and characterization of FeCrCoAlMn_{0.5}Mo_{0.1} high-entropy alloy coating by ultrasonic assisted laser cladding. *J. Alloys Compd.* **2020**, *835*, 155449. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Progress in Microstructure Design and Control of High-Hardness Fe-Based Alloy Coatings via Laser Cladding

Lipei Liu ¹, Yinghua Lin ^{1,*}, Longsheng Peng ^{2,3}, Xin Kang ^{4,*} and Xinlin Wang ¹

¹ Hunan Province Key Laboratory for Ultra-Fast Micro/Nano Technology and Advanced Laser Manufacture, College of Mechanical Engineering, University of South China, Hengyang 421001, China; lipeiiliu97@163.com (L.L.); wxl_ly000@aliyun.com (X.W.)

² Hunan Lifang Roller Co., Ltd., Hengyang 421681, China; flslfls@163.com

³ Hunan Advanced Manufacturing Engineering Technology Research Center for High Wear-Resistant Alloy Materials, Hengyang 421681, China

⁴ School of Mechanical, Electrical and Information Engineering, Putian University, Putian 351100, China

* Correspondence: lyh351258@163.com (Y.L.); tokangxin@163.com (X.K.)

Abstract: High-hardness iron-based alloy coatings are extensively utilized in aerospace, automotive, and industrial equipment due to their exceptional wear resistance and long service life. Laser cladding has emerged as one of the primary techniques for fabricating these coatings, owing to its rapid cooling and dense microstructure characteristics. However, the production of high-hardness iron-based alloy coatings via laser cladding continues to face numerous challenges, particularly when controlling the morphology, quantity, and distribution of the reinforcing phases, which can lead to cracking during processing and service, thus compromising their usability. The cracks of the cladding layer will be suppressed through good microstructure design and control, resulting in a wide range of performance for high-hardness Fe-based alloy coatings. This paper reviews recent advancements in the design and control of the organization and structure of high-hardness iron-based alloy coatings from the perspectives of material composition, processing parameters, and external assistance techniques. It summarizes the properties and applications of various materials, including different alloying elements, ceramic particles, and rare earth oxides, while systematically discussing how processing parameters influence microstructure and performance. Additionally, the mechanisms by which external auxiliary energy fields affect the melt pool and solidified microstructure during laser cladding are elucidated. Finally, the future development directions of laser cladding technology for high-hardness iron-based coatings are anticipated, emphasizing the need for further quantification of the optimal coupling relationships among the gain effects of composite energy fields.

Keywords: laser cladding; surface strengthening; Fe-based alloy; high hardness; microstructure design and control

1. Introduction

As critical equipment components face increasingly stringent operating conditions and as materials science continues to evolve [1,2], there is a heightened demand for the development and application of high-hardness coatings [3]. Compared to traditional methods such as plasma welding and thermal spraying, laser cladding offers significant advantages in producing high-hardness coatings. This is due to its rapid cooling rate, high deposition efficiency, and capability to produce fine and dense microstructures in the formed component [4–6]. However, the rapid heating and cooling characteristics inherent in laser cladding [7,8], along with the differences in melting point and thermal conductivity of the coating materials [9,10], can result in high temperature gradients during the coating formation process, leading to elevated residual stresses, stress accumulation, and solidification segregation. These factors collectively increase the susceptibility to cracking. Particularly when preparing high-hardness coatings using laser cladding, the

balance—or competing relationship [11]—between strength and toughness can further intensify the cracking phenomena. Such cracking issues pose significant challenges to the broad adoption of these coatings in industrial settings.

Compared to Co-based [12] and Ni-based [13] alloys, the primary advantage of Fe-based alloys is their widespread availability and affordability [14]. Furthermore, as the matrix materials for many engineering components in contemporary applications are primarily steel-based structural materials, utilizing iron-based cladding materials ensures excellent wetting properties, resulting in a robust bond with the substrate [15–17]. However, laser cladding with iron-based alloy powder has certain limitations. These include poor self-fusibility, reduced oxidation resistance, and susceptibility to porosity and inclusions [18–20]. Moreover, high-hardness iron-based coatings often have a higher concentration of brittle phases, such as borides and carbides [19], which can induce cracking during the rapid thermal cycling inherent in the cladding process. These phenomena can cause coating failures and render the coating's microstructure inadequate for the stringent requirements posed by high-load friction and wear components [21]. The precise structural design and regulation of laser-cladded high-hardness iron-based alloy coatings are necessary to suppress the initiation and propagation of intergranular cracks during their manufacturing and operational phases, thereby enhancing the surface properties of coatings, including wear resistance, corrosion resistance, and high-temperature oxidation resistance. Advancing these methods is crucial for promoting the application of high-hardness iron-based alloy laser cladding.

Concerning the microstructural design and regulation of high-hardness Fe-based alloy coatings, this study first delves into the impact of the coating material's composition (alloy elements, ceramic particles, and rare earth oxides) on the microstructure and attributes of the coatings. Next, it highlights the regulatory influences of laser process parameters (such as laser power, scanning speed, and powder feeding rate) and auxiliary treatment processes on the solidification microstructure and coating properties. Finally, challenges encountered in the preparation of laser-cladded high-hardness Fe-based alloy coatings are detailed and examined, and prospective research directions are outlined.

2. Composition of Coating Materials

The performance of the cladding layer is predominantly determined by the cladding material [22]. Therefore, a logical and scientific design of the cladding powder formula emerges as a vital aspect of experimental research. Beyond aligning with requirements such as similarity in melting points, superior wettability, and comparable thermal expansion coefficients, the design of cladding materials should also leverage their inherent performance advantages. An appropriate composition design of the powder material is pivotal for achieving high-quality alloy coatings. Considering these aspects, we present a review of the current research endeavors focused on enhancing the performance of Fe-based alloy coatings. This enhancement is achieved by modifying alloy elements, incorporating ceramic particles, and adjusting the composition ratios of cladding materials with the addition of rare earth oxides.

2.1. Alloy Element Design

Owing to the distinct atomic sizes, chemical properties, and structural characteristics of various elements, their ability to impede dislocation motion directly contributes to the alloy's high strength. Techniques such as altering the lattice structure of the matrix to facilitate grain refinement and increasing the quenching capacity of the matrix can indirectly enhance the alloy's strength. Broadly, different alloy elements exert varied influences on their resulting microstructures and their comprehensive properties [23]. It becomes essential, then, to account for the impacts of these diverse elements on the microstructure and properties and to judiciously select alloy elements in line with laser cladding specifics. Therefore, an in-depth comprehension of the mechanisms behind the influences of these

alloy elements is instrumental in the development of high-performance alloy coatings. Table 1 summarizes the mechanisms of action for common alloying elements.

Table 1. Mechanisms of common elements.

Element	Mechanism
B	The addition of this element can enhance carbon activity and promote the formation of carbides [24,25].
Si	The addition of this element can enhance both dislocation strengthening and solid solution strengthening [26].
Mo	The addition of this element can increase the lattice distortion, easily refine the alloy structure, and improve the hardness and other properties [27].
Nb	The addition of this element can increase the lattice distortion and the high-hardness Laves phase which is easy to precipitate, thus improving the hardness of the coating [28].
V	The addition of this element can enhance grain refinement strengthening and improve the corrosion resistance of the coating [29].
Mn	The addition of this element can enhance austenite stability and reduce the permeability of the coating [30].
Cr	The addition of this element can enhance both grain refinement strengthening and solid solution strengthening [31].

B elements exhibit a lower diffusion rate within hard phase structures and possess a reduced solubility in the metallic matrix. The enrichment of B elements can influence phase transformations and decrease the energy required for phase formation. The types of eutectic carbides in conventional high-strength iron-based coatings are primarily M_2C , MC , and M_6C , which are characterized by their limited ductility. On the other hand, M_3C demonstrates superior fracture toughness. Lentz et al. [24,25] found that introducing an appropriate quantity of B elements can promote the precipitation of the Fe_3C eutectic structure within iron-based composite materials. B elements can also enhance the carbon activity in the liquid phase, enabling the easier precipitation of Fe_3C eutectic structures even in regions with diminished carbon content. Feng et al. [32] incorporated trace amounts of B while fabricating a 42CrMo iron-based coating. As illustrated in Figure 1, with a progressive increase in the B content of the coating, the reinforcing phase transformed from NbC-type carbides to $Cr_{23}C_6$ -type carbides, ultimately transitioning into Fe_3C -type carbides. Integrating B proves beneficial in lowering the formation energy of Fe_3C . Upon reaching a B content of 0.75%, a eutectic microstructure composed of Fe_3C -type carbides and γ -Fe is formed, with a hardness exceeding 900 HV_{0.5}. (The value 0.5 indicates the Vickers hardness measured under a load of 500 g, while 0.1, 0.12, 0.2, 0.3, and 1 in the following text represent the Vickers hardness measured under loads of 100 g, 120 g, 200 g, 300 g, and 1000 g, respectively). Under this condition, the coating exhibits peak compressive strength and ductility.

The incorporation of Si elements is pivotal in laser cladding. It effectively inhibits grain growth and facilitates grain refinement. Wang et al. [33] investigated the impact of Si content on the microstructure and performance of FeCoNiBSiNb laser-cladded coatings. An optimal amount of Si suppresses the formation and growth of dendritic structures, yielding a more homogeneous coating microstructure. The coating's average hardness surged from 719 HV_{0.1} (without Si) to 930 HV_{0.1}, paired with an increase of approximately 700 MPa in fracture strength. In another study, Liang et al. [34] integrated single-crystal silicon powder in varying mass fractions to enhance the quality of Fe60 alloy coatings. Their findings suggested that an appropriate Si content improved the bonding efficacy between the substrate and the coating while also enhancing the microstructural homogeneity. At a mass ratio of 20:1, the coating hardness peaked at 66 HRC. Additionally, Dong et al. [26] observed that in 316 L stainless steel coatings, the introduced Si elements accumulated as nano-sized

silicon dioxide particles at the cellular substructure's grain boundaries. Under the influence of thermal stresses during solidification, these nano silicon dioxide particles induced the formation of dense dislocation structures around them. Such dislocation structures disrupted the growth of columnar solidification structures, enhancing the formation of cellular structures. This process improves the coating's performance and microstructure.

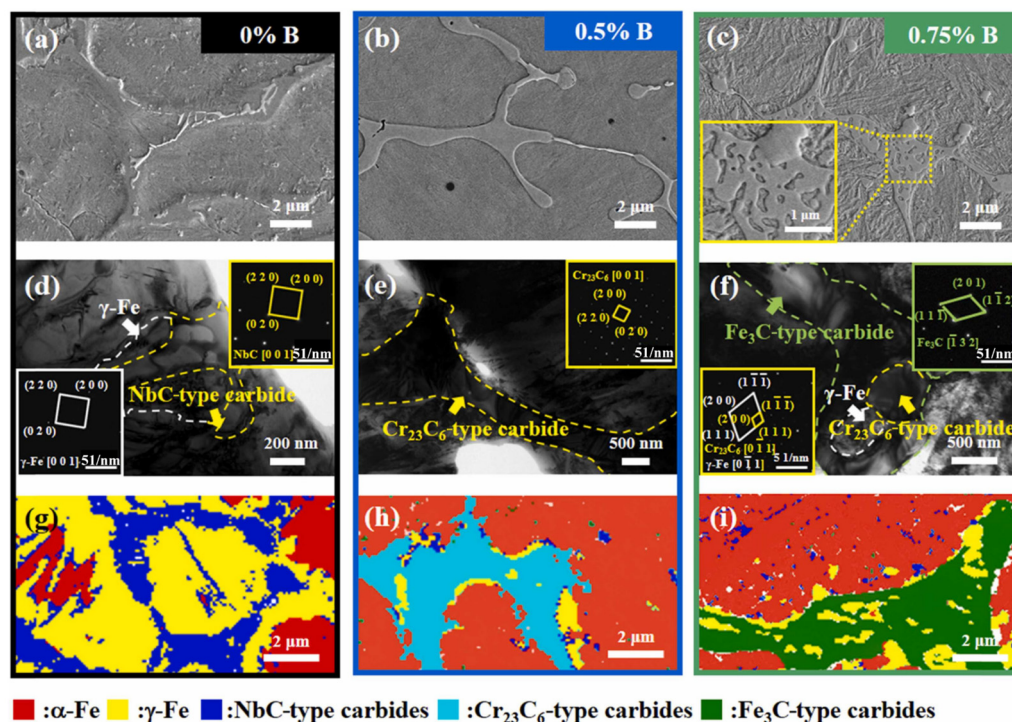


Figure 1. Carbides present in 0% B, 0.5% B, and 0.75% B coatings: (a–c) scanning electron microscopy images of carbides; (d–f) transmission electron microscopy images of eutectic structure and corresponding selected area electron diffraction of carbides; and (g–i) phase image of carbides [32].

Mo is a vital alloying element in steel and cast iron, renowned for its pronounced hardenability and solid-solution-strengthening effects. Li et al. [27] found that incorporating Mo into Fe901 alloy coatings refines the grain structure and promotes the formation of hard phase Mo_2FeB_2 . Mo tends to aggregate near grain boundaries, facilitating both grain refinement and solid solution strengthening. The average hardness of the coating with 4.8 wt% Mo content reached 720.2 HV_{0.2}, approximately 3.6 times that of the substrate. In a separate study, Chen et al. [35] prepared Fe-Mo coatings with varying Mo content on 65 Mn steel plowshares. Introducing Mo caused the precipitation of brittle phases, such as the σ phase, distributed along grain boundaries, resulting in a minor decline in coating impact toughness. However, as the Mo content increased, dendritic growth was promoted, leading to finer grain sizes. Consequently, the coating hardness peaked at 894 HV_{0.12}, nearly double that of the matrix. Cao et al. [36] investigated the influence of Mo content on the microstructure and properties of Fe-Cr-Ni-B-Si composite coatings. An optimal Mo content transformed the Fe-based composite coatings' microstructure from coarse columnar grains into a disordered amorphous matrix, accompanied by the generation of nano-precipitates. This transformation significantly increased the coatings' microhardness to 1100 HV_{0.5} and improved their resistance to plastic deformation. Ma et al. [37] performed laser cladding of iron-based coatings with varying Mo content on Q235 steel surfaces. With increasing Mo content, the coating's structure progressively refined. The content of high-hardness $\text{M}_{23}(\text{C}, \text{B})_6$ -type boron carbides in the eutectic structure increased while the formation of the softer $\text{M}_7(\text{C}, \text{B})_3$ -type boron carbides diminished. This wear resistance improvement resulted in coating microhardness levels consistently exceeding 700 HV_{0.5}, with only minor variations.

Compared to other elements, Nb possesses a notably large atomic radius, low solubility with other elements during solidification, and a propensity to cluster at the solid–liquid interface, inhibiting grain growth. Wang et al. [38] fabricated Fe–Cr–Mo–Co–C–B–Nb alloy coatings on 45 steel surfaces with Nb mass fractions of 0%, 2%, 4%, and 6%. As demonstrated in Figure 2, the crystalline zone at the interface between the substrate and the coating diminishes with increasing Nb content. From the enlarged view of A in Figure 2a, it can be seen that there are many pores in the bonding zones without Nb addition. The inclusion of Nb results in the disappearance of pores in the bonding zone, leading to a more cohesive interface and improved bonding strength. Additionally, introducing a modest amount of Nb to both low-carbon steel and stainless steel not only causes significant lattice distortion but also promotes the formation of fine secondary phases, substantially enhancing the mechanical attributes of the cladding layer. In a separate study, Liu et al. [28] infused varying Nb concentrations into 316 L stainless steel cladding coatings. As the Nb content increased, lattice distortion occurred, bolstering the solid solution effect, refining the grain size, and augmenting the formation of new Laves phases. These factors enhanced the coating's hardness. Moreover, with the integration of Nb, it accumulates on the surface, forming an oxidized Nb film. Coatings containing a 1% Nb mass fraction demonstrated superior corrosion resistance. However, an excessive Nb presence increased susceptibility to corrosion, consequently compromising the coating's corrosion resistance.

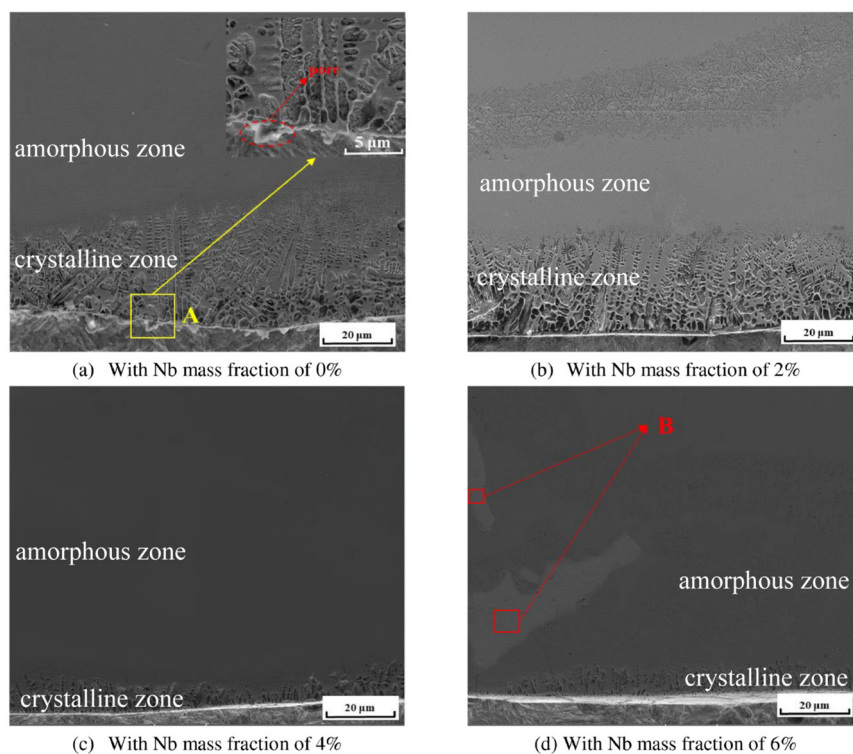


Figure 2. Microstructure of the coatings with different Nb mass fractions [38]. (“A” refers to the yellow boxed area in (a), with an enlarged view of “A” in the upper right corner. “B” refers to the white area in (d), while the white area is rich in Nb and Mo elements.).

In iron-based alloys, constituent elements vary in atomic size, chemical properties, and structural characteristics. The interactions among these elements result in the formation of diverse alloy phases. The attributes, structure, and concentration of these phases directly influence the alloy's performance. Addressing the need for laser cladding re-manufacturing of corrosion-resistant and wear-resistant critical components, Shan et al. [39] utilized a “material genetics” design approach based on classical phase theory for iron-based alloys. They established a material gene design database system, emphasizing key gene designs pertinent to corrosion and wear. Their optimization yielded a novel 50Cr12Ni3Mo2W6Co5BiTi3CeO₂

iron-based alloy composition. In contrast to the 50Cr6Ni2Y alloy prepared using traditional composition design methods, this new iron-based alloy coating exhibited enhanced resistance to corrosion and wear. Yao et al. [40] employed a supersaturated solid solution alloy design to fabricate Fe-C-Cr-Ni-Mo-W-V-Ti-Ce powder. The resultant coating featured martensite, residual austenite, and in situ-generated reinforcing particles devoid of surface cracks. Achieving a hardness of 65 HRC, its hardness, wear resistance, and toughness surpassed that of the substrate. In real-world applications, the interplays between alloy composition, microstructure, and performance are intricate. Contemporary research often focuses on the impact of individual element contents on coating performance. It is crucial to delve deeper into understanding the interaction mechanisms among the constituent elements and to consider both microstructure and performance from the outset of material development.

2.2. Adding Ceramic Particles

Beyond incorporating specific elements for second-phase strengthening, introducing ceramic particles into iron-based alloys is another method to form reinforcing phases, which enhances the wear resistance of the coatings. This is accomplished using either the “direct addition” or the “in situ synthesis” method. By merging the high ductility and toughness of metallic materials with the exceptional qualities of ceramics—such as high hardness, wear resistance, and corrosion resistance—a synergistic effect emerges, considerably improving the service performance of components. Table 2 provides a detailed comparison of the addition methods, hard particles, and the resulting mechanical properties of iron-based alloy coatings reinforced with ceramic particles.

Table 2. Ceramic particle-reinforced iron-based coating.

Addition Method	Hard Particles	Phase Composition	Hardness	Mechanical Properties	Ref.
Directly added	WC	FCC, WC, M_6C	874 HV _{0.2}	No cracks; microhardness increased by 4.2 times; significant wear resistance improvement	[41]
Directly added	WC-14Co	α -Fe, γ -Fe, WC, MoC, $M_{23}C_6$	937.6 HV _{0.1}	No cracks; significantly improved microhardness; reduced wear amount	[42]
Directly added	WC	γ austenite, ϵ martensite, Fe_6W_6C	650 HV _{0.2}	No cracks; microhardness increased by over 2 times; friction coefficient reduced by 1/4	[43]
In situ synthesis	WC	α -Fe, (Cr, W) ₂₃ C ₆ , WC	827 HV _{0.5}	Hardness increased by 1.43 times; significant friction coefficient decrease	[44]
In situ synthesis	TiC	Fe, FeTiO ₃ , TiC	950 HV _{0.1}	No cracks; hardness was 3 times higher than matrix	[45]
In situ synthesis	TiC	Ferrite, Fe ₃ C, TiC, TiCx, FeTi, Fe ₂ Ti	1022 HV _{0.2}	Microhardness and wear resistance increased with the increase in TiC or TiCx content	[46]
Directly added	Cr ₃ C ₂ + MoS ₂	Fe-Cr-Ni, (Cr, Fe) ₂₃ C ₆ , MoS ₂ , CrS	746 HV _{0.2}	Significantly improved wear resistance	[47]
Directly added	NiCr-Cr ₃ C ₂	Martensite, Cr ₃ C ₂ , Cr ₇ C ₃ , (Cr·Fe) ₇ C ₃	1100 HV _{0.2}	Higher thermal fatigue resistance and wear resistance than matrix	[48]
In situ synthesis	NbC	NbC, Fe ₂ B, B ₄ C, solid solution	866 HV _{0.5}	Significantly improved hardness; abrasive wear shifted to adhesive wear	[49]
In situ synthesis	VC	α -Fe, VC, M ₇ C ₃ , M ₂₃ C ₆ (M: Cr and Fe)	850 HV _{0.2}	Uniform microhardness distribution; significantly improved hardness and wear resistance	[50]
In situ synthesis	Al ₂ O ₃	γ -Fe, Fe ₃ C, (Cr, Fe) ₇ C ₃ , Al ₂ O ₃	725 HV _{0.1}	Significantly increased microhardness of coating and heat-affected zone	[51]

2.2.1. Direct Addition of Ceramic Particles

The direct addition approach entails the mechanical mixing of ceramic particles with metal powder. Due to ceramics' high melting point, only a small portion of these particles melt during the laser cladding process. The remaining unmelted ceramic particles function as reinforcing phases, providing strengthening effects [52,53].

When ceramic particles are added in insufficient quantities, they fail to provide adequate reinforcement. On the other hand, excessive addition leads to significant disparities in physical properties, such as thermal expansion coefficients, melting points, and wetting behavior, between the composite material and the matrix. These disparities can lead to increased thermal stresses and a rise in the content of eutectic phases as the volume fraction of ceramic particles increases. Furthermore, the distribution of these eutectic phases becomes more uneven, resulting in a more brittle coating with a higher susceptibility to cracking [54,55]. Thus, to effectively enhance service performance, it is crucial to control the mass fraction of the added ceramic particles to produce high-quality coatings free of cracks or voids. Lu et al. [56] examined the impact of varying WC content on the microstructural characteristics and wear performance of Fe104 alloy coatings. The W and C elements diffused into the iron matrix, and as WC content increased, a portion of $\text{Fe}_3\text{W}_3\text{C}$ transitioned into the more stable and harder $\text{Fe}_6\text{W}_6\text{C}$ phase. This led to an improved microhardness and wear resistance of the coating. Zhu and colleagues [57] employed laser cladding technology to produce 410 martensitic stainless steel coatings with different TiC ceramic particle concentrations. The inclusion of TiC ceramic particles notably refined the lamellar martensite. When the content reached 10 wt%, the coating's hardness surged to 634 HV_{0.2}, a significant increase compared to the 462 HV_{0.2} hardness of the TiC-free coating. However, laser-cladded coatings with a high 15 wt% TiC content exhibited microcracks and pores.

The size of ceramic particles can influence their solubility, thereby affecting the microstructure and properties of the coatings. Li et al. [58] found that small-sized WC had a positive effect on the uniform refinement of the organization of Fe-based composite coatings, while the opposite was true for large-sized WC. Utilizing laser cladding technology, Qi et al. [59] developed Fe-WC composite coatings and noted that the combustion loss rate of WC particles was inversely proportional to the average particle size of localized WC particles. Zou et al. [60] generated WC powder via plasma rotating electrode atomization and found that smaller WC particles facilitated enhanced wear resistance.

2.2.2. In Situ Synthesis of Ceramic Particles

The direct addition method offers a wide range of material choices, a straightforward preparation process, and controllable particle sizes. However, it is susceptible to poor interface bonding due to differences in thermal material properties, as well as issues related to the burning of ceramic phases. These issues can lead to coating cracking or delamination, which can significantly reduce the coating's lifespan [61]. In 1976, Soviet scholars introduced the concept of in situ composite materials, where different elements or compounds undergo chemical reactions under specific conditions, producing one or more ceramic phase particles within the metal matrix [62]. Compared to the direct addition method, in situ synthesis mitigates concerns related to surface contamination between the matrix material and ceramic particles. Moreover, in situ-synthesized ceramic reinforcing phases are uniformly dispersed and distributed within the matrix, ensuring optimal wetting and interface bonding properties with the matrix [63,64]. Chen et al. [49] used a mixture of Nb and boron carbide powder to produce in situ NbC-reinforced iron-based coatings on medium carbon steel surfaces. Figure 3 illustrates the principle of in situ laser cladding for generating NbC ceramic particles. The composite coatings primarily consist of reinforcing phases (NbC, Fe_2B , and B_4C) and the matrix (solid solution). In situ-formed NbC particles at grain boundaries enable dispersion and fine-crystal strengthening effects. Ren et al. [65] employed ultra-high-speed laser cladding technology to fabricate defect-free in situ VC-reinforced X-M6V coatings. In situ synthesis allows the coating to avoid stress concentration caused by the aggregation of reinforcing phases, ensuring a more uniform

particle distribution. The extremely high cooling rate, combined with uniform VC precipitation, contributes to both fine-crystal strengthening and second-phase strengthening, thus enhancing the coating's hardness and wear resistance. The coating's low wear loss and reduced surface roughness indicate its suitability for use with minimal or no subsequent finishing. This synergistic approach of ultra-high-speed laser cladding and in situ synthesis holds potential for broader applications in ceramic-reinforced composite coatings.

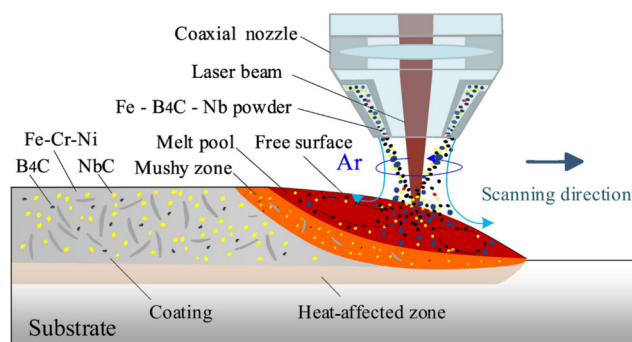


Figure 3. Principle of in situ ceramic particle synthesis via laser cladding [49].

Due to the poor wetting between ceramics and the metal matrix, the bonding interface between the ceramic and metal matrix can become a potential source of cracks under alternating stresses. This issue significantly diminishes the wear resistance and corrosion resistance of single ceramic-reinforced coatings. In composite ceramics, ceramic particles interact with each other, effectively preventing the detachment of ceramic particles from the coating matrix [66]. This has made them an emerging focus in industrial applications. Zhu et al. [67] successfully fabricated an $\text{Al}_2\text{O}_3/\text{TiC}$ composite ceramic coating on a 16Mn steel substrate using Fe60 alloy powder and Ti_3SiC_2 particles. They observed that the TiC carbides of $\text{Al}_2\text{O}_3/\text{TiC}$ composite ceramics have a dragging effect on the Al_2O_3 precipitates and prevent the reinforcements from being ripped out from the matrix.

2.3. Addition of Rare Earth Oxides

Rare earth elements, often termed “industrial gold”, are prized for their unique electron structure and highly reactive chemical properties. In metallurgy, they are frequently utilized as spheroidizing and nucleating agents to enhance casting quality. Upon interaction with oxygen and sulfur, rare earth elements readily form high-melting-point oxides and sulfides, thereby facilitating the deoxidation, desulfurization, and morphological transformation of inclusions. Appropriately introducing rare earth elements into laser cladding powders can effectively control the coating's microstructure, improve its morphology, and enhance its surface properties [68,69].

During the cooling process of coatings, rare earth oxides can serve as crystallization nuclei, increasing nucleation rates. They tend to accumulate near grain boundaries, obstructing grain growth and thereby improving the coating's hardness and wear resistance [70]. Jiang et al. [71] added Y_2O_3 when preparing FeCrAlTiC coatings and found that Y_2O_3 reacted with TiC near the grain boundaries to form two oxides, $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 , which changed the morphology of TiC from short rod-like to spherical, resulting in a decrease in the wetting ratio at the grain boundaries. Compared to the coatings without Y_2O_3 , the microhardness of the coatings increased by 9.88%. Wang et al. [72] aimed to prevent the formation of coarse columnar grains during the cladding process by introducing varying quantities of La_2O_3 into the coating, as depicted in Figure 4. Coatings containing 1 wt% La_2O_3 displayed no significant columnar grains. However, in 2 wt% La_2O_3 coatings, a minimal presence of columnar crystals was noted. Compared to La_2O_3 -free coatings, the columnar crystals in the 2 wt% La_2O_3 coating were confined mainly to the interface, and both their size and quantity were reduced.

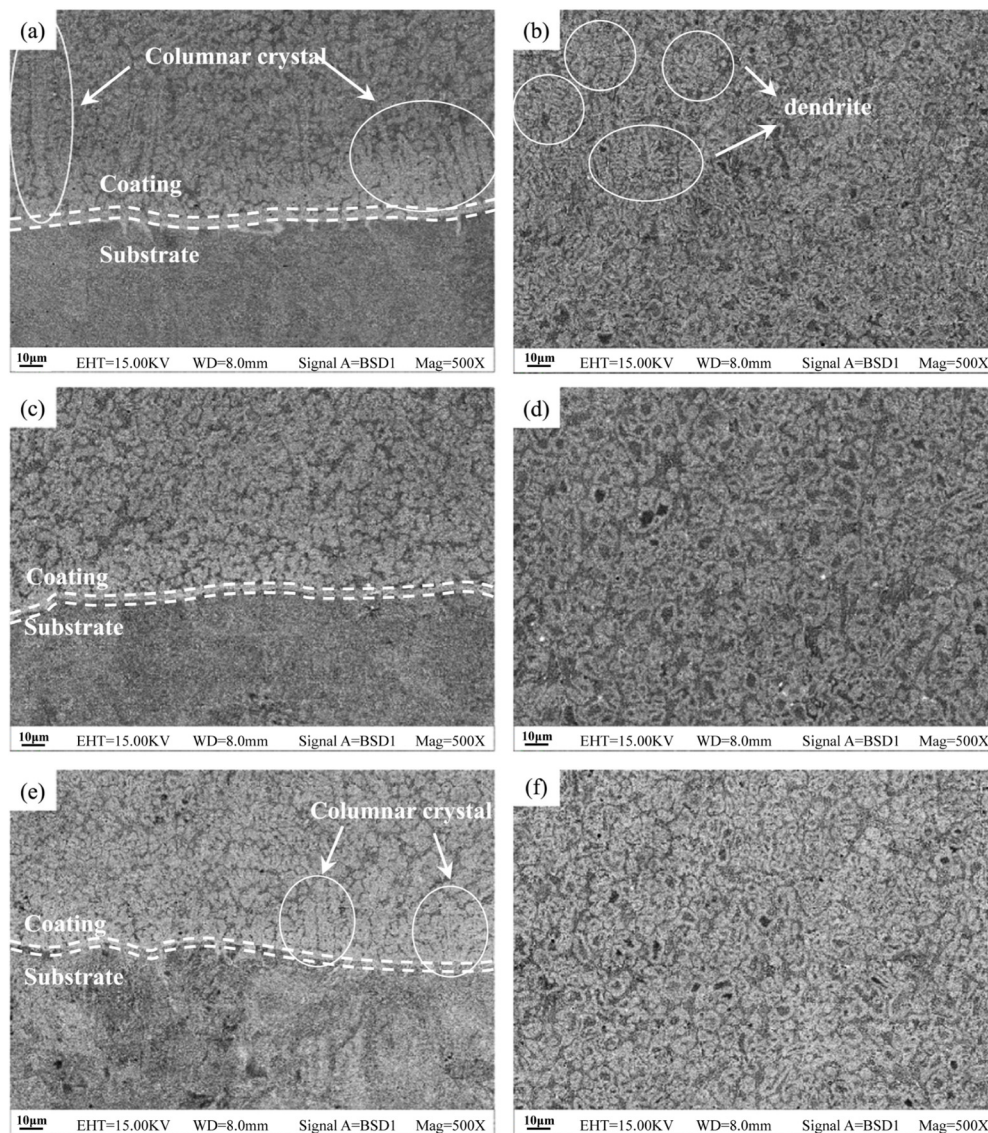


Figure 4. Microstructure of the interfacial binding region and the middle part of the coating: (a,b) 0 wt% La_2O_3 ; (c,d) 1 wt% La_2O_3 ; and (e,f) 2 wt% La_2O_3 [72].

An appropriate addition of rare earth elements can enhance the coating's microstructure, modify the morphology of ceramic phase particles, and ensure their uniform distribution in the cladding layer. Cai et al. [73] used laser cladding to prepare TiC/Fe-based composite coatings with CeO_2 on the surface of Cr_{12}MoV steel. The research revealed that in the absence of rare earth elements, the TiC ceramic particles exhibited irregular shapes, significant size variations, and a degree of agglomeration. An appropriate addition of rare earth elements effectively promoted the spheroidization and refinement of ceramic particles, ensuring a homogeneous distribution. However, adding excessive rare earth elements can cause ceramic particle burning loss, inhibit the formation of secondary precipitates, and result in particle agglomeration. Chen et al. [74] assessed the impact of adding varying amounts of CeO_2 on the microstructure and performance of laser-cladded ceramic-reinforced $\text{Fe}_{78.5}\text{Cr}_{15.6}\text{Ni}_{4.0}\text{Si}_{0.7}$ coatings. They identified that when the CeO_2 content exceeded 3%, no TiC particles precipitated within the coating. An excess of rare earth elements suppressed the secondary precipitation of TiC ceramic particles after the initial TiC ceramic particles decomposed into Ti and C elements.

Rare earth elements have a high affinity for oxygen, preventing the oxidation of other reactive alloying elements. This attribute significantly enhances the coatings' resistance to high-temperature oxidation and corrosion. Zhang et al. [75] examined the high-temperature oxidation resistance of iron-based composite coatings containing the rare earth oxide Y_2O_3 at 600 °C. Y_2O_3 aggregates at grain boundaries, reducing the diffusion of metal ions towards grain boundaries. This considerably diminishes the corrosion rate associated with gas-phase oxidation and inhibits the surface oxidation of the cladding layer.

3. Laser Cladding Process Parameters

Beyond the primary consideration of cladding material, adjusting laser process parameters can directly influence the coating's microstructure and its formative quality. These process parameters are intricately connected to the coating's structural properties; modifying them reflects changes in the interactions among the laser, powder, and substrate [18]. Variations in these parameters can impact the heat accumulation during the cladding process [76], cooling rates of the molten pool [77], thermal cycling pattern [78], and Marangoni flow behavior [79]. Consequently, these changes can affect the coating's microstructure, performance, and surface quality. Among these, laser power, scanning speed, and powder feed rate have the more significant impact on coating quality [80].

3.1. Laser Power

Laser power is one of the most critical parameters in laser cladding, directly influencing the microstructure and properties of the clad layer. Excessive laser power can cause the over-sintering of the powder, exacerbating deformation and cracking in the cladding layer. Conversely, insufficient laser power can result in the incomplete melting of the powder material, leading to issues such as voids and balling. Within a certain range, adjusting the laser power and changing the power density can regulate the cladding layer's depth, promoting dynamic solidification and reducing defects such as cracks and pores. Mao et al. [81] analyzed the differences in the microstructure and microhardness of iron-based alloy coatings at two laser power levels: 2.5 kW and 2.8 kW. They observed that, within a specific power range, as the laser power increased, the melt pool absorbed more heat. This extended the solidification time, enhanced substrate melting, increased dilution, expanded dendrite size, and promoted directional solidification. As a result, the hardness of the coatings decreased from 864–984 $HV_{0.3}$ to 660–851 $HV_{0.3}$. Xie et al. [82] prepared Fe314 alloy cladding layers on an EA4T steel substrate using various laser powers (1.5 kW, 1.8 kW, 2.1 kW, and 2.4 kW). As shown in Figure 5, with an increase in laser power, the melt pool absorbed more heat. This prolonged the time the melt pool remained at a high-temperature state, allowing more time for grain growth. This led to the formation of larger columnar grains and diminished the effect of fine-grain strengthening. Consequently, the coating's microhardness decreased with increasing laser power.

3.2. Scanning Speed

Scanning speed has a similar impact to that of laser power. When other process parameters are kept constant, an exceedingly low laser scanning speed prolongs the interaction time between the laser beam and the cladding powder. This elevates the coating temperature and intensifies substrate melting and dilution, resulting in a decline in the surface quality and wear resistance of the cladding layer. On the other hand, an excessively high scanning speed reduces the interaction time between the laser beam and the cladding powder, diminishing dilution and impairing the metallurgical bonding between the coating and the substrate, thereby reducing wear resistance. Jiao et al. [83] deposited a layer of T15M high-speed steel alloy powder onto a Q235 substrate at different scanning speeds (100 mm/min, 200 mm/min, and 300 mm/min). Among the three, the coating produced at a scanning speed of 200 mm/min exhibited the smallest grain size, highest solid solubility, and most substantial average hardness, reaching 1050 $HV_{0.1}$. However, as the scanning speed escalated to 300 mm/min, the wear performance of the coating deteriorated, with

a notable amount of material peeling off. Li et al. [84] utilized high-speed laser cladding technology to deposit an Fe-Co-B-Si-Nb amorphous coating on the surface of 45 medium carbon steel at varying scanning speeds. A large volume fraction of amorphous phases and some dendrites was contained within the coating. The distances between secondary dendrite arms and cooling rates in different areas of the high-speed laser-cladded samples under varying scanning speeds are illustrated in Figure 6. As the scanning speed increased, the distance between secondary dendrite arms decreased, and the cooling rate increased. At high scanning speeds, the ability to form amorphous structures significantly improved, resulting in a refined microstructure, an increased volume fraction of the amorphous phase, and a significant enhancement in the hardness of the laser-cladded coating. The peak hardness at the top of the coating was observed to reach up to 1215.9 HV_{0.1}. Sun et al. [85] demonstrated that as the scanning speed increases, the product of the $G \cdot R$ (temperature gradient * grain growth rate) in B-containing Cr17Ni2 coatings also increases, resulting in finer lath martensite and Cr₂B phases and, consequently, higher coating hardness.

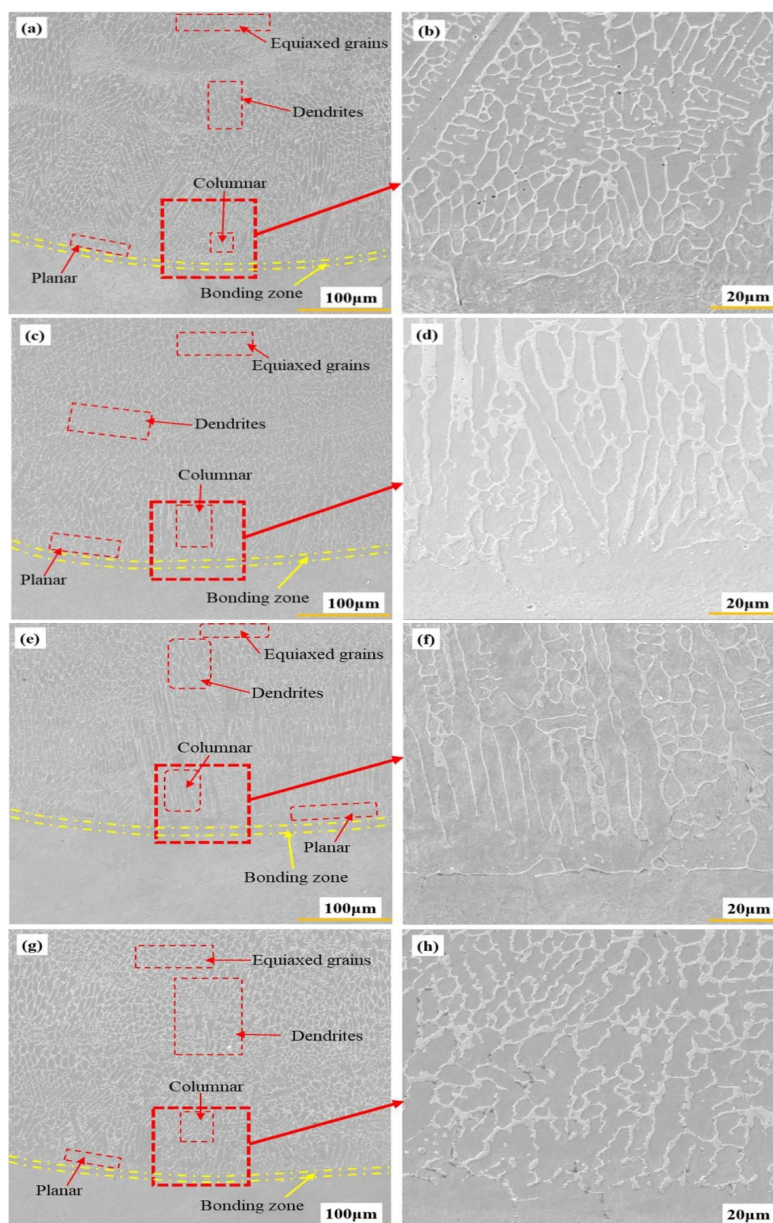


Figure 5. Microstructure of cladding layer at different laser powers: (a,b) 1.5 kW; (c,d) 1.8 kW; (e,f) 2.1 kW; and (g,h) 2.4 kW [82].

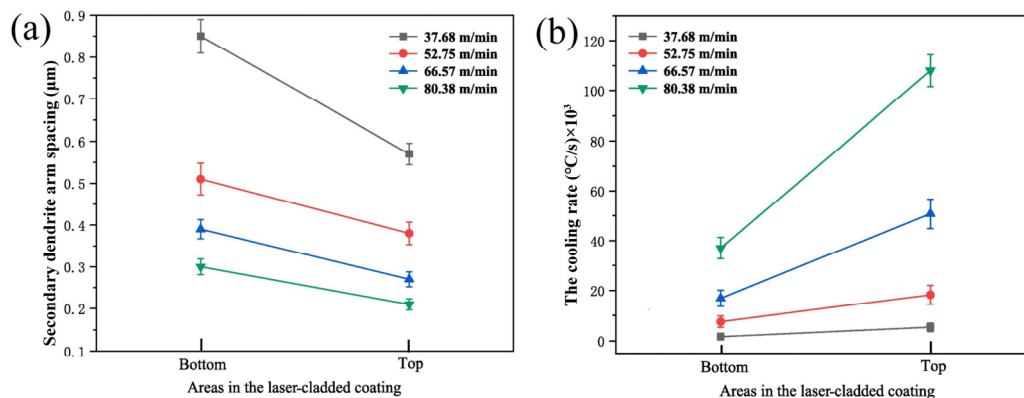


Figure 6. Distance between secondary dendrite arms (a) and the cooling rate (b) of the coating during laser cladding at varying scanning speeds [84].

3.3. Powder Feed Rate

The powder feed rate refers to the mass of powder introduced into the melt pool per unit time. Selecting an appropriate powder feed rate can mitigate issues such as powder accumulation, uneven heating, and excessive sintering. Wang et al. [86] employed a high-speed powder feeding method to fabricate an iron-based alloy coating on a 27SiMn steel substrate. Compared to the conventional gravity powder feeding (25 g/min), the microstructure of the coating developed through high-speed powder feeding (60 g/min) transitioned from coarse columnar crystals to uniformly distributed small grains. The total energy consumption was only 75.5% of that required by the gravity powder feeding process, allowing for efficient coating production at reduced energy levels. The grain refinement contributed to an increased hardness and improved wear resistance of the coating. Bartkowski et al. [87] prepared Fe/WC metal matrix composite coatings on low-carbon steel surfaces using two distinct powder feed rates (6.25 g/min and 12.5 g/min). At lower powder feed rates, as the laser power increased, the number of cracks decreased, with microhardness values ranging between 1150 HV_{0.1} and 1200 HV_{0.1}. In contrast, higher powder feed rates led to increased coating thickness with no observed cracks and microhardness values ranging from 1200 HV_{0.1} to 1400 HV_{0.1}. Budde et al. [88] studied the effects of process parameters on the geometry and process stability in laser hot-wire cladding of AISI 52100, finding that a lower wire feed rate (1.5 m/min) resulted in a more stable geometry compared to a higher feed rate (2 m/min).

3.4. Coverage of Shielding Gas

By creating a protective atmosphere, the shielding gas is employed to prevent oxidation and the intrusion of other harmful gasses into the processing space, thereby reducing pore formation and enhancing the density and uniformity of the overlay layer. To effectively avoid unacceptable oxidation during the cladding process, the dimensions of the area sufficiently covered with shielding gas are relevant. This area is referred to as the “effective protective region” [89]. The effective protection region was defined by Ding et al. [90] and Li et al. [89] as the area in which oxygen concentration was below 2000 ppm. The influence of the shielding gas coverage on the laser hot-wire cladding process of high-carbon cladding material AISI 52100 was investigated by Budde et al. [91]. It was found that an increased shielding gas coverage resulted in a reduced ablation rate of alloying elements and fewer pores, along with a nearly halved average dilution rate. The average hardness of the cladding layer was significantly increased. Bernauer et al. [92] designed a new local shielding gas nozzle based on fluid dynamics principles. Through simulations, they explored how the gas flow rate influences gas coverage, finding that an increase in the flow rate can expand the coverage area of the shielding gas.

3.5. Process Parameter Optimization

It is noteworthy that the actual laser cladding process is influenced by the combined effects of multiple parameters, whose interactions contribute to the complex nonlinear relationship between the process parameters and the quality of the cladded layer. Extensive experimentation is often required to optimize these parameters to achieve a high-quality and high-performance cladding layer.

Du et al. [93] adjusted the laser specific energy E_s ($E_s = P/(DV)$, where E_s (J/mm²) is the laser specific energy, P (W) is the laser power, D (mm) is the spot diameter, and V (mm/s) is the scanning speed) by changing the laser power and scanning speed, and found that with the increase in the specific laser energy, the undercooling degree of Fe60 coating increased during the solidification process, the nucleation rate accelerated, the coating grains became finer and more uniform, and the coating hardness reached 744.2 HV_{0.2}. Through the multi-objective optimization of the process parameters of 17-4PH/B4C coating via multilayer laser cladding, Luo et al. [94] found that the factors influencing coating hardness in order of significance are powder feed rate > overlap rate > laser power > scanning speed. The cladding layer produced with the optimal parameters exhibited a microhardness of 784.5 HV_{0.2}, approximately four times higher than that of the substrate. Patrycja Wołosz et al. [95] found that the refinement of the microstructure in H13 coatings depends on the scanning speed and the size of the laser spot. The highest hardness achieved under different process parameters reached 800 HV_{0.1}. Due to the rapid heating and cooling characteristics of laser cladding, the molten pool exists for a very short duration, resulting in complex interactions among the process parameters. As a result, relying solely on the optimization of process parameters to control the microstructure and properties of the coating has certain limitations. Reddy et al. [96] optimized the process parameters for the laser cladding of SHS7170 iron-based alloy coatings and found that the porosity of the coatings was independent of the process parameters, being primarily determined by the cladding material.

4. External Field-Assisted Treatments

Reasonable cladding material design and the optimization of cladding process parameters can reduce the defects in the coating to a certain extent, but it is still difficult to completely eliminate the cracks and other defects in the microstructure of the high-hardness iron-based coating. In recent years, researchers have combined the external field-assisted technology with laser cladding technology. Through the application of heat treatment, ultrasonic vibration field, electromagnetic field, and other energy fields (as shown in Figure 7), the convection movement of melt is affected, and the temperature field and solute distribution are more uniform. These technologies have played an important role in tissue refinement, defect elimination, and performance improvement.

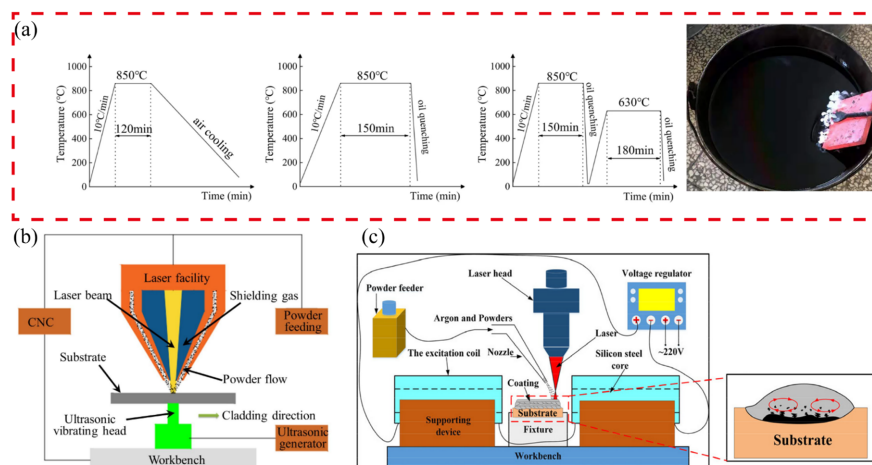


Figure 7. Schematic illustration the heat treatment processes and quenching process (a) [97], induction heating-assisted laser cladding (b) [98], and electromagnetic field-assisted laser cladding (c) [99].

4.1. Heat Treatment Assistance

Heat treatment is a material processing technique that uses controlled heating and cooling to induce phase transformations or structural changes in the solid state. The primary goal is to improve material properties. Strategies such as simultaneous heating and post-heating systems on substrates have been employed for this purpose. The use of tempering, diffusion annealing, and other heat treatment techniques facilitate the diffusion of alloying elements, promoting a more uniform distribution. This approach aids in mitigating the high residual stresses typically encountered during the laser cladding process, ultimately optimizing and enhancing the microstructure and performance of the cladding layer. Wang et al. [100] investigated the mechanisms of post-heat treatment and deep cooling treatment to improve the microhardness of martensitic stainless steel coatings. In the post-heat treatment phase, Cr_{23}C_6 particles precipitated from the austenite, leading to diminished levels of C and Cr content. This spurred the formation of martensite, raising the hardness to 700 HV₁. A subsequent deep cooling treatment triggered a phase transition to martensite, further reducing residual austenite content and elevating the coating's hardness to 760 HV₁. Guo et al. [101] employed laser cladding technology to produce Fe60 coatings on a C45E4 steel substrate. They heated the coating to 1050 °C and sustained this temperature for 30 min, followed by cooling in ambient air. This heat treatment process released residual stresses and carbon atoms within the body-centered cubic lattice structure, decreasing deformation and susceptibility to cracks. While the microhardness dropped from 800 HV₁ before the heat treatment to 650 HV₁ after it, the precipitation hardening effect from newly formed carbide particles in the dendrites increased the coating's ultimate tensile strength from 450 MPa to 550 MPa. Gong et al. [102] subjected FeCrNi laser-cladded coatings to heat treatment in the temperature range of 800 °C to 1000 °C. Their findings indicated grain refinement within the coating and the effective elimination of the softening region. This led to a notable enhancement in the tensile strength of the laser-cladded components.

By adjusting laser scanning strategies, in situ laser heat treatment can be achieved. Shi et al. [103] introduced laser idle time between each cladding track, as illustrated in Figure 8, to control the in situ quenching and tempering sequence. The laser idle time between tracks allows the previous track to cool to near room temperature, facilitating a complete martensitic transformation. Consequently, in situ tempering occurs when overlapping tracks pass through. Compared to the 300M steel substrate material, the overall tensile properties of the $\Delta t_{\text{track}} = 80$ s sample were restored, with a 38% increase in ductility. The yield strength and maximum tensile strength decreased only by 5%–10%, and the wear rate was substantially reduced, yielding excellent overall performance. Gao et al. [104] conducted high-speed re-melting experiments on a titanium-doped iron-based alloy coating, achieving the refinement of the coating. As the re-melting scan speed increased, both the area of the refinement zone and grain size significantly decreased. Rashid et al. [105] utilized laser reheat post-treatment (LPHT) to repair 300 M high-strength steel cladding layers. They found that M_{23}C_6 carbides, present in the as-deposited state, dissolved into the martensitic matrix. This led to an increase in the volume of residual austenite and a minor decline in cladding layer hardness. However, the additional laser re-heating of the cladding layer resulted in a uniform distribution of tempered martensite, eliminating localized tempering caused by overlap between passes. LPHT can be effectively employed for the localized control of the microstructure in the laser-cladded repaired parts by tuning the laser reheat parameters. Compared to traditional heat treatment processes, methods such as laser quenching and laser re-melting are more suitable for localized heat treatment requirements. These methods not only significantly shorten the processing cycle but also avoid issues of deformation and high energy consumption that are typical of overall heat treatment processes.

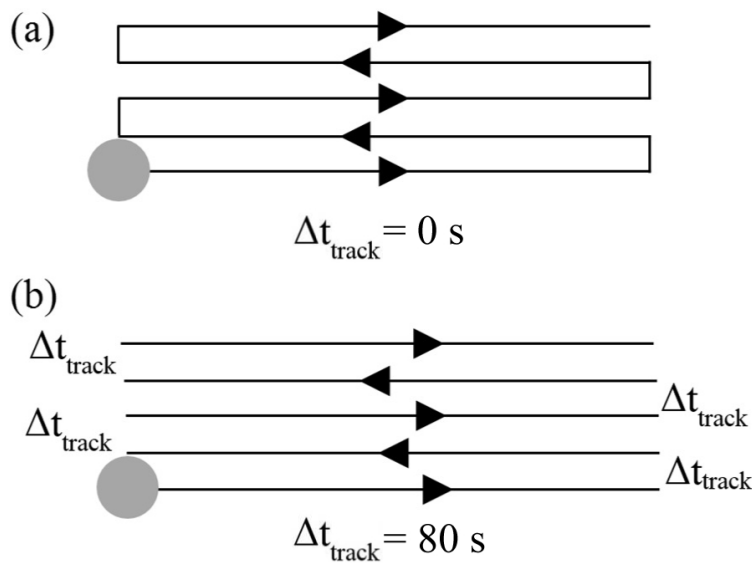


Figure 8. Scan paths with different idle times: (a) continuous deposit; (b) deposit with a laser idle time of 80 s [103].

4.2. Ultrasonic Vibration Assistance

Ultrasonic vibration-assisted laser cladding technology leverages the synergistic effects of ultrasonic cavitation and acoustic streaming. These effects influence the liquid-phase flow and temperature field distribution within the molten pool, thereby regulating the microstructure and element distribution of the coating [106,107]. Implementing ultrasonic vibration improves the flowability of the liquid metal [108], decreasing the incidence of porosity defects caused by material evaporation and molten pool collapse. It also reduces the temperature gradient within the coating, alleviates thermal stresses, and addresses crack defects [109]. Concurrently, this technology can fragment columnar dendrites, resulting in a finer and more uniformly distributed coating structure [110].

Xu et al. [111] applied ultrasonic vibration assistance during the laser cladding process to deposit an Fe901 alloy coating onto the surface of GCr15 bearing steel. Their results indicated that with the application of ultrasonic vibration, the growth of columnar grains was disrupted, leading to the formation of fine equiaxed grains in the coating. This application of ultrasonic vibration increased the microhardness from 742.6 HV_{0.2} to 783.8 HV_{0.2} and notably reduced the friction coefficient. Xiao et al. [98] utilized laser cladding equipment, as depicted in Figure 7b, to produce Fe₄₁Co₇Cr₁₅Mo₁₄C₁₅B₆Y₂ amorphous coatings both with and without ultrasonic vibration. Although the top microhardness of both coatings was similar (approximately 1100 HV_{0.2}), the application of ultrasonic vibration increased the thickness of the crystalline region at the bottom of the coating by 46 μm, resulting in a wavy distribution. Furthermore, the microhardness of the transition zone increased by 75 μm. Yao et al. [112] integrated ultrasound into the laser cladding process and identified that the ultrasound significantly reduced the local aggregation of WC particles, promoting a more uniform distribution of WC particles and suppressing crack initiation. Wang et al. [113] examined the properties of 3540Fe/CeO₂ alloy coatings prepared via laser cladding with varying ultrasonic vibration angles. The study revealed that the cladding layer's microstructure, when aided by ultrasonic vibration, consisted of fine equiaxed grains and dendrites, indicating a substantial improvement in grain structure refinement. When subjected to a 45° ultrasonic vibration, the coating's surface appeared smooth and devoid of defects such as cracks and pores, and exhibited the highest average microhardness, reaching 1148 HV_{0.1}. This had a significant positive impact on wear resistance.

Excessive energy absorbed by the molten pool due to ultrasonic vibration can prolong its solidification time, leading to grain growth and the formation of coarser grains. Liu et al. [114] observed that ultrasonic power exerted a nonlinear effect on the coating's microstructure. Within a suitable range of ultrasonic power, the grain refinement in the cladding layer was significant. However, when the power exceeded 750 W, the grain size increased. From the studies mentioned, it is evident that alterations in ultrasonic vibration process parameters can influence the microstructure of the cladding layer. By optimizing ultrasonic vibration process parameters in conjunction with laser cladding process parameters, the surface performance of the coating can be further improved. However, this requires further in-depth theoretical and experimental research.

4.3. Electromagnetic Field Assistance

Electromagnetic field-assisted laser cladding technology leverages the interaction between an electromagnetic field and the metal melt, generating electromagnetic forces that alter the convective motion and the processes of heat and mass transfer within the melt. This, in turn, affects the solidification process, leading to a reduction in supercooling and the refinement of the solidified microstructure [115,116]. The electromagnetic field assistance can be categorized into three main types: single magnetic fields (including steady-state, alternating, and rotating magnetic fields), single electric fields (including direct current, alternating current, and pulsed electric fields), and combined electromagnetic fields, each with various configurations.

Ouyang et al. [117] observed that applying an electrostatic field opposite to the laser scanning direction (Figure 9c) can enhance the diffusion and convection of elements within the molten pool, thereby promoting the directional solidification of the laser cladding layer and resulting in the formation of columnar grains. Conversely, applying an electrostatic field aligned with the laser scanning direction (Figure 9d) was found to suppress the diffusion and convection of elements in the molten pool, leading to an orderly mushy solidification and the development of an ultrafine grain structure in the cladding layer. Li et al. [118] established a three-dimensional numerical model for magnetic field-assisted laser cladding, which included chemical species transport, magnetic fields, fluid flow, heat transfer, and dynamic networks. As shown in Figure 10, when the induced magnetic field force and convection velocity acted in opposite directions (Figure 10(a2)), the addition of the magnetic field restricted the flow of the molten metal toward the edges of the molten pool, shortened the length and duration of the molten metal, and increased the maximum cooling rate at the solidification interface (Figure 10(b1–b4)), thus leading to a decrease in grain size. This conclusion was also confirmed by observations of the microstructure in the cladding layer (Figure 10(c1–c3)). Huang et al. [99] utilized electromagnetic field assistance to produce 4 mm thick Fe901 coatings on a Cr₁₂MoV substrate via multilayer laser cladding. The incorporation of the electromagnetic field mitigated cracking defects in the laser-cladded coating. The stirring effect induced by the electromagnetic field disrupted the growth of columnar dendrites, leading to grain refinement and improved the fatigue and wear resistance of the coating. Chen et al. [119] investigated the impact of the electromagnetic field on the microstructure and mechanical properties of Fe901/Al₂O₃ metal matrix composite coatings. Their findings highlighted that Lorentz forces, combined with Joule heating effects, increased the nucleation rate of grains, intensified the flow within the molten pool, disrupted the coarse columnar dendrites, and refined the coating structure. The microhardness increased from 782 HV_{0.2} to 866.4 HV_{0.2}, and the predominant wear mechanism transitioned from adhesive wear to abrasive wear.

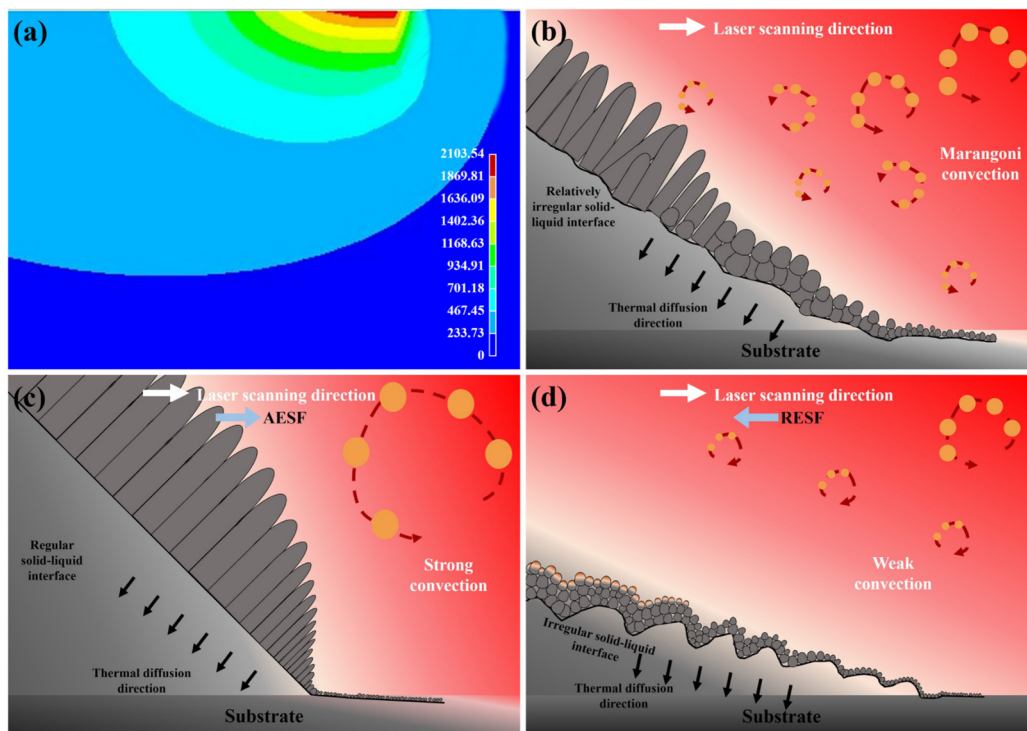


Figure 9. Schematic diagram for the simulated temperature distribution of laser cladding 316 L stainless steel powders (a) and schematic diagram showing the crystal growth and convection in the laser cladding layer with different fabrication states (b–d) [117].

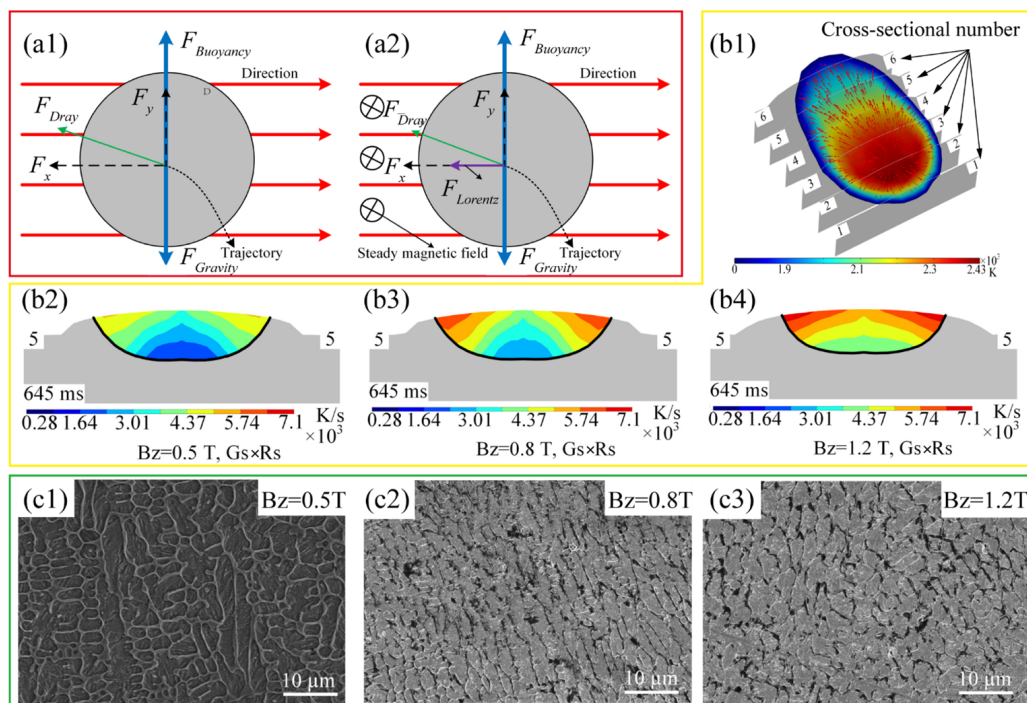


Figure 10. (a1,a2) Force analysis of melt pool liquid; (b1) cross-section positions; (b2–b4) cross-section cooling rates at different magnetic fields; and (c1–c3) microstructures at different magnetic fields [118].

4.4. Additive-Equivalent Hybrid Manufacturing

The technology of additive-equivalent hybrid manufacturing introduces mechanical force fields and thermal fields during the additive phase or subsequent post-processing,

based on processes such as rolling, forging [120], hammering, and shot peening, to induce plastic deformation at specific depths within the additive layers. This approach enhances the grain morphology, microstructure, and stress state of the deposited material, enabling effective control over the macroscopic mechanical properties and ultimately improving the fatigue life of the formed materials. Chen et al. [121] prepared Fe-based alloy coatings on a 27SiMn substrate through laser cladding. It was observed that after undergoing ultrasonic high-frequency micro-forging (UH-FM), the surface layer of the coating was broken and refined, and a gradient structure appeared. A part of the fcc phase was transformed into the bcc phase, which increased the resistance of dislocation movement, and the hardness of the coating increased. Cai et al. [122] observed that after rolling, the tops of the columnar grains in the FeCoCrNi alloy coatings produced by laser cladding exhibited increased width and a noticeable inclination. Zhang et al. [123] combined laser deposition technology with shot peening and discovered that the yield strength of the Fe-based alloy coatings produced by this hybrid process was significantly enhanced. Additionally, some coarse columnar grains were refined, leading to a reduction in grain size heterogeneity and an overall improvement in the microstructure.

4.5. Assistance from Multiple Physical Fields

The control effects of single energy fields, such as ultrasonic fields, electromagnetic fields, and thermal fields, on defects like porosity and cracks in the cladding layer each have their advantages in different application areas. However, issues still arise with the beneficial effects produced during the laser cladding process, such as the attenuation of ultrasound during transmission, the complexity of electromagnetic field equipment, and the uneven temperature distribution in thermal fields. The technology of multi physics-assisted laser cladding involves the coupling of various physical energy fields to leverage their synergistic effects, thereby addressing the limitations of single-process techniques and extending the capabilities for the organization and performance regulation of high-hardness iron-based alloy coatings. Zhou et al. [124] developed a preheating and ultrasonic composite-assisted laser additive manufacturing method, comparing the effects of single energy fields and composite energy fields on the microstructure and properties of the 24CrNiMoY coating. It was found that the synergistic effect of the dual fields had a more significant influence on the coating's density, phase composition, grain size, and strength–ductility matching properties. Zheng et al. [125] combined ultrasonic waves with traditional rolling processes to investigate the impact of the hybrid process on the surface quality of Fe-based alloy coatings, comparing it with conventional rolling. It was observed that the coatings produced through the hybrid process exhibited finer grain sizes, with surface roughness reduced to only one-quarter of that of the traditionally rolled coatings, and both hardness and residual compressive stress were found to be higher than those of the coatings subjected to conventional rolling.

5. Conclusions

In recent decades, there has been significant advancement in the preparation of high-hardness iron-based alloy coatings using laser cladding, particularly in terms of cladding material composition, laser processing techniques, and the optimization of coating performance. However, due to persistent issues with coating defects and cost considerations, its broad industrial application remains limited. To realize coatings that exhibit metallurgical bonding with the substrate and deliver satisfactory performance, future research should focus on the areas outlined in Table 3.

Table 3. Future research directions and focus areas.

Improvement Direction	Measures	Expected Performance	Potential Drawbacks
Improvement of iron-based alloy powders	Combining the characteristics of non-equilibrium solidification in laser cladding and considering different reinforcement and repair targets, a database will be established using digital manufacturing technology.	Establishing a predictive model for the relationship between material composition, microstructure, and properties to effectively address the issue of cracking	Extensive experimental validation is still required.
Optimization of process parameters	By integrating digital manufacturing technology, process parameters can be dynamically adjusted through real-time monitoring and feedback systems.	Improving the stability and repeatability of coating quality	It may increase the complexity and cost of the system.
Composite energy field	Exploring the coupling effects of the composite energy field and optimizing the energy field parameters and application methods	Effectively suppressing the generation of defects by extending the limits of coating microstructure and performance control	The specific effects of different energy field parameters are difficult to quantify.

Author Contributions: Conceptualization, methodology, and investigation, L.L. and Y.L.; formal analysis, supervision, and writing—review and editing, Y.L., X.K., L.P. and X.W.; writing—original draft preparation, L.L.; project administration and funding acquisition, Y.L. and X.W. All authors have read and agreed to the published version of the manuscript.

Funding: The research work was financially supported by the Key Technology Innovation and Industrialization Project of Fujian Province (No. 2023XQ017), the Natural Science Foundation of Hunan Province of China (No. 2024JJ5336), the Natural Science Foundation of Hunan Province of China—Provincial and Municipal Joint Fund (No. 2022JJ50019), the Hengyang Guiding Plan Project (No. hyzdxjh202101), and the University of South China Talent Introduction Project (No. 210XQD017).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the manuscript.

Conflicts of Interest: Author Longsheng Peng was employed by Hunan Lifang Roller Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Shi, Y.; Xia, Q.; Xie, M.; Zhou, Q.; Hua, D.; Chai, L.; Shi, T.; Eder, S.J.; Wang, H.; Wang, P.; et al. Insights into irradiation-affected structural evolution and mechanical behavior of amorphous carbon. *Acta Mater.* **2024**, *281*, 120424. [CrossRef]
- Zhou, Q.; Luo, D.; Hua, D.; Ye, W.; Li, S.; Zou, Q.; Chen, Z.; Wang, H. Design and characterization of metallic glass/graphene multilayer with excellent nanowear properties. *Friction* **2022**, *10*, 1913–1926. [CrossRef]
- Li, L.; Yao, C.; Huang, J.; Feng, K.; Li, Z. Characteristics of interdendritic residual austenite in laser cladding of high hardness iron-based coating. *Chin. J. Lasers* **2017**, *44*, 0302011.
- Trojan, K.; Ocelík, V.; Čapek, J.; Čech, J.; Canelo-Yubero, D.; Ganev, N.; Kolařík, K.; De Hosson, J.T.M. Microstructure and mechanical properties of laser additive manufactured H13 tool steel. *Metals* **2022**, *12*, 243. [CrossRef]
- Shi, X.; Wen, D.; Wang, S.; Wang, G.; Zhang, M.; Liao, J.; Xu, C. Investigation on friction and wear performance of laser cladding Ni-based alloy coating on brake disc. *Optik* **2021**, *242*, 167227. [CrossRef]
- Pellizzari, M.; Zhao, Z.; Bosetti, P.; Perini, M. Optimizing direct laser metal deposition of H13 cladding on CuBe alloy substrate. *Surf. Coat. Technol.* **2022**, *432*, 128084. [CrossRef]
- Zuojiang, S.; Yu, H.; Jiang, X.; Gao, W.; Sun, D. A thermal field FEM of titanium alloy coating on low-carbon steel by laser cladding with experimental validation. *Surf. Coat. Technol.* **2022**, *452*, 129113. [CrossRef]
- Wang, J.; Timokhina, I.; Sharp, K.; Shekhter, A.; Liu, Q. Microstructure and precipitation behaviours of laser clad 7075 aluminium alloy. *Surf. Coat. Technol.* **2022**, *445*, 128726. [CrossRef]

9. Zhu, L.; Xue, P.; Lan, Q.; Meng, G.; Ren, Y.; Yang, Z.; Xu, P.; Liu, Z. Recent research and development status of laser cladding: A review. *Opt. Laser Technol.* **2021**, *138*, 106915. [CrossRef]
10. Dmitrieva, A.; Klimova-Korsmik, O.; Gushchina, M.O.; Korsmik, R.; Zadykhan, G.; Tukov, S. Effect of the laser cladding parameters on the crack formation and microstructure during nickel superalloy gas turbine engines repair. *Metals* **2023**, *13*, 393. [CrossRef]
11. Ritchie, R.O. The conflicts between strength and toughness. *Nat. Mater.* **2011**, *10*, 817–822. [CrossRef] [PubMed]
12. Ouyang, C.; Wang, R.; Bai, Q.; Chen, Z.; Yan, X. Aging strengthening treatment of laser cladding Co-based alloy coating. *Mater. Lett.* **2022**, *313*, 131746. [CrossRef]
13. Awasthi, R.; Limaye, P.K.; Kumar, S.; Kushwaha, R.P.; Viswanadham, C.S.; Srivastava, D.; Soni, N.L.; Patel, R.J.; Dey, G.K. Wear characteristics of Ni-based hardfacing alloy deposited on stainless steel substrate by laser cladding. *Metall. Mater. Trans. A* **2015**, *46*, 1237. [CrossRef]
14. Wang, C.; Wang, W.; Ding, S.; Gong, P.; Gao, Y. Preparation and tribological properties of laser cladding iron based wear resistant coatings. *Chin. J. Lasers* **2022**, *49*, 137–147.
15. Yang, Y.-l.; Zhou, L.-l.; Chen, H.-b.; Wang, J.; Qiao, H.C.; Lu, Y.; Qin, G.-w. Laser shock peening Fe-based coatings for enhancing wear and corrosion resistance. *Mater. Sci. Technol.* **2021**, *37*, 1214–1224. [CrossRef]
16. Yang, P.; Song, Y.; Wang, J.; Hu, F.; Xie, L. Semiconductor laser cladding of an Fe-based alloy on nodular cast iron. *Weld. World* **2021**, *65*, 785–792. [CrossRef]
17. Ding, H.; Mu, X.; Zhu, Y.; Yang, W.; Xiao, Q.; Wang, W.; Liu, Q.; Guo, J.; Zhou, Z. Effect of laser claddings of Fe-based alloy powder with different concentrations of WS₂ on the mechanical and tribological properties of railway wheel. *Wear* **2022**, *488–489*, 204174. [CrossRef]
18. Xie, Z.; Liu, C.; Wu, Q.; Chen, S.; Liang, J. A review on the preparation of high hard and wear resistant coatings by laser cladding. *Surf. Technol.* **2022**, *52*, 25–40.
19. Li, Q.; Fu, H. Research progress in laser cladding of iron based wear-resistant alloys. *J. B. Univ. Technol.* **2013**, *39*, 1552–1560.
20. Aghasibeig, M.; Fredriksson, H. Laser cladding of a featureless iron-based alloy. *Surf. Coat. Technol.* **2012**, *209*, 32–37. [CrossRef]
21. Feng, K.; Guo, Y.; Feng, Y.; Yao, C.; Zhu, Y.; Zhang, Q.; Li, Z. Microstructure controlling and properties of laser clad high strength and high toughness Fe-based coatings. *Acta Metall. Sin. Engl. Lett.* **2022**, *58*, 513–528.
22. Jiang, M.; Sun, S.; Wang, J.; Wang, P.; Sun, X.; Shao, J.; Liu, J.; Cao, A.; Sun, W.; Chen, X. Research progress in wear resistance of high entropy alloy coatings prepared by laser cladding. *J. Mater. Eng.* **2022**, *50*, 18–32.
23. Zhou, Q.; Jiao, Z.; Huang, Z.; Shi, Y.; Li, Y.; Ying, C.; Wang, H.; Cavalcanti Pinto, H.; Greiner, C.; Liu, W. Wear-resistant CrCoNi nanocrystalline film via friction-driven surface segregation. *Acta Mater.* **2024**, *279*, 120299. [CrossRef]
24. Lentz, J.; Röttger, A.; Theisen, W. Mechanism of the Fe₃(B, C) and Fe₂₃(C, B)₆ solid-state transformation in the hypoeutectic region of the Fe-C-B system. *Acta Mater.* **2016**, *119*, 80–91. [CrossRef]
25. Lentz, J.; Röttger, A.; Theisen, W. Hardness and modulus of Fe₂B, Fe₃(C, B), and Fe₂₃(C, B)₆ borides and carboborides in the Fe-C-B system. *Mater. Charact.* **2018**, *135*, 192–202. [CrossRef]
26. Dong, G.; You, H.; Mao, K.; Yuan, N.; Ge, M.; Yu, X.; Zhang, Q.; Yao, J. Effect of Si element content on the manufacturing process and corrosion performance of laser clad 316L. *Surf. Technol.* **2024**, *53*, 179–190.
27. Li, Q.; Wang, Q.; Zhang, L.; Chen, D.; Jin, H.; Li, J.; Zhang, J. Microstructure, wear and electrochemical behaviors of laser cladding Fe-based coatings with various molybdenum contents. *Mater. Res. Express* **2022**, *9*, 026504. [CrossRef]
28. Liu, X.; Wang, H.; Liu, Y.; Wang, C.; Song, Q.; Cui, H.; Zhang, C.; Huang, K. The effect of Nb content on microstructure and properties of laser cladding 316L SS coating. *Surf. Coat. Technol.* **2021**, *425*, 127684. [CrossRef]
29. Yang, Y.; Xing, Y.; Chen, H.; Liu, Z.; Wang, B.; Qiao, H.; Zhang, E. Improving wear and corrosion resistance of U71Mn rail steel subjected to laser in-situ fabrication of Fe based Cr–V coatings. *Wear* **2024**, *546–547*, 205312. [CrossRef]
30. Yang, J.; Miao, X.; Wang, X.; Yang, F. Influence of Mn additions on the microstructure and magnetic properties of FeNiCr/60% WC composite coating produced by laser cladding. *Int. J. Refract. Hard. Met.* **2014**, *46*, 58–64. [CrossRef]
31. Shang, F.; Xu, Z.; Chen, J.; Chen, L.; Lu, S.; Wang, S.; Jing, X.; Dubovyi, O. Effect of Cr on wear resistance and mechanism of preset-powder laser cladding T15 alloy steel coating. *J. Mater. Res. Technol.* **2024**, *29*, 4991–4999. [CrossRef]
32. Feng, Y.; Pang, X.; Feng, K.; Feng, Y.; Li, Z. Study on microstructure and compressive properties of Fe-C-W-Cr-V-Nb coating with boron addition. *J. Alloys Compd.* **2022**, *904*, 163986. [CrossRef]
33. Wang, Q.; Bai, X.; Sun, B.; Liu, J.; Cai, Z.; Liang, X.; Shen, B. Influence of Si on tribological behavior of laser clad Fe-based amorphous/crystalline composite coatings. *Surf. Coat. Technol.* **2021**, *405*, 126570. [CrossRef]
34. Liang, Z.; Zhan, J.; Shi, W.; Xie, Y.; Huang, J.; An, F. The effect of Si addition amount on Fe-based alloy laser cladding coating. *Appl. Laser* **2020**, *40*, 593–597.
35. Chen, K.; Yang, X.; Li, W.; Xia, G.; Wang, S.; Wang, K. Study on the wear and corrosion resistance of Fe–Mo coatings on 65Mn steel ploughshares by laser cladding. *Appl. Phys. A* **2022**, *128*, 795. [CrossRef]
36. Cao, S.; Liang, J.; Zhou, J. Evolution in microstructure features and properties of Mo-containing Fe-Cr-Ni-B-Si composite coatings by laser cladding. *Mater. Charact.* **2022**, *188*, 111926. [CrossRef]
37. Ma, X.; Wang, K.; Fu, H.; Ju, J.; Lei, Y.; Yi, D. Effect of Mo content on microstructure and properties of laser cladding Fe-based alloy coatings. *Surf. Rev. Lett.* **2018**, *25*, 1850077.

38. Wang, H.Z.; Cheng, Y.H.; Yang, J.Y.; Wang, Q.Q. Microstructure and properties of laser clad Fe-based amorphous alloy coatings containing Nb powder. *J. Non-Cryst. Solids* **2020**, *550*, 120351. [CrossRef]
39. Shan, B.; Chen, J.; Chen, S.; Ma, M.; Ni, L.; Shang, F.; Zhou, L. Laser cladding of Fe-based corrosion and wear-resistant alloy: Genetic design, microstructure, and properties. *Surf. Coat. Technol.* **2022**, *433*, 128117. [CrossRef]
40. Yao, C.; Xu, B.; Huang, J.; Zhang, P.; Li, Z.; Wu, Y. Microstructure design of controlling crack of Fe-based laser cladding layer. *China Surf. Eng.* **2010**, *23*, 74–79+83.
41. Chen, L.; Lan, Y.; Cheng, Y.; Zeng, J.; Ma, Y.; Yu, S.; Ding, Z.; Liu, B.; Zhang, J.; Peng, H.; et al. Friction behavior and wear mechanism of laser clad FeNiCr-WC composite coatings in comparison with different friction pairs. *J. Mater. Res. Technol.* **2024**, *31*, 1956–1973. [CrossRef]
42. Zhang, X.; Lu, W.; Guo, H.; Huo, F.; Chen, H.; Qiu, K.; Yang, B.; Wang, J. Effect of WC–Co addition on tribological and cracking behavior of laser clad Fe-based amorphous/crystalline composite coatings. *J. Mater. Sci.* **2023**, *58*, 11804–11819. [CrossRef]
43. Liu, C.; Xu, P.; Pang, C.; Zha, G.; Ouyang, Z.; Chen, J. Phase transformation in Fe–Mn–Si SMA/WC composite coating developed by laser cladding. *Mater. Chem. Phys.* **2021**, *267*, 124595. [CrossRef]
44. Li, J.; Zhu, Z.; Peng, Y.; Shen, G. Phase evolution and wear resistance of in-situ synthesized (Cr, W)₂₃C₆-WC composite ceramics reinforced Fe-based composite coatings produced by laser cladding. *Vacuum* **2021**, *190*, 110242. [CrossRef]
45. Xu, N.; Zhang, Q.; Yao, J. Microstructure of in-site synthesis TiC hardened coating by laser irradiation. *Chin. J. Lasers* **2010**, *37*, 2653–2657.
46. Zhang, Z.; Wang, X.; Zhang, Q.; Liang, Y.; Ren, L.; Li, X. Fabrication of Fe-based composite coatings reinforced by TiC particles and its microstructure and wear resistance of 40Cr gear steel by low energy pulsed laser cladding. *Opt. Laser Technol.* **2019**, *119*, 105622. [CrossRef]
47. Li, A.; Wei, C.; Liu, J.; Zhou, W.; Wang, H.; Kuang, S. Microstructure, friction and wear properties of laser cladding Fe-based Cr₃C₂/MoS₂ coatings. *China Surf. Eng.* **2015**, *28*, 77–85.
48. Li, H.; Gao, Q.; Li, K.; Li, B. Properties of surface laser cladding H13/NiCr-Cr₃C₂ composite powder cladding layer. *Chin. J. Lasers* **2018**, *48*, 163–172.
49. Chen, L.; Yu, T.; Xu, P.; Zhang, B. In-situ NbC reinforced Fe-based coating by laser cladding: Simulation and experiment. *Surf. Coat. Technol.* **2021**, *412*, 127027. [CrossRef]
50. Aramide, B.; Jamiru, T.; Pityana, S.; Sadiku, R.; Popoola, P. Scanning speed effect on the microstructure, hardness, wear, and corrosion performance of VC-Cr₃C₂ reinforced laser claddings on steel baseplate for tillage application. *Trans. Indian Inst. Met.* **2022**, *75*, 2149–2157. [CrossRef]
51. Tan, H.; Luo, Z.; Li, Y.; Yan, F.; Duan, R. Microstructure and wear resistance of Al₂O₃–M₇C₃/Fe composite coatings produced by laser controlled reactive synthesis. *Opt. Laser Technol.* **2015**, *68*, 11–17. [CrossRef]
52. Fomin, V.M.; Malikov, A.G.; Golyshv, A.A.; Bulina, N.V.; Gulov, M.A.; Vitoshkin, I.E.; Brusentseva, T.A.; Filippov, A.A.; Mishin, A.V. Structural-phase state and mechanical properties of a laser cladding titanium matrix composite based on Ti64 alloy and TiB₂ ceramics. *Phys. Mesomech.* **2024**, *27*, 1–15. [CrossRef]
53. Naizabekov, A.; Samodurova, M.; Bodrov, E.; Lezhnev, S.; Samoilova, O.; Trofimov, E.; Mikhailov, D.; Litvinyuk, K.; Trofimova, S.; Latfulina, Y.; et al. Use of laser cladding for the synthesis of coatings from high-entropy alloys reinforced with ceramic particles. *Case Stud. Constr. Mater.* **2023**, *19*, e02541. [CrossRef]
54. Wang, J.; Li, L.; Tao, W. Crack initiation and propagation behavior of WC particles reinforced Fe-based metal matrix composite produced by laser melting deposition. *Opt. Laser Technol.* **2016**, *82*, 170–182. [CrossRef]
55. Li, W.; Yang, X.; Wang, S.; Duan, D.; Li, F.; Qiao, Y.; Liu, Y.; Liu, X. The effect of WC content on the bonding strength and mechanical properties of WC/Ni60 coatings of brake disc. *Opt. Laser Technol.* **2022**, *149*, 107822. [CrossRef]
56. Lu, J.Z.; Cao, J.; Lu, H.F.; Zhang, L.Y.; Luo, K.Y. Wear properties and microstructural analyses of Fe-based coatings with various WC contents on H13 die steel by laser cladding. *Surf. Coat. Technol.* **2019**, *369*, 228–237. [CrossRef]
57. Zhu, H.; Ouyang, M.; Hu, J.; Zhang, J.; Qiu, C. Design and development of TiC-reinforced 410 martensitic stainless steel coatings fabricated by laser cladding. *Ceram. Int.* **2021**, *47*, 12505–12513. [CrossRef]
58. Li, J.; Zhu, Z.; Peng, Y.; Shen, G. A comparative study on microstructure evolution and wear resistance of different-sized tungsten carbide modified Fe-based laser cladding coatings. *Opt. Laser Technol.* **2022**, *147*, 107672. [CrossRef]
59. Xiao, Q.; Sun, W.L.; Yang, K.x.; Xing, X.f.; Chen, Z.h.; Zhou, H.n.; Lu, J. Wear mechanisms and micro-evaluation on WC particles investigation of WC-Fe composite coatings fabricated by laser cladding. *Surf. Coat. Technol.* **2021**, *420*, 127341. [CrossRef]
60. Zou, L.; Liu, X.; Wang, L.; Xie, H.; Cai, Y. Effects of cast tungsten carbide powder on wear resistance of laser cladding ceramic particle reinforced iron matrix composite. *Rare Met. Mater. Eng.* **2017**, *46*, 1126–1131.
61. Chen, T.; Deng, Z.; Liu, D.; Zhu, X.; Xiong, Y. Bioinert TiC ceramic coating prepared by laser cladding: Microstructures, wear resistance, and cytocompatibility of the coating. *Surf. Coat. Technol.* **2021**, *423*, 127635. [CrossRef]
62. Xu, L.; Xiao, R.; Qu, G.; Wang, D. In situ synthesized graded TiC particulate reinforced Ni-based composite coating prepared by laser cladding. *J. Phys. Conf. Ser.* **2021**, *1820*, 012050. [CrossRef]
63. Richardson, P.; Cuskelly, D.; Brandt, M.; Kisi, E. Microstructural analysis of in-situ reacted Ti₂AlC MAX phase composite coating by laser cladding. *Surf. Coat. Technol.* **2020**, *385*, 125360. [CrossRef]
64. Adesina, O.S.; Popoola, A.P.I.; Pityana, S.L.; Oloruntoba, D.T. Microstructural and tribological behavior of in situ synthesized Ti/Co coatings on Ti-6Al-4V alloy using laser surface cladding technique. *Int. J. Adv. Manuf. Tech.* **2018**, *95*, 1265–1280. [CrossRef]

65. Ren, Y.; Li, L.; Zhou, Y.; Wang, S. In situ synthesized VC reinforced Fe-based coating by using extreme high-speed laser cladding. *Mater. Lett.* **2022**, *315*, 131962. [CrossRef]
66. Weng, F.; Yu, H.; Chen, C.; Liu, J.; Zhao, L.; Dai, J. Fabrication of Co-based coatings on titanium alloy by laser cladding with CeO₂ addition. *Mater. Manuf. Process.* **2016**, *31*, 1461–1467. [CrossRef]
67. Zhu, Z.; Li, J.; Peng, Y.; Shen, G. In-situ synthesized novel eyeball-like Al₂O₃/TiC composite ceramics reinforced Fe-based alloy coating produced by laser cladding. *Surf. Coat. Technol.* **2020**, *391*, 125671. [CrossRef]
68. Mohammed, S.; Balu, P.; Ahmed, A.; Zhang, Z.; Kovacevic, R. Improvement of wear resistance of the nickel based alloy mixed with rare earth elements by high power direct diode laser cladding. *Lasers Manuf. Mater. Process.* **2019**, *6*, 173–188. [CrossRef]
69. Das, A.K. Effect of rare earth oxide additive in coating deposited by laser cladding: A review. *Mater. Today Proc.* **2022**, *52*, 1558–1564. [CrossRef]
70. Quazi, M.M.; Fazal, M.A.; Haseeb, A.S.M.A.; Yusof, F.; Masjuki, H.H.; Arslan, A. Effect of rare earth elements and their oxides on tribo-mechanical performance of laser claddings: A review. *J. Rare Earths* **2016**, *34*, 549–564. [CrossRef]
71. Jiang, H.; Zhao, X.; Cao, S.; Wang, D.; Zhu, Q.; Lei, Y. Improvement of the mechanical properties and LBE cavitation erosion resistance of laser clad FeCrAlTiC coating by Y₂O₃ addition. *Mater. Lett.* **2022**, *326*, 132882. [CrossRef]
72. Wang, Q.; Yang, J.; Niu, W.; Li, Y.; Mao, X.; Wang, Y.; Zhang, K. Effect of La₂O₃ on microstructure and properties of Fe-based alloy coatings by laser cladding. *Optik* **2021**, *245*, 167653. [CrossRef]
73. Cai, Y.; Luo, Z.; Chen, Y.; Ao, S. Influence of CeO₂ on tribological behaviour of TiC/Fe-based composite coating. *Surf. Eng.* **2017**, *33*, 936–943. [CrossRef]
74. Chen, L.; Zhao, Y.; Guan, C.; Yu, T. Effects of CeO₂ addition on microstructure and properties of ceramics reinforced Fe-based coatings by laser cladding. *Int. J. Adv. Manuf. Technol.* **2021**, *115*, 2581–2593. [CrossRef]
75. Zhang, M.; Wang, X.H.; Qu, K.L.; Liu, S.S. Effect of rare earth oxide on microstructure and high temperature oxidation properties of laser cladding coatings on 5CrNiMo die steel substrate. *Opt. Laser Technol.* **2019**, *119*, 105597. [CrossRef]
76. Yu, W.; Ma, P.; Bai, W.; Chen, J. Numerical simulation of temperature field and stress field in 316L/Aisi304 laser cladding with different scanning strategies. *Chin. J. Lasers* **2021**, *48*, 18–29.
77. Fan, S.; Mao, J.; Xie, S.; Wang, L.; Yao, Z.; Chen, Z.; Yao, J. Effect of pulsed/continuous double-beam hybrid laser cladding on microstructure of 316L stainless steel. *Chin. J. Lasers* **2023**, *50*, 80–90.
78. Muvvala, G.; Patra Karmakar, D.; Nath, A.K. Online monitoring of thermo-cycles and its correlation with microstructure in laser cladding of nickel based super alloy. *Opt. Lasers Eng.* **2017**, *88*, 139–152. [CrossRef]
79. Chen, C.; Meiping, W.; Rui, H.; Yuling, G.; Xiaojin, M. Understanding stellite-6 coating prepared by laser cladding: Convection and columnar-to-equiaxed transition. *Opt. Laser Technol.* **2022**, *149*, 107885. [CrossRef]
80. Wang, K.; Liu, W.; Hong, Y.; Sohan, H.M.S.; Tong, Y.; Hu, Y.; Zhang, M.; Zhang, J.; Xiang, D.; Fu, H.; et al. An overview of technological parameter optimization in the case of laser cladding. *Coatings* **2023**, *13*, 496. [CrossRef]
81. Mao, J.; Feng, A.; Cheng, B.; Li, Z.; Wu, H.; Huang, Y.; Zhang, H. Microstructure and friction and wear properties of Fe-based alloy coatings by laser cladding. *Hot Work. Technol.* **2017**, *46*, 139–142.
82. Xie, Y.; Chen, W.; Liang, L.; Huang, B.; Zhuang, J. Influence of laser power on the microstructure and properties of Fe314 alloy cladding layer on EA4T steel. *Weld. World* **2022**, *66*, 1551–1563. [CrossRef]
83. Jiao, X.; Wang, J.; Wang, C.; Gong, Z.; Pang, X.; Xiong, S.M. Effect of laser scanning speed on microstructure and wear properties of T15M cladding coating fabricated by laser cladding technology. *Opt. Lasers Eng.* **2018**, *110*, 163–171. [CrossRef]
84. Li, R.; Yuan, W.; Yue, H.; Zhu, Y. Study on microstructure and properties of Fe-based amorphous composite coating by high-speed laser cladding. *Opt. Laser Technol.* **2022**, *146*, 107574. [CrossRef]
85. Sun, Z.; Du, C.; Yu, Z.; Long, Y.; Ren, X. Effect of cladding speed on the microstructure and hardness of high-hardness B-bearing Cr17Ni2 coating. *J. Mater. Res. Technol.* **2024**, *31*, 668–678. [CrossRef]
86. Wang, Q.; Qian, R.; Yang, J.; Niu, W.; Zhou, L.; Pan, X.; Su, C. Effect of high-speed powder feeding on microstructure and tribological properties of Fe-based coatings by laser cladding. *Coatings* **2021**, *11*, 1456. [CrossRef]
87. Bartkowski, D.; Bartkowska, A.; Jurči, P. Laser cladding process of Fe/WC metal matrix composite coatings on low carbon steel using Yb: YAG disk laser. *Opt. Laser Technol.* **2021**, *136*, 106784. [CrossRef]
88. Budde, L.; Biester, K.; Lammers, M.; Hermsdorf, J.; Kaierle, S.; Overmeyer, L. Influence of process parameters on single weld seam geometry and process stability in Laser Hot-Wire Cladding of AISI 52100. *Adv. Ind. Manuf. Eng.* **2023**, *7*, 100122. [CrossRef]
89. Li, G.; Zhang, J.; Shi, T.; Shi, J.; Cheng, D.; Lu, L.; Shi, S. Experimental investigation on laser metal deposition of Ti-6Al-4V alloy with coaxial local shielding gas nozzle. *J. Mater. Eng. Perform.* **2020**, *29*, 7821–7829. [CrossRef]
90. Ding, J.; Colegrove, P.; Martina, F.; Williams, S.; Wiktorowicz, R.; Palt, M.R. Development of a laminar flow local shielding device for wire + arc additive manufacture. *J. Mater. Process. Technol.* **2015**, *226*, 99–105. [CrossRef]
91. Budde, L.; Biester, K.; Coors, T.; Faqiri, M.Y.; Lammers, M.; Hermsdorf, J.; Hassel, T.; Pape, F.; Overmeyer, L. Influence of shielding gas coverage during laser hot-wire cladding with high carbon steel. *Int. J. Adv. Manuf. Technol.* **2023**, *127*, 3195–3207. [CrossRef]
92. Bernauer, C.; Meininger, L.; Zapata, A.; Zhao, X.; Baehr, S.; Zaeh, M.F. Design and investigation of a novel local shielding gas concept for laser metal deposition with coaxial wire feeding. *Appl. Sci.* **2023**, *13*, 5121. [CrossRef]
93. Du, Y.; Peng, Y.; Mao, K.; He, G.; Zhang, L. Effect of laser specific energy on mechanical properties of Fe60 coatings by laser cladding. *Opt. Laser Technol.* **2024**, *172*, 110497. [CrossRef]

94. Luo, D.; Liu, C.; Wang, C.; Wang, Y.; Wang, X.; Zhao, J.; Jiang, S. Optimization of multilayer laser cladding process parameters based on NSGA-II-MOPSO algorithm. *Opt. Laser Technol.* **2024**, *176*, 111025. [CrossRef]
95. Wotosz, P.; Baran, A.; Polański, M. The influence of laser engineered net shaping (LENS™) technological parameters on the laser deposition efficiency and properties of H13 (AISI) steel. *J. Alloys Compd.* **2020**, *823*, 153840. [CrossRef]
96. Reddy, L.; Preston, S.P.; Shipway, P.H.; Davis, C.; Hussain, T. Process parameter optimisation of laser clad iron based alloy: Predictive models of deposition efficiency, porosity and dilution. *Surf. Coat. Technol.* **2018**, *349*, 198–207. [CrossRef]
97. Yingtao, Z.; Yongliang, M.; Gang, W.; Xiulin, J.; Zhichao, L. Experimental study on the wear properties of 42CrMo steel with different microstructures and T15 laser cladding. *J. Mater. Eng. Perform.* **2022**, *31*, 4232–4241. [CrossRef]
98. Xiao, M.; Jiang, F. Microstructural evolution of Fe-based amorphous alloy coatings via ultrasonic vibration-assisted laser cladding. *Mater. Lett.* **2022**, *322*, 132520. [CrossRef]
99. Huang, L.; Zhou, J.; Xu, J.; Huo, K.; He, W.; Meng, X.K.; Huang, S. Microstructure and wear resistance of electromagnetic field assisted multi-layer laser clad Fe901 coating. *Surf. Coat. Technol.* **2020**, *395*, 125876. [CrossRef]
100. Wang, X.L.; Huang, A.R.; Shang, C.J.; Xie, Z.J. Characterization of the cladding layer by laser cladding of 9Cr18Mo powder on 3Cr14 martensitic stainless steel and the impact of martensite obtained through post heat treatment on hardness. *Mater. Today Commun.* **2022**, *32*, 104057. [CrossRef]
101. Guo, W.; Li, X.; Ding, N.; Liu, G.; He, J.; Tian, L.; Chen, L.; Zairi, F. Microstructure characteristics and mechanical properties of a laser clad Fe-based martensitic stainless steel coating. *Surf. Coat. Technol.* **2021**, *408*, 126795. [CrossRef]
102. Gong, F.-b.; Shen, J.; Gao, R.-h.; Zhang, T.; Xie, X.; Li, Y. Influence of heat treatment on microstructure and mechanical properties of FeCrNi coating produced by laser cladding. *Trans. Nonferr. Metal. Soc.* **2016**, *26*, 2117–2125. [CrossRef]
103. Da Sun, S.; Fabijanic, D.; Barr, C.; Liu, Q.; Walker, K.; Matthews, N.; Orchowski, N.; Easton, M.; Brandt, M. In-situ quench and tempering for microstructure control and enhanced mechanical properties of laser clad AISI 420 stainless steel powder on 300M steel substrates. *Surf. Coat. Technol.* **2018**, *333*, 210–219. [CrossRef]
104. Gao, W.; Zhao, S.; Wang, Y.; Zhang, Z.; Zhou, C.; Lin, X. Refinement of Fe-based alloy doped Ti cladding layer. *Surf. Coat. Technol.* **2015**, *270*, 16–23. [CrossRef]
105. Rahman Rashid, R.A.; Nazari, K.A.; Barr, C.; Palanisamy, S.; Orchowski, N.; Matthews, N.; Dargusch, M.S. Effect of laser reheat post-treatment on the microstructural characteristics of laser-clad ultra-high strength steel. *Surf. Coat. Technol.* **2019**, *372*, 93–102. [CrossRef]
106. Zhu, L.; Yang, Z.; Xin, B.; Wang, S.; Meng, G.; Ning, J.; Xue, P. Microstructure and mechanical properties of parts formed by ultrasonic vibration-assisted laser cladding of Inconel 718. *Surf. Coat. Technol.* **2021**, *410*, 126964. [CrossRef]
107. Liu, W.; Mi, G.; Li, L.; Chen, X.; Pan, Y.; Zhai, F.; Miao, H. Research progress of effect of auxiliary treatment on microstructure and properties of laser cladding layer. *Mater. Rep.* **2023**, *37*, 200–206.
108. Yao, Z.; Shen, Q.; Ge, H.; Wang, Z.; Dong, G.; Ye, Z.; Li, L.; Yao, J. Influence of ultrasound on the wetting behavior of molten pool in laser cladding. *Surf. Technol.* **2022**, *51*, 20–29.
109. Xiao, M.; Jiang, F.; Guo, C.; Song, H.; Dong, T. Investigation on microstructure and mechanical properties of Fe-based amorphous coatings prepared via laser cladding assisted with ultrasonic vibration. *Opt. Laser Technol.* **2023**, *162*, 109294. [CrossRef]
110. Han, X.; Li, C.; Yang, Y.; Gao, X.; Gao, H. Experimental research on the influence of ultrasonic vibrations on the laser cladding process of a disc laser. *Surf. Coat. Technol.* **2021**, *406*, 126750. [CrossRef]
111. Xu, J.; Zhou, J.; Tan, W.; Huang, S.; Wang, S.; He, W. Ultrasonic vibration on wear property of laser cladding Fe-based coating. *Surf. Eng.* **2018**, *36*, 1–9. [CrossRef]
112. Yao, Z.; Wang, F.; Sun, Z.; Chen, Z.; Liu, R.; Yao, J. Effects of ultrasound on distribution of laser melt injected WC reinforced particles on stainless steel substrate surface. *Chin. J. Lasers* **2023**, *50*, 100–109.
113. Wang, Y.; Liu, S.; Zhang, X.; Liu, Y.; Li, R. Experiments and analyses of 3540Fe/CeO₂ coatings by ultrasonic vibration assisted laser cladding. *China Mech. Eng.* **2018**, *29*, 2600–2605.
114. Liu, L.; Feng, M.; Wang, X.; Cui, Y.; Jia, Z.; Li, J. Microstructure analysis of laser cladding strengthening layer on H13 die steel surface assisted by ultrasonic. *Trans. China Weld. Inst.* **2021**, *42*, 85–90+96+102.
115. Wang, Q.; Zhang, L.; Li, Q.; Zhang, J.; Ban, C. Research progress of electromagnetic field assisted laser cladding technology. *Surf. Technol.* **2023**, *52*, 166–179.
116. Lin, Y.; Yuan, Y.; Wang, L.; Hu, Y.; Zhang, Q.; Yao, J. Effect of electric-magnetic compound field on the microstructure and crack in solidified Ni60 alloy. *Acta Metall. Sin.* **2021**, *54*, 1442–1450.
117. Ouyang, W.; Xu, Z.; Chao, Y.; Liu, Y.; Luo, W.; Jiao, J.; Sheng, L.; Zhang, W. Effect of electrostatic field on microstructure and mechanical properties of the 316L stainless steel modified layer fabricated by laser cladding. *Mater. Charact.* **2022**, *191*, 112123. [CrossRef]
118. Li, G.; Wang, Z.; Yao, L.; Xie, D.; Chen, G. Concentration mixing and melt pool solidification behavior during the magnetic field assisted laser cladding of Fe-Cr-based alloy on 45 steel surface. *Surf. Coat. Technol.* **2022**, *445*, 128732. [CrossRef]
119. Chen, Y.; Zhou, J.; Li, P.; Huo, K.; Meng, X.K. Effect of electromagnetic field on wear resistance of Fe901/Al₂O₃ metal matrix composite coating prepared by laser cladding. *Materials* **2022**, *15*, 1531. [CrossRef]
120. Pape, F.; Coors, T.; Barroi, A.; Hermsdorf, J.; Mildebrath, M.; Hassel, T.; Kaierle, S.; Matthias, T.; Chugreev, A.; Chugreeva, A.; et al. Tribological study on tailored-formed axial bearing washers. *Tribol. Online* **2018**, *13*, 320–326. [CrossRef]

121. Chen, C.; Bai, Q.; Zhao, C.; Li, Q.; Zhang, S. Effect of ultrasonic high-frequency micro-forging on the wear resistance of a Fe-base alloy coating deposited by high-speed laser cladding process. *Vacuum* **2024**, *221*, 112934. [CrossRef]
122. Cai, Y.; Shan, M.; Cui, Y.; Manladan, S.M.; Lv, X.; Zhu, L.; Sun, D.; Wang, T.; Han, J. Microstructure and properties of FeCoCrNi high entropy alloy produced by laser melting deposition. *J. Alloys Compd.* **2021**, *887*, 161323. [CrossRef]
123. Zhang, X.; Huang, S.; Li, D.; Geng, J.; Yang, F.; Li, Q. An approach to improve the microstructure and mechanical properties: A hybrid manufacturing of laser directed energy deposition and shot peening. *Addit. Manuf.* **2022**, *55*, 102686. [CrossRef]
124. Zhou, L.; Chen, S.; Jia, W.; Cui, T.; Liang, J. Effects of preheating-ultrasonic synergistic on the microstructure and strength-ductility of 24CrNiMoY alloy steel by laser directed energy deposition. *Mater. Sci. Eng. A* **2023**, *863*, 144463. [CrossRef]
125. Zheng, K.; Lin, Y.; Cai, J.; Lei, C. Corrosion resistance and tribological properties of laser cladding layer of H13 die steel strengthened by ultrasonic rolling. *Chin. J. Mech. Eng.* **2022**, *32*, 137. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Effects of Nanosecond-Pulsed Laser Milling on the Surface Properties of Al₂O₃ Ceramics

Zhaomei Xu ¹, Zhengye Zhang ², Qi Sun ², Jiale Xu ³, Zhao Meng ², Yizhi Liu ⁴ and Xiankai Meng ^{2,*}

¹ Faculty of Mechanical & Material Engineering, Huaiyin Institute of Technology, Huaian 223003, China

² School of Mechanical Engineering, Jiangsu University, Zhenjiang 212013, China

³ Department of Intelligent Equipment, Changzhou College of Information Technology, Changzhou 213164, China

⁴ Suzhou Leader Harmonious Drive Technology Limited, Suzhou 215101, China

* Correspondence: mengdetiankong10@126.com

Abstract: The effect of nanosecond-pulsed laser milling on the surficial microstructure of Al₂O₃ ceramics is studied in this work. The macrostructure, microstructure, surface roughness, and milling depth of the ceramics are analyzed via scanning electron microscopy and confocal laser scanning microscopy. The results reveal that the surface roughness and the milling depth of Al₂O₃ ceramics increase with increasing laser power, laser repetition rate, and scanning times. After nanosecond-pulsed laser milling, cavities as well as molten and granular solidified structures are observed on the Al₂O₃ ceramic surface, which indicate that the main mechanism of nanolaser milling is the melting and gasification caused by the interaction between the laser and the material.

Keywords: laser technology; laser milling; Al₂O₃ ceramics; surface morphology; surface roughness; milling depth

1. Introduction

Al₂O₃ ceramics are a kind of industrial material with good wear resistance, high temperature resistance, and corrosion resistance, attributes which provide chemical stability under harsh conditions and allow their widespread use in the aerospace industry, chemical machinery, and biomedicine [1,2]. At the same time, Al₂O₃ is one of the most important materials for fusion technology [3]. However, the traditional processing methods such as mechanical grinding and polishing fail to meet stringent demands related to the dimensional accuracy, shape and position error, and processing quality of Al₂O₃ ceramics. In order to achieve good structural matching between the ceramic components, the latter requires post-treatment. In that regard, laser milling is a recently developed advanced manufacturing technology, enabling material to be removed instantly through melting or gasification under the laser thermal effect and thus providing a novel way of processing ceramics [4,5].

In recent years, various studies on the laser milling of ceramics have been performed in several countries. In one particularly relevant study, alumina and aluminum nitride were machined with nanosecond lasers by Preusch et al. [6]. Using high-pulse overlaps and fluence of 64 J/cm², they were able to achieve material removal rates of up to 94 mm³/h and 135 mm³/h for alumina and aluminum nitride, respectively. Jian Li et al. [7] studied the impact of the short wavelength of 532 nm and the pulse width of 6 ns on the milling volume and quality of Y-TZP ceramics. The optimal milling quality of the ceramics could be attained at the blind hole diameter of 500 µm and with 200 µm wide and 100 µm high square grooves. Yinbo Zhu et al. [8] investigated the effect of single-pulse shock parameters on the milling surface quality at the laser (Nd: YAG) wavelength of 1.064 µm, observing a noticeable influence of the scanning speed on the surface roughness. Luo et al. [9] performed the milling of Y-TZP ceramics with an Nd: YAG laser, avoiding cracks.

In particular, the best surface-processing quality and the largest material removal rate could be attained by establishing the optimal processing parameters (laser power of 11.3 W, laser repetition rate of 30 kHz, and milling speed of 50 mm/s). Muneer [10] studied ways to optimize multi-response problems associated with micro-milling of Al_2O_3 ceramics, finding that laser beam overlap and the use of a high-power laser beam significantly affected the milling depth. The milling surface roughness and the material removal rate were found to be predominantly influenced by the laser beam intensity and pulse repetition rate. A comparative analysis was performed by Parry et al. [11] using nano- and picosecond lasers while machining zirconia ceramics. They demonstrated that crack-free surfaces with good surface finish can be produced with picosecond lasers. Flexural strength was also found to be satisfactory using the four-point bend test. Yibas et al. [12] conducted an irradiation test of Al_2O_3 ceramics with a 2 kW laser power in a nitrogen environment, observing the formation of a molten layer on the material surface which resulted in a decrease in surface roughness and an increase in surface hardness. Kibria et al. [13] investigated laser microturning of cylindrical Al_2O_3 ceramics, focusing on the effect of continuous point overlap and circumferential overlap rates on surface roughness and the trend of turning depth with each process parameter. However, the effect of nanosecond laser parameters on the macrostructure and microstructure of Al_2O_3 ceramics remains unclear and requires a thorough investigation.

In the present work, we aimed to perform nanosecond-pulsed laser milling of Al_2O_3 ceramics to elucidate the influence of milling parameters on the macrostructure and microstructure of the ceramic surface. In this article, the surface formation mechanism is characterized via scanning electron microscopy (SEM) and confocal laser scanning microscopy. Special attention is paid to the impact of processing parameters on the surface roughness and milling depth of Al_2O_3 ceramics, thus providing new prospects for optimization of nanolaser milling.

2. Materials and Methods

2.1. Materials

The Al_2O_3 ceramic is a kind of multi-phase solid material which comprises metallic and nonmetallic elements. Prior to the experiments, the Al_2O_3 ceramic specimen was divided using a special cutting machine into pieces with the dimensions of 30 mm × 15 mm × 4 mm, as shown in Figure 1a. Their properties are shown in Table 1. The chemical composition of the specimen, obtained using an energy-dispersive spectrometer (EDS), is shown in Figure 1b.

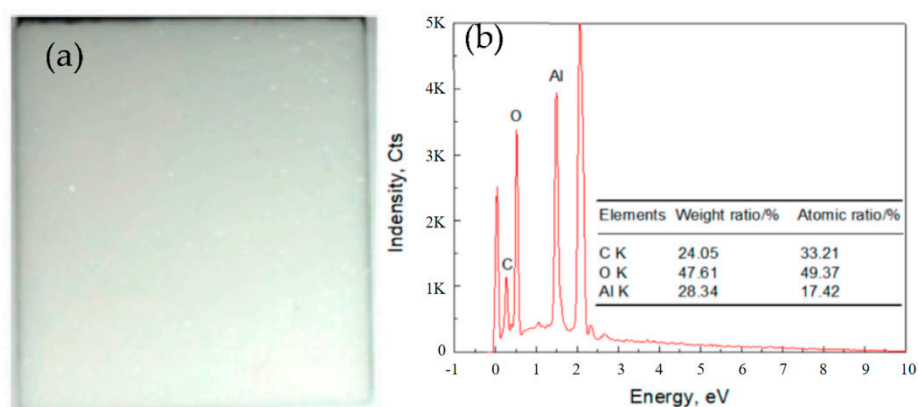


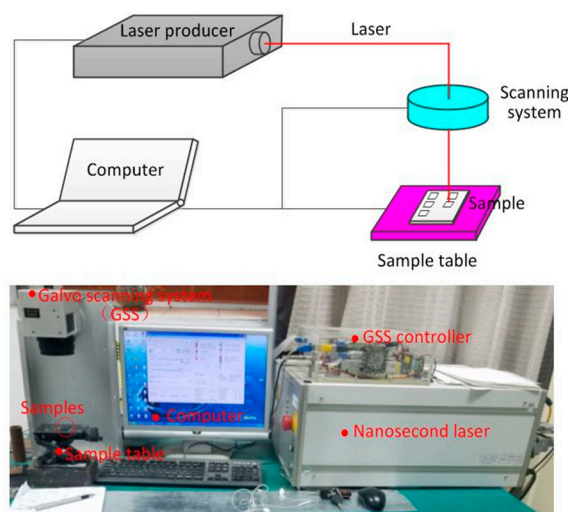
Figure 1. (a) Al_2O_3 ceramic and (b) its chemical composition.

Table 1. Al₂O₃ ceramic properties.

Density (g/cm ³)	Absorption Coefficient	Index of Refraction	Reflectivity	Coefficient of Thermal Expansion ($\times 10^{-6}/K$)	Thermal Conductivity (W/m•K)
3.5	0.85	1.3~2.7	0.051~0.153	7.2	24

2.2. Laser Milling

The milling of ceramics was performed using a YLP-HP100 nanosecond-pulsed fiber laser (Germany IPG company, Munich, Germany) at the laser power of 100 W, the pulse width of 100 ns, the wavelength of 1060 nm, the adjustable pulse repetition rate of 2~100 kHz, and the beam diameter of 50 μ m. The milling setup consisted of a laser, a water-cooling system, a PC, a high-speed scanning galvanometer, a control system, and a sample table (see Figure 2). The milling path and milling speed were controlled by a high-speed galvanometer, allowing for milling speed adjustments in the range of 20–8000 mm/s.

**Figure 2.** Schematic of a laser milling experimental system.

The milling process was conducted with varying laser-processing parameters including laser power, pulse repetition rate, and milling time. According to multi-time and single-factor experimental results, the optimal milling parameters were as follows: between three and nine milling operations with a laser power of 20–40 W, a pulse repetition rate of 35–50 kHz, and a laser beam overlap of 75–90%.

2.3. Surface Morphology

After laser milling, the surface macrostructural characteristics of Al₂O₃ ceramics, in particular, the surface roughness (S_a) and the milling depth (M_d), were measured using a VK-X160 confocal laser scanning microscope (Japan KEYENCE Company, Osaka, Japan). The surface microstructure of Al₂O₃ ceramics was studied by means of a Merlin Compact field-emission scanning electron microscope (FE-SEM, ZEISS, Jena, Germany).

2.4. XRD Experiment

XRD tests were carried out on the material using a D8 ADVANCE-type X-ray diffractometer (Bruker, Karlsruhe, Germany). The diffraction analysis process took place as follows. The cut specimens were first cleaned with anhydrous ethanol and then radiated on the X-ray diffractometer using Cu-K α rays ($\lambda = 0.15406$ nm), scanning at a speed of 5°/min over the 20–90° range with a step width of 0.01°.

3. Results and Discussion

3.1. The Effect of Laser Power on Surface Roughness and Milling Depth

Figure 3 displays the microstructure of the Al_2O_3 ceramic's surface after laser milling at different laser powers (here, the pulse repetition rate was 40 kHz and the number of milling operations was three). Plenty of cavities and melt were found on the surface treated at laser powers of 25 W and 30 W. Raising the laser power to 35 W and 40 W led to the emergence of some granular-like solidified structures the sizes of which increased with the increase in laser power. When the laser power increases, the laser milling surface temperature increases, material vaporization is evident, and the depth of the holes it causes increases significantly, worsening the surface roughness.

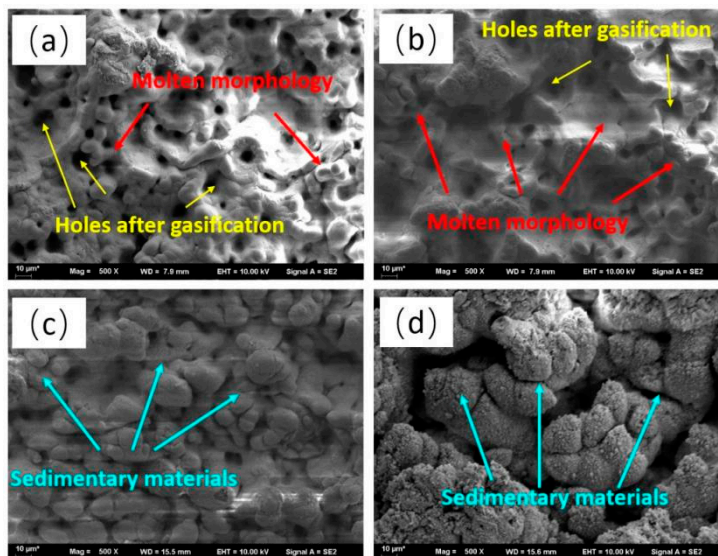


Figure 3. Surface microstructure after laser milling at different laser powers: (a) 25 W; (b) 30 W; (c) 35 W; (d) 40 W.

The laser power as one of the milling parameters could influence the surface quality prominently. The rise of temperature caused by a single-pulse laser beam with a single pulse width or single pulse time can be described as [14]:

$$\Delta T = \frac{P\gamma}{\pi\kappa d^2} \sqrt{\frac{4\alpha\tau}{\pi}} \quad (1)$$

where ΔT is the change in the temperature of the ceramic, γ is the laser absorption rate of the material surface, κ is the thermal conduction rate, α is the thermal diffusion rate of the ceramic, τ is the laser pulse width, P is the laser power, and d is the laser beam diameter. According to formula (1), the surface temperature of the material is proportional to the laser power. Therefore, at laser powers of 25 W and 30 W, the cavities on the surface during the laser milling are mainly caused by the partial gasification of the material, whereas the molten layer is the product of melting and solidification processes. In turn, increases in the laser power to 35 W and 40 W intensify the gasification. Under the action of a jet driving force caused by gasification, the melt spatters the treated surface, forming the granular solidified structure. Higher laser powers lead to increasingly stronger jet driving forces, which result in larger areas of spattered liquid substance and larger dimensions of solidified structures.

The surface roughness after milling at different laser powers (with a laser repetition rate of 40 kHz and three milling operations) is presented in Figure 4. The results show that the surface roughness after laser milling increases with higher laser power. The surface roughness after laser milling at the laser power of 40 W reaches $10.671 \mu\text{m}$, which is about 2.35 times higher than that at the laser power of 20 W. This means that the surface roughness

increases with the increase in laser power until it approaches saturation. This is because the surface temperature increases with the laser power, intensifying the gasification and augmenting the number of cavities and their depth. In turn, the splashed melt leads to the emergence of many solidified particles on the surface, thus dramatically increasing the surface roughness.

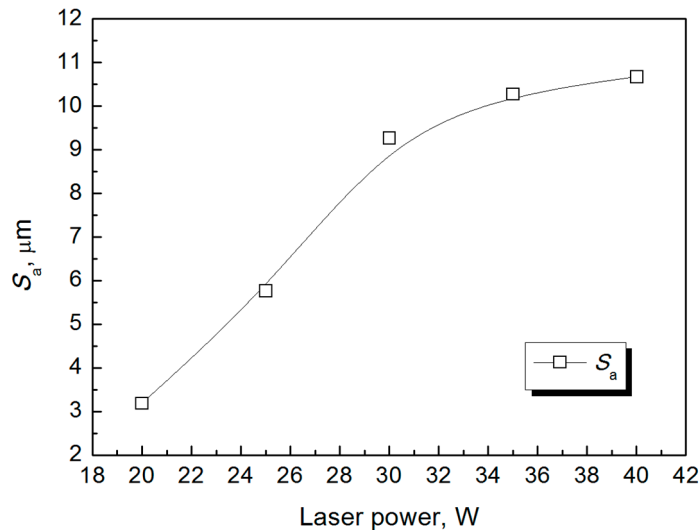


Figure 4. Surface roughness after laser milling at different laser powers.

Figure 5 shows the milling depth evolving with the laser power (the laser repetition rate is 40 kHz and the number of milling processes is three). As seen in Figure 5, when the laser power is 20 W or 40 W, the average laser milling depth is found to be 33.277 μm or 182.653 μm, respectively, i.e., the higher the laser power, the larger the milling depth. The relationship between the laser processing depth of the material and the incident laser power is described as [15]:

$$h = \frac{1}{l} \ln \left(\frac{4P}{I_{th} \pi d^2 f} \right) \quad (2)$$

where h is the processing depth, l is the absorption rate, and I_{th} is the ablation threshold of the material. At a constant laser repetition rate, the laser processing depth is, therefore, proportional to the laser power, as can be seen from formula (2).

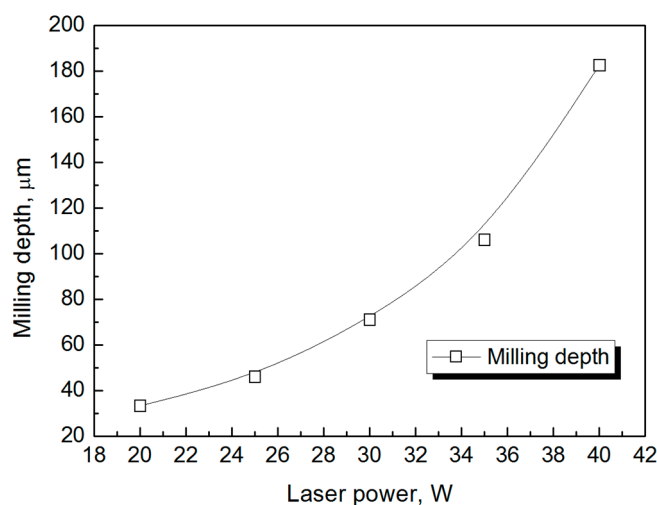


Figure 5. Milling depth at different laser powers.

3.2. The Effect of the Laser Repetition Rate on Surface Roughness and Milling Depth

Figure 6 displays the surface roughness of the ceramic after laser milling at different laser repetition rates (here, the laser power is 30 W and the number of milling operations is three). As seen from the images, the surface roughness increases from 7.812 μm to 11.04 μm (i.e., by 41.3%) with an increasing laser repetition rate from 30 kHz to 50 kHz. It is worth noting that the laser repetition rate influences the pulse time distribution: higher rates of laser repetitions correspond with smaller time intervals, causing increases in temperature and, consequently, surface roughness. The laser processing provides the options of extreme cooling and fast heating thanks to changes of the laser repetition rate, which cause slight differences of the temperature caused by the overlapping of laser beams. There is no evidence of increases in the surface roughness due to such changes in the laser pulse rate.

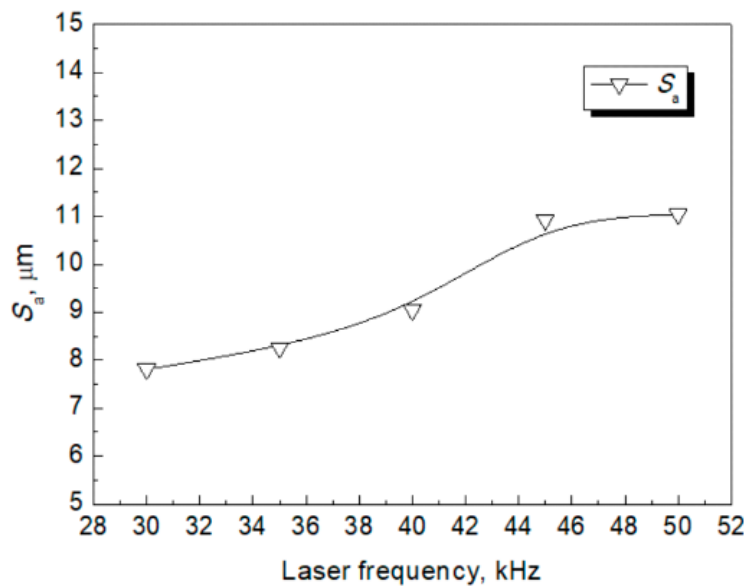


Figure 6. Surface roughness after laser milling at different pulse frequencies.

Figure 7 depicts the change in the milling depth at different pulse repetition rates (the laser power is 30 W and the number of milling operations is three). According to the results, the milling depth drastically increases from 38.141 μm to 81.63 μm as the pulse repetition rate rises from 30 kHz to 50 kHz.

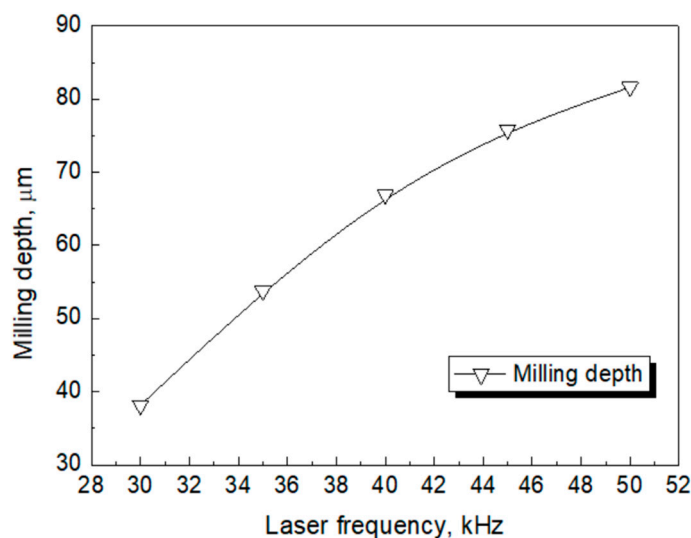


Figure 7. Milling depth after laser milling at different pulse repetition rates.

3.3. The Influence of the Number of Milling Processes on Surface Roughness and Milling Depth

Figures 8 and 9 depict the surface microstructure and the surface roughness after laser milling with various numbers of milling processes. After three milling treatments, the surface microstructure reveals mainly cavities and melt caused by gasification, whereas the surface roughness is as high as $9.78\ \mu\text{m}$. Applying five milling operations results in the emergence of a granular solidified structure on the surface, partially covering the cavities and melt. In turn, the surface roughness increases to $10.48\ \mu\text{m}$. Once the ceramic surface is exposed to nine milling operations, the grains which comprise part of the solidified structure become larger and the surface roughness rises to $11.88\ \mu\text{m}$.

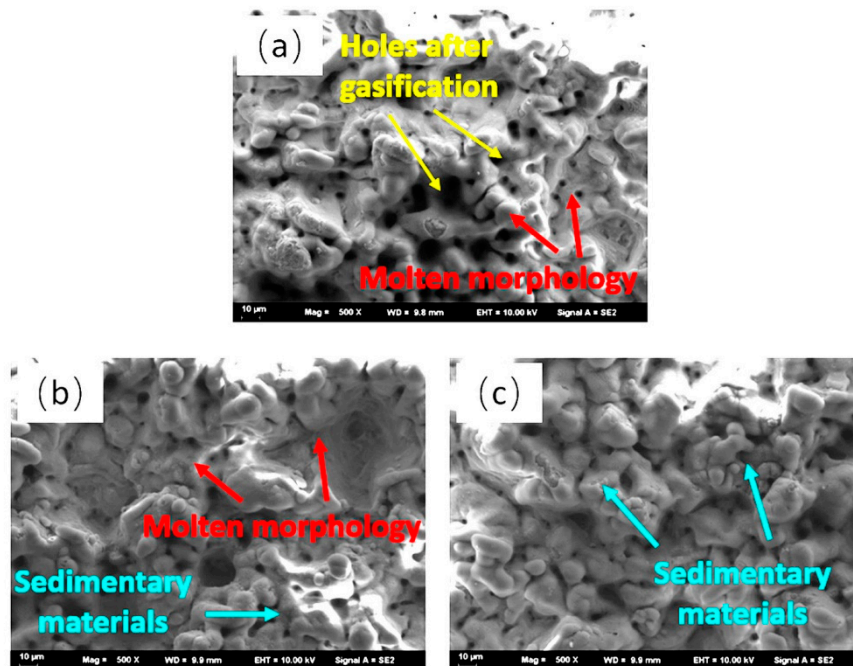


Figure 8. Surface microstructure after laser milling with different numbers of milling processes: (a) three; (b) five; (c) nine times.

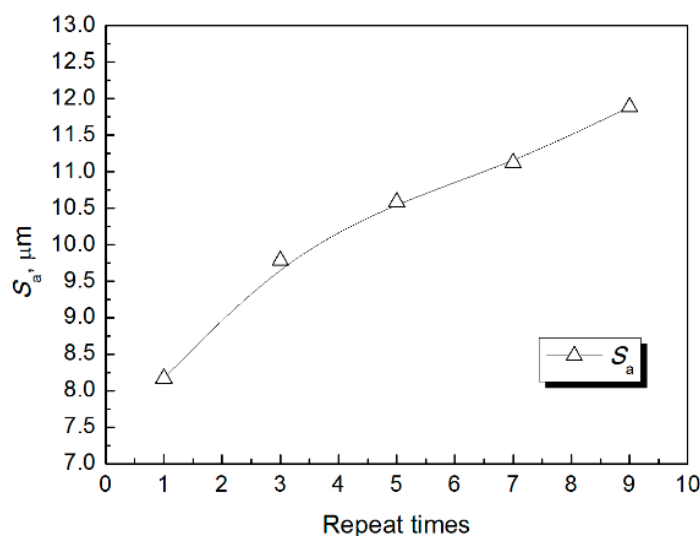


Figure 9. Surface roughness after laser milling with different numbers of milling processes.

Figure 10 depicts the milling depth as a function of the number of milling operations. Even though the milling depth increases with additional milling processes, the extent of the

increase gradually slows as the number of repetitions rises. For instance, the milling depth after three and five milling processes reaches $47.50\ \mu\text{m}$ and $67.38\ \mu\text{m}$, respectively, thus increasing by 41.9%. In turn, after seven and nine treatments, the milling depth reaches $80.56\ \mu\text{m}$ and $85.46\ \mu\text{m}$, respectively, i.e., an increase of only 6.1%. This is because the surface microstructure after three or fewer milling processes exhibits cavities and melt, which undergo gasification and are easily removed from the surface with subsequent milling. At the same time, an increase in the milling processes makes the granular-like solidified structure enlarge and raises the melting point, which weakens the impact of milling and, hence, slows the increases in the milling depth.

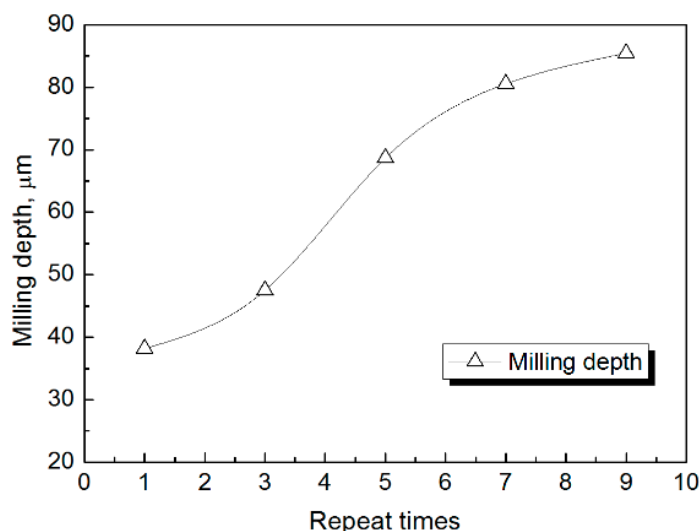


Figure 10. Milling depth after different numbers of milling operations.

3.4. The Mechanism of Nanosecond-Pulsed Laser Milling

The XRD results of the Al_2O_3 specimens before and after laser milling are shown in Figure 11, from which it is evident that the diffraction peaks of the specimens did not change significantly during laser milling, so the composition and structure of the Al_2O_3 specimens did not change.

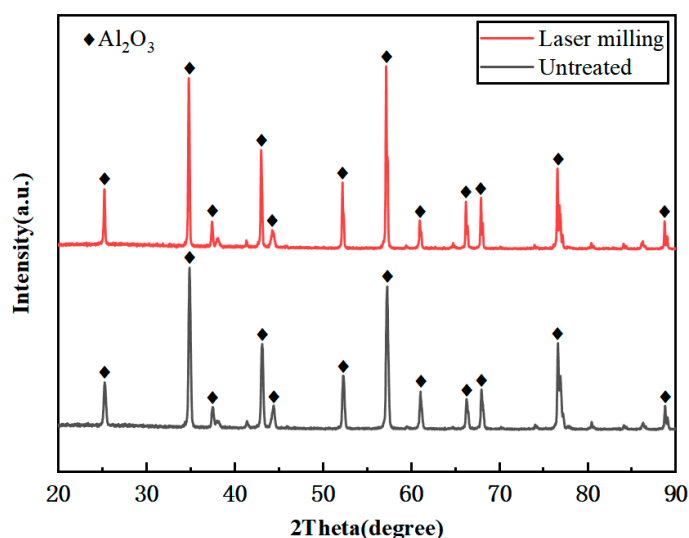


Figure 11. XRD results of specimens before and after laser milling.

Based on the data from Figures 3 and 8, the surface microstructure of Al_2O_3 ceramics takes a micron-grade granular structure, with submicron shrinkage cavities and molten

structure. Furthermore, the interaction between the laser beam and the material induces the emergence of high-temperature ions. As the ions' temperature increases to the material's melting point, the ceramic begins to melt with the formation of the molten structure. When the ions' temperature increases to the material's boiling point, the ceramic surface undergoes gasification, causing the appearance of corrosion pits and cavities. A further increase in the temperature of the ions makes them blast and hit the ceramic surface at an extremely high speed, thereby generating a shock wave. Under the action of the latter, the droplets and the gasification material from the molten pool are deposited on the surface of the specimen and micron-grade granular-like structures form after solidification (see Figure 12). Therefore, the dominant mechanisms of nanosecond-pulsed laser milling of Al_2O_3 ceramics consist of melting and gasification of the material surface.

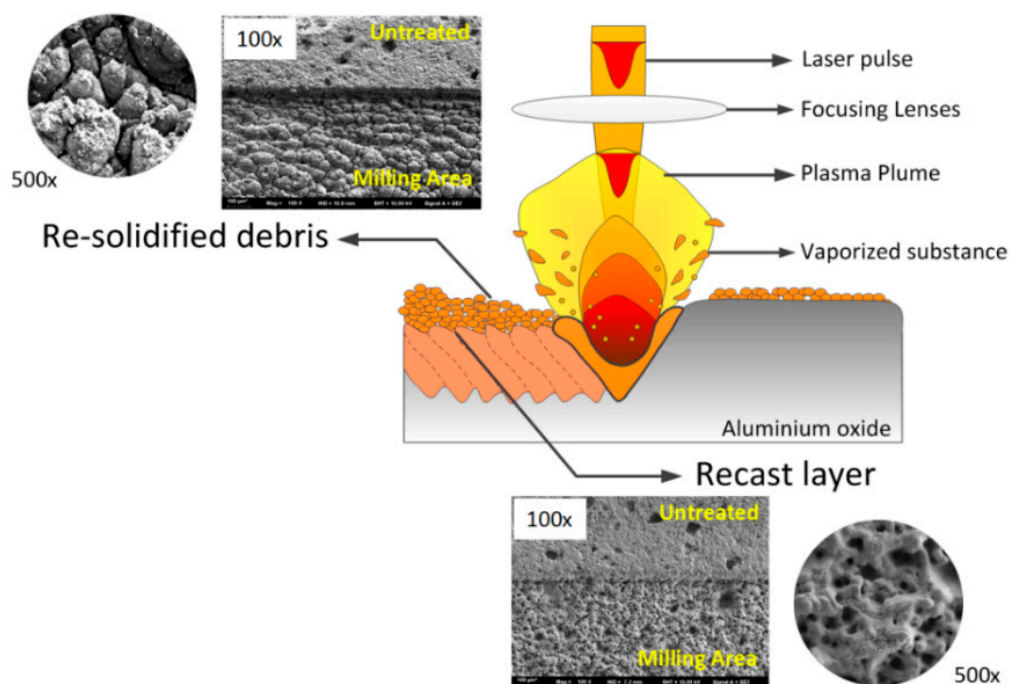


Figure 12. Formation mechanism of surface microstructure of Al_2O_3 ceramics after laser milling.

4. Conclusions

In this work, a nanosecond laser was used to mill Al_2O_3 ceramics, and the effect of laser milling on the surface microstructure, surface roughness, and milling depth was investigated. Based on the findings of the study, the following conclusions can be drawn:

- (1) The laser-induced temperature on the ceramic's surface rose and the surface roughness increased with increases in laser power, pulse repetition rate, and number of milling operations. This was due to morphological peculiarities of the ceramic surface, associated with cavities, melt, and granular structure;
- (2) The increases in laser power, pulse repetition rate, and number of milling processes led to enhancement of the laser-induced gasification on the Al_2O_3 ceramic surface, which increased the volume of departed material and the milling depth;
- (3) After nanosecond-pulsed laser milling, the surface morphology of the Al_2O_3 ceramic exhibited cavities and melt caused by the material melting and the formation of the granular solidified structure as a result of gasification. Accordingly, we propose that melting and gasification were acting synchronously during the laser milling, thereby laying the foundation for the main mechanism of nanosecond-pulsed laser milling in the removal of the materials.

Therefore, the ability to elucidate processes occurring in ceramics under the impact of nanosecond pulses, shown in the present research, opens new prospects for optimization of nanosecond-pulsed laser milling of materials.

Author Contributions: Conceptualization and validation, Z.X.; writing—original draft preparation and visualization, Z.Z.; formal analysis and methodology, Q.S.; resources, J.X.; supervision, Z.M.; investigation, Y.L.; writing—review and editing, X.M. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the Jiangsu Province Advanced Manufacturing Technology Key Laboratory Open Fund (grant no. HGAMTL-1808), China Postdoctoral Science Foundation (grant No. 2021M691309), Jiangsu Province Postdoctoral Science Foundation (grant no. 2021K245B), Natural Science Research of the Jiangsu Higher Education Institutions of China (grant no. 20KJB460016), and Changzhou Sci and Tech Program (grant no. CJ20210034).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are grateful to the Jiangsu University Analytical Testing Center for providing equipment support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hu, M. Current status of advanced ceramics and its development trend. *China Powder Ind.* **2018**, *5*, 15–17.
2. Hacker, J.; Motz, G.; Ziegler, G. *Ceramic Materials and Components for Engines*; World Scientific: Singapore, 2001.
3. Popov, A.I.; Lushchik, A.; Shablonin, E.; Vasil'chenko, E.; Kotomin, E.A.; Moskina, A.M.; Kuzovkov, V.N. Comparison of the F-type center thermal annealing in heavy-ion and neutron irradiated Al_2O_3 single crystals. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2018**, *433*, 93–97. [CrossRef]
4. Samant, A.N.; Dahotre, N.B. Laser machining of structural ceramics—A review. *J. Eur. Ceram. Soc.* **2009**, *29*, 969–993. [CrossRef]
5. Genna, S.; Leone, C.; Lopresto, V. An experimental study on the surface mechanisms formation during the laser milling of PMMA. *Polym. Compos.* **2015**, *36*, 1063–1071. [CrossRef]
6. Preusch, F.; Adelmann, B.; Hellmann, R. Micromachining of AlN and Al_2O_3 using fiber laser. *Micromachines* **2014**, *5*, 1051–1060. [CrossRef]
7. Jian, L.; Lingfei, J.; Yan, H. Experimental Study on Milling of Y-TZP Ceramic by 532 nm Laser. *Chin. J. Lasers* **2015**, *42*, 0806002. [CrossRef]
8. Yinbo, Z. Numerical simulation and experimental investigation on laser milling of Al_2O_3 ceramic. *China Mech. Eng. Soc.* **2010**, *3*, 5502.
9. Luo, Y.; Wang, X. Morphology investigation of removal particles during laser cutting of Al_2O_3 , ceramics based on vapor-to-melt ratio. *J. Mater. Process. Technol.* **2018**, *255*, 340–346. [CrossRef]
10. Muneer, K.M.; Usama, U.; Abdulrahman, A. Optimization of laser micro milling of alumina ceramic using radial basis functions and MOGA-II. *Int. J. Adv. Manuf. Technol.* **2017**, *91*, 2017–2029.
11. Parry, J.P.; Shephard, J.D.; Hand, D.P.; Moorhouse, C.; Jones, N.; Weston, N. Laser Micromachining of Zirconia (Y-TZP) Ceramics in the Picosecond Regime and the Impact on Material Strength. *Int. J. Appl. Ceram. Technol.* **2011**, *8*, 163–171. [CrossRef]
12. Yilbas, B.S.; Ali, H.; Khaled, M. Laser gas assisted texturing of alumina surfaces and effects of environmental dry mud solution on surface characteristics. *Ceram. Int.* **2016**, *42*, 396–404. [CrossRef]
13. Kibria, G.; Doloi, B.; Bhattacharyya, B. Investigation into the effect of overlap factors and process parameters on surface roughness and machined depth during micro-turning process with Nd: YAG laser. *Opt. Laser Technol.* **2014**, *60*, 90–98. [CrossRef]
14. Watkins, K.G.; Curran, C.; Lee, J. Two new mechanisms for laser cleaning using Nd: YAG sources. *J. Cult. Herit.* **2003**, *4*, 59–64. [CrossRef]
15. Lippert, T.; Hauer, M.; Phipps, C.R. Fundamentals and applications of polymers designed for laser ablation. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *77*, 259–264. [CrossRef]

Article

An Analysis of the Morphology Evolution of YG8 Cemented Carbide by Laser Ablation in the Liquid Phase

Yujie Fan, Kang Zhao *, Mengjie Hao, Jing Xia, Xiaoyan Guan and Fanghua Liu

School of Mechanical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China; fanyujie@just.edu.cn (Y.F.); haomengjie1029@163.com (M.H.); xiajingdumi@yeah.net (J.X.); guanxiaoyankb@163.com (X.G.); cylfhua@163.com (F.L.)

* Correspondence: zhaokang20210312@163.com; Tel.: +86-151-6227-8063

Abstract: To explore the influence of the number of laser ablations on the shape, geometry, and taper of the pitting structure by laser ablation in the liquid phase, three-dimensional confocal microscopy was used to quantitatively characterize the shape of the surface dotting texture of YG8 cemented carbide and analyze the evolution of the morphology based on the liquid-assisted laser ablation test. The results show that the surface pitting structure of YG8 cemented carbide evolves from a micro-convexity to a crater with the increase in the number of laser ablations, and the bottom of the crater produces a convexity after 7 ablations, the shape of the crater evolves to a trapezoidal shape after 13 ablations, and the shape is stable. The size of the dot texture increases with the number of laser ablations and reaches a maximum value of 396 μm in diameter and 149 μm in depth at the 10th and 12th ablations, respectively. The taper of the dot texture showed a trend of decreasing, increasing, and then decreasing with the increase in the number of laser ablations, and the taper was stable with more than seven ablations. This study lays a theoretical foundation for the control of the dot texture morphology on the surface of YG8 cemented carbide by laser ablation in a liquid-phase environment.

Keywords: laser technique; liquid-phase environment; dotting texture shape; taper

1. Introduction

Cemented carbide is an alloy material made from hard compounds of refractory metals and bonding metals by powder metallurgy and is widely used in various mechanical engineering equipment and cutting tools. However, high loads and wear are often accompanied during use. Currently, laser ablation of surface microstructures is an effective means to address wear and tear.

Zhang et al. [1] used a high-ultraviolet nanosecond laser to prepare textures on the surface of YG8 cemented carbide, and the optimal texture parameters had a good effect on the friction reduction and wear resistance of the cemented carbide surface. He et al. [2] demonstrated that laser ablation of cemented carbide circular pitted microtextured (CPMT) surfaces resulted in better friction performance than smooth surfaces. Xin et al. [3] found that the microcircular texture of cemented carbide traps impurities and reduces abrasive wear on the cemented carbide surface. Niu et al. [4] searched for the optimal parameters of surface properties by changing the density, diameter, and depth of the weaving area on the surface of medium carbon steel; the best property was obtained for surfaces textured with a depth of 10 μm , area density of 10%, and diameter of 100 μm . Its coefficient of friction was reduced by 38 per cent, and the experiment proved that the depth of the crater is the main factor affecting the friction and wear properties. The surfaces textured optimum depths can effectively prolong the steady state and reduce friction and wear in the variation state, which results in a longer sliding distance in the starved lubrication. Zhang et al. [1] studied the weaving width and area ratio and the influence on the friction reduction and wear properties and found that the optimal parameters of the weaving have a better gain on the friction reduction and wear properties of the surface of the cemented carbide in the

dry friction and solid lubrication states. When the texture width and area ratio parameter combination was 40 μm (45%) and 100 μm (45%), the friction coefficient was reduced from 0.301 to 0.287 and 0.275, respectively. Therefore, it is particularly important to control the size and shape of microtextures. Yang et al. [5] used a conventional two-temperature model (TTM) to optimize laser processing parameters, an optimized hole depth increase of 50 μm , smooth walls, and no residual stresses to improve the quality of turbine blades and blade film cooling holes, thereby improving engine performance. Serguei P. Murzin et al. [6] laser ablated microtextures on the surface of silicon carbide ceramics, which were used to reduce the coefficient of friction of a rolling bearing in operation; the results demonstrate that the laser treatment reduces the coefficient of friction by more than 30 per cent compared to the initial structure. Erkan Öztürk [7] used a laser to ablate microtextures on a tool to enhance machining performances in dry hard turning by decreasing friction between tool and chip, reducing adhesion, reducing cutting forces, and improving wear mechanisms. Aniket Roushan et al. [8] reduced the cutting forces, cutting temperatures, surface roughness, and tool wear by changing the surface morphology parameters of the ablated weave on the tool, which improved machining performance. Above, it can be seen that changing the surface morphology and improving the shape is beneficial in improving the workability and reducing the coefficient of friction. Xin et al. [3] statistically quantified the friction force, coefficient of friction, and wear rate of microcircular weave by the preparation parameters (weave spacing, weave diameter) and geometrical parameters (laser ablation power, ablation speed, number of ablations) and found that the scanning speed, laser power, and the diameter of the microcircular weave have a large effect on the surface properties of the tungsten carbide and that the optimal preparation parameters (laser power: 70 W; scanning times: seven times; scanning speed: 1600 mm/s) can effectively reduce the friction force and the coefficient of friction.

However, most laser processing of carbide surface texture is carried out in air, which is prone to the effect of heat accumulation [9]. Jia et al. [10] studied underwater femtosecond laser ablation of SiC and found that the microporosity depth and the material removal rate increased gradually with the increasing energy of a single pulse and inhibited the occurrence of oxidation reaction, which resulted in a cleaner processed surface. S. vander Linden et al. [11] found that in picosecond-pulsed underwater laser ablation of silicon, the volume of material removed per pulse was better than that in the air environment. Yu et al. [12] found that liquid-phase laser ablation of silicon nitride can effectively inhibit oxidation, but it will reduce the rate of material removal, and with the increase of scanning speed, the surface roughness increases, and the depth of laser ablation decreases. Zhou et al. [13] utilized water-assisted laser ablation in the different water layers and found that the liquid-phase ablation environment can get clearer micrographs and smaller heat-affected zones, the liquid-phase environment makes the inner wall of the grooves clean and smooth, and the depth of the grooves decreases with the increase of the liquid-phase flow rate. PANG Minghua et al. [14] processed YT15 cemented carbide in a liquid-phase environment and found that the micro-pit distribution on the surface of liquid-phase assisted laser processing is more uniform (with basically no oxidation and recasting of molten material), the assisting liquid plays a cooling and protecting role on the laser processing surface, and the surface contact angle is minimized (55°). In addition, the friction coefficient of the surface texture processed by liquid-phase-assisted laser processing is the smallest, and the wear amount is improved to a certain extent. Yang et al. [4] found that the quality of laser microtextures is very important for aerospace turbine blades and blade film cooling holes, in which the diameter–depth variation of ablation is related to the effective surface area of ablation, laser intensity, ablation time, number of pulses, the energy of a single pulse, and the target material of ablation. Zhu et al. [15] found that the pit taper is related to the angle of laser ablation and the number of ablation times, and the edge quality of microtextured structures can be effectively improved by the method of laser compensation.

Existing research has demonstrated that liquid-phase laser ablation produces good morphology, lessens the formation of recast layers and cracks, and enhances the heat-

building effect during laser ablation and the recasting phenomenon during processing. Nevertheless, the influence of liquid-phase-assisted laser ablation on YG8 cemented carbide has not been reported. To investigate the impact of ablation times on the morphology of liquid-phase laser ablation of YG8 cemented carbide, this study uses a mixed liquid of anhydrous ethanol and hydrogen peroxide as a propellant to facilitate laser ablation processing of YG8 cemented carbide. There is a significant improvement in the ablation morphology compared with other machining processes [1], and it is particularly outstanding for the reduction of heat-affected zones, recast layers, and cracks [16], which provides a theoretical basis for the machining and shape control of the point weave structure on the surface of YG8 cemented carbide. This research has some guiding significance for the use of laser ablation to achieve high-quality shapes, sizes, and taper controls in key industrial areas such as in the machining and manufacturing of micro-tools [7], engine fuel injectors, and cooling holes in turbine blades [5].

2. Materials and Methods

2.1. Test Material

The test material was YG8 cemented carbide, with a size of $20\text{ mm} \times 20\text{ mm} \times 5\text{ mm}$. Sandpapers with 800 mesh, 1000 mesh, and 2000 mesh were used to polish the surface, and then the surface was polished to the roughness $Ra < 0.8\text{ }\mu\text{m}$, and finally cleaned with deionized water and acetone, and then left to dry naturally in the air for spare parts.

2.2. Test Equipment

The laser system was a Nd: YAG laser with a wavelength of 1064 nm and a pulse width of 15 ns . The laser energy density was 200 J/mm^2 , the pulse frequency was 20 KHZ , the spot diameter was $350\text{ }\mu\text{m}$, and the number of ablations ranged from 1 to 14.

The auxiliary liquid is a mixture of hydrogen peroxide and anhydrous ethanol in the ratio of 30:1 by volume, controlled by volumetric measurement of the workpiece at a height of 1 mm above the liquid surface. Figure 1 is the schematic diagram of the liquid-phase laser processing process, and the surface dot-woven array is shown in Figure 1. In total, ten sets of experiments were performed in which the room temperature was controlled to be constant at 20° to ensure the reproducibility and robustness of the observed effects.

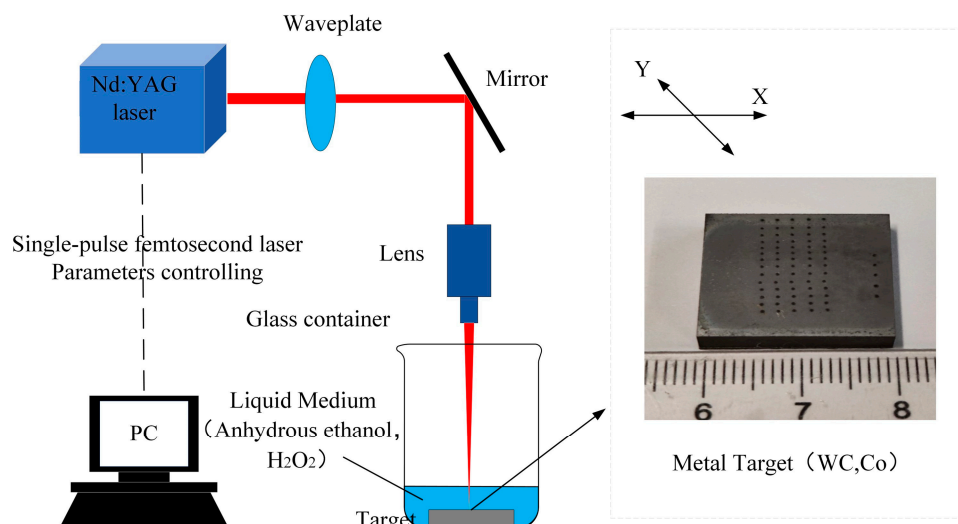


Figure 1. Schematic diagram of laser processing technology in liquid phase.

3. Results and Discussion

3.1. Analysis of the Shape Evolution of the Laser Ablation Dot Texture in a Liquid-Phase Environment

(1) Three-dimensional morphology of laser ablation dot texture in liquid-phase environment

Figure 2 shows the three-dimensional morphology of the dot texture of the YG8 cemented carbide surface ablated by laser in a liquid-phase environment. It is evident that as the number of ablations increases, more material is gradually removed from the ablated surface, the center region of the dot texture changes from a slight bump to a pit, and the pit's depth increases gradually. In contrast, the edge region of the bump structure's dot texture does not significantly change as the number of ablations increases and produces very little recast melt.

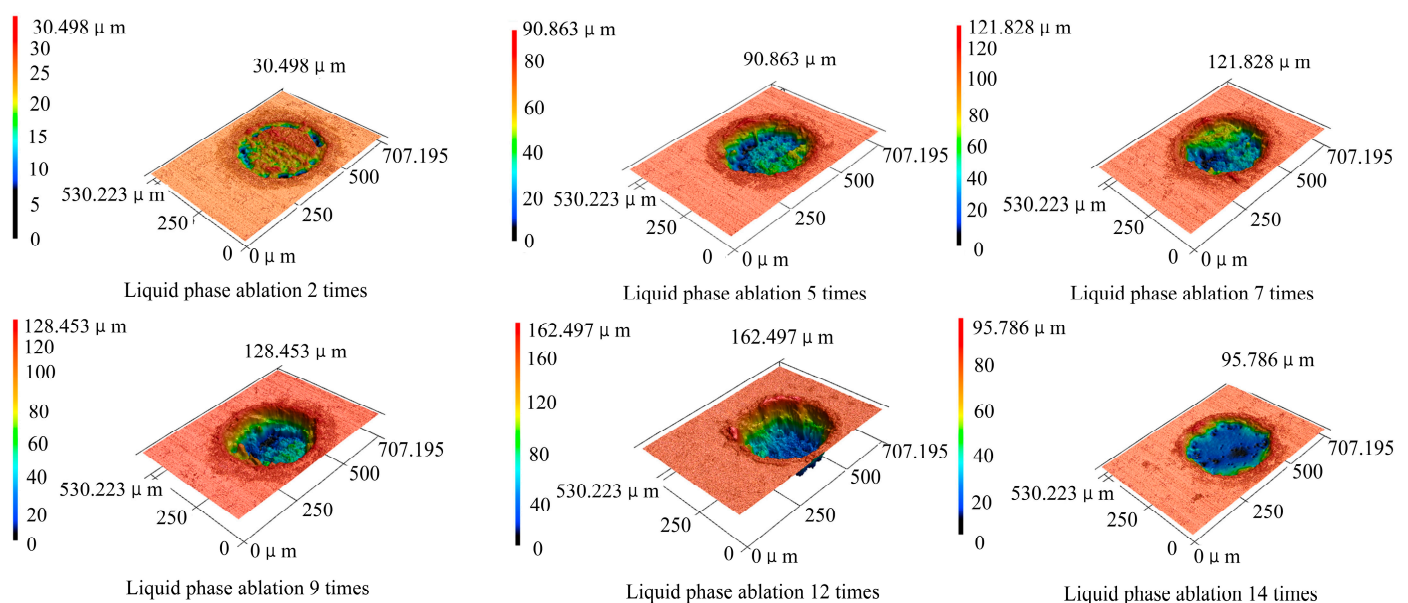


Figure 2. Three-dimensional morphology of dot texture of YG8 cemented carbide surface by laser ablation in liquid phase.

(2) Laser ablation of dot texture two-dimensional profiles in a liquid-phase environment

Figure 3 shows the two-dimensional contours of the dot texturing centers for different numbers of liquid-phase ablations. It can be seen that when the number of ablation is one, there is a bump around the dot texture, and the ablation shape of the substrate surface is a crater at this time. This is because the substrate surface will create a local melt pool during one ablation. The melt will then flow outward from the melt pool's center under the recoil pressure, creating a micro-pit on the substrate surface and a pit surrounding the micro-bumps [17]. The ablated surface of the substrate is convex when the number of ablations is two. This is because as the number of ablations increases, remelting takes place in the ablated area of the substrate, the temperature in the melt pool's center is at its highest, and surface tension causes a strong inward Marangoni flow [18], which causes the melt to flow to the melt pool's center and eventually form a convex shape.

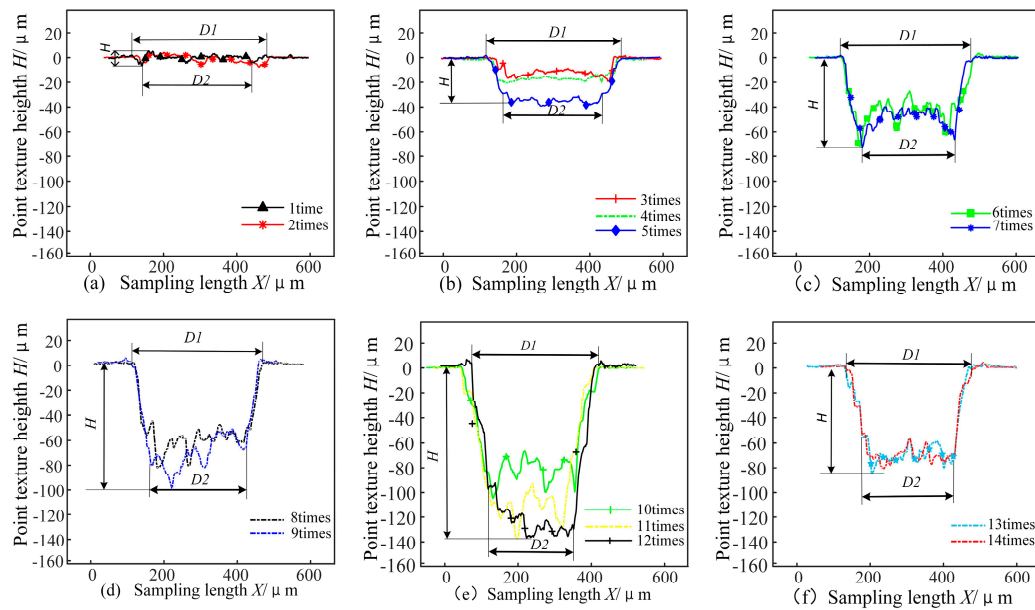


Figure 3. Two-dimensional profile of the center diameter of dot texture under different ablation times.

When there are more than three ablations, a pit gradually forms in the center. This is due to the increase in the number of ablations, resulting in the accumulation of heat, and because the center part of the bulge is subjected to the most heat, part of the material reaches the ablation threshold, and the material removal phenomenon takes place [19]. When the number of ablations reaches five, rapid ablation begins. At this point, the energy in the center of the protruding part of the melt gradually starts to accumulate, and the liquid acts as a propellant, which gradually forms a pit with depth, and the depth of the pit is more uniformly ablated. However, due to the recoil pressure, the melt at the bottom of the pit will be extruded, and the liquid will gradually take away most of the removed material and melt, thus reducing the accumulation of material [20]. At 9–12 times into the steady ablation stage, both the ablation depth and recoil pressure increase, resulting in smoother ablation [21].

When there are 12 to 14 laser ablations, the depth of the pit decreases with a small convex shape around it. During this period, the bottom of the pit produces a plasma shielding effect [22], and with the increase of the depth of the liquid through the laser, loss increases, which in turn weakens the laser ablation effect on the pit, resulting in a decrease in the depth of the ablation pit. As the substrate absorbs a large amount of heat in a short period, the recoil pressure formed by the material in the center of the melt pool is too large, which causes the liquid bubbles to explode, leading to the intensification of the flow of the melt at the bottom of the pit and spreading to the surrounding area of the pit and forming a part of the molten material around the pit.

(3) Dimensional changes of laser ablation dot texture in liquid-phase environments

Figure 4 shows the graphs of the variation of the weaving height and the top and bottom diameters of the laser-ablated spots with the number of ablations in the liquid-phase environment. It can be seen that when the laser ablates 1–2 times, the diameter and depth of the top of the dot texture decreases with the increase of laser energy, and the diameter and depth of the top of the crater are up to 330 μm and 6 μm , respectively, and the ablation efficiency is lower than that of the thermal expansion efficiency at this time, and thus the micro-bump is generated. At 3–5 times ablation, the diameter and depth of the texture increase with the rise of laser energy. This happens because of the increase of heat absorption in the center part of the micro-bump material and liquid, resulting in the reduction of the material. After rapid ablation, a pit with a larger diameter and depth is formed. The top of the pit reaches a diameter of 380 μm and a depth of 39 μm

after the 5th ablation. At 5–8 ablations, the top and bottom diameters of the dot texture show a decreasing trend, while the depth ablation of the dot-textured changes faster due to the creation of a bulge at the bottom of the pit, which in turn reduces the ablation of the bottom edge of the pit. At 8–10 ablations, the diameter and depth of the dot texture increase rapidly, the ablation of the bottom edge of the pit increases, and the efficiency of the liquid-propelled ablation is greater than the energy loss, with a maximum diameter and depth of 396 μm and 114 μm of the dot texture, respectively. At 11–12 times, the diameter of the dot texture decreases with the increase of the depth of the dot texture because the ablation center is shifted to the center of the dot texture, and the maximum depth of the dot texture is 149 μm . Finally, at the 13th to 14th times of ablation, the diameter and depth of the dot texture change slowly with the increase of the laser energy density, and the diameter and depth of the dot texture stabilize at around 353 μm and 85 μm , respectively. As the number of laser times increases, the energy generated also accumulates. This leads to a greater loss of energy through liquid ablation, and the substrate material is continuously heated by the laser to form a plasma [23]. The plasma, with the increase in the laser energy density of the laser beam formation, has a certain shielding effect, so the ablation depth decreases and then tends to be stabilized.

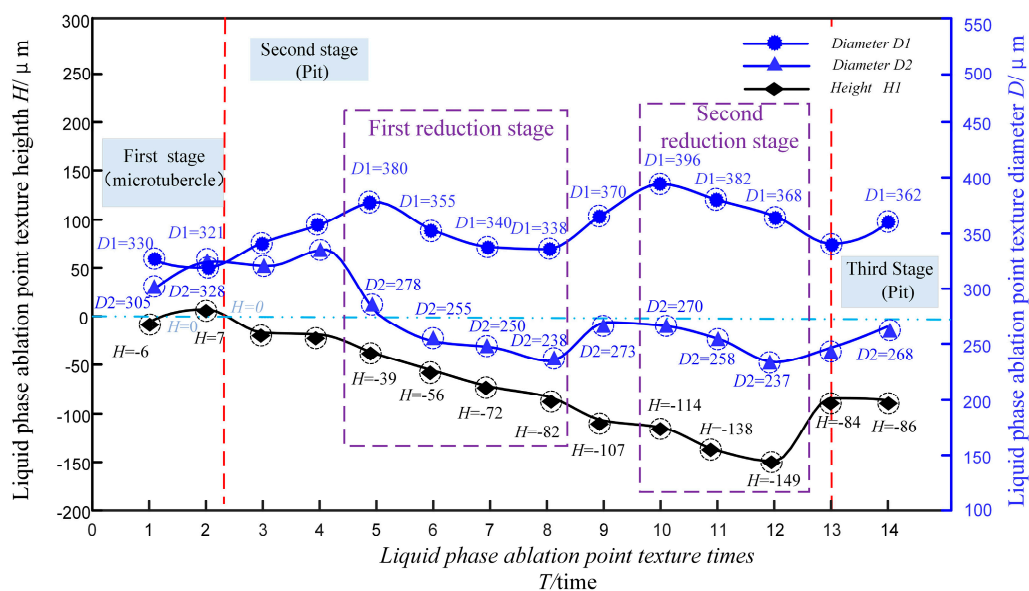


Figure 4. Changes in the height and diameter of the dot texture with the number of ablations in the liquid phase.

(4) Modeling the shape evolution of laser ablation dot texture in a liquid-phase environment

Figure 5 shows the shape evolution model of the YG8 cemented carbide dot structure with the number of liquid-phase laser ablation. It can be divided into six stages. Stage 1: evaporation stage. The number of ablations is 1–2, and the workpiece produces a small number of pits and bumps. This stage of ablation does not produce much energy, the impact on the workpiece is limited, and the surface of the workpiece removes fewer substances. And then, as the surface of the YG8 reaches the boiling point and forms upward metal vapor, the liquid surface begins to produce an evaporation phenomenon [24]. Stage 2 is the molten pool stage. The number of ablations is 3–5, the surface material melts and forms a molten pool, and the workpiece is also gradually subjected to thermal expansion and radiates around [25]. Stage 3: the molten pool vortex. The number of ablations is 6–7, with the increase in the number of ablations producing a larger recoil pressure exacerbating the depression of the molten pool, in which double vortex is obvious; it is caused by the natural convection in the molten pool and the Marangoni convection [26].

The natural convection is driven by buoyancy forces of the density of the liquid metal affected by temperature. It causes the hot melt to float. Marangoni convection occurs when the surface tension of a liquid metal is affected by a temperature gradient, causing the high-temperature melt to flow towards the low-temperature region. The combined effect creates a center-edge-bottom-center vortex path in the melt pool. According to the conservation of momentum, the high-temperature melt flows towards the low-temperature region and exerts a downward recoil pressure on the melt pool. Stage 4: high-pressure melt pool. The number of ablations is 8–9. The surface of the melt pool shows high pressure and high velocity, while the pressure and velocity inside the melt pool are low, so the heat is transferred to the inside, and the vortices converge toward the center of the melt pool as the temperature and velocity decreases, generating upward velocity vectors at the surface of the melt pool, the downward trend is suppressed [27]. However, the upward flow rate on both sides of the melt pool is very high [28], and the pressure inside the melt pool is very high, which remains downward ablated by surface tension and buoyancy. Stage 5: the melt pool recoil. The number of ablations is 10–12. With the increase of ablation depth, the vortex inside the melt pool weakens, which inhibits the surface depression; this stage of the melt pool surface produces upward velocity vectors, which inhibits the downward tendency to reach its peak. Stage 6: shielding and stacking. The number of ablations is 13–14. The melt pool is kept oscillating under recoil pressure, surface tension, buoyancy, and gravity, and the plasma produced by its ablation produces a shielding effect on the laser ablation [29], resulting in the buildup of the molten cladding, and the laser ablation has no significant change on the melt pool, thus achieving dynamic equilibrium.

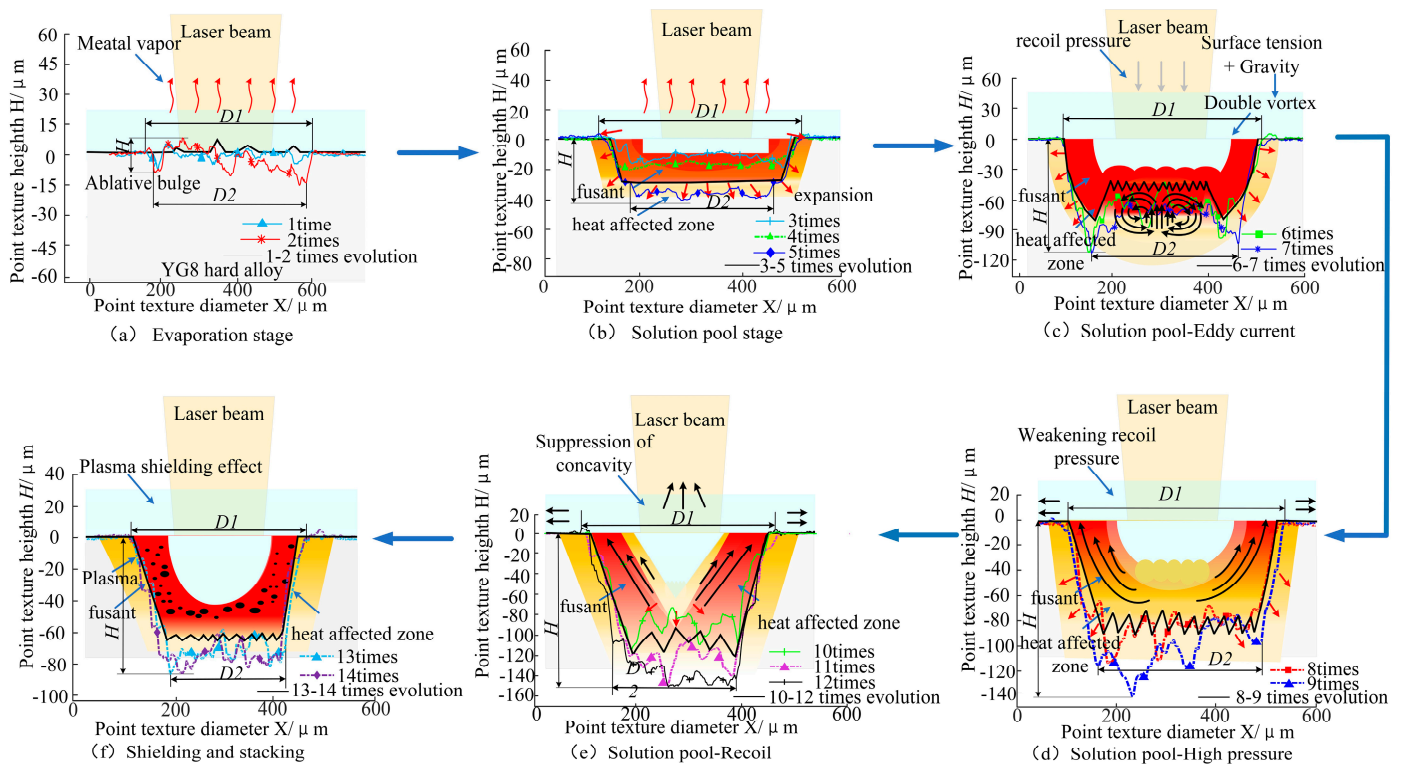


Figure 5. Shape evolution model of dot texture induced by laser ablation in liquid-phase environment.

3.2. Analysis of the Taper of Ablation Dot Texture Craters in Liquid-Phase Environments

Figure 6 shows a schematic diagram of the dot texturing taper of the liquid-phase laser ablation, whose taper V is calculated by the following formula:

$$V = \frac{D1 - D2}{H} \times 100\% \quad (1)$$

where the depth of the hole cross-section is H , and $D1$ and $D2$ are the diameters of the top and bottom surfaces of the pit, respectively [30].

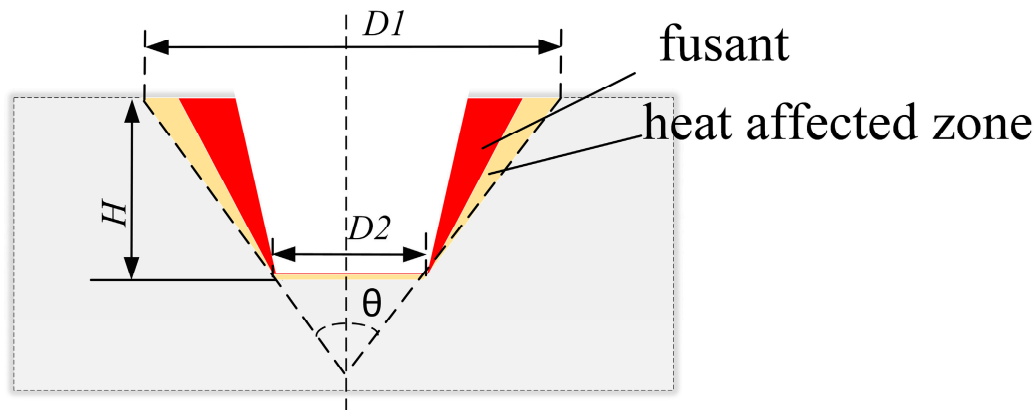


Figure 6. Schematic diagram of the taper of the dot texture.

As shown in Figure 5, after two ablations, the taper of the dot texture is 4.17, and the number of laser ablations in the initial stage is less than after crater removal, with the hole taper being larger. The taper of 5 times ablation is 2.62; as the number of ablations increases, the pit removal increases, and the hole taper decreases gradually. The taper of 7 times ablation is 1.25, which enters into the stage of rapid ablation, and the center of the pit ablation is gathered in the middle; as shown in Figure 5d–f, the rate of laser ablation slows down gradually in this stage, and the depth of ablation tends to be stabilized due to plasma shielding effect, the taper is stabilized at about one.

Figure 7 shows the graph of the taper variation of laser-ablated dot texture with the number of ablations in the liquid-phase environment, and it can be seen that the taper shows a decreasing, then increasing, and then decreasing trend with the increase of the number of ablations. The taper trend is divided into three stages [31]: The first stage is unstable because the initial ablation number is small (1~2), and the change in diameter difference between the top and bottom of the dot texture will increase, while the depth change is small, and the taper fluctuation range is large. The second stage is the stabilization stage when the number of ablations is 3–4, the ablation rate is accelerated, the diameter and depth of the pit top and bottom increase simultaneously, and the calculated value is smaller according to the taper equation. At the fifth ablation, the diameter of the top of the pit increases while the bottom decreases, and the difference between the diameters of the top and bottom increases more rapidly than the depth, resulting in taper increases to 2.62. At the sixth ablation, the top and bottom diameters of the dot texture decrease while the depth gradually increases, so the taper decreases. The third stage is 7–14 times of stabilization; the difference between the diameters of the top and bottom of the crater and the ablation depth have the same trend, so the taper fluctuates in a certain range.

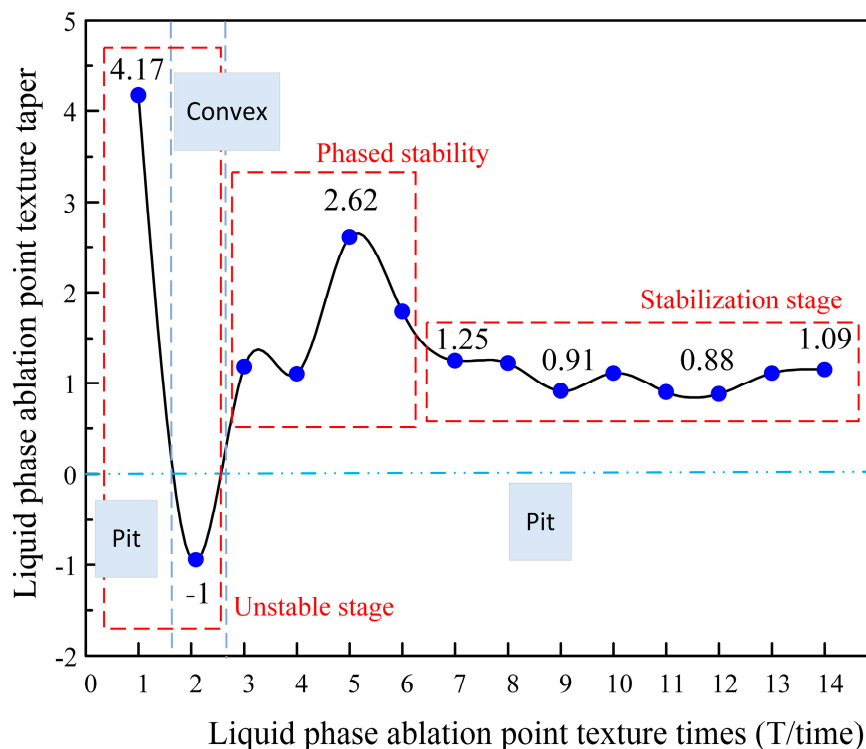


Figure 7. Change of taper of dot texture with the number of ablations in the liquid phase.

4. Conclusions

In this study, the liquid-phase laser ablation technique was used to investigate the effect pattern of the number of laser ablations on the liquid-phase laser ablation of YG8 cemented carbide. There are three findings as follows.

(1) Laser ablation of YG8 cemented carbide morphology was divided into six stages: The first stage was the evaporation stage, where the shape of the convex and small size changed. The second stage was the melt pool stage, the heat-affected zone began to expand, and the shape of the ablation was a trapezoidal shape, the more regular shape. The third stage was the melt pool vortex: the bottom of the pit produced a rise and characteristics of a pressure vortex. The fourth stage was the high-pressure melt pool: the bottom of the pit rise disappeared, and with it, the pressure vortex disappeared, and the shape took on an irregular trapezoidal shape. The fifth stage was the molten pool recoil: The shape evolved into a trapezoidal shape with a smaller taper, and the ablation depth was suppressed. And the final stage was shielding and stacking: the pits' shape changed to a more regular trapezoidal form with a smaller taper, and the shape was stabilized due to the plasma shielding effect.

(2) The number of laser ablations had a significant effect on the geometry of the surface texture. When the number of laser ablations was varied from 1 to 4 and 8 to 10, the diameter and depth of the top and bottom of the dot texture showed an increasing trend. The number of ablations was 5–8 and 10–12, the diameter of the dot texture decreased, and the depth increased. After more than 13 ablations, the diameter of the texture pits increased, the depth decreased, and the dot texture size changed slowly.

(3) The number of laser ablations had a great influence on the taper of the pits, with an overall trend of decreasing, increasing, and then decreasing. When the number of laser ablations was 3–4, the taper of the pits was small; when the number of ablations was more than 7, the taper of the pits tended to stabilize gradually.

This study reveals the effect and mechanism of the number of liquid-phase laser ablation on the surface dot texture morphological changes of YG8 cemented carbide and achieves the control of liquid-phase laser ablation dot texture geometry and size. Since the methodology study was limited to the morphological changes induced by the specific

workpiece type and the number of laser ablations, parameters such as laser power density, pulse width, etc., are a step toward unexplored machining properties in future studies. This research is expected to be applied to rolling bearings, cutting tools, aero engine blades, and other transmission parts.

Author Contributions: Conceptualization and validation, Y.F.; writing—original draft preparation and visualization, K.Z.; formal analysis and methodology, M.H.; resources, J.X.; supervision, X.G.; investigation, F.L.; writing—review and editing, Y.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 12202167.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors are grateful to the School of Mechanical Engineering, Jiangsu University of Science and Technology, for providing equipment support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, Z.; Lu, W.; He, Y.; Zhou, G. Research on optimal laser texture parameters about antifriction characteristics of cemented carbide surface. *Int. J. Refract. Met. Hard Mater.* **2019**, *82*, 287–296. [CrossRef]
2. He, C.; Yang, S.; Zheng, M. Analysis of synergistic friction reduction effect on micro-textured cemented carbide surface by laser processing. *Opt. Laser Technol.* **2022**, *155*, 108343. [CrossRef]
3. Tong, X.; Gou, Y.; Yu, S. Anti-wear and anti-friction performance of cemented carbide under the interaction of micro-circular texture preparation and geometric parameters. *Mater. Sci. Eng. B* **2021**, *268*, 115116. [CrossRef]
4. Niu, Y.; Pang, X.; Yue, S.; Shangguan, B.; Zhang, Y. The friction and wear behavior of laser textured surfaces in non-conformal contact under starved lubrication. *Wear* **2021**, *476*, 203723. [CrossRef]
5. Yang, Z.; Ji, P.; Zhang, Z.; Ju, Y.; Wang, Z.; Zhang, Q.; Wang, C.; Xu, W. Fundamental 3D simulation of the femtosecond laser ablation for cooling hole drilling on Ni and Fe based aero-engine components. *Opt. Commun.* **2020**, *475*, 126237. [CrossRef]
6. Murzin, S.P.; Balyakin, V.B. Microstructuring the surface of silicon carbide ceramic by laser action for reducing friction losses in rolling bearings. *Opt. Laser Technol.* **2017**, *88*, 96–98. [CrossRef]
7. Öztürk, E. FEM and statistical-based assessment of AISI-4140 dry hard turning using micro-textured insert. *J. Manuf. Process.* **2022**, *81*, 290–300. [CrossRef]
8. Ahuir-Torres, J.I.; Arenas, M.A.; Perrie, W.; de Damborenea, J. Influence of laser parameters in surface texturing of Ti6Al4V and AA2024-T3 alloys. *Opt. Lasers Eng.* **2018**, *103*, 100–109. [CrossRef]
9. Temmler, A.; Braun, K.; Uluz, E. Heat accumulation and surface roughness evolution in CO₂ nanosecond laser ablation of quartz glass. *Opt. Laser Technol.* **2021**, *144*, 107426. [CrossRef]
10. Wei, J.; Yuan, S.; Zhang, J.; Zhou, N.; Zhang, W.; Li, J.; An, W.; Gao, M.; Fu, Y. Removal mechanism of SiC/SiC composites by underwater femtosecond laser ablation. *J. Eur. Ceram. Soc.* **2022**, *42*, 5380–5390. [CrossRef]
11. van der Linden, S.; Hagmeijer, R.; Römer, G. Picosecond pulsed underwater laser ablation of silicon and stainless steel: Comparing crater analysis methods and analysing dependence of crater characteristics on water layer thickness. *Appl. Surf. Sci.* **2020**, *540*, 148005. [CrossRef]
12. Yu, X.; Jiang, L.; Luan, Q.; Cai, Y.; Song, Q.; Wang, B.; Liu, Z. Investigation of mechanism and surface morphology on the femtosecond laser ablation of silicon nitride under different auxiliary processing environments. *Ceram. Int.* **2023**, *49*, 13425–13434. [CrossRef]
13. Zhou, J.; Huang, Y.-X.; Zhao, Y.-W.; Jiao, H.; Liu, Q.-Y.; Long, Y.-H. Study on water-assisted laser ablation mechanism based on water layer characteristics. *Opt. Commun.* **2019**, *450*, 112–121. [CrossRef]
14. Pang, M.-H.; Zhai, S.-J.; Feng, Q.-G.; Zhang, Q.-C.; Ma, L.-J. Preparation and tribological properties of cemented carbide Surface texture by liquid-phase assisted laser. *Tribology* **2021**, *42*, 1001–1011.
15. Zhu, Q.; Fan, P.; Li, N.; Carlson, T.; Cui, B.; Silvain, J.-F.; Hudgins, J.L.; Lu, Y.F. Femtosecond-laser sharp shaping of millimeter-scale geometries with vertical sidewalls. *Int. J. Extreme Manuf.* **2021**, *3*, 045001. [CrossRef]
16. Zhang, N.; Yang, D.; Liu, G. Preparation of YG8 hard alloy surface groove weave and its friction reduction properties. *Mech. Eng. Mater.* **2020**, *44*, 38–41+56.
17. Qian, Y.; Jiang, M.; Zhang, Z.; Huang, H.; Yan, J. On the transformation between micro-concave and micro-convex in nanosecond laser ablation of a Zr-based metallic glass. *J. Manuf. Process.* **2021**, *68*, 1114–1122. [CrossRef]

18. Wang, X.S.; Xu, W.T.; Liu, L.; Zhang, Z.W.; Jin, M.F.; Kang, M. Magnetic-field-assisted fabrication of micro-convex domes using long pulse laser. *Appl. Phys. A* **2017**, *123*, 592. [CrossRef]
19. Hua, X.J.; Zhang, J.L.; Xie, X.; Ping, G.F. Laser Concave/Convex Micro-Texture Process of GCr15 Bearing Steel Surface. *Chin. J. Lasers* **2019**, *46*, 94–100.
20. Zhang, Y.; He, X.; Yu, G.; Li, S.; Tian, C.; Ning, W.; Zhang, Y. Dynamic evolution of keyhole during multi-pulse drilling with a millisecond laser on 304 stainless steel. *Opt. Laser Technol.* **2022**, *152*, 108151. [CrossRef]
21. Zhao, W.; Yu, Z.; Hu, J. Numerical simulation and experimental analysis on nanosecond laser ablation of titanium alloy. *J. Manuf. Process.* **2023**, *99*, 138–151. [CrossRef]
22. Li, Q.; Yang, L.; Hou, C.; Adeyemi, O.; Chen, C.; Wang, Y. Surface ablation properties and morphology evolution of K24 nickel based superalloy with femtosecond laser percussion drilling. *Opt. Lasers Eng.* **2019**, *114*, 22–30. [CrossRef]
23. Fu, Y.H.; Liu, Q.X.; Ye, Y.X.; Hua, X.J.; Kang, Z.Y.; Fu, H. Research on laser surface micro texturing processing of single pulse intervals. *Chin. J. Lasers* **2015**, *42*, 1203005.
24. Jing, X.; Wang, J.; Song, X.; Chen, Y.; Jaffery, S.H.I. A comparative investigation on micro-channel by using direct laser ablation and liquid-assisted laser ablation on zirconia. *Ceram. Int.* **2023**, *49*, 31871–31880. [CrossRef]
25. Cai, S.; Xiong, W.; Wang, F.; Tao, Y.; Ming, X.; Sun, X.; Zeng, X. Expansion property of plasma plume for laser ablation of materials. *J. Alloys Compd.* **2018**, *773*, 1075–1088. [CrossRef]
26. Rudenko, A.; Abou-Saleh, A.; Pigeon, F.; Maclair, C.; Garrelie, F.; Stoian, R.; Colombier, J.P. High-frequency periodic patterns driven by non-radiative fields coupled with Marangoni convection instabilities on laser-excited metal surfaces. *Acta Mater.* **2020**, *194*, 93–105. [CrossRef]
27. Liu, B.; Wang, C.; Mi, G. Simulation of the removal mechanism of thermo-oxidized layer and surface morphological evolution on TA15 alloy under nanosecond pulsed laser ablation by multiphase flow model. *J. Manuf. Process.* **2021**, *69*, 69–83. [CrossRef]
28. Sharma, S.; Mandal, V.; Ramakrishna, S.A.; Ramkumar, J. Numerical simulation of melt pool oscillations and protuberance in pulsed laser micro melting of SS304 for surface texturing applications. *J. Manuf. Process.* **2019**, *39*, 282–294. [CrossRef]
29. Chen, T.; Chen, X.; Liu, G.; Zhang, X.; Zhang, W. Research on the ablation mechanism and ablation threshold of CMC-SiCf/SiC by using dual-beam coupling nanosecond laser. *Ceram. Int.* **2022**, *48*, 24822–24839. [CrossRef]
30. Qingliang, S.; Tiyan, W.; Qiang, S.; Fang, Y.; Hejun, L.; Fu, M.W. Unraveling of the laser drilling of carbon/carbon composites: Ablation mechanisms, shape evolution, and damage evaluation. *Int. J. Mach. Tools Manuf.* **2023**, *184*, 103978. [CrossRef]
31. Gu, Z.; He, Y.; Yang, J.; Fu, Y.; Ji, J.; Zhang, Y.; Li, J.; Liu, G. Dual-path micro-holes process for 0Cr17Ni7Al stainless steel thin plate with picosecond laser. *J. Manuf. Process.* **2023**, *101*, 1224–1233. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Adhesion Strength and Anti-Corrosion Performance of Ceramic Coating on Laser-Textured Aluminum Alloy

Changfeng Fan ^{1,2}, Xue Wang ^{3,*}, Xiaoli Yin ¹, Wei Huang ^{1,4}, Yujie Da ¹, Hao Jiang ¹, Jingfeng Cao ¹, Yongchao Gai ¹ and Wangwang Zhang ⁵

¹ College of Intelligent Manufacturing and Control Engineering, Shandong Institute of Petroleum and Chemical Technology, Shandong 257061, China; fancf2015@hotmail.com (C.F.); yinxl@sdipect.edu.cn (X.Y.); hwei18231303568@163.com (W.H.); dayujie0731@163.com (Y.D.); 17661250686@163.com (H.J.); y18853008092@163.com (J.C.); gaiyongchao2025@163.com (Y.G.)

² Key Laboratory of Mechanical Surface Engineering and Tribology, Shandong Institute of Petroleum and Chemical Technology, Shandong 257061, China

³ College of Chemical Engineering, China University of Petroleum, Shandong 266580, China

⁴ Dongying Pinmo Import and Export Co., Ltd., Shandong 257061, China

⁵ Dongying City Infrastructure Pipeline Natural Gas Limited Liability Company, Shandong 257061, China; shilong19891225@126.com

* Correspondence: xuewang0822@163.com

Abstract: Laser surface texturing and micro-arc oxidation provide excellent approaches to enhance the adhesion strength and anti-corrosion performance of adhesive bonding interfaces in aluminum alloys, which can be applied in the field of automotive light weighting. Herein, micro-arc oxidation coatings were fabricated on the laser-textured aluminum surface under the voltage of 500 V for various treatment times (5 min, 15 min, 30 min, 60 min). The anti-corrosion performance of ceramic coatings on the laser-textured surface was analyzed using electrochemical measurements. The results of electrochemical measurement indicate that the coating on the sample surface presents two time constants corresponding to a dual-layer structure. The sample grown under 500 V for 60 min exhibits excellent protective performance with a value of $1.3 \times 10^7 \text{ ohm}\cdot\text{cm}^2$. The adhesion strength of laser-textured ceramic coating is improved compared with the as-received substrate. The sample treated with 500 V for 30 min exhibits the highest bonding strength with a value of 52 MPa. The wider pores and bulges for the sample grown in 60 min would introduce microcracks and consequently reduce the adhesion strength.

Keywords: micro-arc oxidation; laser texture; aluminum alloy; electrochemical measurement; adhesive bonding

1. Introduction

Aluminum alloy, known for its exceptional combination of low density and high strength, has become an essential material in various industries, such as automotive [1] and aerospace industries [2]. The application in lightweight structural components effectively enhances performance [3,4]. Their light weight contributes to fuel economy, reducing the overall weight of the vehicle without compromising the structural integrity in the automotive industry, while the aerospace industry relies on aluminum alloys for their structural components, due to their strength-to-weight ratio, corrosion resistance, and compatibility with manufacturing processes. However, aluminum alloys present specific weldability challenges, especially when joining dissimilar materials. Adhesive bonding, an efficient, cost-effective, and environmentally friendly processing technique, has emerged as an alternative. It not only reduces the structural weight by about 25%–30% compared to traditional methods like riveting and welding, but also provides advantages including decreased stress concentrations at joints, corrosion resistance, and efficiency [5,6].

The surface modification of aluminum plays a central role in determining adhesion strength and durability for applications. Laser texturing has attracted much attention by creating diverse micro- and nanostructures with many advantages [7]. F. Lambiase et al. treated aluminum surfaces before joining to enhance the mechanical interlock between substrates by laser texturing [8]. Wan et al. demonstrated that laser treatment induces physicochemical changes, increasing joint strength by 374% and transitioning the failure mode from interfacial to mixed [9]. However, adhesive joints encountered the degradation and poor durability stemming from the interfacial corrosion in humid, hot environments. In light of this, Bora et al. investigated laser texturing and silane treatment on adhesive performance [10]. Notably, silane treatment's effect on interfacial bond strength is unpredictable and may reduce interfacial bond strength.

Micro-arc oxidation (MAO) is considered an eco-friendly and effective surface treatment for aluminum. MAO exploits transient high-temperature and high-pressure conditions created by an electrical discharge in an electrolyte solution to promote in situ generation of oxide ceramic films on metal surfaces, including magnesium, aluminum, and titanium. The electrical parameters have a significant impact on the discharge energy, ultimately influencing the microstructure of the ceramic coating. Wang et al. emphasized that coatings with remarkable corrosion resistance can be obtained by controlling process parameters [11]. Many studies have explored the corrosion resistance of MAO-treated aluminum surfaces, confirming its effectiveness. The corrosion resistance performance is closely associated with process parameters and electrolyte composition. Tran et al. achieved rapid growth of the micro-arc oxidation layer and improved corrosion resistance and hardness by adding ammonia to the sodium silicate electrolyte solution [12], while Wang et al. adjusted the electrical parameters to obtain a coating with improved corrosion resistance [13]. The dense ceramic coatings exhibit excellent corrosion properties [14–16]. Furthermore, Guan et al. involved the MAO treatment of valve metal surfaces, resulting in significant adhesive property improvements [17]. The mechanical bond strength is further improved as the coating roughness and micropore size on the surface increase. Physical interlocking of the ceramic coating and substrate contributes to excellent adhesion [18–21]. These ceramic coatings exhibit high bonding strength and other advantages such as excellent durability, corrosion resistance, and insulation. Micro-arc oxidation application has the potential to significantly improve the surface strength and corrosion resistance of aluminum alloys [22–24]. However, less attention has been paid to correlations between laser surface texturing and MAO on the adhesion strength of the 5052 aluminum alloy.

In this work, 20 W nanosecond pulsed laser pulses were used to fabricate microholes in the 5052 aluminum alloy substrate. We investigated the impact of micro-arc oxidation treatment time on the corrosion resistance and adhesion strength performance of the laser-textured surface. The aim was to evaluate the performance of the combination of laser surface texturing and micro-arc oxidation on adhesion strength. The influence of micro-arc oxidation time on the adhesion strength of laser microtextured surfaces will be elucidated. Other parameters, such as the electrolyte, voltage, and current density, will not be discussed in this study. The micromorphology of ceramic coatings was characterized by scanning electron microscopy (SEM) and analyzed using an energy-dispersive spectrometer (EDS). The corrosion resistance was evaluated on an electrochemical workstation. The adhesion strength was measured by the pull-out method.

The objective is to determine the optimal parameters for the micro-arc oxidation application of aluminum alloys, providing both theoretical information and technical support for the advancement of lightweight materials in the automotive industry. The combination of increased strength and suitable surface properties can lead to the development of lightweight components with improved durability and corrosion resistance. The study not only contributes to ongoing efforts in materials science for automotive applications but also highlights the importance of surface engineering techniques in pushing the limits of performance and functionality of lightweight materials.

2. Materials and Methods

2.1. Material and Coating Preparation

The chemical compositions of the 5052 aluminum alloy used in this research are shown in Table 1. Plates with a thickness of 2 mm were cut to dimensions of 25 mm × 50 mm.

Table 1. Chemical composition of 5052 aluminum alloy (in wt%).

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Al
Content	0.06	0.21	0.01	0.01	2.66	0.19	0.01	Bal.

The samples were polished using sandpaper until they reached a grit of #2400, after which they were dipped into a 4 g/L NaOH solution at 80 °C for 10 min. Afterwards, the samples were soaked in a 10% HCl solution at room temperature for 2 min and subsequently washed with deionized water.

2.2. Laser Surface Texturing and Micro-Arc Oxidation Treatment

The nanosecond laser system (KX-200) is represented in Figure 1 with a schematic illustration. Samples were mounted on a 3-dimensional translation stage. A 20 W pulsed laser was used to generate a sinusoidal pattern on aluminum, as shown in Figure 1. The scanning speed was set at 1000 mm/s. This study aims to investigate and improve adhesion strength through combined laser microtexturing and micro-arc oxidation. The distinction in bonding strength is also influenced by laser texturing parameters. Further information is essential to elucidate this point.

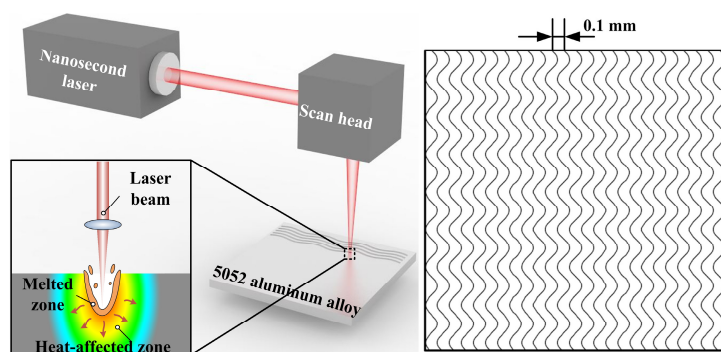


Figure 1. Schematic illustration of the nanosecond laser system.

A series of samples was obtained by micro-arc oxidation using the experimental system shown in Figure 2. The silicate electrolyte with KOH (4 g/L) and K_2TiF_6 (5 g/L) was introduced. Micro-arc oxidation was conducted at 750 Hz, with a positive-to-negative duty ratio of 35% and a current density of 2 A/dm². The laser-textured substrate was treated with various treatment times, as shown in Table 2. The voltage was selected as 500 V for micro-arc oxidation. To remove residual alkali solution on the ceramic coating surface and prevent erosion, the fabricated samples were immersed into deionized water with 5–10 min ultrasonication treatment and then dried.

Table 2. The treatment method and treatment time utilized in this study.

No.	Surface Treatment	MAO Voltage (V)	MAO Time (min)
1	As-received	-	-
2	LST	-	-
3	LST + MAO	500	30
4	LST + MAO	500	5
5	LST + MAO	500	15
6	LST + MAO	60	60

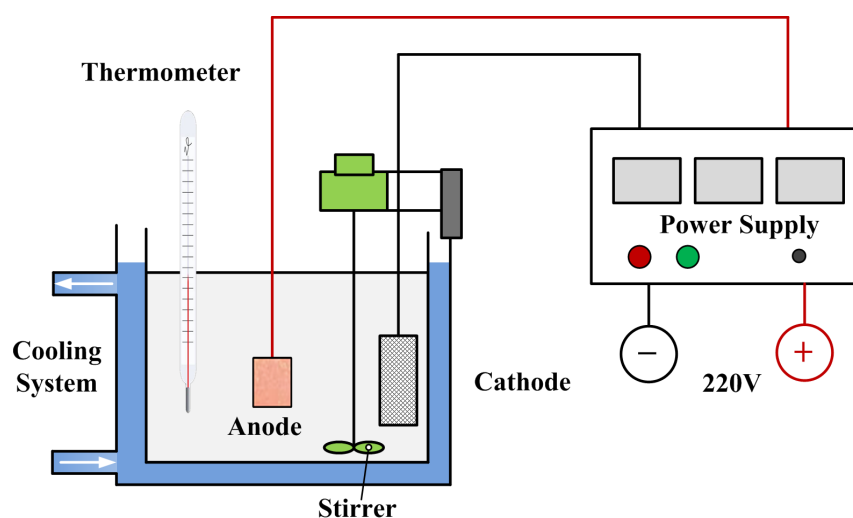


Figure 2. The micro-arc oxidation experimental system.

2.3. Characterization Methods and Electrochemical Measurement

MAO ceramic coatings were observed via scanning electron microscope (SEM, SUS3800, Hitachi, Tokyo, Japan). The texture geometry was evaluated by the 3D profile measurement microscope (VHX-5000, KEYENCE, Osaka, Japan). Energy-dispersive X-ray spectroscopy (EDS) characterized element distribution and content on the ceramic coatings.

Electrochemical measurements were carried out by an electrochemical workstation with a 3.5 wt% NaCl solution (Reference 3000, Gamry, Warminster, PA, USA). A three-electrode system was employed with the sample as the working electrode. A platinum mesh was regarded as the counter electrode. The reference electrode was selected as an Ag/AgCl electrode (3M KCl). Potentiodynamic (DP) measurements were conducted with the scanning rate of 1 mV/s (over ± 0.1 V vs. open circuit potential). Electrochemical impedance spectroscopy was performed with the following characteristics: exposure area of 1 cm², frequency from 100 kHz to 0.01 Hz with the voltage amplitude of 20 mV. Acquired data were analyzed using Zview software (Version 3.2) with specified equivalent circuit models to obtain comprehensive information on the electrochemical behavior of the measured samples.

2.4. Characterization Methods and Electrochemical Measurement

The epoxy (AV138M-1, ARALDITE, Basel, Switzerland) was selected as the adhesive in this study. The base and hardener of the two-component coating were completely blended together. The coating was placed in a ventilated environment at 25 °C for seven days to carry out the follow-up test. The adhesion strength for the interface was evaluated based on the ASTM D4541-2017 standard test method [25].

3. Results and Discussion

The ablation signature indicates sequential layer-by-layer removal of material, similar to the ablation observed in Al₂O₃ when fabricated with a picosecond laser [26]. As depicted in Figure 3a, a distinct microwall-like structure is formed due to the melted and recast material. This phenomenon is further emphasized by the inward flow of the molten material stemming from the impact of laser pulses. The presence of the microwall structure above the aluminum substrate increases the depth, which is positive to the enhancement of adhesion strength.

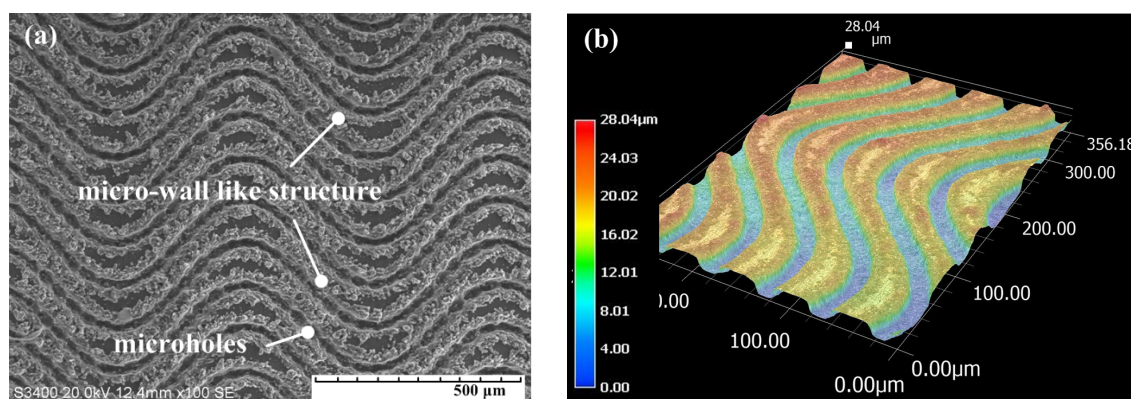


Figure 3. SEM top-view of laser texture (a) and 3D profile microscope images (b) of aluminum surface.

Figure 3b indicates the 3D profile microscope images of the aluminum surface with the microtexture. Microvalleys with complex structures were fabricated by nanosecond laser ablation, reaching a vertical depth of approximately 28 μm . During nanosecond laser ablation of the aluminum surface to create lines, many nanoparticles and microparticles were removed and then deposited along the sides of the ablated lines. These particles were redeposited along two sides of the ablated lines. The depth illustrates nonuniformity. Rims and valleys can be observed. This inhomogeneity arises from the formation and expulsion of molten material owing to local high pressure during laser texturing. The formation of recast material both within and around the concealed microholes contributes to the growth of microwalls surrounding blind micropores.

The SEM surface morphology of the ceramic layers on the laser-textured aluminum surface grown at 500 V for 30 min is depicted in Figure 4. A porous structure is observed. The sample develops an in situ MAO ceramic coating on the laser-textured substrate. The aluminum surface has a microtextured structure with ridges and valleys (Figure 4b) in addition to micro-nanoholes in the micro-arc oxidation coating. It is worth emphasizing that applying high voltage causes electrical sparks stemming from a higher electrical current. The strong electric avalanches lead to the initiation of wider micropores. When the voltage applied is high, the positive voltage more easily suffers from the breakdown potential of the ceramic coating. Consequently, lots of electron avalanches occur in the vicinity of the anode leading to more pore initiation. The consolidation of the structural pores is a result of the high-energy sparks [27]. The ceramic coating is subjected to high electric current in order to sinter it. The laser-textured aluminum substrate has more concave and convex microstructuring than the as-received aluminum alloy with faster molten oxidation in protruding parts. The bonding strength would be affected. According to the EDS mapping results shown in Figure 5, element mapping of Al, O, Si, Mg, and Ti indicates that these elements are homogeneously distributed in the coating. The surface analysis results from the EDS are presented in Table 3, giving an indication of the proportion for each element. The analysis showed that Al and O were found in the film, occupying a large proportion, whereas Si, Mg, and Ti account for relatively smaller proportions. The ceramic coating is mostly composed of silicon–oxygen, magnesium–oxygen, and titanium–oxygen compounds. Silicon–oxygen compounds have an influence on the roughness of the MAO coating. The presence of titanium–oxygen compounds can positively enhance the corrosion properties.

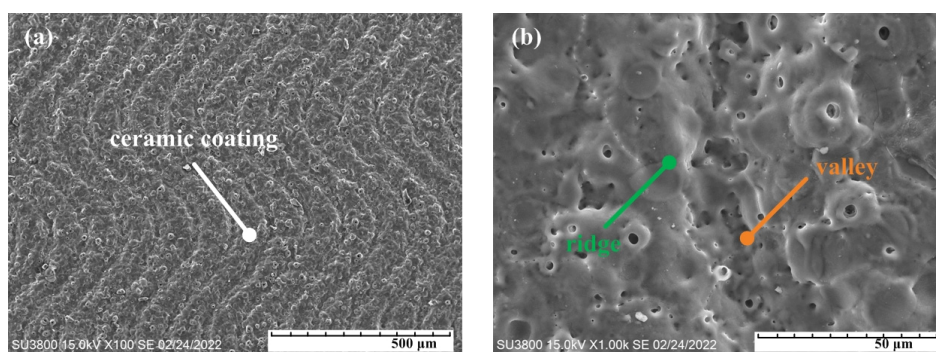


Figure 4. SEM top-view of the MAO coatings on laser-textured aluminum substrate grown at 500 V for 30 min. (a) 100 $\times$. (b) 1000 $\times$.

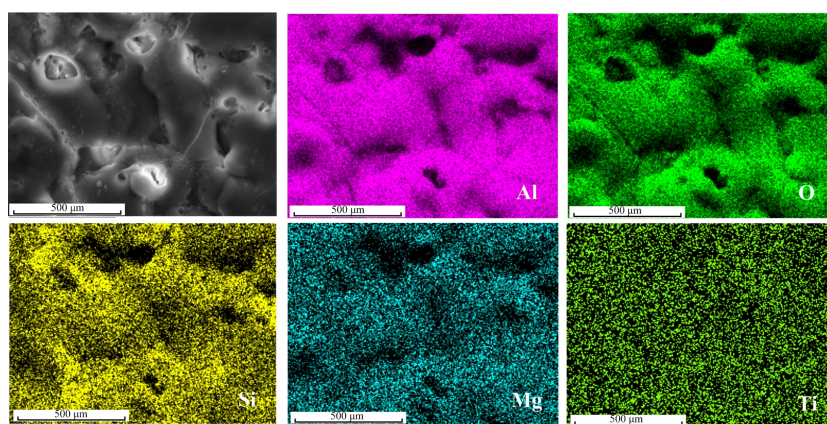


Figure 5. EDS elemental mapping of laser-textured aluminum with MAO treatment at 500 V for 30 min.

Table 3. The compositions on surfaces from EDS analysis (wt%).

Elements	Al	O	Si	Mg	Ti
content	43.79	41.20	5.81	4.51	3.75

The coating that was developed at a voltage of 500 V displayed a suitable morphology and chemical composition. Herein, the textured samples were fabricated by micro-arc oxidation at 500 V for 5 min, 15 min, and 60 min. It is worth reminding that the growth time of 30 min was investigated earlier. Figure 6 illustrates the impact of growth time on the surface morphology of the coatings. It can be observed that the diameter of pores increases over the treatment time, whereas there are cracks and breakdowns on the coarse surface [28]. The diameter of the micropore is appropriately 3 μm for the ceramic coating grown under the condition of 500 V for 30 min. The formation of a structural pore through an electrical spark increases its susceptibility to subsequent electron avalanches due to its lower breakdown voltage compared to non-porous areas. Furthermore, the sequential occurrence of electrical sparks at a single point leads to larger pores. The coating became exfoliative and coarse when the applied voltage exceeded a critical value for an extended treatment time, making optimization impossible to a certain extent. Jiang et al. demonstrated that high voltage in the electrolyte led to the occurrence of intense sparking arcs, resulting in negative consequences like the thermal cracking of coatings [29]. A lot of bulges can generate under the condition of 500 V for 60 min. The formation of wider pores and bulges initiates microcracks, which in turn reduce the surface area and subsequently weaken the adhesion between the coating and the substrate.

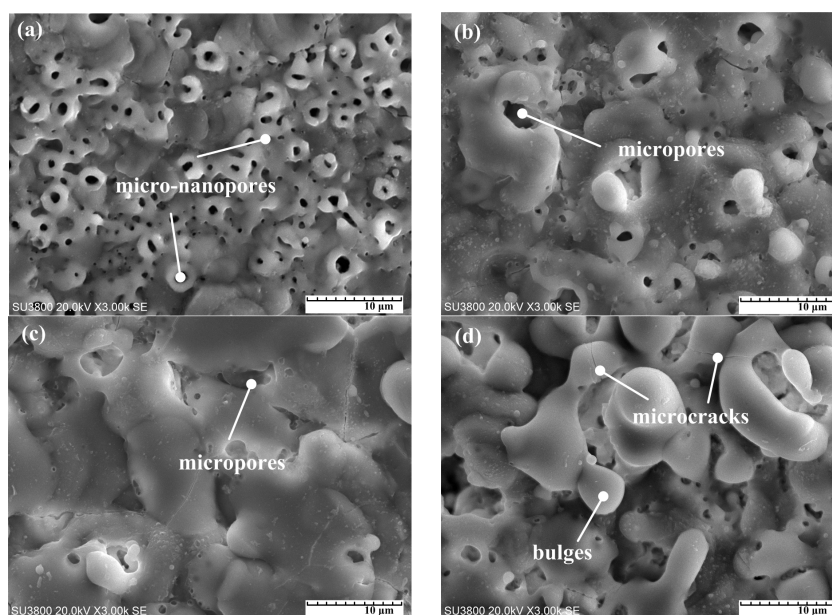


Figure 6. SEM top-view of the micro-arc oxidation coatings grown under the voltage of 500 V for different times: (a) 5 min, (b) 15 min, (c) 30 min, (d) 60 min.

The potentiodynamic polarization curves of the coatings are illustrated in Figure 7. The results show that the corrosion potential of ceramic coatings is almost similar to that on the substrate. However, the MAO coating exhibits a relatively lower current density, which can be related to the presence of metal oxides in the coatings. Based on Figure 7a, it can be observed that the coatings display a consistent decrease in corrosion current density as the voltages increase, while corrosion potential and polarization resistance continuously increase. A low corrosion current density suggests a good corrosion resistance. The corrosion potential and polarization resistance of the bare substrate are -680 mV and $0.69 \mu\text{A}/\text{cm}^2$, respectively. These values slightly increase to -650 mV and $0.63 \mu\text{A}/\text{cm}^2$ for the laser-textured surface. The ceramic coating after LST exhibits a maximum of -616 mV and $4.47 \text{ nA}/\text{cm}^2$, respectively. The current density dropped almost two orders of magnitude compared to that of the substrate. Figure 7b illustrates the potentiodynamic polarization curves of ceramic coatings obtained under 500 V with different treatment time. The corrosion current density noticeably decreases as the treatment time increases, reaching a minimum of $2.04 \text{ nA}/\text{cm}^2$ after 60 min. The current density of the MAO sample was more than 100 times lower than that of the substrate.

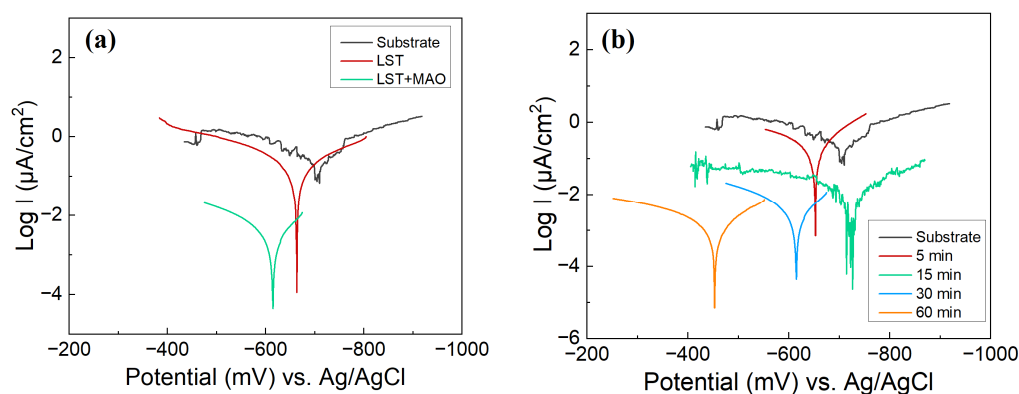


Figure 7. Polarization curve for (a) different surface treatment on 5052 aluminum alloy and (b) different MAO treatment time at 500 V.

Figure 8a illustrates impedance spectra in the Nyquist plot for the aluminum substrate with/without laser texturing and micro-arc oxidation. Generally, the relationship between resistance and capacitance in charge transfer processes can be reflected by the impedance arc in the Nyquist plots. The radius of the arc on the impedance is directly proportional to the corrosion resistance of the sample. A larger radius indicates better corrosion resistance [30–32]. The Nyquist plots of the substrate with/without laser texturing indicate similar electrochemical behavior. Poor corrosion resistance can be observed in the substrate for $1.04 \times 10^5 \text{ ohm}\cdot\text{cm}^2$. However, micro-arc oxidation coating can effectively enhance the impedance. Laser microtexturing mainly affects the microscopic surface morphology of the substrate, while micro-arc oxidation leads to the formation of a ceramic coating between the substrate and electrolyte, showing the possibility of excellent corrosion resistance. The Nyquist plot shows its high impedance characteristics. The complex plane of coating grown on the textured surface at 500 V for 30 min was manifested as a straight line, which exhibits the highest impedance with about $2 \times 10^6 \text{ ohm}\cdot\text{cm}^2$.

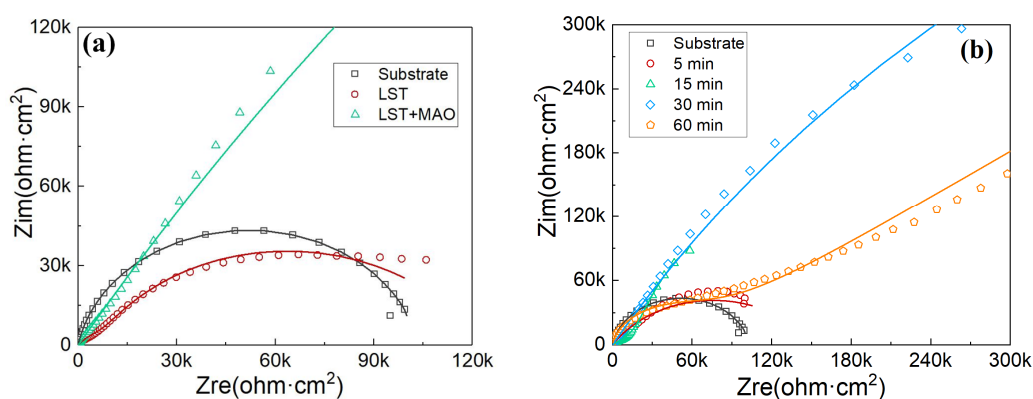


Figure 8. EIS spectra for (a) different surface treatment on 5052 aluminum alloy and (b) different MAO treatment time at 500 V.

Figure 8b shows the Nyquist and Bode plots of micro-arc oxidation coatings grown under different treatment times. The Nyquist plot of the sample grown under 500 V for 60 min displays a large arc that does not end in the low-frequency range, which indicates the excellent protective performance. The compressed arc, implying two overlapping time constants, can be deduced from the Nyquist plots for all samples. As the micro-arc oxidation time increases, the thickness of the ceramic coating continues to increase, thus leading to a corresponding increase in its impedance. The values of the impedance modulus increased remarkably from $1.16 \times 10^5 \text{ ohm}\cdot\text{cm}^2$ to more than $10^7 \text{ ohm}\cdot\text{cm}^2$. The sample grown at 500 V for 60 min displays a very high impedance with a value of $1.3 \times 10^7 \text{ ohm}\cdot\text{cm}^2$.

Figure 9 illustrates the equivalent circuit to elucidate the EIS spectra for the samples with and without micro-arc oxidized coatings. Model A and model B are employed to fit the EIS spectra of the substrate and textured sample with ceramic coating, respectively. Constant phase elements (CPEs) are incorporated into the equivalent circuit. R_e represents the electrolyte resistance. R_1 and CPE_1 indicate the equivalent resistance and capacitance of the outer layer of the coating, while R_2 and CPE_2 represent the equivalent resistance and capacitance of the inner layer of the coating. Generally, the condensed inner layer exhibits better corrosion resistance for external corrosive ions, resulting in higher impedance values. Conversely, the micro-arc oxidation outer layer of the coating is thinner and contains certain voids, facilitating the passage of corrosive ions and thus leading to a relatively lower impedance value. Polarization resistance R_{pl} ($R_{pl} = R_1 + R_2$) is commonly considered as a parameter to evaluate the protective performance. The sample fabricated under the condition of 500 V for 60 min exhibits the highest resistance value of $1.3 \times 10^7 \text{ ohm}\cdot\text{cm}^2$, indicating the best corrosion resistance among the samples. This suggests that this is an appropriate voltage to reduce the number and size of pores. Moreover, the formed oxides

such as Al_2O_3 and TiO_2 can obstruct the erosion of corrosive ions, enhancing the corrosion resistance of the ceramic coating [33,34].

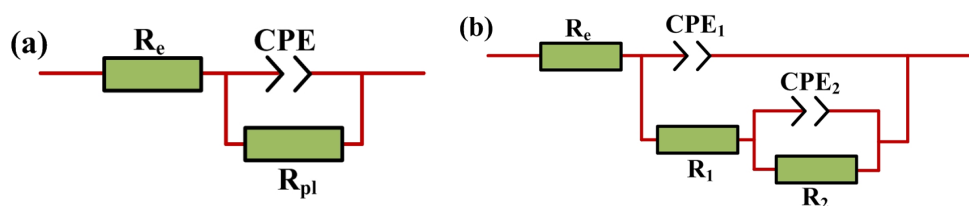


Figure 9. Equivalent circuit diagrams of EIS for aluminum alloy with various surface treatments and MAO treatment times. (a) Model A. (b) Model B.

Sandblasting is widely regarded as a method of surface treatment, but noise and dust from sandblasting may be detrimental to the environment. Furthermore, as indicated in Table 4, preliminary experimental studies show slightly lower adhesion strength in the samples with sandblasting + MAO treatment compared to those treated with LST + MAO. The combination of laser microtexturing and micro-arc oxidation can create a structure on the substrate similar to a gecko's foot pad, which can increase adhesion strength. The laser microtexturing treatment is at the center of our attention here. The tensile test results of the substrate with and without laser texture and micro-arc oxidation are revealed in Figure 10. Compared with the bare substrate, the textured sample shows an adhesion strength improvement of 65% with 33 MPa. The textured sample with micro-arc oxidation illustrates improved adhesion strength with the value of 52 MPa. According to the SEM graphs, it is clear that in samples without MAO treatment, the adhesive components are damaged at the interface between the adhesive layer and the substrate. In contrast, for samples subjected to MAO treatment, the adhesive layer exhibited fractures, resulting in cohesive failure. This result can be relevant to the porous surface of the aluminum. The presence of pores on the surface would promote a mechanical interlock between the oxide layer and the adhesive. When the ceramic coating is subjected to tensile loading, the distribution and configuration of pores in fact lead to weaknesses in the bonds [35]. The textured aluminum treated with micro-arc oxidation exhibits enhanced adhesive strength from 33 MPa to the maximum of 52 MPa. Laser texturing effectively minimizes both breakage and delamination of MAO coatings, consequently reducing the formation of the peeling layer. This is achieved by forming an oxide layer after undergoing micro-arc oxidation treatment. It can be observed that the textured sample with/without micro-arc oxidation exhibits a similar fractured morphology characterized by an identical pattern. However, it is important to note that the sample without ceramic coating presents adhesive failure, while the textured sample with micro-arc oxidation indicates cohesive fracture.

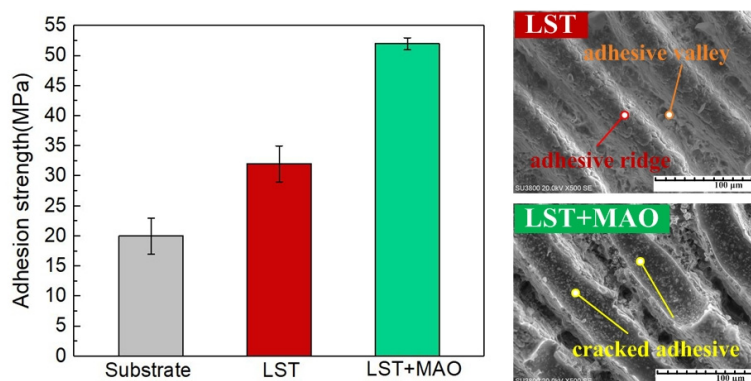
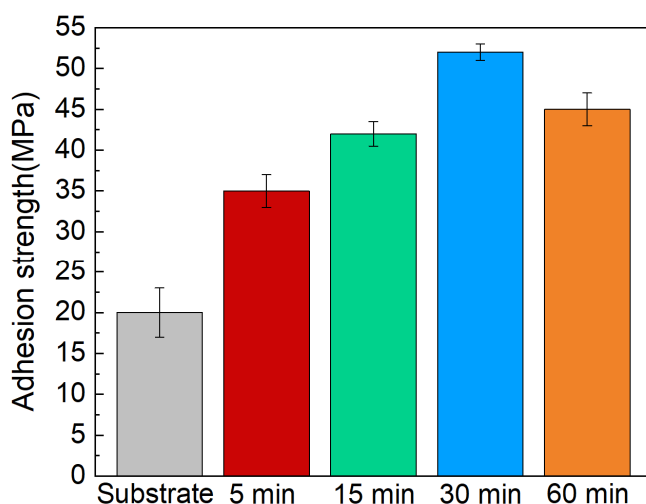


Figure 10. Adhesion strength of aluminum alloy under different surface treatments.

Table 4. The adhesion strength for different surface treatments.

Surface Treatment	Adhesion Strength (MPa)
As-received	20 ± 3
Sandblasting	30 ± 1.5
LST	33 ± 3
Sandblasting + MAO	46 ± 1.5
LST + MAO	52 ± 1

Figure 11 illustrates the tensile test results of the ceramic coatings grown at 500 V with treatment times. The adhesion strength gradually increases during 5 to 30 min of micro-arc oxidation treatment. However, as the treatment time extends to 60 min, the adhesion strength decreases slightly to 45 MPa. It may be suggested that the presence of the oxide layer determined the bond strength of the aluminum–epoxy system. The findings of this research align with previous studies that attribute decreased bond strength to the presence of a thick oxide layer on the metal surface [36]. The wider pores and bulges for the sample grown in 60 min shown in Figure 6d would introduce the microcracks and consequently reduce the bonding strength between the coating and the substrate. Contrarily, Figure 6c revealed a compact and smooth structure with minimal large pores. This feature is advantageous as it enhances the effective contact area between the coating and the substrate while also preventing any potential breakage or spalling.

**Figure 11.** Adhesion strength of laser-textured aluminum alloy under different MAO treatment times.

4. Conclusions

This study investigated the influence of micro-arc oxidation treatment times on the adhesion strength and corrosion mechanism of ceramic coating on laser-textured 5052 aluminum alloy. The size of pores increases with the applied voltage because of the higher electrical current flowing through the electrochemical cell. The diameter of the micropore is appropriately 3 μm for the MAO coating grown under the condition of 500 V for 30 min. The Nyquist plot of the sample grown under 500 V for 60 min displays a large arc, which indicates an excellent protective performance with a value of $1.3 \times 10^7 \text{ ohm}\cdot\text{cm}^2$. The textured aluminum treated with micro-arc oxidation exhibits enhanced adhesive strength ranging from 33 MPa to 52 MPa. The sample without ceramic coating presents adhesive failure, while the textured sample with micro-arc oxidation indicates cohesive fracture. The sample treated with 500 V for 30 min exhibits the highest bonding strength. The wider pores and bulges for the sample grown in 60 min would introduce the microcracks and consequently reduce the bonding strength between the coating and the substrate. This study mainly focuses on the combined effects of laser microtexturing and micro-arc oxidation

on the adhesion strength of the aluminum alloy surface. Several parameters play a role in this process, such as laser microtexture pattern, laser processing parameters, electrical parameters for micro-arc oxidation, and electrolyte composition. Further information is essential to explore and elucidate the influence of these factors.

Author Contributions: Conceptualization, C.F.; methodology, X.W. and X.Y.; investigation, W.H., Y.D. and H.J.; formal analysis, J.C.; data curation, Y.G.; writing—original draft preparation, C.F.; writing—review and editing, X.W., X.Y. and W.Z.; funding acquisition, C.F., X.W. and X.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by Dongying Science and Technology Development Foundation (DJ2020016, FZ20220027) and Shandong Provincial Natural Science Foundation (ZR2022QE186, ZR2021ME180, ZR2023QE139).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The corresponding author can provide the data supporting the findings of this study upon reasonable request.

Conflicts of Interest: Author Wei Huang was employed by Dongying Pinmo Import and Export Limited Liability Company. Author Wangwang Zhang was employed by Dongying City Infrastructure Pipeline Natural Gas Limited Liability Company. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Jin, Q.H.; Chen, J.; Peng, L.M.; Li, Z.Y.; Yan, X.; Li, C.X.; Hou, C.C.; Yuan, M.Y. Research progress in joining of carbon fiber-reinforced polymer composites and aluminum/magnesium alloys. *J. Mater. Eng.* **2022**, *50*, 15–24.
- Zhang, J.; Dai, W.; Wang, X.; Wang, Y.; Yue, H.; Li, Q.; Yang, X.; Guo, C.; Li, C. Micro-arc oxidation of Al Alloys: Mechanism, microstructure, surface properties, and fatigue damage behavior. *J. Mater. Res. Technol.* **2023**, *23*, 4307–4333. [CrossRef]
- Wang, S.; Peng, X.; Yang, Y.; Wang, S.; Wu, M.; Hu, P.; Fu, C. Insight into microstructure evolution and corrosion mechanisms of K₂ZrF₆/Al₂O₃-doped hot-dip aluminum/micro-arc oxidation coatings. *Coatings* **2023**, *13*, 1543. [CrossRef]
- Li, L.; Yang, E.; Yan, Z.; Xie, X.; Wei, W.; Li, W. Effect of pre-anodized film on micro-arc oxidation process of 6063 aluminum alloy. *Materials* **2022**, *15*, 5221. [CrossRef] [PubMed]
- Budzik, M.K.; Wolfahrt, M.; Reis, P.; Kozłowski, M.; Sena-Cruz, J.; Papadakis, L.; Nasr Saleh, M.; Machalicka, K.V.; Teixeira de Freitas, S.; Vassilopoulos, A.P. Testing mechanical performance of adhesively bonded composite joints in engineering applications: An Overview. *J. Adhes.* **2021**, *98*, 2133–2209. [CrossRef]
- Gong, W.; Ma, R.; Du, A.; Zhao, X.; Fan, Y. The effects of the pre-anodized film thickness on growth mechanism of plasma electrolytic oxidation coatings on the 1060 Al substrate. *Materials* **2023**, *16*, 5922. [CrossRef] [PubMed]
- Zou, X.; Liu, L.; Chen, T.; Wu, L.; Chen, K.; Kong, L.; Wang, M. Laser surface treatment to enhance the adhesive bonding between steel and CFRP: Effect of laser spot overlapping and Pulse Fluence. *Opt. Laser Technol.* **2023**, *159*, 109002. [CrossRef]
- Lambiase, F.; Yanala, P.B.; Leone, C.; Paoletti, A. Influence of laser texturing strategy on thermomechanical joining of AA7075 aluminum alloy and Peek. *Compos. Struct.* **2023**, *315*, 116974. [CrossRef]
- Wan, H.; Min, J.; Lin, J. Experimental and theoretical studies on laser treatment strategies for improving shear bonding strength of structural adhesive joints with cast aluminum. *Compos. Struct.* **2022**, *279*, 114831. [CrossRef]
- Bora, M.; Çoban, O.; Akman, E.; Oztoprak, B.G.; Kutluk, T. Comparison of novel surface treatments of al 2024 alloy for Al/CFRP adhesive bonded joints. *Int. J. Adhes. Adhes.* **2020**, *103*, 102721. [CrossRef]
- Wang, S.Q.; Wang, Y.M.; Zou, Y.C.; Chen, G.L.; Wang, Z.; Ouyang, J.H.; Jia, D.C.; Zhou, Y. Generation, tailoring and functional applications of micro-nano pores in microarc oxidation coating: A critical review. *Surf. Eng.* **2021**, *50*, 1–22. [CrossRef]
- Tran, Q.P.; Sun, J.K.; Kuo, Y.C.; Tseng, C.Y.; He, J.L.; Chin, T.S. Anomalous layer-thickening during micro-arc oxidation of 6061 al alloy. *J. Alloys Compd.* **2017**, *697*, 326–332. [CrossRef]
- Wang, P.; Wei, W.X.; Pu, J.; Zhou, X.L.; Cao, W.J.; Xiao, Y.T.; Gong, Z.Y.; Hu, J. Effect of current density on characteristics of 2024 aluminum alloy micro arc oxidation coatings with titanium dioxide particles. *Int. J. Electrochem. Sci.* **2019**, *14*, 4338–4349. [CrossRef]
- Yang, G.; Lü, X.; Bai, Y.; Cui, H.; Jin, Z. The effects of current density on the phase composition and microstructure properties of micro-arc oxidation coating. *J. Alloys Compd.* **2002**, *345*, 196–200.
- Arunnelliappan, T.; Kishore Babu, N.; Rama Krishna, L.; Rameshbabu, N. Influence of frequency and duty cycle on microstructure of plasma electrolytic oxidized AA7075 and the correlation to its corrosion behavior. *Surf. Coat. Technol.* **2015**, *280*, 136–147. [CrossRef]

16. Zhang, J.; Fan, Y.; Zhao, X.; Ma, R.; Du, A.; Cao, X. Influence of duty cycle on the growth behavior and wear resistance of micro-arc oxidation coatings on hot dip aluminized cast iron. *Surf. Coat. Technol.* **2018**, *337*, 141–149. [CrossRef]
17. Li, Y.; Guan, Y.; Zhang, Z.; Ynag, S. Enhanced bond strength for micro-arc oxidation coating on magnesium alloy via laser surface microstructuring. *Appl. Surf. Sci.* **2019**, *478*, 866–871. [CrossRef]
18. Wang, P.; Wu, T.; Xiao, Y.T.; Pu, J.; Guo, X.Y. Effects of $\text{Ce}(\text{SO}_4)_2$ concentration on the properties of micro-arc oxidation coatings on ZL108 aluminum alloys. *Mater. Lett.* **2016**, *182*, 27–31. [CrossRef]
19. Xin, S.G.; Song, L.X.; Zhao, R.G.; Hu, X.F. Microstructure and adhesion strength of Al-Si-O micro-arc oxidation coating. *J. Inorg. Mater.* **2006**, *21*, 493–498.
20. Egorkin, V.S.; Gnedenkov, S.V.; Sinebryukhov, S.L.; Vyaliy, I.E.; Gnedenkov, A.S.; Chizhikov, R.G. Increasing thickness and protective properties of PEO-coatings on aluminum alloy. *Surf. Coat. Technol.* **2018**, *334*, 29–42. [CrossRef]
21. Polat, A.; Makaraci, M.; Usta, M. Influence of sodium silicate concentration on structural and tribological properties of microarc oxidation coatings on 2017A aluminum alloy substrate. *J. Alloys Compd.* **2010**, *504*, 519–526. [CrossRef]
22. Li, Q.B.; Liu, C.C.; Yang, W.B.; Liang, J. Growth mechanism and adhesion of PEO coatings on 2024Al alloy. *Surf. Eng.* **2016**, *33*, 760–766. [CrossRef]
23. Gecu, R.; Yurekturk, Y.; Tekoglu, E.; Muhaffel, F.; Karaaslan, A. Improving wear resistance of 304 stainless steel reinforced AA7075 aluminum matrix composite by micro-arc oxidation. *Surf. Coat. Technol.* **2019**, *368*, 15–24. [CrossRef]
24. Zhang, K.; Yu, S. Preparation of wear and corrosion resistant micro-arc oxidation coating on 7N01 aluminum alloy. *Surf. Coat. Technol.* **2020**, *388*, 125453. [CrossRef]
25. ASTM D4541-17; Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers. ASTM: West Conshohocken, PA, USA, 2022.
26. Jagdheesh, R. Fabrication of a superhydrophobic Al_2O_3 Surface using picosecond laser pulses. *Langmuir* **2014**, *30*, 12067–12073. [CrossRef] [PubMed]
27. Clyne, T.W.; Troughton, S.C. A review of recent work on discharge characteristics during plasma electrolytic oxidation of various metals. *Int. Mater. Rev.* **2018**, *64*, 127–162. [CrossRef]
28. Mohedano, M.; Serdechnova, M.; Starykevich, M.; Karpushenkov, S.; Bouali, A.C.; Ferreira, M.G.S.; Zheludkevich, M.L. Active protective PEO coatings on AA2024: Role of voltage on in-situ LDH Growth. *Mater. Des.* **2017**, *120*, 36–46. [CrossRef]
29. Jiang, X.Z.; Lu, S.; Tang, L.; Wang, Z.X.; Chen, J. Influence of negative voltage on micro-arc oxidation of magnesium alloy under two steps voltage-increasing mode. *Key Eng. Mater.* **2013**, *575*, 472–476. [CrossRef]
30. Wang, S.D.; Xu, D.K.; Wang, B.J.; Sheng, L.Y.; Qiao, Y.X.; Han, E.-H.; Dong, C. Influence of phase dissolution and hydrogen absorption on the stress corrosion cracking behavior of Mg-7% Gd-5% Y-1% Nd-0.5% Zr alloy in 3.5 wt.% NaCl solution. *Corros. Sci.* **2018**, *142*, 185–200. [CrossRef]
31. Chen, X.W.; Li, M.L.; Zhang, D.F.; Cai, L.P.; Ren, P.; Hu, J.; Liao, D.D. Corrosion resistance of MoS_2 -modified titanium alloy micro-arc oxidation coating. *Surf. Coat. Technol.* **2022**, *433*, 128127. [CrossRef]
32. Wang, S.D.; Xu, D.K.; Chen, X.B.; Han, E.H.; Dong, C. Effect of heat treatment on the corrosion resistance and mechanical properties of an as-forged Mg-Zn-Y-Zr alloy. *Corros. Sci.* **2015**, *92*, 228–236. [CrossRef]
33. Li, C.; Goei, R.; Li, Y.; Shi, J.; Liu, F.; Li, B.; Gao, Y.; Li, Y.; Li, S.; Tok, A.I. Effect of chromium on erosion-corrosion properties of ZrO_2 - Al_2O_3 particles reinforced FE-based composites in artificial seawater slurries. *Corros. Sci.* **2022**, *198*, 110138. [CrossRef]
34. Li, J.; Ma, C.; Wang, J.; Bian, D.; Zhao, Y. Effect of pore content and pH on the corrosion behavior of hydrophobic ceramic coatings. *Int. J. Appl. Ceram. Technol.* **2022**, *20*, 1624–1635. [CrossRef]
35. Hsieh, S.F.; Ou, S.F.; Chou, C.K. The influence of the substrate on the adhesive strength of the micro-arc oxidation coating developed on TiNi shape memory alloy. *Appl. Surf. Sci.* **2017**, *392*, 581–589. [CrossRef]
36. Li, J.X.; Zhang, Y.M.; Han, Y.; Zhao, Y.M. Effects of micro-arc oxidation on bond strength of titanium to porcelain. *Surf. Coat. Technol.* **2010**, *204*, 1252–1258. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Post-Wear Surface Morphology Assessment of Selective Laser Melting (SLM) AlSi10Mg Specimens after Heat Exposure to Different Gas Flames

Maaz Akhtar ^{1,*}, Muhammad Muzamil ², Muhammad Samiuddin ³, Naser Alsaleh ¹, Rashid Khan ¹, Mahad Ali Khan ², Joy Djuansjah ¹, Ali Khursheed Siddiqui ¹ and Arfan Majeed ⁴

¹ Mechanical and Industrial Engineering Department, College of Engineering, Imam Mohammad Ibn Saud Islamic University, Riyadh 11432, Saudi Arabia; naalsaleh@imamu.edu.sa (N.A.); rakhan@imamu.edu.sa (R.K.); jrdjuansjah@imamu.edu.sa (J.D.); aksiddiqui@imamu.edu.sa (A.K.S.)

² Mechanical Engineering Department, NED University of Engineering & Technology, Karachi 75270, Pakistan; muzamil@neduet.edu.pk (M.M.); mahadali97@hotmail.com (M.A.K.)

³ Metallurgical Engineering Department, NED University of Engineering & Technology, Karachi 75270, Pakistan; engr.sami@neduet.edu.pk

⁴ School of Mechanical Engineering, Northwestern Polytechnical University, Xi'an 710072, China; amajeed@mail.nwpu.edu.cn

* Correspondence: maakhtar@imamu.edu.sa

Abstract: The wear surface morphology of AlSi10Mg specimens, originally manufactured using selective laser melting (SLM), has been analyzed in the context of exposure to heat from gas flames. The first stage of the experimental work included the performance of surface heat-exposure on SLM-prepared specimens through oxyacetylene gas welding. Gas welding was utilized with three different flames, namely; reducing, neutral, and oxidizing on the as-built specimens of SLM. The post-surface-treated specimens were subjected to pin-on-disk wear testing against fixed parameters. After the performance of wear testing at two different radii, the mass loss of each of the four types of specimens was calculated including the three specimens exposed to heat along with the as-built specimens. The results showed that the maximum amount of mass losses at 24 mm and 30 mm radii belongs to the neutral flame specimens and the least was for the as-built condition specimens. Upon analysis, the heat-exposure specimens through all three types of gas flames resulted in an increase in the amount of mass in contrast to the as-built specimens. Moreover, the morphologies of the developed wear tracks at surfaces were examined using the scanning electron microscope (SEM) for the understating of the mechanism.

Keywords: SLM; heat-exposure; wear testing; wear tracks; gas welding; AlSi10Mg

1. Introduction

The term additive manufacturing (AM) is most commonly renowned with the word 3D printing with the help of layer-by-layer deposition of material in the creation of prototypes and complex geometries along with controlling waste over substantive manufacturing and customized production [1]. This technology has equal applications for all types of industries but especially demanding for aerospace, medical, electrical vehicles, and critical jigs and fixtures production. However, the research studies are being conducted extensively in the direction of materials and process optimization. Overall, additive manufacturing has shown great potential for transforming the manufacturing industry with ongoing research focusing on further improving the technology and expanding its applications [2].

Aluminum alloys have found a wide range of applications considering and fulfilling the lightweight criterion for the automotive, aerospace, machine construction, and electronic appliances as well as for the domestic utensils [3]. Aluminum alloys such as Al-Si, Al-Mg-Si, Al-Cu, and Al-Zn have been identified as resourceful alloys for multiple

applications along with the capability of displaying higher mechanical behavior upon the generation of fine precipitates [4] in the matrix. Currently, among the additive manufacturing techniques, Laser Powder Bed Fusion (LPBF) is one of the most preferred additive techniques to produce metallic components with having integration with a high-power laser source for melting, and become commercially known as Selective Laser Melting (SLM). The SLM is also expected to revolutionize the manufacturing industry by providing ease in the cycle of design and flexibility in the time and material utilization by also considering the geometrical complexity, defect-free, and fully dense parts of high quality [5,6]. AlSi10Mg is one of the most frequently used aluminum alloys that is integrated with SLM and exhibits good mechanical behavior in as-built conditions [7]. The authors are particularly concerned with assessing the wear surface morphology of SLM AlSi10Mg alloy with surface heat exposure from gas flames.

Many additively prepared aluminum alloys including the AlSi10Mg have the potential to be used for static and dynamic performances in the automobile and aerospace sector like in casted conditions. However, sometimes the elevation of temperature approaches more than 150 °C while operating for a long duration. This can potentially reduce the mechanical behavior of the developed component causing the coarsening and dissolution of the developed precipitates even more pronounced in the cases of heat-treatable aluminum alloys [8]. This will also reduce the useful and service life of the potentially sliding components. However, a good tribological assessment in terms of the wearing of these components can help find the remaining life and associated reliability. There are only two possible cases to increase the life of the components; one is to reduce the friction by providing good lubrication while the other is to prior assessment and proactive prediction of wear behavior according to tentative working conditions where it is fitted [9].

To connect with one of the above-discussed situations where the temperature is also an associated case from any utilized or surrounding commonly fabrication techniques such as electric arc and gas welding. Surface heat exposure (melting) is a developed process that locally affects, melts, and solidifies a thin layer from the material's surface. Possibly this study can be treated as a simulator to find the changes in surface properties and functionalities. Therefore, high energy sources are considered such as electric arc, gas flames, laser, electron, and plasma beam sources for instantaneous melting and further rapid solidification resulting in changes in composition, microstructure, and ultimately the consequence on the mechanical behavior. The famous post-surface remelting techniques for the above objective are laser surface remelting (LSM), electron beam surface remelting, and plasma surface remelting [10,11].

From the available different techniques, LSM is frequently used for wide applications for surface remelting that utilize a high-power laser beam for melting. The procedure involves localized remelting of the surface, which ultimately changes the microstructure and mechanical behavior in contrast to the base material properties. However, the exact performance is most likely dependent on operating parameters like laser power, exposure time, and spot size [12]. Furthermore, surface remelting through an electron beam is also a high-tech operation and also demonstrated an appreciated potential to remelt the surface, which tailors the surface properties of metallic materials. The applications of remelting even prior electroplated with Ni and Ni-WC, and subsequently remelted the surface through electron beam to withstand extreme temperature and high strength alloys such as Ti-6Al-4V (TC4) [13] and titanium grade 2 (TA2) [14] is also reported to improve the further surface hardness and wear resistance. Several studies have also disclosed the consideration of plasma beam remelting as a good alternative source [15] with key characteristics and advantages including superior metallurgical bond formation, ease of operation, high efficiency of heating, and minimal dimensional changes along with localized hardening [16].

The process of providing surface heat-exposure can also be carried out through oxy-acetylene gas welding operations using different types of flames, such as neutral, carburizing, and oxidizing flames, to analyze the results on surfaces. This operation is relatively very cheap in comparison with the above-discussed remelting cases and opens a window

to execute post-surface heat exposure on the low-temperature lightweight alloys prepared through additive manufacturing. The importance and the industrial application of the presented work is to integrate and explore the detrimental effects created on the aluminum alloys against heat exposure, which were previously cold worked, heat treated, or fabricated from specialized processes for higher mechanical behavior. The exposure to heat may be experienced as a result of exceeding operational factors including leakage of hot gases, high-temperature generation near engine components; maintenance procedures nearby section joining-repair causing repeated heat cycle; or accidental fire. In a similar context, the cold-worked hole fasteners of aluminum alloy that were provided with the benefit of compressive residual stresses to delay the crack initiation and growth; experienced higher fatigue growth rates when exposed to a temperature of 150 °C [17,18]. In addition, Jabra et al. [19] explored the effect of thermal exposure on different aluminum alloy plates in different conditions, and reported a reduction in the strength and hardness. However, Ceschini et al. [20] planned to study the effect of thermal exposure on A356 aluminum alloy in the casted form to report their mechanical properties; the ultimate tensile strength and yield strength are reported to decrease by 32% and 40%, respectively, after thermal exposure at 210 °C for 41 h. This was attributed to the coarsening of precipitates after the exposure to heat. Therefore, exposure to heat is also critical to assess the high cost and performance processes such as SLM where higher mechanical behavior is expected by the user, and even become more severe for heat treatable sensitive alloys such as AlSi10Mg.

As far as the AlSi10Mg is concerned, a typically heat-treatable alloy with good casting properties along with widely investigated AM alloy with SLM process. Moreover, several studies have reported extremely fine microstructure that promotes better mechanical behavior in the as-built condition in contrast to solution and T6 heat treatment conditions [21,22]. The coarsening of the microstructure and the disruption of the Si-network while solution treatment induces ductility and less resistance to wear, and prolonged holding for T6 treatment causes porosity growing is the probable contribution in the reduction of mechanical behavior comparable to as-built condition. Despite the higher number of studies reporting the aforementioned behavior considering mechanical properties, process parameter optimization, and morphological studies, only a few research studies available in the literature report the wear behavior of AlSi10Mg alloy. Tonolini et al. [23] presented a comprehensive wear behavior comparison of AlSi10Mg considering the as-built, and T6 heat treatment along with the gravity casting of similar alloy. The as-built AM specimens exhibit the lowest wear rate, whereas the heat-treatable specimens depicted the worst wear behavior in contrast to other cases. Another work by Park et al. [24] highlighted the comparison of mass loss against the as-built, direct aging, and T6 treatment specimens reported a decrease in the hardness value at the T6 treatment condition but a slight improvement in the mass loss in comparison to the as-built specimens.

Despite the current trend in the utilization of the above high-cost heat sources to remelt the surface and heat-treatment procedures, the exposure of gas welding source on the surface of AlSi10Mg alloy behavior is not available and the tribological behavior findings are overall unclear. This executed work is focused precisely on the sliding wear behavior considering the heat exposure through a gas welding heat source. Moreover, the change in the surface properties based on heat treatments such as solution heat treatment and age hardening have been a point of focus for quite some time. However, the study on the change in surface behavior through heat-exposure considering gas welding with various flames is a topic less discovered. This research gap was identified and the major aim of this paper is to study the possibilities of heat exposure on AlSi10Mg alloy through gas welding by deploying various flames. Nevertheless, high stresses can be created at any time in severe operating and working conditions and leave the specimens in the previously mentioned more ductile and less wear-resistant state. Eventually, the pin-on-disc test was selected to execute the wear testing and the SEM images to understand the wear track mechanisms of the as-built and heat-exposure surfaces from gas flames.

2. Experimental and Methodology

The roadmap to execute the overall work is given in Figure 1, which further divides the work into seven major tasks, including the experimentation execution for specimen preparation and conducting the wear testing. However, the details of SLM specimens, surface heat-exposure through oxyacetylene gas flames, and further performance of wear testing are presented under the domain of this heading; while the processing and post-processing of the obtained wear testing results including the macro analysis of wear tracks, microstructure/elemental mapping, and SEM analysis of wear mechanism are presented and described under the next section as illustrated in Figure 1.

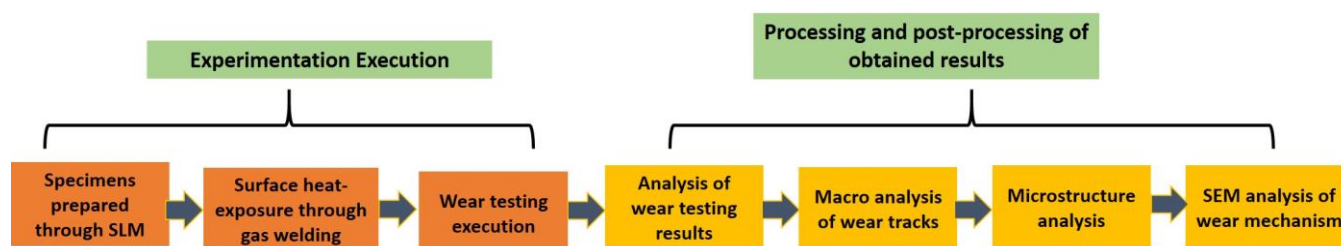


Figure 1. Roadmap to execute the overall work; categorically highlighting the experimentation execution, and processing and post-processing of obtained results.

2.1. Fabrication of AlSi10Mg Specimens through SLM

The SLM 280HL (SLM Solutions, Lübeck, Germany) facility is used to prepare the specimens. The gas-atomized powder of AlSi10Mg was used for the experimentation, the particle sizes ranged from 15 μm to 58 μm [25]. Moreover, the selection of parameters is important for the SLM process in achieving a defect-free structure, good mechanical properties, and maximum relative density. Several researchers have reported different parameters for the printing of specimens to optimize the process. For this work, the optimal process parameters are used from the author's preliminary studies on different targeted themes such as explicit mechanical behavior and heat treatment behavior [26,27] of SLM specimens. These considered parameters are given in Table 1. The 2.5 mm wall thickness SLM specimens were fabricated as similarly produced in the previous study [26] based on parameters given in Table 1. The schematic illustration of the fabrication of specimens is provided in Figure 2.

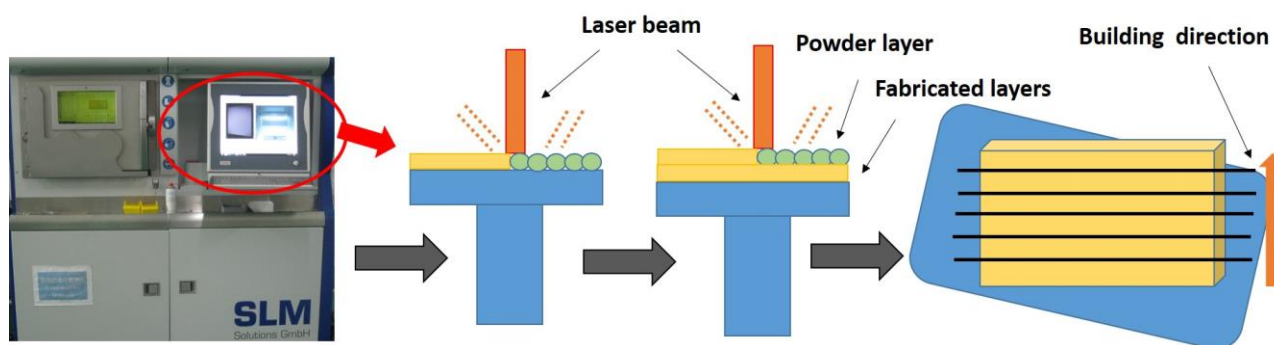


Figure 2. Schematic representation of process starting from the SLM machine where the powder is fused layer by layer in the building orientation in the vertical z-axis direction on checkboard.

Table 1. Processing parameters and their values for the SLM processing [27].

Technical/Processing Parameters	Values/Description
Laser power (kW)	0.32
Scan Speed (m/s)	0.90
Hatch distance (mm)	0.08
Slice thickness (mm)	0.03
Beam focus diameter (mm)	0.08
Scanning strategy	67° with checkerboard
Building direction	Vertical
Building substrate plate	280.0 mm × 280.0 mm × 70.0 mm (L × W × H)

2.2. Execution of Surface Heat Exposure from Gas Flames

The prime purpose of the presented research work is to provide heat exposure to the surface of SLM-prepared specimens through gas flames from welding torch and their further assessment of behavior through wear testing. Three principal types of flames can be used from gas welding torch, neutral, oxidizing, and carburizing, each with its unique characteristics and applications towards joining. In gas welding, the most common type of flame is the neutral flame, which is created by combining equal amounts of oxygen and acetylene gas, and its chemical composition is balanced, resulting in a clean and stable flame. The neutral flame has a light blue inner cone that is bordered by a darker blue outer cone and is appropriate for welding most common metals.

The oxidizing flame is created by increasing the flow of oxygen while decreasing the flow of acetylene. This flame has a higher oxygen concentration, resulting in a hotter and more intense flame. It has a short inner cone and a long, pointed outer cone. The carburizing flame is created by raising the acetylene flow while decreasing the oxygen flow. This flame contains more acetylene, resulting in a reducing environment that can allow carbon to be absorbed into the weld or surface. It has a long, bright inner cone and a smaller, less visible outer cone. The parameters involved in executing the work are to open the oxygen and acetylene cylinders at 4 Psi and 5 Psi pressures, respectively. The physical setup of the gas welding is equipped with the adjusting knobs of gas mixtures at the torch. After the flame was created, the surface was heated in a single pass. After exposure, the specimen was cooled in air before being subjected to wear testing at two different radii.

2.3. Wear Testing Execution

As highlighted in Figure 1, wear testing execution is the prime and major objective of this study, to find out which flame type experiences the most and least mass loss after the execution of the test. Both the as-built specimen and each of the surface-treated specimens underwent wear testing. Therefore, in addition to the as-built specimen, wear testing was carried out sequentially on all three distinctly flame-surface melted specimens. ASTM G99-05 standard [28] test method is followed to execute the wear testing with a pin on the disc apparatus. This standard covers a laboratory procedure for the determination of wear mass during sliding using a pin-on-disc apparatus. To execute this test based on ASTM G99-05, a pin is required which is positioned perpendicular usually a flat circular disc. However, either the pin specimen or disc specimen may revolve or rotate causing the formation of circular tracks. In this study, a stationary pin is used against a flat fixture plate, which held the SLM-prepared specimens.

The further emphasis and guidelines from ASTM G99-05 involve; the equipment requires a motor drive to rotate the disc at the specified velocity, a revolution counter (such as a tachometer) to measure the speed, a holder that holds the pin in place and apply a test force proportional to the mass of the weight, and an electronic mass balance having a sensitivity of 0.1 mg to measure the mass loss. From this wear testing system, load, speed, and sliding distance are the possible test parameters from ASTM G99-05 while temperature and atmosphere may also be accounted for. For this work, tungsten carbide is utilized as

a superior static pin (stationary), and the mass loss is measured from a revolving special disk-fixture carrying the SLM specimens.

Based on the above information from ASTM G99-05, the time and radius of the disc-fixture to achieve the desired sliding distances of testing and rotating speed (Revolution per Minute (RPM)) are the constant controllable factors in the study to execute the wear testing and further proceed to mass loss measurements. First, the disk fixture was set to rotate continuously for 90 s while being subjected to wear testing, and the duration was monitored using a stopwatch. Secondly, once the specimen is securely placed into the fixture slot, the speed controller is activated, and the rotating speed is set using the built-in regulator with the machine to a range of 227–228 PRM. Lastly, the radius between the tip of the pin and the center of the rotating disk-fixture was calculated using the meter ruler. The experiment included two sets of values, the first with a radius of 24 mm and the second with a radius of 30 mm.

The in-house fabricated wear-testing device as shown in Figure 3 was used for testing that had a pin holder attached to the loading lever, formally called a pin-on-disc machine. The sequence of wear testing machine adjustment is pictorially illustrated in Figure 3. As highlighted in Figure 3a, a fixture is placed onto the rotating disc that has a slot to fix the under-observation specimen and is tightened using the Allen key. The radius of the wear testing machine needed to adjust at the 24 mm and 30 mm radii, which is possible due to the sliding mechanism provision provided in the machine. As highlighted in Figure 3a, the wear testing machine used for this work is shown along with the rotating disc and a dead load of 1 kg at the edge of the lever. The fixture having two slots placed onto the disc holder is separately shown in Figure 3b. One slot of the fixture was used to place the SLM fabricated AlSi10Mg specimen while the other is a dummy, filled with the steel piece for balance. A tachometer was used to monitor and ensure the speed of the disc as highlighted in Figure 3c, and a controller box was in Figure 3d. The observed values for the mass losses while performing wear testing, one at 24 mm and the other at 30 mm radius are provided in Table 2. Before and after the execution of testing, the electronic mass-balance device with a sensitivity of three digits was used to measure the mass loss. Moreover, the microstructure analysis is also executed using the optical microscope considering the standardized practices of grinding and polishing, which were etched by Keller's reagent to reveal the structure. In addition, the wear surface analysis is executed to ensure the type of wear and characterized through SEM (Zeiss, Oberkochen, Germany), and the elemental mapping analysis of the cross-sections done on energy-dispersive X-ray spectroscopy (EDX) equipped with SEM.



Figure 3. Execution sequence of wear testing; (a) wear testing machine, (b) fixture having two slots placed onto the disc holder is separately (c) tachometer, (d) controller box.

Table 2. Shows the mass difference and percentage of mass loss when wear testing is performed at 24 mm and 30 mm radius.

Wear Testing Radius	Specimen	Mass before Wear Testing (g)	Mass after Wear Testing (g)	Mass Difference (g)	Percentage of Mass Loss (%)
Wear Testing at R = 24 mm	As-Built	0.498	0.485	0.013	2.610
	Carburizing	0.470	0.453	0.017	3.617
	Neutral	0.470	0.450	0.020	4.255
	Oxidizing	0.474	0.457	0.017	3.586
Wear Testing at R = 30 mm	As-Built	0.485	0.473	0.012	2.474
	Carburizing	0.453	0.439	0.014	3.090
	Neutral	0.453	0.436	0.017	3.752
	Oxidizing	0.457	0.441	0.016	3.501

3. Results and Discussion

3.1. Mass Loss Analysis after Wear Testing

The developed alloy performance of AlSi10Mg through SLM can be controlled and analyzed from two perspectives. The first is the material's developed behavior against the additive manufacturing process to analyze the as-built properties including tensile strength, surface roughness, relative density, porosities, and microstructural features. However, this understanding is already in consideration and presented gradually [29,30] in multiple studies. The other side is the execution by changing the operating conditions and parameters such as applied normal load, sliding distance, lubricating condition, or the testing in harsh conditions integrating with temperature and acidic environment against any specific post-heat heat exposure and heat-treatment to assess the positive and negative impact. The subsequent sections featured the effect of oxyacetylene gas flame exposure and its influence on the surface of SLM-prepared specimens in terms of mass losses.

The results of the pin-on-disc wear testing in the as-built and after the surface exposure from gas flames are presented in Table 2. For assessing the results of the wear testing, the difference in the masses of the specimens was noted before and after the experimentation. Initially, the masses were measured using an electronic weight balance and afterward, the masses were again measured after the post-surface exposure of wear testing. The experimentation was executed at two different radii, i.e., at 24 mm and 30 mm. The subsequent mass losses before and after the testing, mass differences, and the percentage of mass losses are highlighted in Table 2.

Table 2 shows that the surface gas flame-treated specimens maintained a higher mass loss for every type of flame for both the considered radii than the as-built condition specimen of SLM. For the execution at a 24 mm radius, the mass loss difference is 0.017, 0.020, and 0.016 g for carburizing, neutral, and oxidizing flames in contrast to the value of 0.013 g for as-built conditions. Besides the 30 mm radius, the mass loss differences are 0.014, 0.017, and 0.016 g for carburizing, neutral, and oxidizing flames respectively when compared to the value of as-built, which is just 0.012 g. The mass loss values for the heat exposure specimens at the three flames conferred almost the same values at 24 mm except for the neutral flame, while these values are progressively higher than the obtained value of an as-built specimen. Anyhow, the variation in the mass loss at a 30 mm radius is more evident within the three types of flames. The lowest mass difference is captured for the carburizing flame, and the ultimate for the neutral flame, but a similar progressive increment in the mass loss is allied with the 24 mm radius corresponding to the as-built specimen.

Figure 4 plots the graphical comparison in terms of the mass loss difference for the carburizing, neutral, and oxidizing flames at 24 mm and 30 mm of radii used in the wear testing with the as-built obtained values. However, purely to plot the percentage of mass loss is not fruitful as the initial mass of the specimens is not constant or the same. It is observed that the smallest block of mass loss belongs to the as-built condition with the

values of 0.013 and 0.012 g at 24 mm and 30 mm radii, respectively, as well as the percentage of mass loss, which is graphically shown at the bottom of Figure 4. However, the other percentage of mass losses after the heat exposure from different flames is given in Table 2 in comparison with the as-built SLM. The exact mass loss block for carburizing flames is plotted just above the as-built block, which is the increasing one in comparison to the as-built condition but the lowest mass loss percentage in contrast to other gas welding flames. Nevertheless, the oxidizing flame performed better in terms of percentage and difference at both the radii of 24 mm and 30 mm when compared to the percentage and values of neutral flame. Concisely, it is evident that the maximum percentages of mass losses occurred when the specimens were provided with heat exposure through the oxyacetylene gas flames subject to the same testing condition.

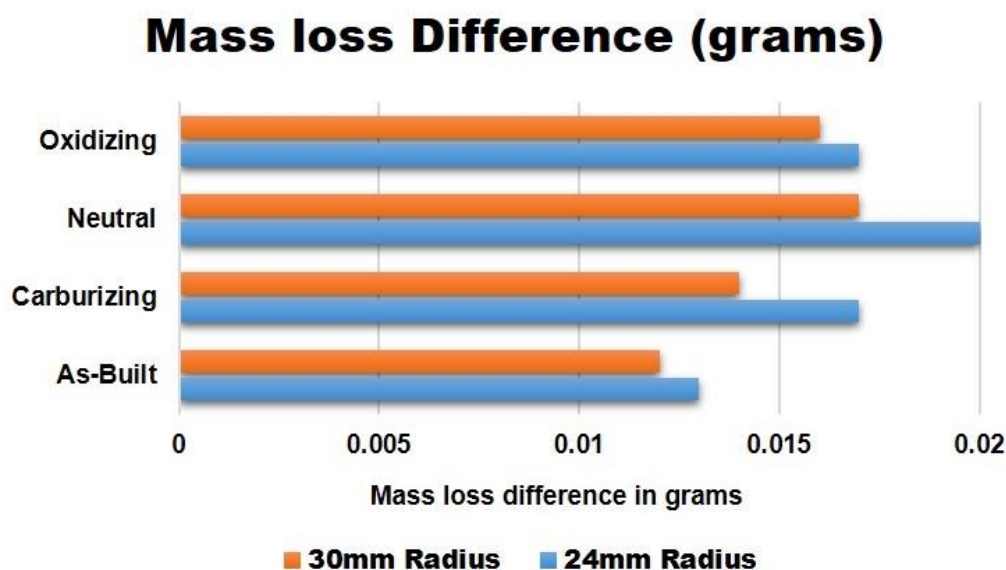


Figure 4. Difference of mass loss block for all three gas flames and as-built condition specimen at 24 mm and 30 mm radii.

The surface developed through the SLM process in the as-built condition is more resistant to the penetration of asperities against the wearing as concluded from the results depicted in Table 2 and Figure 4. The primary cause for this behavior arises from the strengthening provided by the structure developed in the as-built condition of the SLM process, while the higher mass loss behavior is connected and explained in the subsequent Section 3.3 of Microstructure [4]. However, it is also noticed that the grain size plays a critical role against the sliding action while performing the wear testing [21]. The oxyacetylene gas flames reduce the grain size prior developed from the process in the as-built condition at the localized surface. As a result, when the normal load applied to the surface it ultimately transmitted directly from the weak top surface and offered low resistance to wear. The other argument for the higher mass loss percentages is the curvature developed at the melted surface, as shown in the next Section 3.2, is eventually responsible for supporting the normal applied load. This causes easy exhibitance of the counterface pin asperities to the weak and soft aluminum melted surface having large grains and curvature, which offers low resistance and increased mass loss percentages in contrast to the as-built SLM specimen.

3.2. Macro Analysis of Wear-Track Images and Cross-Sections

Figures 5–8 show the macro images of the worn surfaces i.e., the wear tracks of the as-built, carburize, neutral, and oxidizing flames generated from the oxyacetylene gas welding respectively. According to the captured macro images, the as-built and the heat exposure specimens revealed sharp grooves but of different morphological shapes. In comparison to grooves developed on the as-built surfaces, the grooves of the dry sliding wear test from

gas flames exposure are more severe in deformation along with an elliptical impression established at the top surfaces.

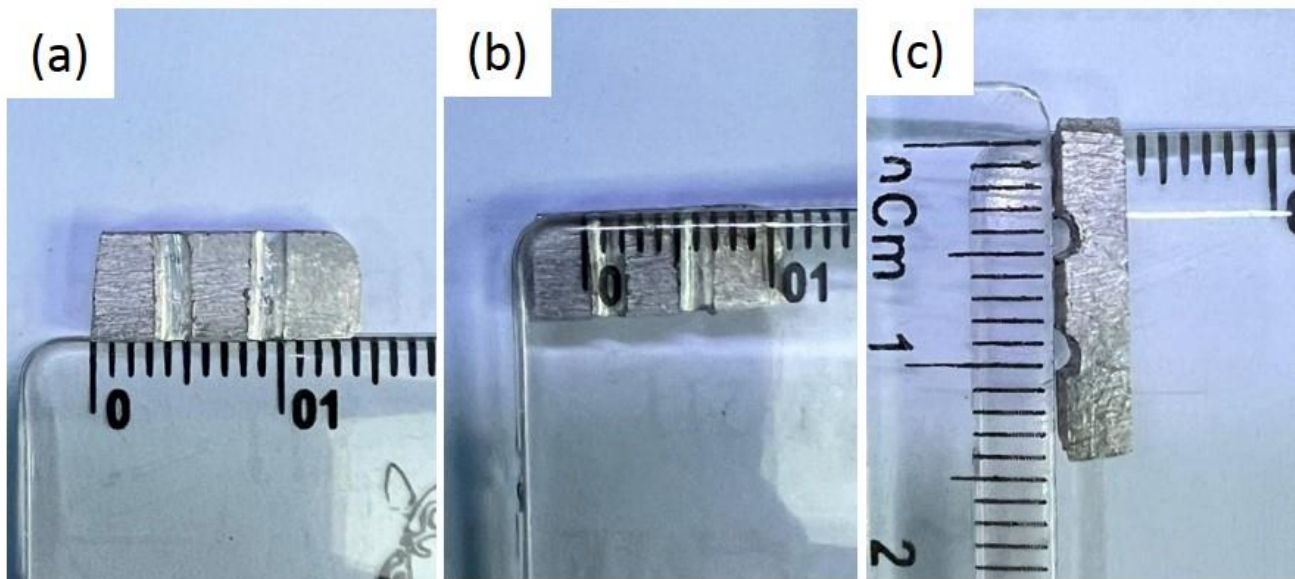


Figure 5. Macro images of the As-built specimens wear tracks; (a) the top view of both the wear tracks grooves (b) wear track images with scale (c) side view morphology of the grooves.

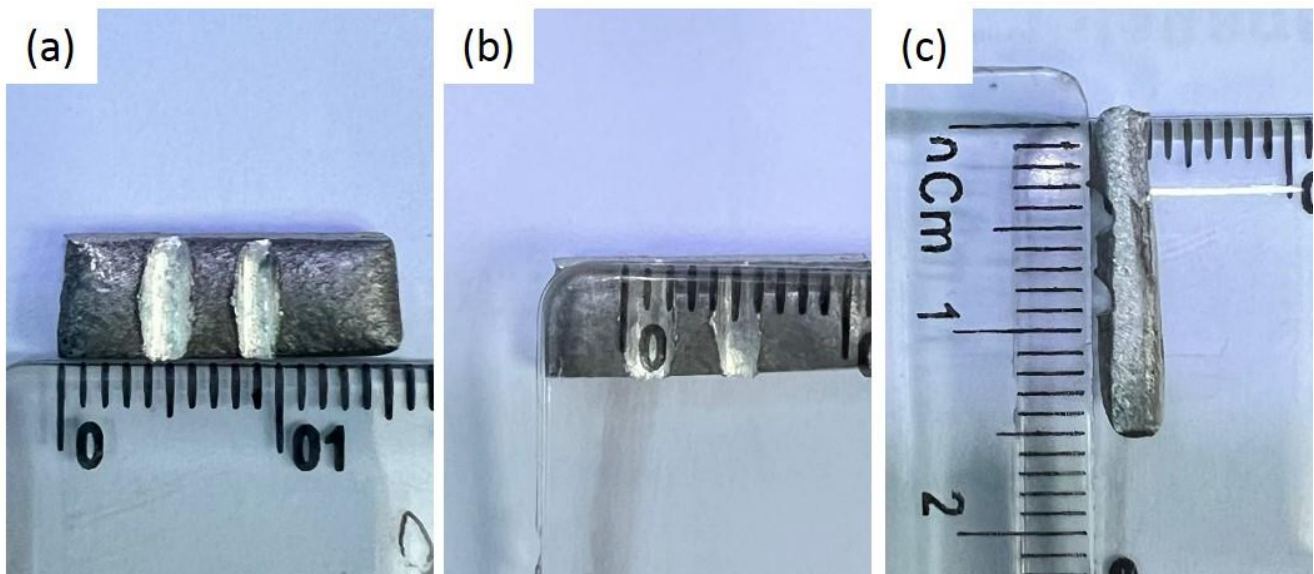


Figure 6. Macro wear track images of the heat exposure specimens through the carburizing flame; (a) the top view of the specimen when placed flat on the surface (b) wear track image with scale (c) side view morphology of the wear tracks grooves.

The worn macro surfaces of the as-built specimens are shown in Figure 5a–c, which revealed that the width and depth are almost identical for both the radii at 24 mm and 30 mm. Evidently, the worn track width cannot exceed the dimension of 1.3 mm for both radii as highlighted in Figure 5a–c. However, the width of the tracks is consistent and confined at the top opening and subsurface. Moreover, the surface is notably deformed after the sliding duration of 90 s along with the mechanical thermal wear also played their part as the tip of the pin is in continuous contact with the disc and got heated due to high revolution speeds of 228 RPM. When comparing with the mass loss of heat exposure specimens as given in

Table 2, the as-built specimens had relatively less mass loss. The wear grooves are not too deep and widely opened to be distorted and present as the specimens had tried to counter the situation from the built-in abrasive rough surface against the counterface part of the pin. Even, the developed and frozen structure helps in arresting the deformation at the surface from this natural condition while printing with SLM.

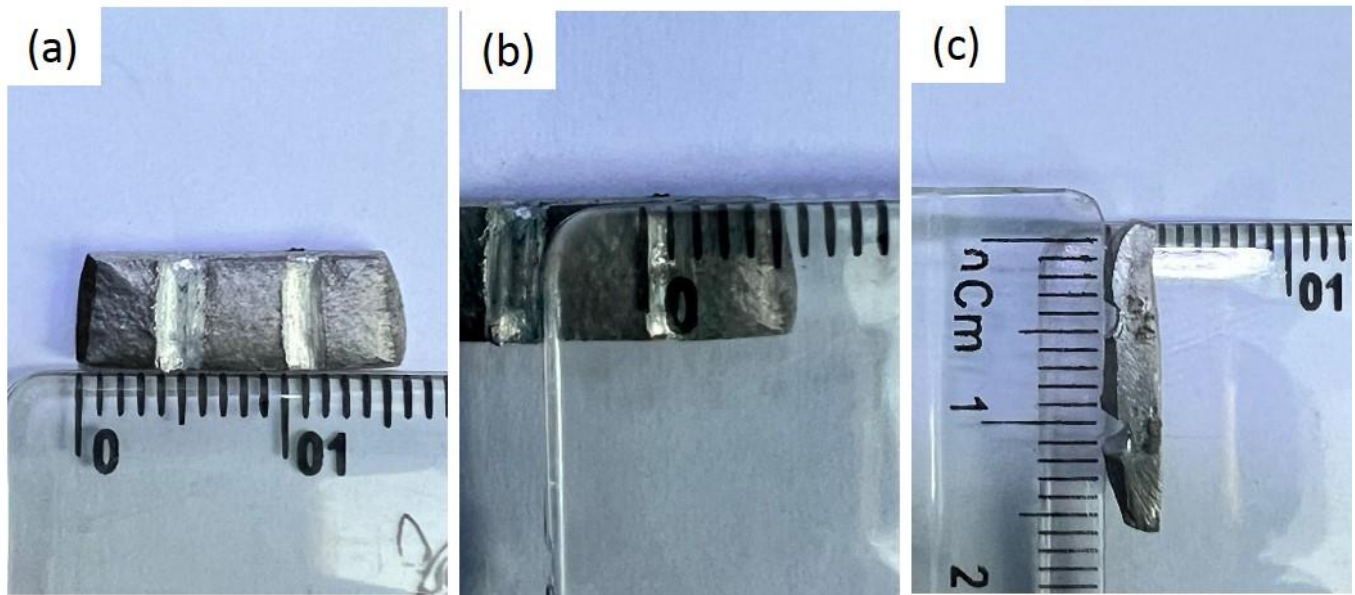


Figure 7. Macro wear track images of the heat exposure specimens through the neutral flame; (a) the top view of the specimen when placed flat on the surface (b) wear track image with scale (c) side view morphology of the wear tracks grooves.

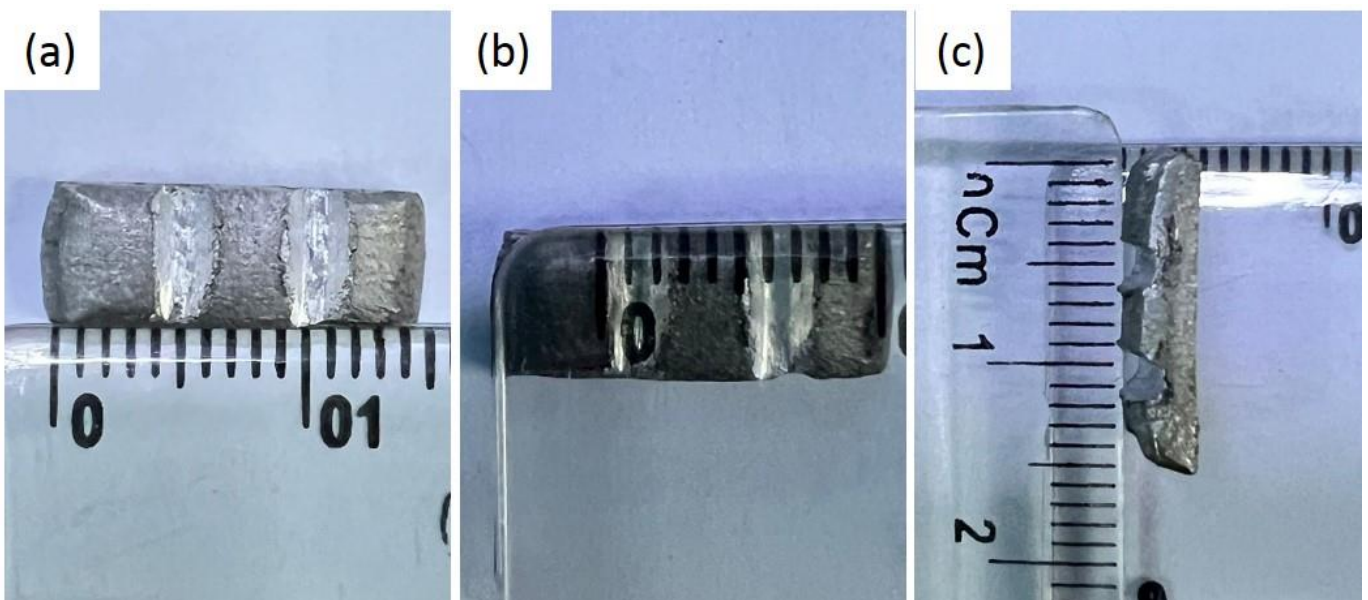


Figure 8. Macro wear track images of the heat exposure specimens through the oxidizing flame; (a) the top view of the specimen when placed flat on the surface (b) wear track image with scale (c) side view morphology of the wear tracks grooves.

Similarly, the developed morphologies of the wear tracks after carburizing, neutral, and oxidizing flames are given in Figures 6–8 respectively. The Figures revealed that the width of the worn tracks increased significantly and approached the value of greater

than 1.8 mm. Specifically, the wear tracks that went through surface heat exposure based on the carburizing flame are shown a bit more deeper and have a larger width track as highlighted in Figure 6a–c in contrast to Figure 5a–c. This is mainly due to the easy initiation of the plastic deformation due to the comparatively developed soft surface being ploughed against the sliding wear. The width and the morphology of both the worn track surfaces of all of the flames are highlighted in Figures 6a,b, 7a,b and 8a,b with a similar characteristic of wide-opened tracks at the top.

The wear tracks taken from two radii of the specimen surfaces exposed through neutral gas flames are given in Figure 7a–c. Extreme pullout surfaces and deep elliptical grooves are shown and resulted for both the radii as depicted in Figure 7a–c for the case of neutral flames. The wear tracks formed in Figure 7a,c have shown deeper troughs thus showing that more mass loss has occurred when compared to the other flames. However, at 24 mm the mass loss with the neutral flame was almost the highest but at 30 mm neutral flame had comparable mass loss with the other flames. The obtained macro images of wear tracks developed after the oxidizing flames are given in Figure 8a–c. As it is evident from the captured wear tracks and results in Table 2; the mass loss was quite significant as compared to the as-built specimen. Nevertheless, when compared to the other gas flames, the oxidizing flame had a relatively lower value of mass losses. The more important characteristics developed from the wear tracks obtained after the heat exposure are; first, the worn-out surfaces and tracks are smoother and brighter than the as-built condition SLM specimens due to ease of plastic deformation with relatively less rough zones. Second, the top surface is severely deformed from sliding wear along with baldy affected in terms of dimensional stability.

In addition, the fine details of the cross-sections after the wear testing of as-built and gas flame-exposed specimens are presented with the aid of SEM images in Figure 9. These presented cross-sections (Figure 9) are in agreement with captured macro images provided in Figures 5–8 in terms of the worn surface features. Similarly, a confirmation of confined and consistent tracks of as-built SLM specimens are highlighted in Figure 9a,b, which were previously featured at the macro-scale in Figure 5a–c. Moreover, a bit deeper and larger in width wear tracks are confirmed from the SEM images presented in Figure 9c–h after the heat exposure from gas flames. However, the distinct feature of porosity is clearly evident at the cross-sections in Figure 9 after the heat exposure from gas flames that directs the higher mass losses, which was not apparent from the macro wear tracks from Figures 5–8. According to Figure 9, as-built fabricated specimens have shown fewer pores (Figure 9a,b), and higher porosities are evident at the cross-sections of heat exposure specimens from gas flames in Figure 9c–h. The porosities are generally characterized at the macro and micro level porosities, where the cracks are developed from macro porosities, and micro porosities become more prominent and critical [31] after heat treatment and heat exposure. A very limited amount of micro porosities are indicated (with arrows) for the as-built condition specimens in Figure 9a,b, while a series of patches of micro and macro porosities are apparent after the gas flame exposure. The cross-sections of 30 mm and 24 mm radii of carburizing flames are provided in Figure 9c,d, where both the images are divided into upper and bottom regions for a better understanding. The mixture of micro and macro sizes of circular porosities are available at the upper region (highlighted with white arrows) for both the tracks, and gradually the density decreases as moves to the bottom region (highlighted with red arrows). Moreover, the cluster and patches of dense micro and macro porosities are available at the upper regions, and the macro porosities became more pronounced and opened at the bottom regions of neutral flames as provided in Figure 9e,f. This is the ultimate reason for providing higher mass loss values for neutral flame as indicated in Table 2. Furthermore, the cross-sections of oxidizing flames depicted in Figure 9g,h revealed less dense areas of micro and macro porosities in contrast to the other two flames but periodically covered with the evidence of micro-pores. The possible reason for the formation of higher porosities after exposure to gas flames is the demolished melt pool and dissolution of the eutectic cellular structure of Si, where

the migration, coalescences of micro-pores, and already trapped gas pores agglomeration become easier [32].

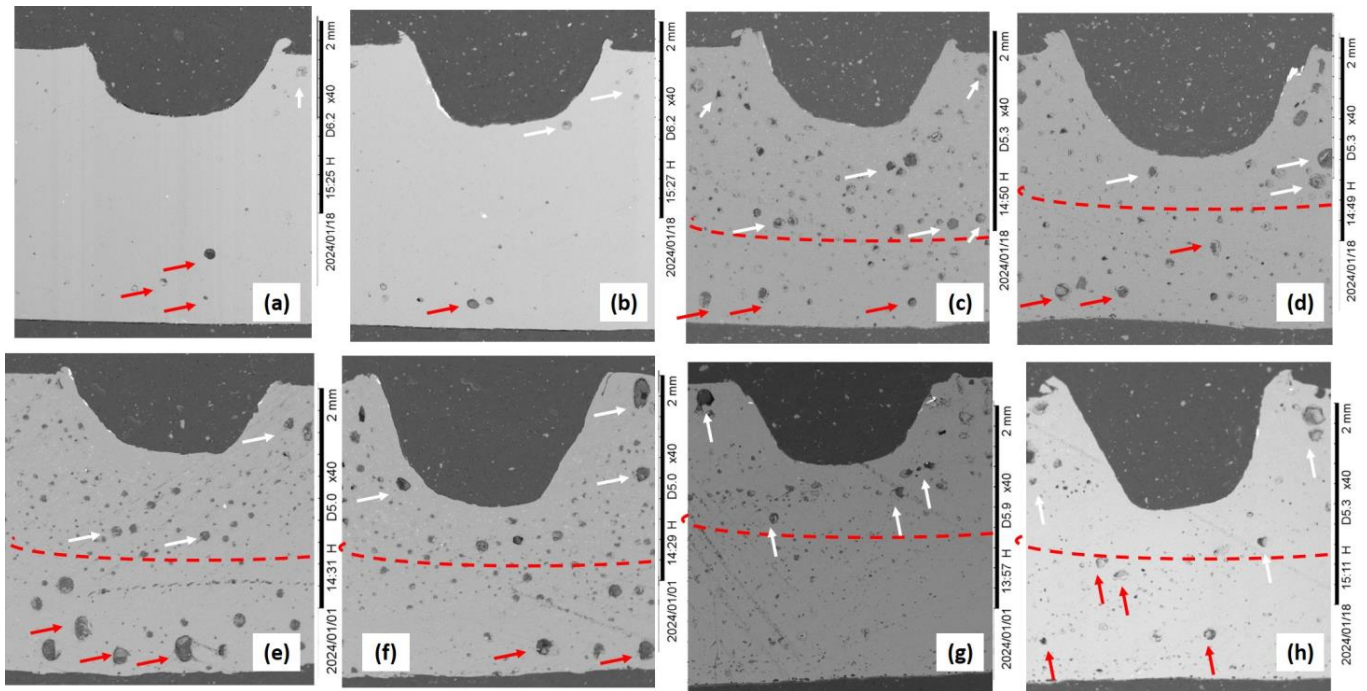


Figure 9. SEM images of the Cross-Sections after wear testing; (a,b) as-built specimen at 30 mm and 24 mm radii, respectively; (c,d) heat exposure from carburizing gas flame, tested at 30 mm and 24 radii respectively; (e,f) heat exposure from neutral gas flame, tested at 30 mm and 24 radii respectively; (g,h) heat exposure from oxidizing gas flame, tested at 30 mm and 24 radii, respectively.

3.3. Microstructure and EDX Analysis of Heat-Exposure Specimens

Due to the rapid melting and rapid solidification cycles of the process, the microstructural aspect creates a stronger influence on mechanical behavior due to the generation of fine cellular grain structure enriched with Si nano size particle/network in the as-built condition. While taking the references from the studies on solution treatment and age hardening; the large-size globalized Si particles are formed in the microstructure with the loss of the interconnected network [33]. This ultimately causes a growth in the Si-particles that further induces ductility and softness in the Al-matrix [27]. Possibly, a similar situation of solution treatment has arisen where the network of Si-rich cell boundaries was completely broken and the Si particle network dissolves in the matrix at the application of surface heat-exposure from the gas flames. The effect of heat-exposure from the carburizing and neutral flames on the microstructure is presented in Figure 10. It is evident in Figure 10a,b that the inherited enriched Si cellular network of SLM is completely dissolved in the matrix, and even the coarser large Si particle density is quite low after the exposure from carburizing and neutral flames. However, very few coarse Si particles were observed in Figure 10a,b, which are highlighted in the form of patches and clusters. It is observed that the density of undissolved or coarse Si particles is relatively higher for the case of carburizing flame in Figure 10a than neutral flame exposure given in Figure 10b. The reason for the existence of large/coarse Si particles at a few places involved the growth of particles at the expense of smaller ones, or otherwise the incomplete dissolving of the Si-based network in the matrix.

As highlighted in Table 2, the as-built specimens offered higher resistance in terms of low mass loss due to the ultrafine cellular structure, where the supersaturated cells are decorated with the network of eutectic Si. These cell boundaries show an interconnected network consisting of eutectic Si particles with a very small amount of Mg_2Si phase [34]. This characteristic microstructure is the ultimate reason for offering the low mass loss in

the wear testing. However, when the surface exposed to heat through gas flames, shows a completely different microstructure; the signs of the Si cellular structure completely vanish. As highlighted in Figure 10a,b, a completely broken or dissolved cellular structure only existed, which is the ultimate sign and reason for showing higher mass loss after exposure to gas flames. Moreover, the cellular structure of eutectic Si is transformed into the bimodal distribution of coarse and fine particles [22], which is distributed in the matrix of microstructure given in Figure 10a,b. The more concentrated patches of coarse Si particles are gathered after carburizing flames shown in Figure 10a, which relatively offered more resistance to wear in contrast to neutral flames where the network is completely dissolved. Thus, very few signs of clustering and coarse particle patches are exhibited in Figure 10b.

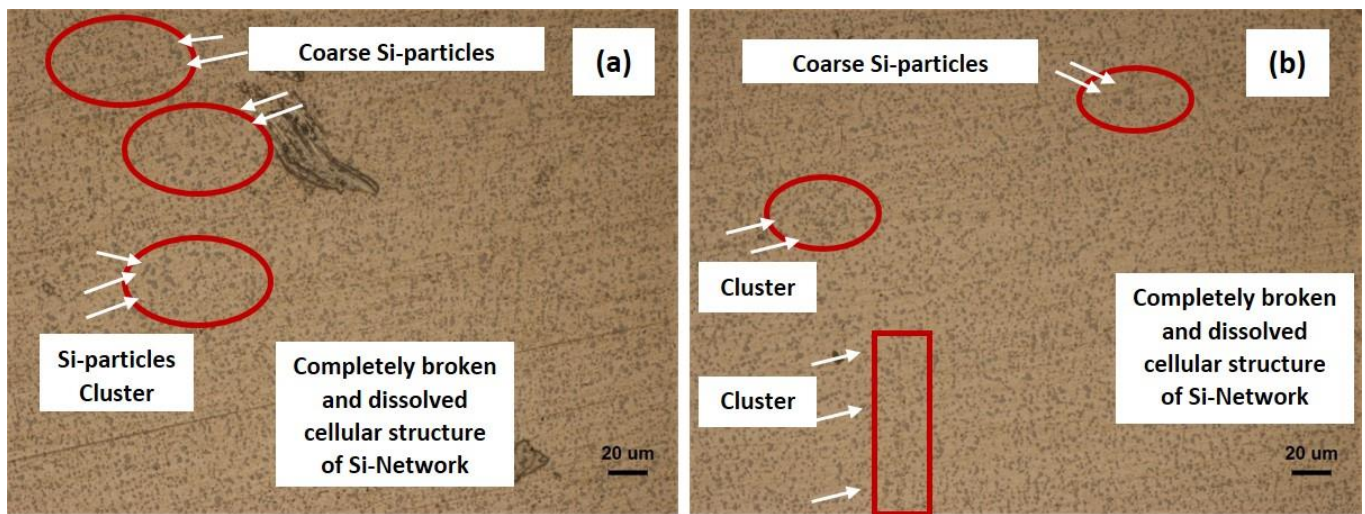


Figure 10. Optical microstructure after heat-exposure from gas flames (a) carburizing flame exposure, (b) neutral flame exposure.

The cross-sectional examination of the wear tracks is conducted to assess the elemental distribution variations through elemental mapping using SEM-EDX. The obtained EDX mapped locations of the as-built, carburized, neutral, and oxidized specimens are presented in Figure 11a–h, respectively. Figure 11a,b illustrates the as-built specimen, revealing the distinct elemental Si cellular network rings, marked separately in Figure 11b. These elemental Si cellular rings are possible due to rapid cooling from the SLM process, where the supersaturated Si gets trapped in the α -Al matrix, and the remaining residual Si gets settled or segregated at the cellular formed boundaries [35]. The elemental bar intensity highlights the low peak of Si as a result of this formed supersaturated solution. In addition, the minute existence of Mg_2Si is also possible at the inside melt pool boundary where Mg reacts with the eutectic Si forming Mg_2Si phases at the sub-cell boundaries [36]. For this reason, the elemental mapping boundaries of Si and Mg are slightly overlapped as depicted and observable in Figure 11b.

Figure 11c,d depicted the surface EDX elemental mapping after the heat exposure to the carburizing flame. The cellular Si network is nearly eradicated after the exposure of heat, as also confirmed by optical microstructures, where the coarsening of the melt pool boundary is exhibited along with the existence of nearly circular discontinuous Si particles. As highlighted in Figure 11d, discontinuous Si elemental mapping is evident with large circular and undissolved Si particle patches. Moreover, the elemental bar intensity highlights the slightly high peak of Mg, which may be caused by the formation of Mg_2Si .

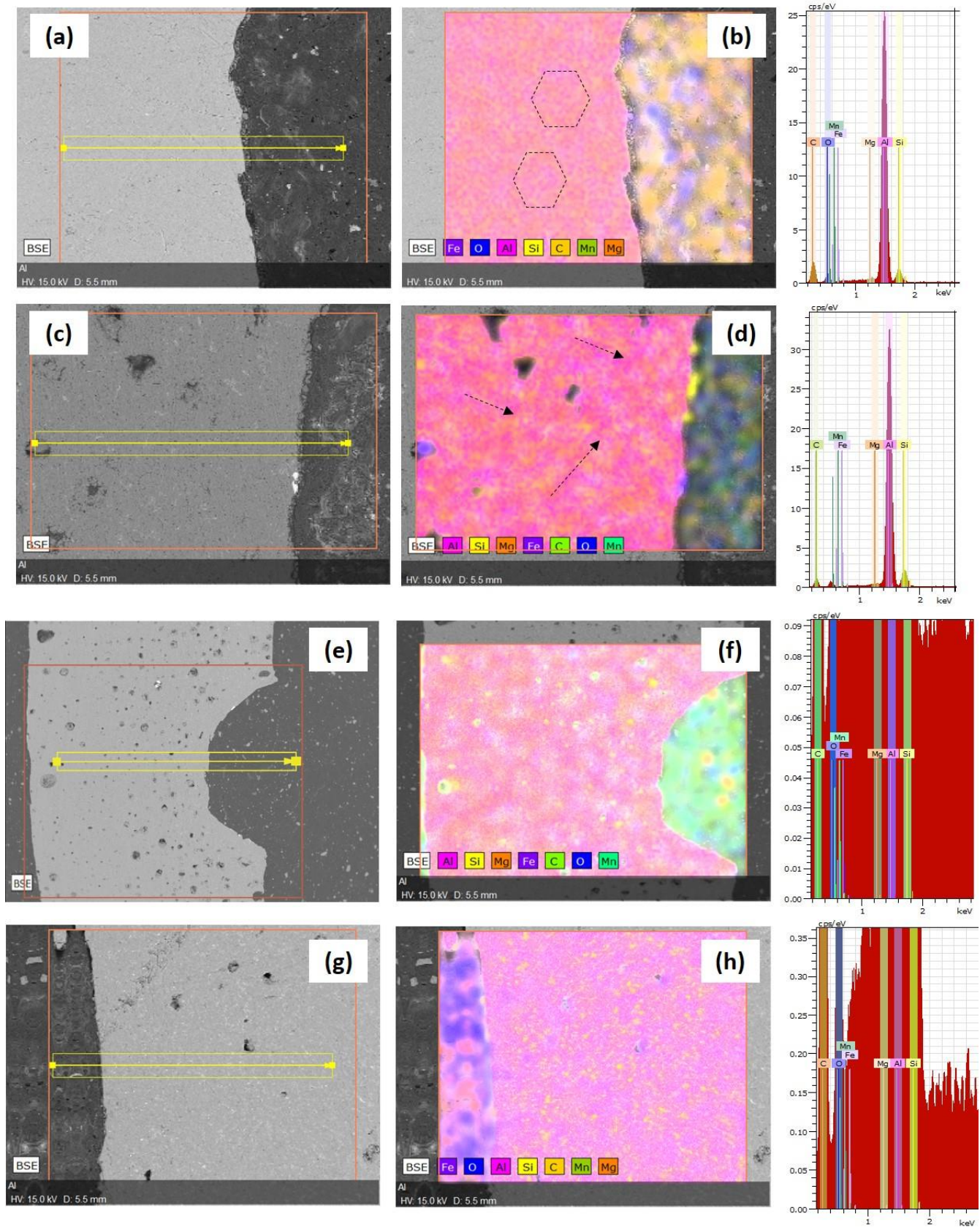


Figure 11. EDX elemental mapping of the cross section of Wear track with different flames; (a,b) as-built condition SLM, (c,d) carburizing flame exposure, (e,f) neutral flame exposure, and (g,h) oxidizing flame exposure.

However, the neutral flame mapping is presented in Figure 11e,f where the Si-rich cellular network is completely broken and transformed into coarse isolated Si particles [37]. The scattered elemental distribution of Si over the selected surface is visible in Figure 11f. The higher intensity elemental peak of Si is visible attributed to the amount of Si rejected from the α -Al matrix to form coarse particles of Si at the expense and dissolution of the eutectic Si-network. This effect caused a declination in the supersaturation of the α -Al matrix due to the precipitation of dissolved Si, which is the ultimate reason for showing higher mass loss values, as provided in Table 2. Furthermore, with the oxidized flame (Figure 11g,h), the Si content underwent complete dissolution, resulting in the elimination of the Si network structure and the formation of coarse Si particles due to the agglomeration and the precipitation from the saturated α -Al matrix [38]. A discontinuous and scattered coarse Si elemental distribution is visible in Figure 11h. The formation of Mg_2Si was also drastically reduced in the oxidized flame, indicating a significant alteration in the elemental composition.

3.4. SEM Analysis of the Worn Surfaces after Heat-Exposure

To better understand the effect of surface remelting through oxyacetylene flames on the wear mechanism of AlSi10Mg, the developed morphologies concerning the wear types on wear tracks are analyzed through SEM images as given in Figures 12–14 for carburizing, neutral, and oxidizing flames, respectively. Figure 12a–c shows the wear track developed for a 24 mm radius while Figure 12d–f is for a 30 mm radius after the exposure from carburizing flame. Before discussing the exact wear mechanism, the width of the abrasion groove for 24 mm is greater than 30 mm as superficially a deep furrow is visible in the middle of Figure 12a. In contrast, a well-confined groove in terms of the shallow furrow is obtained for 30 mm radius as shown in Figure 12d, which caused a dominant decrement in the percentage of mass loss from 3.617% to 3.09% from 24 mm to 30 mm radius as also given in Table 2.

The evaluation of the wear mechanism as a function of carburizing flame against the observed SEM images is illustrated in Figure 12a–f. The obtained wear patterns indicated that adhesive wear is the prevalent wear mechanism for both the wear tracks. However, starting with the generation of an abrasion groove that developed against the interaction of the sliding pin and the SLM-prepared remelted surface; the wearing away of the material is the abrasion that grew in the ellipsoidal shape along the major axis in the same direction of sliding. This ellipsoidal-shaped abrasion groove is highlighted in Figure 12a,d for 24 mm and 30 mm radii and shows extensive plastic deformation. A large amount of adhered material on the side of grooves has existed that buildup significant material [39], which is often characteristic for the cases of pin-on-disc testing. This material buildup and plastic deformation are categorically highlighted in Figure 12a and 12d, and also in the enlarged detail of Section-A in Figures 12b and 12e respectively. This ultimately suggests that the adhesion is the predominant wear mechanism [40] and causes a higher mass loss specifically for the 24 mm radius.

The magnified SEM images shown in Figure 12b,c,e,f revealed no traces of abrasive wear except a limited region highlighted in Figure 12b, which showed the signs of wear debris adjacent to the wear track boundary. In contrast, a minute percentage of delamination existed in Figure 12e,f whereas no significant sign in Figure 12a–c. Furthermore, the sideways examination of the groove revealed the ridges and micro-groove valleys for 24 mm and 30 mm radii highlighted in Figure 12b and 12e that are magnified in Figure 12c and 12f, respectively. It is important to note that the wear testing is executed under an externally applied normal load with a repeated number of cycles that cause extreme deformation where the sliding pin is able to penetrate from the top surface and create an abrasion groove at the center of the track [41]. This pin also pushed the upper edge of the groove and created the sequential ridges valley while traveling circumferentially as highlighted in Figure 12c. The ridges are concentrated centrally seem like microcutting, and reduce gradually as moving towards the trailing edge of the specimen. On the contrary, the

wear track of 30 mm showed micro or sub-groove valley as depicted in Figure 12f, which is a sign of difficulty in the plastic deformation and improved resistance as highlighted in Table 2. The morphology of this magnified region exhibited the absence of coarse deep ploughing as previously observed in Figure 12c, and showed the patches of craters and scratching against the sliding surface as depicted in Figure 12e.

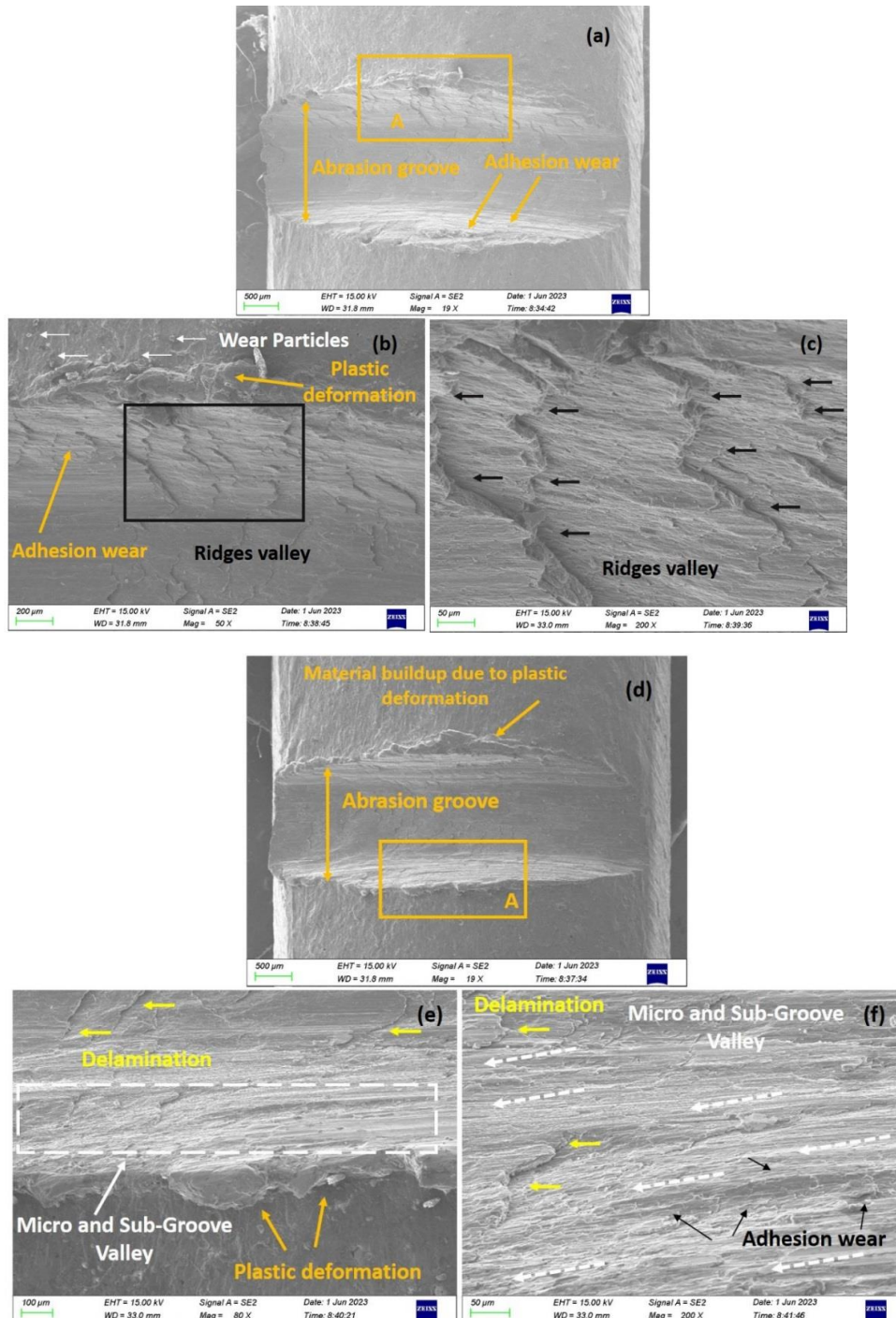


Figure 12. SEM wear track images of carburizing flame; (a–c) belong to 24 mm radius, (a) elliptical abrasion groove against dry sliding, (b) expanded view of the area of track [A], (c) expanded view of the ridges valley; (d–f) belong to 30 mm radius, (d) elliptical abrasion groove against dry sliding, (e) expanded view of the area of track [A], (f) expanded view of the micro and sub-groove valley highlighted in Figure 12e.

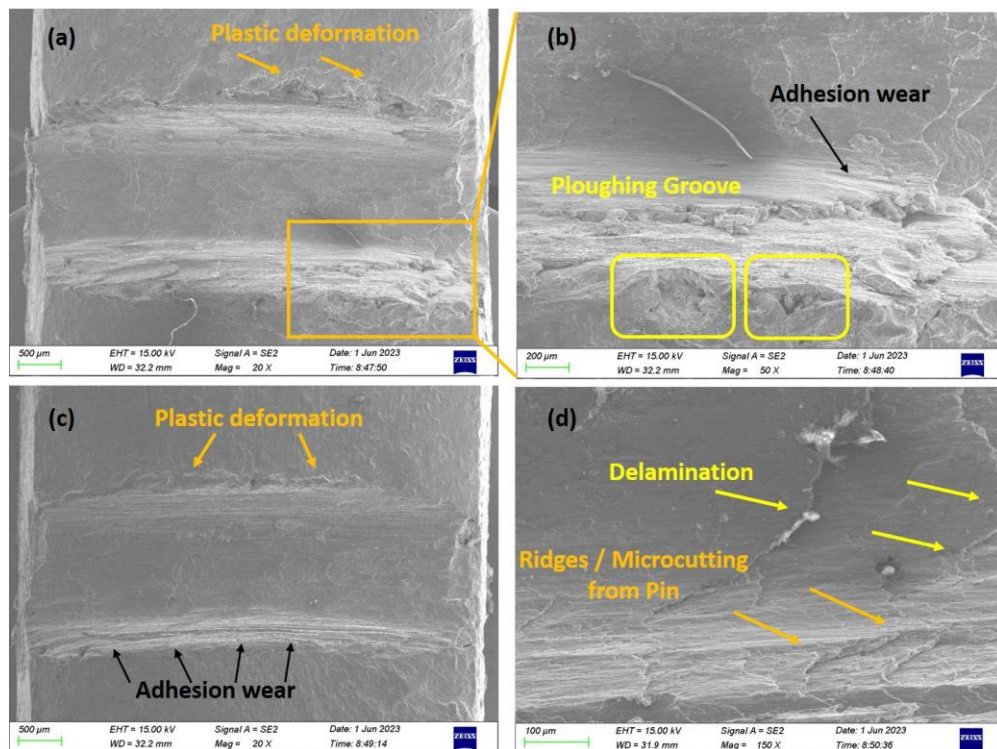


Figure 13. SEM wear track images of neutral flame; (a,b) belong to 24 mm radius, (a) deep ploughing abrasion groove against dry sliding, (b) expanded view of the trailing edge highlighting ploughing and macro ridges; (c,d) belong to 30 mm radius, (c) abrasion groove highlighting adhesion, (d) bottom sideways expanded view.

The representative wear attributes of neural flame surface remelting for both radii are presented in Figure 13a–d. The SEM images in Figure 13a–c showed extended widths of the wear tracks in comparison with the previous case of carburizing. Visually a deep ploughing furrow is obtained for 24 mm radius wear track along with decent plastic flow during sliding, while relatively constrictive but widened furrow plastic deformation is observed for 30 mm radius. Again, the observed morphologies indicated in Figure 13a,c are ubiquitous towards the adhesive wear mechanism. The magnified images of the worn surfaces given in Figure 13b,d also revealed other in-detailed topology features. A considerable portion of Figure 13b is covered with deep adhesive wear characteristics with severe ploughing and macro ridges at the trailing edge. Moreover, the complete ploughing of grains that pulled out from the surface and generated the small pits is also highlighted in Figure 13b. The track shown in Figure 13a represents the creation of higher contact stresses by frictional heat induced during sliding [42] in contrast to a larger radius track of 30 mm. In addition, the magnified image in Figure 13d exhibits the signs of delamination prominently at various places. While the sideways examination of a similar track in Figure 13d, the limited ridges valley also developed by pushing the pin along the edge of the abrasion groove.

The effect of oxidizing flame remelting on the worn surface of the SLM-prepared specimen is shown in Figure 14a–d. The presented wear tracks are developed against the static pin and the rotating fixture carrying the SLM specimens at 24 mm and 30 mm radii given in Figure 14a,b and Figure 14c,d respectively. The soft aluminum surface developed an abrasion groove against oxidizing flames similar to the previous cases of carburizing and neutral flames. The condition of the developed wear tracks for oxidizing flames is not as severe as obtained for the neutral flame, and comparable to carburizing flame but with observable topological features. The widths of the obtained tracks are possibly similar to Figure 12a–f but the extended transferred sideways are obtained for 24 mm and 30 mm radii with a nature of longitudinal rough patches accumulated on either side of abrasion

tracks given in Figures 14a and 14c, respectively. Each sideways is brightly self-illuminated on either side of the groove and is also highlighted in Figure 14a,c.

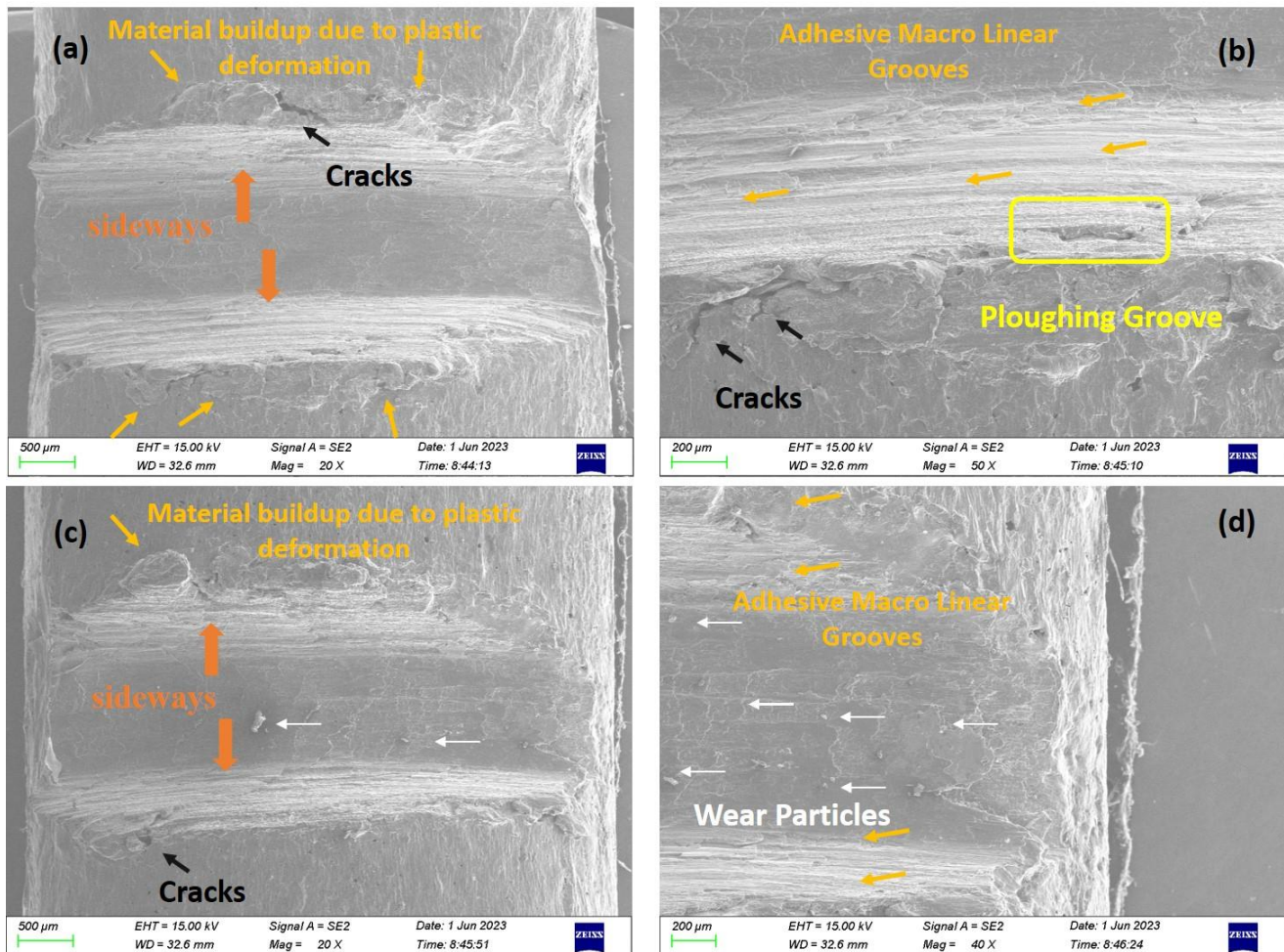


Figure 14. SEM wear track images of oxidizing flame; (a,b) belong to 24 mm radius, (a) abrasion groove at the center, (b) expanded view of bottom sideways; (c,d) belong to 30 mm radius, (c) abrasion groove highlighting both the sideways, (d) expanded view of trailing edge.

The magnified images of both the radii are given in Figure 14b,d, where the considerable portion is based on adhesive wear along with the directional macro linear grooves that were produced due to sliding wear against the reciprocating nature of contact. The typical characteristic behavior of adhesive wear is prevalent due to the nature of two contacting surfaces; where the transfer or loss of mass from a less strengthened surface in the dry non-lubricating condition exhibits. Based on this wear mechanism, categorically the lump of buildup material against the plastic deformation on either side of the wear tracks is represented in Figure 14a,c. Moreover, the high contact stressed wear track of a 24 mm radius also demonstrated the visible fissures of pullout on the eve of opened cracks available at the boundary of grooves, which is highlighted, with black color, in Figure 14a–c. Furthermore, the creation of good passive coating also resists and prolongs the removal of material under the fixed RPM for wear testing, here the generation of a dense aluminum oxide layer due to the condition provided in the oxidizing flame also existed. This layer also acts like a solid lubricant and helps in reducing the coefficient of friction [10], and is further indicative of minor abrasive wear contribution. The presence of pullout and ejected oxide particles from the wear track surface is evident in Figure 14c,d as separately highlighted with white color arrows. As depicted in Table 2, the difference in mass loss for

oxidizing is almost comparable to carburizing and lesser than the neutral flames, which is possible due to the generation of oxide flame that contributes as a passive blocking while the bright extended sideways could be due the slight contribution of abrasive wear along with adhesion.

4. Conclusions

The characteristics, features, and behavior of developed wear tracks of the SLM fabricated AlSi10Mg alloy specimens have been studied considering the pin-on-disc wear testing. The following conclusions are drawn after the heat exposure from different flames oxyacetylene gas welding:

1. The wear testing of the as-built SLM specimen exhibits the lowest mass loss of all of the surface exposure specimens through different flames. Moreover, the smallest block of mass loss also belongs to the as-built SLM condition with almost identical values at 24 mm and 30 mm radii, respectively.
2. The wear behavior of SLM AlSi10Mg specimens exhibits nuanced responses to distinct heat exposures. Notably, the neutral flame produces the highest mass losses at both the 24 mm and 30 mm radii. However, carburizing and oxidizing flames yield lower mass losses in contrast to the neutral flame but higher values than the as-built condition specimens. These findings underscore the influence of heat exposure on wear characteristics, offering insights for tailored applications.
3. By comparing the macro morphology of the developed wear tracks; the width of the built-in SLM specimens is sharp and consistent throughout the length though an elliptical impression; which is more widened at the center for the cases of heat exposure specimens. Even, the signs of extreme deformation with a bit more deeper and larger in width tracks for all of the flames, including carburizing, neutral, and oxidizing, are available along with badly affected dimensional stability.
4. The observed wear pattern for all types of flames indicated that adhesive wear is the prevalent wear mechanism for both the wear tracks. A large amount of adhered amount exhibited on both sideways due to plastic deformation along with the ridges valley and micro-groove valley at 24 mm and 30 mm radii for carburizing flame are the highlighted features. However, severe ploughing, macro ridges, ploughing of grains, and delamination are the wear mechanism features of the neutral flame. SEM analysis revealed extended sideways carrying rough patches of macro linear groove in the direction of sliding for the oxidizing flame.

Author Contributions: Conceptualization, M.A., M.M. and N.A.; methodology, M.A., M.M., R.K. and J.D.; validation, M.M., M.S. and A.M.; writing—original draft preparation, M.A., M.M., M.A.K., R.K. and A.K.S.; writing—review and editing, M.A., M.M., N.A., M.S., R.K., J.D. and A.M.; visualization, M.M.; supervision, M.A. All authors have read and agreed to the published version of the manuscript.

Funding: The work was supported and funded by the Deanship of Scientific Research at Imam Mohammad Ibn Saud Islamic University (IMSIU) (grant number IMSIU-RG23104).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Duran, M.M.; Moro, G.; Zhang, Y.; Islam, A. 3D printing of silicone and polyurethane elastomers for medical device application: A review. *Adv. Ind. Manuf. Eng.* **2023**, *7*, 100125. [CrossRef]
2. Pramanik, J.; Brahma, B.; Pradhan, S.; Senapati, M.R.; Samal, A.K.; Pani, S.K. 3D printing application in biomedical—A review. *Mater. Today Proc.* **2023**, in press. [CrossRef]

3. Ajibola, O.O.; Adebayo, A.O.; Borisade, S.G.; Owa, A.F.; Ige, O.O. Characterisation and tribological behaviour of zinc-aluminium (Zn-Al) alloy under dry sliding reciprocating ball on disk tribometer. *Mater. Today Proc.* **2021**, *38*, 1140–1146. [CrossRef]
4. Haque, M.S.; Rokon, S.N.; Kaiser, M.S. Strengthening and softening behavior of non-heat-treatable aluminum alloys subject to deformation and annealing treatment. *Mater. Today Proc.* **2023**, *82*, 151–157. [CrossRef]
5. Wang, L.F.; Sun, J.; Yu, X.L.; Shi, Y.; Zhu, X.G.; Cheng, L.Y.; Liang, H.H.; Yan, B.; Guo, L.J. Enhancement in mechanical properties of selectively laser-melted AlSi10Mg aluminum alloys by T6-like heat treatment. *Mater. Sci. Eng. A* **2018**, *734*, 299–310. [CrossRef]
6. Wang, J.; Zhu, R.; Liu, Y.; Zhang, L. Understanding melt pool characteristics in laser powder bed fusion: An overview of single-and multi-track melt pools for process optimization. *Adv. Powder Mater.* **2023**, *2*, 100137. [CrossRef]
7. Read, N.; Wang, W.; Essa, K.; Attallah, M.M. Selective laser melting of AlSi10Mg alloy: Process optimisation and mechanical properties development. *Mater. Des. (1980–2015)* **2015**, *65*, 417–424.
8. Dinaharan, I.; Gladston, J.A.K.; Selvam, J.D.R.; Jen, T.C. Influence of particle content and temperature on dry sliding wear behavior of rice husk ash reinforced AA6061 slurry cast aluminum matrix composites. *Tribol. Int.* **2023**, *183*, 108406. [CrossRef]
9. Akram, S.; Babutskyi, A.; Chrysanthou, A.; Montalvão, D.; Whiting, M.J.; Pizurova, N. Improvement of the wear resistance of nickel-aluminium bronze and 2014-T6 aluminium alloy by application of alternating magnetic field treatment. *Wear* **2021**, *480*, 203940. [CrossRef]
10. Bukhari, S.M.A.; Husnain, N.; Siddiqui, F.A.; Anwar, M.T.; Khosa, A.A.; Imran, M.; Qureshi, T.H.; Ahmad, R. Effect of laser surface remelting on Microstructure, mechanical properties and tribological properties of metals and alloys: A review. *Opt. Laser Technol.* **2023**, *165*, 109588. [CrossRef]
11. Li, F.; Zhang, T.; Chen, C.; Liu, X.; Zhou, K. Constructing an ultrahard layer on the surface of Ti₃AlC₂ ceramics via electron beam surface remelting. *Mater. Lett.* **2021**, *301*, 130315. [CrossRef]
12. Ciubotariu, C.R.; Frunzăverde, D.; Mărginean, G.; Șerban, V.A.; Birdeanu, A.V. Optimization of the laser remelting process for HVOF-sprayed Stellite 6 wear resistant coatings. *Opt. Laser Technol.* **2016**, *77*, 98–103. [CrossRef]
13. Wu, Z.; Wang, W.; Li, X.; Yan, M.; Li, Y. Microstructure and mechanical properties of Ti-6Al-4V prepared by nickel preplating and electron beam surface remelting. *J. Mater. Process. Technol.* **2019**, *271*, 420–428. [CrossRef]
14. Li, Y.; Song, P.; Wang, W.; Lei, M.; Li, X. Microstructure and wear resistance of a Ni-WC composite coating on titanium grade 2 obtained by electroplating and electron beam remelting. *Mater. Charact.* **2020**, *170*, 110674. [CrossRef]
15. Chari, V.S.; Jhavar, S. Surface properties modification of SS316L using plasma beam remelting (PBR) and its applications in additive manufacturing. *Trans. Indian Natl. Acad. Eng.* **2021**, *6*, 1017–1025. [CrossRef]
16. Pan, W.X.; Meng, X.; Li, G.; Fei, Q.X.; Wu, C.K. Feasibility of laminar plasma-jet hardening of cast iron surface. *Surf. Coat. Technol.* **2005**, *197*, 345–350. [CrossRef]
17. Clark, D.A.; Johnson, W.S. Temperature effects on fatigue performance of cold expanded holes in 7050-T7451 aluminum alloy. *Int. J. Fatigue* **2003**, *25*, 159–165. [CrossRef]
18. Lacarac, V.D.; Smith, D.J.; Pavier, M.J. The effect of cold expansion on fatigue crack growth from open holes at room and high temperature. *Int. J. Fatigue* **2001**, *23*, 161–170. [CrossRef]
19. Jabra, J.; Romios, M.; Lai, J.; Lee, E.; Setiawan, M.; Ogren, J.R.; Clark, R.; Oppenheim, T.; Es-Said, O.S.; Lee, E.W.; et al. The effect of thermal exposure on the mechanical properties of 2099-T6 die forgings, 2099-T83 extrusions, 7075-T7651 plate, 7085-T7452 die forgings, 7085-T7651 plate, and 2397-T87 plate aluminum alloys. *J. Mater. Eng. Perform.* **2006**, *15*, 601–607. [CrossRef]
20. Ceschini, L.; Morri, A.; Morri, A.; Rotundo, F.; Toschi, S. Heat treatment response and influence of overaging on mechanical properties of C355 cast aluminum alloy. *Metall. Ital.* **2014**, *5*, 11–17.
21. Zhou, L.; Mehta, A.; Schulz, E.; McWilliams, B.; Cho, K.; Sohn, Y. Microstructure, precipitates and hardness of selective-ly laser melted AlSi10Mg alloy before and after heat treatment. *Mater. Charact.* **2018**, *143*, 5–17. [CrossRef]
22. Alghamdi, F.; Song, X.; Hadadzadeh, A.; Shalchi-Amirkhiz, B.; Mohammadi, M.; Haghshenas, M. Post heat treatment of additive manufactured AlSi10Mg: On silicon morphology, texture and small-scale properties. *Mater. Sci. Eng. A* **2020**, *783*, 139296. [CrossRef]
23. Tonolini, P.; Montesano, L.; Tocci, M.; Pola, A.; Gelfi, M. Wear behavior of AlSi10Mg alloy produced by laser-based powder bed fusion and gravity casting. *Adv. Eng. Mater.* **2021**, *23*, 2100147. [CrossRef]
24. Park, T.H.; Baek, M.S.; Sohn, Y.; Lee, K.A. Effect of post-heat treatment on the wear properties of AlSi10Mg alloy manufactured by selective laser melting. *Arch. Metall. Mater.* **2020**, *65*, 1073–1080. [CrossRef]
25. Zhang, Y.; Majeed, A.; Muzamil, M.; Lv, J.; Peng, T.; Patel, V. Investigation for macro mechanical behavior explicitly for thin-walled parts of AlSi10Mg alloy using selective laser melting technique. *J. Manuf. Process.* **2021**, *66*, 269–280. [CrossRef]
26. Majeed, A.; Muzamil, M.; Lv, J.; Liu, B.; Ahmad, F. Heat treatment influences densification and porosity of AlSi10Mg alloy thin-walled parts manufactured by selective laser melting technique. *J. Braz. Soc. Mech. Sci. Eng.* **2019**, *41*, 267. [CrossRef]
27. Majeed, A.; Muzamil, M.; Khan, M.A.; Malik, E.H.; Huzaifa, M.; Lv, J.; Dar, N.U. Comprehensive Mechanical Behavior of Thin-Walled Additively-Manufactured Parts of AlSi10Mg by SLM in As-Built, Post-Solution, and Aging Treatment Conditions. *JOM* **2023**, *75*, 3067–3082. [CrossRef]
28. ASTM G99-05; Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus. ASTM International: West Conshohocken, PA, USA, 2006; Volume 5, pp. 1–6.
29. Hammond, V.; Schuch, M.; Bleckmann, M. The influence of a process interruption on tensile properties of AlSi10Mg samples produced by selective laser melting. *Rapid Prototyp. J.* **2019**, *25*, 1442–1452. [CrossRef]

30. Maconachie, T.; Leary, M.; Zhang, J.; Medvedev, A.; Sarker, A.; Ruan, D.; Lu, G.; Faruque, O.; Brandt, M. Effect of build orientation on the quasi-static and dynamic response of SLM AlSi10Mg. *Mater. Sci. Eng. A* **2020**, *788*, 139445. [CrossRef]
31. Galy, C.; Le Guen, E.; Lacoste, E.; Arvieu, C. Main defects observed in aluminum alloy parts produced by SLM: From causes to consequences. *Addit. Manuf.* **2018**, *22*, 165–175. [CrossRef]
32. Tabatabaei, N.; Zarei-Hanzaki, A.; Moshiri, A.; Abedi, H.R. The effect of heat treatment on the room and high temperature mechanical properties of AlSi10Mg alloy fabricated by selective laser melting. *J. Mater. Res. Technol.* **2023**, *23*, 6039–6053. [CrossRef]
33. Strauß, L.; Lübbecke, S.; Löwisch, G. Optimizing the Solution Annealing of Additively Manufactured AlSi10Mg. *HTM J. Heat Treat. Mater.* **2023**, *78*, 300–316. [CrossRef]
34. Li, W.; Li, S.; Liu, J.; Zhang, A.; Zhou, Y.; Wei, Q.; Yan, C.; Shi, Y. Effect of heat treatment on AlSi10Mg alloy fabricated by selective laser melting: Microstructure evolution, mechanical properties and fracture mechanism. *Mater. Sci. Eng. A* **2016**, *663*, 116–125. [CrossRef]
35. Wei, P.; Wei, Z.Y.; Chen, Z.; Du, J.; He, Y.Y.; Li, J.F.; Zhou, Y.T. The AlSi10Mg samples produced by selective laser melting: Single track, densification, microstructure and mechanical behavior. *Appl. Surf. Sci.* **2017**, *408*, 38–50. [CrossRef]
36. Fousová, M.; Dvorský, D.; Michalcová, A.; Vojtěch, D. Changes in the microstructure and mechanical properties of additively manufactured AlSi10Mg alloy after exposure to elevated temperatures. *Mater. Charact.* **2018**, *137*, 119–126. [CrossRef]
37. Wei, P.; Chen, Z.; Zhang, S.; Fang, X.; Lu, B.; Zhang, L.; Wei, Z. Effect of T6 heat treatment on the surface tribological and corrosion properties of AlSi10Mg samples produced by selective laser melting. *Mater. Charact.* **2021**, *171*, 110769. [CrossRef]
38. Kempf, A.; Hilgenberg, K. Influence of heat treatments on AlSi10Mg specimens manufactured with different laser powder bed fusion machines. *Mater. Sci. Eng. A* **2021**, *818*, 141371. [CrossRef]
39. McConnell, J.E.; Segall, A.E.; Eden, T.J. The Dry Sliding Behavior of Al₂O₃ Transformed, Hypereutectic, 2xxx, and 7xxx, Aluminum Alloys Under Simulated Wire–Rope Induced Wear. *Tribol. Trans.* **2006**, *49*, 563–573. [CrossRef]
40. D’Amato, C.; Buhagiar, J.; Betts, J.C. Tribological characteristics of an A356 aluminium alloy laser surface alloyed with nickel and Ni–Ti–C. *Appl. Surf. Sci.* **2014**, *313*, 720–729. [CrossRef]
41. Rajamure, R.S.; Vora, H.D.; Gupta, N.; Karewar, S.; Srinivasan, S.G.; Dahotre, N.B. Laser surface alloying of molybdenum on aluminum for enhanced wear resistance. *Surf. Coat. Technol.* **2014**, *258*, 337–342. [CrossRef]
42. Zhang, Y.; Lei, G.; Luo, K.; Chen, P.; Kong, C.; Yu, H. Tribological behavior of high-entropy alloy particle reinforced aluminum matrix composites and their key impacting factors. *Tribol. Int.* **2022**, *175*, 107868. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Microstructure and Impact Toughness of Laser-Arc Hybrid Welded Joint of Medium-Thick TC4 Titanium Alloy

Peng Luo ^{1,2}, Wanxi Feng ², Gang Zu ³, Linyin Luo ² and Jun Xiao ^{1,*}

¹ College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), Nanjing 210016, China; luopeng_1983@163.com

² Avic General Huanan Aircraft Industry Co., Ltd., Zhuhai 519040, China

³ Tang Shan Iron and Steel Group Co., Ltd., Tangshan 063000, China

* Correspondence: j.xiao@nuaa.edu.cn

Abstract: This study delves into the impact toughness of medium-thick (12 mm thick) titanium alloy joints crafted through a multi-layer, multi-pass welding technique that blends laser-arc (MIG) hybrid welding technology. Microstructural scrutiny, employing optical microscopy, SEM and TEM, unveils a consistent composition across weld passes, with prevailing α/α' phases interspersed with some β phase, resulting in basket-weave structures primarily dominated by acicular α' martensite. However, upper regions exhibit Widmanstatten microstructures, potentially undermining joint toughness. Hardness testing indicates higher values in cosmetic layers (~420 HV) compared to backing layers and bending tests manifest superior toughness in lower joint regions, attributed to smaller grain sizes induced by repetitive welding thermal cycles. Impact toughness assessment unveils diminished values in the weld metal (WM) compared to the heat-affected zone (HAZ) and base material (BM), amounting to 91.3% of the base metal's absorption energy. This decrement is ascribed to heightened porosity in upper regions and variations in grain size and phase composition due to multi-layer, multi-pass welding. Microstructural analysis proximal to failure sites suggests one mechanism wherein crack propagation is impeded by the β phase at acute crack angles. In essence, this study not only underscores the practicality of laser-MIG hybrid welding for medium-thick TC4 alloy plates but also underscores the reliability of joint mechanical properties.

Keywords: titanium welding; laser-MIG hybrid welding; microstructural analysis; impact toughness; medium-thick welded joint

1. Introduction

Titanium alloys have gained significant attention in various industries due to their exceptional mechanical properties, including a high strength-to-weight ratio, excellent corrosion resistance, and biocompatibility [1–3]. These properties make titanium alloys ideal for critical applications such as aerospace components, medical implants, and sporting equipment. Especially in the actual industrial generation and manufacturing, such as shipbuilding, aviation, and other fields, the medium-thick cross-section TC4 titanium alloy is being used more and more widely [4,5]. For this reason, in the manufacturing process of some large complex structures, TC4 alloys with medium-thick sections need to be welded for practical use. However, welding titanium alloys presents challenges due to their high reactivity with atmospheric gases and susceptibility to welding metal (WM) and heat-affected zone (HAZ) embrittlement [1,6,7]. Traditional metal inert gas (MIG) arc welding techniques often result in limited weld penetration depth, narrow weld width, and the formation of weld defects, such as porosity and cracking, particularly in medium-thick or thick sections of titanium alloys [8,9].

To overcome these challenges and enhance the mechanical properties of welded joints, researchers have explored various welding techniques, including gas tungsten arc

welding (GTAW), plasma arc welding (PAW), electron beam welding (EBW), and laser beam welding (LBW) [1,10–13]. Among these techniques, laser beam welding has emerged as a promising method for joining titanium alloys due to its high energy density, minimal heat input, and precise control over the welding process [14,15]. Furthermore, several researchers have explored the integration of artificial intelligence algorithms and alternative strategies to enhance the monitoring and adjustment of the welding process [16,17]; yet, challenges persist in the welding of titanium alloys, specifically concerning these process issues. To mitigate these constraints, innovative hybrid welding techniques, merging laser welding with supplementary welding methods, have been introduced. Notably, the laser-MIG hybrid welding technique has emerged as a significant advancement, offering enhanced penetration depth, increased weld width, and improved modulation of weld microstructure [18]. In addition, the use of arc bridging ability can achieve a synergistic effect of “1 + 1 > 2”. Laser-arc hybrid welding only needs a few layers of thick plate, which significantly improves the efficiency compared with traditional MIG welding. By combining the advantages of both laser and MIG welding processes, laser-MIG hybrid welding offers a potential solution to overcome the challenges associated with traditional laser welding techniques and produce high-quality welded joints in titanium alloys [7,18].

In recent years, there has been a growing interest in utilizing laser-MIG hybrid welding for titanium alloys. Several studies have explored the microstructural characteristics, mechanical properties, and optimization of process parameters in laser-MIG hybrid welded titanium alloy joints [1,7]. For instance, Su et al. [19] investigated the impact of heat input (E) on the microstructure and tensile strength of 15 mm thick TC4 alloy plate joints fabricated through laser-MIG hybrid welding. They observed that increasing heat input prolonged the residence time of α' martensite in the high-temperature phase transformation region, leading to thicker α' phases and increased β thickness, along with the presence of dislocations in α' . Moreover, higher heat input resulted in reduced tensile strength. Brandizzi et al. [20] examined the laser-MIG hybrid welding process for 3 mm thick TC4 alloy and identified the optimal welding parameters by analyzing the cross-section morphology of the weld. Compared to laser welding, laser-MIG hybrid welding achieved well-formed welds with lower heat input, mitigating the risk of weld collapse observed in laser welding. Chen et al. [21] explored the influence of defocusing amount on porosity defects in laser-MIG welding of titanium alloy. Their welding simulation revealed that welding pores primarily resulted from keyhole collapse. Increasing the defocusing amount reduced laser energy density, shallowed the keyhole depth, and weakened the eddy current of the molten pool metal, suppressing keyhole-type pore defects. Fan et al. [22] conducted single-pass welding tests on 5 mm thick TC4 alloy plates using laser-TIG hybrid welding. Their findings demonstrated that increasing welding current improved the tensile strength of the welded joint. Yang et al. [23] performed butt welding tests on 6 mm thick titanium alloy plates by adjusting process parameters in laser-arc hybrid welding. They found that laser-arc hybrid welding allowed for higher welding speed and lower heat input compared to traditional arc welding. Additionally, the laser-induced concentration of arc energy improved microhardness by refining grain structures in the WM and HAZ. Li et al. [14] compared laser-MIG hybrid welding and laser welding joints of 4 mm Ti-Al-Zr-Fe alloy, revealing that the former method produced joints with higher ductility. Optimal parameter settings ensured defect-free welds with no surface oxidation, pores, cracks, or insufficient penetration. Laser-MIG hybrid welding also demonstrated significant advantages in joining dissimilar titanium alloy-gold alloys. Gao et al. [24] utilized laser-arc hybrid welding to connect dissimilar Ti6Al4V titanium alloy with AISI316 stainless steel, investigating the effects of welding parameters on weld bead shape, microstructure, mechanical properties, and fracture behavior.

However, scholars mostly focus on the study of thin titanium alloys. For large thick plates, some scholars adopt narrow-gap laser-arc hybrid welding and beam shaping to improve the weld formation and performance [25,26], but there are still few studies on the laser-MIG hybrid welding parameters and their effects on the joint performance of TC4

medium-thick cross-section alloy, so further studies are needed [9]. In this study, the feasibility and mechanical performance of laser-MIG hybrid welding for joining medium-thick titanium alloy plates is investigated. Specifically, this study focuses on the microstructural characteristics, hardness distribution, and impact toughness of the welded joints fabricated using a multi-layer, multi-pass laser-MIG hybrid welding technique. By comprehensively characterizing the microstructure and mechanical properties of the welded joints, this research aims to provide insights into the optimization of laser-MIG hybrid welding parameters and the enhancement of joint performance in titanium alloy applications.

2. Experimental Details

2.1. Material

The base material (BM) used is TC4, also known as Ti-6Al-4V, which is one of the $\alpha + \beta$ titanium alloys. This material, with a thickness of 12 mm, was fabricated through the hot rolling process by Baoti Co. Ltd., Baoji, China. The dimensions of the test specimens are $150 \times 100 \times 12$ mm. TC4 wire with a diameter of 1.2 mm is used for welding, with its composition detailed in Table 1. The mechanical properties of both the BM and the wire are presented in Table 2.

Table 1. Element of TC4 alloy.

Element	Al	V	Fe	C	N	H	O	Ti
TC4 alloy	6.2	4.05	0.13	0.016	0.007	0.0008	0.131	Bal.
TC4 welding wire	5.96	4.01	0.10	0.012	0.007	0.0001	0.126	Bal.

Table 2. Physical properties of TC4 alloy at 20 °C.

	Yield Stress $R_{p0.2}$ (MPa)	Ultimate Stress R_m (MPa)	Elongation A (%)
TC4 alloy	922	986	13.8
TC4 welding wire	895	993	15.5

2.2. Laser-Arc Hybrid Welding System

The primary equipment utilized during the welding process is depicted in Figure 1. The laser-arc hybrid welding system, as shown in Figure 1a, consists of a FANUC robot (FANUC, Oshino-mura, Japan), an IPG Photonics YLS-10000 laser (IPG, New York, NY, USA) with a 10 kW maximum power, 0.6 mm spot diameter, 300 mm focal length, and a Fronius TPS4000 arc welder (Fronius International GmbH, Pettenbach, Austria). As illustrated in Figure 1b, the laser-MIG hybrid welding process for medium-thickness plates adopts a leading laser and trailing arc configuration, with the laser beam angled at approximately 85° horizontally and 60° between the laser and the arc. The distance between the laser beam and the arc is approximately 2.5 mm. A shroud containing 99.999% pure argon gas is employed during welding to prevent adverse reactions between titanium alloy and atmospheric elements at high temperatures, ensuring weld quality. Additionally, high-purity argon serves as the backing gas for the weld.

The dimensions of the laser-MIG hybrid welded titanium alloy specimens are illustrated in Figure 2a, featuring a zero gap, 5 mm blunt edge, and double-sided bevel angle of 30°. Figure 2b depicts the welding sequence and pass distribution, comprising the 1st#, 2nd#, and 3rd# passes corresponding to the back weld, packing weld, and cosmetic weld layers, respectively. The welding process parameters for the weld joint, determined through preliminary testing and adjustments, are detailed in Table 3.

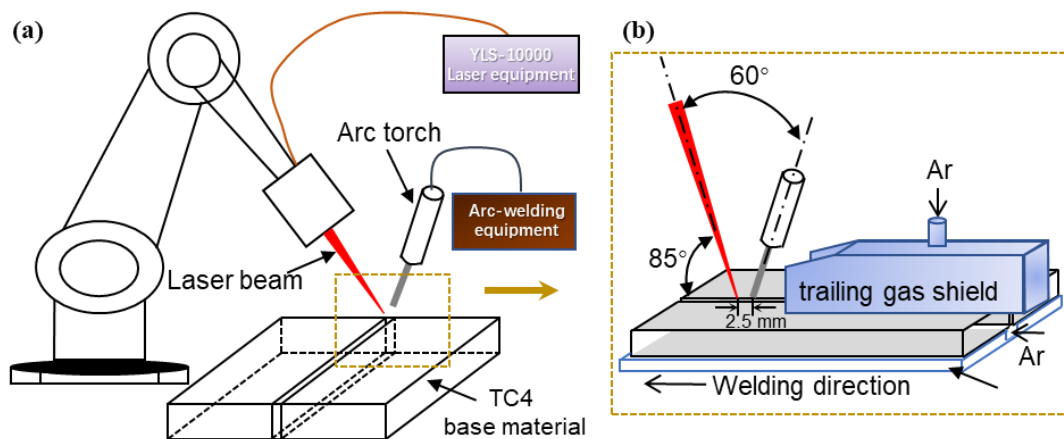


Figure 1. (a) Schematic diagram of the laser-arc hybrid welding process; (b) Schematic diagram of TC4 plate butt welding.

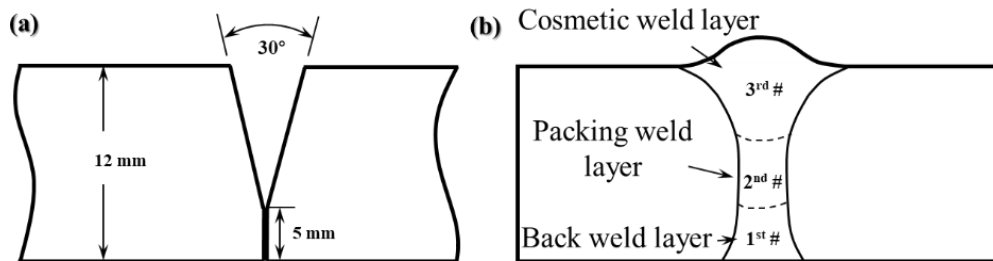


Figure 2. (a) Schematic diagram size of laser-MIG hybrid TC4 joint; (b) schematic diagram of welding sequence and distribution of welding passes.

Table 3. Parameters of TC4 alloy laser-MIG hybrid welding process.

Number	Welding Pass	Laser Power (kW)	Welding Speed (mm/s)	Wire Feed Rate (m/min)
1st #	Back weld layer	4500	10	10
2nd #	Packing weld layer	4000	10	9
3rd #	Cosmetic weld layer	6000	16	15

2.3. Microstructure, Hardness, Bending and Impact Properties Tests

The overview diagram of the sampling position of weld properties is shown in Figure 3. Each pair of plates should be tested in the middle of the weld as far as possible.

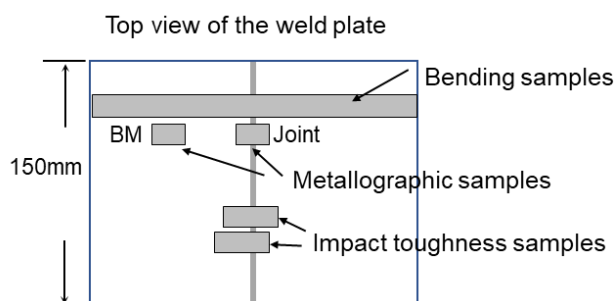


Figure 3. Schematic diagram of sampling position.

2.3.1. Microstructure Characterization

To analyze the characteristics and properties of the laser-arc hybrid welded titanium alloy joint, the microstructure of the joint and BM samples requires characterization and analysis. Initially, metallographic samples are obtained by wire cutting perpendicular to the

weld seam, followed by grinding with sandpaper, polishing, and etching in Keller's reagent ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O} = 1:3:16$) for approximately 25~30 s. Subsequently, the microstructure of the joint is observed and analyzed using a Zeiss optical microscope (OM, ZEISS temi, Shanghai, China), a scanning electron microscope (SEM, ZEISS Gemini 300, Oberkochen, Germany), and a transmission electron microscope (TEM, FEI Tecnai F20, Thermo Fisher Scientific, Waltham, MA, USA). Among them, the TEM samples were prepared using an EM Precision Cutter (Model EM-PC300, Shanghai, China) to slice ultrathin sections. These sections were then thinned to electron transparency using an ion milling machine (Model IM4000, Shanghai, China). The final thickness was monitored under a light microscope to ensure optimal electron transmittance for TEM analysis.

2.3.2. XRD Test

The XRD analysis was conducted using a Panalytical Empyrean diffractometer equipped with a $\text{Cu K}\alpha$ radiation source. The scanning speed was set to $1^\circ/\text{min}$, covering a 2θ range from 30° to 80° . This setup ensures comprehensive coverage and detailed data collection for accurate phase identification and lattice parameter calculations.

2.3.3. Hardness Test

The schematic diagram of hardness testing positions is shown in Figure 4, utilizing an HVS-20 Vickers microhardness tester, with tests conducted in accordance with GB/T 4340.1 [27]. During testing, the ambient temperature is maintained at approximately 20°C , with a load of 1 kg applied for 15 s and a step size of approximately 0.5 mm for each indentation.

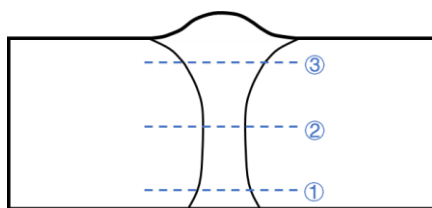


Figure 4. Schematic representation of the position of hardness tests.

2.3.4. Bending Test

Bend testing, a common method for assessing mechanical properties, is conducted to evaluate the plasticity and bonding strength between the weld and the BM, with tests carried out in accordance with GB/T 2653 standards [28]. Rectangular bend specimens measuring $200 \times 20 \times 10$ mm are cut from the test plates, and the specimens are fixed during testing. The three-point bending apparatus, with a bending core diameter of approximately 40 mm and capable of bending angles up to 180° , is used to apply a continuous force at the midpoint between the supports until the specimen bends to the specified angle or exhibits visible cracking. The same parameter should be tested at least 3 times, and the corresponding data should be processed.

2.3.5. Impact Toughness Test

The impact toughness testing equipment used is the PTM220 impact tester, with tests performed at least 3 times once a weld layer in accordance with GB/T 2650 standards [29]. Figure 5 illustrates the sampling scheme for impact test specimens of the titanium alloy welded joint, with several specimens taken along a plane perpendicular to the weld direction from both the HAZ and WM. Figure 5b provides a schematic diagram of the specimen dimensions, with the impact fracture surfaces observed using an SEM (ZEISS Gemini 300, Oberkochen, Germany).

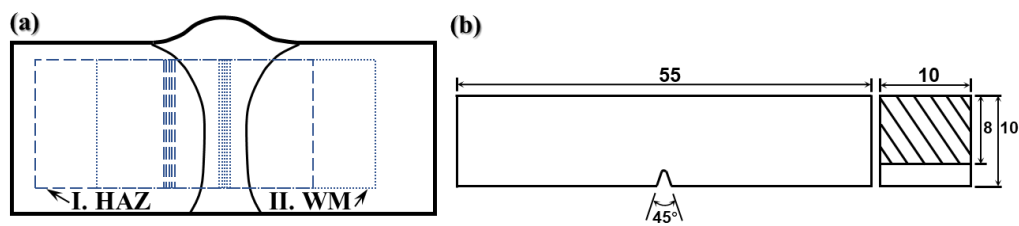


Figure 5. (a) Diagram of positions of impact toughness test specimens; (b) size of specimens (mm).

3. Results and Discussion

3.1. Microstructure Analysis

The microstructure of the BM is illustrated in Figure 6, and it is observed longitudinally from the rolling direction perpendicular to the plate, where the lighter areas represent equiaxed primary α phases, and the darker areas depict lamellar $\alpha + \beta$ phases distributed along the edges of the α phase, with an average grain size of 5 μm .

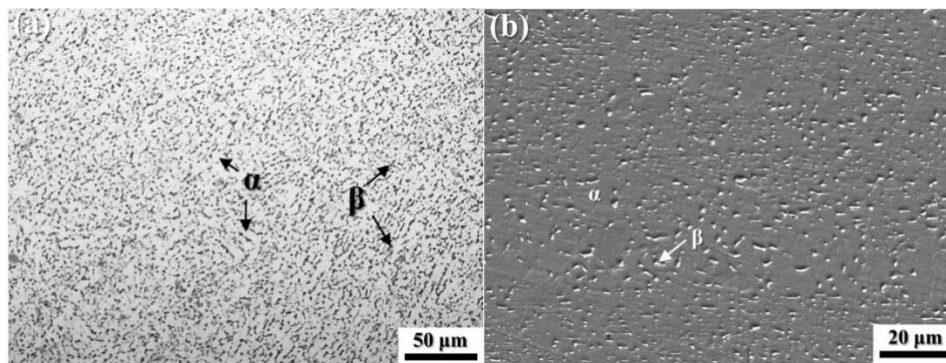


Figure 6. Microstructure of TC4 base metal by: (a) OM; (b) SEM.

Figure 7a displays the metallographic cross-section of the titanium alloy laser-MIG hybrid welded joint, where the upper and lower surfaces are ground to approximately “10 mm” thickness. The WM and HAZ exhibit an overall V-shaped nail-like characteristic, with the filler layer in the middle occupying a smaller area distribution proportion. Moreover, the grain size of the weld bead in the 3rd# layer is noticeably larger than that at the bottom (1st# layer). Within the WM, there are a few equiaxed grains, and numerous columnar grains exist on both sides of the weld, with these columnar grains nucleating at the interface between the BM and the weld and growing toward the center of the weld. During the solidification process of the molten pool, the temperature at the center of the weld is higher than at the sides, causing the grains to grow along the temperature gradient and in the direction of columnar grain growth. As the columnar grains grow, the solid-liquid interface moves toward the center of the weld, increasing the undercooling. Meanwhile, the temperature at the center of the weld decreases over time, inhibiting the growth of existing grains and promoting the formation of new grains, ultimately leading to the formation of uniformly sized equiaxed grains [27]. In Figure 7b, the macroscopic morphology of the root and cosmetic layer weld beads on both the upper and lower surfaces under these parameter conditions is presented. The weld bead surfaces appear silver-white without any oxidation phenomenon, and there is minimal spatter on the weld bead surface, indicating overall good formability.

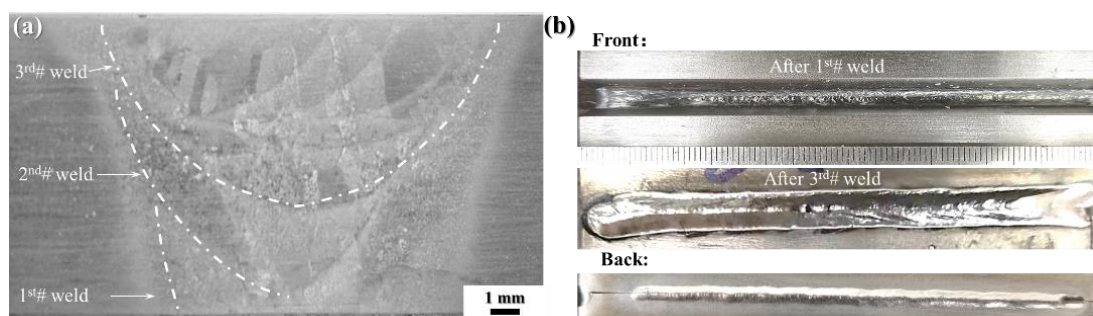


Figure 7. (a) The microstructure distribution of the welded joint; (b) Macroscopic morphology of the weld.

Figure 8 depicts the microstructure and distribution of the weld bead in the 3rd# cosmetic layer of the joint at low magnification (OM) and high magnification (SEM) under a microscope. In Figure 8a, the grain size within the joint ranges from 200 to 600 μm , with numerous α' martensite needle-like structures distributed within the β primary grain boundaries. Figure 8b illustrates the approximately vertical distribution of α' martensite needle-like structures, forming a basket-weave microstructure. This is attributed to the rapid cooling during the welding process, leading to the transformation of the β phase into α' . Due to the high nucleation rate of α' in different orientations, the size of α' clusters decreases, and the α' needles widen and shorten within the original columnar grains. The α' martensite nucleates and grows within the original columnar grains, intertwining with each other, forming needle-like martensite with a certain orientation relationship, and terminating upon encountering grain boundaries.

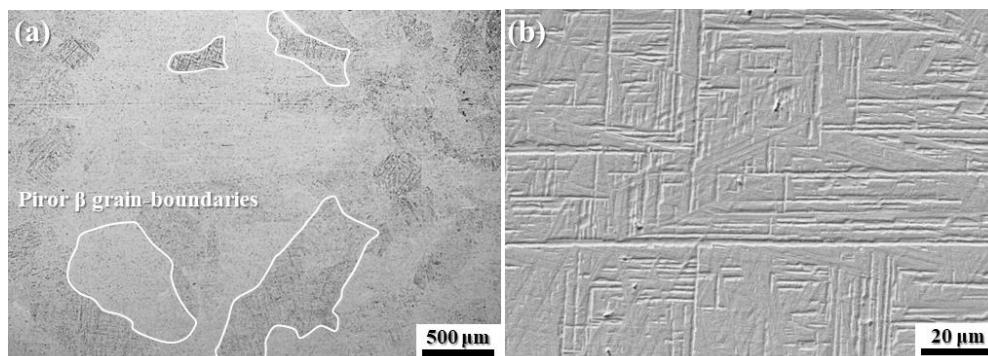


Figure 8. Microstructure of WM of the laser-MIG hybrid welded TC4 joint: (a) OM; (b) SEM.

Figure 9 illustrates the microstructural morphology of the WM and HAZ within the corresponding regions of the three weld passes in the joint. Due to slower cooling rates at the center of the weld bead, the surrounding columnar grains exert a certain hindrance to temperature reduction. Consequently, after heating and temperature elevation, there is minimal change in temperature once it decreases to a certain extent, leading to rapid grain coarsening in the WM and the appearance of some larger equiaxed grain structures. Comparing Figure 9a,c,e, it is evident that the grain size in the 3rd# layer weld bead is significantly larger than that in the previous two passes. The width of the columnar grains is approximately 400 μm in the 3rd# layer weld bead, whereas the grain size in the 1st# layer weld bead is only about 220 μm , with the majority being equiaxed grains. This is primarily attributed to the different welding thermal cycles experienced by the weld beads in different layers.

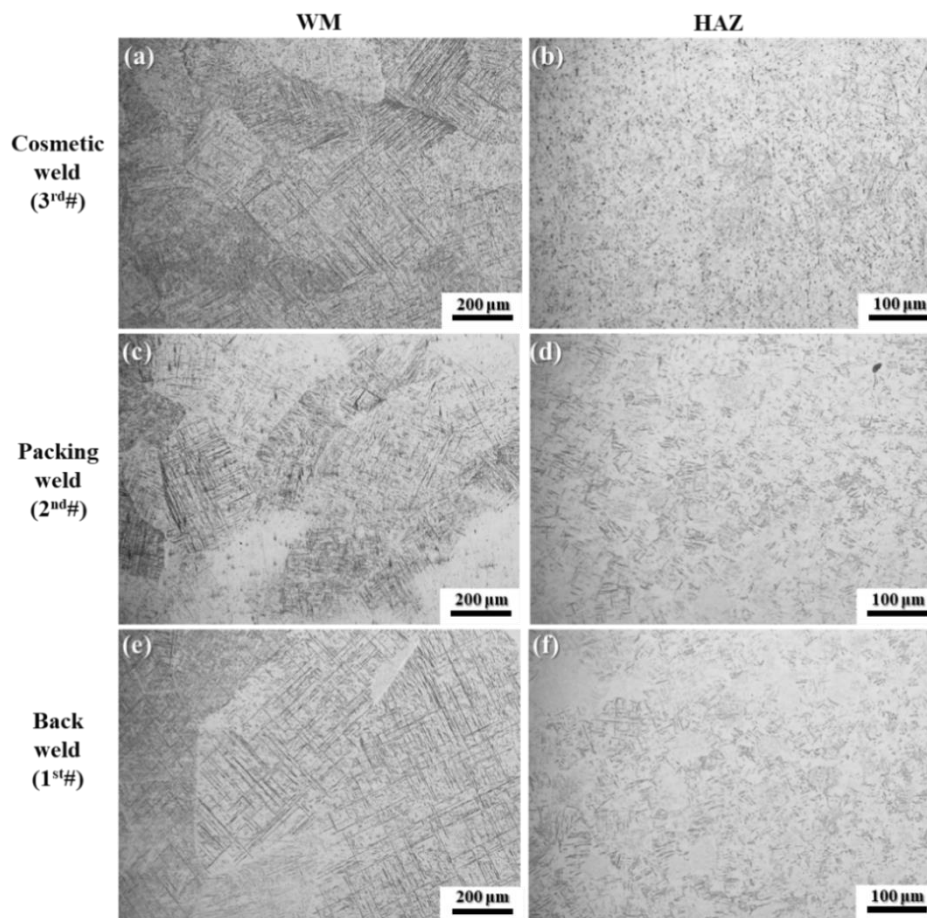


Figure 9. Microstructure of the different zones of laser-MIG hybrid welded TC4 joint. (a) WM in 3rd# weld; (b) HAZ in 3rd# weld; (c) WM in 2nd# weld; (d) HAZ in 2nd# weld; (e) WM in 1st# weld; (f) HAZ in 1st# weld.

The bottom weld bead undergoes a second heating-cooling cycle while being welded over the upper layers, with the peak temperature relatively lower compared to the first cycle [28]. However, it is still possible to reach the temperature for $\beta \rightarrow \alpha'$ transformation. Due to the secondary thermal cycle, the cooling rate accelerates compared to the previous cycle, preventing the grains from growing. This effectively anneals the bottom weld bead, to some extent enhancing the uniformity of its microstructure distribution. Basket-weave structures are observed in all three layers, with coarse Widmanstätten microstructures formed near the β grain boundaries in the WM of the 2nd# and 3rd# layers. These structures result from the rapid cooling after the transformation from the primary β phase, above the $\beta \rightarrow \alpha'$ transformation point, forming either α' lamellae or $\alpha' + \beta$ lamellae within the grains.

The microstructural morphology of the HAZ at the three locations exhibits minimal differences in size. The HAZ is influenced by the heat from the WM, reaching the temperature for α phase to β phase transformation. Rapid grain growth occurs in the β phase, with smaller primary β grains near the WM due to slower cooling rates and longer dwell times at high temperatures. After cooling, the microstructure transforms into α' martensite, forming an interlocking basket-weave structure. In areas closer to the BM, where the cooling rates are faster, the dwell time in the β phase is shorter, resulting in finer α' grains. In the transition zone between the HAZ and the BM, the dwell time in the β phase is even shorter, leading to the formation of secondary α' , with some untransformed α phases fused together to form blocky α phases [29]. Upon completion of cooling, a mixture of secondary α' and blocky α phases forms the microstructure.

3.2. XRD Analysis

Figure 10 presents the micro-area XRD spectra of different weld passes within the same weld bead. There are no significant differences in grain orientation among the different layers, with the majority consisting of α/α' phases. The β phase only appears at the peak (110), which is close to the position of the α' peak (0002). Compared to the two layers below the joint, the diffraction intensity of the hexagonal crystal system grains is relatively higher. Particularly, in the 3rd# cosmetic layer weld bead, the diffraction intensity of the (10–11) crystal orientation is significantly higher, indicating a distinct orientation of α/α' phases in the cosmetic layer. This is attributed to the differences in microstructural distribution and size generated during the solidification process of the molten pool, as well as the fewer thermal cycles experienced by the upper weld bead during the multi-pass welding process compared to the lower layers.

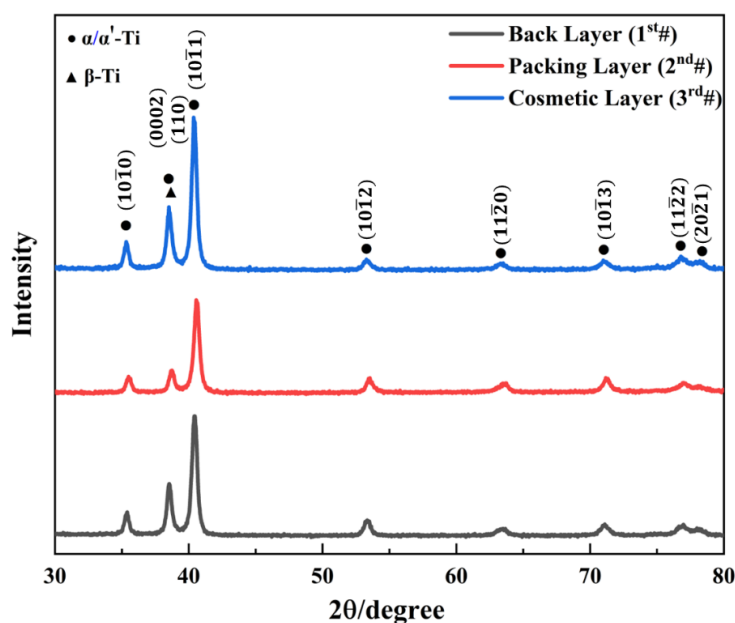


Figure 10. XRD results of different zones of the welded joint.

3.3. Mechanical Properties of the Joint

Hardness Analysis

The hardness curve, as depicted in Figure 11, exhibits a convex profile, indicating that the hardness in the vicinity of the weld bead's center is significantly higher than that in the BM. As is depicted, Figure 11a–c shows the horizontal hardness test results of the three layers of the weld, respectively. Near the HAZ, the hardness reaches a relative peak, gradually decreasing toward the HAZ and the BM transition. Due to the close elemental composition between the weld bead and the BM and the gradual decrease in fusion degree, the energy for nucleation on semi-melted grains in the fusion zone is minimal. Therefore, during the solidification of the weld pool, nuclei are first formed near the fusion zone and grow toward the center of the weld pool in the form of columnar grains. As the columnar grains continue to grow and migrate, they push lower-melting-point solutes or impurities toward the center of the weld pool. Consequently, due to the segregation effect, a large amount of relatively large α' phases are generated within the weld bead, resulting in slightly lower hardness values in the middle of the weld bead compared to the HAZ. Vertically, the hardness value is highest in the cosmetic weld (3rd#), reaching approximately 440 HV. The increased hardness in WM of titanium alloy welding is primarily due to the microstructure formed by rapid cooling during the welding process. In the WM, rapid cooling can lead to the formation of fine, hardened α' martensitic phases. This fine martensitic structure is much harder than the original structure of the titanium alloy, thus

increasing the overall hardness of the welded area [30]. This is also related to the observed distribution of Widmanstatten structures [31,32]. The overall variation in hardness values of the 2nd# and 1st# weld passes is less pronounced compared to the upper layer (3rd#), with hardness values in the weld bead zone approximately 420 HV.

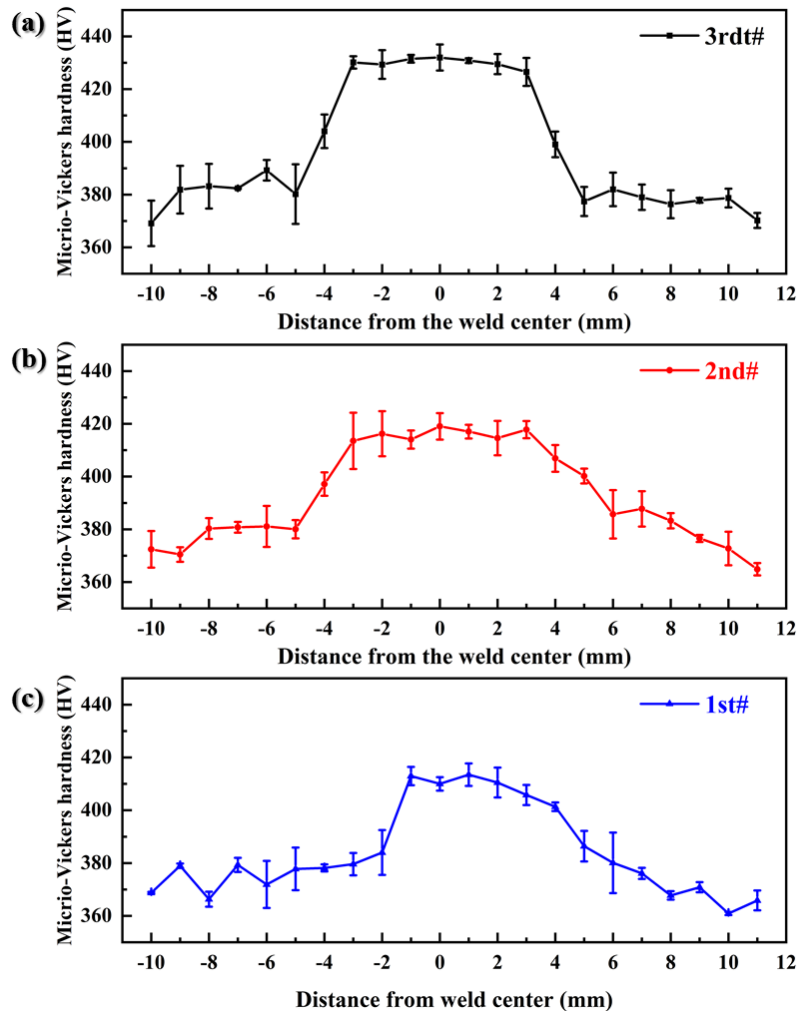


Figure 11. Hardness distribution of laser-MIG hybrid welded TC4 alloy joint: (a) 3rd# layer, (b) 2nd# layer, (c) 1st# layer.

3.4. Bending Test

Table 4 provides the test results for both face bend and root bend tests. The data in groups 1–3 correspond to the micro-zone positions sampled from the upper (3rd#), middle (2nd#), and lower (1st#) parts of the joint, respectively. It can be observed that the test forces in the root bend tests are generally slightly higher than those in the positive bend tests. Particularly in the third group of specimens, the test force in the root bend test reaches 31.41 kN, which is slightly higher than the highest value of 30.10 kN in the positive bend test. The standard deviations of the test forces for positive bending and back bending are 0.08 and 0.69, respectively. This indicates that the joint's load-bearing capacity under root bending loading is slightly higher than that under face bending loading, indicating better toughness performance. The bending results reveal that the bending performance of the 3rd# weld bead is superior to that of the 1st# and 2nd# weld beads, which may be attributed to the microstructure size in the WM region.

Table 4. Results of the bending test.

Number	Mode	Bending Angle (°)	Bending Force (kN)	Average Force (kN)	Standard Deviation
1-1	Face bending	9.4	30.05	30.02	0.08
2-1		14.8	29.90		
3-1		15.7	30.10		
1-2	Root bending	9.6	31.41	30.96	0.69
2-2		13.2	31.49		
3-2		25.1	29.98		

This disparity in bending performance can be correlated to the microstructural characteristics observed within the WM. Specifically, the superior performance of the 3rd# weld bead suggests a finer and more homogeneous microstructure, which is known to enhance the toughness and load-bearing capacity of the material under stress. Furthermore, the observed standard deviations imply a more consistent mechanical behavior in the face bend tests compared to the root bend tests, potentially indicating a more uniform distribution of residual stresses and microstructural features across the tested zones. Future studies could further elucidate these relationships by correlating microstructural features with mechanical properties across different sections of the weld joint, as has been suggested in the literature [33,34]. This comprehensive approach can offer deeper insights into the influence of welding parameters on joint performance.

3.5. Room-Temperature Impact Toughness

3.5.1. Impact Toughness Analysis

The results of the room-temperature impact performance in different micro zones of the joint are shown in Table 5. The impact absorption energy in the WM is minimal, only 30.6 J, while in the HAZ, it is 33.3 J, reaching a level close to that of the BM (33.5 J). The WM remains the most brittle part of the joint in terms of toughness, whereas the HAZ exhibits better impact toughness compared to the WM, likely due to smaller dimensions and a smoother transition in grain size. These findings suggest that HAZ demonstrates enhanced toughness properties, likely due to the thermal cycling experienced during the welding process, which may refine the grain structure or alter the phase composition, thus improving the impact resistance. The BM, with an impact absorption energy of 33.5 J, shows the highest toughness, indicating that the original material properties are largely preserved outside of the direct influence of welding heat. Additionally, the variance in impact absorption energy, represented by the standard deviations, indicates a level of inconsistency within the zones, with the WM area showing a higher variability (standard deviation of 2.18) compared to the HAZ (standard deviation of 1.90). This variation could be attributed to factors such as welding speed, temperature gradients, and material flow during the welding process, which can introduce heterogeneities in the microstructure, particularly in the WM. The difference between the WM and HAZ impact toughness also highlights the right combination can minimize the adverse effects of welding on the microstructure and enhance the overall performance of the welded joint [35,36].

Table 5. Results of impact toughness test in different locations. (Unit of A_{kv} : J).

Number	WM	HAZ	BM
1	33.1	34.0	34.0
2	31.0	30.7	33.0
3	27.8	35.2	33.5
Average (J)	30.6	33.3	33.5
Standard Deviation	2.18	1.90	0.41

Figure 12 illustrates the macroscopic morphology of the impact fracture surfaces corresponding to the results in Table 5. It can be observed that the fracture surfaces of all three

regions consist of a fibrous zone near the notch, a bright and radially patterned radiative zone, and shear lips extending along the 45° direction, displaying typical characteristics of ductile fracture. The fracture surface in the BM appears relatively flat and smooth, without obvious defects. In the HAZ, some minor pores are present in the radiative zone, while the shear lips exhibit some larger pores. In the WM, both the radiative zone and the shear lips feature pores of notably differing sizes (approximately 30–50 µm), exhibiting a clustered distribution, particularly as observed in Figure 12(a2,a3). This phenomenon primarily stems from the collapse and closure of keyhole pores during the welding process, culminating in process-induced porosity [9,37]. Such pores are likely to diminish the impact absorption energy of the WM, consequently reducing its toughness and resulting in a divergence from the anticipated optimal weld toughness. The specimens in group number 1 exhibit better impact toughness in all regions, with the fracture surface being the flattest, smoothest, and showing clear ductile fracture characteristics, with the least number of pores and defects.

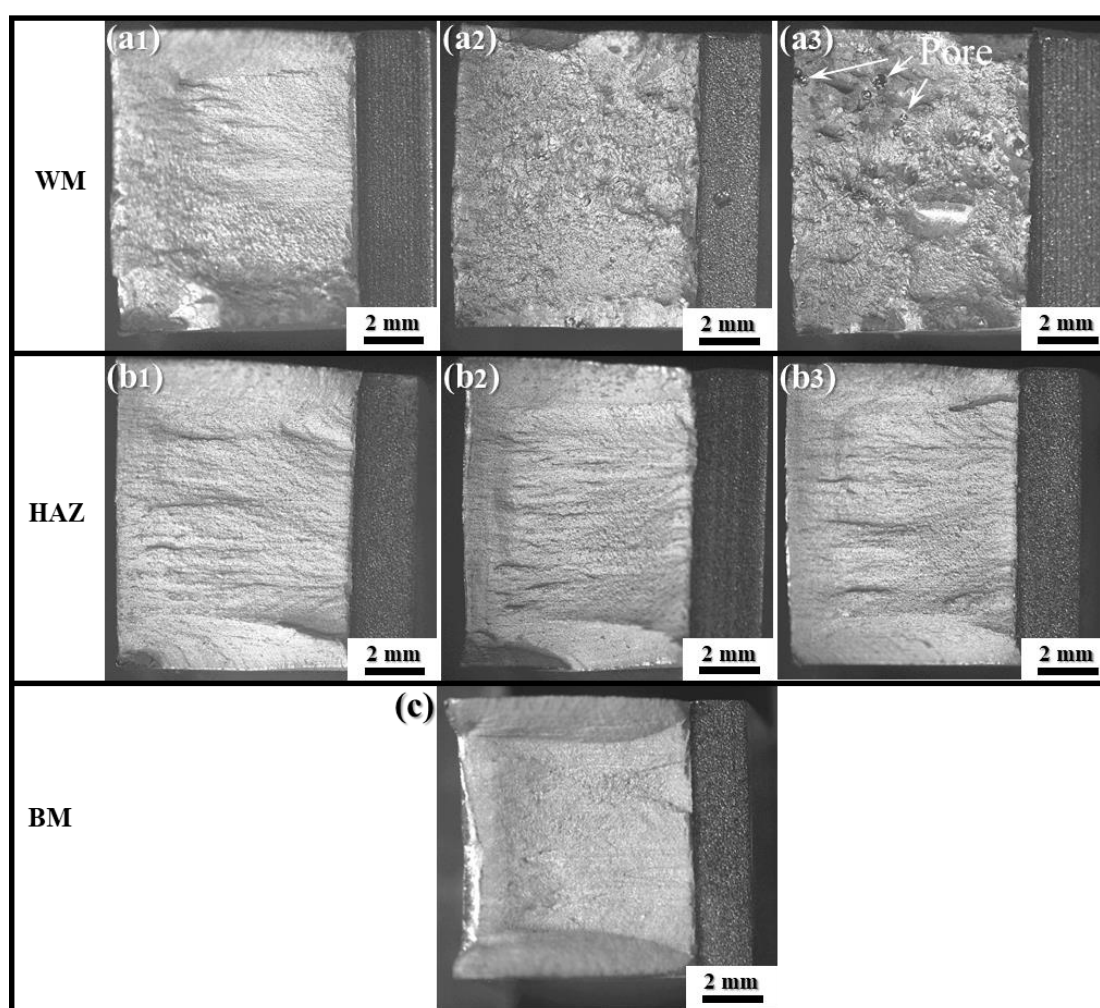


Figure 12. Macroscopic fracture morphology of laser-MIG hybrid welded TC4 joint: (a1–a3) sampled WM as the center; (b1–b3) sampled HAZ as the center; (c) sampled BM as the center.

The microstructure characterization of the impact fracture surface in the WM, which exhibits better impact toughness, from the first group of samples is depicted in Figure 13(a1,a2). The fracture surface in the fibrous zone shows numerous and unevenly sized dimples, indicating a ductile-brittle mixed fracture. These dimples, formed by the accumulation of microvoids or pores under the action of external force, exhibit ductile fracture characteristics. The radiative zone displays deep micropores clustered in a river-like pattern, along with some larger micropores that represent tearing dimples. The parabolic direction of the

tearing dimples indicates the crack source, accelerating local ductile fracture. The central part of the fibrous zone is mainly composed of unevenly sized equiaxed dimples, indicating good plasticity, with a small portion showing river-like patterns. The interweaving distribution of numerous dimples and a few river-like patterns suggests a ductile fracture, indicating relatively good toughness. Additionally, there is a large shallow pit and a large micropore, which have minimal impact on the overall impact performance. The fibrous zone exhibits similar-sized and evenly distributed dimples.

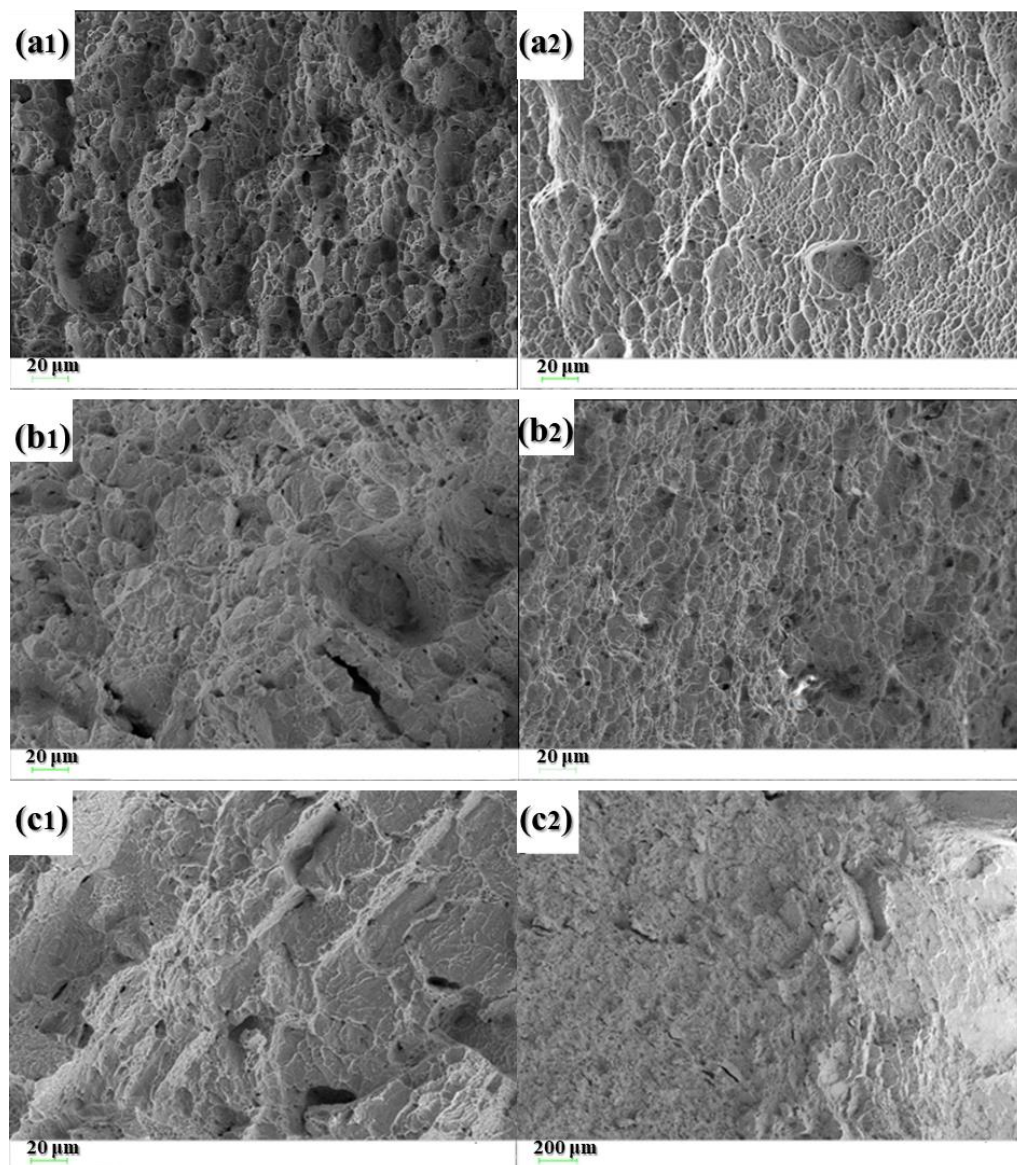


Figure 13. Impact fracture analysis of WM of TC4-welded-joint: (a1,a2) fibrous area; (b1,b2) radiation area; (c1,c2) shear lip area.

In Figure 13(b1), the radiative zone of the fracture surface shows dimples of varying sizes, with small dimples interweaving to form a net-like structure, while larger dimples are accompanied by cleavage planes. Micropores are clustered on the planar river-like pattern, with one larger micropore representing a tearing dimple. Near the shear lips, as shown in Figure 13(b2), the radiative zone of the fracture surface exhibits numerous small, deep, and densely packed dimples, characteristic of ductile fracture. Additionally, there are some cleavage planes distributed and relatively fewer deep micropores and large micropores.

The presence of second-phase inclusions within the micropores contributes to its relatively good toughness, which is associated with smaller grain size in the lower part of the WM.

Figure 13(c1) elucidates the detection of numerous significant cleavage steps and tear ridges present in the shear lips area, with dimples of differing scales dispersed across the cleavage terraces, primarily illustrating transgranular fracture phenomena. In Figure 13(c2), this area is mainly composed of river-like steps and numerous small cleavage steps, along with abundant tiny tear ridges. The specimen uniformly exhibits traits indicative of brittle fracture throughout. This phenomenon is primarily attributed to the persistent presence of α' martensite and Widmanstatten structures within the weld zone [38]. The coalescence of these microstructural features significantly elevates the brittleness of the matrix. Consequently, such brittle characteristics are prominently manifested during the terminal phase of impact-induced fracturing. Overall, the analysis indicates that, while maintaining welding quality, the impact toughness of the WM can be maintained at a relatively good level, closely approximating that of the BM [39].

In comparison to existing literature, our study demonstrates superior impact toughness in the WM and HAZ of titanium alloy weld joints. Although the impact performance of the weld zone has not exceeded that of the base material, it still demonstrates commendably good performance. Specifically, our findings indicate that the impact absorption energy shows enhanced toughness compared to the research by Balasubramanian et al. [36]. Furthermore, the study by Cui et al. [40] reveals that although the impact toughness of the weld metal does not surpass that of the base material, the presence of high-angle grain boundaries positively contributes to the impact toughness. This suggests that our welding process may offer optimized conditions that preserve or enhance joint performance without compromising material toughness.

3.5.2. Failure Mechanism of Impact Performance

To enhance the analysis of the microstructural factors contributing to impact crack failure, we employed TEM to examine the microstructure adjacent to the crack. We selected samples located near the impact fracture surface of the WM for detailed TEM characterization, as illustrated in Figure 14. The analysis of bright-field images and selected area electron diffraction (SAED) results revealed the presence of a small amount of β phase between the lamellar α/α' phases, confirming the validity of the XRD and microscopic structure analyses. Characterization showed the existence of a small number of dislocations within some α/α' phases, while the β phase was precisely located at the interfaces. When subjected to external impact loads, the main impediments to crack propagation are concentrated at the interfaces near the β phase, as these interfaces typically have higher strain capacities. Therefore, they can initially resist external loads, and when many such interfaces appear, they can hinder further crack propagation.

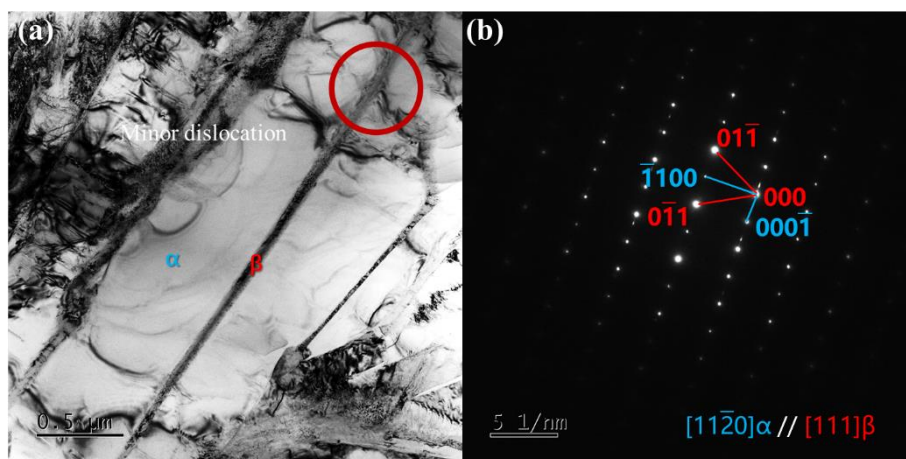


Figure 14. (a) TEM image of the microstructure near the fracture; (b) the diffraction spots.

Figure 15 illustrates a schematic diagram of a failure mechanism based on the results analysis. It is generally believed that during the impact process, cracks originate from micropores generated by plastic deformation due to external impact forces [41]. As the micropores expand, microscopic cracks penetrate columnar grains, mainly propagating along internal phase boundaries. When the angle of the phase boundary reaches the minimum energy for fracture, the crack continues to propagate. However, when the angle between the phase boundary and the crack propagation angle is small, the ability of crack propagation decreases, eventually leading to its cessation.

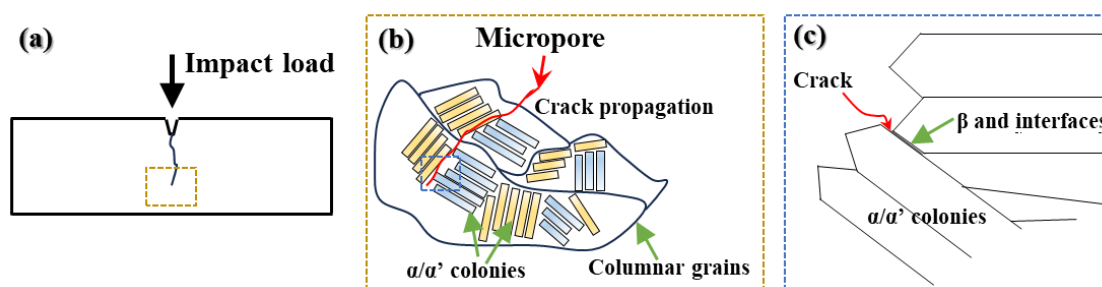


Figure 15. Schematic diagram of a failure mechanism of impact performance in WM of the joint: (a) impact diagram; (b) the enlarged area in (a); (c) the enlarged area in (b).

4. Conclusions

This study employed multi-layer multi-pass welding to complete the laser-MIG hybrid welding of 12 mm thick titanium alloy, and through performance testing and characterization, the following findings were made:

(1) Minor differences were observed in the microstructure among different passes, with all exhibiting α/α' phases and a minor presence of β phases, predominantly in basket-weave structures, primarily consisting of needle-like α' martensite. However, it was noted that the upper regions tended to display Widmanstatten structures, which are less conducive to the enhancement of joint toughness.

(2) The upper layer of the 12 mm laser-MIG composite multi-layer multi-pass weld exhibited the highest hardness value, peaking at approximately 420 HV. This contrasted with the lower weld seam, which displayed a smaller hardness peak and variances in bending performance across different passes. Crucially, the toughness in the lower part of the joint weld seam outperformed that in the upper part, correlating with the refined grain size due to repetitive welding heat cycles, highlighting the intricate interplay between welding parameters and mechanical properties.

(3) The impact performance within the weld seam area did not reach the levels of the HAZ or the base metal, attaining 91.3% of the base metal's impact absorption capacity. This reduction in toughness, particularly in the upper section, can primarily be attributed to an increased presence of pores. Furthermore, the variation in grain size and phase content due to multi-layer multi-pass welding creates a differential in toughness across distinct areas of the fracture surface, illustrating the complex relationship between microstructure and mechanical properties in welded joints.

(4) Analysis of the microstructure near the failure surface allows us to delineate a failure mechanism: the initiation of cracks stems from the expansion of micropores during deformation. The existing β phase between the α phases and at their interfaces acts as an effective barrier against further expansion when the crack propagation angle remains small, elucidating the intricate fracture behavior of welded joints under stress.

Author Contributions: Conceptualization, J.X. and P.L.; methodology, W.F.; software, G.Z.; validation, P.L. and L.L.; formal analysis, W.F.; investigation, G.Z.; resources, J.X.; data curation, G.Z.; writing—original draft preparation, P.L.; writing—review and editing, J.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research received to external funding.

Institutional Review Board Statement: There are no ethical issues with this study.

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Auwal, S.T.; Ramesh, S.; Yusof, F.; Manladan, S.M. A review on laser beam welding of titanium alloys. *Int. J. Adv. Manuf. Technol.* **2018**, *97*, 1071–1098. [CrossRef]
2. Guo, P.; Zhao, Y.; Zeng, W.; Hong, Q. The effect of microstructure on the mechanical properties of TC4-DT titanium alloys. *Mater. Sci. Eng. A* **2013**, *563*, 106–111. [CrossRef]
3. Cui, C.; Hu, B.; Zhao, L.; Liu, S. Titanium alloy production technology, market prospects and industry development. *Mater. Des.* **2011**, *32*, 1684–1691. [CrossRef]
4. Wen, P.; Yelkenci, D.; Chen, J.; Chang, B.; Du, D.; Shan, J. Numerical analysis of the effect of welding positions on formation quality during laser welding of TC4 titanium alloy parts in aerospace industry. *J. Laser Appl.* **2019**, *31*, 022401. [CrossRef]
5. Schneider, A.; Gumenyuk, A.; Lammers, M.; Malletschek, A.; Rethmeier, M. Laser Beam Welding of Thick Titanium Sheets in the Field of Marine Technology. *Phys. Procedia* **2014**, *56*, 582–590. [CrossRef]
6. Akman, E.; Demir, A.; Canel, T.; Sınmazçelik, T. Laser welding of Ti6Al4V titanium alloys. *J. Mater. Process. Technol.* **2009**, *209*, 3705–3713. [CrossRef]
7. Sun, Y.Y.; Wang, P.; Lu, S.L.; Li, L.Q.; Nai, M.L.S.; Wei, J. Laser welding of electron beam melted Ti-6Al-4V to wrought Ti-6Al-4V: Effect of welding angle on microstructure and mechanical properties. *J. Alloys Compd.* **2019**, *782*, 967–972. [CrossRef]
8. Yuan, T.; Li, Y.; Ren, X.; Jiang, X.; Zhao, P. Effect of Pulse Current on Grain Refinement in Ti6Al4V Welds during Pulsed Plasma Arc Welding. *J. Mater. Eng. Perform.* **2023**. [CrossRef]
9. Su, R.; Li, H.; Chen, H.; Wang, H.; Wang, W.; Wang, D.; Guo, J. Stability analysis and porosity inhibition mechanism of oscillating laser-arc hybrid welding process for medium-thick plate TC4 titanium alloy. *Opt. Laser Technol.* **2024**, *174*, 110569. [CrossRef]
10. Junaid, M.; Baig, M.N.; Shamir, M.; Khan, F.N.; Rehman, K.; Haider, J. A comparative study of pulsed laser and pulsed TIG welding of Ti-5Al-2.5Sn titanium alloy sheet. *J. Mater. Process. Technol.* **2017**, *242*, 24–38. [CrossRef]
11. Pragatheswaran, T.; Rajakumar, S.; Balasubramanian, V. Optimization of the weld characteristics of plasma-arc welded titanium alloy joints: An experimental study. *Mater. Manuf. Process.* **2021**, *37*, 896–907. [CrossRef]
12. Gao, F.; Li, P.; Jiang, P.; Liao, Z. The effect of constraint conditions on microstructure and properties of titanium alloy electron beam welding. *Mater. Sci. Eng. A* **2018**, *721*, 117–124. [CrossRef]
13. Chen, J.; Li, H.; Liu, Y.; Zhao, X.; Cai, Y.; Chen, H.; Chen, Y.; Feng, A.; Wang, H.; Sun, Z. Deformation behavior and microstructure characteristics of the laser-welded Ti-6Al-4V joint under variable amplitude fatigue. *Mater. Charact.* **2023**, *196*, 112606. [CrossRef]
14. Li, R.; Li, Z.; Zhu, Y.; Rong, L. A comparative study of laser beam welding and laser-MIG hybrid welding of Ti-Al-Zr-Fe titanium alloy. *Mater. Sci. Eng. A* **2011**, *528*, 1138–1142. [CrossRef]
15. Chatterjee, S.; Mahapatra, S.S.; Bharadwaj, V.; Upadhyay, B.N.; Bindra, K.S.; Thomas, J. Parametric appraisal of mechanical and metallurgical behavior of butt welded joints using pulsed Nd:YAG laser on thin sheets of AISI 316. *Opt. Laser Technol.* **2019**, *117*, 186–199. [CrossRef]
16. Nam, K.; Ki, H. One camera-based laser keyhole welding monitoring system using deep learning. *J. Manuf. Process.* **2023**, *104*, 17–27. [CrossRef]
17. Chatterjee, S.; Mahapatra, S.S.; Lamberti, L.; Pruncu, C.I. Prediction of welding responses using AI approach: Adaptive neuro-fuzzy inference system and genetic programming. *J. Braz. Soc. Mech. Sci. Eng.* **2022**, *44*, 53. [CrossRef]
18. Zhan, X.; Liu, J.; Chen, J.; Peng, Q.; Wei, Y.; Zhao, Y. Parameter optimization of multi-pass multi-layer MIG welded joint for invar alloy. *Int. J. Adv. Manuf. Technol.* **2016**, *87*, 601–613. [CrossRef]
19. Su, X.; Tao, W.; Chen, Y.; Fu, J. Microstructure and Tensile Property of the Joint of Laser-MIG Hybrid Welded Thick-Section TC4 Alloy. *Metals* **2018**, *8*, 1002. [CrossRef]
20. Brandizzi, M.; Satriano, A.A.; Tricarico, L. CO₂ Laser—MIG Hybrid Welding of Titanium Alloy. *Adv. Mater. Res.* **2011**, *264–265*, 1270–1280. [CrossRef]
21. Chen, S.; Luo, S.; Yu, H.; Geng, H.; Xu, G.; Li, R.; Tian, Y. Effect of beam defocusing on porosity formation in laser-MIG hybrid welded TA2 titanium alloy joints. *J. Manuf. Process.* **2020**, *58*, 1221–1231. [CrossRef]
22. Fan, H.; Zhou, P.; Li, J.; Huang, J.; Ni, Y.; Hui, Y. Microstructure and Mechanical Properties of Arc Zone and Laser Zone of TC4 Titanium Alloy Laser-TIG Hybrid Welded Joint. *Metals* **2022**, *12*, 1854. [CrossRef]
23. Yang, H.Y.; Xu, X.K.; Ba, X.L.; Tao, X.K.; Liu, L.M. Process and mechanism of low power laser-double arc welding of titanium alloy plate. *Trans. China Weld. Inst.* **2022**, *43*, 12–19. [CrossRef]
24. Gao, M.; Chen, C.; Wang, L.; Wang, Z.; Zeng, X. Laser-Arc Hybrid Welding of Dissimilar Titanium Alloy and Stainless Steel Using Copper Wire. *Metall. Mater. Trans. A* **2015**, *46*, 2007–2020. [CrossRef]
25. Yu, J.; Cai, C.; Xie, J.; Chen, Z.; Chen, H. Keyhole stability, arc behavior, and molten pool flow in narrow-gap oscillating laser-arc hybrid welding of titanium alloy. *Int. J. Heat Mass Transf.* **2024**, *220*, 124922. [CrossRef]

26. Liu, J.; Zhan, X.; Gao, Z.; Yan, T.; Zhou, Z. Microstructure and stress distribution of TC4 titanium alloy joint using laser-multi-pass-narrow-gap welding. *Int. J. Adv. Manuf. Technol.* **2020**, *108*, 3725–3735. [CrossRef]
27. Zhan, X.; Bu, H.; Gao, Q.; Yan, T.; Ling, W. Temperature field simulation and grain morphology on laser welding-brazing between Ti-6Al-4V and 1050 aluminum alloy. *Mater. Res. Express* **2019**, *6*, 056551. [CrossRef]
28. Liu, J.; Yang, T.; Zhuang, Y.; Li, L.; Huang, M.; Su, X.; Dong, S. Micro-crystallographically revealing the plasticity-evolved behaviors of thick Ti-6Al-4V laser-arc hybrid welded joint. *J. Mater. Res. Technol.* **2024**, *28*, 459–467. [CrossRef]
29. Rominiyi, A.L.; Mashinini, P.M. A critical review of microstructure and mechanical properties of laser welded similar and dissimilar titanium alloy joints. *J. Adv. Join. Process.* **2024**, *9*, 100191. [CrossRef]
30. Matsumoto, H.; Yoneda, H.; Sato, K.; Kurosu, S.; Maire, E.; Fabregue, D.; Konno, T.J.; Chiba, A. Room-temperature ductility of Ti-6Al-4V alloy with α' martensite microstructure. *Mater. Sci. Eng. A* **2011**, *528*, 1512–1520. [CrossRef]
31. Zhang, Y.; Xin, R.; Guo, B.; Wang, K.; Liu, Q. Influence of alternate grain boundary α on the development of Widmanstätten microstructure in TC21 Ti alloy. *Mater. Charact.* **2021**, *177*, 111162. [CrossRef]
32. Ma, Y.; Youssef, S.S.; Feng, X.; Wang, H.; Huang, S.; Qiu, J.; Lei, J.; Yang, R. Fatigue crack tip plastic zone of $\alpha + \beta$ titanium alloy with Widmanstätten microstructure. *J. Mater. Sci. Technol.* **2018**, *34*, 2107–2115. [CrossRef]
33. Wei, P.; Wu, M.; Liu, D.; Liang, Y.; Zhao, Z. Face Bend Property of 7N01-T4 Aluminum Alloy MIG Welded Joint by Using Different Welding Wires. *Metals* **2022**, *12*, 873. [CrossRef]
34. Luo, C.; Zhao, Y.; Cao, Y.; Zhao, L.; Shan, J. Effect of laser heat treatment on bending property of laser welded joints of low-alloy ultra-high strength steel. *J. Laser Appl.* **2019**, *31*, 032011. [CrossRef]
35. Liu, Y.; Chen, Q.; Chen, J.; Yang, J.; Dong, S. Development of a novel fabricating thin-walled TA2 titanium tube via high-frequency induction welding. *Prog. Nat. Sci. Mater. Int.* **2024**, (in press). [CrossRef]
36. Balasubramanian, T.S.; Balakrishnan, M.; Balasubramanian, V.; Manickam, M.A.M. Influence of welding processes on microstructure, tensile and impact properties of Ti-6Al-4V alloy joints. *Trans. Nonferrous Met. Soc. China* **2011**, *21*, 1253–1262. [CrossRef]
37. Huang, J.L.; Warnken, N.; Gebelin, J.-C.; Strangwood, M.; Reed, R.C. On the mechanism of porosity formation during welding of titanium alloys. *Acta Mater.* **2012**, *60*, 3215–3225. [CrossRef]
38. Dewangan, S.; Mohapatra, S.K.; Sharma, A. An assessment into mechanical properties and microstructural behavior of TIG welded Ti-6Al-4V titanium alloy. *Grey Syst. Theory Appl.* **2020**, *10*, 281–292. [CrossRef]
39. Sun, L.; Wang, M.; Huang, L.; Fang, N.; Wu, P.; Huang, R.; Xu, K.; Wang, X.; Qin, J.; Li, S.; et al. Comparative study on laser welding thick-walled TC4 titanium alloy with flux-cored wire and cable wire. *Materials* **2023**, *16*, 1509. [CrossRef] [PubMed]
40. Bagheri, F.; Madoliat, R.; Sedighi, M.; Asgari, A. Rubber-assisted pre-hemming process: A parametric study. *J. Manuf. Process.* **2019**, *38*, 328–337. [CrossRef]
41. Esfahani Yeganeh, V.; Li, P. Effect of beam offset on microstructure and mechanical properties of dissimilar electron beam welded high temperature titanium alloys. *Mater. Des.* **2017**, *124*, 78–86. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Influence of Scanning Strategy and Post-Treatment on Cracks and Mechanical Properties of Selective-Laser-Melted K438 Superalloy

Bin Zhang, Hua Yan *, Zhisheng Xia, Peilei Zhang, Haichuan Shi and Qinghua Lu

School of Materials Science and Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; bin2030@126.com (B.Z.); xzsfzth@163.com (Z.X.); oxidpl@126.com (P.Z.); shc0010@126.com (H.S.); luqh@sues.edu.cn (Q.L.)

* Correspondence: yanhua@foxmail.com; Tel.: +86-216-779-1412

Abstract: The feasibility of manufacturing high-performance components with complex structures is limited due to cracks in some superalloys fabricated by selective laser melting (SLM). By controlling the main process parameters such as scanning strategy, the adverse effects of cracks can be effectively reduced. In this paper, the effects of two different SLM scanning strategies with island and ‘back-and-forth’ and post-heat treatment on the cracks and mechanical properties of selective-laser-melted (SLMed) K438 alloy were investigated. The results show that the SLM method of the ‘back-and-forth’ scanning strategy had better lap and interlayer rotation angles and a more uniform distribution of laser energy compared with the island scanning strategy. The residual stress accumulation was reduced and crack formation was inhibited under this scanning strategy owing to the cooling and shrinkage process. In addition, the dislocation motion was hindered by the formation of uniformly dispersed MC carbides and γ' phases during the SLM K438 alloy process, which resulted in the density of the as-built SLMed K438 alloy being up to 99.34%, the hardness up to 9.6 GPa, and the tensile strength up to 1309 MPa. After post-heat treatment, the fine secondary γ' phases were precipitated and dispersed uniformly in the Ni matrix, which effectively improved the Young’s modulus and tensile strength of the alloy by dispersing the stress-concentrated area.

Keywords: K438 nickel-based superalloy; selective laser melting (SLM); scanning strategy; mechanical properties; heat treatment; crack

1. Introduction

Selective laser melting (SLM) is one of the most widely used additive manufacturing (AM) technologies for metallic materials [1]. With continuous improvements in SLM technology, many alloys, including Ti alloys [2], Al alloys [3], nickel-based superalloys [4], and certain steels, can be successfully processed using SLM, leading to high densities and favorable mechanical properties [5]. The SLM process demonstrates outstanding performance in the fabrication of nickel-based superalloys and has clear advantages over other additive manufacturing processes in terms of geometric complexity, high efficiency, flexibility, and cost-effectiveness compared to conventional manufacturing methods [6–8].

With the development of SLM technology, the SLMed nickel-based alloys have been widely used. For instance, K438 alloy components play a vital role in both marine and aerospace industries, which must withstand high temperatures and stresses [9–11]. The K438 superalloy has complex chemical properties, including Co, Cr, Al, Ti, and Mo [12]. It is mainly composed of disordered (γ) substrates, ordered (γ') particles, and various carbides, which are enhanced by solid solution strengthening, grain boundary strengthening, and precipitation strengthening [13,14]. Furthermore, K438 heat resistance, corrosion resistance, toughness, plasticity, and other properties and its reinforcement mechanism are closely related. The primary method of reinforcement in K438 alloys is the precipitation of

intermetallic compounds, particularly $\text{Ni}_3(\text{Al}, \text{Ti})$, resulting in the formation of γ' particles within the FCC phase. These alloys display remarkable properties resulting from the solid solution strengthening of Co and Mo in the matrix, enhanced oxidation resistance due to a high Cr content, the γ -phase precipitation strengthening of Al and Ti, the dispersion strengthening through MC and M_{23}C_6 carbides and boride-forming elements, and the combined effects of multiple strengthening mechanisms [15,16]. This combination of strengthening mechanisms gives K438 high-temperature alloys their exceptional properties. These alloys are especially favored for aero-engine blades and gas turbines due to their exceptional thermal stability and resistance to thermal corrosion [17–19]. Even at elevated temperatures ranging from 540 °C to 1000 °C, nickel-based superalloys maintain excellent mechanical and physical properties.

Although their superior resistance to high temperatures, SLMed K438 alloys are susceptible to extensive cracks caused by precipitation and cooling stresses during the rapid solidification and shrinkage stages of the forming process [20]. The high contents of Al and Ti ($\text{Al} + \text{Ti} > 6\%$) in these high-temperature alloys, where γ' serves as the strengthening phase, increase their vulnerability to cracking during forming, thus impacting the final material properties [21]. The primary types of cracking observed in K438 alloys are liquefaction cracking (LC), solidification cracking (SC), and ductility dip cracking (DDC) [22,23]. Liquefaction cracking mainly occurs at grain boundaries, while ductility dip cracking (DDC) results from low-melting eutectics of $\gamma + \gamma'$, carbides, and borides [24,25]. DDC complements liquefaction cracking during the growth phase. For instance, Xu et al. [26] investigated the liquefaction cracking mechanism of the high-temperature alloy IN-738LC. They observed that the semi-continuous $\gamma + \gamma'$ eutectic at the grain boundary, dispersed during the process of grain boundary liquefaction, locally melted and formed a liquefaction crack through the rupture of the liquid film. Additionally, Zhang et al. [23] explored crack propagation in the high-temperature alloy IN738 using laser melting deposition (LMD) techniques. They identified that microscopic liquefaction cracks initiated at the center along extended straight grain boundaries and propagated due to the coupling effect of LMD. In an attempt to address hot tearing at high temperatures, Heydari et al. [27] conducted a study where the element Zr (0.01 wt.%~0.04 wt.%) content in K438 high-temperature alloys was varied. The results indicated that a higher Zr content prevents grain aggregation at grain boundaries but increases the alloy's susceptibility to hot tearing. Crack failure caused by cracking is a common and very serious failure mode. Considering the influence of cracks, the methods of adjusting process parameters and post-treatment are commonly used to reduce the harm caused by cracks.

Many researchers carried out the influence of process parameters on the mechanical properties and overall quality of AM products. By varying the process parameters (laser power, scan rate, scan spacing, layer thickness, and scanning strategy), defects in the material forming process could be reduced. These defects were a critical factor in the final properties of the material [5,28]. However, few studies have changed the scanning strategy to observe the internal structural properties of alloys. As the motion pattern of the energy beam in space, the scanning strategy is coupling influence by the direction and sequence of the scanning, the vector rotation angle, and the vector length. During SLM, the high-speed motion of the energy beam leads to rapid changes in temperature distribution, which triggers high residual stresses and inhomogeneous deformation, affecting product quality [29]. Therefore, more and more studies have been conducted to enhance the product quality of SLM by optimizing the scanning strategy. Rashi et al. [30] improved the mechanical properties of 17-4PH stainless steels produced by SLM by changing the number of laser scans per layer in the scanning strategy. It was found that by using a scanning strategy of two laser scans per layer of powder, the hardness of the samples increased by 44% and the relative density was approximately 0.06%~0.08% higher. Xu et al. [31] investigated the histo-mechanical properties of 24CrNiMo low alloy steel produced by SLM using four scanning strategies and found that the continuous scanning strategy with a 90° interlayer transition tended to have an equilibrium temperature field, higher relative

density, minimal residual stress, and the best surface quality. Furthermore, Nong et al. [32] found that densification, microstructure, crystalline structure, and mechanical properties could be tailored by SLM using different scanning strategies by comparing four continuous scanning strategies with different angles on the histological properties of 15-5PH stainless steel prepared by SLM. The above researches show that scanning strategy can significantly improve the formability of SLMed superalloy, which has good scientific research value.

Moreover, post-treatment of the specimen is crucial to enhance the internal integrity of the alloy. The microstructure of an alloy significantly influences its mechanical properties. Factors such as high residual stresses, excessive internal porosity, and susceptibility to cracking can impact the final mechanical properties of the material. A suitable post-treatment program can be developed to achieve excellent mechanical properties. For instance, Cao et al. [33] examined the mechanical properties of IN718 produced by SLM and subjected to 1080 °C homogenization heat treatment. They discovered that an appropriate amount of δ phase, under the influence of the homogenization temperature, acts as a stabilizer on the grain boundaries, thereby enhancing the grain boundary strength and extending the creep rupture life of the sample. Additionally, Luo et al. [34] investigated the Inconel 718 alloy produced through selective laser melting with various heat treatments. Their findings demonstrated that a suitable heat treatment significantly improved the corrosion resistance of the specimens by reducing micro-segregation and modifying the shape of the second phase. The heat treatment of the nickel-based K438 alloy primarily involved a solid solution and aging treatment processes. The solid solution treatment dissolved all the γ' particles in the substrate, while the aging treatment led to the reprecipitation of dense and homogeneous γ' particles of an appropriate size. Sotov et al. [35] compared the effects of standard heat treatment and hot isostatic pressing (HIP) conditions on the behavior of the IN738 alloy. They observed an increase in the yield strength at 900 °C for both heat treatments. Wongbunyakul et al. [36] investigated the microstructural properties of the IN738 alloy with different temperatures and times of solid solution and aging treatments. They noted that decreasing aging treatment times and increasing solid solution treatment temperatures resulted in a consistent decrease in the size and area fraction of γ' particles, resulting in finer γ' particles and hardness values above 450 HV.

Thus, this study focuses on the effects of different scanning strategies and post-treatment on the density of existing K438 alloy materials, type of crack production, characterization of the microstructure, and mechanical properties. In particular, the relationship between the two scanning strategies and crack formation in the printing process was systematically studied. The microstructure was used to deeply analyze the root causes of cracks and the internal mechanism leading to differences in mechanical properties. On this basis, the subsequent effects on cracks and mechanical properties were further explored through post-treatment. The findings of this research can contribute to the advancement of selective laser melting technology by providing guidelines for optimizing the processing parameters and post-treatment methods to achieve the superior short columnar dendritic microstructure and higher hardness and tensile strength of K438 alloy samples. Ultimately, this can lead to the development of high-performance products with improved reliability and durability, benefiting industries that rely on K438 alloys for their applications.

2. Experiments

2.1. Fabrication of K438 Alloy

The K438 alloy powder was prepared using gas atomization and supplied by Avimetalam. Table 1 provides the chemical composition and composition content of the K438 alloy powder. The particle size distribution of the powders was determined by laser diffraction: 19.0 μm , 33.3 μm , and 56.2 μm for D10, D50, and D90, respectively. It was observed by SEM that most of the powders had good sphericity and a smooth surface, and a few powders had depressions or protrusions, but this did not affect the overall fluidity of the powder, as shown in Figure 1.

Table 1. Chemical composition and content of K438 alloy.

Element	C	Ta	Mo	W	Ti	Al	Co	Cr	Ni
Content (wt.%)	0.1–0.2	1.5–2.0	1.5–2.0	2.4–2.8	3.0–3.5	3.2–3.7	8.0–9.0	15.5–16.3	Bal.

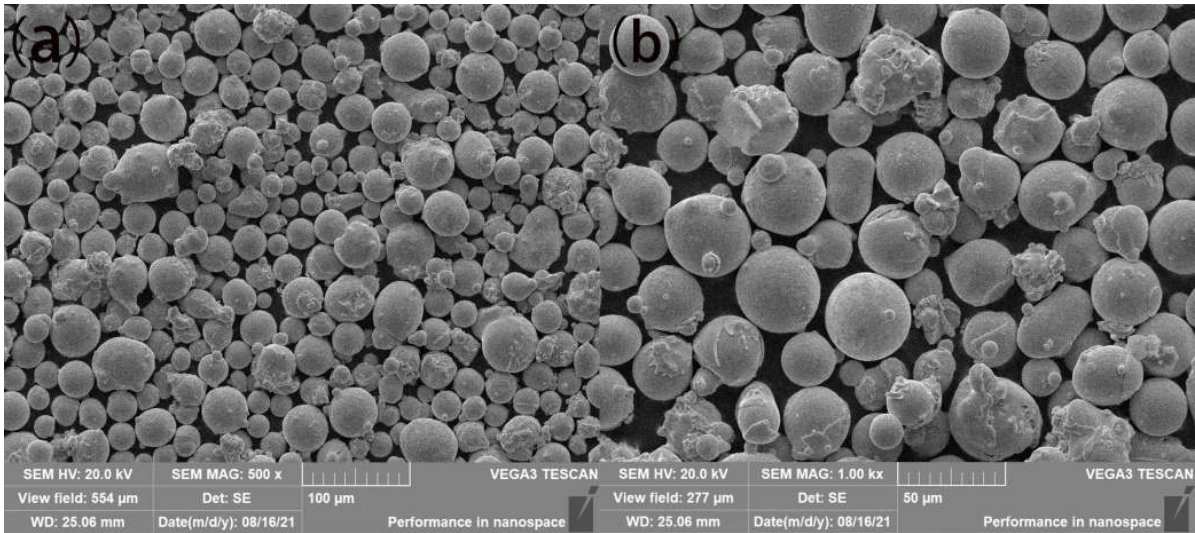


Figure 1. SEM of K438 powder at different magnifications, (a) low power SEM and (b) enlargement SEM.

The SLMed K438 alloy specimens were printed by a machine named M2 cusing system (Concept Laser Company, Bayern, Germany). The laser was an IPG fibre laser with a maximum power of 400 W and a spot diameter of 270 µm. Scanning processes using a high-speed scanning scope controlled forming accuracy. An isolated air precision powder feeding structure controlled the oxygen content below 50 ppm using highly pure nitrogen (99.99%) for protection. The SLM equipment schematic diagram is shown in Figure 2.

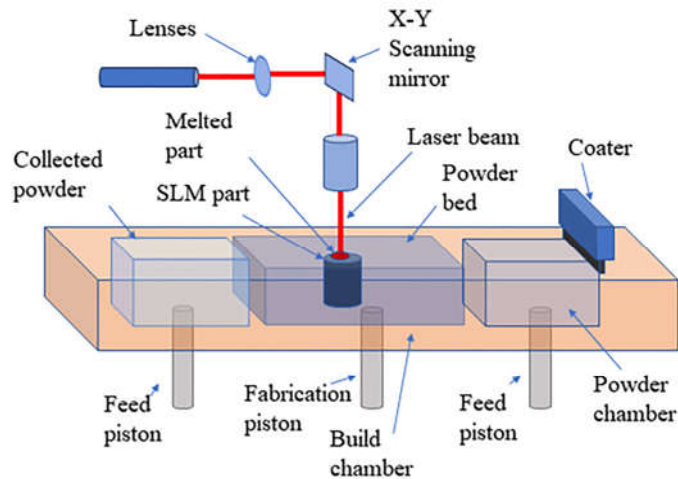


Figure 2. Equipment schematic of SLM.

2.2. Experimental Parameters

In this experiment, the following laser parameters were used: laser power of 370 W, scanning speed of 700 mm/s, scanning spacing of 0.13 mm, and spot diameter of 270 µm. The SLMed K438 alloy sample is shown in Figure 2a. As shown in Figure 3c, two different scanning strategies were used to SLM with the same basic process parameters. The specimens with the ‘back-and-forth’ scanning strategy were labeled as S1 while those with

the island scanning strategy were labeled as S2. 'Back-and-forth' scanning strategy is 67° rotation of the adjacent layer scanning vector and all scan lines parallel to each other. This scanning strategy implemented a non-regional, evenly distributed diagonal scanning method. Island scanning strategy is 90° rotation of scan vector between adjacent islands. After completing one region, the next region was scanned along the diagonal direction to reduce the laser energy concentration. This process was repeated until one layer of printing was completed. This scanning strategy divided the printing area into rectangular areas evenly, and the scanning directions of adjacent areas were perpendicular to each other.

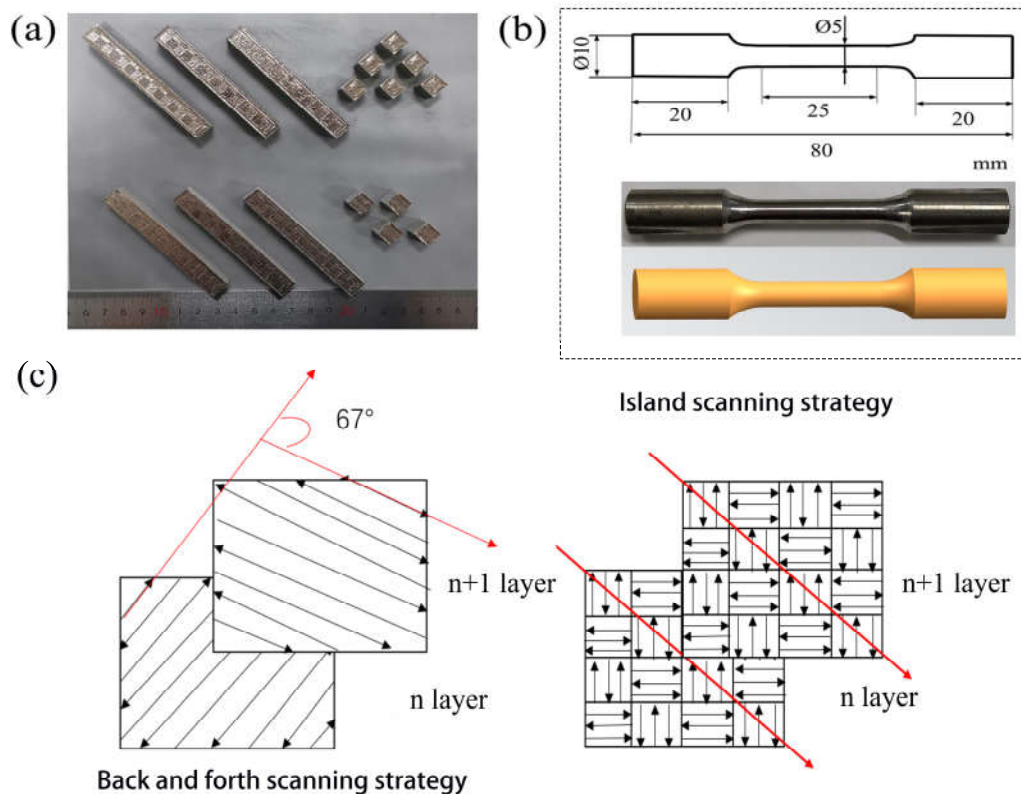


Figure 3. Schematic diagram of scanning strategies: (a) sample preparation of as-built samples; (b) tensile test sample size; (c) 'back-and-forth' and island scanning strategies.

The post-treatment procedure consisted of two steps. First, the specimens were subjected to solid solution treatment at 1120°C for a duration of 2 h and subsequent air cooling. The aging treatment was carried out at 850°C for a duration of 24 h and air-cooling subsequently. The post-treated S1 and S2 specimens are denoted by HTS1 and HTS2, respectively. The standard process parameters of K438 were used for the standard post-treatment (solid solution treatment and aging treatment) of the samples after employing different scanning strategies to observe the tissue evolution and mechanical properties after the different scanning strategies and post-treatment.

In addition, oxide films and impurities were removed from the substrate surface using a sandblaster on a substrate made of nickel-based alloy with a thickness of 20 mm. The substrate was kept at a temperature of 200°C during the whole preparation and manufacturing process. At least two exposures were made in order to minimize heat dissipation gradients and prevent warping, chipping, and distortion when melting the initial layer of powder. Two different scanning strategies (island scanning strategy and 'back-and-forth' scanning strategy) were used to prepare a square sample to study the microstructure of a K438 alloy with a size of $10\text{ mm} \times 10\text{ mm} \times 10\text{ mm}$. In addition, in order to study its tensile properties, a rectangular block with a size of $10\text{ mm} \times 10\text{ mm} \times 80\text{ mm}$ was prepared and processed into a round rod-shaped tensile specimen that met the requirements,

as shown in Figure 3a,b. The SLMed samples were separated from the substrate plate by wire electrical discharge machining. After post-treatment, mechanical lapping was used for preparing microstructure observation samples and then mechanically polished with a 50 nm particle-sized suspension. The samples were then etched in a Kalling etchant (11 m C₂H₅OH, 11 mL HCl acid, 0.5 ml CuCl₂) for 30 s to observe the morphology, followed by immersion in an etchant (25 g FeCl₃, 25 mL HCl, 100 mL H₂O) for 20 s to observe the phase morphology after etching. Subsequently, the sample was cleaned with alcohol using an ultrasonic cleaner for 30 min to remove surface impurities. After drying, the samples were placed in a drying oven for tissue observation.

2.3. Characterization

The experimental samples were analyzed to determine their density, hardness, tensile properties, and microstructural characteristics using various scanning strategies and post-treatment. The density of the K438 alloy was determined using Archimedes' method by the average of the five measurements with a balance precision of ± 0.0001 g. Microstructure analysis was conducted using the optical microscope, scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS), and electron backscatter diffraction (EBSD). X'pert Pro X-ray diffraction (XRD) was employed to examine and analyze the phase composition of the samples, using a Cu target with a goniometer movement step of 0.02° and a test angle range of 10° to 100° . Additionally, continuous stiffness measurements (CSMs) were performed using the nanoindenter, employing a standard Brinell diamond indenter probe. The measurements were carried out using a constant strain rate of 0.05/s. The experiments involved an approximate displacement of 800 nm (using a 100 μ m radius indenter), a maximum load of 50 mN, and a dwell time of 20 s. To ensure consistency in variables, five tensile specimens were tested with all specimens oriented transversely parallel to the substrate.

3. Results and Discussion

3.1. Density

Figure 4 illustrates the trend in alloy density under various scanning strategies and post-treatment conditions. The densities of the alloys were calculated by equation $\rho = \rho_p / \rho_0 \times 100\%$ for different scanning strategies, with a theoretical density of 8177.1 kg/m³. ρ_p is the measured density of the specimen block and ρ_0 is the theoretical density of the K438 alloy. Significant differences in density between the scanning strategies were observed with a difference of 0.21%, and the 'back-and-forth' scanning strategy (S1) resulted in a higher density of 99.34%, as opposed to 99.13% for the island scanning strategy (S2).

The use of the 'back-and-forth' scanning strategy resulted in higher densities. This can be attributed to the unique role of the 'back-and-forth' scanning strategy in the process of scanning. Rotating the direction of the scanning vector by 67° between adjacent layers resulted in a more uniform heat flow rotation and the alternate formation of a molten pool, leading to a uniform temperature gradient and complete melting of the particles, resulting in higher densities [37,38]. The island scanning strategy often started or ended the laser run at the overlap. The acceleration or deceleration of the laser at these locations resulted in it staying for longer, causing an increased local heat input at this point [39]. This led to the formation of a deeper molten pool, making it difficult for gas to escape from the melt. As a result, the overlap may have contained more small pores in comparison to other regions of the formed part. The existence of these pores eventually reduced overall density.

As shown in Figure 5, in laser scanning, due to the Gaussian energy distribution of the laser beam, the central energy is higher and the peripheral energy is lower. The solidified single-track molten pool also has a higher center and lower edges. In contrast to the island scanning remelting mode (no inter-layer rotation), the use of the 'back-and-forth' scanning strategy with a 67° rotation between each layer compensated for the height difference between the center and the edges caused by scanning the previous layer. This

ensured that the overall height difference across the sample surface remained less than the thickness of the single layer of powder, resulting in a more uniform powder distribution and higher density. Inter-layer scanning modes with different scanning strategies caused different melting and solidification modes within the alloy, resulting in different melting and residual stress distributions due to the rapid melting and solidification processes of the alloy. Such differences within the alloy also led to different formations of defects such as cracks, pores, and unmelted pores. Therefore, in the experiments, different scanning strategies led to differences in the densities of the alloys, even if other process parameters were kept constant.

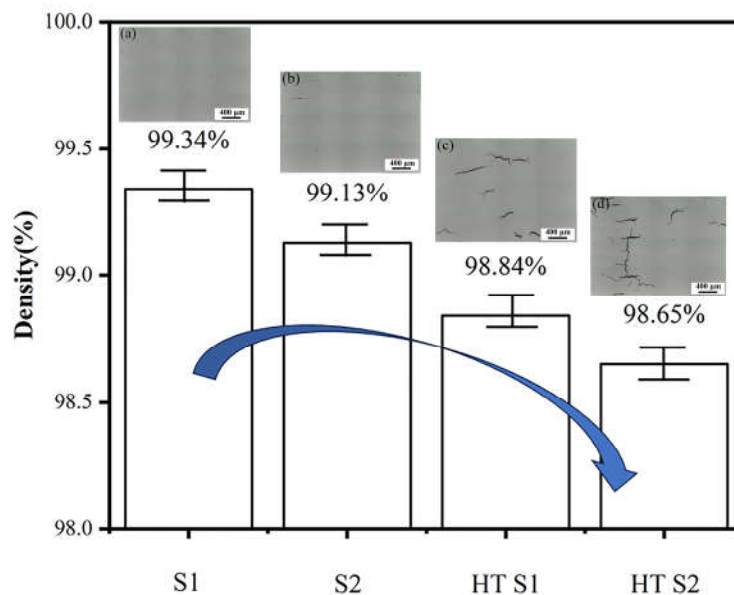


Figure 4. Density of different scanning strategies and post-treatment, (a) Surface OM of S1, (b) Surface OM of S2, (c) cracks of HT S1 and (d) cracks of HT S2.

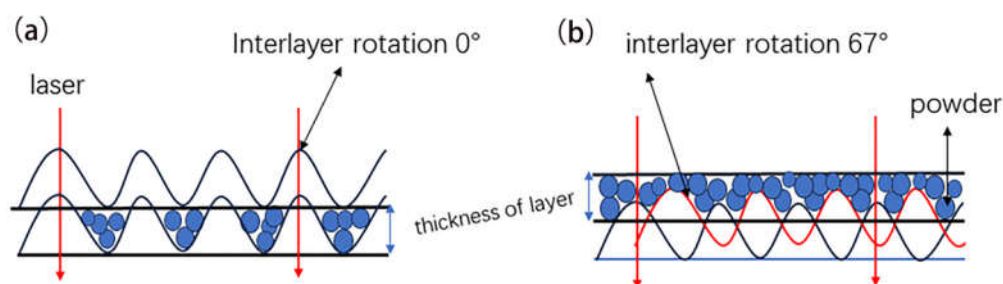


Figure 5. Schematic diagram of powder with different interlayer rotation angles under the same layer thickness, (a) island scanning remelting mode and (b) 'back-and-forth' scanning mode.

As a result of the post-treatment, the density of the alloys with the island scanning strategy and the 'back-and-forth' scanning strategy was reduced by 0.5% and 0.48%, respectively. During the post-treatment process, the crack morphology changed from fine to coarse, and the number of cracks increased significantly. After the aging treatment, recrystallized grains were generated near the original grain boundaries and inside the grains. As the size of the grains and grain boundaries increased, cracks were generated at the grain boundaries and propagated along the grain boundaries. At the same time, the solid solution treatment released residual stresses, contributing to the formation of microcracks. These microcracks could extend and penetrate the interior of the material to form pores and the cracks could expand into larger coarse cracks, leading to a decrease in the density of the post-treatment alloy.

3.2. Distribution and Types of Cracks

In general, by varying fundamental process parameters such as laser power and scan speed, one can regulate the depth and width of the molten pool, influence its morphology, adjust the melting efficiency, and influence the size of the solidification grains. These parameter variations directly affect the microstructure and properties of the material, reducing internal alloy defects while maintaining consistent formation patterns. Consequently, by independently modifying the scanning strategy of the alloy and subsequently modifying the laser scanning path and the overlap pattern, it becomes possible to more effectively discern the influence of different scanning strategies on internal crack defects within the alloy at the microscopic level. To further investigate the effects of different scanning strategies leading to internal cracks in the alloy, SEM images showing crack trends after different scanning strategies and post-treatment were analyzed as shown in Figure 6.

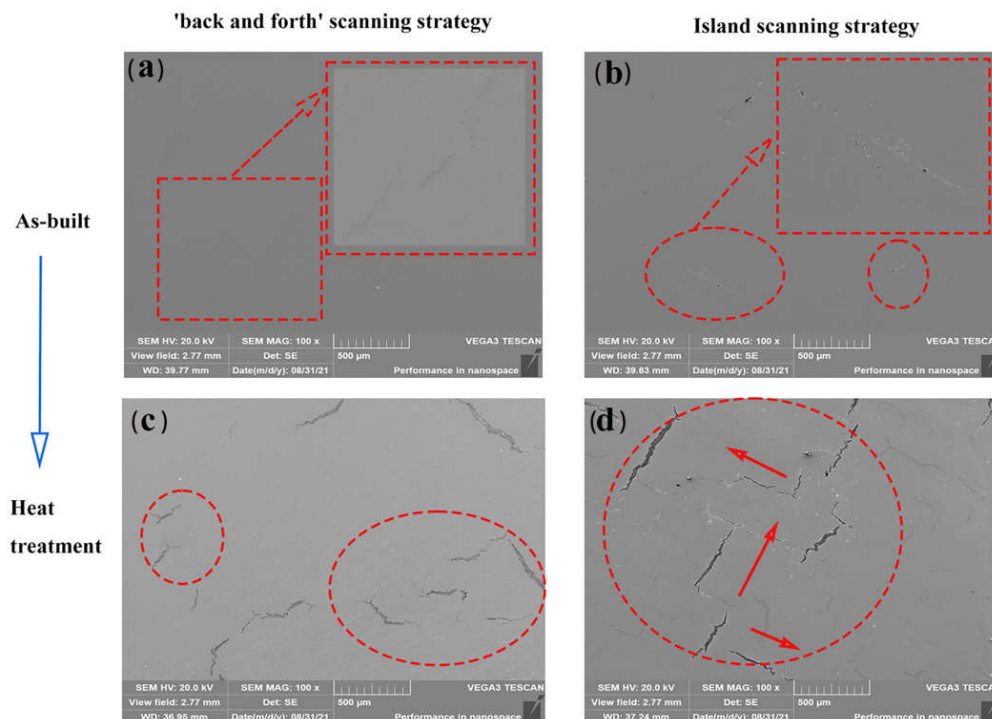


Figure 6. SEM images of cracks trend after different scanning strategies and post-treatment, (a) cracks of S1, (b) cracks of S2, (c) cracks of HT S1 and (d) cracks of HT S2.

The alloys exhibited good forming quality when utilizing the ‘back-and-forth’ scanning strategy. The resulting surfaces exhibited smooth and uniform characteristics. The surface of the alloy revealed no visible holes or defects. The present micro-cracks, uniformly oriented, had sizes ranging from 182 to 245 μm , as shown in Figure 6a. This is because the laser vector of the ‘back-and-forth’ scanning strategy was parallel and opposite in many directions to maintain the residual stress at a low level, the distribution tended to be average, and the cracks were not easy to produce [40]. In contrast, utilizing the island scanning strategy increased the number of defects within the K438 alloy, as well as the appearance of pores and keyhole defects. Due to the remelting of the substrate in the overlap during the laser scanning process and concentration effect of the energy in the lap region, irregularly shaped and sized keyhole defects were generated and remained in the next layer. Two different types of vertically extending cracks were observed, with perpendicular directions, both approximately 250 μm in size, as illustrated in Figure 6b.

A comparison of the crack characteristics with the two scanning strategies reveals significant differences in their crack extension directions. The crack extension direction within the alloy had a close relationship with the laser scanning strategy, instead of being

randomly generated. The explanation for this phenomenon has two aspects. Firstly, in the 'back-and-forth' scanning strategy, the scanning directions within the same layer were parallel and opposite to each other. In this strategy, after completing the previous scanning vector, the next scanning vector was initiated in the higher-temperature region. This led to decreasing the temperature gradient and reducing the residual stress [41]. However, as the scanning process proceeded towards the central region, the laser single-scan path became longer, leading to an increase in the temperature gradient and a gradual increase in the residual stress [42]. This produced a number of cracks in the same direction. The multi-partition scanning mechanism in the island scanning strategy resulted in a shorter single laser scanning path compared to the non-partitioned 'back-and-forth' scanning strategy. This led to a more even melting and solidification rate of the powder at different locations, resulting in lower residual stress. Furthermore, repetitive melting and solidification caused a high laser energy input, which increased the thermal contraction effect of the liquid phase in the molten pool, further intensifying the level of residual stress [43,44]. While the temperature gradient inside individual islands was low, it became high at the boundaries where cracks were more likely to form in the lap region. In the island scanning strategy, the laser scanning paths were perpendicular to each other at the lap region, which aligned with the direction of the crack vector. Hence, the length of scanning vectors and the lap pattern have a direct impact on crack formation in this alloy, and there exists a strong relationship between the scanning vector and the crack vector [45].

The surface crack states obtained after post-treatment with two different scanning strategies are shown in Figure 6c,d. The number of cracks on the alloy surface increased after the post-treatment, and originally elongated cracks gradually developed into coarser and longer structures, as observed. Fine, irregularly orientated short cracks with a size of about 200–500 μm also surrounded these coarse cracks. This phenomenon can be attributed to the effect of the solid solution aging treatment, which resulted in the melting of the original coarse grains in the alloy and the precipitation of fine recrystallized grains in the grain boundary regions. The presence of recrystallized grains increased the number of grain boundaries and, when internal stresses were applied to the material, these stresses tended to be concentrated at the grain boundaries. Since grain boundaries were regions of discontinuity in the crystal structure, this stress concentration led to plastic deformation near the grain boundary and stress concentration cracks.

Cracking is a common defect problem during selective laser melting under conditions of high temperature, high stress, welding, and solidification. The main cracking types include liquefaction cracking (LC), solidification cracking (SC), ductility dip cracking (DDC), and strain-age cracking after post-treatment. Liquefaction cracking is a common type in high-temperature alloys, and its occurrence is mainly related to the segregation of the alloy composition. Using the K438 alloy as an example, during fast cooling, elements that form γ' phases, such as Al and Ti, accumulate in the intergranular liquid phase and precipitate γ' phases and γ - γ' eutectic mixtures at grain boundaries, resulting in localized variation in composition. This deviation in composition results in a non-uniform distribution of composition in the solidification area, and the inhomogeneous γ' phase tends to diffuse into the matrix and decompose again during melting. Due to the high cooling rate, the diffusion effect is limited. Therefore, MC or γ phases that would normally be present are now surrounded by a high concentration of MC or γ phases, resulting in the formation of a thin film consisting of a low melting point eutectic composition at the grain boundaries. As shown in Figure 7, the formation of the above-mentioned film contributes to the liquefaction of the grain boundaries during melting. However, the liquefied grain boundaries are unable to withstand the stresses, leading to the formation of liquefaction cracks [46].

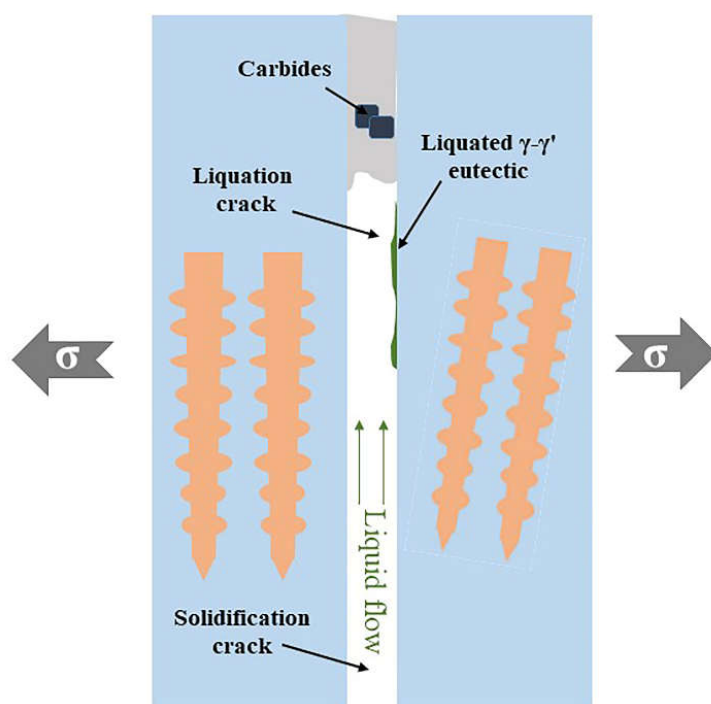


Figure 7. Schematic diagram of the initiation of liquation and solidification cracks in the overlapping zone.

The initiation stage of liquation and solidification cracks in the overlapping zone was examined. Solidification cracks are formed during the cooling and solidification of the liquid molten pool. They are distributed between the grain boundaries of the solidified grains or between the cellular crystals and extend along the coarse cellular crystal tissue to form long cracks. Solidification cracks are related to the residual stress state, solidification, and segregation of the alloy. In Figure 8a, the residual stresses at the laser lap are high due to the internal laser lap of the alloy. The greater the solidification temperature range of the alloy, the more likely it is that solidification cracks will form. Figure 8a illustrates that solidification cracks are closely linked to the residual stress, solidification processes, and segregation phenomena within the alloy. Solidification cracks in nickel-based, high-temperature alloys mainly stem from inter-dendrites of high-melting-point carbides and shrinkage holes formed in the final stage of solidification. The overlap of the laser in the alloy results in relatively high residual stress in the region of overlap. It is worth noting that the formation of solidification cracks is more probable in alloys with a wider solidification temperature range. During the cooling and solidification of the liquid molten pool, these solidification cracks appear and are distributed along the grain boundaries of the solidified grains or between cellular crystals, eventually propagating along the coarse cellular crystals to form long, extended cracks.

Figure 8b,d demonstrate the common characteristics of ductility dip cracking. This phenomenon typically takes place within the heat-affected area of reheated weld metal or base metal at homologation temperatures ranging from 0.4 to 0.9 [47]. These kinds of cracks are identified by edges that mostly feature straight and long triangular grain boundaries, as well as serrated grain boundaries and slip cracks adjacent to carbides or eutectics. In metals, ductile tilt cracks usually stem from grain boundaries formed by liquefaction cracks that emerge when alloy grain boundaries experience considerable residual stress exceeding the bond strength of the interface. Ductility dip cracks are usually short and thin-shaped. The formation of such cracks is due to multiple factors, including the macroscopic thermal stresses that arise during the welding process, solidification stresses, and local stresses generated by the precipitation of $M_{23}C_6$ carbides at grain boundaries [48].

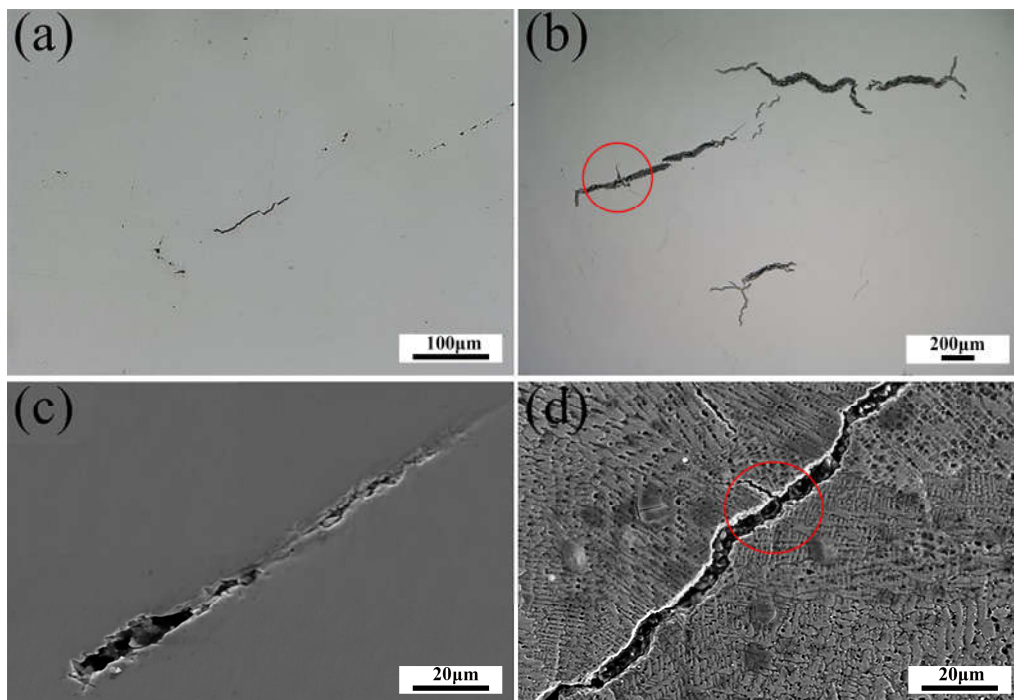


Figure 8. Cracks by OM and SEM: (a,c) S1; (b,d) HT S1.

3.3. Microstructure Characterization

Significant changes in microstructure were observed after changing the scanning strategy for the selective laser melting of the K438 alloy. In Figure 9a,a', it can be seen that the 'back-and-forth' scanning strategy, with the laser scanning perpendicular to the direction of the build, resulted in a specific microstructure with parallel orbital structures. Within the single-track structure, we could observe the presence of perpendicularly oriented cellular crystals near the edges of the tracks and a homogeneous cellular crystal structure in the center of the tracks. Due to the adjacent layer rotation of 67° in the 'back-and-forth' scanning strategy, the size of different columnar dendrites changed with the scanning direction. The elongated cellular crystals were remelted by the laser in subsequent layers, resulting in shorter columnar dendritic structures with lengths of $5\text{--}15\text{ }\mu\text{m}$. This columnar dendritic structure tended to have more grain boundaries and finer grains, effectively inhibiting crack propagation. Furthermore, the grain boundaries, as regions of lower strength in the material, could play a role in inhibiting crack propagation. Fine grain structures could also limit the movement of dislocations at the grain boundaries, further improving the crack propagation resistance of the material. When adjacent tracks were scanned by the laser, local heating led to thermal expansion and cooling led to the contraction of the material. When the heat-affected regions of two adjacent tracks overlapped, compressive stresses caused by thermal stress and cooling contraction developed between the adjacent regions. This compressive stress helped to tightly bond the material around the grain boundaries, reducing the propagation of grain boundary defects and cracks.

As shown in Figure 9b,b', we could clearly observe distinct melting channel boundaries that were perpendicular to each other. This was typically characterize an island scanning strategy. The island scanning strategy divided the scan region into multiple islands, and each island was a radiation unit with different radiation directions [44,49]. As a result, the island scanning strategy dissipated heat faster than a conventional unidirectional scanning strategy, and heat did not accumulate significantly between regions, so the quality of the forming inside each island was better. However, in Figure 9b, some small cracks through the grain perpendicular to the grain boundary is revealed by SEM. The formation of these cracks was related to the presence of a 90° transition in the island scanning strategy, which

led to an increase in the temperature gradient in the lap region and a consequent increase in residual stress, thus contributing to crack formation.

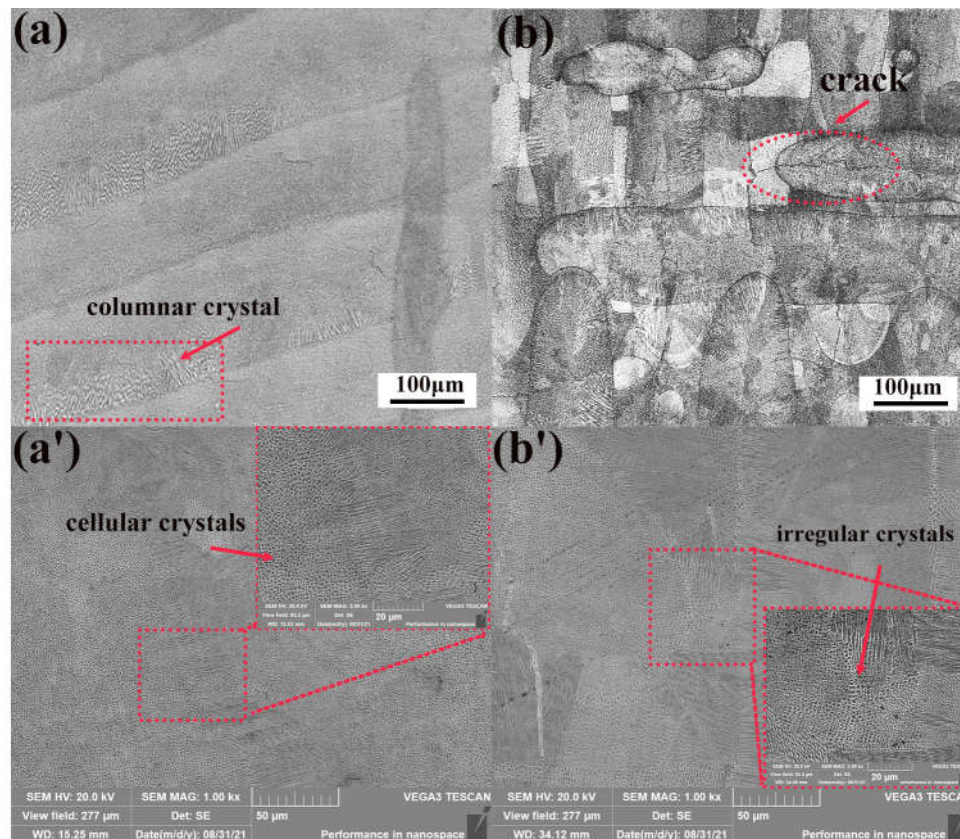


Figure 9. Metallographic structure and SEM images of samples under different scanning strategies: (a,a') S1; (b,b') S2.

When low melting point eutectic phases are present in the grain boundaries of high-temperature, nickel-based alloys, carbide precipitation can occur during cooling due to their high thermal expansion coefficient. As a result, large shrinkage stresses are generated during melting and solidification, and these stresses can initiate cracking along the solid–liquid interface and the formation of small solidification cracks near the grain boundaries [50]. In this case, the two directions of the melting channels are connected, but the connected regions show a mixed morphology of columnar and cellular crystals. Due to the characteristics of the island scanning strategy, where each island undergoes rapid solidification through different cooling directions, a mixture of short and thin cellular crystals as well as cellular crystals with different orientations and irregular morphology are produced.

Figure 10 shows the micrographs under both scanning strategies after standard post-treatment. As can be seen from the Figure 10, the orbital structure of the two scanning strategies were disappeared and the grain growth was affected by the migration of the grain boundary after post heat treatment processing. However, a large number of refined recrystallized crystals (columnar subcrystals, honeycomb subcrystals) emerged near the original crystal boundary. The reason for this phenomenon is due to the decrease in the grain boundary resulting the binding force could not support the internal stress and the dislocations moved to the grain boundaries. A large number of dislocations causes the orientation difference of the grain boundary to increase and the proportion of the apparent angular crystal boundary ($\theta > 15^\circ$) gradually increase. Those refined recrystallized crystals hindered the growth of recrystallized grains and causing irregular forces at the grain boundary.

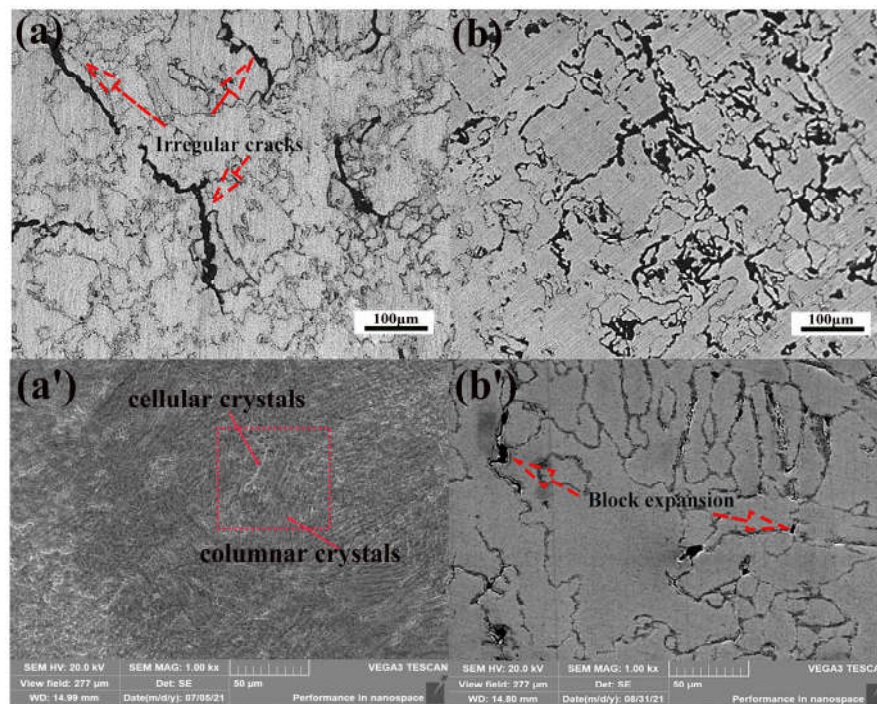


Figure 10. Metallographic structure and SEM images of samples subjected to various post-treatment conditions: (a,a') HT S1; (b,b') HT S2.

After aging treatment, elements such as Al, Ti, and Ni in the alloy precipitated from the grain boundaries and formed a large number of $M_{23}C_6$ carbides with the carbon in the matrix, forming banded regions of carbide distribution. This carbide precipitation adversely affected the plastic deformation capability of the grain boundary region, making it more brittle and reducing the plasticity of the grain boundary. When external stress was applied to the grain boundary region, cracks easily formed and propagated along the grain boundary due to the difficulty of plastic deformation in the brittle grain boundary. In addition, phase transformations during heat treatment were another important factor in crack formation, such as the dissolution of the γ' phase during solid solution treatment and the precipitation of the secondary γ' phase during aging treatment. These phase transformations led to changes in grain structure and size, causing an accumulation of stresses. If these stresses exceed the strength limit of the alloy, cracks can form from the phase interface. However, residual stresses in the alloy can also be released by cracks. Once a crack has formed, the thermal expansion of the alloy is limited and energy is rapidly released through the crack expansion region, reducing the temperature gradient and thus slowing the rate of crack expansion. This inherent stress release can counteract to some extent the crack expansion caused by stress build-up, helping to limit further crack expansion.

Figure 11 displays the orientation image microscopy (OIM) maps in the XY plane, based on the inverse pole figure (IPF), for both scanning strategies and post-treatment [51]. In this representation, the [001] orientation is depicted in red, the (101) orientation in green, and the (011) orientation in blue. The grain structure of both scanning strategies primarily consisted of columnar and equiaxed crystals in the as-built state. As illustrated in Figure 11a, under the 'back-and-forth' scanning strategy, the cellular crystals exhibited a pronounced (001) orientation. Notably, different particles exhibited different color changes, indicating that the rotation angle between continuous layers led to significant orientation differences. On the other hand, in the island scanning strategy depicted in Figure 11c, attributed to the substantial 90° orientation difference between the scanning directions of adjacent islands, coupled with directional solidification within each island, the grains exhibit different orientations due to the variation in cooling rates among neighboring

cellular crystals. Additionally, at the grain boundaries of the cellular crystals, there was the presence of unevenly sized equiaxed crystals. Following the standard post-treatment, the number of cellular crystals noticeably increased, and a considerable population of recrystallized grains with comparable colors emerged within the sample.

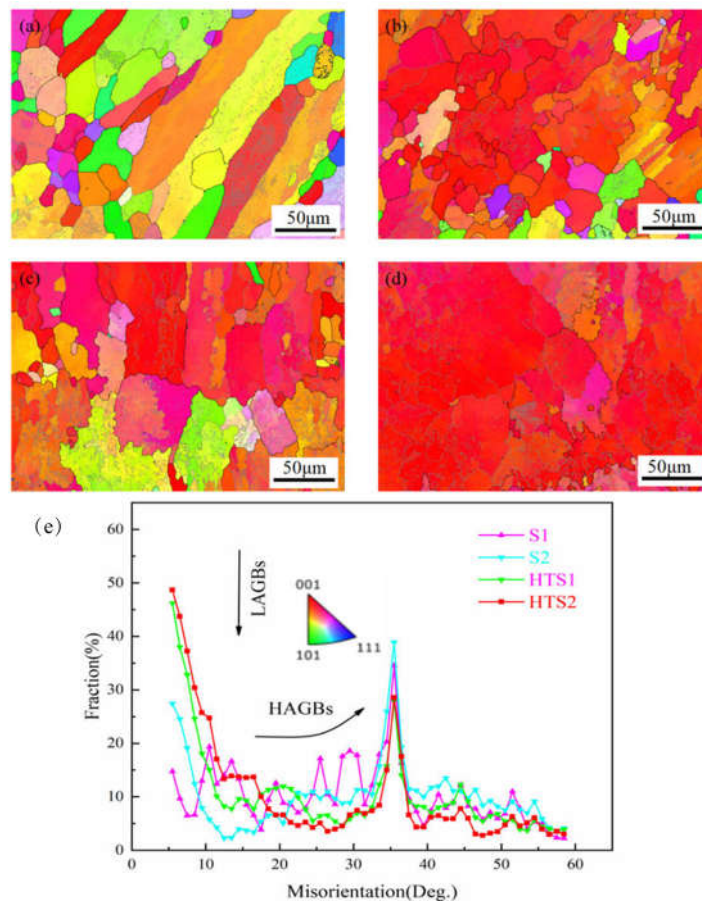


Figure 11. OIM images in the X-Y plane based on different scanning strategies and post-treatment conditions: (a) S1; (b) HT S1; (c) S2; (d) HT S2; (e) misorientation angle distribution.

Due to minimal grain deformation, the recrystallized grains exhibited a low orientation gradient. While the coarse grains underwent SLM and aging treatment, resulting in the formation of uniformly sized equiaxed grains, as illustrated in Figure 11b,d. Grain boundaries displaying misorientation angles ranging from 2° to 15° were classified as low-angle grain boundaries (LAGBs), whereas those with larger misorientation angles were considered high-angle grain boundaries (HAGBs). Dislocations migrated along the grain boundaries, being absorbed by both the grain boundaries and the LAGBs, thus leading to the conversion of LAGBs into HAGBs [52]. Notably, the significant peak increase in HAGBs occurred at approximately 35° . The HAGBs exhibited numerous intricate agglomerates, and fine equiaxed grains were observed within the grains. Subgrain nucleation were mainly occurred in the subgrains, as shown in Figure 11e. After post-treatment, the smaller misorientation meant that the orientation difference of grain boundaries was smaller and the grain boundaries were more stable. In addition, the size of the misorientation also affected the behavior of crystal defects and grain boundary migration in the crystal. The smaller misorientation could reduce the dislocation density of the grain boundary, thereby improving the tensile strength of the material.

K438 is a precipitation-strengthened alloy, with its strengthening effect mainly achieved through the dislocation hindering mechanism of γ' phases and carbides. To verify the presence and variation of the strengthening phases and carbides in the alloy, both the

as-printed alloy and heat-treated samples were analyzed using X-ray diffraction (XRD) patterns, as depicted in Figure 12c. Upon comparison with the physical phase cards in the standard physical phase database (PDF database), several well-defined diffraction peaks were detected in the prepared samples. These peaks corresponded to the matrix γ phase of the FCC structure and the (111), (200), and (220) crystallographic planes of the reinforced γ' phase of the K438 alloy. SEM images were used to observe the morphological evolution of the γ' phase under the 'back-and-forth' scanning strategy. During the as-built process, the austenitic matrix underwent the transient nucleation and growth of γ' phases due to rapid melting and solidification induced by SLM and higher laser temperature. The γ' phases in the alloy exhibited a square structure. Variations in cooling rates resulting from different scanning strategies caused differences in the sizes of γ' phases in different parts of the alloy. The larger γ' phase, illustrated in Figure 12a, measured approximately 8.5 μm and was surrounded by several nanoscale, fine γ' phases.

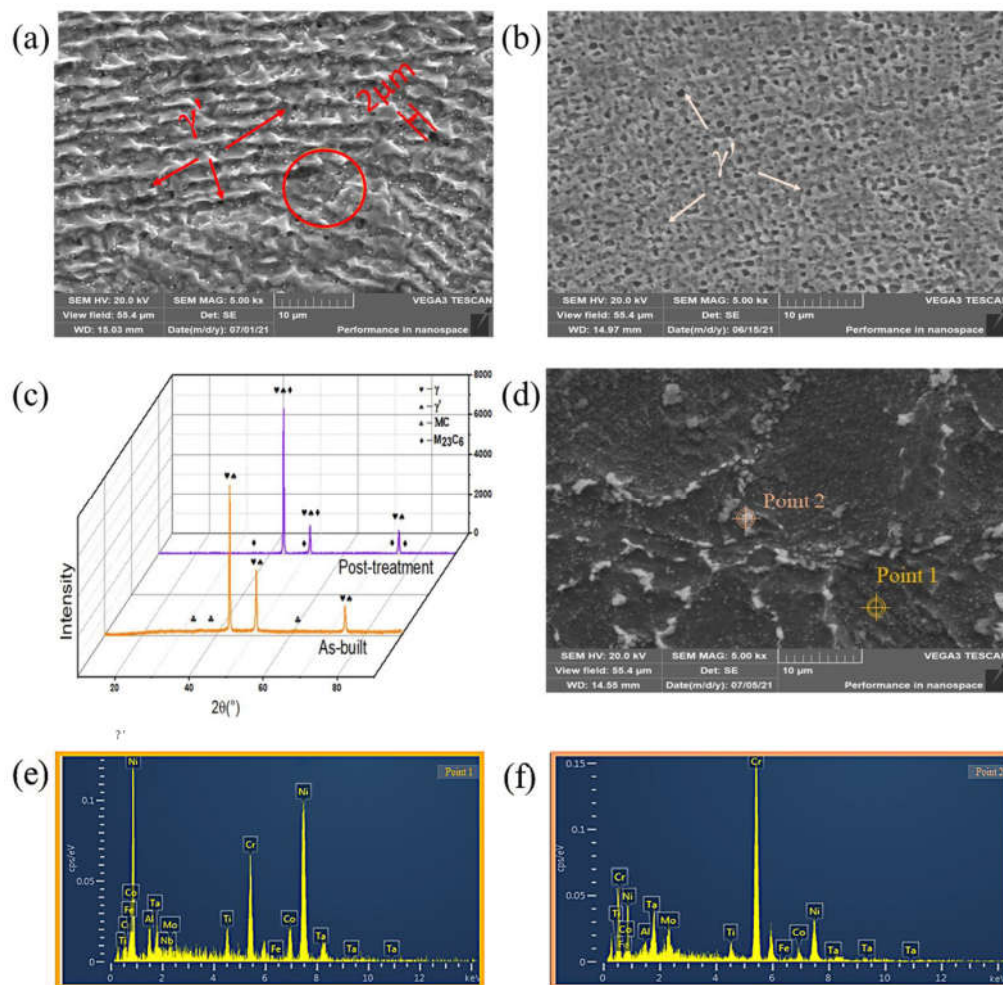


Figure 12. 'Back-and-forth' scanning strategy γ' phase evolution: (a) print state; (b) post-processing; (c) XRD diffraction pattern of the specimen post-treatment; (d–f) EDS analysis of carbide of HT S1.

After post-treatment, the γ' precipitated phases melted at around 1170 °C. The coarse square γ' phase within the material dissolved, resulting in the precipitation of a homogeneous mixture of fine γ' phases, consisting of both square and round shapes, with an average size of approximately 0.1 μm , as shown in Figure 12b. The interfacial and strain energies influenced the variation of the shape of the γ' phase in the solid solution. At low temperatures, there was an increased mismatch between the γ and γ' phases, and the shape of the γ' phase was primarily influenced by the strain energy. Since the strain energy was

smaller for a square compared to a sphere, the γ' phase exhibited a regular square shape. Conversely, at high temperatures, the mismatch between the γ and γ' phases decreased, and the shape of the γ' phase was predominantly determined by the interfacial energy. As the interfacial energy of a sphere is lower than that of a square, the γ' phase tended to adopt a spherical shape.

The generation and distribution of carbides significantly affected the overall performance of the K438 alloy during its selective laser melting and post-treatment process. For this reason, it was crucial to conduct an in-depth study of how carbides were generated and distributed. The K438 alloy commonly had two types of incipient carbides that were present at the grain boundaries and within its grains during initial processing and post-treatment. The presence of such carbides had a dual effect: the pinning effect of dislocations hindered the movement of dislocations, strengthening the alloy. Additionally, due to the accumulation of carbides in the grain boundary region, the plasticity of the grain boundaries was reduced, internal stresses within the alloy increased, and grain boundaries became prone to cracking. After the post-treatment of the alloy, continuous white carbides were found to aggregate along the grain boundaries. EDS analysis reveals that the continuous carbides and the fine granular carbides are dispersed in the grains of HT S1, as shown in Figure 12d–f. Combined with XRD analysis shows the presence of Ta, Mo, Nb, and Ti elements, which readily combined with C elements to form MC carbides after post-treatment, as shown in Figure 12c.

Furthermore, the EDS of the diffuse white particles in Figure 12d shows that these elements, which are prone to MC carbide formation, were mainly distributed in the white particles, indicating that MC carbides were diffusely distributed in the matrix and could effectively inhibit cracking, as shown in Figure 12e. In addition, in Figure 12a, many white particles were uniformly dispersed in the matrix within the red outline. The continuously distributed coarse carbides at grain boundaries were $M_{23}C_6$ carbides, which was due to the decomposition of MC to $M_{23}C_6$ after solid solution treatment ($MC + \gamma \rightarrow M_{23}C_6 + \gamma'$) and the precipitation of secondary $M_{23}C_6$ carbides at eutectic fronts or grain boundaries during long-term aging treatment, as shown in Figure 12f. Previous studies have shown that carbides are accumulated at grain and subgrain boundaries, which reduces the grain boundary plasticity and increases the risk of cracks generation.

3.4. Mechanical Properties

3.4.1. Nanoindentation

The load-displacement curves of the K438 alloy with different scanning strategies and post-treatment conditions are depicted in Figure 13. It can be observed from the graphs that the plastic phase curves for S1 and S2 had almost equal lengths and slopes at maximum load, indicating that the parts under these two scanning strategies had similar plastic behavior. However, the plastic phase curve of HTS1 post-treatment was not much different from that of S1, indicating that post-treatment had little effect on the plasticity of S1. In contrast, the plastic stage curve of HTS2 became steeper, indicating that the post-treatment reduced the plasticity of S2. After post-treatment with different scanning strategies, a large number of square γ phases disappeared, while fine secondary γ phases precipitated and grew uniformly in the matrix, resulting in an increase in the Young's modulus of the alloy. Five imprints were taken for each sample, and the data in Table 2 were obtained by averaging the five values. The Young's modulus of HT S1 and HT S2 increased by 18 GPa and 27 GPa, respectively.

The island scanning strategy employed a square scanning area and a 90° rotation for each layer, which impacted the hardness. However, the laser overlap region experienced more crack propagation, which made suppression difficult. In contrast, the 'back-and-forth' scanning strategy changed the laser scanning direction significantly by 67° after creating a layer, which limited crack expansion. The morphological and distribution analyses of the crack revealed its control of the changing direction of neighboring molten pool dendrites. The Young's modulus of the alloys increased with different scanning strategies, while

the hardness significantly decreased after post-treatment. The hardness of HT S2 was reduced to 8.2 GPa. In the post-treatment process, a significant number of square γ' phases disappeared, while fine secondary γ' phases precipitated and grew uniformly in the matrix. Accordingly, the strength of the alloys was effectively improved. However, during the heat treatment of solid materials, particularly high-temperature annealing or aging treatment, the primary grains continued to grow. This growth resulted in an increase in grain size, which led to a decrease in the alloy's hardness, as demonstrated in Figure 11.

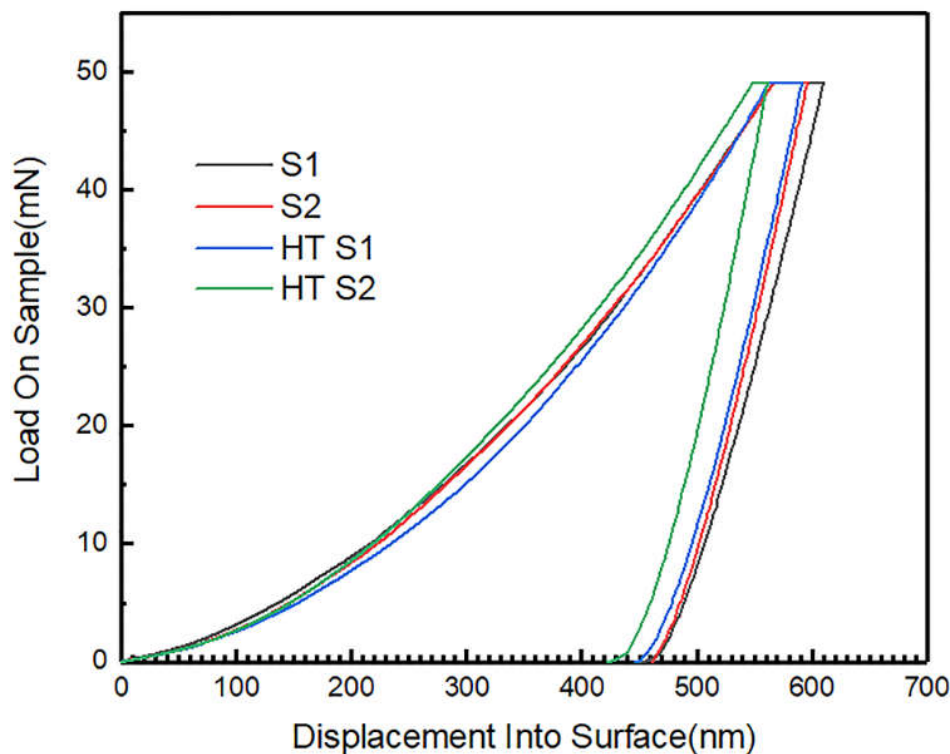


Figure 13. Load displacement curve under different scanning strategies and post-treatment.

Table 2. Hardness and Young's modulus of samples under different scanning strategies and post-treatment.

Sample	Hardness (GPa)	Young's Modulus (GPa)
S1	9.6 ± 0.2	179 ± 3
S2	8.7 ± 0.3	190 ± 1
HT S1	9.1 ± 0.2	197 ± 2
HT S2	8.2 ± 0.1	217 ± 2

After post-treatment, the huge square γ phase in the alloy disappeared and the fine secondary γ phase precipitated, grew, and was uniformly dispersed in the matrix, as shown in Figure 12a,b. At the same time, the K438 alloy was mainly affected by precipitation strengthening. Uniform distribution of fine carbides hinders dislocation motion, which increases the ability of precipitation strengthening and improves the strength of the SLMed K438 superalloy. After aging treatment, many uniformly recrystallized grains adhered to the original grain boundaries and precipitated out. The large amount of $M_{23}C_6$ carbides precipitated on the grain boundary increased the sensitivity of the cracks, increased the initiation of liquefaction cracking along the grain boundary, and reduced the plasticity of the alloy.

3.4.2. Tensile Properties

The ‘back-and-forth’ scanning strategy with a 67° interlayer rotation angle effectively suppressed crack initiation and propagation in the SLMed K438 alloy. The strength of the alloy was effectively maintained, resulting in a higher tensile strength (1309 MPa), as shown in Figure 14. The irregular arrangement of cellular crystals with different orientations in the island scanning strategy led to a diversity of crystal growth directions. This variety allowed the material to undergo plastic deformation in multiple directions during stretching, which enhanced the material’s ductility [53,54]. Compared to the ‘back-and-forth’ scanning strategy, the island scanning strategy exhibited a higher ultimate strain (3.24%). This was because the island scanning strategy involved a 90° rotation direction between adjacent islands, enabling the internal stresses in the two directions within the alloy to be constrained by each other in the positive stress stretching state, which enhanced the toughness of the alloy. Nevertheless, the island scanning strategy led to an increase in cracks at the overlap, which caused the tensile strength of the alloy (1256 MPa) to decrease, as shown in Figure 14. In contrast, the tensile strength of HTS1 and HTS2 was higher than that of S1 and S2 because of the uniform distribution of MC carbides and γ' phases in the matrix after post-treatment.

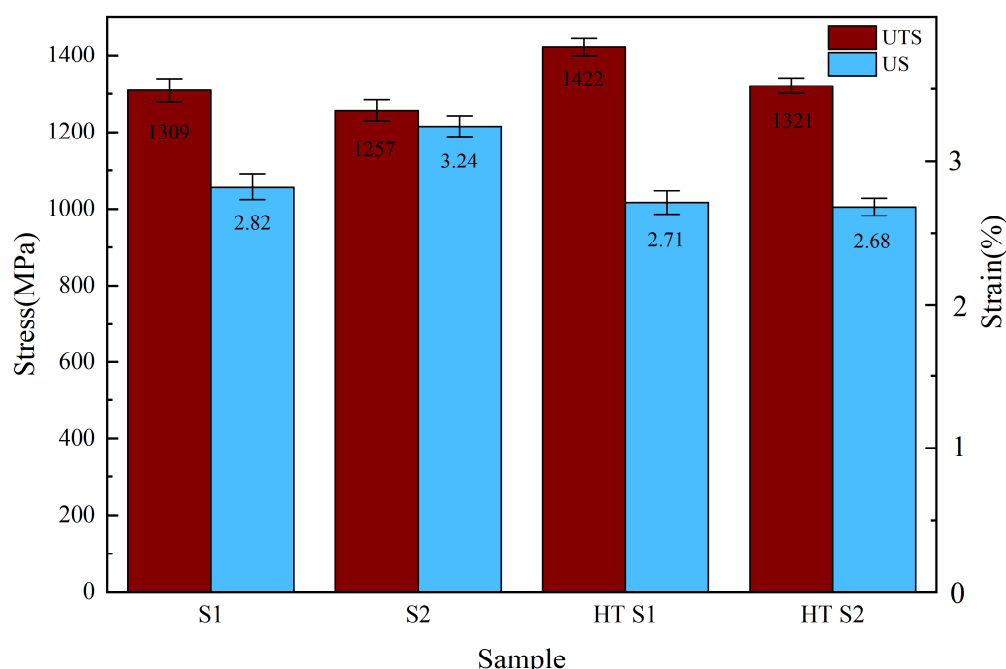


Figure 14. Tensile data with different scanning strategies and heat treatment.

During the solid solution treatment stage, the large γ' phase inside the alloy melted, resulting in the transformation of several diffusely distributed MC carbides into $M_{23}C_6$ carbides. In contrast, during the aging treatment stage, the precipitation of secondary $M_{23}C_6$ carbides at the grain boundaries was accompanied by the uniform precipitation of fine γ' phases throughout the alloy. As these precipitated phases were uniformly distributed, cracks propagated between different phases, diminishing the stress concentration region and thus enhancing the ultimate tensile strength of the alloy. Although the precipitated phase out could hinder the dislocation motion and improve the overall strength of the alloy, the stress concentration increased the sensitivity of the grain and sub-grain boundary cracking, produced more strain aging cracks, and reduced the ultimate strain of the alloy.

To carry out a thorough analysis of the tensile properties of the samples in the as-built state and after post-treatment using different scanning strategies, we examined the fracture characteristics through micro-fracture morphology, as illustrated in Figure 15. The fracture surfaces of specimens, whether in the as-built state or after post-treatment, predominantly displayed quasi-cleavage planes and cleavage ladders. These characteristics

were significantly correlated with reduced elongation. The fracture process involved two crucial stages, namely, the formation and extension of cracks [55].

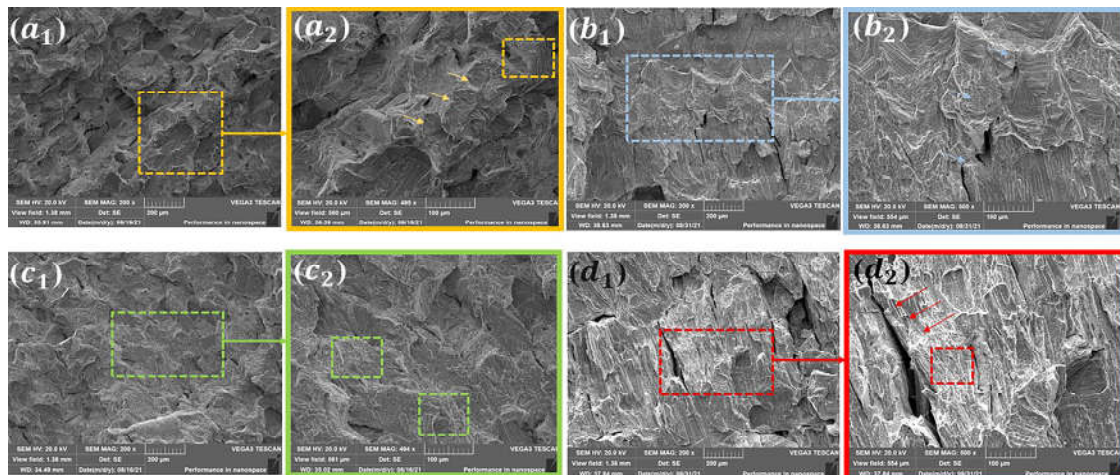


Figure 15. SEM images of tensile fracture morphology. (a1,a2) S1 sample, (b1,b2) S2 sample, (c1,c2) HTS1 sample, (d1,d2) HTS2 sample.

On the fracture surface of S1 shown in Figure 15(a2), there were a few dimples. These dimples were generated while deforming the specimen and grew rapidly along the tearing prongs, eventually forming a perforated fracture indicating ductile fracture mode. However, quasi-cleavage planes and cleavage ladders were observed in the region pointed out by the arrows. This implies that the fracture surfaces separated along specific crystalline surfaces, indicating the presence of brittle fracture modes. The ‘back-and-forth’ scanning method resulted in a combination of ductile and brittle fracture modes. The fracture surface of S2 shown in Figure 15(b2) reveals numerous small, irregular cracks expanding along the grain boundaries in the direction of the main cracks, resulting in herringbone shapes and cleavage ladders, which is a characteristic of the brittle fracture mode. The brittle fracture was related not only to the distribution of the second-phase particles but also to the high internal stress at the laser overlap caused by the island scanning strategy, which promoted crack extension and the formation of brittle fracture patterns [56]. Despite the presence of dimples in some areas, brittle fracture dominated, causing the island scanning strategy to display a mixed fracture pattern.

In summary, there is a significant relationship between the fracture mode and the scanning strategy. This could be attributed to the high-speed scanning and cooling rate of the laser, which resulted in the uneven microstructure of the material. Distinct variations in grain size and grain boundary distribution may have existed in different regions, causing different ductile and brittle properties in local areas, which, in turn, resulted in a mixed mode of ductile and brittle fracture. As a result, the SLM process frequently exhibited mixed fracture modes in selective laser melting [57,58].

In Figure 15(c2), the area of the dimples in the cracks after post-treatment is significantly reduced, and the brittle fracture part is increased, indicating that the precipitation of secondary $M_{23}C_6$ carbides at the grain boundary and the stress concentration reduced the plasticity of the alloy, which is consistent with the previous ultimate strain data. As shown in Figure 15(d2), due to the existence of a large number of cleavage ladders, there was a typical transgranular fracture feature, indicating that the plasticity was greatly reduced. The generation and extension of the cracks were mainly concentrated in the interior of the grains, which hindered the maintenance of the elongation of the sample.

4. Conclusions

- (1) Under the ‘back-and-forth’ scanning strategy, the material achieved the highest density and hardness of 99.74% and 9.61 GPa, respectively. In contrast, the island scanning strategy resulted in a density of 99.34% and hardness of 8.70 GPa. The interlayer rotation of the ‘back-and-forth’ scanning strategy made the molten pool more uniform and dense, thereby improving the density and hardness.
- (2) Liquefaction cracking (LC), solidification cracking (SC), and ductility dip cracking (DDC) were produced during printing. In the two scanning strategies, the interlayer rotation angle of 67° and the partition scanning characteristics helped to reduce the generation of cracks. On the contrary, the longer scanning line length and the overlapping area of the laser easily caused cracks. The scanning vector directly affected the crack vector.
- (3) The interlayer rotation of the ‘back-and-forth’ scanning strategy formed a shorter dendritic structure. In contrast, the partition characteristics and diversified heat dissipation directions of the island scanning strategy led to the anisotropy of the grains, and the plasticity reached the highest at 3.24%.
- (4) After post-processing, stress was easily released at the crack tip and produced strain-age cracking. The MC phase was decomposed into $M_{23}C_6$ and precipitated at the grain boundary, which reduced the plasticity of the material. The misorientation of grain was reduced, and the secondary γ' phase precipitated and grew to be uniformly dispersed in the matrix. The highest Young’s modulus (217.44 GPa) and the highest tensile strength (1421.71 MPa) of the material were achieved.

Author Contributions: B.Z., Z.X., H.Y. and H.S. conceived the idea; Z.X. and B.Z. conducted the experiments and analyses; B.Z., H.Y., P.Z., Q.L. and H.S. provided the data; all authors contributed to the writing and revisions. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by China Postdoctoral Science Foundation (2021M7010380) and Class III Peak Discipline of Shanghai—Materials Science and Engineering (High-Energy Beam Intelligent Processing and Green Manufacturing).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Deng, D.; Eriksson, R.; Peng, R.L.; Moverare, J. On the Dwell-Fatigue Crack Propagation Behavior of a High-Strength Ni-Base Superalloy Manufactured by Selective Laser Melting. *Metall. Mater. Trans. A-Phys. Metall. Mater. Sci.* **2020**, *51*, 962–972. [CrossRef]
2. Lenders, S.; Thoene, M.; Riemer, A.; Niendorf, T.; Troester, T.; Richard, H.A.; Maier, H.J. On the mechanical behaviour of titanium alloy TiAl₆V₄ manufactured by selective laser melting: Fatigue resistance and crack growth performance. *Int. J. Fatigue* **2013**, *48*, 300–307. [CrossRef]
3. DebRoy, T.; Wei, H.L.; Zuback, J.S.; Mukherjee, T.; Elmer, J.W.; Milewski, J.O.; Beese, A.M.; Wilson-Heid, A.; De, A.; Zhang, W. Additive manufacturing of metallic components—Process, structure and properties. *Prog. Mater. Sci.* **2018**, *92*, 112–224. [CrossRef]
4. Banoth, S.; Li, C.-W.; Hiratsuka, Y.; Kakehi, K. The Effect of Recrystallization on Creep Properties of Alloy IN939 Fabricated by Selective Laser Melting Process. *Metals* **2020**, *10*, 1016. [CrossRef]
5. Cloots, M.; Uggowitzer, P.J.; Wegener, K. Investigations on the microstructure and crack formation of IN738LC samples processed by selective laser melting using Gaussian and doughnut profiles. *Mater. Des.* **2016**, *89*, 770–784. [CrossRef]
6. Sabelkin, V.P.; Cobb, G.R.; Shelton, T.E.; Hartsfield, M.N.; Newell, D.J.; O’Hara, R.P.; Kemnitz, R.A. Mitigation of anisotropic fatigue in nickel alloy 718 manufactured via selective laser melting. *Mater. Des.* **2019**, *182*, 108095. [CrossRef]
7. Wang, Z.; Guan, K.; Gao, M.; Li, X.; Chen, X.; Zeng, X. The microstructure and mechanical properties of deposited-IN718 by selective laser melting. *J. Alloys Compd.* **2012**, *513*, 518–523. [CrossRef]
8. Murr, L.E.; Martinez, E.; Pan, X.M.; Gaytan, S.M.; Castro, J.A.; Terrazas, C.A.; Medina, F.; Wicker, R.B.; Abbott, D.H. Microstructures of Rene 142 nickel-based superalloy fabricated by electron beam melting. *Acta Mater.* **2013**, *61*, 4289–4296. [CrossRef]

9. Liu, G.; Du, D.; Wang, K.; Pu, Z.; Chang, B. Epitaxial growth behavior and stray grains formation mechanism during laser surface re-melting of directionally solidified nickel-based superalloys. *J. Alloys Compd.* **2021**, *853*, 157325. [CrossRef]
10. Divya, V.D.; Munoz-Moreno, R.; Messe, O.M.D.M.; Barnard, J.S.; Baker, S.; Illston, T.; Stone, H.J. Microstructure of selective laser melted CM247LC nickel-based superalloy and its evolution through heat treatment. *Mater. Charact.* **2016**, *114*, 62–74. [CrossRef]
11. Sui, S.; Tan, H.; Chen, J.; Zhong, C.; Li, Z.; Fan, W.; Gasser, A.; Huang, W. The influence of Laves phases on the room temperature tensile properties of Inconel 718 fabricated by powder feeding laser additive manufacturing. *Acta Mater.* **2019**, *164*, 413–427. [CrossRef]
12. Yang, J.; Li, F.; Wang, Z.; Zeng, X. Cracking behavior and control of Rene 104 superalloy produced by direct laser fabrication. *J. Mater. Process. Technol.* **2015**, *225*, 229–239. [CrossRef]
13. Maleki, V.; Omidvar, H.; Rahimpour, M.-r. Effect of gap size on microstructure of transient liquid phase bonded IN-738LC superalloy. *Trans. Nonferrous Met. Soc. China* **2016**, *26*, 437–447. [CrossRef]
14. Pilehrood, A.E.; Omidvar, H.; Shamsipur, A.; Sajuri, Z. Influence of transient liquid phase bonding followed by homogenization on the fatigue lifetimes of inconel 738 at elevated temperature. *J. Manuf. Process.* **2020**, *55*, 348–358. [CrossRef]
15. Egbewande, A.T.; Buckson, R.A.; Ojo, O.A. Analysis of laser beam weldability of Inconel 738 superalloy. *Mater. Charact.* **2010**, *61*, 569–574. [CrossRef]
16. Tang, Y.T.; Ghoussoub, J.N.; Panwisawas, C.; Collins, D.M.; Amirkhanlou, S.; Clark, J.W.; Németh, A.A.; Graham McCartney, D.; Reed, R.C. The effect of heat treatment on tensile yielding response of the new superalloy ABD-900AM for additive manufacturing. In *Superalloys 2020, Proceedings of the 14th International Symposium on Superalloys*; Springer: Cham, Switzerland, 2020; pp. 1055–1065.
17. Zhu, L.; Zhu, S.; Wang, F. Hot corrosion behaviour of a Ni plus CrAlYSiN composite coating in Na₂SO₄-25 wt.% NaCl melt. *Appl. Surf. Sci.* **2013**, *268*, 103–110. [CrossRef]
18. Yu, X.; Song, P.; He, X.; Khan, A.; Huang, T.; Li, C.; Li, Q.; Lu, K.; Chen, K.; Lu, J. Influence of the combined-effect of NaCl and Na₂SO₄ on the hot corrosion behaviour of aluminide coating on Ni-based alloys. *J. Alloys Compd.* **2019**, *790*, 228–239. [CrossRef]
19. Jalilvand, V.; Omidvar, H.; Shakeri, H.R.; Rahimpour, M.R. A Study on the Effect of Process Parameters on the Properties of Joint in TLP-Bonded Inconel 738LC Superalloy. *Metall. Mater. Trans. B-Process Metall. Mater. Process. Sci.* **2013**, *44*, 1222–1231. [CrossRef]
20. Ye, Y.; Wei, J.; Zou, G.; Long, W.; Bai, H.; Wu, A.; Liu, L. Microstructure of diffusion-brazing repaired IN738LC superalloy with uneven surface defect gap width. *Sci. Technol. Weld. Join.* **2017**, *22*, 617–626. [CrossRef]
21. Zhong, M.; Sun, H.; Liu, W.; Zhu, X.; He, J. Boundary liquation and interface cracking characterization in laser deposition of Inconel 738 on directionally solidified Ni-based superalloy. *Scr. Mater.* **2005**, *53*, 159–164. [CrossRef]
22. Hollaender, D.; Kulawinski, D.; Weidner, A.; Thiele, M.; Biermann, H.; Gampe, U. Small-scale specimen testing for fatigue life assessment of service-exposed industrial gas turbine blades. *Int. J. Fatigue* **2016**, *92*, 262–271. [CrossRef]
23. Zhang, X.; Chen, H.; Xu, L.; Xu, J.; Ren, X.; Chen, X. Cracking mechanism and susceptibility of laser melting deposited Inconel 738 superalloy. *Mater. Des.* **2019**, *183*, 108105. [CrossRef]
24. Kuhn, F.; Zeismann, F.; Brueckner-Foit, A.; Kadau, K.; Gravett, P. Crack paths in the superalloy IN738 in aged conditions. *Eng. Fract. Mech.* **2013**, *108*, 275–284. [CrossRef]
25. Ramakrishnan, A.; Dinda, G.P. Direct laser metal deposition of Inconel 738. *Mater. Sci. Eng. A-Struct. Mater. Prop. Microstruct. Process.* **2019**, *740*, 1–13. [CrossRef]
26. Xu, J.; Lin, X.; Zhao, Y.; Guo, P.; Wen, X.; Li, Q.; Yang, H.; Dong, H.; Xue, L.; Huang, W. HAZ Liquation Cracking Mechanism of IN-738LC Superalloy Prepared by Laser Solid Forming. *Metall. Mater. Trans. A-Phys. Metall. Mater. Sci. A* **2018**, *49*, 5118–5136. [CrossRef]
27. Heydari, D.; Fard, A.S.; Bakhshi, A.; Drezet, J.M. Hot tearing in polycrystalline Ni-based IN738LC superalloy: Influence of Zr content. *J. Mater. Process. Technol.* **2014**, *214*, 681–687. [CrossRef]
28. Carter, L.N.; Martin, C.; Withers, P.J.; Attallah, M.M. The influence of the laser scan strategy on grain structure and cracking behaviour in SLM powder-bed fabricated nickel superalloy. *J. Alloys Compd.* **2014**, *615*, 338–347. [CrossRef]
29. Jia, H.; Sun, H.; Wang, H.; Wu, Y.; Wang, H. Scanning strategy in selective laser melting (SLM): A review. *Int. J. Adv. Manuf. Technol.* **2021**, *113*, 2413–2435. [CrossRef]
30. Rashid, R.; Masood, S.H.; Ruan, D.; Palanisamy, S.; Rashid, R.A.R.; Brandt, M. Effect of scan strategy on density and metallurgical properties of 17-4PH parts printed by Selective Laser Melting (SLM). *J. Mater. Process. Technol.* **2017**, *249*, 502–511. [CrossRef]
31. Tang, X.; Zhang, S.; Zhang, C.; Chen, J.; Zhang, J.; Liu, Y. Optimization of laser energy density and scanning strategy on the forming quality of 24CrNiMo low alloy steel manufactured by SLM. *Mater. Charact.* **2020**, *170*, 110718. [CrossRef]
32. Nong, X.D.; Zhou, X.L. Effect of scanning strategy on the microstructure, texture, and mechanical properties of 15-5PH stainless steel processed by selective laser melting. *Mater. Charact.* **2021**, *174*, 111012. [CrossRef]
33. Cao, M.; Zhang, D.; Gao, Y.; Chen, R.; Huang, G.; Feng, Z.; Poprawe, R.; Schleifenbaum, J.H.; Ziegler, S. The effect of homogenization temperature on the microstructure and high temperature mechanical performance of SLM-fabricated IN718 alloy. *Mater. Sci. Eng. A* **2021**, *801*, 140427. [CrossRef]
34. Luo, S.; Huang, W.; Yang, H.; Yang, J.; Wang, Z.; Zeng, X. Microstructural evolution and corrosion behaviors of Inconel 718 alloy produced by selective laser melting following different heat treatments. *Addit. Manuf.* **2019**, *30*, 100875. [CrossRef]

35. Sotov, A.V.; Agapovichev, A.V.; Smelov, V.G.; Kokareva, V.V.; Dmitrieva, M.O.; Melnikov, A.A.; Golanov, S.P.; Anurov, Y.M. Investigation of the IN-738 superalloy microstructure and mechanical properties for the manufacturing of gas turbine engine nozzle guide vane by selective laser melting. *Int. J. Adv. Manuf. Technol.* **2020**, *107*, 2525–2535. [CrossRef]
36. Wongbunyakul, P.; Visuttiptitukul, P.; Wangyao, P.; Lothongkum, G.; Sricharoenchai, P. Effect of Reheat Treatment on Microstructural Refurbishment and Hardness of the As-cast Inconel 738. *High Temp. Mater. Process.* **2014**, *33*, 453–461. [CrossRef]
37. Bhardwaj, T.; Shukla, M. Effect of laser scanning strategies on texture, physical and mechanical properties of laser sintered maraging steel. *Mater. Sci. Eng. A* **2018**, *734*, 102–109. [CrossRef]
38. Yadroitsev, I.; Smurov, I. Selective laser melting technology: From the single laser melted track stability to 3D parts of complex shape. *Phys. Procedia* **2010**, *5*, 551–560. [CrossRef]
39. Tian, Y.; Tomus, D.; Rometsch, P.; Wu, X. Influences of processing parameters on surface roughness of Hastelloy X produced by selective laser melting. *Addit. Manuf.* **2017**, *13*, 103–112. [CrossRef]
40. Amirjan, M.; Sakiani, H. Effect of scanning strategy and speed on the microstructure and mechanical properties of selective laser melted IN718 nickel-based superalloy. *Int. J. Adv. Manuf. Technol.* **2019**, *103*, 1769–1780. [CrossRef]
41. Sharma, R.; Kumar, A. Track-scale simulations of selective laser melting to investigate development and mitigation of thermal stresses. *Lasers Manuf. Mater. Process.* **2019**, *6*, 464–492. [CrossRef]
42. Salman, O.; Brenne, F.; Niendorf, T.; Eckert, J.; Prashanth, K.; He, T.; Scudino, S. Impact of the scanning strategy on the mechanical behavior of 316L steel synthesized by selective laser melting. *J. Manuf. Process.* **2019**, *45*, 255–261. [CrossRef]
43. Liu, Y.; Yang, Y.; Wang, D. A study on the residual stress during selective laser melting (SLM) of metallic powder. *Int. J. Adv. Manuf. Technol.* **2016**, *87*, 647–656. [CrossRef]
44. Promoppatum, P.; Yao, S.-C. Influence of scanning length and energy input on residual stress reduction in metal additive manufacturing: Numerical and experimental studies. *J. Manuf. Process.* **2020**, *49*, 247–259. [CrossRef]
45. Dimitrov, D.; Becker, T.H.; Yadroitsev, I.; Booyesen, G. On the impact of different system strategies on the material performance of selective laser melting-manufactured Ti6Al4V components. *South Afr. J. Ind. Eng.* **2016**, *27*, 184–191. [CrossRef]
46. Wang, X.-j.; Liu, L.; Huang, T.-w.; Yang, W.-c.; Yue, Q.-z.; He, C.; Zhang, J.; Fu, H.-z. Grain boundary precipitation behavior in Re-containing nickel-based directionally solidified superalloys with carbon and boron additions. *Vacuum* **2020**, *179*, 109483. [CrossRef]
47. Nippes, E.F.; Grotke, G.; Savage, W.F. *Further Studies of the Hot-Ductility of High-Temperature Alloys*; Welding Research Council: Shaker Heights, OH, USA, 1957.
48. Young, G.; Capobianco, T.; Penik, M.; Morris, B.; McGee, J. The mechanism of ductility dip cracking in nickel-chromium alloys. *Weld. J.* **2008**, *87*, 31–43.
49. Wang, L.; Jiang, X.; Zhu, Y.; Ding, Z.; Zhu, X.; Sun, J.; Yan, B. Investigation of performance and residual stress generation of AlSi10Mg processed by selective laser melting. *Adv. Mater. Sci. Eng.* **2018**, *2018*, 7814039. [CrossRef]
50. Sun, X.; Song, W.; Liang, J.; Li, J.; Zhou, Y. Research and development in materials and processes of superalloy fabricated by laser additive manufacturing. *Acta Met. Sin* **2021**, *57*, 1471–1483.
51. Xu, J.; Ding, Y.; Gao, Y.; Wang, H.; Hu, Y.; Zhang, D. Grain refinement and crack inhibition of hard-to-weld Inconel 738 alloy by altering the scanning strategy during selective laser melting. *Mater. Des.* **2021**, *209*, 109940. [CrossRef]
52. Liu, H.; Ushioda, K.; Fujii, H. Elucidation of interface joining mechanism during friction stir welding through Cu/Cu-10Zn interfacial observations. *Acta Mater.* **2019**, *166*, 324–334. [CrossRef]
53. Huo, H.; Liang, Z.; Zhang, A.; Zhang, X.; Zhang, J.; Wang, Y. Anisotropy of mechanical properties of laser-cladding-deposited TC4 titanium alloy containing boron. *Chin. J. Lasers* **2019**, *46*, 1202008. [CrossRef]
54. Zhang, J.; Zhang, A.; Wang, H.; Zhang, X.; Wang, Y. Microstructure and anisotropy of high performance TC4 obtained by micro forging laser cladding deposition. *Chin. J. Lasers* **2019**, *46*, 0402009. [CrossRef]
55. Bieniawski, Z.T. Mechanism of brittle fracture of rock: Part I—Theory of the fracture process. *Int. J. Rock Mech. Min. Sci. Geomech. Abstr.* **1967**, *4*, 395–406. [CrossRef]
56. Kale, A.B.; Singh, J.; Kim, B.-K.; Kim, D.-I.; Choi, S.-H. Effect of initial microstructure on the deformation heterogeneities of 316L stainless steels fabricated by selective laser melting processing. *J. Mater. Res. Technol.* **2020**, *9*, 8867–8883. [CrossRef]
57. Yang, S.; Han, Q.; Yin, Y.; Gao, J.; Zhang, Z.; Gu, Y.; Low, K.W.Q. Effects of micrometer-sized TiB₂ on crack mitigation, mechanical and electrochemical performance of a Ni-based alloy fabricated by selective laser melting. *Opt. Laser Technol.* **2021**, *142*, 107240. [CrossRef]
58. Zhang, L.; Song, B.; Fu, J.J.; Wei, S.S.; Yang, L.; Yan, C.Z.; Li, H.; Gao, L.; Shi, Y.S. Topology-optimized lattice structures with simultaneously high stiffness and light weight fabricated by selective laser melting: Design, manufacturing and characterization. *J. Manuf. Process.* **2020**, *56*, 1166–1177. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Macroscopic Characteristic and Properties of Inconel 625 Cladding Layers on a Cylinder Liner Based on Laser Cladding Assisted by a Steady-State Magnetic Field

Xinlin Wang, Jing Zhu *, Yongchang Tian, Jinkun Jiang and Tianmin Guan *

School of Mechanical Engineering, Dalian Jiaotong University, Dalian 116028, China; wxl_me@djtu.edu.cn (X.W.); s45542568@163.com (Y.T.); jiangjinkundybala@163.com (J.J.)

* Correspondence: zj_dlme@163.com (J.Z.); gtm@djtu.edu.cn (T.G.)

Abstract: Cylinder liners, which are an vital part of marine diesel engines, are prone to damage owing to the pool working conditions of reciprocating friction and electrochemical corrosion. As a burgeoning manufacturing technology, laser cladding has a prospective application on repairing and performance enhancement of cylinder liners. The performance of cladding layers on cylinder liners reported by current studies is not satisfactory. The laser cladding, assisted by the steady state magnetic field on the cylinder liner, is an effectual method to cover the shortage. However, there are few studies about that. In this study, single-track Inconel 625 cladding layers were carried out on a cylinder liner, assisted by a steady-state magnetic field. The effects of the magnetic field intensity and direction on the geometrical characteristics (width, height, penetration, and dilution ratio), microstructure, phase composition, microhardness, wear resistance, and corrosion resistance were investigated. According to the results obtained, adding a magnetic field with a small magnetic field intensity can significantly enhance the flatness, hardness, friction, wear resistance, and corrosion resistance of the cladding layer. Applying a magnetic field in the horizontal direction was conducive to improving the corrosion resistance of the sample. With the application of a vertical magnetic field, the microhardness increased, and wear resistance, as well as the flatness of the cladding layer, were improved.

Keywords: cylinder liner; laser cladding; steady-state magnetic field; geometrical characteristics; mechanical properties

1. Introduction

The cylinder liner is a vital part of the diesel engine, which is an important piece of power equipment, but its working environment is very harsh [1–3]. The common failure forms of cylinder liners include wear and corrosion. The wear of the cylinder liner is caused by a combination of physical, chemical, and mechanical factors, and can be divided into abrasive wear, corrosion wear, and adhesive corrosion [4,5]. The corrosion forms of cylinder liners mainly include oxygen absorption corrosion, hydrogen evolution corrosion, and oxygen concentration corrosion [6–8]. Premature damage and scrapping of cylinder liners will lead to a waste of resources, so repairing cylinder liners is significant. Common repairing methods of cylinder liners include welding, plating, thermal spray, laser cladding technology, etc. However, parts repaired by welding technology are prone to thermal stress and deformation, with low bonding strength and limited coating thickness [9,10]. For the plating technology, the pretreatment process of workpiece surface is complex, tedious, and has a high cost. In addition, insufficient pretreatment or mistakes during operation may lead to rapid loss of coating and short service life after repairing. Thermal spraying technology makes the workpiece prone to porosity and oxide inclusion. Sometimes, the hardness and impact performance are unsatisfactory, which means the coating is easy to peel off [11]. Compared to the traditional repairing technology, laser cladding technology

is a cost-effective way to significantly improve the surface properties of materials, such as wear, corrosion, heat, oxidation, and fatigue resistance. During the laser cladding process, a laser beam is used to melt a powder material onto a thin layer of the substrate surface. The melted powder material then quickly solidifies to form a surface cladding layer. This process results in a layer with a low dilution rate and excellent bonding properties with the substrate. [12]. Therefore, the use of laser cladding to repair cylinder liner has become more popular lately. This method has gained attention due to its effectiveness.

The laser cladding processing is highly affected by the technological conditions. The thermal stress and phase transition stress caused by the large temperature gradient easily cause cracks. Cracks not only reduce coating's performance, but also shorten its service life, which is one of the important reasons hindering the popularization of laser cladding technology. Additionally, the coating's surface is uneven and fluctuates after laser cladding, which needs machining treatment. To solve the problems existing during laser processing, auxiliary treatment by external fields, such as the thermal, electromagnetic, and vibration fields, is a promising method [13–15]. The external energy field is combined with a thermal energy field provided by a laser to realize the regulation of heat transfer or mass transfer behavior of the molten pool. In particular, laser cladding with steady-state magnetic field assistance has the advantages of simple equipment, multiple control methods, and good control effects. The solidification of the molten pool and grain growth can be controlled, owing to the existence of the electromagnetic braking effect and thermo-magnetofluid effect. Some scholars have studied the steady-state magnetic field-assisted laser cladding, mainly focusing on the flow of the molten pool, composition distribution, and microstructure. M. Bachmann et al. discovered that the steady-state magnetic field can be used to generate induced a Lorentz force to change the shape of the coating in the laser manufacturing process [16,17]. O. Velde et al. used numerical simulation methods to study the effects of static magnetic fields on convection during metal surface growth, and found that static magnetic fields can control eddy currents and improve crystal quality [18]. C. Lee et al. used static stabilizing magnetic fields to suppress the flow on the upper surface of the pool during laser cladding, thus slowing the flow of molten pool, effectively reducing splashing and improving the surface quality of the cladding layer [19]. Q. Kang et al. found that magnetic fields have a significant influence on the defects and properties of laser cladding layers, which could improve element distribution and reduce crack sensitivity [20]. They also found the magnetic field generated a magnetostriction that reduces the elastic modulus, which can improve the cracking and wear resistance [21]. L. Wang et al. focused on the influence of a static magnetic field on the molten pool surface and carried out the cladding experiment, The result pointed out that the resistance generated by a Lorentz force slowed down the flow velocity of the fluid, thus making the molten pool surface smoother due to the effect of magnetic field [22]. T. Hu et al. established a two-dimensional transient cladding model using numerical simulation. It has been found that adding a stable magnetic field in the molten pool can effectively suppress its internal convection [23]. J. Yao et al. conducted a preliminary study using a numerical simulation method, but the mechanism of how a steady-state magnetic field suppressed the surface ripple was not clear. Therefore, they established a two-dimensional transient model of steady-state magnetic field-assisted laser cladding for simulation. It turned out that the steady-state magnetic field intensity interacted with the internal temperature field, flow field, and cladding surface topography and then reduced the dragging force of the WC particles [24].

Therefore, during the laser cladding process, the occurrence of defects such as cracks, pores, and segregation can be reduced by assisting a steady-state magnetic field, which changes the convective state and crystallization characteristics of the molten pool, which promotes the forming quality of the cladding layer. Until now, few studies have been conducted on the auxiliary effects of stable magnetic fields on the distribution of elements in Inconel 625 cladding layers on cylinder liners, and a large number of experiments guided by theoretical models are lacking. In this paper, a steady-state magnetic field was used to

reduce the cracks, smooth the surface, and improve the quality of the cladding layer to improve the surface quality of the cylinder liner.

2. Materials and Methods

2.1. Materials and Experimental Set-Up

Inconel 625 powder, which was produced by Hoganas (Ath, Belgium), was selected as the cladding powder, aiming to strengthen the damaged parts of cylinder liner with its high temperature corrosion, oxidation, and excellent wear resistance [25]. It has a particle size range of 45–150 μm . Grey cast iron HT300, which is a commonly used material for the cylinder liners of marine diesel engines, was used for the substrate with a size of 100 mm $\times$ 50 mm $\times$ 5 mm and surface roughness of 3.6 μm . Table 1 displays the chemical compositions of both the cladding powder and the substrate materials.

Table 1. Chemical composition of Inconel625 and HT300.

Materials	Element Content (wt.%)						
Inconel625	Ni 61.37	Cr 21.41	Mo 8.9	Fe 4.04	Nb 3.44	Al 0.2	C 0.061
HT300	Fe 93.84	C 2.9	Si 1.8	Mn 1.2	S 0.12	P 0.15	

As shown in Figure 1, a laser cladding system was used in this study, including a laser generator (LDF 4000–100, Laserline, Mulheim-Karlich, Germany), a coaxial laser cladding head (YC52, Precitec, Rotenfels, Germany), a six-axis industrial robot (ZH 30/60III, Kuka, Augsburg, Germany), and a gas coaxial powder feeder (RC-PGF-D, Raycham, Anshan, China), as well as a water cooler, air compressor, and other auxiliary equipment.

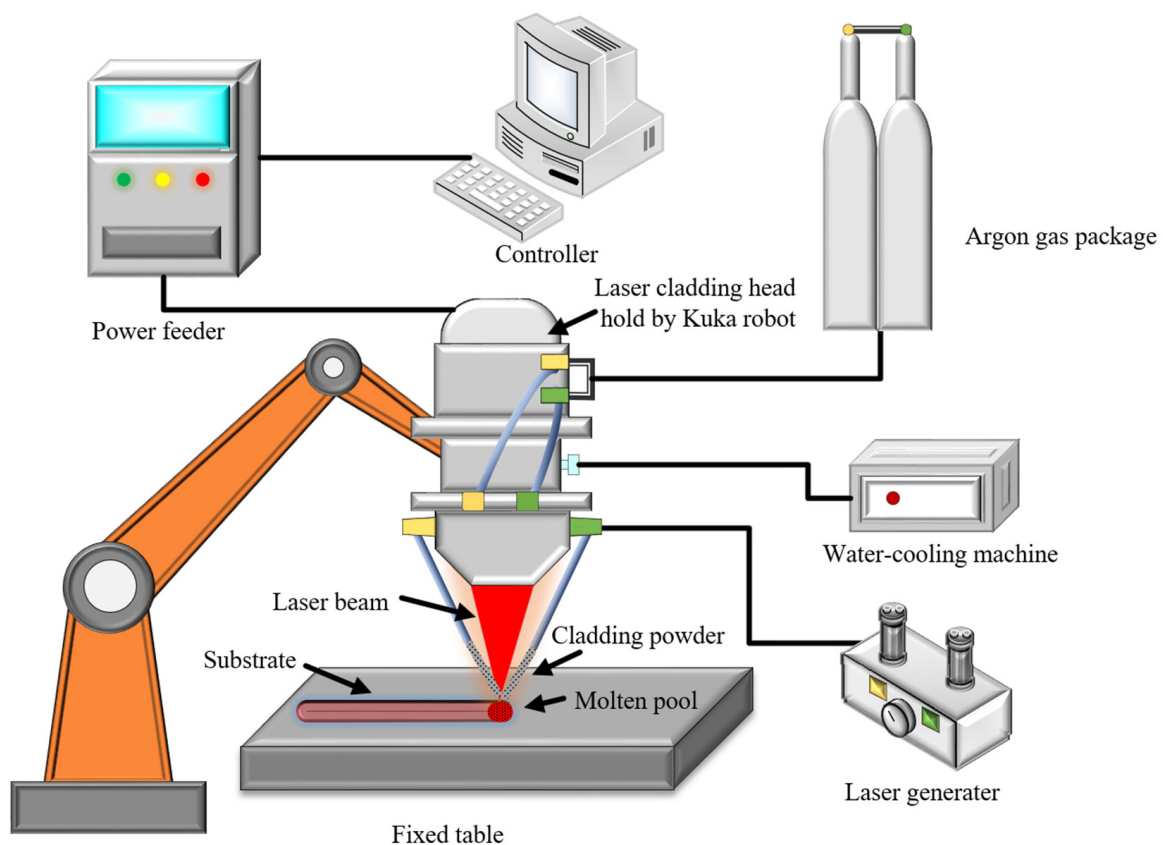


Figure 1. Schematic diagram of laser cladding system.

2.2. Design of Steady-State Magnetic Field and Parameters

The steady-state magnetic field of this experiment was provided by an NdFeb permanent magnet with a size of 100 mm × 100 mm × 50 mm. Magnetic field intensity and direction were used as experimental factors. The magnetic field intensity was adjusted by changing the distance between the magnets. As displayed in Figure 2, the magnetic field directions, including the horizontal left (L), horizontal right (R), vertical upward (U), and vertical down (D), were determined by the relative location between the magnets and molten pool. The laser cladding parameters, which can create the laser cladding layer with a uniform surface morphology and strong matrix bonding, were determined after long-term research and experimental comparison. The specific experimental parameters are shown in Table 2. In the laser cladding process, 99.99% pure Argon gas was used as both the carrier and shielding gas with flow rates of 400 L/h and 600 L/h, respectively. Under the conditions of different magnetic field intensity and direction, the single-track layers were deposited by laser cladding with the mentioned process parameters.

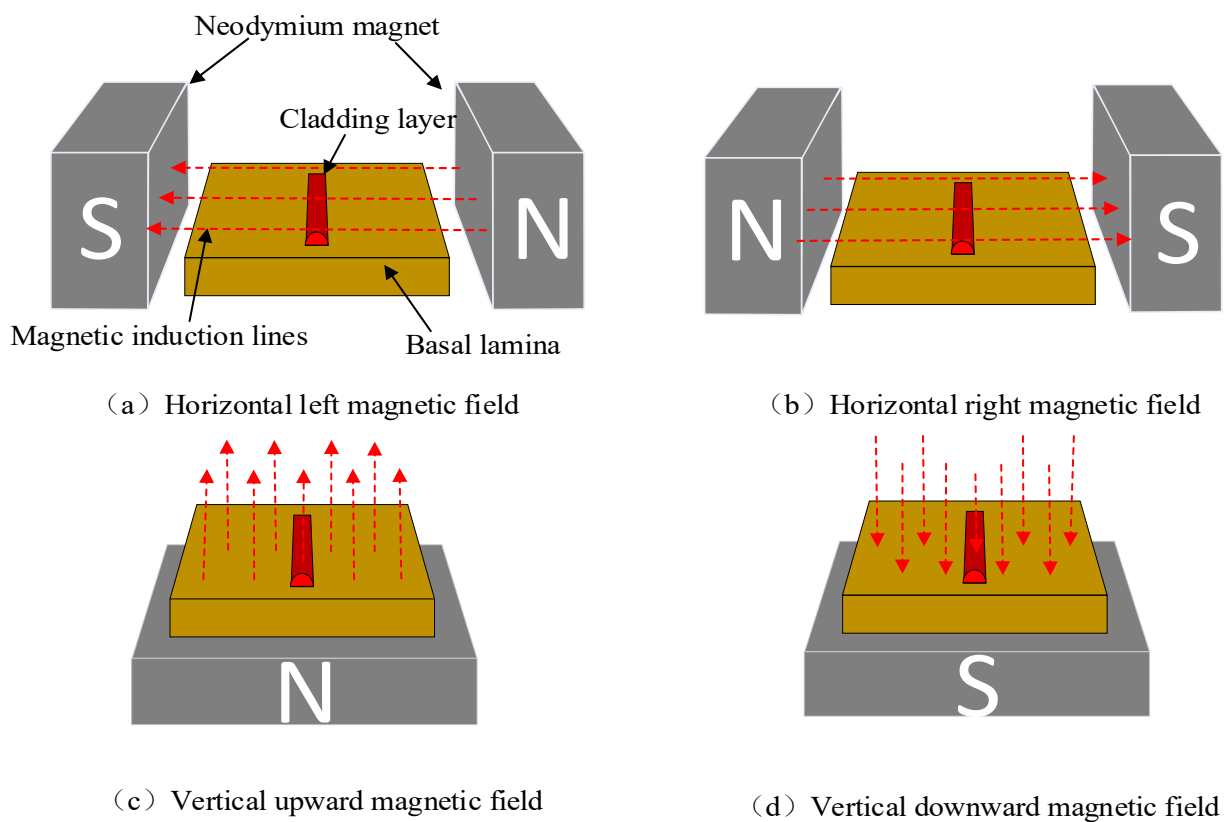


Figure 2. Schematic diagram of magnetic field direction.

Table 2. Experimental parameters.

	Laser Power (W)	Scan Speed (mm/s)	Powder Feed Rate (g/s)	Magnetic Field Intensity (mT)	Field Direction
F1	1200	5	20	0	L
F2				50	
F3				100	
F4				150	
F5				200	
F6	1200	5	20	150	R
F7				150	U
F8				150	D

2.3. Characterization Techniques

The test specimens were obtained by wire spark erosion, and then mechanically ground and polished. The surfaces were then etched in the saturated oxalic acid solution at 5 V DC. The geometric characteristics of the cladding layer (width, depth, height, and dilution) were obtained. The microstructure of the samples were observed using a metallographic microscope (Leica-DMi8, Leica, Wetzlar, Germany). The dilution adopted in this paper was calculated as the ratio of height to depth of cladding layer. The phase composition of cladding layer was analyzed by Empyrean X-ray diffractometer (Empyrean, Panaco, Malvern, The Netherlands), in which the voltage was 40 kV, the current was 40 mA, the Cu target was used as a cathode in the X-ray diffractometer, and the diffraction angle was 20° – 100° . The Vickers microhardness tester (HV-1000, Fangyuan, Jinan, China) was used for measuring the microhardness along the depth direction at the top, middle, and bottom region of the cladding layer, as well as the substrate. As shown in Figure 3, the interval between the measured points of microhardness was 0.1 mm, the load was 1 kg, and the loading time was 15 s. The friction wear testing machine (CETR-UMT, Bruker, Billerica, America) was used to conduct friction wear tests on the substrate and cladding samples, respectively. A tungsten steel ball was used for wear test, the loading force was 50 N, the sliding distance was 15 mm, and the sliding frequency was 1 Hz. Single samples were rubbed at 23°C for 20 min. The samples were weighed and recorded before and after wear tests using electronic balance (FA1004N, Qinghai, Shanghai, China) to calculate the abrasion loss. A three-electrode electrochemical corrosion system (CHR6601, Huachen, Shanghai, China) was used for electrochemical corrosion test where the solvent was NaCl solution with a mass fraction of 3.5%. The measurement range was -0.9 V – 0.2 V . The sampling rate was 0.01 V/s . Corrosion and abrasion tests were performed multiple times to ensure the credibility of the test results.

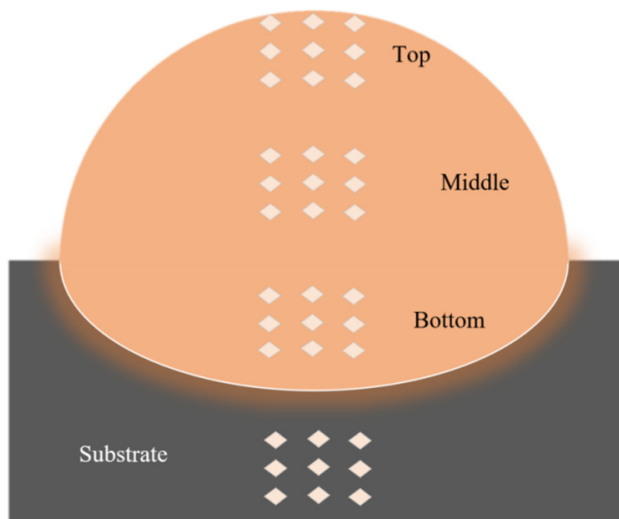


Figure 3. Schematic diagram of the Vickers hardness test.

3. Results and Discussion

3.1. Geometrical Characteristics

As displayed in Figure 4 and Table 3, from the perspective of the macro profile, the molten pool without the addition of a steady-state magnetic field presented a plump oval shape, and the molten pool contained many round pores. The macromorphology of the molten pool changed obviously when a higher intensity steady-state magnetic field was applied. Put another way, the overall macro profile of the cladding layer will be gradually flattened when a higher steady-state magnetic field is applied. This is the result of the interactions between hydrodynamics and electrodynamics. Figure 5 shows the mechanism of the inhibiting effect for the convection of the molten pool during the laser cladding

assisted by the steady-state magnetic field process, where the circle line represents the convection of molten pool, which is determined by the temperature field and v is the flow velocity of the molten pool.

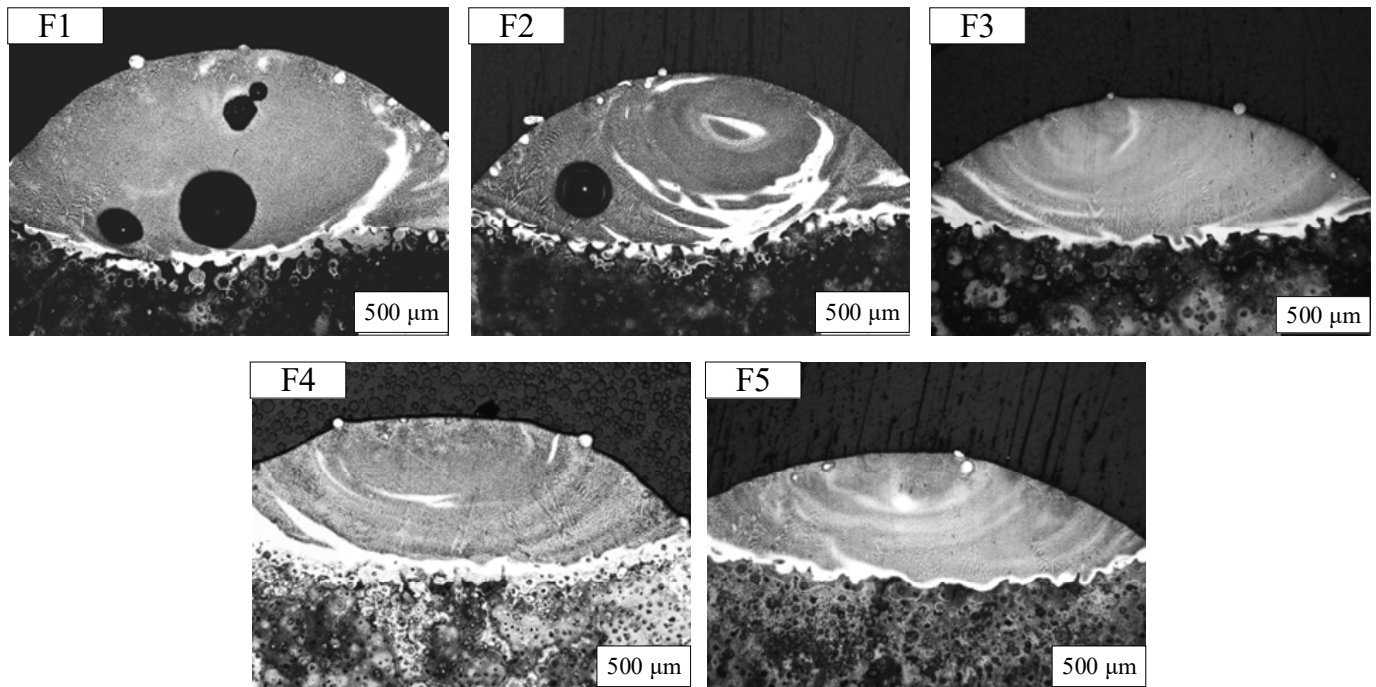


Figure 4. The morphology of the cladding layer under magnetic field intensity of (F1) 0 mT, (F2) 50 mT, (F3) 100 mT, (F4) 150 mT, and (F5) 200 mT.

Table 3. The cross-sectional size and dilution rate data of single-channel cladding layer under various applied steady-state magnetic field strengths.

No.	Melting Width/ μm	Melting Height/ μm	Melting Depth/ μm	Dilution Ratio %
F1	2595.80	704.72	511.83	42.07%
F2	2637.81	652.21	391.44	37.51%
F3	2666.55	602.39	228.23	27.48%
F4	2745.41	586.41	221.3	27.40%
F5	2855.73	537.32	197.97	26.92%

When the molten metal moves in the molten pool along the vertical direction of the magnetic field, an induced current will be generated. Such a moving material with an electric charge will experience the opposite Lorentz force (F_M) in a magnetic field. Therefore, when there is a magnetic field perpendicular to the laser cladding direction, a Lorentz force component, which is offset with the original molten pool motion direction, will appear, which results in a reduction in the convection velocity and the generation of the electromagnetic braking effect [26–29]. Under the condition of the steady-state magnetic field, the induced current (Jw) can be expressed as $\sigma v \times B$, where v is the velocity of fluid and σ is the conductivity of the solution. The expression of the induced Lorenn magnetic force is $J_w \times B$, where the induced electromagnetic force is proportional to the square of the intensity of the magnetic induction, and it can be judged that the direction of the induced electromagnetic force is in the opposite direction to the flow direction of the melt, which has the effect of inhibiting the convection of the molten pool.

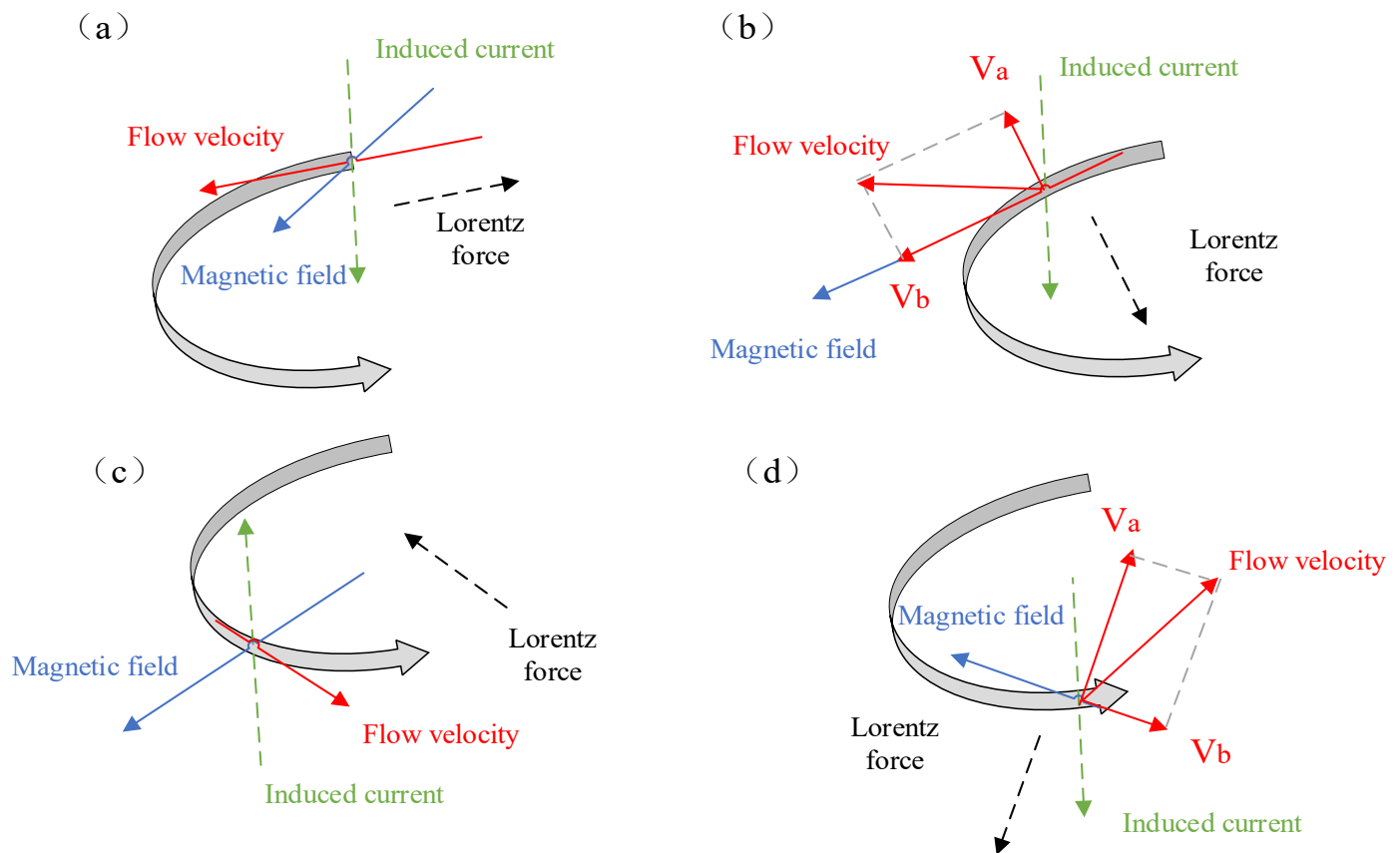


Figure 5. Schematic diagram of the mechanism of magnetic field inhibiting convection: (a) $B \perp V$, (b) $\theta < 90^\circ$, (c) $B \perp V$, (d) $\theta > 90^\circ$.

Due to the weakened convection, the high-temperature melt in the upper part of the molten pool cannot flow down to the bottom, which makes a large amount of the high-temperature melt stay in the top part of the molten pool and, as a result, less substrate was melted. Carbon in the substrate reacted with oxygen at high temperatures to produce pores. A lack of magnetic field assistance led to more substrate, which was melted with the high content of carbon elements, and it easily reacts to produce pores under high temperature conditions. So, the accumulated high-temperature melt in the top part of the molten pool transfers heat to the horizontal direction, which contributes to the increase in the width and reduction in pore defects.

Figure 6 and Table 4 present the morphology and size data of molten pool under different magnetic field directions. It is visible in Figure 6 that, when the horizontal magnetic field was applied, the height and width were higher, but the depth and dilution rate of the molten pool were lower. However, the external stable magnetic field has a limited effect on the width, which mainly depends on the laser cladding process parameters.

The convective movement in the laser molten pool is the fundamental cause of the concave–convex corrugating on the cladding layer’s surface. The steady-state magnetic field can reduce the velocity of the molten pool surface in the normal direction, thus reducing the elevation of the coating and smoothing the coating’s surface. With an increase in magnetic induction, the surface smoothness is further improved. Therefore, the electromagnetic braking effect of the steady-state magnetic field is a favorable factor for decreasing the surface fluctuation.

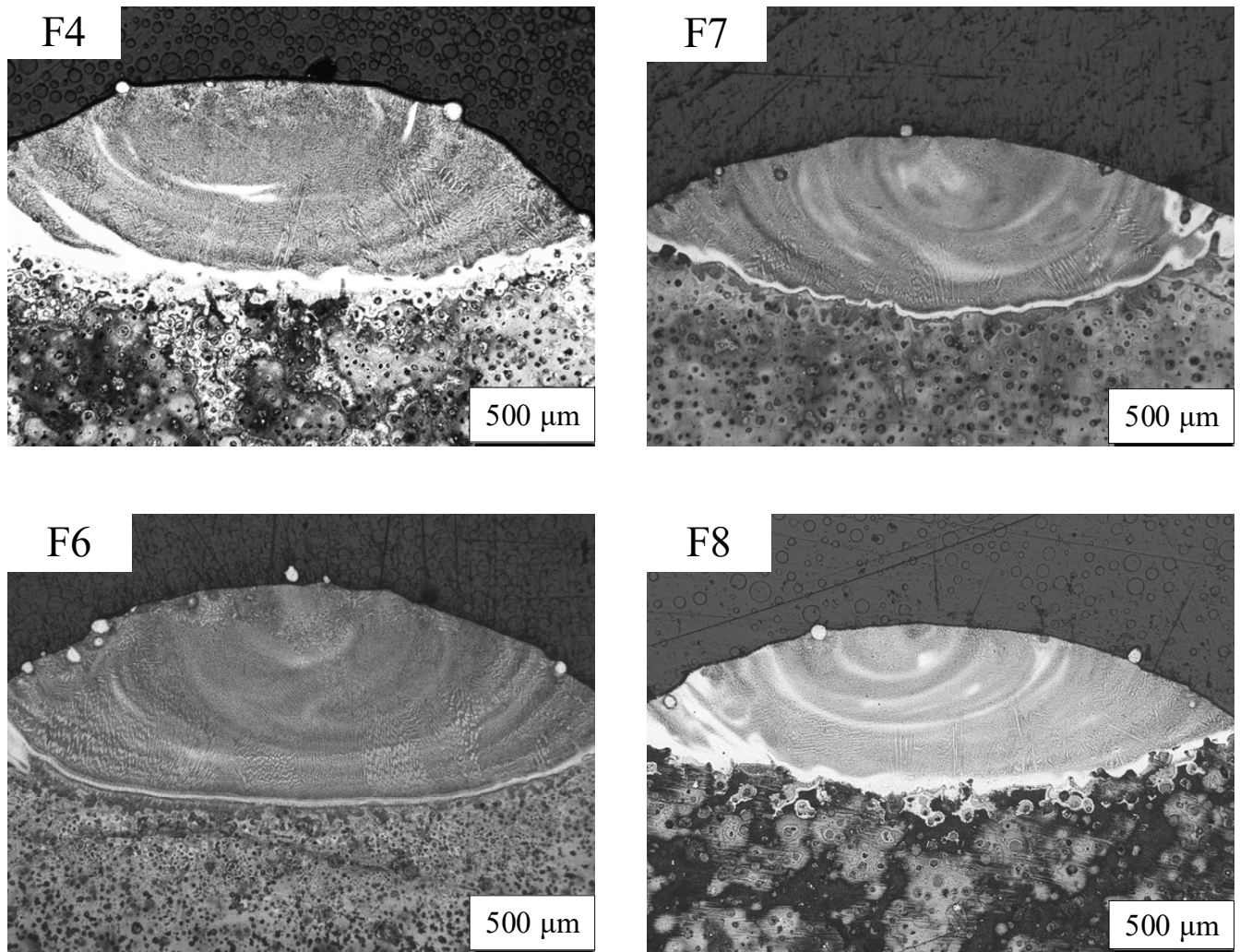


Figure 6. The morphology a of molten pool under magnetic field direction of (F4) left, (F6) right, (F7) upward, and (F8) downward.

Table 4. The data on the cross-sectional size and dilution rate for a single cladding layer has been obtained under magnetic fields in all directions.

No.	Melting Width/ μm	Melting Hight/ μm	Melting Depth/ μm	Dilution Ratio %
F4	2745.41	586.41	221.3	27.40%
F7	2785.04	610.91	229.65	28.35%
F6	2686.1	612.99	242.55	29.99%
F8	2688.98	464.23	320.21	40.82%

3.2. Microstructure

Figure 7 displays the cross-sectional structure of the Inconel 625 cladding layer with different magnetic field intensities. It is visible in Figure 7 that the dendrite growth followed the typical solidification microstructure characteristics of laser cladding; that is, the microstructure mainly changed from planar crystals near the bottom to a cellular and columnar dendritic near the middle, and then to epitaxial crystals near the top along the direction of the cladding height, regardless of whether a steady-state magnetic field was applied. F1 shows the cladding layer without a steady-state magnetic field. The microstructure presented relatively small columnar crystals in the bottom and middle

regions of F1, whose crystal growth direction was mainly towards the maximum heat dissipation direction. Since the isotherm was perpendicular to the heat dissipation direction, the dendrite growth direction was perpendicular to the isotherm of this layer. F2 and F3 shows the microstructure of the cladding layers under the steady-state magnetic fields with magnetic field intensities of 50 mT and 100 mT. The columnar dendrites near the bottom were slightly thicker than those without an applied magnetic field. The convection at the bottom interfered with the external transverse steady magnetic field, and changed the heat flow direction of the cladding layer slightly at a small magnetic field intensity. The growth direction of the dendrite was about 70° – 80° in the horizontal direction. F4 presents the microstructure of the cladding layer when a 150 mT steady-state magnetic field is added. It can be found that a larger range of strong columnar dendrites with more orientation appeared near the bottom. These dendritic stems were arranged neatly, and the growth direction was about 60° – 45° from the horizontal direction. With an increase in the steady-state magnetic field intensity, the electromagnetic braking effect was increasingly stronger, which reduced the velocity of convection. In this case, the primary dendrites grew along the direction of heat flow, but the secondary dendrites were inhibited to a greater extent. In the middle region, there were a large number of dendrites, and many fine equiaxed crystal structures were surrounded between and above each dendrite. F5 is the microstructure with a stable magnetic field intensity increased by 200 mT. Many columnar dendritic crystals with neatly arranged trunks can be found at the bottom and middle. The angle between the growth direction and the horizontal line was reduced to about 45° .

Additionally, compared to the cladding structure without a magnetic field, the dendrites with different directions changed to dense equiaxed structures in the middle and top with an increase in the constant magnetic field intensity. When a low-intensity magnetic field was applied to the solidification of the liquid metal, the temperature gradient at the solidification front decreased with an increased magnetic Taylor number. Simultaneously, the enhancement of the magnetic field intensity increased the induced current in the molten pool, and generated a larger magnetic Taylor number and a smaller temperature gradient, which were conducive to the formation of equiaxed crystals [30]. Therefore, the auxiliary of a stable magnetic field applied during the laser cladding process can reduce the internal energy exchange, the temperature difference of the interface front, and the concentration of the crystallization area of the supercooling degree, and improve the stability of the crystallization front, to promote the creation of numerous equiaxed crystals.

On the other side, under the condition of the steady-state magnetic field, the liquid metal generated a relative flow in the crystallization front, and scoured or fused the formed grains. These broken grain fragments were brought into the molten pool by the convection, and became new nucleation particles, forming a finer crystal structure, promoting the formation of equiaxed crystals, and were conducive to refining the cladding layer structure. Therefore, with an increase in magnetic field intensity, a larger range, denser, and smaller equiaxed crystals ensured excellent performance of the entire cladding layer. Simultaneously, when the constant magnetic field intensity increased, dendrites in different directions were transformed into dense equiaxed crystal structures in the middle and top of the cladding layer. Dendrites also appeared over a wider area, and they were more robust and organized than before.

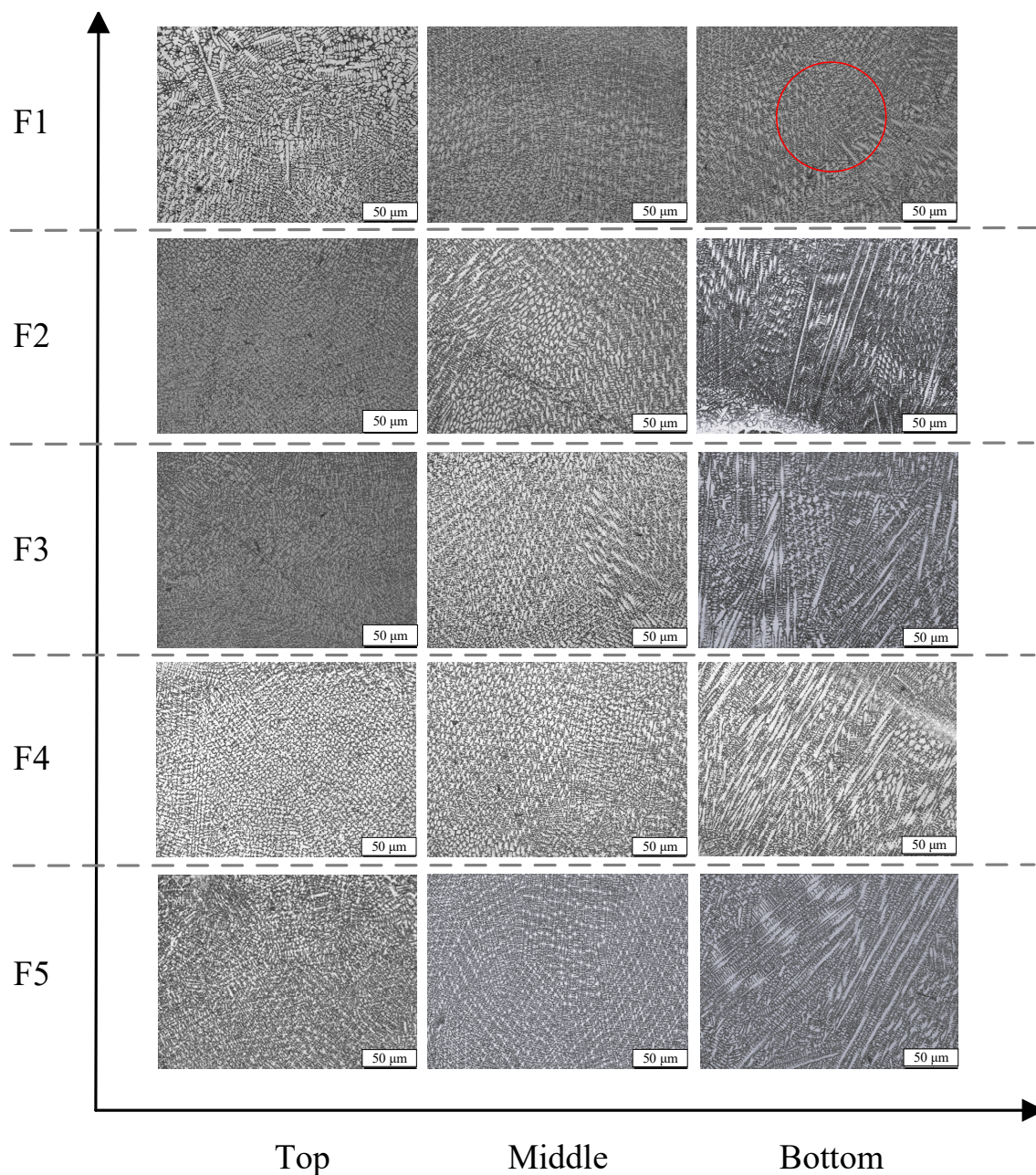


Figure 7. The microstructure of the molten pool under different magnetic field intensities.

Figure 8 shows the direction of the dendritic growth when different magnetic field intensities are used. As observed in Figure 8, a stable magnetic field led to dendrite coarsening, and its growth direction extended towards the direction of maximum heat dissipation. Since the magnetization of the Inconel 625 nickel–iron alloy in a molten state caused changes in magnetization energy, the crystal contained iron, which is easy to magnetize, and the crystal had the magnetic anisotropy. When the paramagnetic substance was magnetized, the magnetic moment of the molecule was parallel to the applied magnetic field direction, so the magnetized axis was biased to the magnetic field direction. The magnetization X_m of Inconel 625 is 50–100, and its magnetic anisotropy is significant when placed in a magnetic field, so that the axis of magnetic anisotropy is deflected towards the magnetic field direction and tends to be parallel to the magnetic field direction. In the cladding layer, the growth direction of dendritic crystals will change when the steady magnetic field is not applied; that is, when the steady magnetic field is applied horizontally

to the left, the dendrites on the right side of the molten pool will be deflected horizontally, and the angle formed between the growth direction and the horizontal direction decreases, leading to a change in the growth mode of dendritic crystals. The influence of a steady magnetic field on dendrite deflection is limited in a complex, convective environment. However, these two factors work together to cause some dendrites to grow along the stable magnetic field direction, and the dendrites show a tendency to grow in that direction. This may be due to the maximum heat dissipation direction of the liquid flow and the horizontal magnetic field. Figure 9 shows the direction of dendritic growth with different directions of magnetic fields with an intensity of 150 mT. It can be seen from Figure 9 that changing the direction of the magnetic field had similar effects on the top and middle regions of the cladding layer. The auxiliary of a steady-state magnetic field made dendritic and cellular crystals stronger and extend towards the direction of maximum heat dissipation. Similarly, compared to the horizontal magnetic field, the vertical magnetic field caused the dendrites to grow at a smaller angle in the vertical direction without any external factors after magnetization; that is, they deflected and tended to grow steadily along the vertical direction.

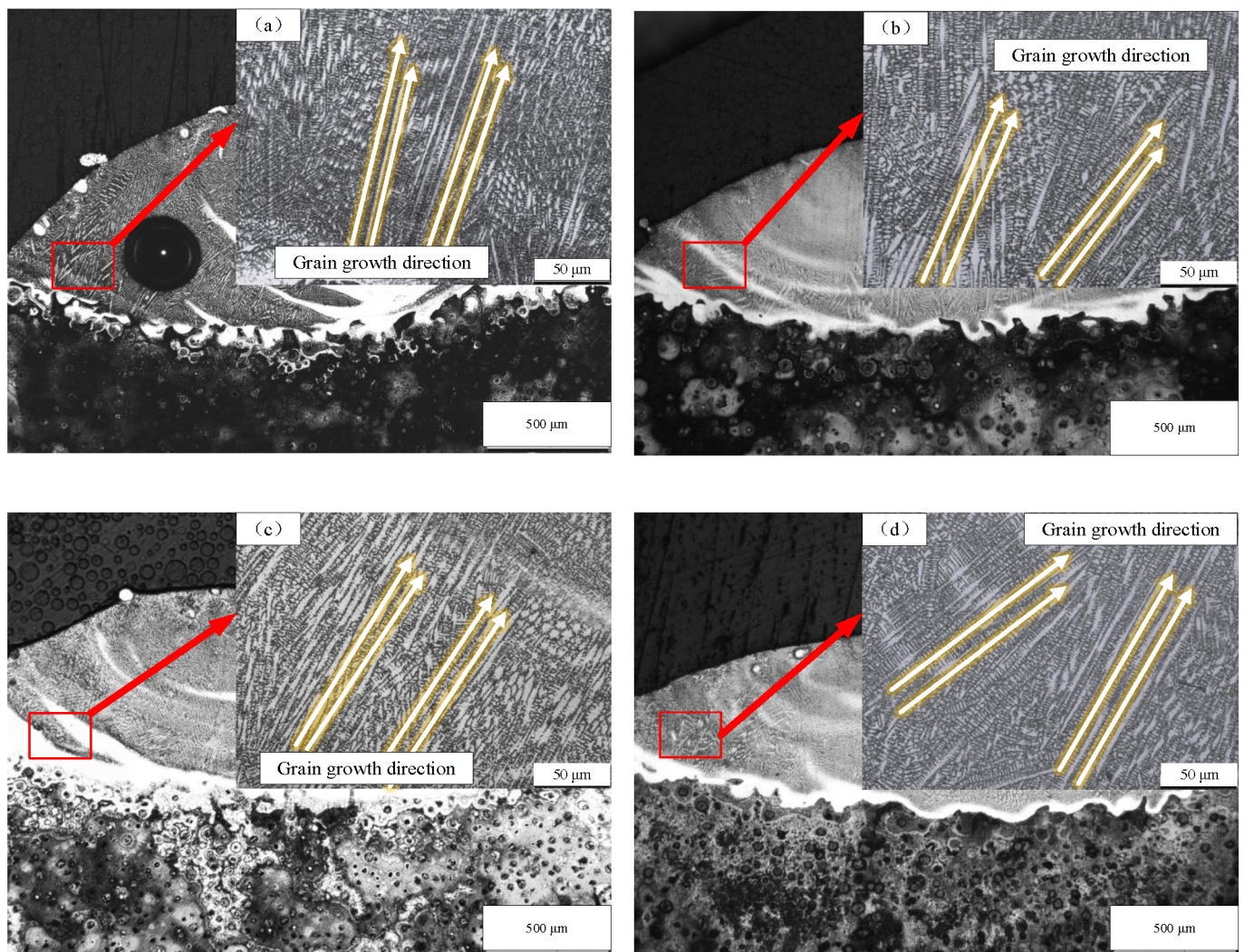


Figure 8. The direction of dendritic growth under magnetic fields with intensities of (a) 50 mT, (b) 100 mT, (c) 150 mT, (d) 200 mT.

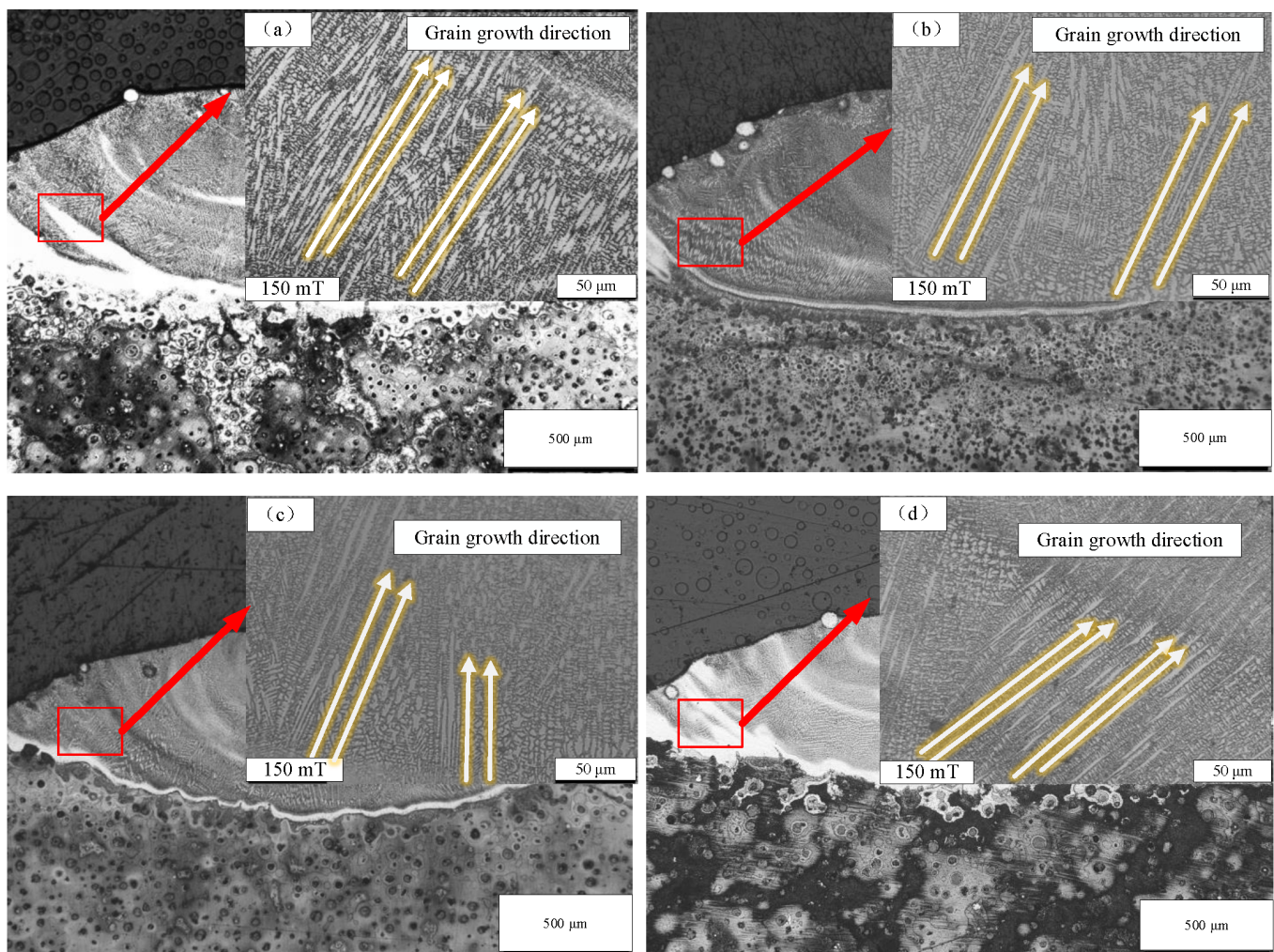


Figure 9. The direction of dendritic growth with the (a) L, (b) R, (c) U, (d) D directions of the magnetic fields with an intensity of 150 mT.

3.3. XRD Pattern Analysis

As displayed in Figure 10, the cladding layer phase was composed of the matrix phase of γ -Ni, the Laves phase of Ni_2Nb , and the strengthened phase of Ni_3Nb , which were all included in the atlas of each experimental group. It is indicated that the composition of the cladding layer phase was not changed. As the steady-state magnetic field intensity increased, the content of γ -Ni increased, and the strengthening phase of Ni_3Nb was enhanced. However, the Laves phase of Ni_2Nb decreased. This effect caused the molten pool to flatten, and increased the surface heat dissipation area, leading to an increase in the cooling rate of the molten pool surface. Therefore, a decrease in the Laves phase is directly related to an increase in the cooling rate. Figure 10b displays that the change in magnetic field direction not only does not change the phase composition, but also has the same level of influence on the phase content. It can be analyzed from Figure 10b that the steady-state magnetic field added in the horizontal direction had a higher diffraction peak than that of the matrix phase and the strengthened phase added in the vertical direction, while the diffraction peak of the Laves phase was lower. When the steady magnetic field with D direction was applied, the cross-section width of the cladding layer was slightly wider than that of the upward magnetic field, and the height and depth of the molten pool were lower, resulting in better surface heat dissipation performance, and a lower content of the Laves phase between dendrites in the molten pool.

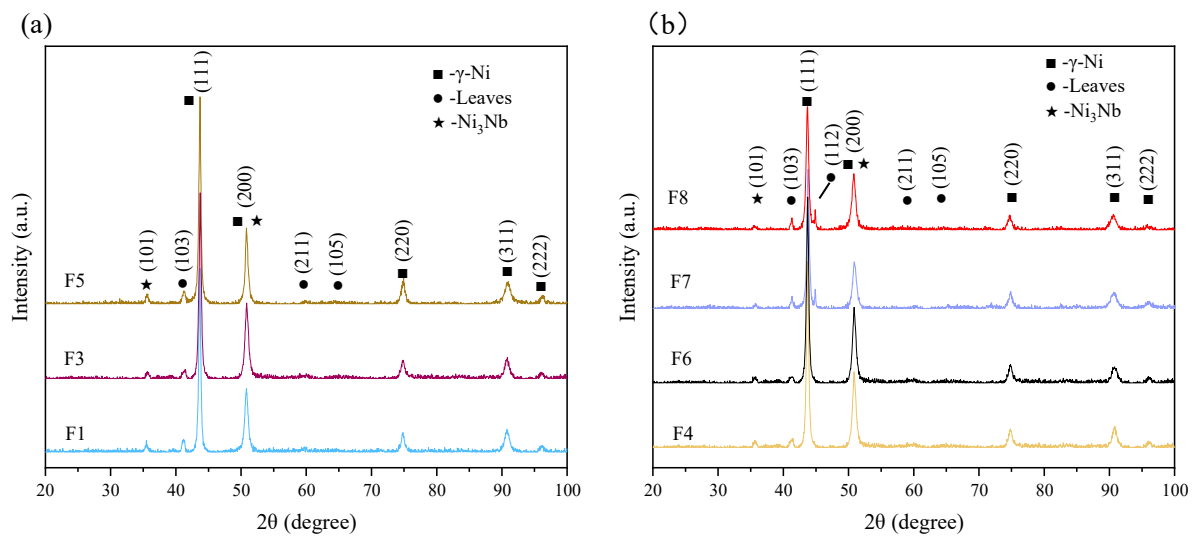


Figure 10. X-ray diffraction spectra of the cladding layers with different: (a) intensities and (b) magnetic field directions.

Table 5 shows the XRD data of the matrix phase γ -Ni on the (111), (200), and (220) crystal planes. The diffraction peak data presented show that the diffraction peaks of the γ -Ni matrix phase on the two crystal planes (111) and (200) all shifted to low angles, indicating that the lattice constant of the γ -Ni matrix phase solid solution changed with an increase in magnetic induction intensity. The matrix phase γ -Ni solid solution lattice constant α is expressed as:

$$\alpha = \frac{\lambda \sqrt{H^2 + K^2 + L^2}}{2 \sin \theta} \quad (1)$$

Table 5. XRD data of matrix phases gamma-Ni on the (111), (200), and (220) crystal planes.

	Crystal Face Index H, K, L	Diffraction Angle ($2\theta/^\circ$)	Lattice Constant (α)	Half-Height Width (B)
F1	(111)	43.772	3.5778	0.3606
F3		43.732	3.5810	0.3985
F5		43.693	3.5840	0.4479
F1	(200)	50.823	3.5888	0.4324
F3		50.823	3.5888	0.6087
F5		50.784	3.5913	0.6117
F1	(220)	74.852	3.5836	0.6072
F3		74.852	3.5836	0.6687
F5		74.930	3.5804	0.6399

The lattice constant, half-width, and height of the matrix phase γ -Ni solid solution increased with an increase in magnetic induction intensity. This indicated that the steady-state magnetic field can not only enhance the solid solubility of the matrix phase γ -Ni, but also refine the grain. In liquid metals, atoms lose their valence electrons to form ions, which move randomly. When a magnetic field is applied, the liquid cuts the magnetic field lines and creates a Lorentz force, causing the ions to rotate around them. Due to the differences in the mass and charge of Ni, Fe, Nb, and Cr, their plasma behaves differently in the molten pool, and various solute particles have a relative motion to the matrix phase under the condition of the magnetic field. This motion enhances the diffusion motion of solute particles in the matrix phase, and eventually leads to an increase in the solute elements in the matrix phase γ -Ni solid solution. The content increase in the γ -Ni solid solution can

stabilize the crystal structure. The enhancement effect increases with the strength of the constant magnetic field.

As shown at the bottom of F1 in Figure 7, a reference line with a radius of 50 μm was drawn on the images to obtain the grain size by determining the number of grains crossing the reference line. The results of the grain sizes are shown in Table 6.

Table 6. Grain size (μm).

	F1	F3	F5
Bottom	3.96	3.58	3.29
Middle	3.46	2.38	2.26
Top	2.24	2.23	2.11
Average	3.22	2.73	2.55

As shown in Tables 3 and 6, after applying a steady-state magnetic field, the grain structure of the entire coating became more refined. This suggests that the thermoelectric magnetofluid effect was the primary factor influencing the solidification process. In the solidification process, the first precipitated solid phase and melt exist at the same time to form a paste zone. The different temperatures between solid phase and liquid phase in the pasting zone will produce a temperature gradient (ΔT) in these two phases, so that the solid/liquid phase has different thermoelectric potential. Generally, the solid/liquid phase is regarded as a closed loop, which generates the thermoelectric potential difference $\Delta V = (\eta_L + \eta_S) \times \Delta T$, generating thermal current J_{TE} , and the expression is [31–33]

$$J_{TE} = \frac{-\sigma_S \sigma_L f_L}{\sigma_S f_S + \sigma_L f_L} (S_S - S_L) T \quad (2)$$

where S_S , S_L are the electrical conductivity; S_S , S_L are the thermoelectric potential ratio; and f_S , f_L are the volume fractions. The thermoelectric force can be expressed by the following formula [31–33]:

$$F_{TE} = \frac{-\sigma_S \sigma_L f_L}{\sigma_S f_S + \sigma_L f_L} (S_S - S_L) \Delta T \times B \quad (3)$$

In the formula, F_{TE} is the thermoelectric force generated by the steady-state magnetic field; B is magnetic induction intensity.

The steady-state magnetic field can produce opposing effects on the solution pool through the electromagnetic braking effect and thermoelectric magnetofluid effect, which promote grain magnetization and dendrite structure fusion. The electromagnetic braking effect can weaken the flow velocity of the fluid, inhibit the formation of equiaxed crystals, and promote the growth of columnar crystals. The thermoelectric magnetic force acting on dendrites by the thermoelectric magnetofluid effect can refine grains [34]. Based on the changes in the macroscopic morphology and microstructure of the coating in this section, it has been observed that a steady-state magnetic field can have an electromagnetic braking effect on the molten pool, which can result in a smoother surface. However, the steady-state magnetic field can also refine the grain structure, which indicates that the steady-state magnetic field also has a thermo-magnetic fluid effect on the molten pool.

3.4. Microhardness

The hardness of a material is an important mechanical property index, which shows the ability of the surface to resist deformation. It is visible in Figure 11 that the hardness of the cladding layer after cladding with the Inconel 625 alloy was above 360 HV, which was much higher than the measured value of 246.3 HV of the matrix gray cast iron. There was a small difference in the hardness between the middle region and the bottom region, but the bottom hardness was slightly lower than that of the middle region, because the middle part of the cladding layer contained significantly more cellular crystal structures, while the bottom was mostly occupied by the dendritic crystal, whose hardness was lower

than the cellular crystal. The hardness of the top was slightly higher than that of the rest region, mainly because of the small G/R at the top of the cladding layer, the large undercooling degree, and the equiaxed crystal structure with a smaller grain size. In addition, with increasing magnetic induction intensity, the microhardness distribution value of the cladding layer showed a gradual increase. This indicates that the strength of the magnetic field has a significant impact on the microhardness of the cladding layer, and the thermoelectric magnetofluid effect played a significant role. The existence of the temperature gradient and the potential difference between the solid and liquid phase formed a closed loop circuit that resulted in the creation of induced current on the newly crystallized dendrites. The current generates a Lorentz force under the condition of the magnetic field, and the Lorentz force acts on the dendrites. Combined with the mechanical scour effect of the Marangoni flow on the dendrites, the crystallized dendrites are broken to form a new nucleation, thus improving the nucleation rate and refining the grains that contribute to the increase in microhardness. As can be seen from Figure 11, the top hardness of the cladding layer under any magnetic field direction was slightly higher than that of the middle and bottom of the cladding layer. From the perspective of different magnetic field directions, the hardness of each region of the cladding layer was the highest when the vertical downward steady magnetic field was added, followed by the vertical upward magnetic field direction, while the hardness difference was small when the horizontal magnetic field was added. The grain size of the magnetic field in the vertical direction was smaller than that of the magnetic field added in the horizontal direction, so the experimental results were consistent with the law of the calculated data.

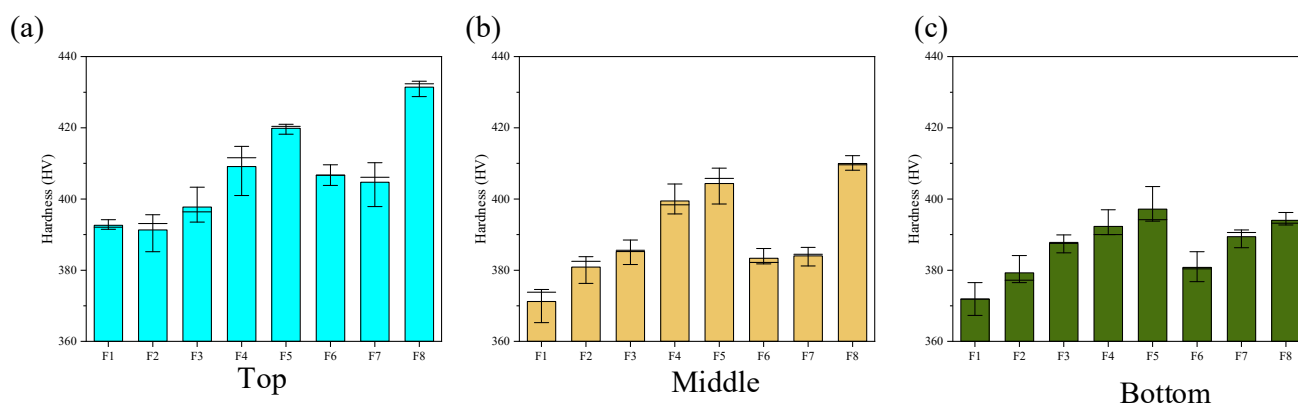


Figure 11. The microhardness of the cladding layers: (a) top; (b) middle; (c) bottom.

It is visible in Figure 11 that the hardness of the cladding layer top part under any magnetic field direction was slightly higher than the middle and bottom. From the perspective of different magnetic field directions, the hardness of each region of the cladding layer was the highest when the vertical downward steady magnetic field was added, followed by the vertical upward magnetic field direction, while the hardness difference was small when the horizontal magnetic field was applied. The vertical direction resulted in a smaller grain size for the magnetic field compared to the horizontal direction, so the experimental results were consistent with the law of the calculated data.

3.5. Wear Resistance

To obtain better wear performance for marine diesel engine cylinder liners, and to study the influence law of a magnetic field on the friction coefficient and wear weight loss of the cladding layer, the magnetic field intensity and magnetic field direction were changed in this section, and the average data were obtained from three wear tests for each sample, respectively.

It is visible in Figure 12 and Table 7 that the wear loss of substrate was the highest. With an increase in magnetic field intensity, the wear loss of the cladding layer decreased to

different degrees. At a magnetic field strength of 200 mT, the cladding layer exhibited the best wear resistance, with a wear mass of approximately 14.4 mg and an average friction coefficient of 0.5902. Compared to the other magnetic field direction, the abrasion loss of the cladding layer fabricated with the R direction presented highest value of 32.4 mg, and the average friction coefficient was 0.72. When the D direction was applied, the abrasion loss was about 16.9 mg, and the average friction coefficient was 0.59, which means the cladding layer presented the optimal wear resistance.

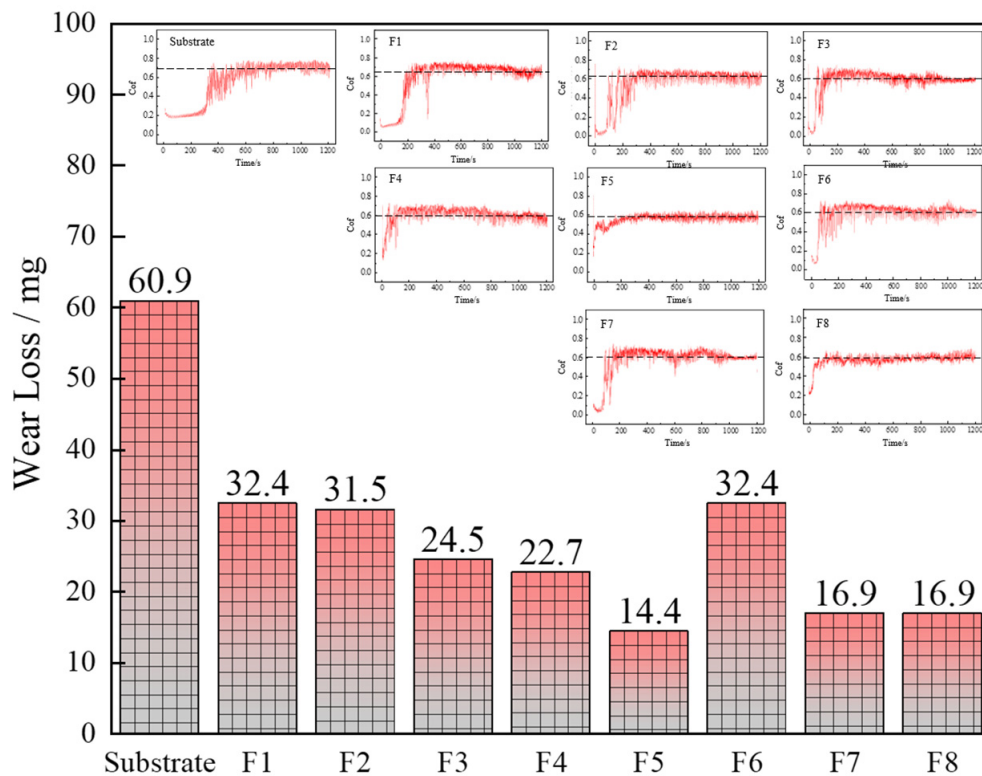


Figure 12. The wear amount and friction coefficient of the cladding layer.

Table 7. The abrasion loss and friction coefficient of the cladding layer.

Sample	Abrasion Loss/mg	Coefficient of Friction
Substrate	60.9	0.704
F1	32.4	0.637
F2	31.5	0.631
F3	24.5	0.613
F4	22.7	0.604
F5	14.4	0.590
F6	32.4	0.633
F7	20.8	0.608
F8	16.9	0.599

The higher the hardness result, the lower the friction coefficient and the abrasion loss, which means the better the friction performance. This is due to the presence of a hardness difference between the friction pairs, which leads to plastic deformation of the softer material, with more material being adhered and torn in a relative motion, producing more abrasion loss and leading to an increase in the friction coefficient. Reducing this hardness difference by increase the hardness of softer material reduces the friction coefficient and the abrasion loss, resulting in a better friction performance.

Figure 13 displays the morphology of the coatings. It is visible that when no magnetic field was applied, there were mainly two types of wear on the surface of the substrate:

abrasive and fatigue wear. The surface of the cladding layer presented an uneven state, and there were a lot of pear grooves, stratified zones, and particulate matter. In addition, under the action of the high uplift caused by the plastic deformation, obviously worn edges can be produced. At the same time, some shallow ploughing and different degrees of spalling, accompanied by severe material transfers and slight cutting, were presented. As shown in F1–F8 of Figure 13, the decrease in the depth of the scratches and the distance between the scratches indicated the positive influence of the magnetic field on the wear resistance of cladding layer. Only a small amount of material fell off the surface, with minimal deformation and scratch depth, at a magnetic field intensity of 200 mT. This is due to the density of equiaxed crystals in the cladding layer, which increased with the magnetic field intensity and resulted in the presence of equiaxed crystal structures, significantly enhancing the overall microhardness of the coating after the magnetic field was applied. In addition, the magnetic field can partially prevent convection during the laser cladding process, and results in a more even distribution of carbide particles. This not only effectively prevented crack propagation, but also enhanced the bonding strength between the carbide particles and the equiaxed matrix. Consequently, the wear resistance of the cladding layer was significantly improved.

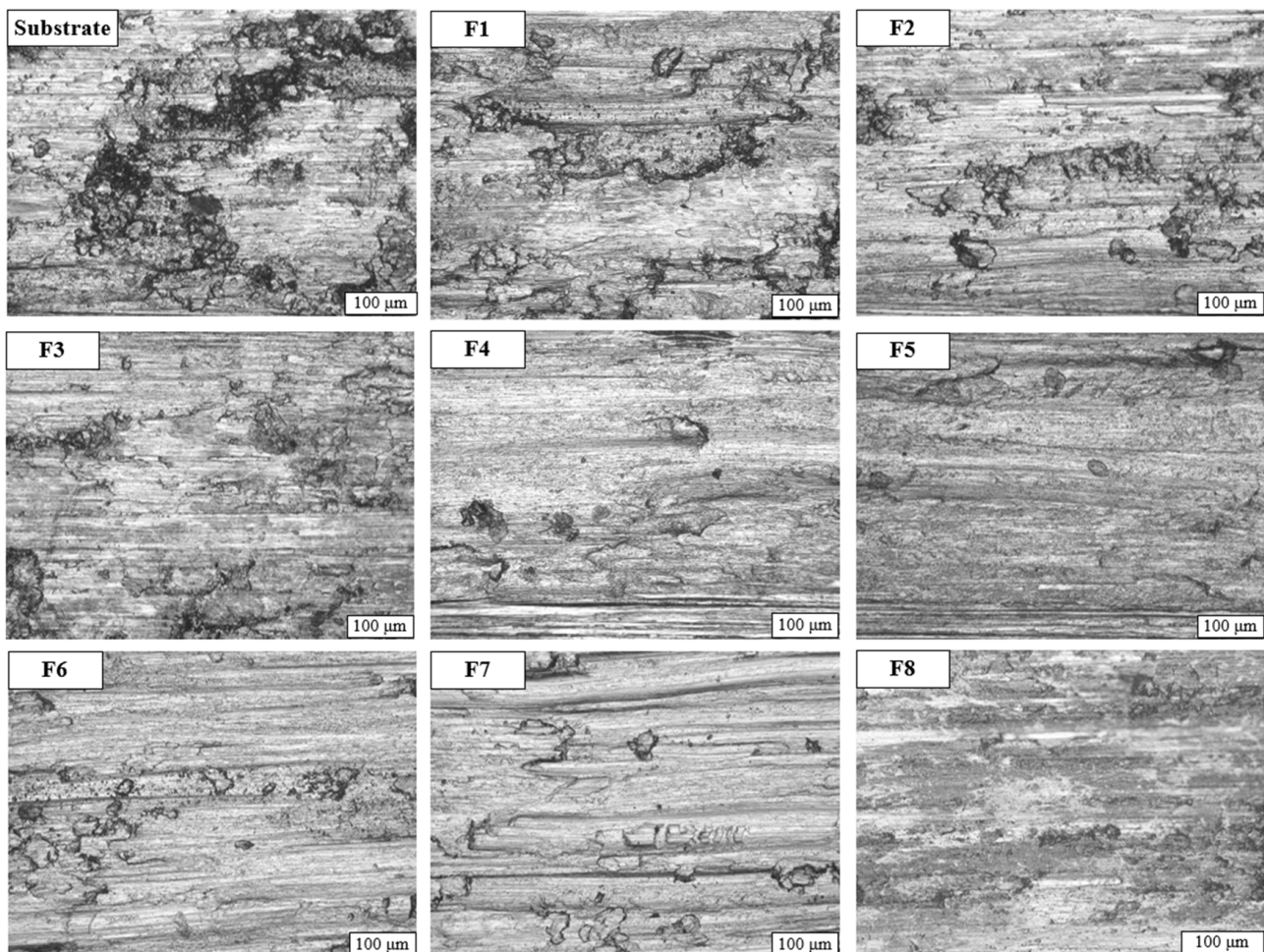


Figure 13. The surface of cladding layer after the wear test.

From the perspective of the magnetic field direction, as shown in F4 and F6–F8 of Figure 13, debris peeling occurred in the samples applied in the U direction, while surface peeling and the furrow phenomenon were relatively alleviated in the samples applied in the D direction, accompanied by some fine and uniform scratches. However, the samples applied in the L and R directions presented ploughing surfaces. Because the

wear performance was related to the hardness of the cladding layer, the hardness was the highest when the downward vertical magnetic field was applied, which showed that the sample had better friction and wear performance.

3.6. Corrosion Resistance Test

The open circuit potential (OCP) of Inconel 625 alloy was measured by applying the steady-state magnetic fields with different directions and intensities. As shown in Figure 14a, the average OCP value of the Inconel 625 cladding layer without a steady-state magnetic field was -0.475 V. When the magnetic field is added, the OCP value fluctuates greatly, and finally stabilizes between -2.5 V and -0.48 V. Compared to no steady-state magnetic field, the potential changed slightly. The higher OCP value indicated a lower corrosion tendency, and vice versa. However, there was no specific rule between the change in potential and magnetic field intensity. It is noteworthy that the OCP value of each cladding layer was higher than that of matrix HT 300 with or without a steady-state magnetic field, which can play a good cathodic protection role and show a small corrosion tendency.

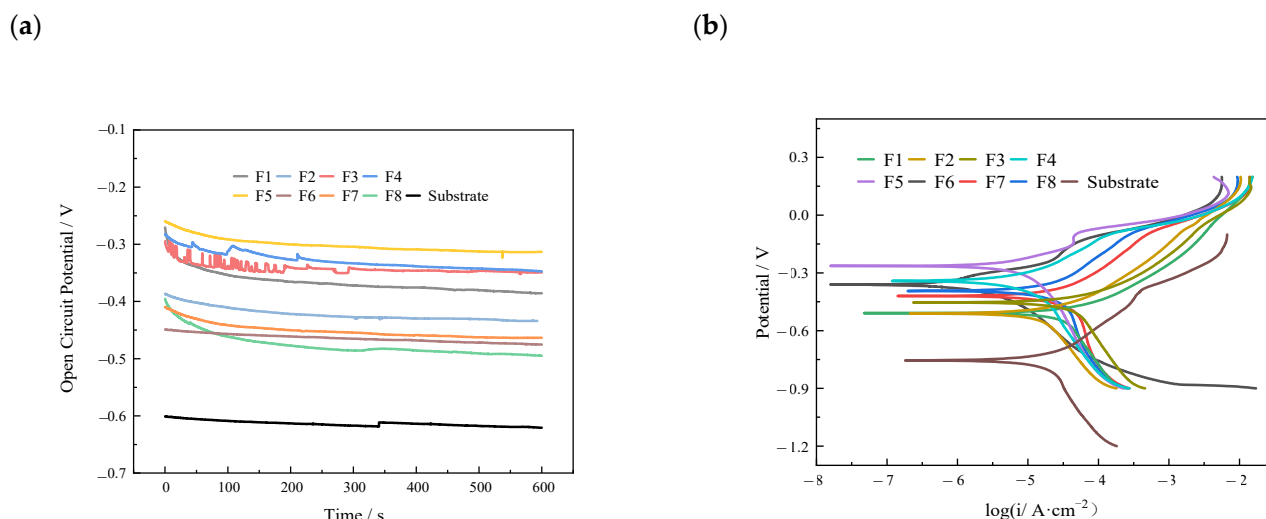


Figure 14. (a) Cladding surface open circuit data diagram, (b) Tafel polarization curve of the cladding layer.

Figure 14b shows the Tafel test curves of the substrate and cladding layers. No obvious passivation occurred within the set $\text{VOCP} \pm 1$ V test range. Meanwhile, the shape and position of all curves were similar and the anode rate slowed down gradually, showing a symmetric relationship independent of self-corrosion potential. As shown in Figure 14, both anode and cathode curves exhibited the characteristics of active dissolution. The shape and position of all curves were similar, and the corrosion rate slowed down as the voltage changed and gradually decreased in the anode region.

It can be seen from Table 8 that the substrate presented the smallest E_{corr} , with a value of -0.76326 V, and the biggest I_{corr} , with a value of $0.0186231 \mu\text{A}/\text{cm}^2$, compared to the cladding layer. That is, the laser cladding layer can enhance the surface to suppress the corrosion. In addition, with the increase in the magnetic field intensity, the E_{corr} increased and the I_{corr} decreased. For instance, the E_{corr} was -0.55655 V, accompanied by the I_{corr} of $0.014997 \mu\text{A}/\text{cm}^2$ when the intensity was 0 mT, and the E_{corr} increased to -0.30288 V, accompanied by the decreased I_{corr} with a value of $0.00035922 \mu\text{A}/\text{cm}^2$ when the intensity of 200 mT was used. This means that an increase in the intensity contributes to an improvement in the corrosion resistance of the cladding layers. Cr, Nb, and other elements are beneficial to increase the corrosion performance, but the precipitation of the Laves phase will injure these strengthening elements, which results in a reduction in the synthesized γ -Ni matrix phase, and thus a decrease in the overall corrosion resistance of the cladding layer. However, the increase in the magnetic field intensity increased

the matrix phase content which, in turn, decreased the harmful Laves phase. Thus, an increase in the magnetic field intensity can improve the corrosion resistance of the cladding layer. Through comparing to the E_{corr} and I_{corr} of the cladding layers created by different magnetic field directions, the cladding layer assisted by the horizontal magnetic field presented the maximum average value of E_{corr} (-0.35354 V) and minimum average value of I_{corr} (0.00529505 $\mu\text{A}/\text{cm}^2$).

Table 8. The self-corrosion potential (E_{corr}) and current density (I_{corr}) of the cladding layer obtained after the Tafel test.

	E_{corr} (V)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
Substrate	-0.76326	0.0186231
F1	-0.55655	0.014997
F2	-0.48133	0.012695
F3	-0.44469	0.010409
F4	-0.33571	0.0068632
F5	-0.30288	0.00035922
F6	-0.37137	0.0037269
F7	-0.41374	0.0095103
F8	-0.42675	0.0093793

4. Conclusions

1. A higher steady-state magnetic field intensity resulted in a slightly wider melting width of the molten pool, but reduced the melting height, depth, and dilution rate. A horizontal magnetic field flattened the molten pool more than a vertical one. Stronger magnetic fields caused the dendritic structure to change into an equiaxed crystal structure with more extensive and stronger columnar dendritic structures at the bottom of the clad layer, biased towards the magnetic field direction.

2. The magnetic field stabilized the crystal structure and refined the grain by increasing the content of the matrix phase and decreasing the content of Laves phase.

3. The cladding layer's microhardness was higher than that of the matrix. A vertical downward steady magnetic field increased the microhardness and wear resistance. The highest hardness, lowest wear amount, and best wear performance were observed with the vertical downward magnetic field.

4. The higher the magnetic field intensity, the better the corrosion resistance of the cladding layer. The corrosion resistance is lower in the vertical direction than in the horizontal direction. Increasing the magnetic field intensity increases the matrix phase content and reduces the harmful Laves phase, leading to improved corrosion resistance of the cladding layer.

Author Contributions: Conceptualization, X.W. and J.Z.; methodology, X.W.; validation, Y.T. and J.J.; formal analysis, J.J.; investigation, Y.T.; writing—original draft preparation, X.W. and Y.T.; writing—review and editing, X.W., Y.T. and J.J.; project administration, T.G.; funding acquisition, X.W. and T.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 52305340, the Natural Science Foundation of Liaoning Province, grant number 2020-BS-206, Liaoning Department of Education Scientific Research Foundation, grant number JDL2020022, and Scientific and technological research program of China National Railway Group Limited, grant number N2021T010.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Pawlus, P.; Koszela, W.; Reizer, R. Surface Texturing of Cylinder Liners: A Review. *Materials* **2022**, *15*, 8629. [CrossRef] [PubMed]
- Li, C.; Chen, X.; Liu, H.; Dong, L.; Jian, H.; Wang, J.; Du, F. Tribological Performance and Scuffing Resistance of Cast-Iron Cylinder Liners and Al-Si Alloy Cylinder Liners. *Coatings* **2023**, *13*, 1951. [CrossRef]
- Peng, E.; Huang, S. Wear performance of cylinder liner surface texturing on cylinder liner–piston ring assembly. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2017**, *232*, 291–306. [CrossRef]
- Rahmani, R.; Rahnejat, H.; Fitzsimons, B.; Dowson, D. The effect of cylinder liner operating temperature on frictional loss and engine emissions in piston ring conjunction. *Appl. Energy* **2017**, *191*, 581. [CrossRef]
- Liu, N.; Wang, C.N.; Xia, Q.; Gao, Y.Y.; Liu, P. Simulation on the effect of cylinder liner and piston ring surface roughness on friction performance. *Mech. Ind.* **2022**, *23*, 8. [CrossRef]
- Alshwawra, A.; Pasligh, H.; Hansen, H.; Dinkelacker, F. Increasing the roundness of deformed cylinder liner in internal combustion engines by using a non-circular liner profile. *Int. J. Engine Res.* **2019**, *22*, 1214–1221. [CrossRef]
- Denkena, B.; Grove, T.; Schmidt, C. Machining of Micro Dimples for Friction Reduction in Cylinder Liners. *Procedia CIRP* **2018**, *78*, 318–322. [CrossRef]
- Alshwawra, A.; Swerih, A.A.; Sakhrieh, A.; Dinkelacker, F. Structural Performance of Additively Manufactured Cylinder Liner—A Numerical Study. *Energies* **2022**, *15*, 8926. [CrossRef]
- Haldar, B.; Saha, P. Identifying defects and problems in laser cladding and suggestions of some remedies for the same. *Mater. Today Proc.* **2018**, *5*, 13090–13101. [CrossRef]
- Kwok, C.T.; Man, H.C.; Cheng, F.T.; Lo, K.H. Developments in laser-based surface engineering processes: With particular reference to protection against cavitation erosion. *Surf. Coat. Technol.* **2016**, *291*, 189–204. [CrossRef]
- Zhang, P.; Liu, Z.; Du, J.; Su, G.; Zhang, J.; Xu, C. On machinability and surface integrity in subsequent machining of additively-manufactured thick coatings: A review. *J. Manuf. Process.* **2020**, *53*, 123–143. [CrossRef]
- Chong, Z.; Sun, Y.; Cheng, W.; Han, C.; Huang, L.; Su, C.; Jiang, L. Enhanced wear and corrosion resistances of AlCoCrFeNi high-entropy alloy coatings via high-speed laser cladding. *Mater. Today Commun.* **2022**, *33*, 104417. [CrossRef]
- Farahmand, P.; Kovacevic, R. Laser cladding assisted with an induction heater (LCAIH) of Ni–60%WC coating. *J. Mater. Process. Technol.* **2015**, *222*, 244–258. [CrossRef]
- Zhang, Z.; Zhang, Y.; Ming, W.; Zhang, Y.; Cao, C.; Zhang, G. A review on magnetic field assisted electrical discharge machining. *J. Manuf. Process.* **2021**, *64*, 694–722. [CrossRef]
- Zhu, L.; Xue, P.; Lan, Q.; Meng, G.; Ren, Y.; Yang, Z.; Xu, P.; Liu, Z. Recent research and development status of laser cladding: A review. *Opt. Laser Technol.* **2021**, *138*, 106915. [CrossRef]
- Bachmann, M.; Avilov, V.; Gumenyuk, A.; Rethmeier, M. Numerical assessment and experimental verification of the influence of the Hartmann effect in laser beam welding processes by steady magnetic fields. *Int. J. Therm. Sci.* **2016**, *101*, 24–34. [CrossRef]
- Bachmann, M.; Avilov, V.; Gumenyuk, A.; Rethmeier, M. About the influence of a steady magnetic field on weld pool dynamics in partial penetration high power laser beam welding of thick aluminium parts. *Int. J. Heat Mass Transf.* **2013**, *60*, 309–321. [CrossRef]
- Velde, O.; Gritzki, R.; Grundmann, R. Numerical investigations of Lorentz force influenced Marangoni convection relevant to aluminum surface alloying. *Int. J. Heat Mass Transf.* **2001**, *44*, 2751–2762. [CrossRef]
- Lee, C.-K.; Lee, W. The effect of magnetic fields for laser welding process using carbon steel. *Int. J. Precis. Eng. Manuf.* **2013**, *14*, 1915–1923. [CrossRef]
- Qi, K.; Yang, Y.; Sun, R.; Hu, G.; Lu, X.; Li, J.; Liang, W.; Jin, K.; Xiong, L. Effect of magnetic field on crack control of Co-based alloy laser cladding. *Opt. Laser Technol.* **2021**, *141*, 107129. [CrossRef]
- Qi, K.; Yang, Y.; Liang, W.; Jin, K.; Xiong, L. Influence of the anomalous elastic modulus on the crack sensitivity and wear properties of laser cladding under the effects of a magnetic field and Cr addition. *Surf. Coat. Technol.* **2021**, *423*, 127575. [CrossRef]
- Wang, L.; Yao, P.H.; Hu, Y.; Song, S.Y. Suppression effect of a steady magnetic field on molten pool during laser remelting. *Appl. Surf. Sci.* **2015**, *351*, 794–802. [CrossRef]
- Hu, Y.; Wang, L.; Yao, J.; Xia, H.; Li, J.; Liu, R. Effects of electromagnetic compound field on the escape behavior of pores in molten pool during laser cladding. *Surf. Coat. Technol.* **2020**, *383*, 125198. [CrossRef]
- Wang, L.; Yao, J.; Hu, Y.; Zhang, Q.; Sun, Z.; Liu, R. Influence of electric-magnetic compound field on the WC particles distribution in laser melt injection. *Surf. Coat. Technol.* **2017**, *315*, 32–43. [CrossRef]
- Carroll, R.I.; Beynon, J.H. Rolling contact fatigue of white etching layer, Part 1: Crack morphology. *Wear* **2007**, *262*, 1253–1266. [CrossRef]
- Fujimoto, K.; Yoshikawa, Y.; Shioya, T. Opening Behaviour Of Surface Crack in Elastic Half-plane Under Hertzian Contact Loading. In *WIT Transactions on Engineering Sciences*; WIT Press: Southampton, UK, 1997; Volume 14.
- Jia, G.W.; Hua, L.; Mao, H.J. The influence of surface layer microstructure evolution of M2 steel cold-ring rolling mandrel roller on fatigue crack initiation. *J. Mater. Process. Technol.* **2007**, *187*, 562–565. [CrossRef]
- Mercado-Solis, R.D.; Talamantes-Silva, J.; Beynon, J.H.; Hernandez-Rodriguez, M.A.L. Modelling surface thermal damage to hot mill rolls. *Wear* **2007**, *263*, 1560–1567. [CrossRef]
- Cerullo, M. Sub-surface Fatigue Crack Growth at Alumina Inclusions in AISI 52100 Roller Bearings. *Procedia Eng.* **2014**, *74*, 333–338. [CrossRef]

30. Ohtsuka, H. Structural control of Fe-based alloys through diffusional solid/solid phase transformations in a high magnetic field. *Sci. Technol. Adv. Mater.* **2008**, *9*, 13004. [CrossRef]
31. Li, X.; Fautrelle, Y.; Zaidat, K.; Gagnoud, A.; Ren, Z.; Moreau, R.; Zhang, Y.; Esling, C. Columnar-to-equiaxed transitions in al-based alloys during directional solidification under a high magnetic field. *J. Cryst. Growth* **2010**, *312*, 267–272. [CrossRef]
32. Shuai, S.S.; Lin, X.; Xiao, W.Q.; Yu, J.B.; Wang, J.; Ren, Z.M. Effect of Transverse Static Magnetic Field on Microstructure of Al-12% Si Alloys Fabricated by Powder-Blow Additive Manufacturing. *Acta Met. Sin.* **2018**, *54*, 926.
33. Li, X.; Gagnoud, A.; Ren, Z.; Fautrelle, Y.; Moreau, R. Investigation of thermoelectric magnetic convection and its effect on solidification structure during directional solidification under a low axial magnetic field. *Acta Mater.* **2009**, *57*, 2180–2197. [CrossRef]
34. Wang, Q.; Zhai, L.L.; Zhang, L.; Zhang, J.W.; Ban, C.Y. Effect of steady magnetic field on microstructure and properties of laser cladding Ni-based alloy coating. *J. Mater. Res. Technol.* **2022**, *17*, 2145–2157. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Experimental Analysis and Wear Prediction Model Based on Friction Heat for Dry Sliding Contact

Qiming Sun and Dayu Zheng *

Harbin University of Commerce, Harbin 150080, China; 15838529560@163.com

* Correspondence: zhengdayu@hrbcu.edu.cn

Abstract: In this study, the influence of the frictional heat effect on the degree of wear is explored from the perspectives of initial contact positive pressure and frictional relative slip velocity. Experiments based on a multifunctional friction and wear machine show that the friction temperature increases with an increase in friction relative velocity and initial normal contact load, which exacerbates the frictional thermal expansion and normal load fluctuation, and with the generation of frictional heat, the normal force fluctuates periodically; the wear mass and temperature in the contact area iterate cyclically, which results in the wear mass increasing. 316L stainless steel, 5A06 aluminium alloy and pure titanium are used in the Archard wear model due to their applications in severe wear environments. Since 316L stainless steel, 5A06 aluminium alloy and pure titanium are mostly used in wear-intensive environments, the Archard wear model is optimised based on the frictional heat effect of these three materials, and the accuracy of the improved model in 316L stainless steel, 5A06 aluminium alloy and pure titanium is improved by 52.6%, 7.4% and 23.9%, respectively, when compared with the conventional model. This study lays a theoretical foundation for the wear prediction models of 316L stainless steel, 5A06 aluminium alloy and pure titanium.

Keywords: Archard; friction thermal expansion; wear; contact pressure

1. Introduction

Nowadays, frictional wear can bring severe consequences to fields such as aviation and healthcare, etc. [1–3], because it can reduce the precision and working life of components, so predicting the wear degree of components is essential. In the mid-1950s, J.F. Archard [4] found that the wear rate is positively correlated with the load in experiments of frictional wear and expounded the relationship of wear mass with material hardness, load, and slip distance as:

$$V = \left(\frac{K}{H} \right) Ps \quad (1)$$

where V denotes the wear mass; K and H represent the wear coefficient and the hardness of materials, respectively; P and s represent the load and the relative slip distance, respectively. Currently, there exist commonly used wear equations in the field of tribology, including the Cattaneo–Mindlin model, the Lim–Ashby model, the Rabinowicz wear model and the Archard wear equation. The Cattaneo–Mindlin model [5] is used to describe the contact problem on solid surfaces, especially when elastic deformation and sliding between the contacting surfaces are taken into account. Sliding between the contact surfaces has important applications. Since the Cattaneo–Mindlin model takes into account small sliding effects, the computational process is relatively complex and requires high computational costs, so a large amount of experimental data or validation is required to determine the parameters in the model, which limits the scope of application for the model. The Lim–Ashby model is an empirical model for describing the wear behaviour of a material, which is based on the material properties' parameters such as the material hardness and elastic modulus to predict the wear behaviour of a material. The material property parameters are used to

predict the wear rate of the material, whereas the Lim–Ashby model [6] considers only some of the material property parameters and may have limitations for complex wear mechanisms and specific working conditions. Rabinowicz’s wear model [7] is an empirical model used to describe friction and wear phenomena. The model is based on parameters, such as contact pressure, sliding velocity and material hardness of the friction surfaces, and is used to predict the wear rate and life, whereas the model is based on some simplifying assumptions, such as uniform contact pressure distribution, which may lead to deviations from the actual situation. So, many workers in the field of tribology predict the working life of components using the Archard wear equation. For example, Guangwei Yu [8] predicted the service life of deep groove ball bearings based on Archard wear theory.

However, some workers in this field pointed out that the factors in the wear equation proposed by J.F. Archard are comprehensive enough. Arvin Taghizadeh Tabrizi et al. [9] indicated that the effect of surface modification was not considered in this equation. According to their studies, the hardness of materials is a fixed value, only involving the hardness of soft surfaces but not that of hard ones. In addition, the authors, who conducted the pin-on-disc wear test after performing the surface modification of titanium by plasma chemical vapor deposition, pointed out that the wear mass is also related to roughness, hardness of soft and hard surfaces, surface roughness and irregular slope. Yanfei Liu et al. [10] put forward that the surface could be damaged during the micromotion of two objects, thus resulting in a tribologically transformed structure (TTS) on their surfaces. The authors adopted alumina balls for the micro-motion experiment on 316L stainless steel, pure copper and $\text{Ti}_6\text{Al}_4\text{V}$, based on which, they indicated that the dynamic change in the TTS layer was not considered in the Archard equation and proposed an optimized Archard model consequently.

Tobias Dyck et al. [11] described the available wear mass of hemispheres and U shapes numerically and established a wear model based on the horizontal distribution of Archard work intensity. As indicated, the surface hardness depended on base materials, as well as bottom and surface courses. Moreover, they discussed the optimization of the Archard equation using theoretical and experimental methods. Generally, scholars optimized the wear equation from the perspective of material hardness, which, in their opinion, could not be constant throughout the process of frictional wear. However, in these studies, they failed to consider the influence of frictional thermal expansion, namely the local expansion of contact materials caused by frictional heat on external load and wear mass.

Wear arises from complex chemical and physical processes, with many key parameters (including sliding velocity, ambient or local temperature [12], applied pressure [13], surface roughness [14]) appearing in a variety of forms (e.g., adhesive wear, abrasive wear, surface fatigue, micromotion wear, erosive wear, corrosive and oxidative wear). Wear consists of many complex mechanisms [15], including contact, friction, inelastic deformation, etc., which make wear a very complex phenomenon. Frictional thermal expansion greatly impacts the mechanical properties of components in the wear process [16]. As the temperature rises, such expansion will become more significant, and the contact load will change more evidently, thus intensifying the wear degree, which cannot be neglected. At present, nevertheless, no reliable wear model has been established to tackle this problem. To fill this gap, a frictional wear model based on the frictional heating effect is proposed in this study by optimizing the Archard equation. Meanwhile, a series of experiments are conducted to verify its precision, which plays an essential role in predicting the reliability of this model and the overall tribological properties of components.

2. Proposal of a Wear Model Based on the Frictional Heating Effect

We believe that friction will lead to a heat-affected zone under the action of normal load and reciprocating motion (Figure 1a). Due to the additional pressure of thermal expansion generated in the contact area of such expansion (Figure 1b), the contact pressure and temperature will increase in this area, resulting in a relatively high-temperature zone (Figure 1c), which, under the effect of thermal expansion at elevated temperatures, will

be worn rapidly (Figure 1d). At this point, the new contact temperature of this area will be higher than the initial one, and the normal contact load will be higher than the initial positive contact pressure due to thermal expansion. Then, after repeating the steps in Figure 1b–d on this basis, the temperature and degree of wear in the contact area increase dramatically with the number of iterative cycles.

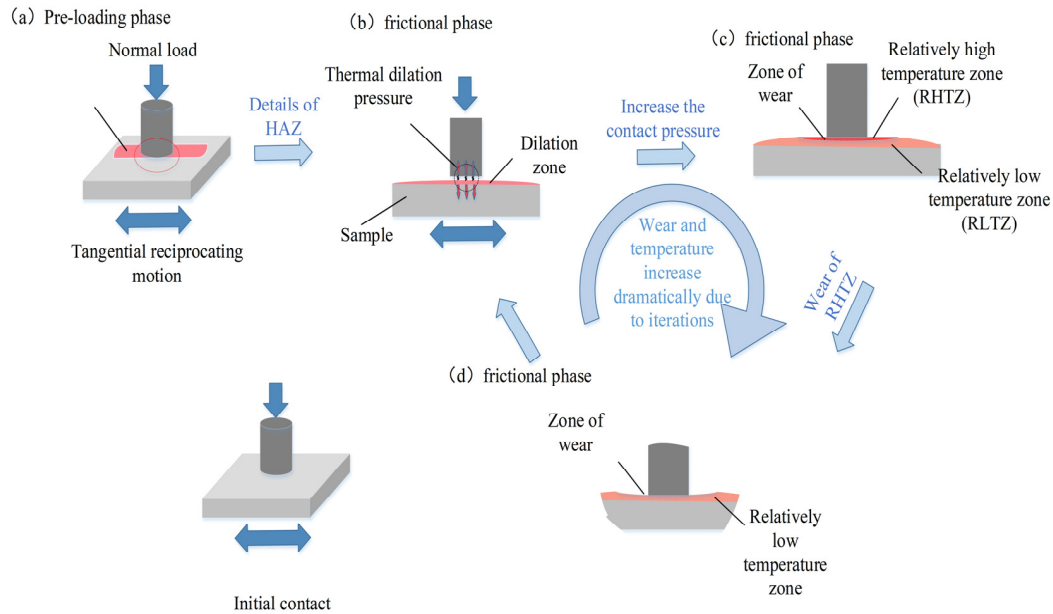


Figure 1. Flow diagram for frictional thermal wear.

On this basis, a model for wear prediction was proposed based on the frictional heating effect in this study:

$$K = \begin{cases} \frac{HM}{P_0 + \sum_{n=1}^n L \rho \int_0^y \int_0^x \Delta P_n ds} & (1) \\ \frac{HM}{[(\Delta T \alpha E) S + P_0] L \rho} & (2) \end{cases} \quad (2)$$

In this equation, H represents the hardness of materials; M represents the wear mass; P_0 represents the initial contact pressure; ΔP_n represents the increment in contact pressure within n dt periods; ΔT represents the temperature difference; α represents the coefficient of thermal expansion; ρ represents the sample density; Z represents the sample length; E represents the elasticity modulus; S represents the contact area; and L represents the relative slip distance. Equation (1) is used when the temperature difference is unknown, while Equation (2) is used when this difference is known.

The derivation is mainly carried out as per the following steps. First, the heat-affected zone in Figure 1 is considered to be regular, as shown in Figure 2. Then, the micro-unit is extracted with a height of Z , a length of dx , and a width of dy . In addition, the change in positive contact pressure within the dt period is considered in this micro-unit, and the equation below shall be made true:

$$n = \left\lceil \frac{t}{dt} \right\rceil \quad (3)$$

where n represents the positive integer; t represents the friction time; and dt represents the micro-unit of t , with its value close to zero. Thus, we can obtain the energy consumed when the frictional work is converted into a heat source:

$$Q = P_0 \mu(t) V(t) dt \gamma \quad (4)$$

In this equation, Q represents the heat energy; P_0 represents the initial positive contact pressure; $\mu(t)$ represents the time function of friction coefficient; $V(t)$ represents the time

function of relative slip velocity; and γ represents the conversion factor of frictional work into heat energy. Thus, the temperature rise can be expressed as:

$$\Delta T = \frac{Q}{Cm_e} \quad (5)$$

where ΔT represents the temperature rise; C represents the specific heat capacity; and m_e represents the mass of the heat-affected zone. Thus, we can obtain the distance of thermal expansion in the Z direction:

$$\Delta l = \Delta T \alpha Z \quad (6)$$

where Δl represents the strain in the Z direction; α represents the coefficient of thermal expansion in this direction; and Z represents the original length of friction parts. The strain in the Z direction is:

$$\varepsilon = \Delta T \alpha \quad (7)$$

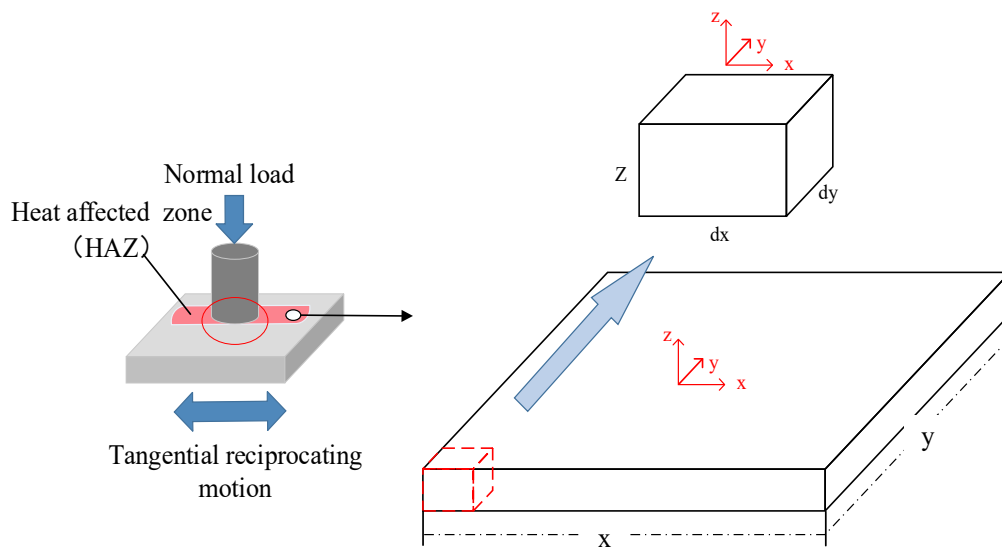


Figure 2. Micrograph for the heat-affected zone of friction.

Thus, we can obtain the increment in normal contact pressure for the micro-unit under the effect of thermal expansion:

$$\Delta P = \varepsilon E dx dy \quad (8)$$

where ΔP represents the increment in normal contact pressure, and E represents the elasticity modulus. Thus, the normal contact pressure of this micro-unit can be expressed as:

$$P_1 = \Delta P_1 + P_0 \quad (9)$$

When the second dt is considered, the following equation can be obtained:

$$P_2 = \Delta P_1 + \Delta P_2 + P_0 \quad (10)$$

When the friction time is t , the equation below is used:

$$P_n = \sum_{n=1}^n \Delta P_n + P_0 \quad (11)$$

Therefore, by considering the whole heat-affected zone, we can obtain the following equation:

$$ds = dx dy \quad (12)$$

$$P_{correction} = P_0 + \sum_{n=1}^n \int_0^y \int_0^x \Delta P_n ds \quad (13)$$

At this point, the modified wear model is expressed as:

$$K = \frac{HM}{P_{\text{correction}} L \rho} \quad (14)$$

where K represents the wear coefficient; H represents the hardness of materials; M represents the wear mass; L represents the relative slip distance; and ρ represents the density of wearing parts.

The simplified equation below can be used when the temperature difference before and after the friction is known:

$$M = \frac{K[(\Delta T \alpha E)S + P_0]L}{H} \quad (15)$$

As mentioned above, this is suitable for dry friction and under heavy load. For electrical contact, theoretically, Equation (4) can add Joule heat:

$$Q = \left(P_0 \mu(t) V(t) + I^2 R(t) \right) dt \gamma \quad (16)$$

In this equation, Q represents the heat energy; P_0 represents the initial positive contact pressure; $\mu(t)$ represents the time function of friction coefficient; $V(t)$ represents the time function of relative slip velocity; I represents the current; $R(t)$ represents the temperature function of resistance; and γ represents the conversion factor of energy into heat. In this study, due to the limitation of experimental conditions, only dry friction is studied, so the heat energy is described in Equation (4).

Experimental Settings

After a large number of pre-experiments and related studies, 16 sets of friction and wear experiments are designed in this section to verify the accuracy of the above wear equations. This study includes three common engineering materials: 316L stainless steel, pure titanium and 5A06 aluminium alloy. Their dimensions are 20 mm × 20 mm × 5 mm, the upper specimen is a cylinder of stainless steel (stainless-steel cylinder diameter of 6 mm), the lower specimens are 316L stainless steel, pure titanium and 5A06 aluminium alloy, the top and bottom specimens are sanded with 800-mesh, 1000-mesh and 2000-mesh sandpaper. Following this, the surface was polished to a roughness of $R_a < 0.8 \mu\text{m}$. The upper and lower specimens were polished with 800-mesh, 1000-mesh and 2000-mesh sandpaper, respectively, and then the surface was polished to a roughness of $R_a < 0.8 \mu\text{m}$ and finally cleaned with deionised water and acetone. It was then placed in the air to dry naturally.

In this study, the system for the friction experiment includes an FTM M30 frictional wear tester, FLIR A615 high-precision thermal infrared imager (Wilsonville, OR, USA) and BSM-220.4 0.1 mg electronic balance (Petra Mechatronics, Dubai, United Arab Emirates). One of the FLIR sensors (temperature range -10° to 150°) has an accuracy of 0.01% FS of the instrumental accuracy. Before the experiment, ultrasonic cleaning was performed, and the mass of the wearing parts (m_0) was measured. Then, the high-precision thermal infrared imager was placed in the position shown in Figure 3a; its operating platform was set with an area for temperature detection in Figure 4a to read the highest temperature of the friction zone in real time, as presented in Figure 4b. In this experiment, samples and pins were fixed onto the reciprocating and Y-stroke modules, respectively (Figure 3b).

Then, the reciprocating platform's parameters, including reciprocating frequency and stroke, initial positive contact pressure and friction time, were set on the platform for the frictional wear experiment. The principle is illustrated in Figure 3c. Pins were moved in the negative direction of Y. Then, when these pins almost touched the samples, they were pressed down constantly at a very low speed till the specific value on the normal force sensor reached the preset initial contact pressure. At this point, the reciprocating module began to run. While samples and pins rubbed against each other, the tangential and normal force fluctuations were measured by tangential and normal force sensors, respectively. The experiments were carried out at room temperature and after friction, ultrasonic cleaning

was carried out to measure the mass of the worn mass (m_{end}) and, finally, the mass of the worn mass ($m_0 - m_{end}$) to ensure the accuracy of the measured mass.

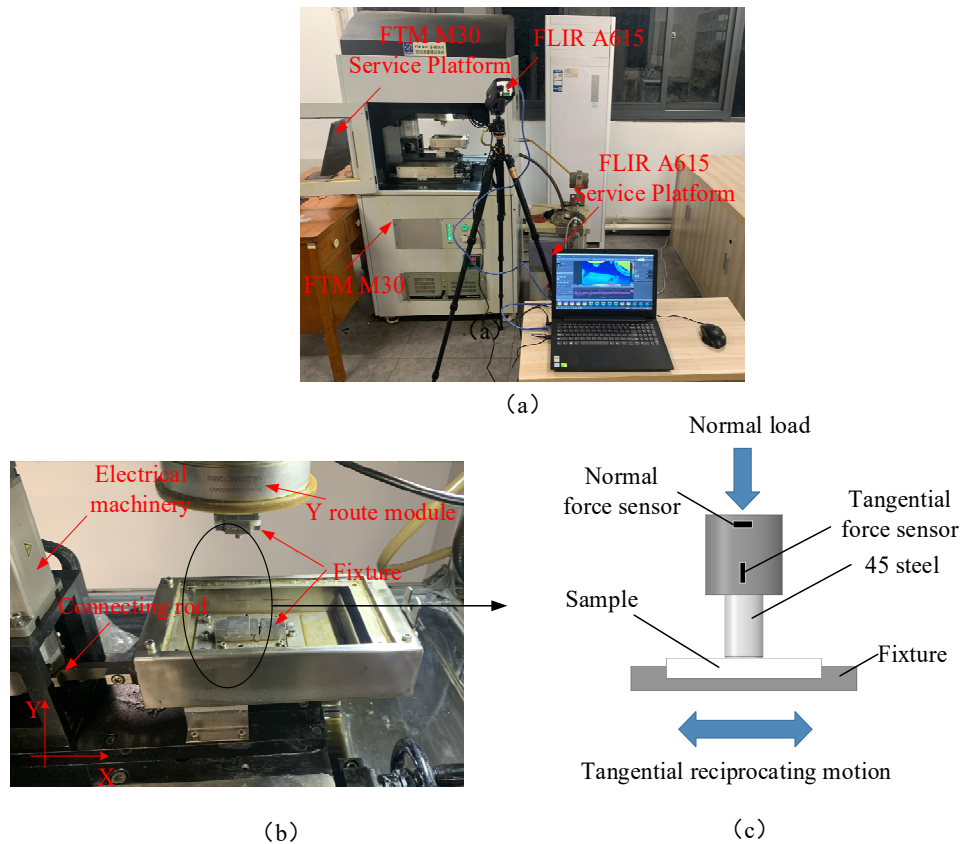


Figure 3. (a) System and operating platform for the experiment on frictional thermal wear. (b) Reciprocating module in the frictional wear experiment. (c) Operating principle of the reciprocating module for frictional wear.

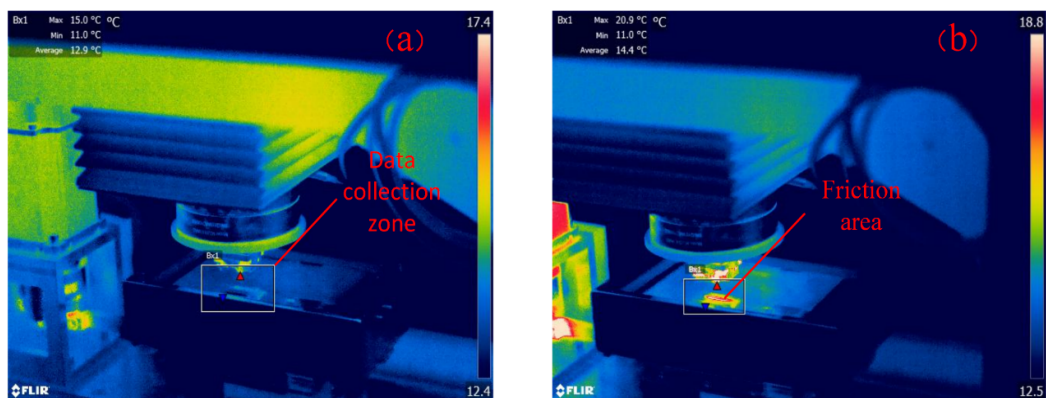


Figure 4. (a) Data collection zone of the high-precision thermal infrared imager (FLIR A615). (b) Collection zone of frictional temperature.

In this study, ten sets of experiments were carried out on 316L stainless steel according to the parameters in Tables 1 and 2, and the average values were obtained to ensure the reliability of the experiments in order to investigate the influence of friction velocity and initial normal load on the frictional heating effect. In addition, three sets of experiments on 316L stainless steel, pure titanium and 5A06 aluminium alloy were also carried out under the conditions listed in Table 3 and averaged to investigate how the thermal expansion caused by this effect affects the normal contact load and wear quality of the different materials.

Table 1. Pressure identical friction frequency reciprocating experimental parameters.

Number	Parameter	Frequency/ (Hz)	Time/ (min)	Pressure/ (N)
1		2	10	40
2		4	5	40
3		6	3.3	40
4		8	2.5	40
5		10	2	40

Table 2. Frequency same friction frequency reciprocation experimental parameters.

Number	Parameter	Frequency/ (Hz)	Time/ (min)	Pressure/ (N)
1		10	10	20
2		10	10	30
3		10	10	40
4		10	10	50
5		10	10	60

Table 3. Parameters of friction frequency reciprocation experiments with different materials.

Number	Parameter	Frequency/ (Hz)	Slip Distance (m)	Pressure/ (N)
316L		2/10	24	40
Pure titanium		2/10	24	40
5A06 aluminium alloy		2/10	24	40

3. Results and Discussion

3.1. Influence of the Initial Positive Contact Pressure on Frictional Heat and Wear Mass

A time–history curve was made for the frictional temperature of 316L stainless steel under different initial positive contact pressures (20 N, 30 N, 40 N, 50 N and 60 N), as shown in Figure 5. Meanwhile, it was smoothed by the neighbourhood averaging method and is presented by the red curve in Figure 5. In the experiment, the reciprocating frequency was set at 10 Hz, and the friction time was controlled at 10 min. It could be seen that the temperature in the friction zone increased with the time. According to Figure 6a, the temperature difference before and after the friction became increasingly larger as the initial positive contact pressure increased. This is due to the fact that during friction, the friction surface may undergo localised plastic deformation due to the two surfaces being under high pressure, causing the friction surface to generate deformation heat. This heat from plastic deformation leads to an increase in the temperature of the friction surface. Thereinto, the difference was minimum under pressure of 20 N, with the value being 2.16 °C; those under 30 N and 40 N had values of 5.24 °C and 5.86 °C, respectively; and the differences under 50 N and 60 N were 7.95 °C and 8.3 °C, respectively. As analysed with Equation (1), the frictional heat energy (Q) increased with the positive contact pressure (F_n) and relative slip distance (L). In addition, the temperature difference (ΔT) was directly proportional to Q . Therefore, when the reciprocating frequency was constant, the frictional temperature increased with the friction time. That is, the larger the value of s , the higher the temperature. In addition, under the same stroke, the temperature difference increased with the positive contact pressure.

$$Q = P\mu\gamma \quad (17)$$

$$\Delta T = \frac{Q}{cm_e} \quad (18)$$

In the above equations, Q denotes the frictional heat energy; P is the normal contact pressure; μ represents the friction coefficient; L represents the relative slip distance; γ represents the conversion factor of frictional work into heat energy; ΔT represents the

temperature difference; c represents the specific heat capacity; and m_e represents the mass of the heat-affected zone. As shown in Figure 6b, the wear mass increased with the positive contact pressure, which was particularly prominent under pressure of 20 N, 30 N and 40 N, corresponding to values of 1.7 mg, 4 mg and 7.7 mg. In addition, this mass showed a similar value of 8.3 mg under 50 N and 40 N and reached the highest value of 12 mg under 60 N. Therefore, it was found that the cycle in Figure 1b–d could be intensified when the frictional temperature increased with the positive contact pressure, thus resulting in a higher wear mass.

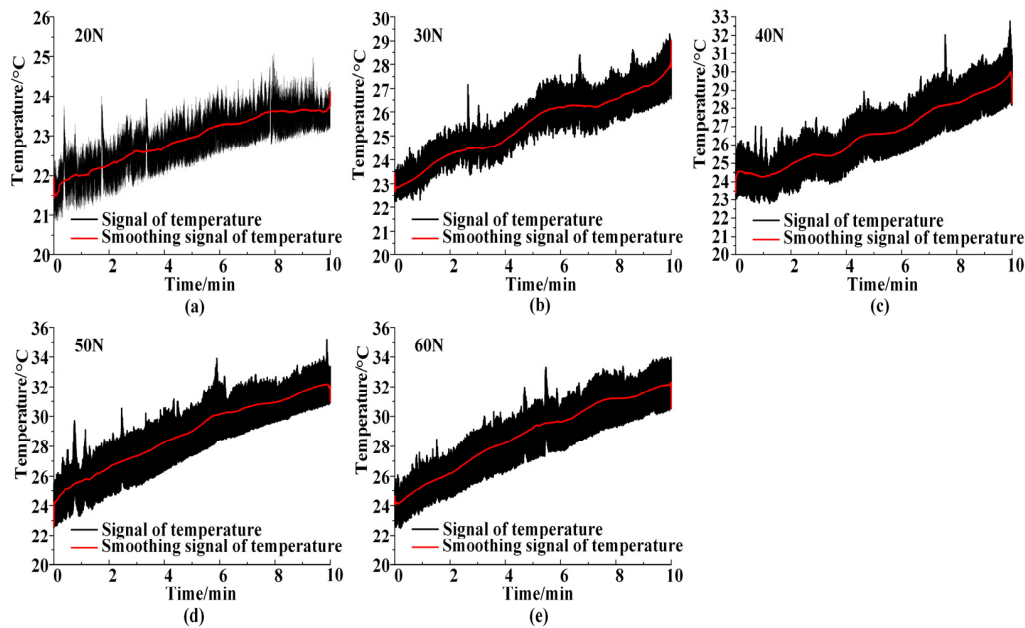


Figure 5. (a–e) Trends of the effect of different initial normal loads from 20–60 N on the friction temperature of 316L stainless steel.

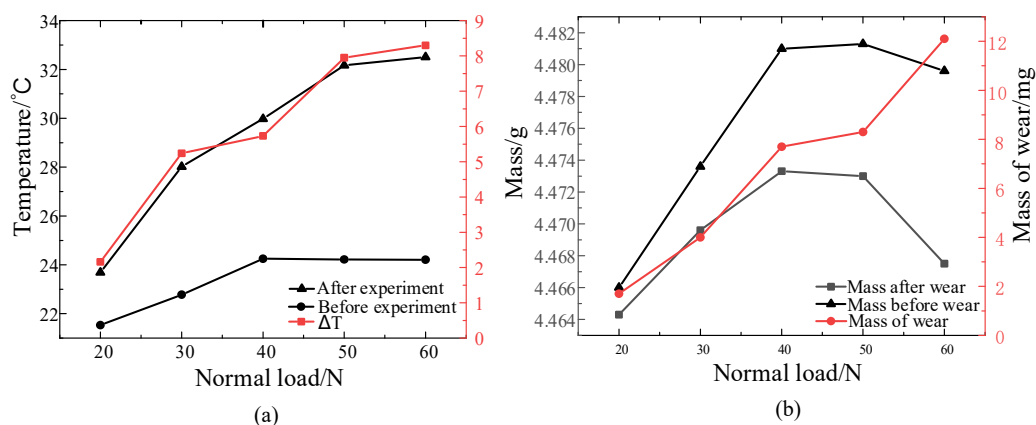


Figure 6. (a) Temperature variation curve of the frictional heat under different initial normal contact loads. (b) Influence curve of the wear mass under different initial normal contact loads.

3.2. Influence of the Reciprocating Frequency on Frictional Heat and Wear Mass

Figure 7 presents a time–history curve for the frictional temperature of 316L stainless steel at different reciprocating frequencies (2 Hz, 4 Hz, 6 Hz, 8 Hz and 10 Hz). In the experiment, this curve was smoothed by the neighbourhood averaging method, as shown by the red curve in Figure 7. Then, the positive contact pressure was set at 40 N, and the relative slip distance was controlled at 24 m. It could be seen that the temperature in the friction zone increased with this distance. For the convenience of comparison, the change in temperature at different reciprocating frequencies is illustrated in Figure 8a.

It was found that the temperature difference before and after friction increased with the increase in frequency. Among them, the smallest temperature difference is $0.21\text{ }^{\circ}\text{C}$ at 2 Hz, the similar temperature difference is $0.9\text{ }^{\circ}\text{C}$ and $1.44\text{ }^{\circ}\text{C}$ at 4 Hz and 6 Hz, and the temperature difference increases significantly at 8 Hz and 10 Hz, which are $2.87\text{ }^{\circ}\text{C}$ and $5.46\text{ }^{\circ}\text{C}$, respectively. Especially in the initial stage of friction, the temperature also increases with the increase in reciprocating frequency. This is because during friction, due to the friction generated by the relative motion of the two surfaces, part of the mechanical energy is converted into thermal energy. These losses of mechanical energy lead to an increase in the temperature of the friction surface.

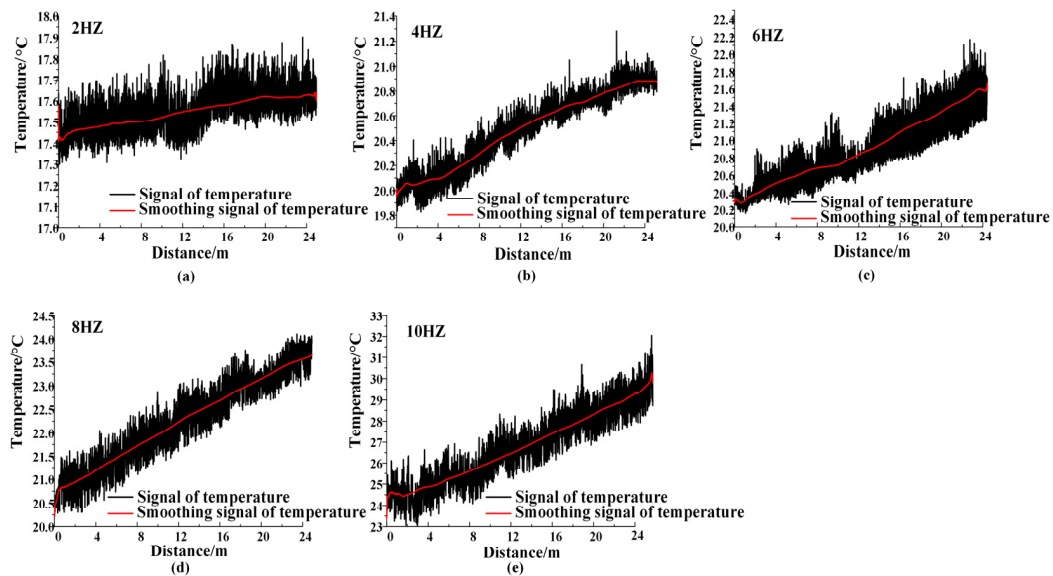


Figure 7. (a–e) Influence trend of different reciprocating frequencies on the frictional temperature of 316L stainless steel.

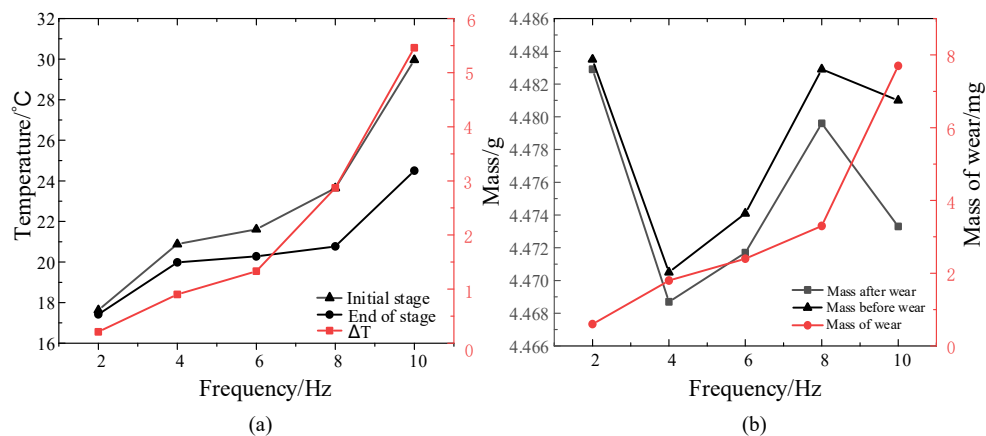


Figure 8. (a) Temperature variation curve of the frictional heat at different reciprocating frequencies. (b) Influence curve of the wear mass at different reciprocating frequencies.

Figure 8b presents the change in wear mass with this frequency: the former increased with the latter. Thereinto, the wear mass was minimum at a frequency of 2 Hz, showing a value of 0.6 mg; it was maximum at 10 Hz, showing a value of 7.7 mg. Meanwhile, this mass increased slowly at 4 Hz, 6 Hz and 8 Hz, with corresponding values of 1.8 mg, 2.4 mg and 3.3 mg. As analysed using Equation (1), when the stroke and initial positive pressure were constant, the frictional work should have been unchanged as well. However, in unit time, the cycle in Figure 4b–d was repeated increasingly with the frequency. Therefore, the phenomenon of heat accumulation became relatively prominent. At the same time,

the temperature rose significantly, and the thermal expansion was intensified. Thus, the normal contact pressure fluctuated, which increased the degree of wear.

3.3. Influence of the Frictional Heating Effect on Normal Contact Load and Wear Mass

Figure 9 shows the wear mass under the same stroke (24 m) and initial positive contact pressure (40 N) but at different reciprocating frequencies (2 Hz and 10 Hz). It was found that the wear mass of pure titanium, 5A06 aluminium alloy and 316L stainless steel was 4.6 mg, 8.1 mg and 1.9 mg, respectively, at a frequency of 10 Hz, while the values were 1.1 mg, 2.2 mg and 0.6 mg, respectively, at 2 Hz. In accordance with the Archard wear equation, this mass is expressed as:

$$M = \rho V \quad (19)$$

where M , ρ , and V represent the mass, density, and the volume. The same material had identical wear volume under the same initial positive contact pressure and stroke. Under such circumstances, the wear mass should be identical as well. However, the error between the actual wear mass of three materials and that predicted by the Archard model was more than 300%, which was not reasonable. By analysing the above equation, it can be found that the frictional heat is not considered, but it is an important factor affecting the frictional wear. This is because the thermal expansion caused by such heat can affect the normal contact pressure, thus influencing the degree of wear. Therefore, this equation shall be optimized.

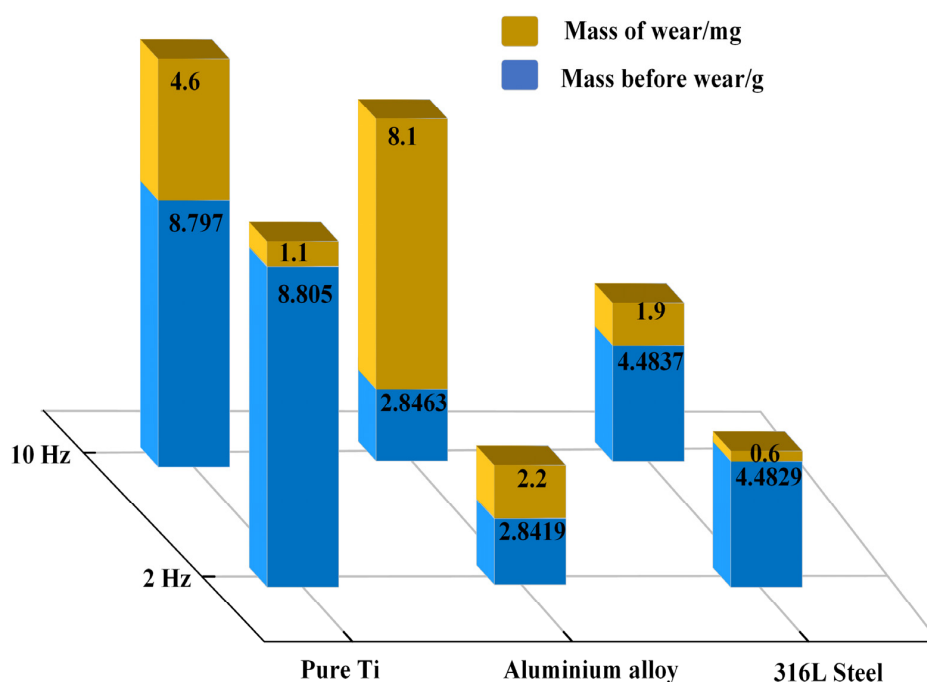


Figure 9. The wear mass of pure titanium, 5A06 aluminium alloy and 316L stainless steel under stroke of 24 m, initial positive contact pressure of 40 N, and reciprocating frequency of 2 Hz and 10 Hz.

Figures 10–12 present the variation curves for the temperature and normal contact pressure of 5A06 aluminium alloy, 316L stainless steel and pure titanium at reciprocating frequencies of 2 Hz and 10 Hz, respectively. First, these curves were smoothed using the neighbourhood averaging method. Then, the initial positive contact pressure was set at 40 N, and the relative slip distance was controlled at 24 m. Under the same stroke, the temperature rise at 10 Hz was more significant than that at 2 Hz. For 5A06 aluminium alloy, the temperature increased by 0.5 °C at 2 Hz but 1.3 °C at 10 Hz. For 316L stainless steel, the temperature increased by 0.3 °C at 2 Hz but 4.5 °C at 10 Hz, showing a more significant rise. For pure titanium, the temperature increased by 1.2 °C at 2 Hz but 4.2 °C at 10 Hz, showing a rising trend. These results are in accordance with the above analysis about the influence of reciprocating frequency on frictional temperature.

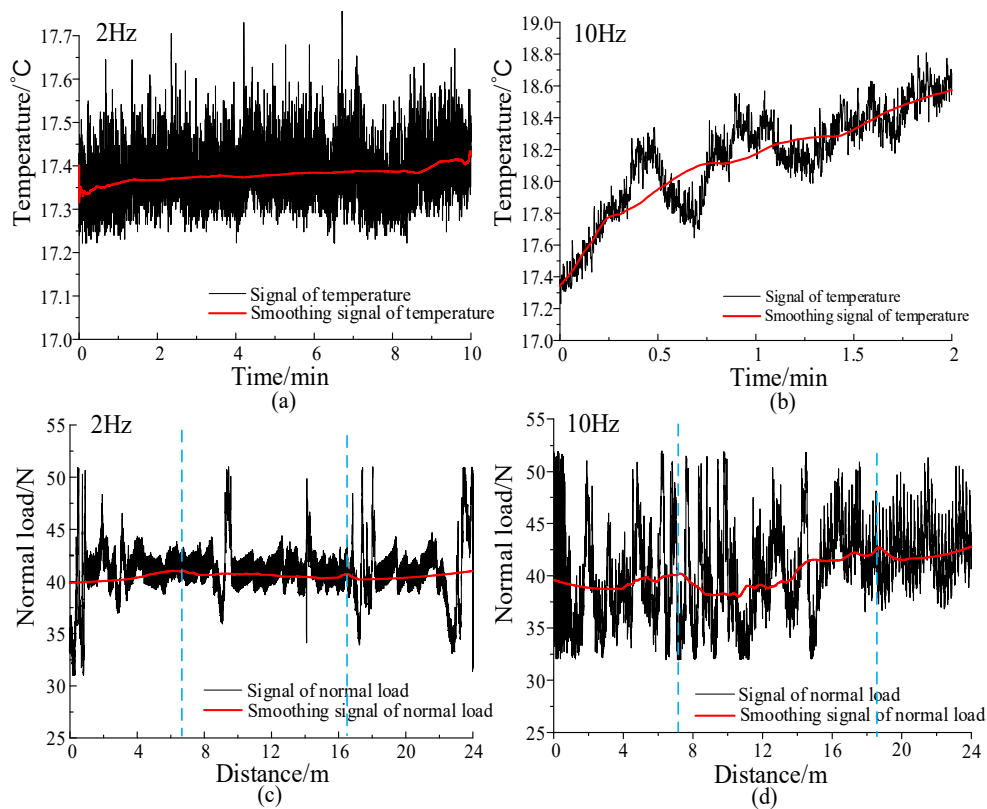


Figure 10. (a–d) Variation curve for the normal contact load of 5A06 aluminium alloy under different frictional heats at the reciprocating frequency of 2 Hz and 10 Hz.

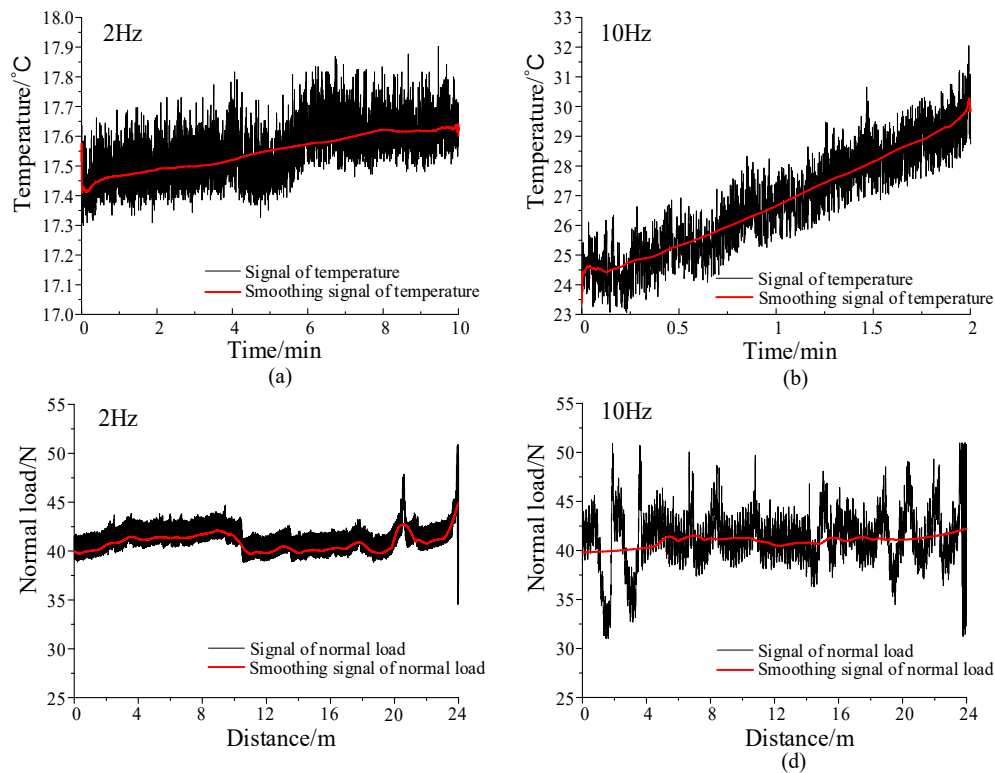


Figure 11. (a–d) Variation curve for the normal contact load of 316L stainless steel under different frictional heats at the reciprocating frequency of 2 Hz and 10 Hz.

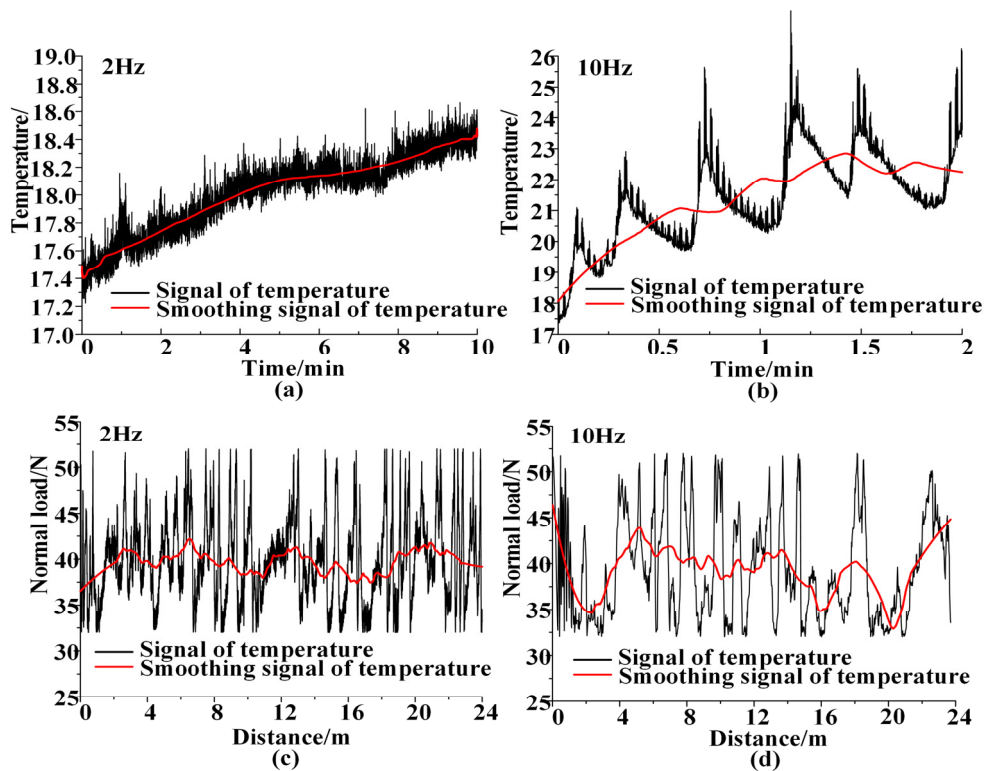


Figure 12. (a–d) Variation curve for the normal contact load of pure titanium under different frictional heats at the reciprocating frequency of 2 Hz and 10 Hz.

Regarding the normal positive contact pressure, the normal load of these three materials at 10 Hz was more fluctuant than that at 2 Hz, which was caused by various factors, such as frictional vibration and systematic noise. When the reciprocating frequency was low, the degree of vibration was also relatively low. However, as this frequency, i.e., the relative velocity, increased, the phenomenon of vibration was more likely to occur. Notably, the normal load of pure titanium fluctuated violently at both frequencies (2 Hz and 10 Hz), as shown in Figure 12. This is because this material has high stiffness and good thermal stability. Hence, in the case of relative friction, the frictional vibration will occur easily, and the whole friction system tends to be unstable [17].

As shown by smooth curves, the normal force was on the rise both at 10 Hz and 2 Hz, showing certain periodic fluctuations. By amplifying the curve of 5A06 aluminium alloy along the Y axis in Figure 10c, it was found (Figure 13) that the normal contact pressure increased in the first segment (Figure 13(I)) due to the frictional thermal expansion, but it declined slightly in the second segment because the relatively high-temperature zone was worn and ground [18] (Figure 13(II)). Furthermore, in the third segment, the worn surface experienced thermal expansion again (Figure 13(III)), which was consistent with the cycle in Figure 1. Thus, the normal positive contact pressure increased, showing certain periodicity. The fluctuation trends for the normal force of 316L stainless steel (Figure 11c,d) and pure titanium (Figure 12c,d) basically accorded with this fluctuating upward trend.

3.4. Model Verification

The proposed model was verified based on the above experimental results. In this study, the wear coefficient was obtained from the Archard equation below:

$$K = \frac{MH}{P_0 L \rho} \quad (20)$$

Due to the inconspicuous influence of frictional thermal expansion on the degree of wear at the reciprocating frequency of 2 Hz, the wear mass of pure titanium, 316L

stainless steel and 5A06 aluminium alloy at this frequency was used to calculate their respective wear coefficients, as shown in Table 4. In addition, this table also includes these materials' elasticity modulus [19–21], yield strength [22–24], density [25–27] and coefficient of thermal expansion [28–30]. Figure 14 shows the actual wear mass and that predicted by modified and Archard models under a stroke of 24 m, initial normal contact load of 40 N and reciprocating frequency of 10 Hz. It can be found that the wear mass predicted by the modified model is more precise than that by the Archard one.

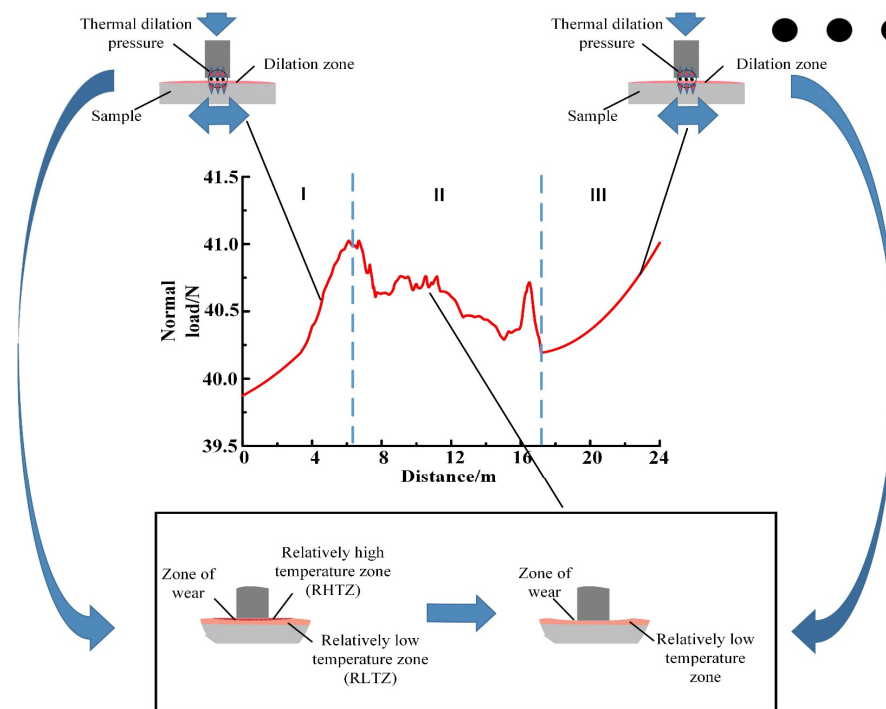


Figure 13. The time–history curve of normal contact load smoothed by neighbourhood averaging method and the wear stage corresponding to different segments.

Table 4. Parameters for 316L stainless steel, pure titanium and 5A06 aluminium alloy.

Material	Parameter	K	E/(Gpa)	H/(Mpa)	ρ (kg/m ³)	APL/ (1/°C)
Pure Ti		2.03×10^{-4}	110	284	4510	10.5×10^{-6}
Aluminum alloy		1.90×10^{-4}	70	224.25	2700	23.6×10^{-6}
316L Steel		0.2×10^{-4}	193	310	7980	17.3×10^{-6}

When the wear mass was predicted by Archard and modified models, the errors for pure titanium were 32.6% and 8.7%, respectively, showing that the latter's precision was improved by 23.9%. For 5A06 aluminium alloy, the errors were 72.8% and 65.4%, respectively, and the precision was improved by 7.4%. For 316L stainless steel, the errors were 68.4% and 15.8%, respectively, and the precision was improved by 52.6%. Thereinto, the errors for the wear mass of 5A06 aluminium alloy predicted by both models were above 50%, which is due to the fact that the hard particles that are produced in the process of friction have a “plough-cutting” effect on this relatively soft material [18].

As shown in Figure 14, the error was relatively large between the actual wear mass and that calculated with the typical Archard model. However, the value calculated with the modified model was closer to the actual one. Therefore, it can be concluded that the modified Archard wear model, with a higher precision, is suitable for the working condition in which the friction time is long and the frictional heat is obvious, for example, the wear prediction of the brake disc.

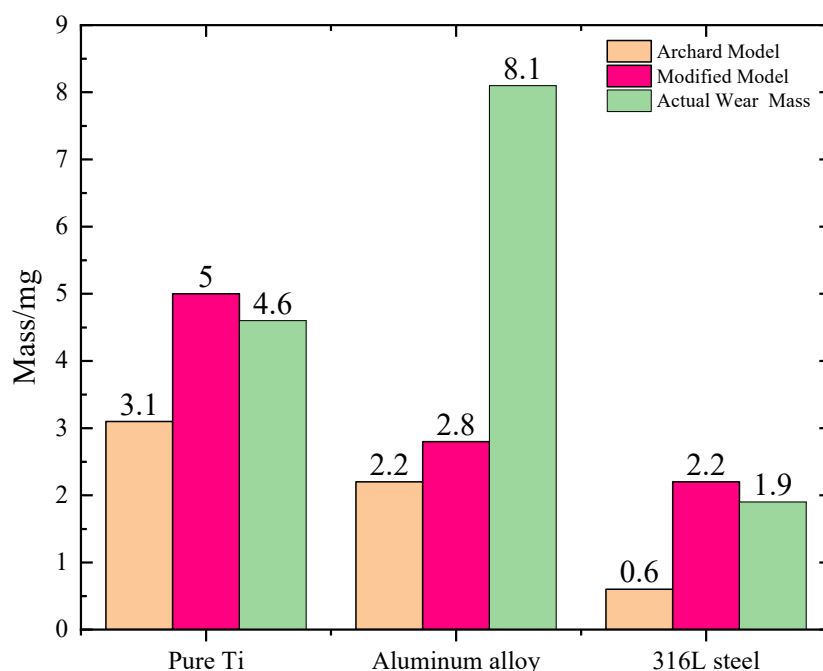


Figure 14. Comparison diagram of the actual wear mass and that calculated with Archard and modified models.

4. Conclusions

In this study, 316L stainless steel was first adopted to reveal the mapping relation of the initial normal contact load, average velocity, frictional heat, and wear mass. Then, based on this finding, the influences of different reciprocating frequencies and temperatures on the normal load were discussed for 316L stainless steel, pure titanium and 5A06 aluminium alloy to explore the mechanism of frictional thermal wear. Finally, a new model for the prediction of wear mass was proposed. The main conclusions are as follows:

- (1) The frictional temperature increases with the initial positive contact pressure, reciprocating frequency and friction time.
- (2) The wear mass also increases with rising temperature.
- (3) The mechanism of frictional thermal wear is analysed. With the generation of frictional heat, the normal force fluctuates periodically, and the wear mass and temperature increase in a cyclic iterative manner in the contact area.
- (4) A wear model based on frictional thermal expansion is proposed. The actual wear mass, the predicted wear mass by the modified model and the predicted wear mass by Archard were measured at a reciprocating frequency of 10 Hz, an initial normal contact load of 40 N and a travel distance of 24 m. The results show that the modified model can predict the wear mass more accurately than the traditional Archard wear model, and the accuracy of the modified model is improved by 52.6%, 7.4% and 23.9% for the 316L stainless steel, the 5A06 aluminium alloy and the pure titanium, respectively. Since the proposed model is limited to specific workpiece types and operating conditions, it will be a reliable model for predicting workpiece material wear under these conditions for future studies.

Author Contributions: Conceptualization and validation, Q.S.; writing—original draft preparation and visualization, D.Z.; formal analysis and methodology, Q.S.; resources, D.Z.; supervision, Q.S.; investigation, D.Z.; writing—review and editing, Q.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Davanageri, M.B.; Narendranath, S.; Kadoli, R. Modeling and Optimization of Wear Rate of AISI 2507 Super Duplex Stainless Steel. *Silicon* **2019**, *11*, 1023–1034. [CrossRef]
2. Rao, T.B.; Ponugoti, G.R. Characterization, Prediction, and Optimization of Dry Sliding Wear Behaviour of Al6061/WC Composites. *Trans. Indian Inst. Met.* **2021**, *74*, 159–178. [CrossRef]
3. Khatkar, S.K.; Verma, R.; Sumankant; Thakur, A.; Sharma, R. Optimization and Effect of Reinforcements on the Sliding Wear Behavior of Self-Lubricating AZ91D-SiC-Gr Hybrid Composites. *Silicon* **2021**, *13*, 1461–1473. [CrossRef]
4. Archard, J.F. Contact and Rubbing of Flat Surfaces. *J. Appl. Phys.* **1953**, *24*, 981–988. [CrossRef]
5. Porter, J.H.; Brake, M.R.W. Towards a predictive, physics-based friction model for the dynamics of jointed structures. *Mech. Syst. Signal Process.* **2023**, *192*, 110210. [CrossRef]
6. Wei, X.K.; Meng, H.F.; He, J.H.; Jia, L.M.; Li, Z.G. Wear analysis and prediction of rigid catenary contact wire and pantograph strip for railway system. *Wear* **2020**, *442*, 203118. [CrossRef]
7. Popov, V.L.; Pohrt, R. Adhesive wear and particle emission: Numerical approach based on asperity-free formulation of Rabinowicz criterion. *Friction* **2018**, *6*, 260–273. [CrossRef]
8. Yu, G.; Xia, W.; Song, Z.; Wu, R.; Wang, S.; Yao, Y. Wear-life analysis of deep groove ball bearings based on Archard wear theory. *J. Mech. Sci. Technol.* **2018**, *32*, 3329–3336. [CrossRef]
9. Tabrizi, A.T.; Aghajani, H.; Saghaian, H.; Laleh, F.F. Correction of Archard Equation for Wear Behavior of Modified Pure Titanium. *Tribol. Int.* **2021**, *155*, 106772. [CrossRef]
10. Yla, B.; Twl, A.; Bdb, C. Dynamic changes of mechanical properties induced by friction in the Archard wear model. *Wear* **2019**, *428*, 366–375. [CrossRef]
11. Dyck, T.; Bund, A. An adaption of the Archard equation for electrical contacts with thin coatings. *Tribol. Int.* **2016**, *102*, 1–9. [CrossRef]
12. Pastewka, L.; Moser, S.; Moseler, M. Atomistic insights into the running-in, lubrication, and failure of hydrogenated diamond-like carbon coatings. *Tribol. Lett.* **2010**, *39*, 49–61. [CrossRef]
13. Aghababaei, R.; Zhao, K. Micromechanics of material detachment during adhesive wear: A numerical assessment of Archard's wear model. *Wear* **2021**, *476*, 203739. [CrossRef]
14. Milanese, E.; Brink, T.; Aghababaei, R.; Molinari, J.-F. Emergence of self-affine surfaces during adhesive wear. *Nat. Commun.* **2019**, *10*, 1116. [CrossRef] [PubMed]
15. Popova, E.; Popov, V.L.; Kim, D.E. 60 years of Rabinowicz' criterion for adhesive wear. *Friction* **2018**, *6*, 341–348. [CrossRef]
16. Lichtenberg, K.; Weidenmann, K.A. Effect of Reinforcement Size and Orientation on the Thermal Expansion Behavior of Metallic Glass Reinforced Metal Matrix Composites Produced by Gas Pressure Infiltration. *Thermochim. Acta* **2017**, *654*, 85–92. [CrossRef]
17. Wu, C.; Chen, F.; Long, X. The self-excited vibration induced by friction of the shaft-hull coupled system with the water-lubricated rubber bearing and its stick-slip phenomenon. *Ocean. Eng.* **2020**, *198*, 107002. [CrossRef]
18. Shan, C.; Zhang, M.; Zhang, S.; Dang, J. Prediction of machining-induced residual stress in orthogonal cutting of Ti6Al4V. *Int. J. Adv. Manuf. Technol.* **2020**, *107*, 2375–2385. [CrossRef]
19. Topolski, K.; Brynk, T.; Garbacz, H. Elastic modulus of nanocrystalline titanium evaluated by cyclic tensile method. *Arch. Civ. Mech. Eng.* **2016**, *16*, 927–934. [CrossRef]
20. Bahri, A.; Guermazi, N.; Bargui, M.; Elleuch, K. Estimation of the elastic modulus of the alumina coated AA1050 aluminum: Modeling and experiments. *Mater. Sci. Eng. A* **2016**, *670*, 188–195. [CrossRef]
21. Ferriell, W.D.; Batt, G.S.; Desjardins, J.D. Finite element validation of 3D American football faceguard structural stiffness models. *Proc. Inst. Mech. Eng. Part P J. Sports Eng. Technol.* **2021**, *235*, 201–211. [CrossRef]
22. Fattah-Alhosseini, A.; Keshavarz, M.K.; Mazaheri, Y.; Ansari, A.R.; Karimi, M. Strengthening mechanisms of nano-grained commercial pure titanium processed by accumulative roll bonding. *Mater. Sci. Eng. A* **2017**, *693*, 164–169. [CrossRef]
23. Li, W. Experimental study on tensile mechanical behaviors of 5A06 aluminum alloy under short time elevated temperature. In Proceedings of the Fourth International Conference on Experimental Mechanics, Singapore, 18–20 November 2009. [CrossRef]
24. Mao, X.; Kang, S.H.; Kim, T.K.; Kim, S.C.; Oh, K.H.; Jang, J. Microstructure and Mechanical Properties of Ultrafine-Grained Austenitic Oxide Dispersion Strengthened Steel. *Metall. Mater. Trans. A* **2016**, *47*, 5334–5343. [CrossRef]
25. Renaudin, P.; Blancard, C.; Faussurier, G.; Noiret, P. Combined Pressure and Electrical-Resistivity Measurements of Warm Dense Aluminum and Titanium Plasmas. *Phys. Rev. Lett.* **2002**, *88*, 215001. [CrossRef]
26. Getmanskii, I.V.; Koval, V.V.; Minyaev, R.M.; Boldyrev, A.I.; Minkin, V.I. Supertetrahedral Aluminum—A New Allotropic Ultralight Crystalline Form of Aluminum. *J. Phys. Chem. C* **2017**, *121*, 22187–22190. [CrossRef]
27. Deng, Y.; Mao, Z.; Yang, N.; Niu, X.; Lu, X. Collaborative Optimization of Density and Surface Roughness of 316L Stainless Steel in Selective Laser Melting. *Materials* **2020**, *13*, 1601. [CrossRef]

28. Zheng, Z.; Eisenlohr, P.; Bieler, T.R.; Pagan, D.C.; Dunne, F.P.E. Heterogeneous Internal Strain Evolution in Commercial Purity Titanium Due to Anisotropic Coefficients of Thermal Expansion. *JOM* **2020**, *72*, 39–47. [CrossRef]
29. Lalet, G.; Kurita, H.; Heintz, J.-M.; Lacombe, G.; Kawasaki, A.; Silvain, J.-F. Thermal expansion coefficient and thermal fatigue of discontinuous carbon fiber-reinforced copper and aluminum matrix composites without interfacial chemical bond. *J. Mater. Sci.* **2014**, *49*, 397–402. [CrossRef]
30. Yakout, M.; Elbestawi, M.A.; Veldhuis, S.C. A study of thermal expansion coefficients and microstructure during selective laser melting of Invar 36 and stainless steel 316L-ScienceDirect. *Addit. Manuf.* **2018**, *24*, 405–418. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Influence of Scanning Paths on the Weld Pool Behavior, Microstructure, and Mechanical Property of AA2060 Al-Li Alloy Joints by Laser Beam Oscillation Welding

Yanbo Song ¹, Ying Liang ^{1,*}, Hongbing Liu ¹, Luchan Lin ², Yanfeng Gao ³, Hua Zhang ³ and Jin Yang ^{1,*}

¹ School of Materials Science and Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; songyanbo97@163.com (Y.S.); lhongbing@163.com (H.L.)

² School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China; luchan.lin@sjtu.edu.cn

³ School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; gaoyf@sues.edu.cn (Y.G.); hzhang@sues.edu.cn (H.Z.)

* Correspondence: liangyinggabi@126.com (Y.L.); jyang@sues.edu.cn (J.Y.)

Abstract: In this paper, the laser beam oscillation welding (LBOW) was utilized to weld a 2 mm thick AA2060 aluminum-lithium (Al-Li) alloy plate. The weld pool behaviors under three scanning paths (pure laser, O-shaped, and ∞ -shaped) were investigated. It was observed that the O-shaped scanning path resulted in the most stable welding process. In addition, the weld macroscopic formation, microstructure, and mechanical property between different paths were studied. The results showed that pure laser and ∞ -shaped patterns produced welding defects such as spatters and collapse during the welding process, while the O-shaped pattern exhibited good macroscopic formation at varying laser powers. The O-shaped pattern promoted the finest grain in the weld center and reduced the heat input during the welding process. The equiaxed grain zone (EQZ) width of the O-shaped pattern is the smallest compared to the other two patterns at high laser power. In addition to this, the O-shaped pattern could effectively reduce the porosity in the weld. When an O-shaped scanning pattern was adopted at the ideal laser power parameter of 3000 W, the microhardness of the weld center increased by approximately 5.6% compared to pure laser mode.

Keywords: aluminum-lithium alloy; laser beam oscillation welding (LBOW); weld pool behavior; microstructure; mechanical property

1. Introduction

Replacing the traditional aeronautical Al alloys with Al-Li alloys is of great value to enhance the comprehensive properties of aerospace equipment [1]. The addition of lithium elements to aluminum alloys results in the formation of Al-Li alloys that retain high-strength, excellent corrosion resistance, and fatigue resistance, while simultaneously reducing specific gravity and enhancing stiffness [2,3]. Consequently, Al-Li alloys hold promising prospects for utilization in contemporary aerospace manufacturing [4,5]. Laser beam welding offers several benefits, including a high energy density, minimal heat input, absence of mechanical contact, and the ability to weld various materials [6,7]. Laser beam welding achieves optimal welds with a high ratio of depth-to-width, a restricted heat-affected zone, minimal deformation, and excellent mechanical qualities due to its significant energy density [8,9]. When the laser beam is welding high-strength aluminum alloys, it will appear to have high reflectivity, spatter, high porosity, and a joint softening phenomenon [10,11]. These problems seriously restrict the application of laser beams in the aluminum alloy welding field. Laser beam oscillation welding (LBOW) is a new type of welding method that uses a galvanometer-type laser head; it can control the beam in a high frequency under different paths, and has many advantages, such as grain refinement, low porosity, and mechanical property strengthening of joints [12,13].

Numerous scholars have conducted studies on the process of laser beam oscillation welding. Thiel [14] demonstrated that the welding efficiency was notably enhanced in laser scanning welding compared to pure laser welding, while the susceptibility of the welding process to focus drift was diminished. The welding process became more efficient as the sensitivity to focal point drift decreased. Ai [15] developed a three-dimensional numerical model to investigate the dynamic behavior characteristics of the weld pool in oscillatory laser welding, and found that the vortices formed in the weld pool-induced complex fluid flow characteristics. Chen [16] employed an ∞ -shaped scanning mode for welding 5052 aluminum alloy. The results showed a significant increase in both the depth and width of the ∞ -shaped weld compared to a pure laser weld. Similarly, Wang [17] utilized three different scanning paths of the laser beam to weld 5A06 aluminum alloy. The experiments demonstrated that the weld seam under infinitely shaped laser path was effective in reducing the porosity of the weld zone. The cooling rate during the welding process was an important factor affecting the mechanical properties of the material [18,19]; LBOW changed the thermal input of conventional lasers, thus the cooling rate changes. Zhang [20] employed an oscillating laser to join mild steel and observed that the oscillating laser effectively restrained grain enlargement by changing the linear velocity of the laser beam, and enhanced the tensile strength of welded joints. Zhang [21] examined the fundamental mechanism of the O-shaped scanning laser welding process by the application of computational fluid dynamics methodology. The results demonstrated that the O-shaped scanning laser diminished the maximum temperature and temperature gradient while generating a novel vortex within the weld pool, which increased the cooling rate of the weld, thus improving the mechanical properties of the weld seam. In a study conducted by Smith [22], dissimilar metal welding tests were performed using a laser scanning welding procedure with an O-shaped scanning pattern. By accurately manipulating the scanning profile, velocity, and laser intensity, it was possible to effectively manage the heat input in the welded joint, increasing the degree of subcooling and improving mechanical properties. Conversely, it allowed for the regulation of the fusion depth of the joint, effectively suppressing the formation of brittle intermetallic compounds during the welding procedure. Nevertheless, the investigation into the impact of different scanning trajectories on the weld pool shape and joint strength lacks thoroughness. This study investigates the forming mechanism of laser beam oscillation welding in the AA2060 Al-Li alloy using three scanning paths, as follows: pure laser, O-shaped, and ∞ -shaped. The research aims to offer fundamental theoretical support for the laser beam oscillation welding process of Al-Li alloy.

2. Experimental Procedures

2.1. Materials

The dimension of the AA2060-T8 Al-Li alloy plate utilized for the experiment was 150 mm $\times$ 50 mm $\times$ 2 mm, and its chemical composition was presented in Table 1. The heat treatment state was T8, which meant that the solid solution treatment was followed by cold deformation and subsequent artificial aging, and the temperature of it was 155 °C.

Table 1. Chemical composition of AA2060-T8 (wt. %) [23].

Element	Cu	Li	Zn	Mg	Mn	Zr	Ag	Si	Fe	Ti	Al
Percent	3.9	0.8	0.32	0.7	0.29	0.1	0.34	0.02	0.02	<0.1	Bal.

2.2. Equipment and Methods

As depicted in Figure 1, the welding experiment employed a single-module continuous fiber laser (MFSC 5000 W-6000 W) with a maximum power output of 6000 W. The laser welding defocusing amount was 0 mm. The laser beam wavelength was 1064 nm, the pass aperture was 30 mm, the quasi-diameter focal length was 100 mm, and the focused spot diameter was 0.2 mm. Pure argon (99.99%) was employed as the shielding gas

with flow rates of 15 L/min. The High-Speed Camera (KeTianjian, Changsha, China) was utilized to capture photographs with an exposure time of 45 ms, a frame rate of 2200 Hz, and a pulse width time of 45 ms. The diagram illustrating the structure of laser welding is shown in Figure 1. The scanning trajectory is depicted in Figure 2. The beam trajectory was determined by the deflection of the beam deflector, which was controlled by two galvanometer motors operating in orthogonal directions. The beam was swiftly shifted within a specific range to achieve scanning trajectories that were pure laser, O-shaped, and ∞ -shaped. The welding parameters are shown in Table 2.

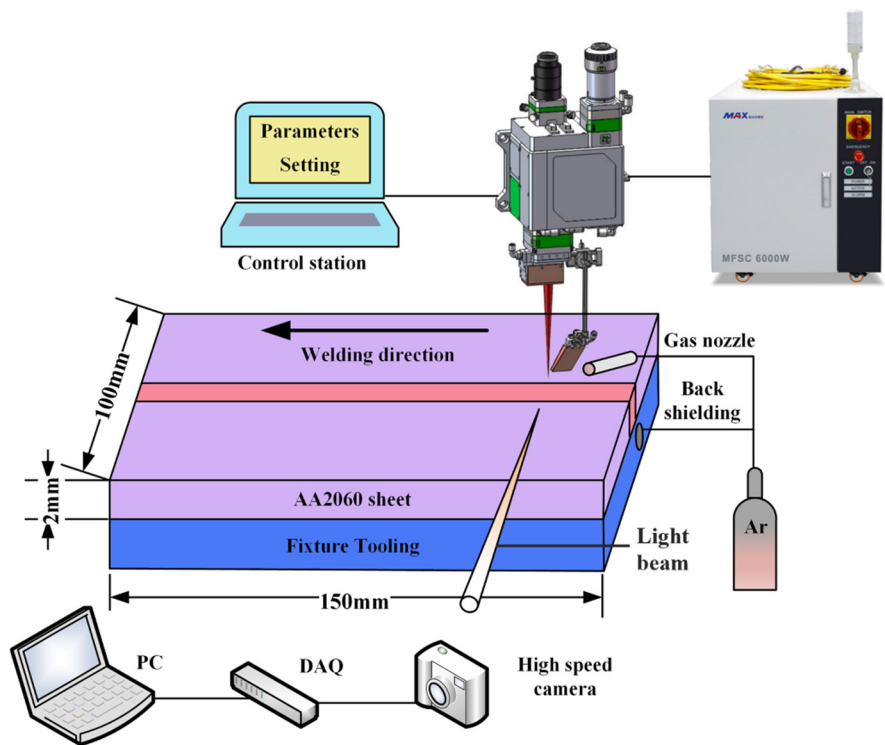


Figure 1. Schematic diagram of the experimental set-up.

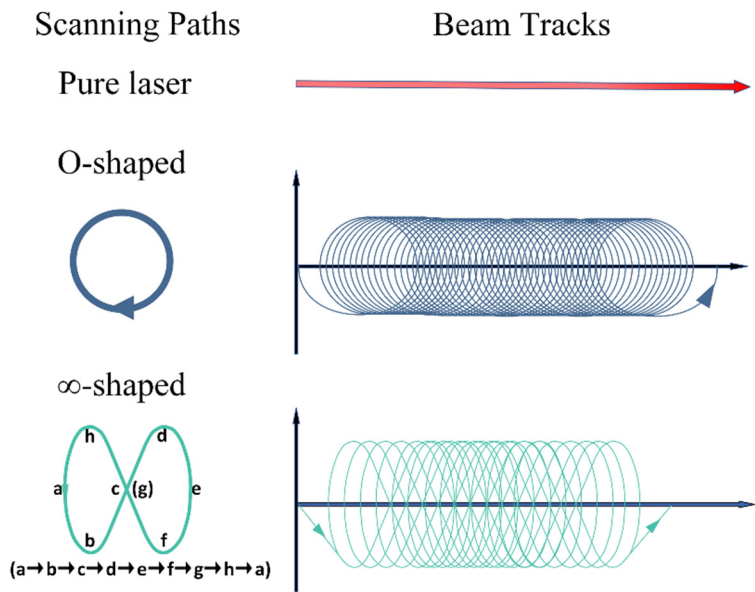
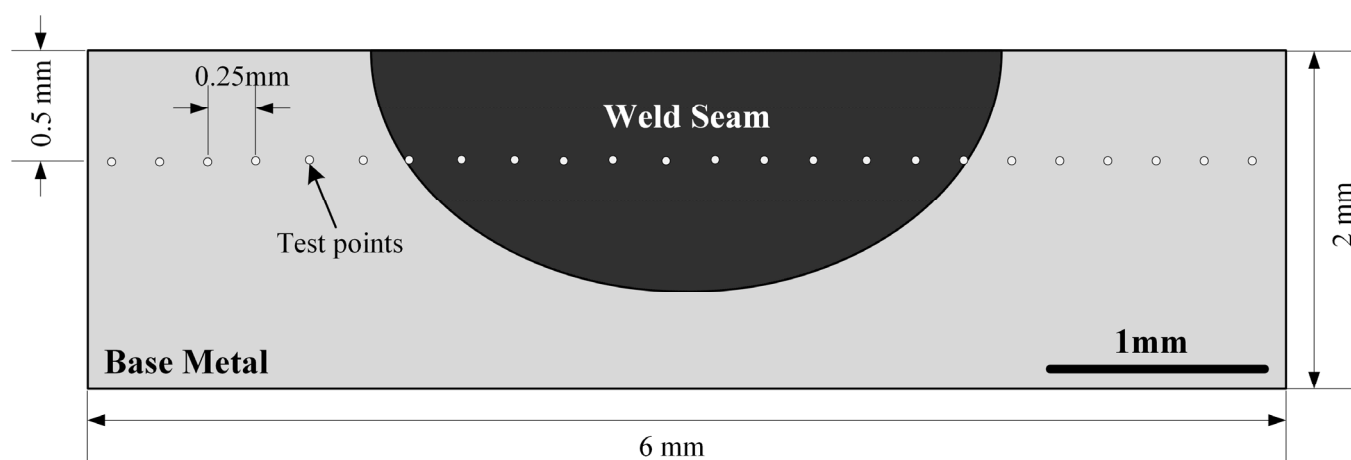


Figure 2. Schematic diagram of the scanning paths and beam tracks.

Table 2. Welding parameters.

Sample	Scanning Path	Laser Power P (W)	Welding Speed V (mm/s)	Scanning Frequency F (Hz)	Scanning Amplitude A (mm)
1	Pure laser	3000	35	0	0
2	O-shaped	3000	35	100	1
3	∞ -shaped	3000	35	100	1
4	Pure laser	3500	35	0	0
5	O-shaped	3500	35	100	1
6	∞ -shaped	3500	35	100	1

Prior to welding, it was necessary to polish and clean the test plate, and then it was wiped with ethanol to eliminate any surface debris and contaminants. After welding, the metallographic specimen was prepared by making a line cut perpendicular to the welding direction. Subsequently, it was corroded using Keller's reagent (with a volume ratio of $\text{H}_2\text{O}:\text{HF}:\text{HCL}:\text{HNO}_3 = 95:1:1.5:2.5$) after embedding, roughing, grinding, and polishing. We utilized the Tescan vega3 scanning electron microscope to observe the microstructure, and employed a Vickers microhardness tester to measure the hardness of the joints. The hardness testing was conducted along the transverse centerline of the joints. As depicted in Figure 3, the hardness sampling points were spaced at intervals of 0.25 mm and 0.5 mm away from the sheet surface. A loading load of 100 g for a sustained loading time of 15 s was applied. As for the microhardness measurement, each microhardness value was the average obtained under the condition of taking three samples for three hardness tests. The confidence interval was 95%, and standard deviation was 1.9% after reviewing the related standards and taking into account experimental errors.

**Figure 3.** Schematic diagram of the microhardness.

3. Results and Discussion

3.1. Macrostructure

Tables 3 and 4 display the impact of scanning pathways on the surface morphology and cross-section morphology of the weld at different laser power levels. Observations reveal that with a laser power of 3000 W, the surface of the pure laser weld exhibits unevenness, noticeable oxidation, a high concentration of spatters surrounding the weld, and a slight undercut. Upon transitioning to the scanning laser welding technique, there is a notable alteration in the surface configuration of the weld. When the scanning path is O-shaped, the width of the weld path increases significantly, resulting in a uniform silver-white fish scale pattern on the weld surface without oxidation. Additionally, the number of spatters around the weld decreases significantly. On the other hand, when the scanning path is ∞ -shaped, the width of the weld path is similar to the O-shaped one. However, the weld surface is less scaly and exhibits better uniformity and smoothness. Nevertheless, when the

laser power is elevated to 3500 W and the scanning path is either pure laser or ∞-shaped, varying levels of undercollapse manifest at the rear end of the weld as a result of heat accumulation, and there is an increased presence of spatter surrounding the weld. At this level of power, the weld production of the O-shaped scanning route remains superior, exhibiting a smooth surface and absence of spatter. Additionally, the breadth of the weld path shows minimal variation at this power level. Hence, it is evident that the utilization of the O-shaped scanning laser welding technique results in improved weld zone formation and enhanced process stability.

Table 3. Surface forming and cross-section morphology of AA2060 weld joints under 3000 W.

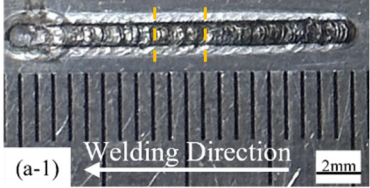
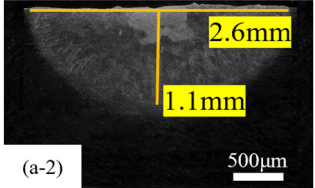
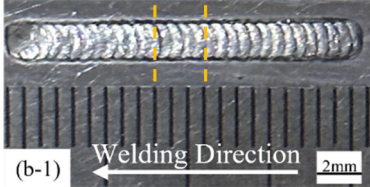
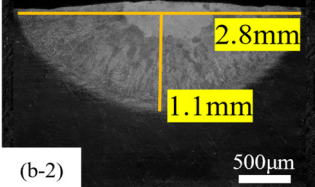
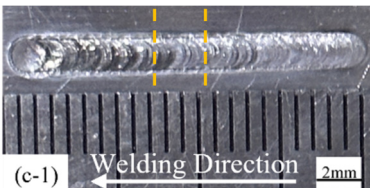
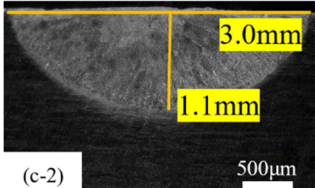
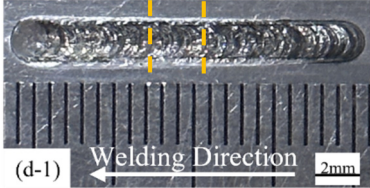
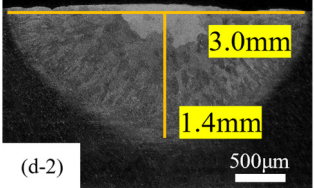
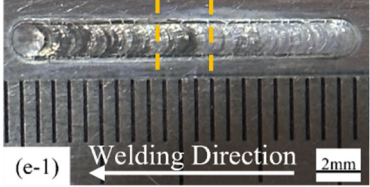
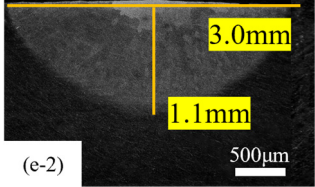
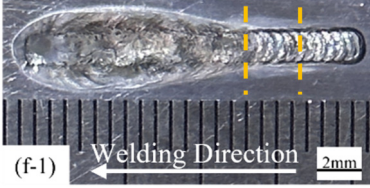
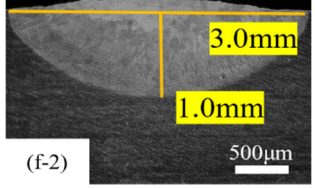
Process Parameters	Top-Surface	Cross-Section
Pure laser		
O-shaped		
∞-shaped		

Table 4. Surface forming and cross-section morphology of AA2060 weld joints under 3500 W.

Process Parameters	Top-Surface	Cross-Section
Pure laser		
O-shaped		
∞-shaped		

As shown in Figure 4, at a laser power of 3000 W, the pure laser produces the smallest weld width in the weld, while the ∞ -shaped scanning path produces the largest melt width. This is because the O-shaped and ∞ -shaped scanning paths increase the heated area of the weld, leading to an increase in weld width. Additionally, when the scanning paths overlap in a straight line, the weld depth of fusion remains relatively unchanged, regardless of the scanning path. It is evident that the scanning path has a more pronounced impact on the width of the melted area when lower power levels are used. Increasing the laser power to 3500 W results in the greatest weld depth of fusion when using the pure laser. Conversely, the ∞ -shaped scanning path yields the smallest weld depth of fusion. However, the weld width remains constant regardless of the scanning path. This is because, at higher power levels, most of the heat is concentrated in the direction of the weld depth of fusion when no swing is applied. On the other hand, the O-shaped and ∞ -shaped paths have weaker effects on the depth of fusion than pure laser due to their larger amplitudes, which causes the heat to propagate more rapidly than pure laser.

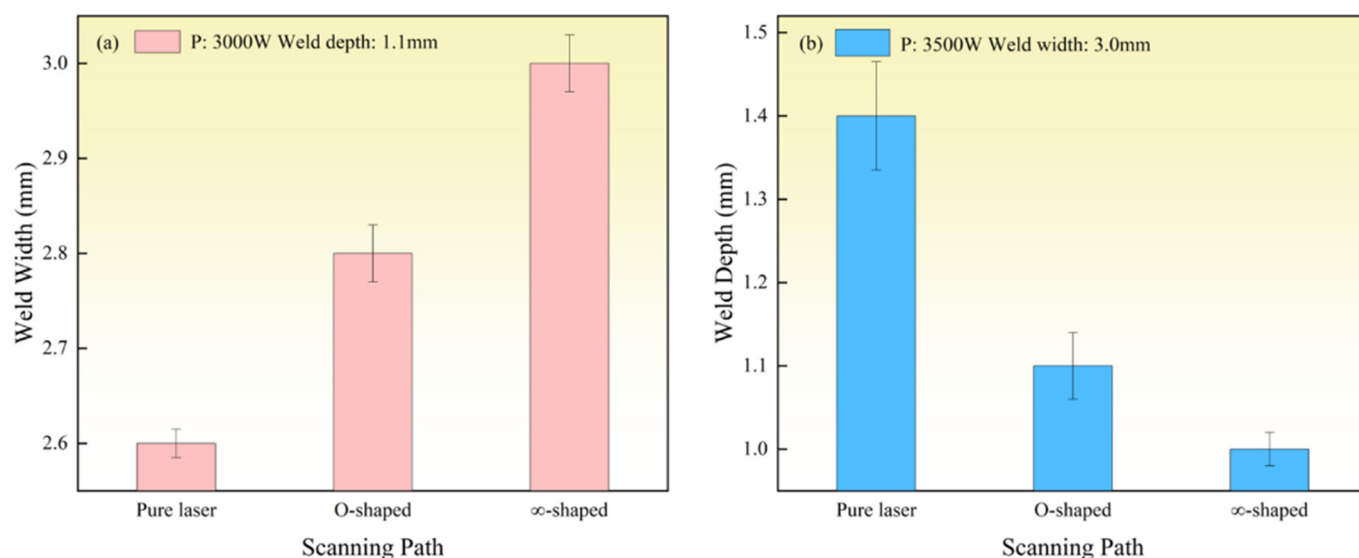


Figure 4. (a) Weld width under different scanning paths and (b) weld depth under different scanning paths.

3.2. Weld Pool Behavior

High-speed cameras were employed to capture the flow behavior of the weld pool throughout a single cycle under each of the three scanning paths in order to examine the process by which welded connections are formed. The resulting data are presented in Figures 5 and 6.

As depicted in Figure 5a, using a 3000 W laser during the pure laser welding process, a significant portion of laser energy is absorbed by the hole, leading to an elevation in the internal temperature of the hole. Instead, it causes substantial fluctuations in the weld pool and the generation of a substantial amount of plasma and metal vapor. The directional movement of the weld pool is caused by the surface tension gradient of the liquid metal, which is influenced by Marangoni convection. In this scenario, the weld pool oscillation causes some of the molten metal to be expelled when the plasma is emitted from the base metal surface. As a result, spatters are prone to forming on the weld surface.

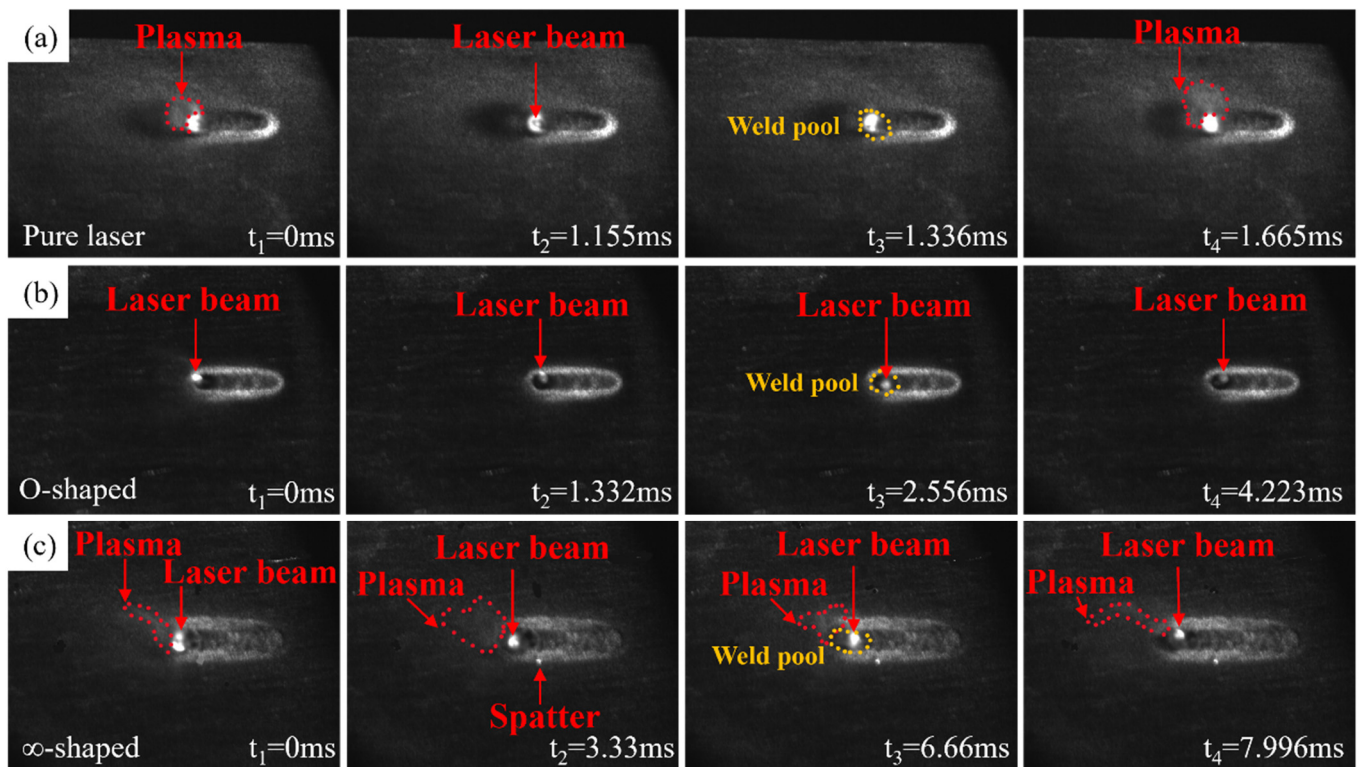


Figure 5. High-speed camera images of 3000 W laser welding: (a) pure laser, (b) O-shaped, and (c) ∞-shaped.

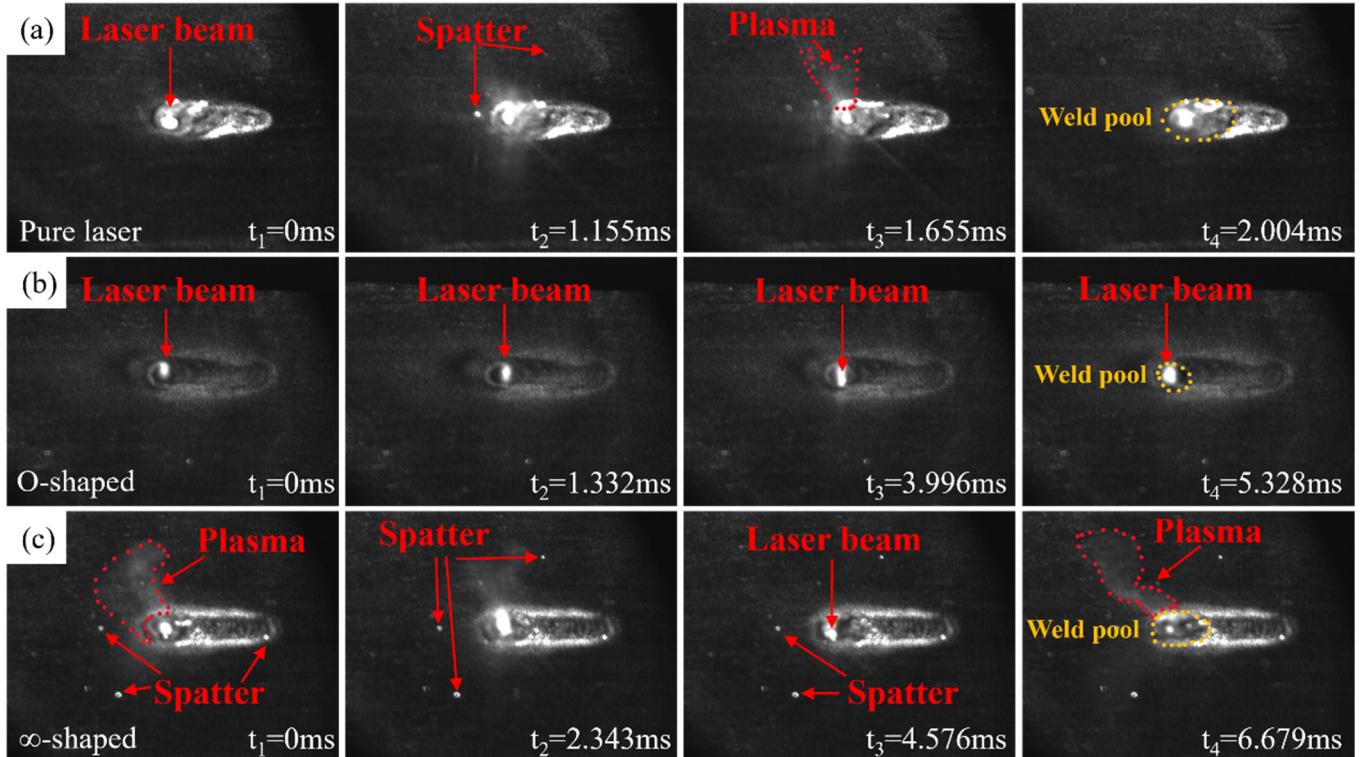


Figure 6. High-speed camera view of 3500 W laser welding: (a) pure laser, (b) O-shaped, and (c) ∞-shaped.

Figure 5b, shows that in the O-shaped scanning welding process, after adopting the O-shaped path, the bursting of plasma/metal vapor is closely related to the change in the laser beam position. As the laser beam position keeps changing, the orientation of plasma also moves, resulting in a decrease in the amount of heat absorbed by the hole. Consequently, this suppresses the bursting of the plasma and the metal vapor. Simultaneously, the velocity of the laser spot's motion is greatly augmented, resulting in the continuous fluctuations in the laser beam position. This dynamic alteration enhances the extent of the impact of the laser beam on the liquid metal, decelerates the rate at which the weld pool cools, reduces the fluctuation of the liquid metal, aids in stabilizing the weld pool, and effectively enhances the uniformity of the weld formation. Furthermore, when compared to the pure laser, the size of the opening in the O-shaped scanning path increases. However, this change in size is relatively gradual and does not exhibit significant fluctuations over time. The high-speed camera shows that the fluctuation of the weld pool surface is relatively smooth, and the splashing phenomenon is significantly reduced.

As can be observed in Figure 5c, in ∞ -shaped scanning path laser welding, the volume of plasma and metal vapor is considerably decreased compared to the pure laser welding condition. In this process, the plasma undergoes minimal oscillation while the laser beam follows a distinct " ∞ " path. The laser beam first melts the alloy at the front end of the weld pool at high temperatures, and then heats the metal at the back end twice as it advances to the back end of the weld pool. The weld pool experiences rapid oscillation, resulting in repeated cycles of cooling, solidification, and heating, leading to a decrease in plasma burst.

As shown in Figure 6a,b, when the laser power is 3500 W, the fluctuation in the size of the weld pool during pure laser and O-shaped scanning welding is comparable to that observed at 3000 W. In Figure 6c, under the ∞ -shaped scanning path, the laser power is elevated, resulting in repeated heating of the weld pool and a substantial increase in heat input. The accumulation of heat results in the concentration of heat in the central and posterior regions of the weld, ultimately resulting in the collapse of the liquefied metal pool and the production of substantial quantities of plasma gas and spatter. This phenomenon suggests that when using high power conditions, the thermal treatment of the weld pool during laser welding with a ∞ -shaped scanning path becomes unstable. This instability leads to a notable rise in plasma gas and spatter, which has a negative impact on the quality of the weld.

Based on the analysis of the laser scanning weld shaping law, it showed that in the LBOW process, the laser beam constantly changes position. This process can produce two effects. Firstly, it stirs the weld pool, increasing the fluidity of the molten metal to become larger compared to a pure laser case, which allows for stable welding even at lower laser power. Secondly, the continuous movement of the laser beam increases the heating range and the volume of the weld pool that reduces the generation of plasma and metal vapors, resulting in a significant reduction of spatter. An extensive analysis of the outcomes in the two conditions of 3000 W and 3500 W demonstrates that O-shaped scanning laser welding is minimally influenced by the laser power, it exhibits the highest level of stability in the welding process, and achieves an optimal weld shape.

3.3. Microstructure

3.3.1. Crystal Morphology

In order to investigate the characteristic of weld microstructure in the Al-Li alloy during various laser scanning path welding procedures, a scanning electron microscope was utilized to examine the weld structure subsequent to welding. Figure 7 is a schematic diagram of the microstructure of an Al-Li alloy joint, and Figure 8 is the metallographic picture of the actual weld. The weld joint is categorized into four regions based on the heat condition, as follows: the base metal (BM), heat-affected zone (HAZ), transition zone (TZ), and weld zone (WZ). The transition zone consists of the equiaxed grain zone (EQZ) and the partially melted zone (PMZ). The EQZ is a unique fine-grain region between the HAZ and WZ of Al-Li alloy. Several studies have examined the process by which

this region is formed [24–26]. Generally, the weld zone includes columnar dendrites and equiaxed dendrites.

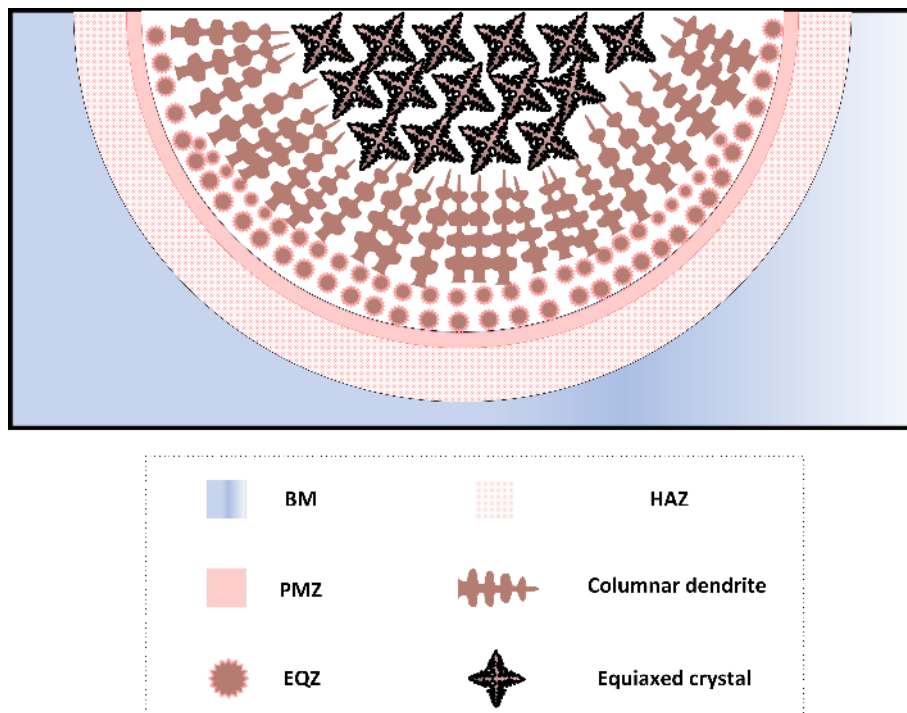


Figure 7. Schematic diagram of microstructure of Al-Li alloy joint.

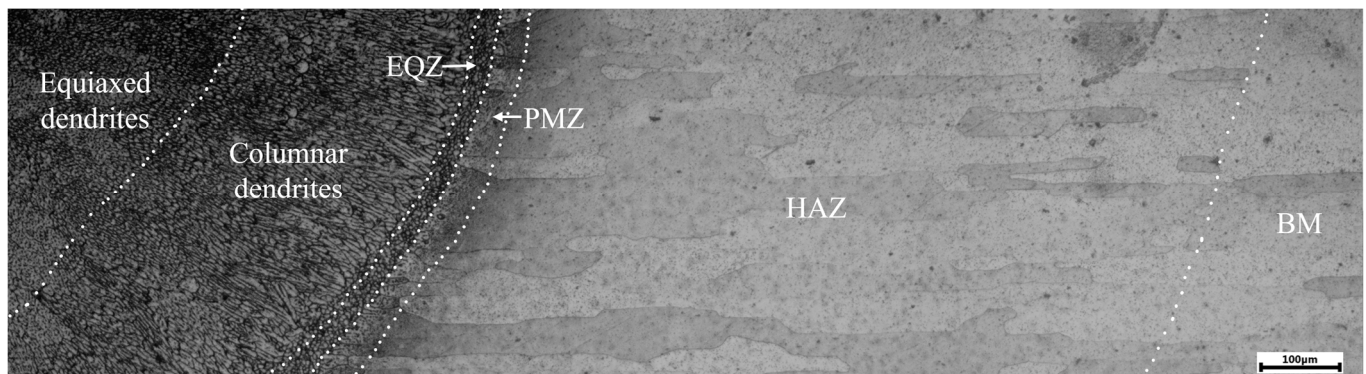


Figure 8. Typical weld metallograph.

During the initial stage of solidification in the weld pool, elevated temperatures and increased welding speeds result in greater temperature differences and faster formation of crystals. In the region of the fusion line near the edge of the weld pool, the temperature is relatively low, making it difficult for the grains to grow, and thus, an EQZ is formed. Figures 9 and 10 show that when the laser power is 3000 W, the EQZ width is 21.76 μm with pure laser, the O-shaped scanning EQZ width is 17.73 μm , and the ∞ -shaped scanning EQZ width is 13.69 μm ; when the laser power is increased to 3500 W, the EQZ width is 18.71 μm with pure laser, the O-shaped scanning EQZ width is 13.73 μm , and the EQZ width of ∞ -shaped scanning is 18.71 μm . Additionally, the width of the columnar dendrites near the fine crystal region also decreases. This phenomenon occurs because the rotational motion of the laser focus alters the temperature gradient of the solid–liquid interface on both sides of the weld pool, specifically in the width direction. As a result, this change affects the process of associative crystallization and ultimately reduces the size of the columnar dendrites. The EQZ zone expands when using ∞ -shaped scanning at 3500 W. The reason for this is

that the ∞ -shaped scanning applies heat to the weld pool after increasing the laser power. This leads to an excessive amount of heat being applied, and causes fragmentation in the columnar dendrites zone.

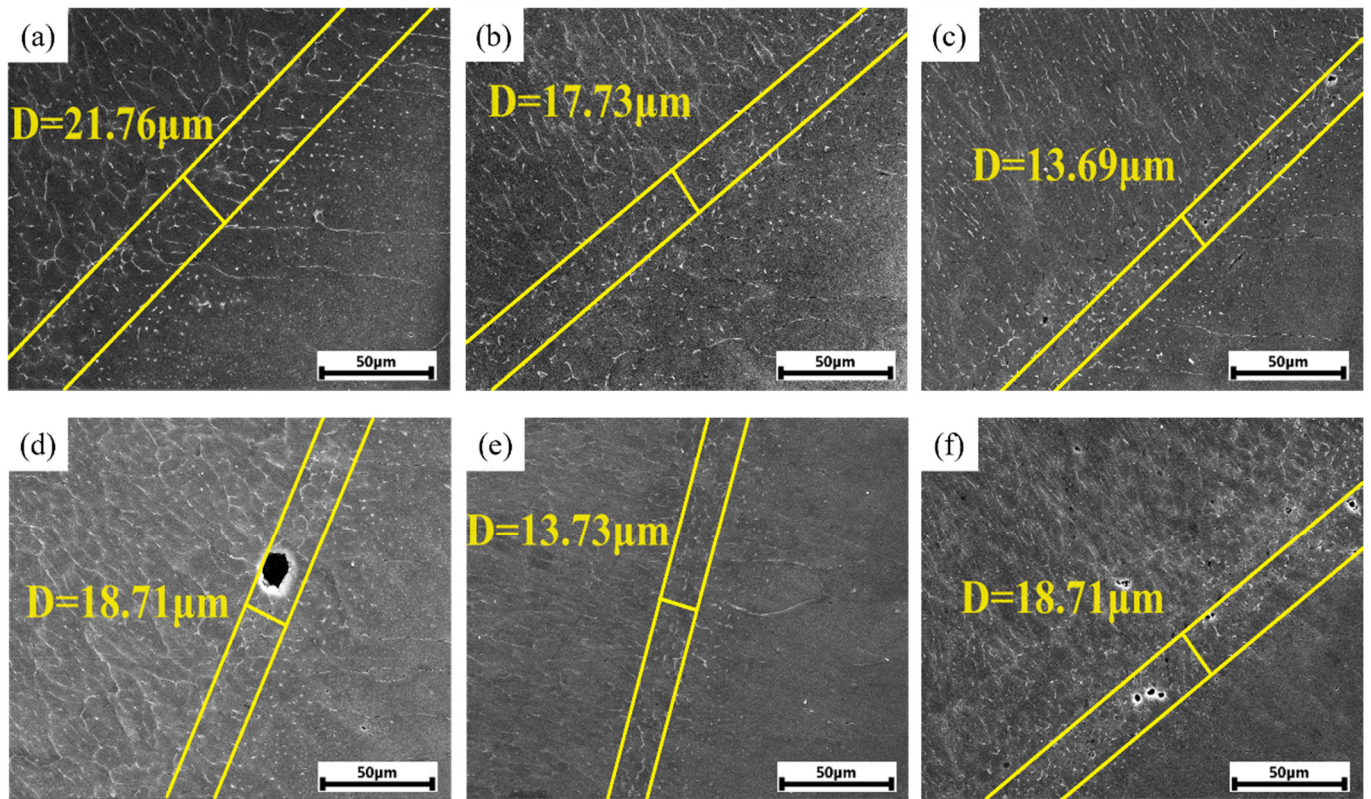


Figure 9. SEM of EQZ: (a) 3000 W pure laser, (b) 3000 W O-shaped, (c) 3000 W ∞ -shaped, (d) 3500 W pure laser, (e) 3500 W O-shaped, and (f) 3500 W ∞ -shaped.

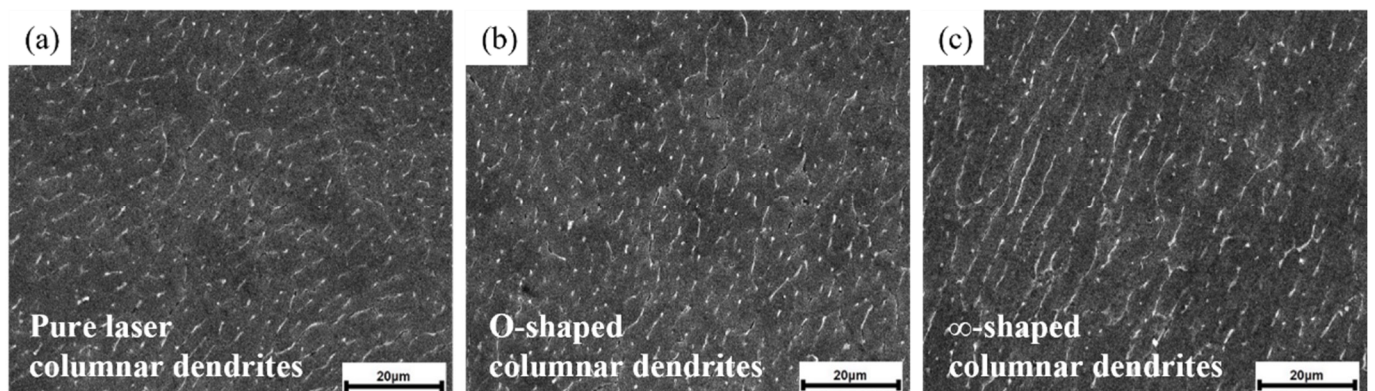


Figure 10. SEM of the columnar dendrites at 3000 W. (a) Pure laser, (b) O-shaped, and (c) ∞ -shaped.

When the laser power is 3000 W, pure laser welding and O-shaped laser welding yields a weld with no pores. ∞ -shaped laser welding has a small number of pores in the EQZ. When the laser power is 3500 W, pure laser welding yields a weld with larger pores. This is due to the rapid cooling of the weld pool, which prevents the gas from overflowing in a timely manner. The O-shaped laser welding process, due to the laser stirring effect in the weld pool and the stability of the welding process, results in the absence of any obvious pores. In contrast, the ∞ -shaped laser welding process, due to the high power welding process instability coupled with a large area of remelting, can easily lead to the inclusion of air in the weld pool, resulting in the formation of pores. The round laser welding, which is

characterized by the laser stirring in the weld pool and the stability of the welding process, does not appear for the formation of any discernible pores. In contrast, the ∞ -shaped laser welding, which is associated with the high power welding process and a large area of remelting, is prone to the inclusion of air in the weld pool, which in turn gives rise to the formation of pores.

Figure 10 shows that the high-speed scanning motion of the laser will make the direction of the heat source in the weld continuously change; according to the theory of grain directional growth, the change in the heat source trajectory will inhibit the growth of the columnar dendrites directionality, and will not lead to the emergence of a significant direction of columnar dendrites [27], which can reduce the tendency of the weld cracks.

Figure 11, shows that the grains in the middle of the weld coarsen after adopting the scanning trajectory. Research has demonstrated [28] that the movement of heat and the redistribution of solute elements during the solidification of a weld greatly impact crystal growth. In the case of laser welding of Al-Cu-Li alloys, the initial phase α -Al (gray area) solidifies first. The alloying elements, including Li, Mg, and Cu, become concentrated at the front of the crystalline structure, forming a eutectic arrangement that precipitates around α -Al. The rotational nature of the laser spot leads to localized repeated heating, greater heat input, and extended grain development time, which results in a certain degree of coarsening of the dendritic organization in the center of the weld.

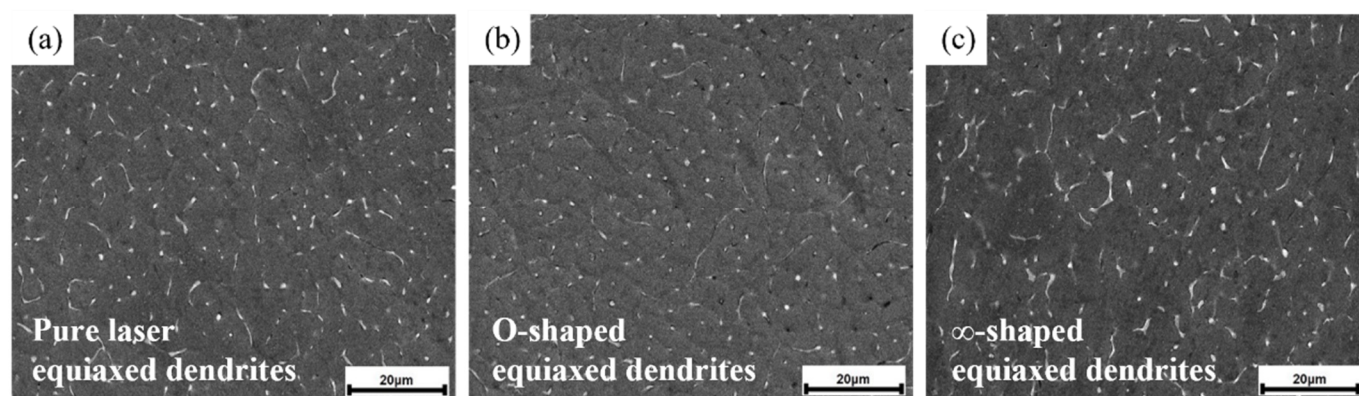


Figure 11. SEM of the equiaxed dendrites at 3000 W. (a) Pure laser, (b) O-shaped, and (c) ∞ -shaped.

It can be seen that high-speed welding under the laser scanning welding process does not cause accelerated cooling of the weld pool, and the cooling time of the weld pool can be prolonged relative to pure laser, which helps the crystal nucleation and grain growth; thus, the fine-grain area in the crystallization can be fully nucleated, and can grow into a dense fine-grain area. At the same time, the laser scanning welding process can achieve high-speed changes in the position of the heat source compared to the pure laser welding process, thus inhibiting the directional growth of grains.

3.3.2. Phase Analysis

Li, as a surfactant, comprises approximately 0.8 at. % of the Al-Li alloy. This facilitates the process of being adsorbed onto the surfaces of Al_3Zr - and Al_3 (Li, Zr)- precipitated particles [29]. Then, sample 2 was selected for phase analysis. As depicted in Figure 12, EQZ is mainly composed of α -Al (96.64% at. Al) and eutectic Al_2Cu phase (90.05 at. % Al, 8.7% at. Cu). The results of the EDS measurements reveal that the Cu content is less than it is in actuality, due to the fact that the EDS results are coming from an electron/material interaction volume, which is certainly greater in volume than the size of the investigated Al_2Cu phases. In this way the Cu content is certainly lower than the real Cu content of the Al_2Cu phase. As shown in Figure 13, the Zr element has a higher content at grain boundaries than in the α -Al matrix. Based on the theory of molten metal crystallization in welded joints [30], as the weld pool cools and solidifies, solutes are redistributed, resulting

in solute enrichment at the solid–liquid interface side of the weld pool. This enrichment causes compositional supercooling. This process results in the creation of equiaxed nuclei within the areas of the weld pool that have not hardened yet, leading to the growth of equiaxed grains. Furthermore, Zr element promotes grain refinement and equiaxed grain formation through its high tendency to segregate to the liquid/solid interface during solidification [31,32]. For EQZ, the distribution of several solute elements was examined to observe the degree of microscopic segregation of the components. As depicted in Figure 13, the elements Cu, Ag, and Zn have an uneven distribution, with a predominant enrichment at the grain borders and in the spaces between dendrites. This is owing to the non-equilibrium crystallization process that happened in the quick solidification of the weld pool, wherein the higher purity Al crystallizes first, and the crystallization front drives the solute elements from the grain center to the border.

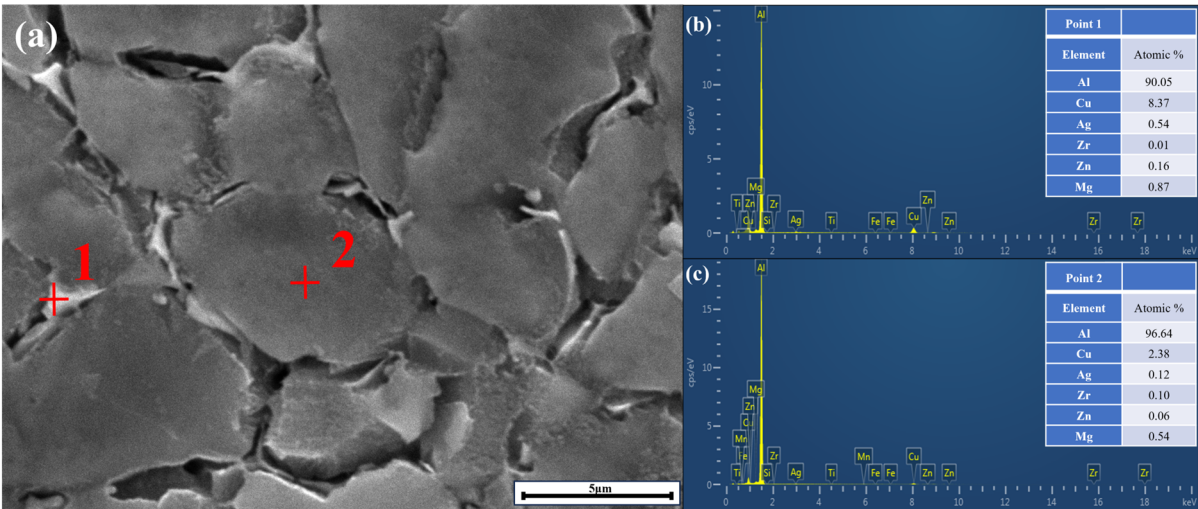


Figure 12. (a) The SEM of EQZ (b,c). The EDS from the zones.

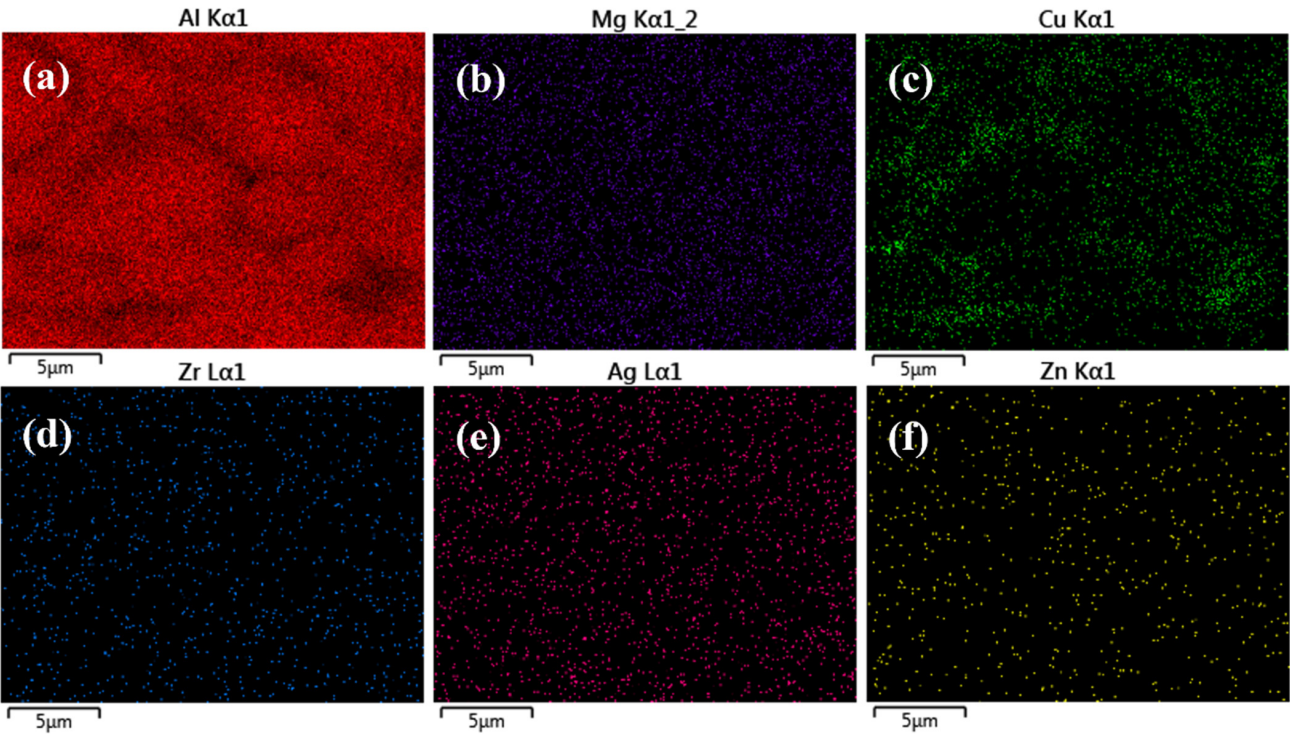


Figure 13. EDS mappings for EQZ. (a) Al, (b) Mg, (c) Cu, (d) Zr, (e) Ag, and (f) Zn.

As made evident in Figure 14, the equiaxed dendrites primarily consist of α -Al solid solution and Al_2Cu eutectic phase, with additional alloying elements being concentrated along the grain boundaries. The EDS analysis reveals that point 3 consists primarily of Al elements (98.21 at. % Al, 0.88 at. % Cu), with lower Cu content compared to the parent material (as shown in Table 1). Points 4 (96.73 at. % Al, 2.41 at. % Cu) and 5 (95.48 at. % Al, 3.45 at. % Cu) exhibit a eutectic structure that is not fully precipitated. As the degree of precipitation increases, the amount of Al decreases, while the content of Cu increases. At point 6, the eutectic phase is fully formed at the borders of the grains, consisting of 92.84 at. % Al and 5.82 at. % Cu. From the Al-Cu binary phase diagram, the maximum solubility of Cu in Al at 548 °C is shown to be 5.65%, whereas the solid solubility of Cu in Al at ambient temperature is 0.05%. The concentration of Cu in the equiaxed dendrites exceeds the maximum amount of Cu that can dissolve in Al. This is due to the rapid solidification and cooling process of the laser weld pool, which expands the solid solubility limit of the alloying elements, and increases the concentration of the alloying elements. As a result, a supersaturated α -Al solid solution is formed in the weld state.

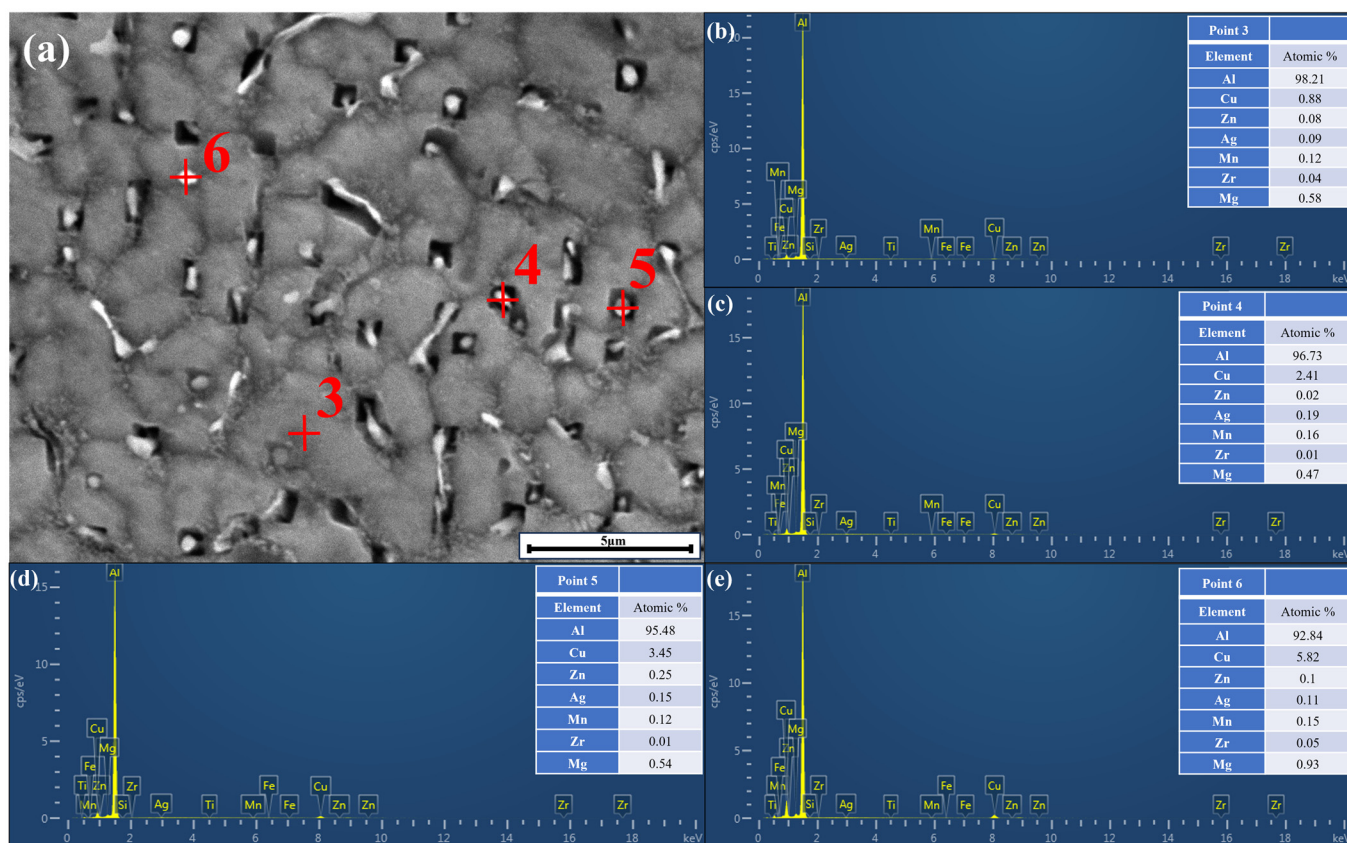


Figure 14. (a) The SEM of equiaxed dendrites. (b–e) The EDS from the zones.

Figure 15 displays the SEM image of the columnar dendrites with EDS spectra, revealing a significant increase in the concentration of Cu elements in the grain boundary precipitates compared to the dendritic center. Conversely, the content of Zr elements is reduced.

As made evident in Figure 16, the grain boundaries and intracrystalline coarse precipitation phases inside the PMZ contain a high concentration of various alloying elements, including both important alloying elements (Cu, Mg, Ag) and ones with a limited diffusion capacity (Fe, Mn). This is because the atomic diffusion coefficients of Fe and Mn are low, preventing them from diffusing into the grain boundaries during the solid-state cooling process of a brief welding heat cycle.

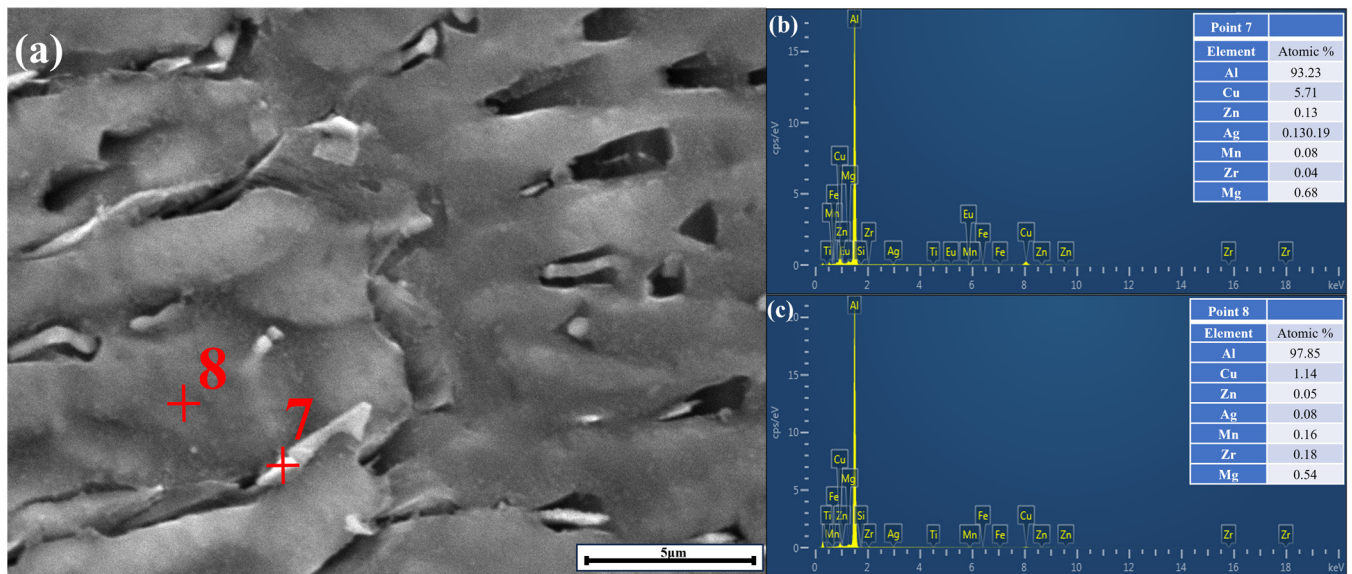


Figure 15. (a) The SEM of the columnar dendrites. (b,c) The EDS from the zones.

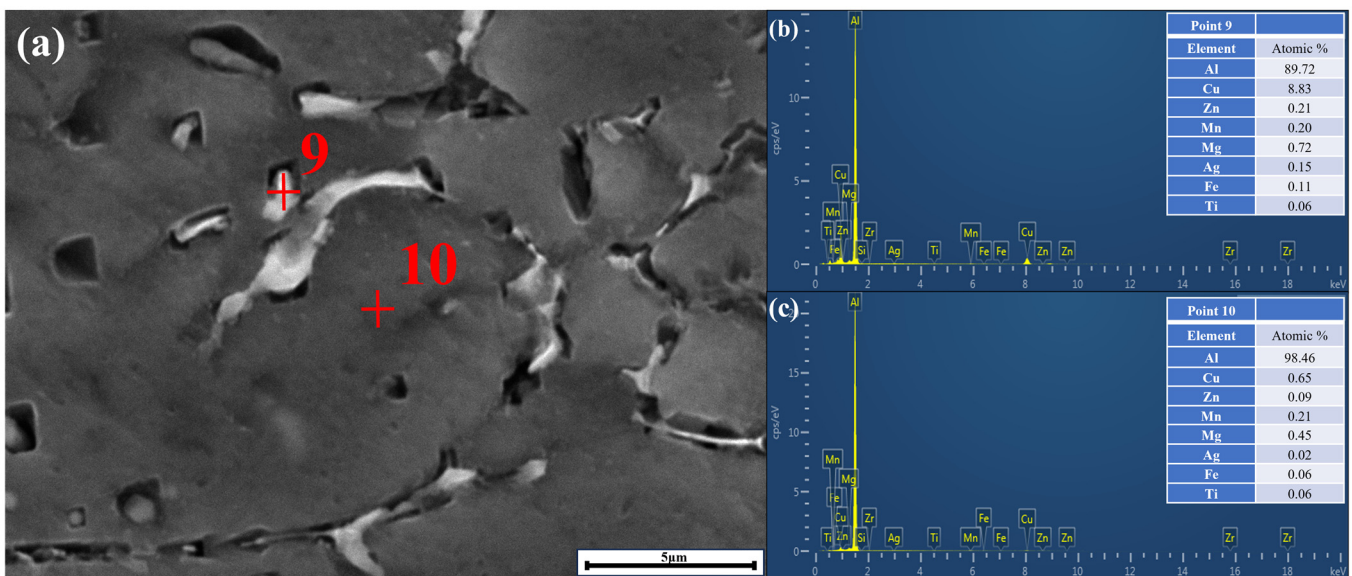


Figure 16. (a) The SEM of PMZ. (b,c) The EDS from the zones.

3.4. Microhardness

A weld joint has equiaxed dendrites, columnar dendrites, EQZ, and PMZ from the center along the direction of the weld fusion line. In Figure 17, it is observed that the microhardness of the weld is low in the equiaxed dendrites. This is due to the fast cooling rate in the center of the weld with low heat input, which may result in the formation of a supersaturated solid solution, leading to low microhardness. As the testing area moves from the equiaxed dendrites to the columnar dendrites area, the microhardness increases. Upon entering the partially melted zone, the microhardness starts to rise rapidly. As the distance between the test point and the center increases, the microhardness quickly returns to the hardness of the base metal.

The comparison reveals that for different powers, low values of microhardness exist in the area of the fusing line for all three. At a power level of 3000 W, the area around the EQZ exhibits a microhardness of approximately 66 HV. However, when the power is increased to 3500 W, the microhardness of the area around the EQZ rises to around 72 HV. During laser welding, the elevated temperature of the base metal adjacent to the fusion line causes

an over-aging phenomenon. This results in the melting of the reinforcing phases inside the base metal, leading to a substantial drop in the microhardness of the HAZ. The scanning path welding procedure does not considerably enhance the softening of the joints in the EQZ. At a power of 3000 W, the equiaxed dendrites microhardness decreases to 40% of the base metal (approximately 65 HV) during the pure laser process. However, when using the O-shaped scanning path process, the hardness of the entire joint becomes more uniform, measuring around 73 HV, which is equivalent to 45.6% of the base metal. Additionally, the microhardness of the joint improves by 5.6% compared to the joint produced through the pure laser process. At a power of 3500 W, the weld microhardness in the equiaxed dendrites is reduced to 41.8% of the base metal microhardness, which is approximately 68 HV, in the pure laser process. In the O-shaped scanning path process, the joint microhardness is more evenly distributed, measuring around 72 HV, which is 44.3% of the base metal hardness. Additionally, the joint microhardness is improved by 2.5% compared to the pure laser process. In the ∞ -shaped scanning path process, the joint microhardness is similar to the O-shaped pattern.

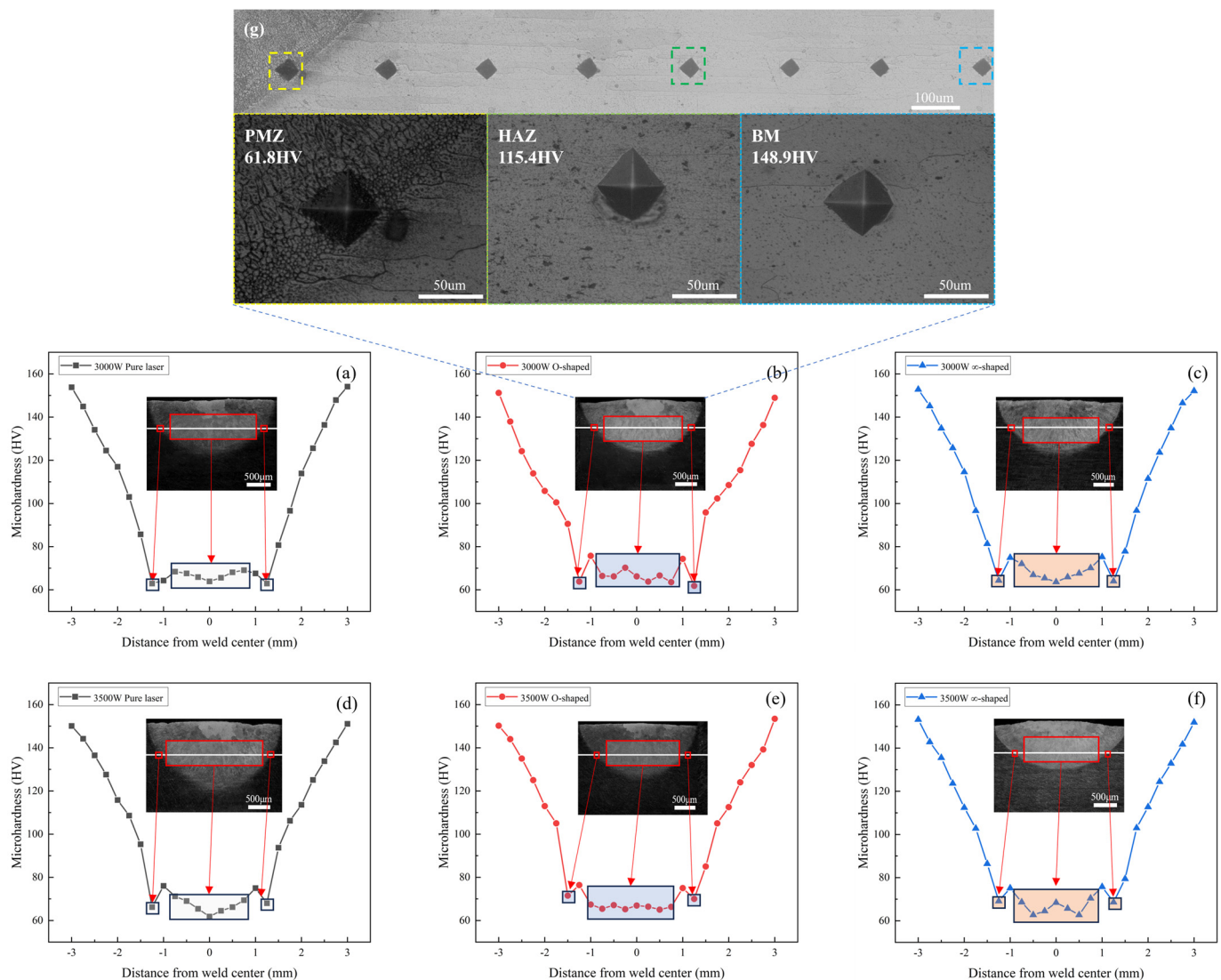


Figure 17. Microhardness distribution of welded joints with different scanning paths. (a–f) Samples 1–6; (g) the track and the value of microhardness in sample 2.

4. Mechanism Analysis

All welding processes used in this experiment are classified as laser heat conduction welding. When using the O-shaped scanning mode, only a small amount of metal evaporated to form vapor depression. As shown in Figure 18, the O-shaped laser beam oscillates in the weld pool, agitating the liquid metal in the weld pool and creating a vortex that reduces the generation of metal vapor and spatters. Additionally, the columnar dendrites in the weld zone are broken up by laser beam, which contributes to the nucleation of fine grains in the center of the weld. Consequently, the O-shaped pattern refines the grain and improves the hardness in the center of the weld when compared to pure laser. At the same time, the O-shaped scanning mode reduces the heat input during the welding process, so the EQZ width of the O-shaped pattern is the smallest compared to the pure laser and ∞ -shaped pattern at high laser power. Due to the stirring effect of the laser, the gas can be overflowed in time, so the weld is basically free of pores made by the O-shaped mode.

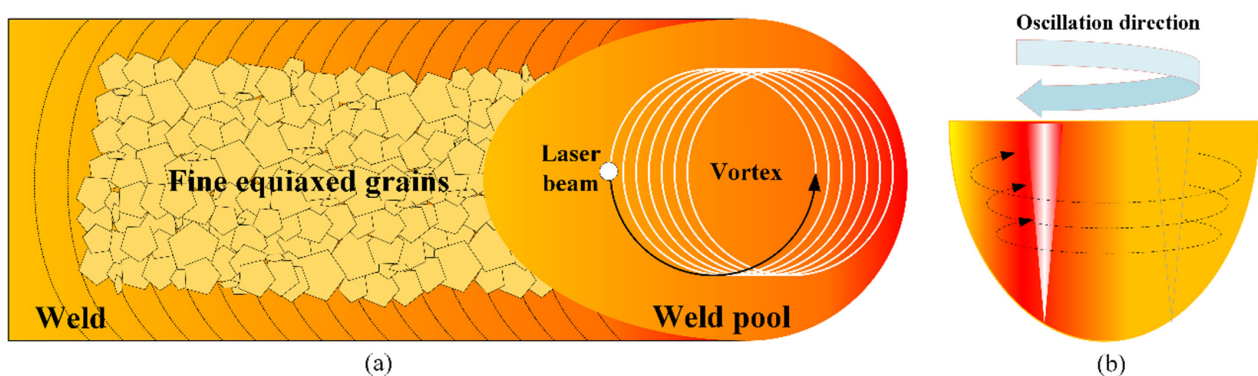


Figure 18. Schematics of weld pool flow and microstructure formation in the O-shaped laser beam welding process: (a) top-surface; (b) cross-section.

5. Conclusions

In this study, the stability of the welding process, the macroscopic forming, and mechanical properties of the weld under three different scanning paths were studied, obtaining O-shaped mode as the optimal scanning path. The flow state of weld pool and the formation mechanism of grain structure in O-shaped mode were revealed. The main conclusions were as follows:

- (1) Laser beam oscillation welding was more effective than pure laser welding in preventing the release of plasma gas and metal vapor from the weld pool, thus reducing spattering. Consequently, the LBOW process was more stable.
- (2) The O-shaped scanning path was more resistant to the impact of laser power and yielded the optimal weld shape in comparison to pure laser and ∞ -shaped scanning paths.
- (3) The Zr element promoted the microstructure formation of EQZ, the equiaxed dendrites and columnar dendrites were mainly composed of α -Al solid solution and Al_2Cu eutectic phase, and PMZ was similar in composition to the base metal.
- (4) LBOW could reduce the width of the EQZ and decrease the pores to improve the mechanical properties of the weld, in which the microhardness of the weld center could be increased by 5.6% under a laser power of 3000 W for O-shaped scanning path laser welding compared to pure laser welding, which means that LBOW provides a small improvement in mechanical properties.

Author Contributions: Conceptualization, Y.L., L.L. and J.Y.; methodology, Y.S. and Y.L.; software, Y.G. and H.Z.; validation, Y.L. and Y.S.; formal analysis, Y.S. and H.Z.; resources, J.Y., H.L., H.Z. and Y.G.; data curation, Y.S., Y.L. and Y.G.; writing—original draft preparation, Y.S.; writing—review and editing, Y.L. and J.Y.; project administration, Y.G., H.Z., H.L. and L.L.; supervision, J.Y. and L.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Shanghai Key Laboratory of Materials Laser Processing and Modification (MLPM), grant number MLPM2022-1.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Li, S.S.; Yue, X.; Li, Q.Y.; Peng, H.L.; Dong, B.X.; Liu, T.S.; Yang, H.Y.; Fan, J.; Shu, S.L.; Qiu, F.; et al. Development and applications of aluminum alloys for aerospace industry. *J. Mater. Res. Technol.* **2023**, *27*, 944–983. [CrossRef]
- Ma, P.P.; Zhan, L.H.; Liu, C.H.; Wang, Q.; Li, H.; Liu, D.B.; Hu, Z.G. Pre-strain-dependent natural ageing and its effect on subsequent artificial ageing of an Al-Cu-Li alloy. *J. Alloys Compd.* **2019**, *790*, 8–19. [CrossRef]
- Zhao, Y.Q.; Wu, Y.F.; Chen, M.L.; Gu, Y.Z.; Zhan, X.H. Research on the stripping performance during dual laser-beam bilateral synchronous welding of 2219 aluminum alloy T-joint for spacecraft. *J. Manuf. Process.* **2019**, *45*, 33–45. [CrossRef]
- Zhang, J.; Wang, C.; Zhang, Y.; Deng, Y.L. Effects of creep aging upon Al-Cu-Li alloy: Strength, toughness and microstructure. *J. Alloys Compd.* **2018**, *764*, 452–459. [CrossRef]
- Dorin, T.; De Geuser, F.; Lefebvre, W.; Sigli, C.; Deschamps, A. Strengthening mechanisms of T₁ precipitates and their influence on the plasticity of an Al-Cu-Li alloy. *Mat. Sci. Eng. A Struct.* **2014**, *605*, 119–126. [CrossRef]
- Jiang, N.; Jiang, M.; Chen, X.; Han, T.; Ma, S.; Chen, Y.; Wang, Z.; Jiang, Y.; Yang, L.; Lei, Z.; et al. Effect of beam oscillation on weld formation, microstructure and mechanical properties in vacuum laser beam welding of thick section 5083 aluminum alloy. *Opt. Laser Technol.* **2024**, *171*, 110408. [CrossRef]
- Zheng, M.; Yang, J.; Xu, J.Y.; Jiang, J.W.; Zhang, H.; Oliveira, J.P.; Lv, X.Q.; Xue, J.; Li, Z.G. Interfacial microstructure and strengthening mechanism of dissimilar laser Al/steel joint via a porous high entropy alloy coating. *J. Mater. Res. Technol.* **2023**, *23*, 3997–4011. [CrossRef]
- Bi, J.; Wu, L.; Liu, Z.; Wang, H.; Li, Q.; Yang, Z. Coupling effect of ultrasonic vibration and beam oscillation on FQZ soften inhibition of laser welded Al-Mg alloy joints. *Mater. Lett. X* **2023**, *18*, 100197. [CrossRef]
- Jiang, J.W.; Oliveira, J.P.; Yang, J.; Zheng, M.; Li, H.Y.; Xu, W.H.; Wu, L.Q.; Dou, T.Y.; Wang, R.J.; Tan, C.W. Effect of defocusing distance on interfacial reaction and mechanical properties of dissimilar laser Al/steel joints with a porous high entropy alloy coating. *Mater. Charact.* **2024**, *210*, 113751. [CrossRef]
- Wang, X.; Luo, Y.P.; Huang, T.; Liu, H.X. Experimental Investigation on Laser Impact Welding of Fe-Based Amorphous Alloys to Crystalline Copper. *Materials* **2017**, *10*, 523. [CrossRef]
- Gong, J.; Li, L.; Meng, S.; Huang, R.; Zou, J.; Cao, H. Study on stability and microstructure properties of oscillating laser welded 5A06 alloy with narrow gap. *Opt. Laser Technol.* **2022**, *155*, 108360. [CrossRef]
- Liu, F.Y.; Tan, C.W.; Wu, L.J.; Gong, X.T.; Chen, B.; Song, X.G.; Zhao, H.Y.; Wang, G.D. Influence of waveforms on Laser-MIG hybrid welding characteristics of 5052 aluminum alloy assisted by magnetic field. *Opt. Laser Technol.* **2020**, *132*, 106508. [CrossRef]
- Chen, C.; Wang, W.Y.; Li, D.Y.; Cai, Y.M.; Zhang, Y.H.; Zhang, K. Effect of beam oscillation on microstructure and properties of laser-TIG hybrid welding of D406A ultra-high strength steel. *J. Manuf. Process.* **2020**, *57*, 798–805. [CrossRef]
- Thiel, C.; Hess, A.; Weber, R.; Graf, T. Stabilization of laser welding processes by means of beam oscillation. *Laser Sources Appl.* **2012**, *8433*, 225–234.
- Ai, Y.; Yu, L.; Huang, Y.; Liu, X. The investigation of molten pool dynamic behaviors during the “∞” shaped oscillating laser welding of aluminum alloy. *Int. J. Therm. Sci.* **2022**, *173*, 107350. [CrossRef]
- Chen, G.Y.; Wang, B.; Mao, S.; Zhong, P.X.; He, J. Research on the “∞”-shaped laser scanning welding process for aluminum alloy. *Opt. Laser Technol.* **2019**, *115*, 32–41. [CrossRef]
- Wang, Z.M.; Oliveira, J.P.; Zeng, Z.; Bu, X.Z.; Peng, B.; Shao, X.Y. Laser beam oscillating welding of 5A06 aluminum alloys: Microstructure, porosity and mechanical properties. *Opt. Laser Technol.* **2019**, *111*, 58–65. [CrossRef]
- Chmelko, V.; Berta, I.; Margetin, M. Influence of Heat Treatment Process to the Fatigue Properties of High Strength Steel. In Proceedings of the 19th International Colloquium on Mechanical Fatigue of Metals (ICMFM), Porto, Portugal, 5–7 September 2018; pp. 35–40.
- Wang, Y.; Wu, G.; Zhang, L.; Guo, Y.; Wang, C.; Li, L.; Xiong, X. Microstructure evolution and mechanical properties of a cast and heat-treated Al–Li–Cu–Mg alloy: Effect of cooling rate during casting. *Mater. Sci. Eng. A* **2023**, *880*, 145366. [CrossRef]
- Zhang, X.D.; Chen, W.Z.; Bao, G.; Zhao, L. Improvement of weld quality using a weaving beam in laser welding. *J. Mater. Sci. Technol.* **2004**, *20*, 633–636.
- Zhang, C.; Li, X.W.; Gao, M. Effects of circular oscillating beam on heat transfer and melt flow of laser melting pool. *J. Mater. Res. Technol.* **2020**, *9*, 9271–9282. [CrossRef]
- Smith, S.; Blackburn, J.; Gittos, M.; Bono, P.D.; Hilton, P. Welding of dissimilar metallic materials using a scanned laser beam. In Proceedings of the ICALEO® 2013: 32nd International Congress on Laser Materials Processing, Laser Microprocessing and Nanomanufacturing, Miami, FL, USA, 6–10 October 2013.

23. Xia, L.; Zhan, X.H.; Yu, H.S.; Xia, P.Y.; Feng, X.S.; Wang, Z.D. Morphology and formation mechanism of equiaxed grains along the fusion boundary in Al-Li alloy weld seam. *Mater. Res. Express* **2018**, *5*, 116523. [CrossRef]
24. Cui, G.; Yang, C. Formation and strengthening mechanism of equiaxial cellular grain zone in AA2195-T8 Al-Cu-Li alloy twin-wire P-VPPA welded joint with Ti-Zr microalloying. *Mat. Sci. Eng. A* **2024**, *896*, 146278. [CrossRef]
25. Peng, S.S.; Zou, J.L.; Li, X.T.; Wu, Q.; Xiao, R.S. Fiber Laser High-Frequency Focus Rotation Spot Welding Process Based on Thermal Conductivity. *Chin. J. Lasers-Zhongguo Jiguang* **2018**, *45*, 1102011. [CrossRef]
26. Han, B.; Chen, Y.B.; Tao, W.; Lei, Z.L.; Li, H.; Guo, S.; Li, P. Nano-indentation investigation on the local softening of equiaxed zone in 2060-T8/2099-T83 aluminum-lithium alloys T-joints welded by double-sided laser beam welding. *J. Alloys Compd.* **2018**, *756*, 145–162. [CrossRef]
27. Lei, X.; Nuam, V.L.; Yuan, Y.; Bai, Y.; Yao, W.; Wang, N. Investigation on laser beam remelted Al-Cu-Li alloy part II: Corrosion behavior and mechanical properties. *J. Alloys Compd.* **2021**, *873*, 159765. [CrossRef]
28. Liu, H.B.; Sun, Y.Y.; Xie, R.S.; Chen, Y.; Chen, S.J. Characterization of microstructure and local mechanical properties of friction rolling additive manufactured Al-Li alloy under repeated thermal-mechanical cycles. *Mater. Charact.* **2023**, *204*, 113169. [CrossRef]
29. Jiang, T.; Zhang, M.; Dai, G.; Shen, Z.; Guo, Y.; Sun, Z.; Li, W. Microstructure evolution and mechanical properties of ultrafine-grained Al-Li alloy fabricated via friction stir additive manufacturing. *Mater. Charact.* **2024**, *209*, 113760. [CrossRef]
30. Wang, X.; Liu, W.; Xu, G.; Zhu, J.; Hu, Q.; Du, B. Numerical analysis of dynamic coupling between the keyhole and molten pool in the rotating laser welding process of aluminum alloy. *Int. J. Adv. Manuf. Technol.* **2022**, *121*, 5491–5502. [CrossRef]
31. Hosseini, S.A.; Abdollah-zadeh, A.; Naffakh-Moosavy, H.; Mehri, A. Elimination of hot cracking in the electron beam welding of AA2024-T351 by controlling the welding speed and heat input. *J. Manuf. Process.* **2019**, *46*, 147–158. [CrossRef]
32. Wang, F.; Liu, Z.; Qiu, D.; Taylor, J.A.; Easton, M.A.; Zhang, M.-X. Revisiting the role of peritectics in grain refinement of Al alloys. *Acta Mater.* **2013**, *61*, 360–370. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Evolutionary Mechanism of Solidification Behavior in the Melt Pool During Disk Laser Cladding with 316L Alloy

Chang Li ^{*,†}, Jiabo Liu [†], Shuchao Li, Fanhong Kong, Xuan Wang, Han Sun and Yichang Sun

School of Mechanical Engineering and Automation, University of Science and Technology Liaoning, Anshan 114051, China; 18104227883@163.com (J.L.); libookchao@163.com (S.L.)

* Correspondence: lichang2323-23@163.com

[†] These authors contributed equally to this work.

Abstract: Laser cladding is an emerging environmentally friendly surface-strengthening technology. During the cladding process, the changes in molten pool temperature and velocity directly affect the solidification process and element distribution. The quantitative revelation of the directional solidification mechanism in the molten pool during the cladding process is crucial for enhancing the quality of the cladding layer. In this study, a multi-field coupling numerical model was developed to simulate the coating process of 316L powder on 45 steel matrices using a disk laser. The instantaneous evolution law of the temperature and flow fields was derived, providing input conditions for simulating microstructure evolution in the molten pool's paste zone. The behavior characteristics of the molten pool were predicted through numerical simulation, and the microstructure evolution was simulated using the phase field method. The phase field model reveals that dendrite formation in the molten pool follows a sequence of plane crystal growth, cell crystal growth, and columnar crystal growth. The dendrites can undergo splitting to form algal structures under conditions of higher cooling rates and lower temperature gradients. The scanning speed of laser cladding (6 mm/s) has minimal impact on dendrite growth; instead, convection within the molten pool primarily influences dendrite growth and tilt and solute distribution.

Keywords: laser cladding; phase field modeling; solidification microstructure; microstructure evolution; convection

1. Introduction

The laser cladding technique is a comprehensive surface-strengthening technology that integrates various disciplines such as materials science, physics, chemistry, and optics. By introducing external strengthening materials into the matrix and achieving a sound metallurgical bond through laser irradiation, its performance can be significantly enhanced [1]. Laser cladding technology presents significant advantages in terms of precision, efficiency, and minimal heat-affected zone, rendering it highly promising for applications in parts remanufacturing, surface repair, and surface strengthening. Coaxial powder feeding is a widely employed technique in laser cladding processes, as shown in Figure 1. The protective gas is conveyed to the molten pool during the cladding process through the flow of metal powder, wherein the metal powder rapidly melts and combines with the matrix to generate a cladding layer exhibiting excellent performance [2,3].

During the laser cladding process, the formation and development of the molten pool play a crucial role in determining the final quality of the cladding layer. A comprehensive understanding of the evolution mechanism of molten pools is essential for predicting their formation. The inner part of the molten pool consists of a combination of metal powder and matrix material. Within a coaxial powder feeding system, not all metal powders are fully melted into the melting pool; only those that fall within it actively contribute to forming the cladding layer. Moreover, it is important to consider both

energy absorption efficiency within the molten pool and energy absorption by the powder flow itself. Simultaneously, variations in powder quantity influence momentum and mass characteristics within the molten pool, thereby further impacting its convection and solidification behavior. Numerical simulation is a highly effective approach for constructing the mathematical model of molten pool evolution [4]. Currently, extensive research has been conducted on numerical simulation of molten pools. Kovalev [5] investigated the impact of powder outlet geometry and substrate distance on powder flux, temperature, and molten pool size. Lei [6] observed that the shape of the melt pool and collective heat-affected zone during NiCrBSi powder cladding on Ti6Al4V substrates was semi-elliptical. C. Li [7] developed a thermal–elastic–plastic flow multi-field coupling cladding model that considered laser light shielding by powder and energy absorption.

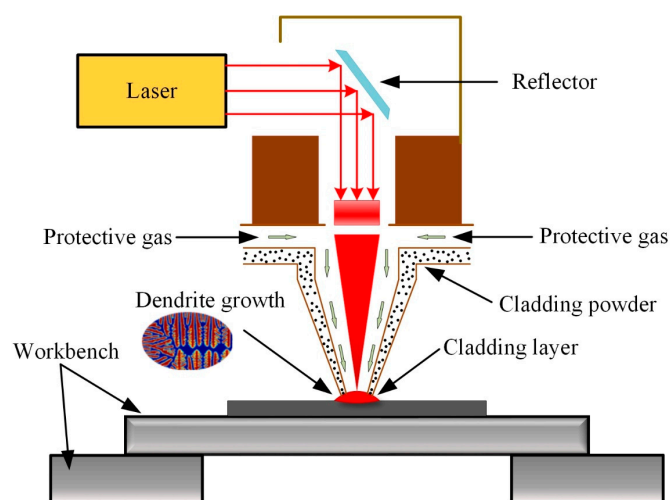


Figure 1. Schematic diagram of the laser cladding principle.

The performance of the cladding layer is determined by its microstructure. Therefore, it is crucial to analyze the microstructure of the cladding layer during laser cladding optimization. A comprehensive understanding of coating material performance and stability can be achieved by investigating microscopic characteristics such as grain size, grain boundary distribution, and crystal structure in the cladding layer. This profound analysis and optimization provide theoretical guidance for obtaining exceptional properties in cladding layers that meet specific requirements across various application fields, thereby promoting widespread adoption and advancement of laser cladding technology. The dendritic crystal structure is the most prevalent form observed during the process of supercooling solidification, and these intricate crystal structures exert significant influences on the mechanical and material properties of the cladding layer. The microstructure in the solidification process can be studied through three primary approaches: deterministic, stochastic, and phase field methods. The deterministic method is a simulation approach for the continuous nucleation model proposed by Oldfield [8]. The instantaneous nucleation model proposed by Hunt [9] considers a specific moment, a given nucleation density, and a growth rate. Randomness methods primarily encompass the Monte Carlo (MC) method [10,11] and the Cellular Automaton (CA) method [12]. The interface model employed in this method is a sharp interface model, which comprises the thermal diffusion equations for both solid and liquid phases. It is crucial to clearly define the boundary condition coupling at the solid–liquid interface while considering factors such as interface mobility, curvature, and heat flux. This aspect poses significant challenges. The phase-field method circumvents these issues by incorporating an ordered parameter ψ (representing the physical state property of each location in the simulated system) into the model. In general, $\psi = 0$ signifies the liquid phase state, while $\psi = 1$ indicates the solid phase state. The entire microstructure can be continuously represented by the sequence parameter ψ , which is bounded between 0 and 1.

In the phase field method, the solid–liquid state is represented by a constant value, while the interface corresponds to the region of order parameter variation. Consequently, the energy term describing interface motion is expressed as a function of $\Delta\psi$. By minimizing the system's free energy and considering the thermodynamic gradient of global thermal effects, both ψ (order parameter) and its gradient function are employed to describe the overall free energy during solidification. The state of the phase in any region is described by the order parameter ψ , which serves as the phase indicator. The parameters and state variables in the phase field method are dependent on this indicator and change solidification. Consequently, the evolution of the phase field can be effectively captured through an energy functional. Notably, there is no longer a need to trace the position of the interface; instead, it can be calculated using the phase field parameters.

The solidification process drives the system towards a low-energy equilibrium state by facilitating the evolution of microstructure, thereby minimizing the free energy of the system. The phase field equation framework couples the thermal and concentration field equations to calculate the microscopic characteristics of the structure, employing a physically driven energy minimization method [13]. This approach considers the contributions of chemical potential, thermal field, and concentration field to the overall free energy system, enabling calculations of dendrite shape, alloy segregation, and solute capture in the paste region. However, this method relies on phase gradient $\Delta\psi$, enthalpy gradient ΔT , and solute concentration Δc [14,15], necessitating accurate deduction of a multivariable well potential function. By incorporating only $\Delta\psi$ as an interfacial motion determinant while adding heat transfer and diffusion equations for solute fields into consideration, significant simplification can be achieved.

Langer [16] and Caginalp [17] formulated the initial phase field equation based on solidification dynamics, subsequently enhancing the phase field model to incorporate anisotropy effects. Kobayashi [18] conducted simulations of two-dimensional dendritic growth with varying degrees of anisotropy using the Ginzburg–Landau free energy potential. Wheeler [19], employing principles of thermodynamic consistency and entropy functional theory, simulated the isothermal solidification phase field model for binary alloys. Karma [20] developed a solidification phase field model for dilute binary alloys, introducing the concept of absolute trapping phases while eliminating non-equilibrium effects arising from interface thickness. Beckermann [21], by investigating the phase field model from columnar to equiaxial, successfully developed a multi-scale model that integrates finite element and random analysis techniques for simulating the microstructure evolution of niobium-based superalloys during the solidification process in laser additive manufacturing. They conducted a comprehensive investigation into the mechanism of dendrite nucleation and growth, the phenomenon of niobium (Nb) segregation, and the formation process of leaf phase particles. Li [22] proposed a multi-field coupling model of the molten pool, revealing that 95% of the cladding layer in the molten pool exhibited columnar dendrite morphology. Qin [23] conducted simulations on the microstructure evolution of thin iron binary alloy within the molten pool, demonstrating that columnar dendrites grew from the bottom of the molten pool following the temperature gradient.

The laser cladding manufacturing process significantly differs from the directional casting solidification process (DS). In DS, heat transfer is unidirectional, with temperature gradients occurring solely in the vertical direction. However, due to the intricate geometry of the paste region and the presence of mobile heat sources, laser cladding exhibits local temperature gradients and convective boundary conditions that actively promote dendrite growth. The convection of melt during the solidification of pure metal into shear flow was simplified by Tonhardt [24]. A corresponding phase field model was established to simulate the dendrite growth process under shear flow conditions, and the influence of convection on the growth morphology of dendrites was investigated. Based on Karma's phase field model, Beckermann and Tong [25] proposed a comprehensive phase field model that incorporates the flow field, enabling simulation of the impact of parameters such as flow velocity and direction on both the advancing velocity and morphological selection of

dendrite tips under forced convection. Therefore, the morphology of dendrite growth is contingent upon the temperature gradient and convection within the solidification pool. To accurately predict microstructure evolution, it is imperative to consider the influence of mobile heat sources and convection in the molten pool. The governing equation $F(\psi, T, c)$ for binary alloy also incorporates a coupled convection term. Most of the above studies use a single perspective to consider the influence of various factors on microstructures. The combination of macroscopical and mesoscopic is rarely used for systematic analysis. During the cladding process, the dendrite growth morphology is not only dependent on the temperature gradient and convection in the solidification pool but also influenced by the heat source moving speed. To accurately predict the evolution of microscopic structures. It is necessary to analyze the convection effect in the molten pool and consider the influence of moving heat sources on the solidification process of the molten pool. In this paper, the heat source moving velocity term and convection term were coupled, respectively, in the governing equation of the binary alloy. The dynamic evolution of microstructure in the laser cladding process is revealed more comprehensively.

In this study, a multi-field coupling numerical model for the process of coating 316L powder with a disc laser on a 45-steel matrix was established. The analysis and calculation of predicting the microstructure development in the cladding layer are compared with the experimental results. The microstructure evolution under moving heat sources and different convection directions was investigated. By employing a solidification model, predictions were made for the spacing and orientation of primary dendrite arms as well as secondary dendrite arms. The dendrite evolution and solute enrichment, induced by the flow field, can be observed through the coupling of the solute field equation. It is of paramount importance to conduct an in-depth investigation into the microstructure evolution of the cladding layer.

2. Experimental Configurations

The growth trend of microstructure in phase field simulation is confirmed through laser cladding experiments conducted in this study. A disk laser model, TruDisk 4000, operating at a power of 1600 W and with an optical fiber minimum diameter of 200 μm , emitting a wavelength of 1030 nm, was employed for the experimental setup. The cladding material utilized was 316L powder. The present study focuses on the analysis of a monorail cladding specimen. Figure 2a shows a monorail cladding specimen with a cladding layer length of approximately 20 mm. To facilitate microstructure observation, the component is divided into two sections: the longitudinal section (shown in Figure 2b) for scanning direction microstructure examination and the cross-section (shown in Figure 2b) for top, middle, and bottom molten pool microstructure observation.

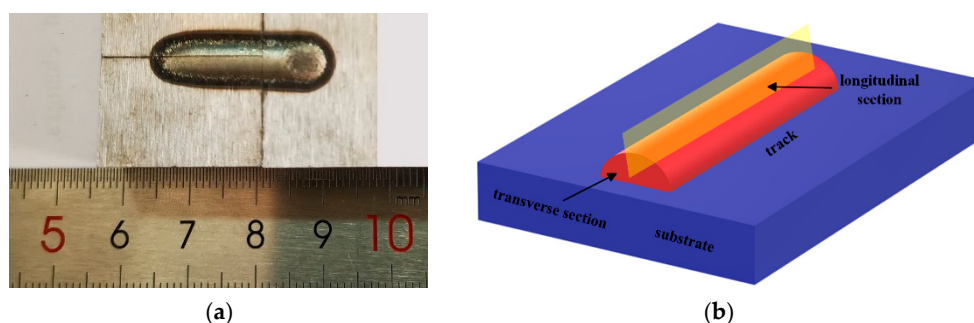


Figure 2. Laser cladding test specimen and cladding diagram. (a) Monorail cladding specimen. (b) Monorail cladding diagram.

3. Modeling of Laser Cladding Process

The molten pool model was established in this section to obtain a three-dimensional estimation of the molten pool, paste zone size, and temperature distribution within the molten pool. As shown in Figure 1, laser cladding employs a coaxial powder feeding

technique, wherein the powder is evenly distributed around the laser beam to form multiple circumferential beams. Additionally, a protective gas (argon) is supplied to the cladding head. The formation of a monorail laser cladding pool was described using fundamental physical assumptions and model formulas.

The underlying assumptions are as follows:

1. The fluid within the molten pool exhibits incompressible Newtonian behavior;
2. Laminar flow characterizes the movement of molten metal within the pool;
3. Powder addition to the substrate follows a Gaussian distribution pattern;
4. The absorption and reflection of laser energy by powder exhibit a linear relationship with the amount delivered.

3.1. Governing Equation

The model data can serve as the initial data and boundary conditions for solidification analysis, thereby establishing the prerequisites for melt pool simulation to enhance model feasibility. In this study, the molten pool model is simulated and predicted using a combination of the finite element method and finite volume method. Additionally, a coupled analysis of the temperature field and flow field is performed to accurately determine the size and temperature gradient of the molten pool. In addition to an expanded range of phase field equations, the numerical calculation of the phase field method becomes challenging due to the necessity of incorporating a coupled solution for fluid flow.

By considering the conservation equations of mass, momentum, and energy in the cladding process, we derive the governing equation for the temperature field (Fourier's law) as follows.

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \nabla T = \nabla \cdot (k \nabla T) - \frac{\partial \Delta H_T}{\partial t} - \rho \mathbf{u} \Delta H_T \quad (1)$$

where ρ represents the density of the molten material, C_p denotes the heat capacity at constant pressure, T signifies the temperature during the cladding process, $\mathbf{u}$ indicates the rate of molten flow, and k stands for thermal conductivity.

The latent heat of the melt is taken into consideration, where ΔH_T represents the latent enthalpy and is expressed as follows:

$$\Delta H_T = \beta_L f_L \quad (2)$$

where β_L is latent heat. f_L is the mass fraction of the fluid, and the expression is as follows:

$$f_L = \begin{cases} 0 & T < T_S \\ \frac{T - T_S}{T_L - T_S} & T_S \leq T \leq T_L \\ 1 & T_L < T \end{cases} \quad (3)$$

where T_S and T_L are the solid–liquid temperatures of the melt.

The flow of molten material within the liquid pool is governed by fluid dynamics. Under the assumed conditions, the continuity equation and Navier–Stokes momentum equation are employed to describe the motion of the fluid.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (4)$$

$$\rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla \cdot (p \mathbf{I}) + \nabla \cdot [\mu_L (\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + D_A \quad (5)$$

where $\mathbf{I}$ is the spatial unit matrix, p is the melt pressure, and μ_L is the dynamic viscosity of the melt.

3.2. Boundary Conditions and Source Terms

During the cladding process, it is not always guaranteed that the powder can be fully absorbed by the molten pool, thus necessitating consideration of surface growth in terms of powder absorption rate [26].

$$V_Z = \frac{2V_f\eta_f}{\rho_f\pi R_f^2} \exp\left[-\frac{2((x-V_st)^2+y^2)}{R_f^2}\right] z \quad (6)$$

where V_f is the powder delivery velocity, η_f is the powder absorption rate, ρ_f is the powder flow density, R_f is the powder flow radius, V_s is the scanning velocity, and z is the unit vector in this direction.

During the solidification process, the size of the melt pool is directly influenced by the velocity of the molten material. As solidification progresses and temperature drops below the liquid phase line, a significant decrease in melt speed occurs. Therefore, the inclusion of an additional drag term in the momentum equation elucidates the observed decrease in velocity:

$$D_A = -\mu_L K_A \mathbf{u} \quad (7)$$

where μ_L represents the temperature-dependent dynamic viscosity, and permeability can be determined using the Kozeny–Carman equation.

$$K_A = K_v \frac{(1-f_L)^2}{f_L^3 + B} \quad (8)$$

The formula incorporates the momentum damping coefficient, K_v , as a constant and B as a minimum value. To prevent division by zero errors, it is essential to restrict the liquid phase fraction f_L within the range of $0 < f_L < 1$.

The static force balance of the liquid metal is disrupted by the uneven temperature distribution in the melting pool, leading to fluid flow driven by the temperature gradient. The gas–liquid interfaces between the molten pool surface and gas exhibit momentum expression as described [27].

$$F_{l/s} = f_s n \kappa_s - \nabla T \frac{df_s}{dT} \quad (9)$$

where f_s is the surface tension, n is the interface normal vector, and κ_s is the interface curvature.

The dominant forces governing the flow of molten metal in a molten pool include gravity, buoyancy, and surface tension. By the Boussinesq approximation principle, the expression for thermal buoyancy resulting from non-isothermal flow can be formulated as follows [28]:

$$F_B = -\rho g \beta_T (T - T_M) \quad (10)$$

where T_M is the melting temperature of the melt, g is the acceleration of gravity, and $9.8 \text{ (m}\cdot\text{s}^{-2}\text{)}$ is taken.

The Marangoni effect is a phenomenon in which the surface tension of a liquid undergoes flow in response to variations in temperature or concentration. The surface tension of the molten pool decreases with increasing temperature, resulting in elevated shear stress near the periphery of the molten pool, thereby inducing lateral expansion and reduced depth of the molten pool [29]. Assuming a linear relationship between temperature and the decrease in surface tension, γ_b can be expressed as $\gamma_b = \gamma_{b0} - \zeta(T - T_M)$. However, this formulation neglects the influence of solute elements present in the molten pool. Therefore, considering thermodynamic principles, an expression accounting for solute elements is proposed [30]:

$$\gamma_b = \gamma_{b0} - \zeta(T - T_M) - R_G T \ln \left[1 + k_L a_i \exp\left(\frac{\Delta H_0}{R_G T}\right) \right] \quad (11)$$

where γ_{b0} is the surface tension of the melt at time T , ζ is the surface tension constant of the temperature coefficient, R_G is the common gas constant, and Γ_S is the saturated excess of the metal surface, the value of which is $1.3 \times 10^{-5} \text{ mol}\cdot\text{m}^{-2}$. a_i is the solute element function under temperature gradient, k_L is the segregation entropy correlation constant, and the value is 3.18×10^{-3} . ΔH_0 is the standard heat of adsorption, with the value $1.67 \times 10^4 \text{ J}\cdot\text{mol}^{-1}$.

3.3. Model Parameters and Mesh Settings

The numerical model was solved using a multi-physics finite element computing platform. A rectangular model of $20 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$ was established. The model used symmetric boundaries along the x–z plane. The whole mesh was divided by free tetrahedral mesh. The maximum cell is 1.6 mm. The intermediate area was refined. The maximum unit is 0.25 mm. The minimum unit is 0.004. The mesh partition contains 131,583 domain units, 5302 boundary units, and 252 side units. The geometric model and meshing are shown in Figure 3. The laser cladding process parameters are shown in Table 1.

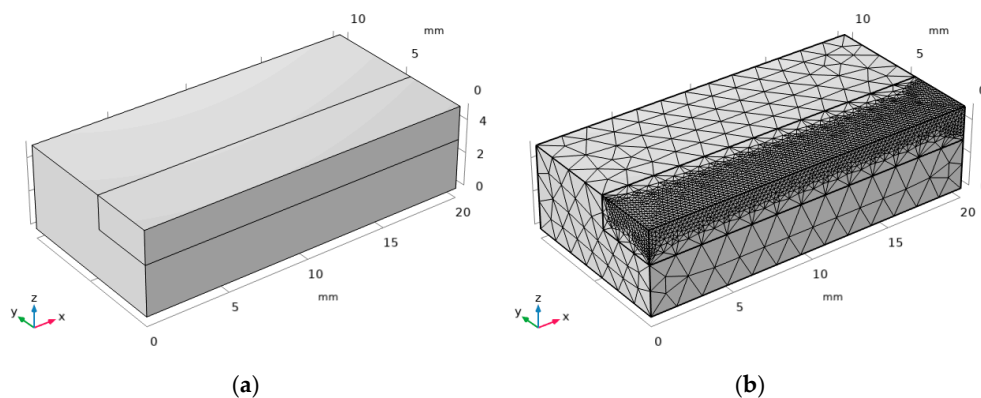


Figure 3. Numerical simulation of process parameters. (a) Geometric model. (b) Meshing.

Table 1. Numerical simulation of process parameters.

Process Parameter	Value
Laser power P_0 /(W)	1000
Spot radius r /(mm)	2.5
Scanning speed v_x /(mm/s)	6
Powder feed velocity V_f /(g/min)	6
Powder flow radius R_f /(mm)	2.5
Ambient temperature T_{amb} /(K)	298.15

3.4. Numerical Analysis and Experimental Verification

The laser cladding process involves non-equilibrium metallurgical solidification, characterized by “hot and cold” conditions, with transient cladding. The physical property parameters of both the powder and matrix exhibit significant fluctuations in response to temperature variations. The CALPHAD method was employed to analyze the thermal properties of both powder and matrix materials as a function of temperature and to simulate the cladding process. Utilizing a multi-physics coupling computing platform, we establish the boundary conditions, source terms, and mesh division while incorporating temperature change physical property parameters to solve the heat transfer equation, continuity equation, and momentum equation.

The longitudinal cross-section of the predicted molten pool is shown in Figure 4a. The transient molten pool is generated by a moving heat source, with the scanning direction aligned with the X-axis and the surface growth direction of the cladding layer aligned with the Z-axis. Laser scanning penetrates through the matrix to obtain a high-temperature transient molten pool. The width of the laser-scanned molten pool is shown in Figure 4b.

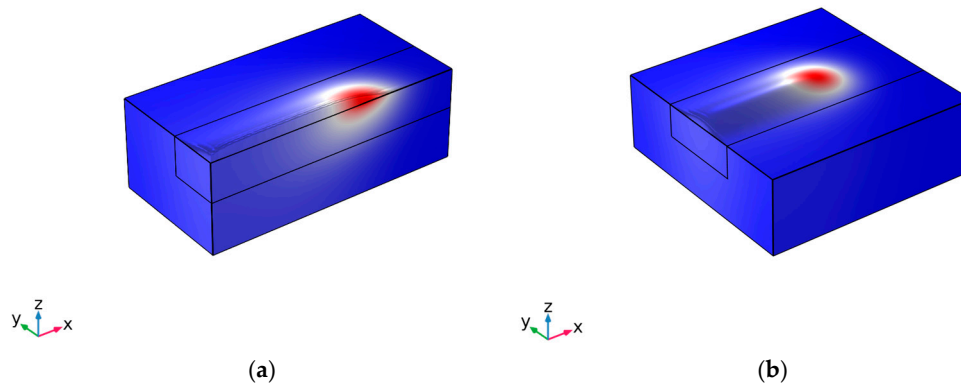


Figure 4. The morphology of the cladding layer was numerically simulated. (a) x–z cross-section morphology of cladding layer. (b) Formation and morphology of the cladding layer.

Figure 5a shows the cladding temperature distribution cloud map at 0.3 s. The figure shows that the maximum temperature of the molten pool reaches 2730 K, surpassing both the melting temperature of the matrix and cladding powder. Consequently, a minute molten pool initiates formation on the surface of the matrix. However, due to the brief duration of laser irradiation, there is limited powder infiltration into the molten pool, resulting in a relatively diminutive molten pool. Under continuous laser energy input, the surface temperature of the matrix exhibits a rapid increase, leading to the accumulation of heat within the matrix. Consequently, an expanding heat-affected zone is observed, resulting in the complete formation of the melt pool at 1.0 s. The transition zone of cladding preheating is observed between the melting and non-melting zones in Figure 5b, with an elliptical molten pool forming near the spot's center, where the maximum temperature reaches 2932 K. Figure 5c,d shows that the maximum cladding temperature of the cladding process is about 2950 K. After laser scanning, the molten pool is cooled and solidified instantly. Obviously, a raised cladding layer is formed behind the laser scanning path.

The laser cladding process induces thermal expansion in the irradiated area of the matrix surface, while the unirradiated region restricts this expansion, leading to internal stress within the matrix and subsequently impacting the quality of the cladding layer. The stress distribution of the matrix at different times is shown in Figure 6. Figure 6a presents a cloud map illustrating the stress distribution in the matrix at 0.3 s. Currently, the heat-affected area is limited, and the maximum matrix stress reaches 277 MPa. Figure 6b shows the cloud image of matrix stress distribution at 1.0 s, revealing that stress levels are low in the center of the spot while circularly distributed stresses dominate its front region, with this area exhibiting maximum stress values. Figure 6c shows the cloud image of matrix stress distribution at 2.0 s, demonstrating an expanding range of stress distribution as laser movement progresses; a long strip-shaped zone of high stress emerges behind laser scanning, reaching up to 294 MPa in terms of matrix stress levels. Figure 6d shows the stress distribution cloud map at 3.0 s. At this time, the stress range of the front end of the spot becomes smaller. The stress region after laser scanning is distributed in a “long strip” shape. The maximum matrix stress is 303 MPa.

Figure 7 shows the cloud diagram of flow field distribution in the molten pool during laser cladding. At the beginning (0.3 s), the flow field in the molten pool was not completely formed, and a small circulation could be seen, and the maximum velocity was 0.23 m/s, as shown in Figure 7a. The formation of Marangoni convection in the melt pool was evident at 1 s, during which time the flow field reached its complete development with a maximum velocity of 0.34 m/s, as shown in Figure 7b. Comparatively, the distribution of the flow field within the molten pool remained essentially unchanged at both 2.0 s and 3.0 s, with only slight variations in flow velocity observed, reaching a maximum value of 0.35 m/s, as shown in Figure 7b–d. According to the numerical simulation results of the flow field, a maximum velocity of 0.35 m/s was selected for analysis of its influence on dendrite growth, with the simulated flow direction being from left to right.

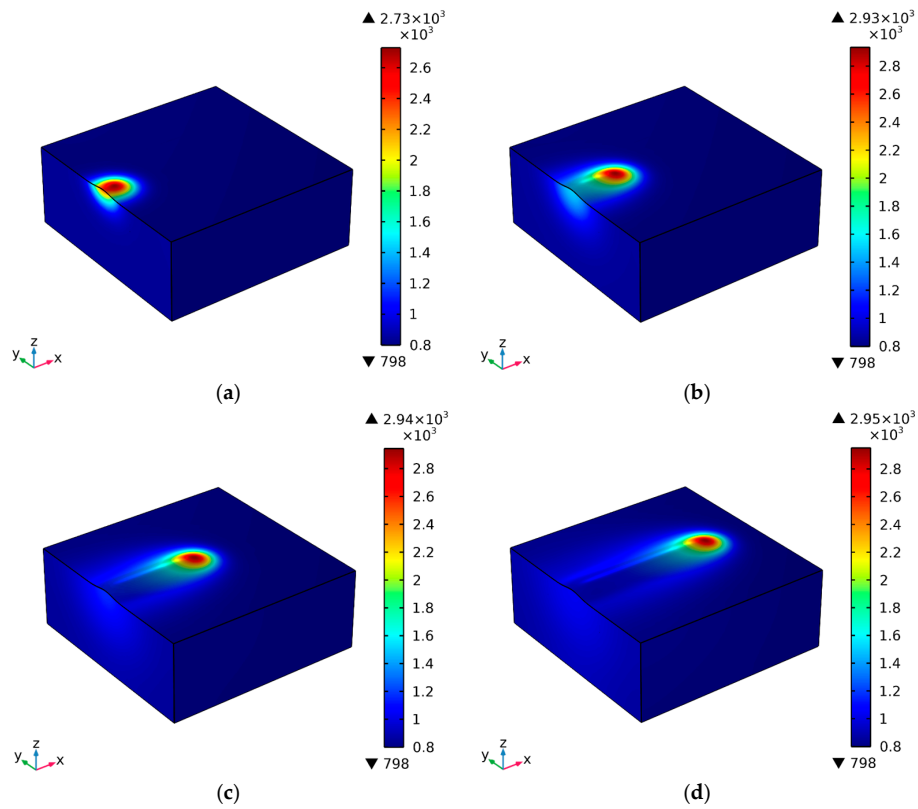


Figure 5. Temperature distribution cloud picture at different times. (a) Temperature distribution at 0.3 s. (b) Temperature distribution at 1.0 s. (c) Temperature distribution at 2.0 s. (d) Temperature distribution at 3.0 s.

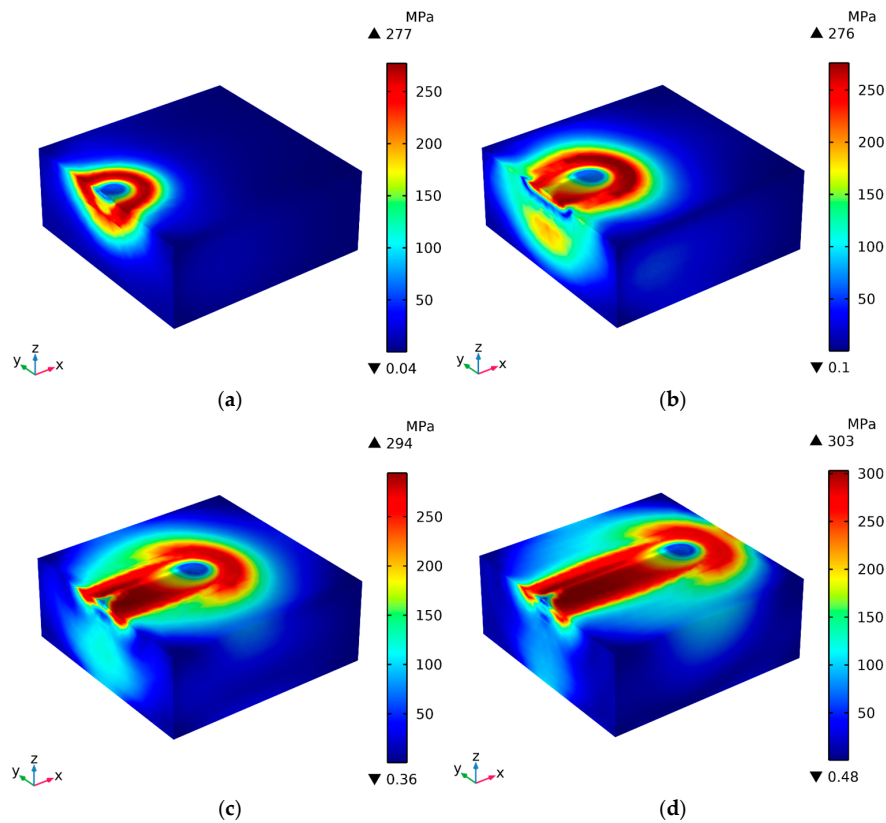


Figure 6. Stress distribution cloud map at different times. (a) The stress distribution at 0.3 s. (b) The stress distribution at 1.0 s. (c) The stress distribution at 2.0 s. (d) The stress distribution at 3.0 s.

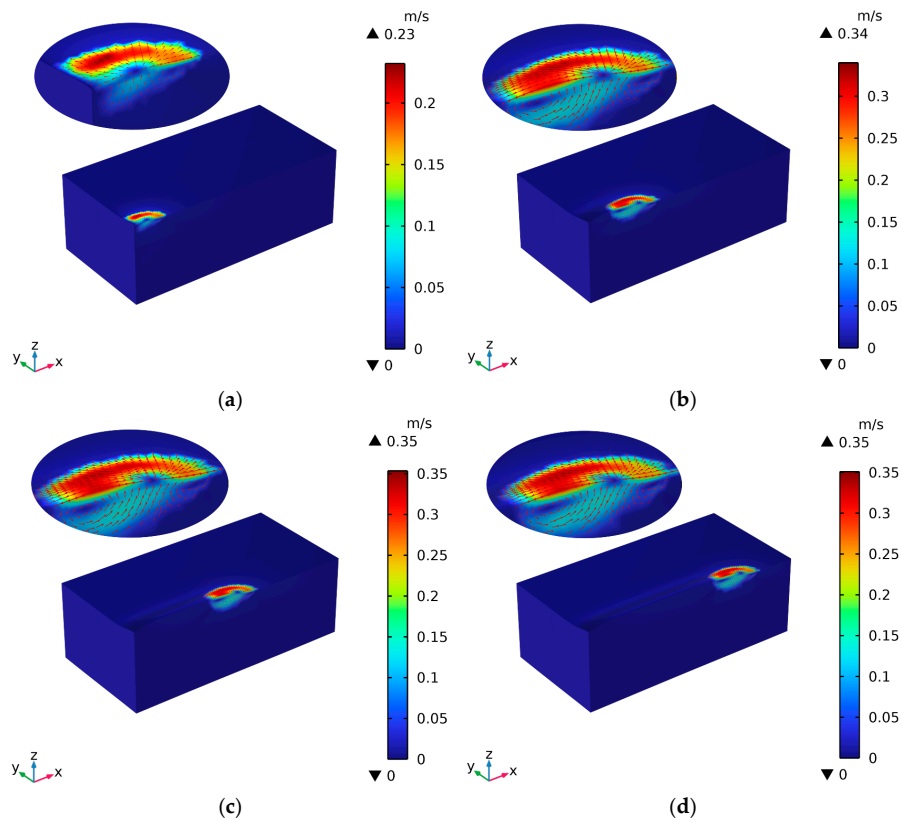


Figure 7. Flow field distribution cloud picture at different times. (a) Velocity distribution at 0.3 s. (b) Velocity distribution at 1.0 s. (c) Velocity distribution at 2.0 s. (d) Velocity distribution at 3.0 s.

To ensure the accuracy of the input conditions for microstructure evolution in the molten pool, a comparison was made between numerical results of macroscopic and experimental observations of cladding layer morphology, as shown in Figure 8. The figure illustrates the cladding layer, with W representing its width and H representing its height. On the left, we present the numerical model calculation result, where the cladding profile has a width of 5.851 mm and a height of 0.682 mm. On the right, we display the scanning electron microscope observation result, which shows a cladding profile width of 5.838 mm and a height of 0.675 mm. Comparative analysis reveals that the experimental results align closely with the numerical simulation results, demonstrating high consistency in terms of heat-affected zone dimensions with an error margin of only 0.22% for width and 1.09% for height, thus validating the effectiveness of our numerical model.

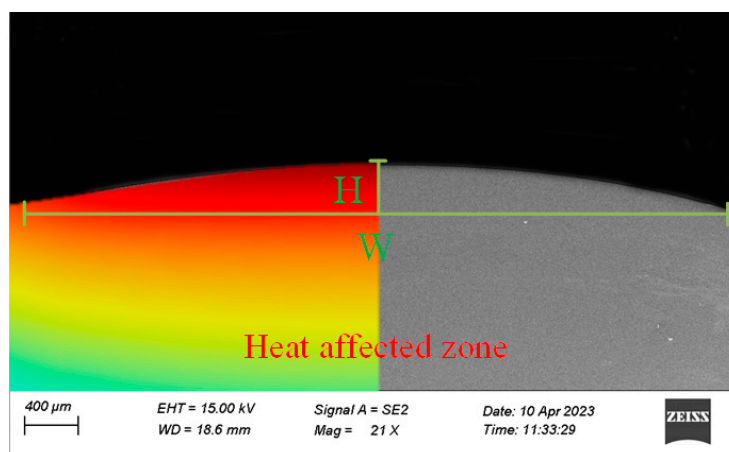


Figure 8. Comparison of cladding morphology and profile.

4. Melt Solidification Simulation

The melt solidification simulation problem involves describing the growth of crystallization in a molten state, originally based on the classical solid phase growth model derived from diffusion theory. The most classical approach is based on the sharp interface model, wherein accurate tracking of the solid–liquid interface motion is necessary to determine changes in its position and shape. However, due to the intricate influence from all directions on dendrite growth in the molten pool, this problem becomes particularly complex [31]. Therefore, a multi-scale method is employed to predict microstructure during dendrite solidification from various directions. The phase field analysis of the supercooled paste region is conducted independently without considering the high-temperature molten pool. To better elucidate the microstructure of the solidification process in the molten pool, the paste region is decomposed into two orthogonal cross-sections. The first section represents the cross-sectional view of the molten pool (Figure 9a), which serves to depict the gradient microstructure within. To address the issue of varying cross-sections, we assume that the interface aligned with the scanning direction exhibits consistent solidification behavior. The subsequent section represents a longitudinal view along the cladding direction (as shown in Figure 9b), which effectively characterizes dendrite growth along the scanning direction of the cladding layer.

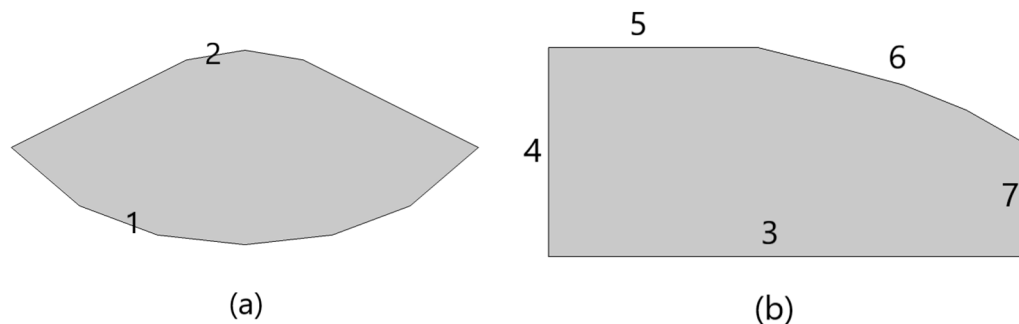


Figure 9. Boundary settings at orthogonal interfaces. (a) Cross sections of boundaries and simulation domains. (b) Longitudinal cross-sections of the boundary and simulation domain (scanning direction).

When simulating the microstructure of the longitudinal section, we set the bottom and left (distal) boundary to the solid-phase line temperature to simulate the boundary conditions of the moving paste region. Meanwhile, due to the continuous release of latent heat, the paste region remains hot.

According to the Ginzburg–Landau theory of free energy [32], within a closed system V , the expression for free energy incorporates the influence of solute:

$$F = \int_V \left[f(\psi, c, T) + \frac{1}{2} \varepsilon^2 (\nabla \psi)^2 + \frac{1}{2} \delta_c (\nabla c)^2 \right] dV \quad (12)$$

where $f(\psi, c, T)$ is the free energy density function, c is the solute concentration, T is the temperature driving term, and ε and δ are the phase field gradient term and solute gradient term, respectively.

In the phase field method, ψ is employed as a scalar quantity representing different states for the solid phase, liquid phase, and interface. Within the phase field model, each point's state value ranges from 0 to 1, where $\psi = 1$ denotes complete solidification and $\psi = 0$ represents complete melting. Building upon the interface relation of Gibbs–Tomson theory, Boettinger et al. [33] established a geometric derivation of the isotropic phase field equation by relating the interface normal velocity to temperature term, liquidus slope, and interface curvature. The resulting equation can be expressed as follows:

$$\frac{1}{\xi_k} \frac{\partial \psi}{\partial t} = \Gamma \left[\nabla^2 \psi + \frac{\psi(2\psi - 1)(1 - \psi)}{d_1} \right] + (T_{eq} - T + m_L(c_l - c_0)) \frac{(\psi(1 - \psi))}{d_1} \quad (13)$$

where ξ_k is the dynamic coefficient, T_{eq} is the equilibrium temperature, and c_l is the liquid phase equilibrium concentration of the binary alloy, c_0 is the initial average concentration of the binary alloy, d_1 is the thickness of the solid–liquid interface, Γ is the Gibbs–Tomson coefficient, and m_L is the liquidus slope of the alloy.

The Equation (13) is thus further refined to incorporate the linear correlation between the interface temperature and the binary phase composition as well as melting temperature: $m = (d_1/2\Gamma) \times (T_L - T_S) \times (1 - T + m_L(c_l - c_0))$. The convergence of the numerical model is enhanced by replacing the linear function with a bounded function: $m = (\alpha/\pi)\arctan\{\gamma[T_M - T + m_L(c_l - c_0)]\}$, where α and γ are constants, and m_L represents the liquidus slope. In this simulation, molten 316L is considered a binary solution, with Fe acting as the solvent and Ni as the solute. The concentration of the aggregated second-phase precipitation is assumed to deviate no more than 14% from the composition of the initial equilibrium concentration solution.

The original equation describing the phase field variables was derived from the minimum energy functional of ψ . For most metallic materials, the surface energy and kinetic coefficients of the solid–liquid interface depend on crystal orientation. Due to the significant impact of anisotropy on crystal growth and dendrite morphology, it is imperative to modify the anisotropy within the phase field model. Building upon the models proposed by Kobayashi [18], Boettinger [14], Wheeler [19], and Zaeem et al. [13]'s approach, this study refines the anisotropic formula for solidified alloy materials. In a two-dimensional model, the diffusion coefficient can be expressed as a function of the growth direction to encompass all members of the opposite sex: θ is defined as $\arctan((\partial\psi/\partial y)/(\partial\psi/\partial x))$, where $\varepsilon = \bar{\varepsilon}\sigma(\theta)$ and $\bar{\varepsilon}(1 + \delta\cos(j(\theta - \theta_0)))$. In this equation, $\bar{\varepsilon}$ represents the anisotropic gradient energy coefficient at the interface, δ denotes the intensity of anisotropy, and j signifies the modulus of anisotropy (symmetry order). The crystal structure of the material presented in this paper is that of face-centered cubic (FCC), with a coordination number of 4. The initial orientation θ_0 for each dendritic dendrite is determined either randomly or by established principles. Consequently, the anisotropic modified phase field equation can be expressed as follows:

$$\tau_0 \frac{\partial\psi}{\partial t} = \nabla \cdot \left(\begin{pmatrix} \varepsilon^2 & -\varepsilon\varepsilon' \\ \varepsilon\varepsilon' & \varepsilon^2 \end{pmatrix} \nabla\psi \right) + \psi(1-\psi)\left(\psi - \frac{1}{2} + m(T, c)\right) \quad (14)$$

where τ_0 is the phase field fitting parameter, $\sigma' = d\sigma(\theta)/d\theta$.

The advancement of the interface in the phase field equation is contingent upon both the temperature field equation and the solute diffusion equation of the binary solution. Considering the volume control of the interface region in the diffusion phase, assuming a time increment of Δt and a phase indicator increment of $\Delta\psi$ in the phase field, $\rho L\Delta\psi$ represents the amount of latent heat produced or consumed. Therefore, by discretizing it in time, the rate of heat change can be expressed as $\rho L\partial\psi/\partial t$. Consequently, the enthalpy variation in the binary system within Δt time is given by $\Delta h = \rho C_p\Delta T - \rho L\Delta\psi$, where the negative sign represents the transition of ψ from liquid phase ($\psi = 0$) to solid phase ($\psi = 1$) during solidification. The equation governing heat transfer is as follows:

$$\frac{\partial T}{\partial t} = \alpha_T \nabla^2 T + \frac{L}{C_p} \frac{\partial\psi}{\partial t} \quad (15)$$

where α_T is the thermal diffusion coefficient ($\alpha_T = k_T/\rho C_p$) and k_T is the thermal conductivity.

The conservation equation was formulated by Karma and Boettinger et al. [11], incorporating the weighted value of the phase field equation for average concentration, resulting in the derivation of the evolution equation for average concentration.

$$\frac{\partial c}{\partial t} = \nabla \cdot [\psi D_S \nabla c_S + (1 - \psi) D_L \nabla c_L] \quad (16)$$

where D_S is the solid phase diffusivity, D_L is the liquid phase diffusivity, and c is the average concentration of the binary alloy solution. The solid phase of the solute concentration for $c_S = k_f c / [(1 - \psi) + k_f \psi]$, the concentration of the solute in the liquid phase for $c_L = c / [(1 - \psi) + k_f \psi]$.

Considering the impact of rapid solidification through laser cladding, to address the issue of non-equilibrium solute field distribution, the determination of the distribution coefficient incorporates the influence of the solidification rate [34]. Therefore, $k_f = (k_{eq} + v/v_{eq}) / (1 + v/v_{eq})$, where k_{eq} and v_{eq} represent equilibrium quantities, and the actual solidification rate is $v = (\partial\psi/\partial t)/(\nabla\psi)$. The final simplified diffusion equation for a binary alloy's solute field can be expressed as follows:

$$\frac{\partial c}{\partial t} = \nabla \cdot \widetilde{D}_k \left[\nabla c + \frac{(1 - k_f)c}{1 + (k_f - 1)\psi} \nabla \psi \right] \quad (17)$$

where $\widetilde{D}_k = D_S + [(D_L - D_S)(1 - \psi)] / (1 + (k_f - 1)\psi)$.

The Equations (14), (16), and (17) are derived under the assumption of negligible convective velocity in the moving heat source. Hence, to incorporate the scanning velocity in the x direction into the longitudinal section (x - z) and modify the coupling equation of (ψ , T , c) [35], we present the following results:

$$\tau_0 \frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial x} \left(\varepsilon \varepsilon' \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\varepsilon \varepsilon' \frac{\partial \psi}{\partial x} \right) + \psi(1 - \psi) \left(\psi - \frac{1}{2} + m(T, c) \right) + \tau_0 v_x \frac{\partial \psi}{\partial x} \quad (18)$$

$$\frac{\partial T}{\partial t} - \frac{L}{2C_p} \frac{\partial \psi}{\partial t} = \alpha_T \nabla^2 T + v_x \frac{\partial T}{\partial x} - \frac{L v_x}{2C_p} \frac{\partial \psi}{\partial x} \quad (19)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \widetilde{D}_k \left[\nabla c + \frac{(1 - k_f)c}{1 + (k_f - 1)\psi} \nabla \psi \right] + v_x \frac{\partial \psi}{\partial t} \quad (20)$$

where v_x follows the scanning direction of the cladding (consistent with V_s).

The dimensionality normalization in the above Equations (18)–(20) is as follows: $T = (T_{actual} - T_S) / (T_L - T_S)$, $l = l_{actual} / l_0$, $t = t_{actual} / \tau$, $v_x = (v_{actual} \tau / l_0)$, where l_0 is the characteristic length scale, τ is the characteristic time scale l_0^2 / α_T , τ_0 is the characteristic constant, and T_L and T_S are the liquid and solid phase temperatures, respectively.

During the laser cladding process, convection is also induced by temperature gradient, concentration gradient, and surface tension in the molten pool. The flow of molten material can impact solute distribution within the pool and influence microstructure growth. The phase field equation of the microstructure [36] with the addition of the convection term is as follows:

$$\tau_0 \frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial x} \left(\varepsilon \varepsilon' \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\varepsilon \varepsilon' \frac{\partial \psi}{\partial x} \right) + \psi(1 - \psi) \left(\psi - \frac{1}{2} + m(T, c) \right) \quad (21)$$

$$\frac{\partial T}{\partial t} + (1 - \psi) v \nabla T = \alpha_T \nabla^2 T + \frac{L}{2C_p} \frac{\partial \psi}{\partial t} \quad (22)$$

$$\frac{\partial c}{\partial t} + \left(\frac{1 - \psi}{1 - \psi + k_f \psi} \right) v \nabla c = \nabla \cdot \widetilde{D}_k \left[\nabla c + \frac{(1 - k_f)c}{1 + (k_f - 1)\psi} \nabla \psi \right] - \nabla j_{at} \quad (23)$$

where v is the velocity of forced convection in the simulation domain and the velocity of the dimensionless liquid phase ($\psi = 0$). μ is the kinematic viscosity of the fluid. The term “ j_{at} ” proposed by Karma et al. [20] represents the anti-solute retention phenomenon. The introduction of the absolute trap term aims to prevent the discrepancy between the diffusion velocity of the solute and the simulated interface moving velocity caused by the dendrite growth rate in simulations.

The detailed boundary conditions for the variables ψ , T , and c can be found in Tables 2 and 3. Figure 9 shows that the dendrite growth nucleated seeds are distributed along borders 4, 5, and 6 on the longitudinal cross-section. The cross-sectional nucleated seed is defined at boundary 1. Additionally, Figure 10 presents the program flow chart of the phase field simulation.

Table 2. Cross-sectional boundary conditions.

Boundary Conditions	ψ	T	c
1	Zero flux	1602.26 K	Zero flux
2	Zero flux	1737.26 K	Zero flux

Table 3. Boundary conditions of the longitudinal section.

Boundary Conditions	ψ	T	c
3	Zero flux	1602.26 K	Zero flux
4	Zero flux	1737.26 K	Zero flux
5	Zero flux	T linearly varying from 1602.26 K to 1737.26 K	Zero flux
6	Zero flux	1737.26 K	c_0
7	Zero flux	1737.26 K	c_L

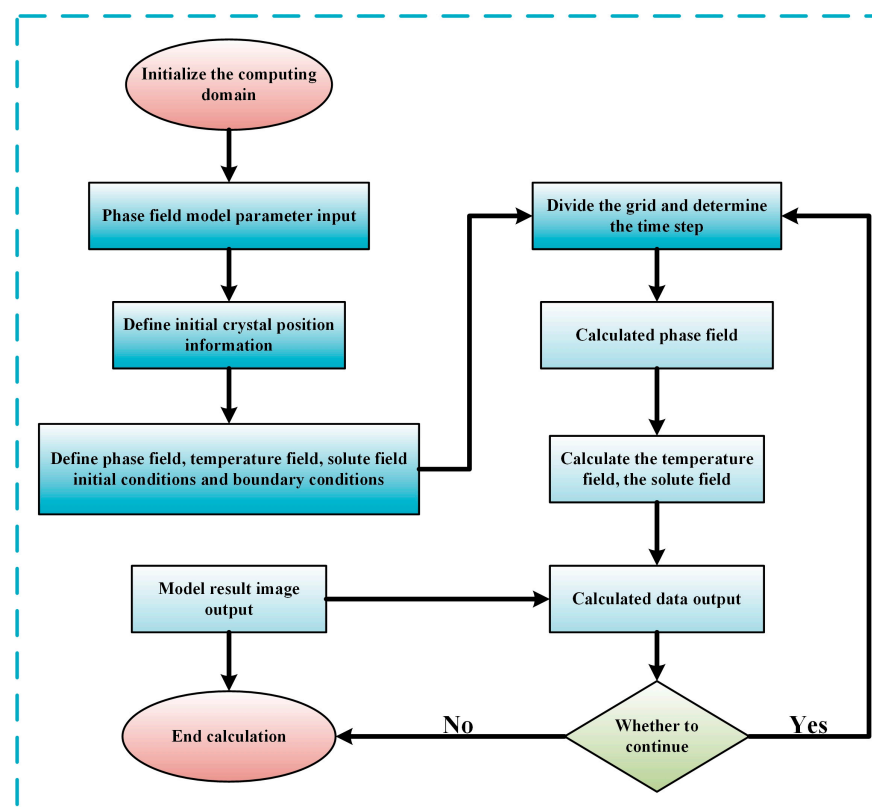


Figure 10. Flow chart of phase field simulation calculation and post-processing.

5. Analysis of Numerical Simulation Results

The finite element method was employed for numerical analysis. The feature length was normalized to $l_0 = 25 \mu\text{m}$, and the mesh was generated using a free triangle mesh approach with a maximum cell size of $l_{\text{mesh}}/l_0 = 0.1$. In the longitudinal section, there were 52,918 units, while in the transverse interface, there were 43,906 units.

The evolution of the crystal during solidification is shown in Figure 11. Initially, the crystal exhibits a planar morphology that subsequently transforms into a cellular

structure due to the influence of temperature and solute gradients. This cellular crystal then undergoes rapid growth and develops directional branches, ultimately forming a dendritic architecture. It is noteworthy that the longitudinal cross-section exhibits variations in the initial temperature of crystal seeds at different boundaries, leading to divergent microstructure growth processes along the three directions. Specifically, the lower section of Figure 11a remains planar, while the left and upper sections tend to cellular crystallization. In Figure 11b, the lower plane has started to transition into cellular crystals, whereas the left and upper regions have displayed indications of lateral branching. This phenomenon arises due to a significant temperature gradient in the left and upper areas, accelerating crystal growth in these regions.

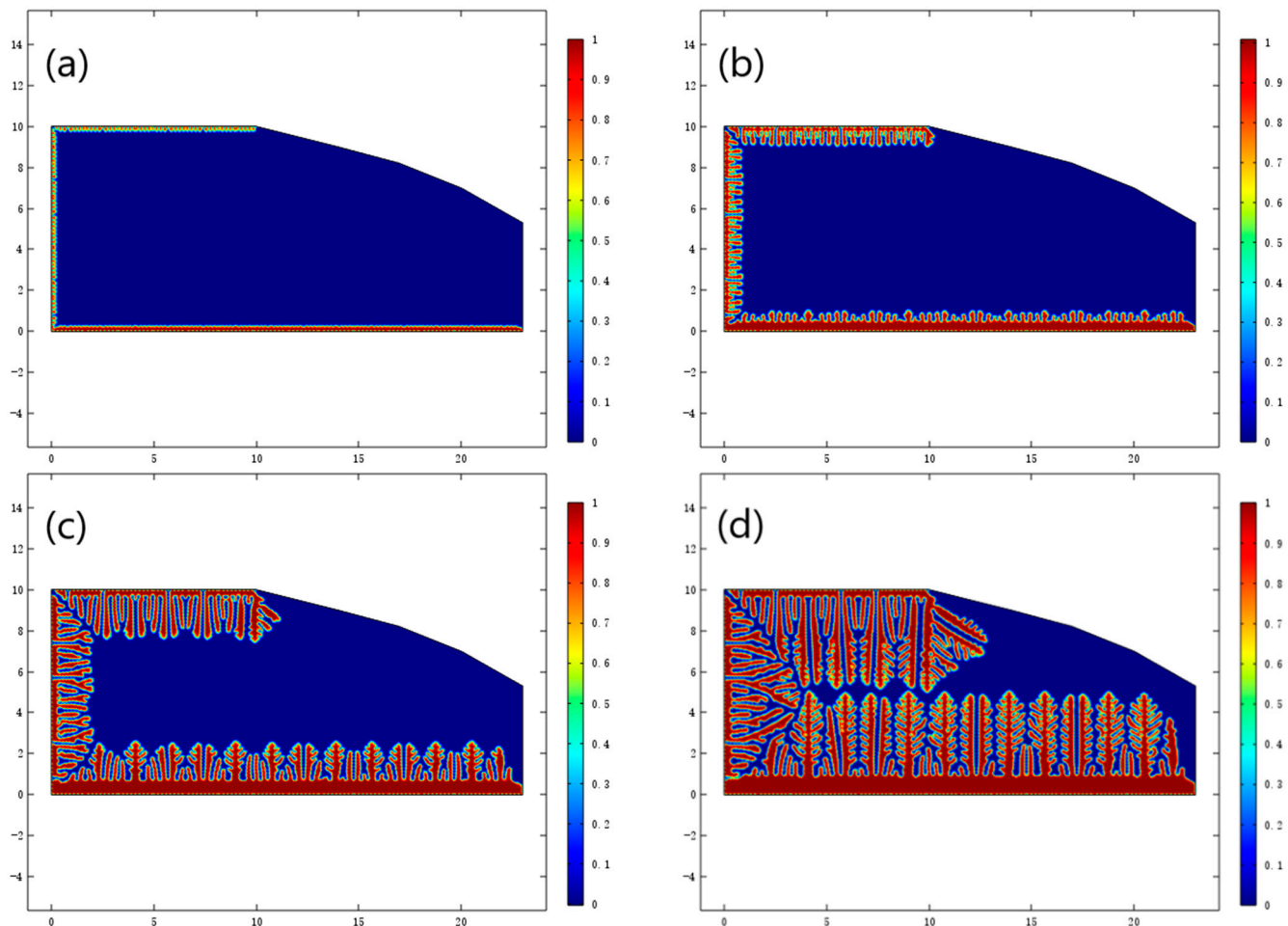


Figure 11. Presents the simulation results of the microstructure growth process in a longitudinal cross-section. (a) At the 200th time step, without accounting for the influence of scanning speed ($v_x = 0$); (b) at the 1000th time step; (c) at the 2500th time step; and (d) at the 4500th time step.

In Figure 11c, it is evident that the crystal tip bifurcates at the left boundary, giving rise to a thick, filamentous structure resembling algae. The formation of seaweed-like structures typically occurs under conditions characterized by a low-temperature gradient and a high cooling rate. This is due to the instability of the solid–liquid propulsion interface, which leads to the continuous division of dendrite tips and the subsequent development of seaweed-like structures [37]. The formation of this algae-like structure is closely linked to the rapid cooling characteristics during laser cladding. It should be noted that the seaweed-like structure represents only one stage in the growth of dendritic structures. As crystal growth continues, the tip of the split dendrite arm gradually diminishes while secondary dendrite arms begin to grow, ultimately forming a complete dendritic structure, as shown in Figure 11d.

In Figure 12a, we investigate the motion of the laser heat source and observe dendrite growth at the 45,000th time step. Compared with the previous Figure 11d, it is evident that there are no significant alterations in dendrite orientation and tip velocity. This can be attributed to the relatively low scanning speed employed during laser cladding, which exerts minimal influence on the solidification process of the molten pool. However, subtle disparities exist in the perpendicular and scanning directions of dendrite arms. In Figure 12a, it is evident that the left secondary dendrites exhibit marginally higher growth rates, while certain dendrites display a slightly greater abundance of left secondary branches. Moreover, as shown in Figure 12b of the experimental results, it is evident that the columnar crystals exhibit a predominantly perpendicular orientation to the molten pool's bottom and remain minimally influenced by natural convection. The figure also shows the morphology of adjacent crystals, which transition from flat bases to cellular, columnar, and equiaxed structures with increasing height.

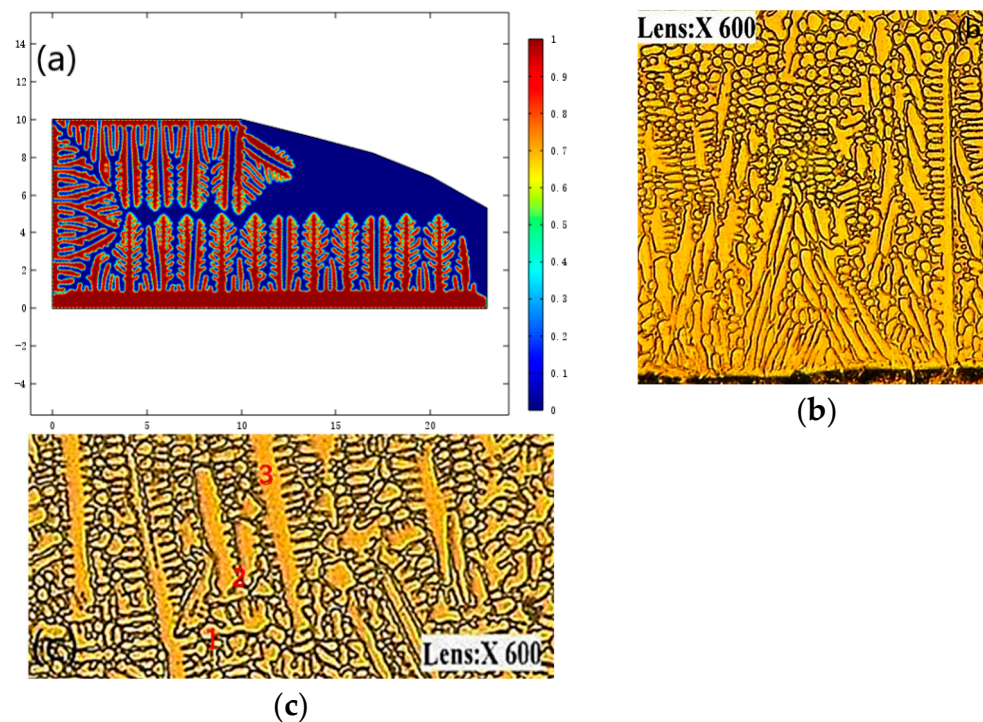


Figure 12. The effects of scanning speed on microstructure simulation and experimental results were investigated. (a) $v_x = 0.028$, corresponding to 4500-time steps. (b) Columnar crystal morphology was observed at the bottom of the longitudinal section. (c) Columnar crystal morphology was observed at the top of the longitudinal section.

The dendrite morphology at the top of the scanning direction is shown in Figure 12c, revealing specific observations. Firstly, the secondary dendrite arm of the columnar crystal fractures at mark 1, resulting in an equiaxed crystal structure formation. Secondly, markers 2 and 3 indicate interference between adjacent dendrites during growth, which restricts the generation of secondary dendrite arms and consequently leads to fewer and smaller dendrites observed within the dendrite gap region. The numerical simulation results also validate this phenomenon, elucidating the influence of competitive growth restriction that enhances the dendrite's diameter structure and ultimately manifests as equiaxed crystal morphology. The remarkable concurrence between experimental observations and numerical simulations strongly unveils the intricate microstructural evolution during solidification.

The distribution of solutes in the dendrite structure is shown in Figure 13. Solute segregation is prominently observed at the root of the dendrites while gradually diminishing as dendrite growth progresses toward the tip. By comparing the solute field scanned

by the laser heat source (Figure 13b), it is evident that the scanning speed exerts an influence, resulting in a slight increase in the content of solute elements between the dendrites and enrichment of solute along the scanning direction. Based on the phase field profiles shown in Figures 11 and 12, it is evident that within the supercooled region, there exists a pronounced inclination of columnar crystals to grow perpendicular to the interface. The presence of similar dendrite structures can also be observed in cross-sections with higher undercooling, as shown in Figure 14. The orientation of dendrites undergoes changes during their growth and approach towards the melt region, or liquidus. The temperature distribution is predominantly influenced by the magnitude of latent heat released at the interface.

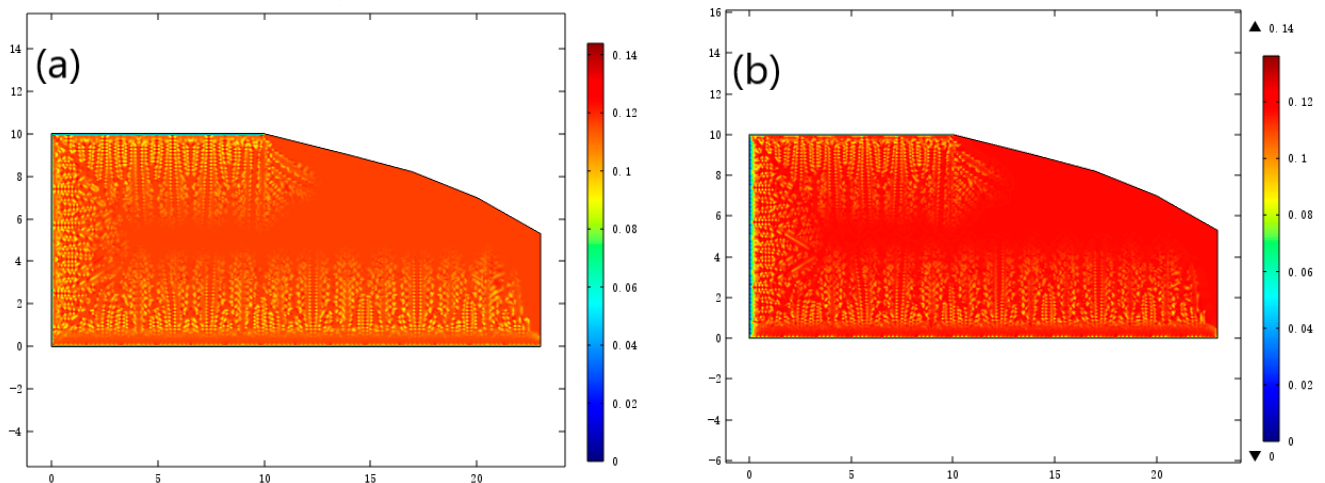


Figure 13. Solute field in longitudinal cross-section at $v_x = 0$ and $v_x = 0.028$ at 45,000 steps. (a) $v_x = 0$ (b) $v_x = 0.028$.

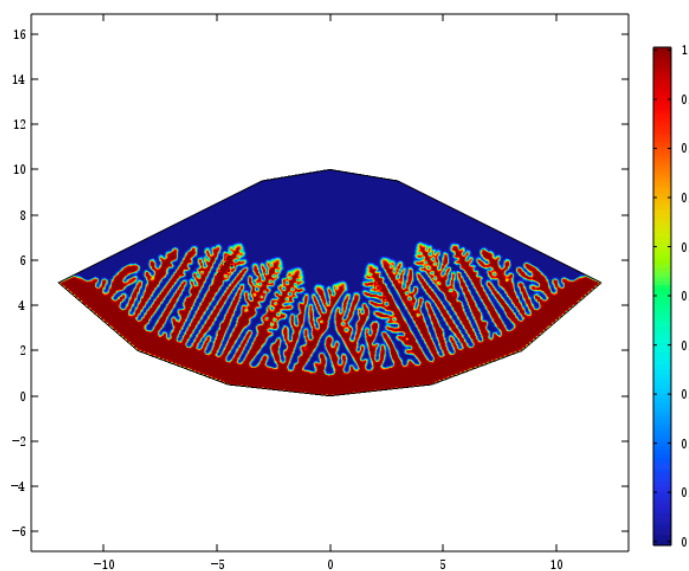


Figure 14. Microstructure of molten pool in cross-section.

The boundary conditions for applying a fixed velocity are shown in Figure 15a. To mitigate the competition between neighboring crystals during columnar crystal growth, it is necessary to increase the spacing between initial crystals. At a dimensionless velocity of $v \approx 2.00$ (equivalent to an actual velocity of 350 mm/s), the growth of cylindrical crystals induces a discernible deflection toward the approaching side, as shown in Figure 15b. In the convective temperature field, the flow effectively washes the oncoming side, facilitating rapid dissipation of latent heat released during solidification. Simultaneously, a portion

of the heat is transported from the oncoming side to the downstream side, resulting in elevated temperatures at the dendrite arm's downstream region, which hinders diffusion. Consequently, there is an accelerated advancement of the solid–liquid boundary toward the oncoming side and a corresponding inclination of dendrites toward this direction. Additionally, the growth rate of secondary dendrite arms is observed to be higher on the oncoming side. In the convective solute field, as shown in Figure 15c, a distinct disparity can be observed between the number and length of secondary dendrite arms on the upstream side compared to those on the downstream side. Within the solute field, the concentration of solute elements is evident in the roots of secondary dendrites [38]. Notably, when contrasted with the downstream side, thinner solute films are present on the upstream side, accompanied by a larger concentration gradient at the solid–liquid interface front and faster growth of dendrite arms.

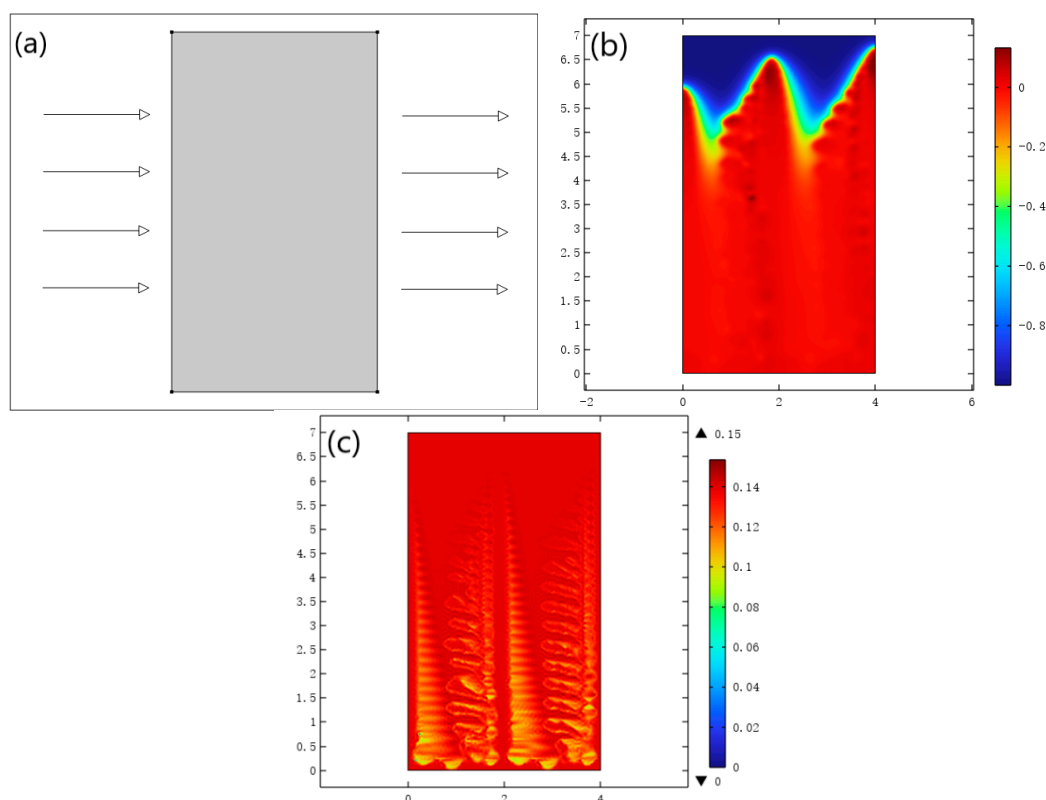


Figure 15. The dendrite morphology of convection flow was considered. (a) Schematic diagram of the calculated region model; (b) temperature field applied against the flow; (c) solute field applied against the flow.

In 2021, Peng et al. [39] used the phase field method to simulate dendrite morphology and solute distribution of Ni-Cu alloy under different unidirectional and mixed convection. The results show that convection has a great influence on dendrite morphology and solute distribution. Convective action causes the dendrites to tilt towards the onstream side, and the secondary dendrite arm tip grows faster on the onstream side. The concentration of solute elements can be seen in the roots of secondary dendrites in the solute field. The growth rate of dendrite arms on the onstream side is faster. In the above study, the numerical simulation of the flow-down dendrite solute field morphology is highly consistent with the results obtained in this paper, which verifies the validity of the model.

6. Conclusions

(1) In this study, a macroscopic multi-field coupling model for laser cladding was established. A phase field model was proposed to describe dendrite growth during solidification and to describe dendrite orientation and solute distribution during contrastive flow.

Quantization reveals the transient evolution of the macroscopic physical field. Among them, the peak temperature field is 2950 K. The peak stress field is 303 Mpa. The peak velocity of the flow field is 0.35 m/s. The input conditions are provided to simulate the microstructure evolution of the paste zone in the molten pool.

(2) The microstructural evolution during the solidification process was predicted. The phase field method was successfully used to reveal the evolution process of crystal microstructure under temperature and solute gradients. The process consists of the transformation of plane-cell crystal, algal structure, and columnar crystal. Accurately predicted the microscopic features of the partial loss of dendritic structure and local fracture caused by competitive growth, as well as the changes in solute distribution.

(3) The influence of heat source scanning speed and convection on solidification microstructure was analyzed. The transverse section of the melt pool at 45,000 steps with different scanning speeds of $v_x = 0$ and $v_x = 0.028$ was compared. The quantitative analysis revealed the dendrite morphology under the non-dimensional flow velocity $v \approx 2.00$ (actual speed 350 mm/s). This study showed that the scanning speed of the moving heat source has a negligible effect on the dendrite growth and orientation in laser cladding. However, the internal temperature gradient and surface tension-induced convection are the main factors affecting the dendrite growth, orientation, and solute distribution.

Author Contributions: C.L. and J.L. acquired the grant and revised the paper; S.L. and F.K. performed modeling and wrote the paper; X.W. extracted and analyzed the data; H.S. and Y.S. checked the grammar. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Applied Basic Research Program of Liaoning Province (2023JH2/101300226), Project for Graduate Education Reform and Technological Innovation and Entrepreneurship of University of Science and Technology Liaoning (2023YJSCX02), Liaoning Province Metallurgical Equipment and Process Control Key Laboratory Open Project (2024KFKT-01), and Liaoning Supported by the Fundamental Research Funds for the Liaoning Universities (2024).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Bayat, M.; Dong, W.; Thorborg, J.; To, A.C.; Hattel, J.H. A review of multi-scale and multi-physics simulations of metal additive manufacturing processes with a focus on modeling strategies. *Addit. Manuf.* **2021**, *47*, 102278. [CrossRef]
2. Santos, E.C.; Shiomi, M.; Osakada, K.; Laoui, T. Rapid manufacturing of metal components by laser forming. *Int. J. Mach. Tool Manufact* **2006**, *46*, 1459–1468. [CrossRef]
3. Kumar, A.; Roy, S. Development of a Theoretical Process Map for Laser Cladding Using a Three-Dimensional Conduction Heat Transfer Model. *Numer. Heat Transf. Part A Appl.* **2009**, *56*, 478–496. [CrossRef]
4. Song, B.; Yu, T.; Jiang, X.; Xi, W.; Lin, X. Development mechanism and solidification morphology of molten pool generated by laser cladding. *Int. J. Therm. Sci.* **2021**, *159*, 106579. [CrossRef]
5. Kovalev, O.B.; Bedenko, D.V.; Zaitsev, A.V. Development and application of laser cladding modeling technique: From coaxial powder feeding to surface deposition and bead formation. *Appl. Math. Model.* **2018**, *57*, 339–359. [CrossRef]
6. Lei, Y.; Sun, R.; Tang, Y.; Niu, W. Numerical simulation of temperature distribution and TiC growth kinetics for high power laser clad TiC/NiCrBSiC composite coatings. *Opt. Laser Technol.* **2012**, *44*, 1141–1147. [CrossRef]
7. Li, C.; Zhang, D.; Gao, X.; Gao, H.; Han, X. Numerical simulation method of the multi-field coupling mechanism for laser cladding 316L powder. *Weld. World* **2022**, *66*, 423–440. [CrossRef]
8. Oldfield, W. A Quantitative Approach to Casting Solidification: Freezing of Cast Iron. 1966. Available online: <https://ntrl.ntis.gov/NTRL/dashboard/searchResults/titleDetail/AD693718.xhtml> (accessed on 13 October 2024).
9. Rappaz, M.; Charbon, C.; Sasikumar, R. About the shape of eutectic grains solidifying in a thermal gradient. *Acta Metall. Mater.* **1994**, *42*, 2365–2374. [CrossRef]
10. Srolovitz, D.J.; Anderson, M.P.; Sahni, P.S.; Grest, G.S. Computer simulation of grain, growth—II. Grain size distribution, topology, and local dynamics. *Acta Metall.* **1984**, *32*, 793–802. [CrossRef]
11. Anderson, M.P.; Grest, G.S.; Srolovitz, D.J. Grain growth in three dimensions: A lattice model. *Scr. Metall.* **1985**, *19*, 2. [CrossRef]

12. Brown, S.G.R.; Bruce, N.B. Three-dimensional cellular automaton models of microstructural evolution during solidification. *J. Mater. Sci.* **1995**, *30*, 1144–1150. [CrossRef]
13. Zaeem, M.A.; Yin, H.; Felicelli, S.D. Modeling dendritic solidification of Al–3% Cu using cellular automaton and phase-field methods. *Appl. Math. Model.* **2013**, *37*, 3495–3503. [CrossRef]
14. Boettinger, W.J.; Warren, J.A.; Beckermann, C.; Karma, A. Phase-field simulation of solidification. *Annu. Rev. Mater. Res.* **2002**, *32*, 163–194. [CrossRef]
15. Bi, Z.; Sekerka, R.F. Phase-field model of solidification of a binary alloy. *Phys. A Stat. Mech. Its Appl.* **1998**, *261*, 95–106. [CrossRef]
16. Langer, J.S. Models of Pattern Formation in First-order Phase Transition. In *Directions in Condensed Matter Physics*; World Scientific: Singapore, 1986; pp. 165–186. [CrossRef]
17. Caginalp, G. The role of microscopic anisotropy in the macroscopic behavior of a phase boundary. *Ann. Phys.* **1986**, *172*, 136–155. [CrossRef]
18. Kobayashi, R. Modeling and numerical simulations of dendritic crystal growth. *Phys. D Nonlinear Phenom.* **1993**, *63*, 410–423. [CrossRef]
19. Wheeler, A.A.; Boettinger, W.J.; McFadden, G.B. Phase-field model for isothermal phase transitions in binary alloys. *Phys. Rev. A* **1992**, *45*, 7424. [CrossRef]
20. Karma, A. Phase-field formulation for quantitative modeling of alloy solidification. *Phys. Rev. Lett.* **2001**, *87*, 115701. [CrossRef]
21. Badillo, A.; Beckermann, C. Phase-field simulation of the columnar-to-equiaxed transition in alloy solidification. *Acta Mater.* **2006**, *54*, 2015–2026. [CrossRef]
22. Kundin, J.; Mushongera, L.; Emmerich, H. Phase-field modeling of microstructure formation during rapid solidification in Inconel 718 superalloy. *Acta Mater.* **2015**, *95*, 343–356. [CrossRef]
23. Qin, Y.; Bao, Y.; DeWitt, S.; Radhakrishnan, B.; Biros, G. Dendrite-resolved, full-melt-pool phase-field simulations to reveal non-steady-state effects and to test an approximate model. *Comput. Mater. Sci.* **2022**, *207*, 111262. [CrossRef]
24. Tonhardt, R.; Amberg, G. Phase-field simulation of dendritic growth in a shear flow. *J. Cryst. Growth* **1998**, *194*, 406–425. [CrossRef]
25. Tong, X.; Beckermann, C.; Karma, A. Velocity and shape selection of dendritic crystals in a forced flow. In *Interactive Dynamics of Convection and Solidification*; Springer: Dordrecht, The Netherlands, 2001; pp. 47–56. [CrossRef]
26. Jia, T.; Li, C.; Jia, S.; Liu, Y.; Han, X. Influence mechanism of active elements on multi-field coupling in laser cladding Fe60 process. *Int. J. Adv. Manuf. Technol.* **2023**, *124*, 411–428. [CrossRef]
27. Song, J.; Chew, Y.; Bi, G.; Yao, X.; Zhang, B.; Bai, J.; Moon, S.K. Numerical and experimental study of laser aided additive manufacturing for melt-pool profile and grain orientation analysis. *Mater. Des.* **2018**, *137*, 286–297. [CrossRef]
28. Morville, S.; Carin, M.; Peyre, P.; Gharbi, M.; Carron, D.; Le Masson, P.; Fabbro, R. 2D longitudinal modeling of heat transfer and fluid flow during multilayered direct laser metal deposition process. *J. Laser Appl.* **2012**, *24*, 032008. [CrossRef]
29. Kruth, J.P.; Badrossamay, M.; Yasa, E.; Deckers, J.; Thijs, L.; Van Humbeeck, J. Part and material properties in selective laser melting of metals. In Proceedings of the 16th International Symposium on Electromachining (ISEM XVI), Shanghai, China, 19–23 April 2010; Shanghai Jiao Tong University Press: Shanghai, China, 2010; pp. 3–14.
30. Hou, S.X.; Zhao, J.K.; Li, Q.; He, L.N.; Zhang, H.Q. Study on the Influencing Factors of Laser Cladding Defects. *Mater. Rep.* **2022**, *36*, 22030105-4. Available online: <http://www.mater-rep.com/CN/Y2022/V36/IZ1/22030105> (accessed on 13 October 2024).
31. Zhu, Y.C.; Yang, G.C.; Wang, J.C.; Zhao, D.W.; Fan, J.F. Multi-phase field simulation of unidirectional solidification for binary eutectic alloys. *Chin. J. Nonferrous Met.* **2005**, *15*, 1026. [CrossRef]
32. Mullins, W.W.; Sekerka, R.F. Morphological stability of a particle growing by diffusion or heat flow. *J. Appl. Phys.* **1963**, *34*, 323–329. [CrossRef]
33. Boettinger, W.J. The structure of directionally solidified two-phase Sn–Cd peritectic alloys. *Metall. Mater. Trans. B* **1974**, *5*, 2023–2031. [CrossRef]
34. Alexiades, V.; Solomon, A.D.; Lunardini, V.J. Mathematical Modeling of Melting and Freezing Processes. *ASME J. Sol. Energy Eng.* **1993**, *115*, 121. [CrossRef]
35. Acharya, R.; Sharon, J.A.; Staroselsky, A. Prediction of microstructure in laser powder bed fusion process. *Acta Mater.* **2017**, *124*, 360–371. [CrossRef]
36. Guo, Z.; Mi, J.; Xiong, S.; Grant, P.S. Phase Field Simulation of Binary Alloy Dendrite Growth Under Thermal- and Forced-Flow Fields: An Implementation of the Parallel-Multigrid Approach. *Metall. Mater. Trans. B* **2013**, *44*, 924–937. [CrossRef]
37. Zhu, C.; Xu, S.; Feng, L.; Han, D.; Wang, K.M. Phase-field model simulations of alloy directional solidification and seaweed-like microstructure evolution based on adaptive finite element method. *Comput. Mater. Sci.* **2019**, *160*, 53–61. [CrossRef]
38. Murakami, K.; Fujiyama, T.; Koike, A.; Okamoto, T. Influence of melt flow on the growth directions of columnar grains and columnar dendrites. *Acta Metall.* **1983**, *31*, 1425–1432. [CrossRef]
39. Peng, X.; Xiao, H.; Li, W.; Yi, B.; Qin, W.; He, H. Simulation of Dendritic Morphology of Ni–Cu Alloy under Convection Based on Phase Field Method. *Shanghai Met.* **2021**, *43*, 69–76. Available online: https://kns.cnki.net/kcms2/article/abstract?v=RE1hRqpi5T0ZXHt5TGTJGPx-kpiKotmBhkMa_u_bBDvuLMIR4hATOu6oINttOUaNIbNRVU4QoydWJZpaieDtBSjm967e5L9Nh_Vd1KW0BCgqi1dAppQ8leWPIbDwgofmkzvmzOG-e48tx6EPV8cBRPKkHosfRs3fk2wBu0nzvXjvLr1SavPx--O9HMP2G82Fjgk4f4ejTRI=&uniplatform=NZKPT&language=CHS (accessed on 13 October 2024).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Simulation of Dendrite Remelting via the Phase-Field Method

Xing Han, Chang Li *, Hao Zhan, Shuchao Li, Jiabo Liu, Fanhong Kong and Xuan Wang

School of Mechanical Engineering and Automation, University of Science and Technology Liaoning, Anshan 114051, China; hanxinggctx@163.com (X.H.)

* Correspondence: lichang2323-23@163.com

Abstract: The solidification of alloys is a key physical phenomenon in advanced material-processing techniques including, but not limited to, casting and welding. Mastering and controlling the solidification process and the way in which microstructure evolution occurs constitute the key to obtaining excellent material properties. The microstructure of a solidified liquid metal is dominated by dendrites. The growth process of these dendrites is extremely sensitive to temperature changes, and even a small change in temperature can significantly affect the growth rate of the dendrite tip. Dendrite remelting is inevitable when the temperature exceeds the critical threshold. In this study, a temperature-induced-dendrite remelting model was established, which was implemented through the coupling of the phase field method (PFM) and finite difference method (FDM). The transient evolution law of dendrite remelting was revealed by simulating dendritic growth and remelting processes. The phase field model showed that the lateral dendrites melt first, the main dendrites melt later, and the main dendrites only shrink but do not melt when the lateral dendrites have not completely melted or the root is not broken. The long lateral branches break into fragments, while the short lateral branches shrink back into the main dendrites. The main dendrites fracture and melt in multiple stages due to inhomogeneity.

Keywords: dendrite growth; phase field method; finite difference method; remelting

1. Introduction

Solidification is a ubiquitous physical phenomenon observed in nature. During the processing of metallic materials—encompassing techniques such as casting, additive manufacturing, and welding—multiple solidification events typically occur, and it is common for a material to undergo one or more solidification processes [1–3]. Solidified molten metal liquid will form dendritic crystals [4]. The growth processes of these dendrites are exceedingly sensitive to temperature changes; even minor changes in temperature affect the growth rate of the tip of the dendrite significantly. A slight increase in temperature results in a deceleration of dendrite tip growth, whereas a slight decrease in temperature accelerates the tip growth rate. When the temperature rises beyond a critical threshold, the phenomenon of dendrite remelting becomes inevitable [5]. The dendrite remelting process is usually accompanied by the dynamic evolution of dendrite morphology, including the morphological reconstruction of the lateral and main dendrite arms, volume contraction, and local melting nonuniformity. This phenomenon exemplifies the intricate interplay of thermodynamic and kinetic behaviors during crystal growth and phase transformation processes. While dendrite remelting exerts a significant influence on alloy solidification structures, the majority of studies to date remain concentrated on macroscopic simulations and experimental microstructural characterization, with numerical modeling of this phenomenon being relatively underexplored.

Dendrite remelting is predominantly governed by two principal driving factors: solute-induced and temperature-induced mechanisms. Neng Ren et al. [6] successfully simulated dendritic growth and remelting under solute-induced conditions by employing a coupled

Cellular Automaton (CA) and Finite Volume Method (FVM). Their model takes into account critical conditions for mechanical fragmentation, alongside dendrite melting and fragmentation induced by convective flow and solute segregation. Peng Xialin et al. [7] employed a coupled phase field method (PFM) and finite difference method (FDM) to simulate and analyze dendritic growth and remelting under solute-induced conditions. Furthermore, this model accounted for the influence of lateral convection and linear flow velocity on the dendrite-remelting process. Previous research predominantly concentrated on solute-induced mechanisms as the primary driving factor, whereas numerical simulations exploring temperature-induced mechanisms remain relatively limited.

The phase field method (PFM) represents a computational method for accurately capturing phase transition interface dynamics throughout the solidification process [8]. At the macroscopic scale, phase transition problems such as solid-state phase transition and droplet phase fusion can be described by using a partial differential equation introduced into the interface [9]. At the microscopic scale, the physical state of the system phase in time and space over the growth domain Ω is described through the ordering parameter $\psi(r,t)$. In dendritic phase field models, the solid phase is typically assigned a $\varphi = 1$, the liquid phase is assigned a $\varphi = 0$, and the interfacial region is represented by $0 < \varphi < 1$ [10]. The PFM is based on the Ginzburg–Landau theory and describes the combined effects of ordering, interfacial diffusion, and thermodynamic driving through differential equations [11,12]. The PFM is also known as a direct simulation method that can track the solid–liquid interface and directly simulate the internal structure of dendrite growth, dendrite morphology, and other microstructures. The phase field method can perfectly solve the complex solid–liquid interface tracking problem, and it can also be coupled with the temperature field and solute field to enable quantitative studies on the growth and evolution of microstructures during metal solidification [13–15]. The finite difference method (FDM) is a commonly used numerical analysis method [16]. The core principle of the FDM involves discretizing the definition domain of a problem into a computational grid and subsequently applying suitable numerical differentiation formulas at the grid nodes to approximate the differential terms, thereby converting the continuous differential equations into the difference equations in discrete form. This process establishes a difference scheme, which is subsequently solved to derive the numerical solution of the original problem.

This study presents a novel temperature-induced dendrite-remelting model. The model was implemented by coupling the phase field method (PFM) with the finite difference method (FDM). The dendritic evolution process, encompassing both dendrite growth and remelting, was simulated, and the transient evolution law of dendrite remelting was revealed. These findings are of great significance for controlling the microstructure and mechanical properties of processed materials.

In summary, a temperature-induced-dendrite-remelting model is established in this paper. The model was implemented via the coupling of the phase field method (PF) and the finite difference method (FDM). The dendrite evolution process, including dendrite growth and dendrite remelting, was successfully simulated, and the transient evolution law of dendrite remelting is revealed herein, constituting findings of great significance for controlling the microstructure and mechanical properties of machined materials.

2. Phase Field Model

2.1. Establishment of Remelting Phase Field Model

Dendrite remelting is a phenomenon in which a dendrite originally in a stable growth state under the condition of an elevated ambient temperature undergoes a phase transition due to a change of temperature field. This results in the migration of its solid–liquid interface toward increasing the volume of the liquid phase, which triggers the localized or overall melting of the crystal [17]. To effectively describe the remelting process of dendrites, this study employs the non-isothermal phase field model, as derived by Kobayashi [18], Boettinger [19], and Zaeem [20]. In order to ensure the accuracy and stability of the numerical simulation, the following assumptions were made during the simulation of the

regrowth of remelted dendrites: (1) the driving force of temperature undercooling during the regrowth of remelted dendrites remained unchanged; (2) the regrowth of adjacent dendrites was restricted by the boundaries on both sides; and (3) the latent heat during dendrite regrowth remained constant. The governing equations for the phase field and temperature field in this model are presented as follows:

$$\frac{\tau_c}{\tilde{\varepsilon}_m^2} \frac{\partial \psi}{\partial t} = \left[\frac{\partial}{\partial x} \left(\frac{\partial \varepsilon^2(\theta)}{\partial \theta} \frac{\partial \psi}{\partial y} \right) - \frac{\partial}{\partial y} \left(\frac{\partial \varepsilon^2(\theta)}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\varepsilon^2(\theta) \psi) \right] + \frac{1}{\tilde{\varepsilon}_m^2} \psi(1-\psi) \left[\psi - \frac{1}{2} + M(\tilde{T}) \right] \quad (1)$$

$$\frac{\partial \tilde{T}}{\partial t} = \alpha_T \nabla^2 \tilde{T} + \frac{L_m}{C_p} \frac{\partial \psi}{\partial t} \quad (2)$$

where τ_c and $\tilde{\varepsilon}_m$ are the interfacial parameters of the phase field, and $\varepsilon(\theta)$ is the anisotropy of each of the solid–liquid interfaces ($\varepsilon(\theta)$ is a function of θ , as given by Equation (3) [21]. $M(\tilde{T})$ is the interface driving term in the phase field equation, where $M > 0$ for the solidified state and $M < 0$ for the melted state, and T_{ap} is the equilibrium temperature during solidification. α_T is the thermal diffusion coefficient of the metal, C_p is the constant pressure heat capacity, L_m is the latent heat, and $\tilde{T}$ is the dimensionless temperature, where $\tilde{T} = (T - T_S)/(T_L - T_S)$ [22]:

$$\varepsilon(\theta) = \bar{\varepsilon} \eta(\theta) = \bar{\varepsilon} (1 + \delta \cos(k_\varepsilon(\theta - \theta_0))) \quad (3)$$

$$\theta = \frac{\nabla \varphi}{|\nabla \varphi|} = \arctan \left(\frac{\partial \varphi / \partial y}{\partial \varphi / \partial x} \right) \quad (4)$$

$$M(T) = \left(\frac{\alpha}{\Pi} \right) \arctan(\sigma(T_{ap} - T)) \quad (5)$$

$$\alpha_T = \frac{l_0^2}{\tau} = \frac{k}{\rho C_p} \quad (6)$$

In the actual solidification process, the solid–liquid interface can be randomly undulated due to solute diffusion, heat flow, and other reasons [23,24]. In order to simulate such random interfacial fluctuations and make the dendrite growth more realistic, random perturbations were added to the phase field equations:

$$\frac{\partial \psi}{\partial t} \rightarrow \frac{\partial \psi}{\partial t} + 16g'(\psi)a^\#r^* \quad (7)$$

where $g'(\psi)$ is the derivative of $g(\psi) = \psi^2(1 - \psi)^2$, $a^\#$ is the perturbation intensity factor (which is time-dependent), and r^* is a random number between -1 and $+1$. To ensure that the perturbation occurs at the interface, the effect of the noise term exists only in the range where $0 \leq \psi \leq 0.5$.

2.2. The Establishment of Geometric Model and the Determination of Boundary Conditions

The finite element computing platform was used to solve the numerical model in this study. According to the characteristics of the dendrite growth, taking into account the cost of the calculation, this section establishes a rectangular model, as shown in Figure 1. Figure 1a depicts the geometrical modeling of the competitive dendrite growth process, and overall mesh delineation was performed by using free triangles. The model contains 9040 cells and 260 boundary cells, with a minimum cell mass is 0.6885.

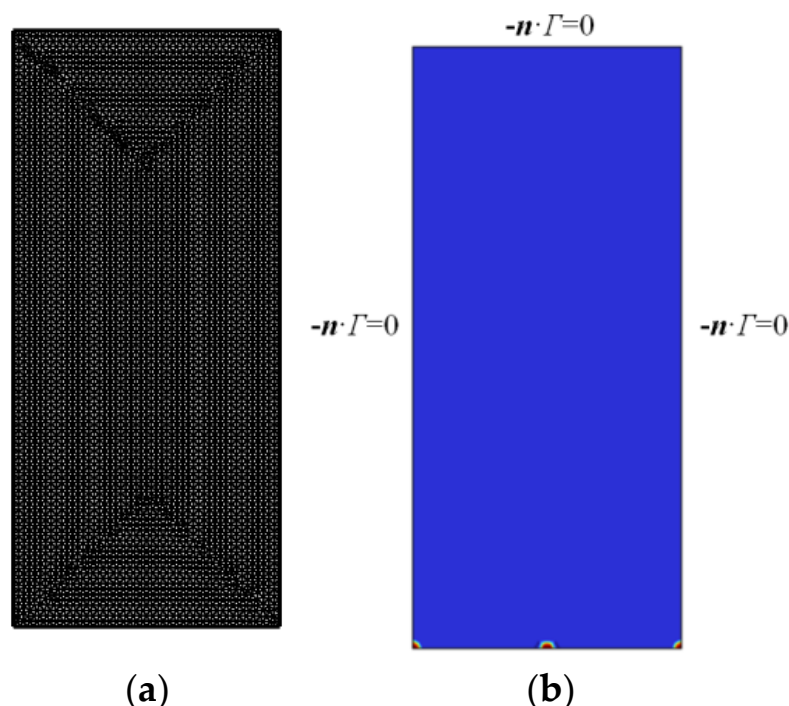


Figure 1. Modeling of dendrite remelting. (a) Dendrite-remelting model meshing. (b) Nucleation positions and boundary conditions for dendrite-remelting setups.

To ensure adequate spacing between crystal nuclei in the initial distribution, providing sufficient room for the growth of secondary dendrite arms, crystal nucleus positions were predefined at the base of the simulation domain. In solving the control equations of the phase field model, it was assumed that the crystal nucleus positions were influenced solely by growth kinetics, free from external interference. Consequently, zero-flux boundary conditions were imposed at the boundaries of the simulation domain, ensuring that both mass and energy transport were zero and preventing external factors from influencing the crystal growth process. This ensured that the simulation results more faithfully represent the actual dendritic growth mechanisms during the remelting process. The predefined crystal nucleus positions and boundary conditions are shown in Figure 1b.

3. Analysis of Dendrite-Remelting Simulation Results

3.1. Dendrite Remelting Process

Figure 2 shows the stable growth states of the dendrites prior to the rise in environmental temperature. As shown in Figure 2a, under the influence of the interface anisotropy, the crystal nucleus shows obvious main dendrite growth in both horizontal and vertical directions, showing the typical preferred orientation characteristics in the dendrite growth process. As shown in Figure 2b, due to the small distance between crystal nuclei in the simulation domain, the main dendrites of adjacent dendrites in the horizontal direction are limited by the competitive behavior of adjacent crystals, resulting in their growth inhibition. However, in the vertical direction, the main dendrites can fully grow along this direction due to the small influence of space limitation, thus exhibiting an obvious growth morphology extending along the vertical direction.

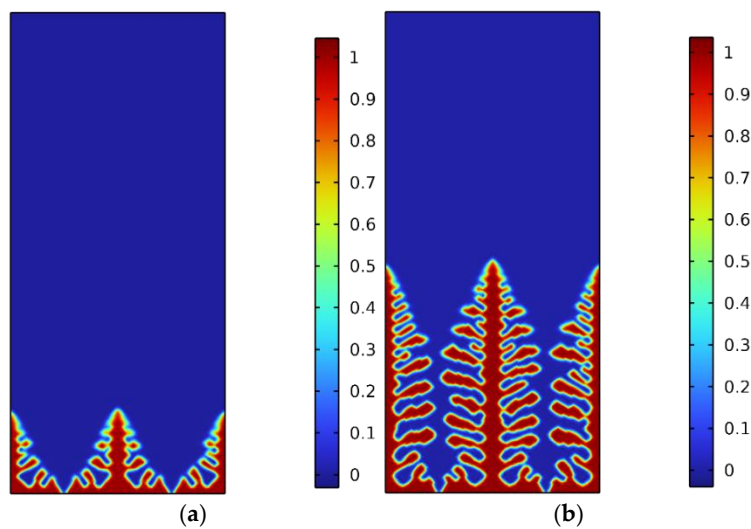


Figure 2. The normal growth process of dendrites within $3000\Delta t$: (a) dendrite morphology at $1000\Delta t$; (b) dendrite morphology at $3000\Delta t$.

After the evolution process reaches $3000\Delta t$, the ambient temperature around the dendrites increases, which causes the dendrites to melt, as shown in Figure 3. As shown in Figure 3a, it can be seen that at the $3005\Delta t$ time step, parts of the lateral dendrites begin to melt, while the main dendrites show an obvious contraction trend. As shown in Figure 3b, with the continuation of the melting process, the overall growth of the dendrites stops, with some of the smaller lateral dendrites having completely melted, while the large lateral dendrites significantly decrease in width and length. As shown in Figure 3c, fracturing occurs at the root position of the lateral dendrites that have not been completely melted at $3030\Delta t$, and it can be seen that the main dendrite arm shows a significant contraction trend. As shown in Figure 3d, most of the lateral dendrites are completely melted at $3040\Delta t$, and the main dendrite arms also show clear signs of melting. As shown in Figure 3, during the remelting process, the main dendrite arms tend to shrink, and the stem width decreases.

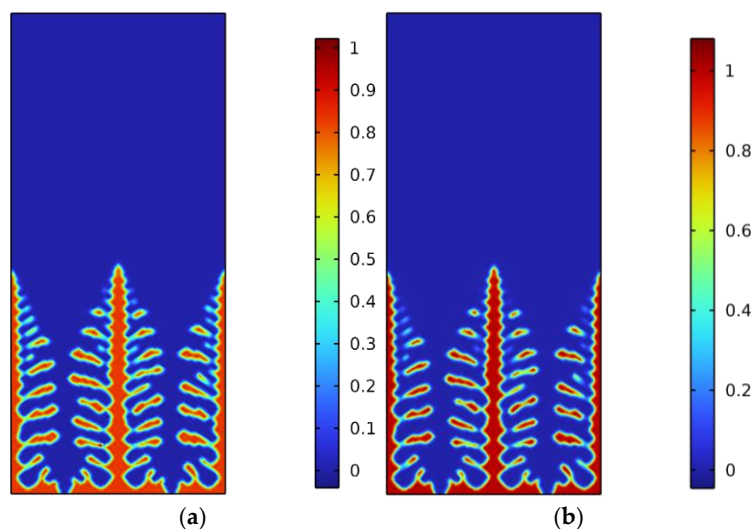


Figure 3. Cont.

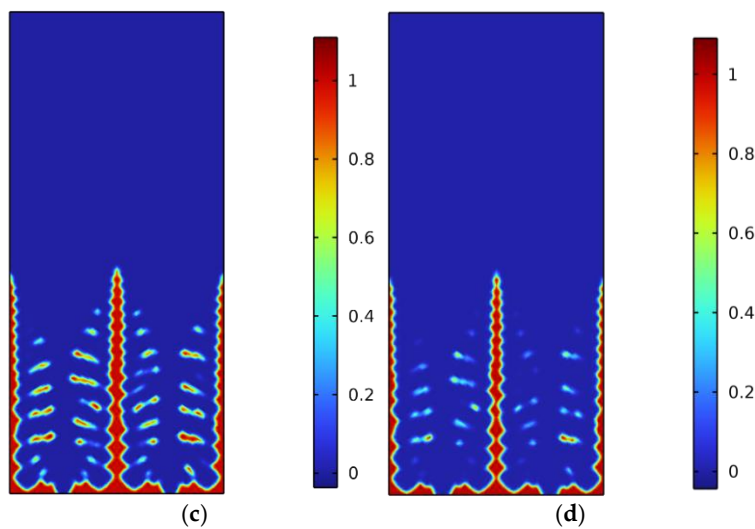


Figure 3. The process of the melting of grown dendrites after $3000\Delta t$: (a) dendrite morphology at $3005\Delta t$; (b) dendrite morphology at $3020\Delta t$; (c) dendrite morphology at $3030\Delta t$; (d) dendrite morphology at $3040\Delta t$.

3.2. Dendrite Remelting Mode in Lateral Dendrite Melting

As shown in Figure 3, during the remelting process, the main dendrite arms exhibit a shrinking trend, and the stem width decreases. The melting behavior of lateral dendrites can be categorized into two typical situations, as shown in Figures 4 and 5. The remelting effect caused by temperature rise and the capillary extrusion effect caused by interface curvature jointly act on the melting process of lateral dendrites. On the one hand, lateral dendrites tend to melt as a whole to maintain the thermodynamic equilibrium at the liquid–solid interface (L/S interface) [25]. On the other hand, the local interface energy difference caused by the negative curvature effect leads to significant capillary extrusion at the root of the lateral dendrites [26], which causes the lateral dendrites to break from the root. In the dendrite remelting process, these two effects compete with each other, resulting in two different melting behaviors of the lateral dendrites.

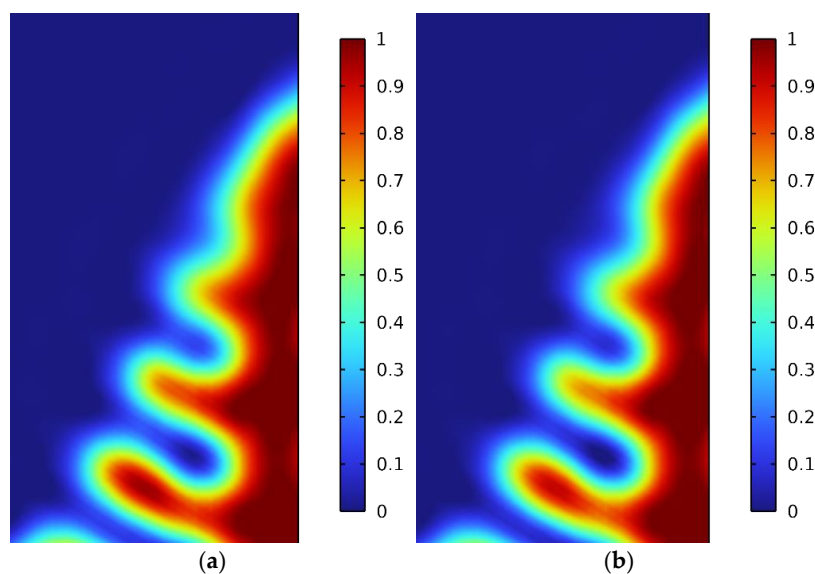


Figure 4. Cont.

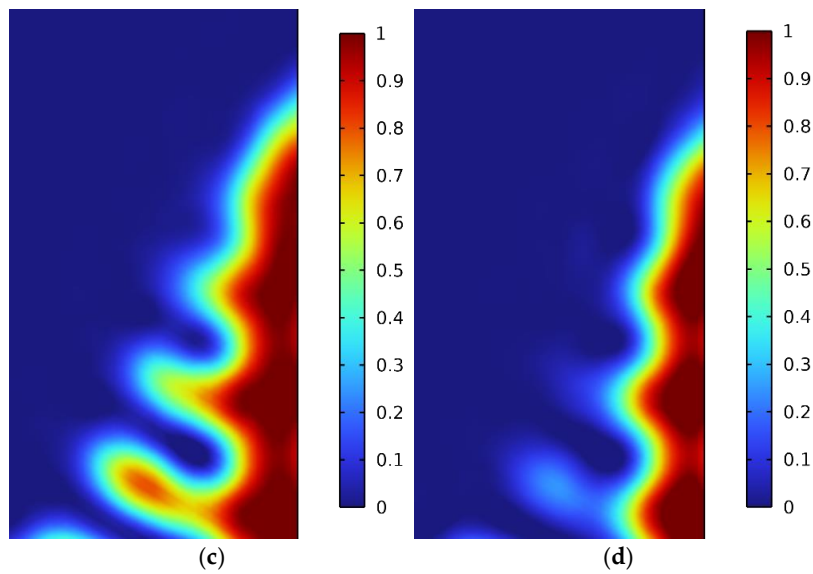


Figure 4. The phenomenon of lateral dendrites retracting into the main dendrite during the melting process. (a) Dendrite morphology at $3000\Delta t$. (b) Dendrite morphology at $3002\Delta t$. (c) Dendrite morphology at $3006\Delta t$. (d) Dendrite morphology at $3018\Delta t$.

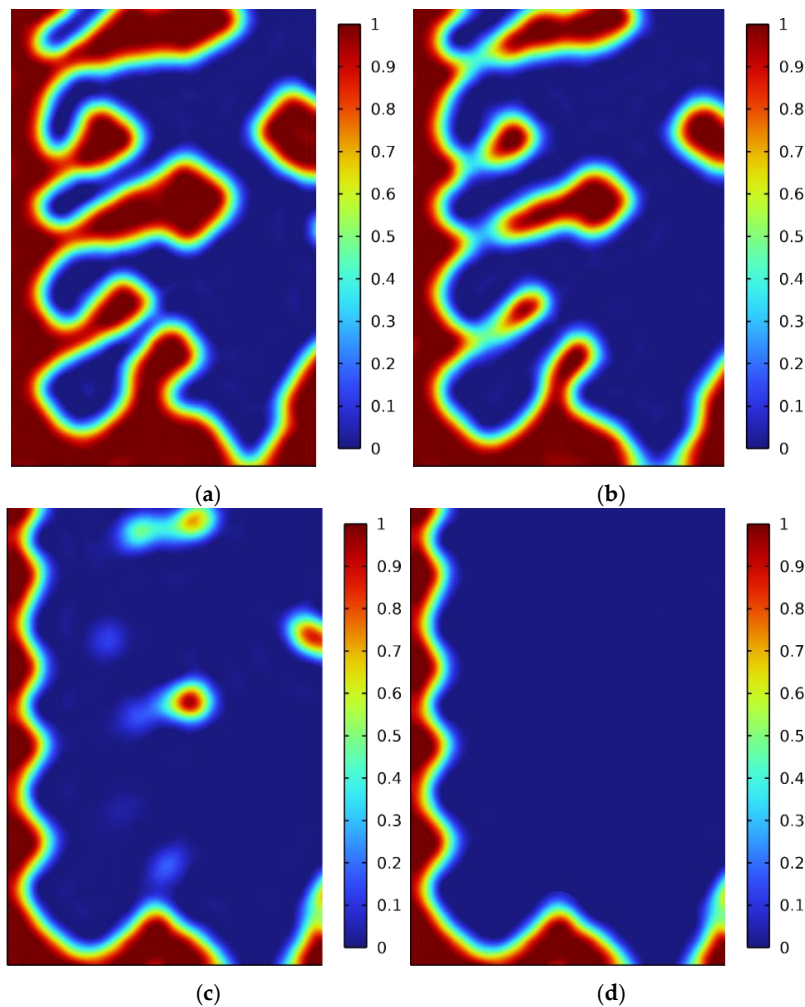


Figure 5. Truncation phenomenon during retraction of melted lateral dendrites. (a) Dendrite morphology at $3000\Delta t$. (b) Dendrite morphology at $3000\Delta t$. (c) Dendrite morphology at $3000\Delta t$. (d) Dendrite morphology at $3000\Delta t$.

As shown in Figure 4a–d, with the increase in ambient temperature, the stem morphology of the lateral dendrites becomes obviously “squeezed”. The lateral dendrites melted before the root fracture until they contracted back into the main dendrites, without forming independent dendrite fragments. The second melting behavior is shown in Figure 5a–d. When the lateral dendrites melt to a certain extent, their roots fracture before completely shrinking back into the main dendrites and then form independent dendrite fragments. At the same time, it can be observed that after the lateral dendrite root fractures, due to the large surface free energy of the dendrite fragments during the melting process, their morphology gradually tends to transition toward a state of minimizing the surface energy. They finally present a nearly spherical melting morphology until completely melting. By observing the whole process of dendrite melting, it can be seen that the longer lateral dendrites show a more significant root fracture tendency, as shown in Figure 3a–d.

The difference between the two kinds of melting behavior reflects the complex competition between the local thermodynamic equilibrium and the capillary effect in the remelting process. In the first case, the thermodynamic equilibrium at the liquid–solid interface (L/S interface) is mainly maintained, and the lateral dendrites shrink from the root back into the main dendrite arm. The second case mainly reflects the influence of capillary compression at the root of the lateral dendrites caused by local interface energy differences caused by the negative curvature effect on lateral dendrite fracture behavior.

3.3. Dendrite Remelting—The Main Dendrite Melting Mode

As the melting process continued, the main dendrites entered the melting stage after the lateral dendrites fractured, as shown in Figure 6. It can be seen in Figure 6a that at $3050\Delta t$, the main dendrites begin to melt rapidly, and their width and length decrease significantly. As shown in Figure 6b, by the time the melting time step reaches $3070\Delta t$, the remaining collateral fragments have all melted into a liquid state. However, due to the heterogeneity in the local dendritic structure and the variability in the melting and fracturing behaviors of the lateral dendrites, the main dendrite fractures along the axial direction and finally splits into several smaller dendrite fragments. As shown in Figure 6c,d, the main dendrite undergoes complete melting between $3070\Delta t$ and $3100\Delta t$. At this stage, the entire dendritic structure has reverted to its initial crystal nucleus state, signifying the completion of the dendrite remelting process.

The dendrite melting process was comprehensively analyzed. As shown in Figures 4 and 6, the overall melting behavior of dendrites is manifested as the gradual melting and fracturing of lateral dendrites, followed by the main dendrites entering the melting stage. The main form of dendrite melting is distinguished by multi-segmented fracturing and melting. This multi-stage fracture behavior may be due to the microstructural characteristics of the main dendrites and the differences in the fracture processes of the lateral dendrites during melting. The complex melting behavior and structure evolution of dendrites during temperature rise has thus been revealed. Theoretical basis and data support have been provided to foster further understanding of the melting mechanism of dendrites under high-temperature conditions.

The above melting process is highly consistent with the experimental observation results obtained by Virkeshwar Kumar [27], indicating that the numerical simulation presented in this paper can accurately reflect the morphological evolution and microstructure changes of dendrites during the remelting process. Thus, the reliability of the model-derived results has been verified.

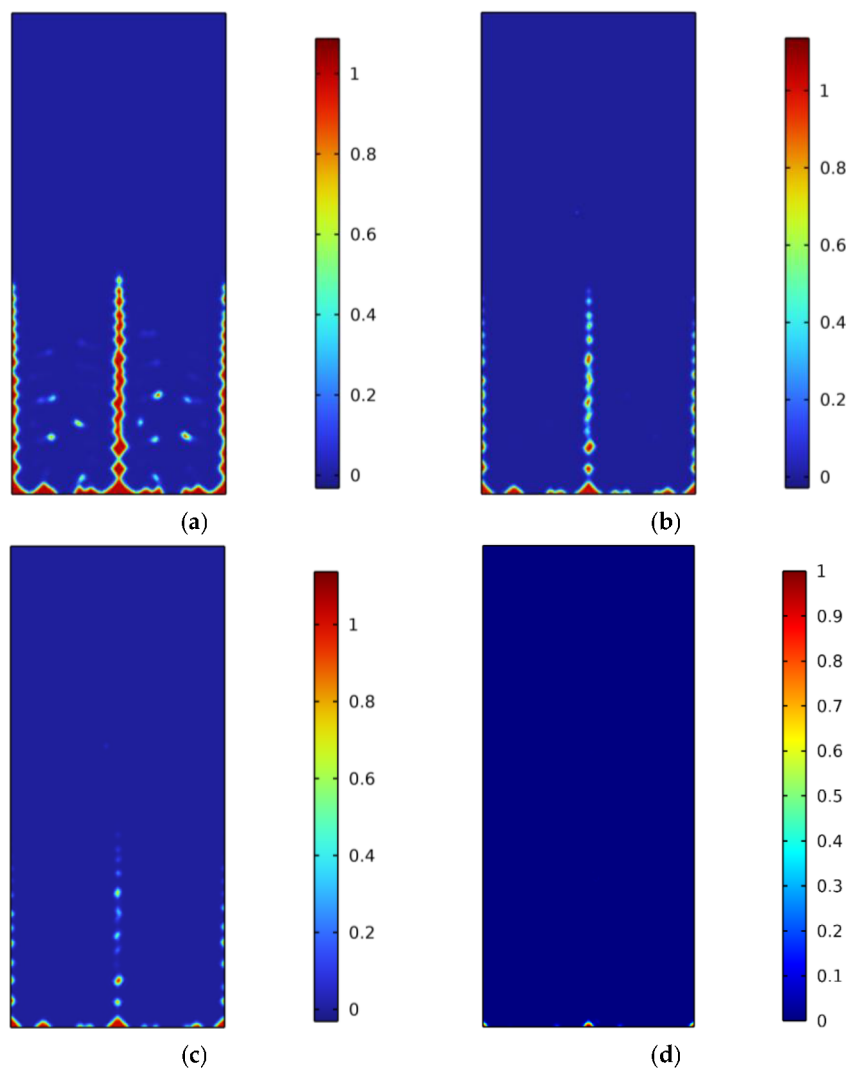


Figure 6. Melting of the primary dendrite arm after the melting of the secondary dendrite arm. (a) Dendrite morphology at $3050\Delta t$. (b) Dendrite morphology at $3050\Delta t$. (c) Dendrite morphology at $3050\Delta t$. (d) Dendrite morphology at $3050\Delta t$.

4. Conclusions

1. Based on the phase field method, a dendrite growth model was established and solved using the finite difference method (FDM), which provided the initial conditions for the solution of the dendrite remelting model. The results show that under the influence of interfacial anisotropy, the crystal nuclei exhibit obvious main dendrite growth in both horizontal and vertical directions, showing the characteristic of a preferred orientation in the process of dendrite growth.
2. Based on the solution data derived from the phase field method and dendrite growth model, a temperature-induced dendrite remelting model was established and solved. The results show that the dendrite remelting process follows a certain sequence, wherein the lateral branches melt the main dendrite first and then melt. When the lateral branches are not completely melted or the root is not broken, the main dendrite stem will shrink to a certain extent but not melt. The melting process of lateral branches consists of the contraction of lateral branches back into the main dendrites and the fracturing of the lateral branches of the main dendrites. The melting process of main dendrites takes the form of multi-stage melting due to the inhomogeneity of the crystal structure and the difference in the melting-induced fracturing of the lateral branches.

Author Contributions: X.H. and C.L. acquired the grant and revised the paper; H.Z. and S.L. performed modeling and wrote the paper; F.K. extracted and analyzed the data; J.L. and X.W. checked the grammar. All authors have read and agreed to the published version of the manuscript.

Funding: The Ministry of Science and Technology of the People's Republic of China provided funding via the following projects: "High-Throughput Design, Preparation, and Characterization of Composite Powders for Special Coatings on Key Components in Metallurgy" (2021YFB3702002); "Applied Basic Research Program of Liaoning Province" (2023JH2/101300226); "Project for Graduate Education Reform and Technological Innovation and Entrepreneurship of University of Science and Technology Liaoning" (2023YJSCX02); "Liaoning Province Metallurgical equipment and process control key laboratory open project fund (2024KFKT-01)"; "Supported by the Fundamental Research Funds for the Liaoning Universities (LJ222410146021)".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Liu, S.; Ding, H.; Chen, R.; Guo, J.; Fu, H. Microstructural evolution and mechanical properties of a Cr-rich β -solidifying TiAl-based alloy prepared by electromagnetic cold crucible continuous casting. *Mater. Sci. Eng. A* **2020**, *798*, 140205. [CrossRef]
2. Zhi, Y.; Jiang, Y.; Ke, D.; Hu, X.; Liu, X. Review on Cellular Automata for Microstructure Simulation of Metallic Materials. *Materials* **2024**, *17*, 1370. [CrossRef] [PubMed]
3. Wang, J.; Wang, H.; Cheng, X.; Zhang, B.; Wu, Y.; Zhang, S.; Tian, X. Prediction of solidification microstructure of titanium aluminum intermetallic alloy by laser surface remelting. *Opt. Laser Technol.* **2022**, *147*, 107606. [CrossRef]
4. Rappaz, M.; Jarry, P.; Kurtuldu, G.; Zollinger, J. Solidification of metallic alloys: Does the structure of the liquid matter? *Metall. Mater. Trans. A* **2020**, *51*, 2651–2664. [CrossRef]
5. Yang, L.; Liu, L.J.; Qin, Q.Y.; Li, J.F. Role of remelting in grain refinement of undercooled single-phase alloys. *Metall. Mater. Trans. A* **2022**, *53*, 3100–3109. [CrossRef]
6. Ren, N.; Li, J.; Bogdan, N.; Xia, M.; Li, J. Simulation of dendritic remelting and fragmentation using coupled cellular automaton and Eulerian multiphase model. *Computational. Mater. Sci.* **2020**, *180*, 109714. [CrossRef]
7. Peng, X.L.; Xiao, H.; Li, W.H.; Yi, B.; Qin, W.; He, H. Simulation of Dendritic Morphology of Ni-Cu Alloy under Convection Based on Phase Field Method. *Shanghai Met.* **2021**, *43*, 69–76.
8. Rojas, R.; Sotomayor, V.; Takaki, T.; Hayashi, K.; Tomiyama, A. A phase field-finite difference lattice Boltzmann method for modeling dendritic growth solidification in the presence of melt convection. *Comput. Math. Appl.* **2022**, *114*, 180–187. [CrossRef]
9. Danilov, D.; Nestler, B. Phase-field simulations of solidification in binary and ternary systems using a finite element method. *J. Cryst. Growth* **2005**, *275*, e177–e182. [CrossRef]
10. Cha, P.R.; Yeon, D.H.; Yoon, J.K. A phase field model for isothermal solidification of multicomponent alloys. *Acta Mater.* **2001**, *49*, 3295–3307. [CrossRef]
11. Gonzalez-Cinca, R.; Folch, R.; Benitez, R.; Ramirez-Piscina, L.; Casademunt, J.; Hernandez-Machado, A. Phase-field models in interfacial pattern formation out of equilibrium. *arXiv* **2003**. [CrossRef]
12. Galfré, A.; Huang, X.; Couenne, F.; Cogné, C. The phase field method—From fundamentals to practical applications in crystal growth. *J. Cryst. Growth* **2023**, *620*, 127334. [CrossRef]
13. Plapp, M. Phase-field models. In *Handbook of Crystal Growth*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 631–668. [CrossRef]
14. Zhu, C.; Jia, J.; Feng, L.; Xiao, R.; Dong, R. Research of three-dimensional dendritic growth using phase-field method based on GPU. *Comput. Mater. Sci.* **2014**, *91*, 146–152. [CrossRef]
15. Kavousi, S.; Gates, A.; Jin, L.; Zaeem, M.A. A temperature-dependent atomistic-informed phase-field model to study dendritic growth. *J. Cryst. Growth* **2022**, *579*, 126461. [CrossRef]
16. Liszka, T.; Orkisz, J. The finite difference method at arbitrary irregular grids and its application in applied mechanics. *Comput. Struct.* **1980**, *11*, 83–95. [CrossRef]
17. Zhang, Q.; Fang, H.; Xue, H.; Pan, S.; Rettenmayr, M.; Zhu, M. Interaction of local solidification and remelting during dendrite coarsening-modeling and comparison with experiments. *Sci. Rep.* **2017**, *7*, 17809. [CrossRef]
18. Kobayashi, R. Modeling and numerical simulations of dendritic crystal growth. *Phys. D Nonlinear Phenom.* **1993**, *63*, 410–423. [CrossRef]
19. Boettinger, W.J.; Warren, J.A.; Beckermann, C.; Karma, A. Phase-field simulation of solidification. *Annu. Rev. Mater. Res.* **2002**, *32*, 163–194. [CrossRef]

20. Zaeem, M.A.; Yin, H.; Felicelli, S.D. Modeling dendritic solidification of Al–3% Cu using cellular automaton and phase-field methods. *Appl. Math. Model.* **2013**, *37*, 3495–3503. [CrossRef]
21. Suzuki, T.; Ode, M.; Kim, S.G.; Kim, W.T. Phase-field model of dendritic growth. *J. Cryst. Growth* **2002**, *237*, 125–131. [CrossRef]
22. Acharya, R.; Sharon, J.A.; Staroselsky, A. Prediction of microstructure in laser powder bed fusion process. *Acta Mater.* **2017**, *124*, 360–371. [CrossRef]
23. Tong, X.; Beckermann, C.; Karma, A.; Li, Q. Phase-field simulations of dendritic crystal growth in a forced flow. *Phys. Rev. E* **2001**, *63*, 061601. [CrossRef] [PubMed]
24. Du, L.; Zhang, R. Phase field simulation of dendrite growth with boundary heat flux. *Integr. Mater. Manuf. Innov.* **2014**, *3*, 225–239. [CrossRef]
25. Sun, D.; Wang, Y.; Yu, H.; Han, Q. A lattice Boltzmann study on dendritic growth of a binary alloy in the presence of melt convection. *Int. J. Heat Mass Transf.* **2018**, *123*, 213–226. [CrossRef]
26. Chen, W.; Hou, H.; Zhang, Y.; Liu, W.; Zhao, Y. Thermal and solute diffusion in α -Mg dendrite growth of Mg-5wt.% Zn alloy: A phase-field study. *J. Mater. Res. Technol.* **2023**, *24*, 8401–8413. [CrossRef]
27. Kumar, V.; Karagadde, S.; Meena, K. Real-Time Strengthening of Natural Convection and Dendrite Fragmentation During Binary Mixture Freezing. In *Conference on Fluid Mechanics and Fluid Power*; Springer Nature: Singapore, 2022; pp. 691–700. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

A Simulation Study on the Effect of Supersonic Ultrasonic Acoustic Streaming on Solidification Dendrite Growth Behavior During Laser Cladding Based on Boundary Coupling

Xing Han, Hao Zhan, Chang Li *, Xuan Wang, Jiabo Liu, Shuchao Li, Qian Sun and Fanhong Kong

School of Mechanical Engineering and Automation, University of Science and Technology Liaoning,
Anshan 114051, China

* Correspondence: lichang2323-23@163.com

Abstract: Laser cladding has unique technical advantages, such as precise heat input control, excellent coating properties, and local selective cladding for complex shape parts, which is a vital branch of surface engineering. During the laser cladding process, the parts are subjected to extreme thermal gradients, leading to the formation of micro-defects such as cracks, pores, and segregation. These defects compromise the serviceability of the components. Ultrasonic vibration can produce thermal, mechanical, cavitation, and acoustic flow effects in the melt pool, which can comprehensively affect the formation and evolution for the microstructure of the melt pool and reduce the microscopic defects of the cladding layer. In this paper, the coupling model of temperature and flow field for the laser cladding of 45 steel 316L was established. The transient evolution laws of temperature and flow field under ultrasonic vibration were revealed from a macroscopic point of view. Based on the phase field method, a numerical model of dendrite growth during laser cladding solidification under ultrasonic vibration was established. The mechanism of the effect of ultrasonic vibration on the solidification dendrite growth during laser cladding was revealed on a mesoscopic scale. Based on the microstructure evolution model of the paste region in the scanning direction of the cladding pool, the effects of a static flow field and acoustic flow on dendrite growth were investigated. The results show that the melt flow changes the heat and mass transfer behaviors at the solidification interface, concurrently changing the dendrites' growth morphology. The acoustic streaming effect increases the flow velocity of the melt pool, which increases the tilt angle of the dendrites to the flow-on side and promotes the growth of secondary dendrite arms on the flow-on side. It improves the solute distribution in the melt pool and reduces elemental segregation.

Keywords: laser cladding; supersonic vibration; acoustic streaming effect; poly dendrite growth; flow field boundary

1. Introduction

Laser cladding is an emerging surface repair technology which adds high-performance materials to the substrate surface [1,2]. With the thermal effect generated by the high-energy-density laser beam, the added material and the substrate material are rapidly melted to achieve metallurgical bonding between the two. Laser cladding can significantly improve the substrate surface properties, including hardness, wear resistance, high temperature stability, and corrosion resistance. Coaxial powder feeding laser cladding has the advantages of unlimited forming size, high flexibility, wide material selectivity, and easy automation. In this paper, the coaxial powder feeding laser cladding method was used in the study, and the schematic is shown in Figure 1.

During the laser cladding process, there are extremely hot and cold characteristics, and a high energy density produces rapid temperature change rates. Micro-defects such as cracks, pores, and tissue segregation are produced, which affect the serviceability of the

parts [3,4]. To further improve the defects and properties for the laser cladding layer, ultrasonic vibration-assisted laser cladding has become the focus of current research. Ultrasonic vibration can produce thermal, mechanical, cavitation, and acoustic flow effects in the melt pool, which comprehensively affect the formation and evolution of the microstructure and reduce the microscopic defects of the cladding layer [5–8]. Introducing ultrasonic vibration into the laser cladding process has important research significance and application value for improving the cladding layer quality and optimizing its performance.

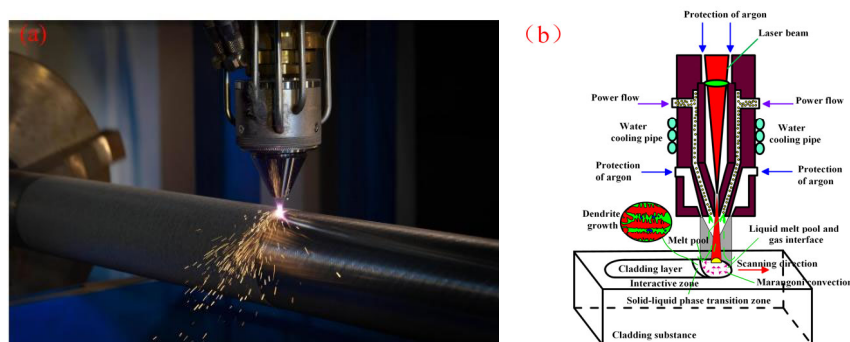


Figure 1. Coaxial laser cladding: (a) physical drawings for laser cladding and (b) schematic of laser cladding process.

Zhuang et al. [9] prepared a 316L cladding layer on a Q345 steel substrate surface and investigated the effect of ultrasonic vibration on the organization of the 316L cladding layer. The results showed that ultrasonic vibration can improve the macroforming quality of the cladding layer and can also significantly refine the cladding layer grain. The average grain size of the cladding layer was reduced by about 42% under the optimum parameters. Song H et al. [10] prepared laser-melted iron-based crystalline/amorphous composite cladding layers with and without ultrasonic vibration. The effect of ultrasonic vibration on the organization evolution of the cladding layer was observed by scanning electron microscopy. The results showed that the amorphous phase content of the fused cladding layer with ultrasonic vibration was increased, the growth of columnar crystals at the interface was suppressed, and the transformation of columnar crystals to equiaxed crystals was promoted along with the refinement of grains. Ma et al. [11] prepared yttria-stabilized zirconia-fused cladding layers on titanium alloy substrates using ultrasonic vibration-assisted laser cladding. The organization of the cladding layer was characterized by scanning electron microscopy. The results showed that ultrasonic vibration could improve the wettability of the cladding layer with the substrate. It reduces the grain size and makes the band structure in the fused cladding layer broken and dispersed. Geng et al. [12] used a phase field model of microstructure evolution in the solidification process of the laser cladding melt pool. The growth process of dendrites at the bottom of the cladding layer of an aluminum–copper alloy was simulated in the arc welding additive manufacturing process. It was found that the growth process of dendrites consists of a linear growth stage, a competitive growth stage, and a stabilization stage. Wu et al. [13] used a phase field model of microstructure evolution in the solidification process of a laser additive manufacturing melt pool. The solidification process of dendrites in additively manufactured Ti-6Al-4V alloys was simulated. It was found that the larger the temperature gradient, scanning velocity, and cooling rate, the smaller the dendrite spacing and the faster the dendrite growth rate. The simulated dendrite morphology and dendrite spacing are in good agreement with the experimental results. Zhang et al. [14] used the phase field model of microstructure evolution during the solidification process in a molten pool. The organizational evolution of the selective laser melting of titanium alloys was investigated. It was found that the dendrites grew along the direction of heat flow. Microsegregation can be observed during the formation of dendrites. The solute enrichment phenomenon exists near the dendrite tip and between the dendrite arms. The temperature gradient and scanning velocity are inversely related to the main dendrite spacing. Sun

et al. [15] conducted a two-dimensional coupling simulation of the macroscopic temperature field and the microscopic tissue growth at the bottom of the melt pool during the laser cladding of pure nickel coaxial powder feed. The phase field method was used to calculate the coupling of the phase field and temperature field in the microscopic region, and the microstructure morphology was obtained. The results showed that the growth direction of the microstructure at the bottom of the melt pool is from the bottom to the top of the melt pool, which is slightly biased towards the laser scanning direction and the competition between the microstructures, which is basically parallel to the direction of heat flow. Li et al. [16] studied the influence of ultrasonic vibration on the fluidity and microstructure for aluminum alloys. The results showed that a sufficient intensity of ultrasonic vibration would cause melt turbulence and destroy the growth of α -Al dendrites, thus achieving the purpose of improving the fluidity. Lian et al. synthesized a Nb-C-reinforced phase in situ on a Ni substrate by ultrasonic vibration-assisted laser cladding and found that ultrasonic vibration could significantly reduce the grain size of the coating without changing the coating phase composition, thus making the coating microstructure finer and more uniform [17]. Lv et al. conducted an experimental analysis on the IN178/WC composite coating with applied ultrasonic vibration. The study showed that the effect of ultrasonic vibration could promote the uniform distribution of WC particles without changing the phase composition, thus improving the microhardness friction and wear properties for the coating [18].

Most of the current studies on ultrasonic-assisted laser cladding tend to use experimental analysis and macroscopic numerical simulations, which cannot directly reveal the dendrite evolution law of the laser cladding solidification process assisted by ultrasonic vibration. Also, it is difficult to quantify the mechanism of ultrasonic vibration assistance on the laser cladding process. In this paper, the mechanism of ultrasonic vibration on the laser cladding process was analyzed from a mesoscopic perspective for melt pool solidification. The effect of ultrasonic vibration and acoustic streaming on the microstructure of the melt pool was directly revealed. A theoretical foundation for optimizing the ultrasonic vibration-assisted laser cladding process was established.

2. Materials and Methodology

2.1. Material Parameterization for Laser Cladding

In this paper, 45 steel was selected as the substrate and 316L powder was selected as the cladding material. In the paper, the thermodynamic simulation software JMatPro 7.0, which is based on the calculated phase diagram method (CALPHAD), was first used to calculate the temperature change physical property parameters of the 45 steel and 316L powder materials. The elemental compositions of the 45 steel and 316L powder are listed in Tables 1 and 2. Fully considering the influence of material physical properties by temperature change is crucial. The temperature change physical property parameter curves for 45 steel and 316L are shown in Figure 2. A 3D numerical model for the laser cladding process was established, and the growth boundary of the solidified microstructure was obtained. The influence of laser scanning velocity parameters on dendrite growth was studied, and the microstructure mechanism of laser scanning velocity and the influence of different scanning velocities on the laser cladding pool were further revealed.

Table 1. Elemental composition of 45 steel (wt%).

Elemental	C	Si	Mn	Cr	Ni	Cu	P	S	Fe
Quantity contained	0.45	0.27	0.65	0.02	0	0.01	0.016	0.007	Bal

Table 2. Elemental composition of 316L powder (wt%).

Elemental	C	Si	Mn	Cr	Ni	P	S	Mo	Fe
Quantity contained	0.08	1.00	2.00	16~18	13	0.045	0.002	2~3	Bal

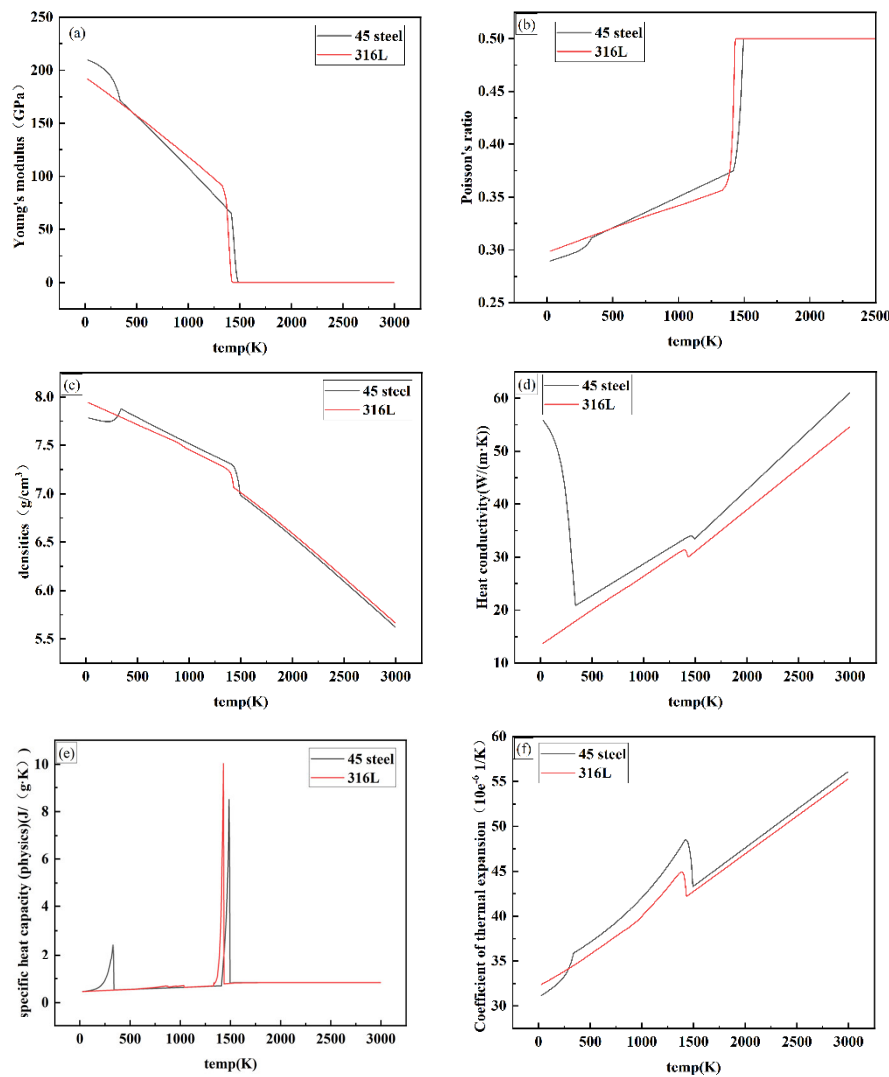


Figure 2. Temperature change physical property parameter curves for 45 steel and 316L. (a) Young's modulus for 45 steel and 316L; (b) Poisson's ratio of 45 steel and 316L; (c) density of 45 steel and 316L; (d) heat conductivity of 45 steel and 316L; (e) specific heat capacity of 45 steel and 316L; (f) coefficient of thermal expansion for 45 steel and 316L.

2.2. Governing Equation for Laser Cladding

The cladding model was established to obtain the 3D model boundary morphology for the melt pool, the size of the paste zone, and the flow velocity in the melt pool. As shown in Figure 1b, the laser cladding powder feeding method adopts a coaxial powder feeding system, in which the powder is distributed around the laser beam in a multi-beam circumferential surrounding. The cladding head is provided with a protective gas (argon). To save time and reduce computational difficulty, basic physical assumptions and model formulas are used in this section to describe the formation of a monorail laser cladding pool [19].

The basic assumptions in the model are as follows:

- (1) The energy density of the laser heat source acting on the melt has a Gaussian distribution;
- (2) The fluid in the melt pool is an incompressible Newtonian fluid;
- (3) The melt metal flow in the melt pool is laminar;
- (4) The impact caused by momentum when the powder enters the melt pool is ignored;
- (5) The loss of heat dissipation caused by the high temperature of the melt is ignored;
- (6) The process of powder addition to the substrate follows a Gaussian distribution;

- (7) The absorption and reflection of the laser energy of the powder are linearly related to the amount of powder delivery.

The above assumptions were used as initial data and boundary conditions for solidification analysis, making the model more feasible. In this paper, based on the finite element method and finite volume method, a predictive cladding pool model is established. The heat–flow coupling can clearly reveal the evolution process of the melt pool. At the same time, the temperature field and the flow field are coupled to obtain the size and temperature gradient for the melt pool.

Considering the conservation equations of mass, momentum, and energy in the cladding process, the governing equation for the temperature field (Fourier's law) is obtained as follows [20–22]:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \nabla T = \nabla \cdot (k \nabla T) - \frac{\partial \Delta H_T}{\partial t} - \rho \mathbf{u} \Delta H_T \quad (1)$$

where ρ is the melt density, C_p is the heat capacity at constant pressure, T is the temperature of the cladding process, $\mathbf{u}$ is the melt flow velocity, and k is the thermal conductivity.

The latent heat of the melt is considered, where ΔH_T is the latent enthalpy and the equation is

$$\Delta H_T = \beta_L f_L \quad (2)$$

where β_L is the latent heat, f_L is the mass fraction of the fluid, and f_L is the function to judge the fluid, the equation of which is

$$f_L = \begin{cases} 0, & T < T_S \\ \frac{T - T_S}{T_L - T_S}, & T_S \leq T \leq T_L \\ 1, & T_L < T \end{cases} \quad (3)$$

where T_S and T_L represent the melt solid and liquidus temperatures, respectively. When f_L is 0, it represents the solid phase; when f_L is 1, it represents the liquid phase.

The melt flow in a melt pool follows hydrodynamics. According to the assumed conditions, the continuity equation and the Navier–Stokes momentum equation describing the fluid motion are expressed as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (4)$$

$$\rho \left[\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla \cdot (p \mathbf{I}) + \nabla \cdot \left[\mu_L (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \right] + D_A \quad (5)$$

where $\mathbf{I}$ is the spatial unit substrate, p is the melt pressure, and μ_L is the dynamic viscosity of the melt.

Melt flow is the main factor affecting the morphology of the melt pool. To better understand the flow state inside the melt pool, the parameter Marangoni number (Ma represents the ratio of thermal capillary force to viscous force) is selected for evaluation, and the equation is as follows:

$$Ma = \frac{d\sigma_t}{dT} \frac{\Delta T R_L}{\mu_L \alpha_0} \quad (6)$$

where R_L is the laser heat source radius, α_0 is the thermal diffusion coefficient of the melt, and $d\sigma_t/dT$ is the temperature gradient coefficient of the surface tension.

2.3. Ultrasonic Vibration Theory

Ultrasonic waves include sound waves with frequencies higher than 20 kHz and vibration waves in objects, which comprise not only a wave mode but also a form of energy transfer [23,24]. There are two main forms of ultrasound, namely power ultrasound and detection ultrasound. In this paper, power ultrasound is selected, which is a kind of

ultrasound with high intensity, and its energy can change the structure and properties of the medium during the transfer process [25,26]. In an elastic medium, power ultrasound causes periodic changes for sound pressure and stress in the medium [27,28]. With the vibration, some of the energy is released in the form of internal energy, resulting in secondary effects such as acoustic flow effects and cavitation effects in a solution and mechanical and thermal effects in solids. Power ultrasound is used in a wide range of industries, including ultrasonic rust removal, ultrasonic brazing, ultrasonic cutting, ultrasonic assisted-casting, and other processes [29–32].

The introduction of ultrasonic vibration is to input an electrical signal through an ultrasonic generator and transform the electrical signal into a mechanical vibration of high-frequency particles through an ultrasonic transducer. This is then reinforced by an amplitude transformer and transmitted to the substrate and metal melt pool [33]. What actually affects the melt pool is the ultrasonic sound field. The ultrasonic vibration equation is

$$X_1 = A \sin(\omega t + \varphi) \quad (7)$$

where X_1 is the displacement of the vibration point of the horn, A is the ultrasonic amplitude, ω is the angular frequency of particle vibration, and φ is the sinusoidal phase angle.

Ultrasonic power and sound intensity are used to measure the energy intensity of sound waves. Power is the total energy passing through a surface per unit of time and is affected by attenuation. The sound intensity represents the energy concentrated in a unit area per unit of time. For a melt pool subjected to ultrasonic vibration, the sound intensity is expressed as follows:

$$I_m = \frac{1}{2} \rho_L c_0 \omega^2 A^2 \quad (8)$$

where c_0 is the ultrasonic propagation velocity in the melt and ρ_L is the medium density.

The sound pressure amplitude is

$$P_m = \sqrt{2 \rho_L I_m c_0} \quad (9)$$

2.4. Acoustic Streaming Effect

When there is strong sound wave propagation in the medium solution, there is often a non-periodic flow, which is called acoustic streaming. The phenomenon of acoustic streaming was first discovered by experimental phenomena. Michael Faraday [34] studied the air vibration phenomenon around an elastic plate under high-velocity vibration and considered the relationship between the motion state of the surrounding air and the vibration. Subsequently, in an experiment, Dvorak found that under a strong amplitude vibration, a small average flow from the amplitude peak to trough would be generated near the wall surface of the Kundt tube, and a backflow phenomenon would be formed in the Kundt tube [1,35]. In the 1940s, Rayleigh [36] carried out theoretical analyses and research on the strange flow phenomena observed in the experiment in plates and Kundt tubes for the first time. In the process of solving the flow control equation, the influence of second-order nonlinear terms on the flow was ignored, and the iterative approximation (successive approximation) method was adopted to solve the control equation. By conducting in-depth theoretical research on this phenomenon, Eckart [37] systematically analyzed the first-order sound field and derived the equation of the force generated in the sound field. The mechanism and properties of the acoustic streaming effect were theoretically described. These theoretical methods provide an important theoretical basis for the follow-up study of acoustic streaming problems.

According to the linear acoustics principle (Hooke's Law), we can assume that an acoustic disturbance of a sinusoidal waveform propagates through a medium [38,39]. In the linear acoustic system, each particle in the medium vibrates sinusoidally according to its initial phase. Therefore, at any point in the liquid medium, the average velocity in time

is zero, meaning that small amplitude sound waves do not produce macroscopic acoustic streaming in a linear medium.

However, in the acoustic field, if the initial state of the liquid medium is stationary, sound flow can be generated during the propagation of the sound wave. Based on the law of conservation of energy, the direction of sound flow must be accompanied by a change in energy. Considering the energy change as the action of a force, it can be inferred that there must be a force in the sound field with a non-zero time average in the Δt time interval. The action of this force may lead to the displacement of the fluid element, which is manifested as the acoustic streaming phenomenon on a macroscopic level.

By studying the propagation process of the first-order sound field, Eckart [37] deduced the directional constant velocity flow caused by the attenuation of sound intensity in the fluid medium, and its calculation equation is as follows:

$$\begin{cases} \vec{F}_1 = -\nabla \langle E_c \rangle \\ 2E_c = \frac{P_1^2}{\rho_L c_L} + \rho_L \vec{v}_s \cdot \vec{v}_s \end{cases} \quad (10)$$

where $\vec{F}_1$ is the driving force acting on the direction of sound flow, ∇E_c is the energy density gradient in the sound field, ρ_L and c_L are the first-order terms of the density and sound propagation velocities of the liquid medium, respectively, P_1 is the pressure, and $\vec{v}_s$ is the second-order term of the displacement velocity of any intermediate particle in the sound field.

In the finite element calculation process, the driving force of acoustic flow is added to the flow equation in the form of a volume force source term, and the calculation equation is as follows [40]:

$$F_m = \frac{1}{2} \text{Re}[\rho_e^* \omega u] + \frac{1}{2} \rho_e^* \left(\text{Re} \left[u_x^* \frac{\partial u}{\partial x} \right] + \text{Re} \left[u_y^* \frac{\partial u}{\partial y} \right] \right) \quad (11)$$

where ρ_e^* is the conjugate complex number of density perturbations, u is the velocity of the particle in the flow field, and u_x and u_y are the velocity components of the particle velocity in the x and y directions, respectively.

When Eckart deduced the theory of acoustic streaming in the process of first-order sound field propagation, the finite amplitude effect of sound vibration was not considered. CTaTHNKO improved the calculation method of acoustic fluid force based on the equations of viscous fluid dynamics. The equation is as follows [41]:

$$F_m = \frac{2\pi^2}{3} \frac{\beta \omega l_m^3}{(1 + Y)^3 c_L^2} \quad (12)$$

where β is the nonlinear coefficient of the medium, ω is the angular frequency of ultrasonic vibration, l_m is the amplitude of the vibration velocity of the contact end face of the horn, $Y = \beta M k x$, M is the Mach number of the fluid, k is the wave number, and x is the distance between the particle and the end face of the horn. According to the calculation results of this equation, it can be concluded that the different positions of the ultrasonic vibration source will cause different equal effects, even in the medium without viscous force. Due to the absorption effect produced by the finite amplitude, the same effects will be produced. Compared with Eckart's acoustic streaming theory, the above equation can calculate the acting volume force of acoustic streaming at different positions in the melt pool.

2.5. Phase Field-Controlling Equations

According to the phase field model of the free energy function, in the case of time dependence, the total free energy must be guaranteed to be brief with time. The phase

field equation for the solidified alloy and the governing equation for the solute field can be deduced as follows [42]:

$$\frac{\partial \psi}{\partial t} = M_\psi \left(-\varepsilon_\psi^2 \nabla^2 \psi + \frac{\partial f(\psi, c, e)}{\partial \psi} \right) \quad (13)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(M_c c (1 - c) \nabla \left(\frac{\partial f(\psi, c, e)}{\partial c} - \varepsilon_c^2 \nabla^2 c \right) \right) \quad (14)$$

According to the principle of classical thermodynamics, the variational equation of F in equilibrium must be satisfied.

$$\frac{\delta F}{\delta \psi} = \frac{\partial f}{\partial \psi} - \varepsilon_\psi^2 \nabla^2 \psi = 0 \quad (15)$$

$$\frac{\delta F}{\delta c} = \frac{\partial f}{\partial c} - \varepsilon_c^2 \nabla^2 c = \text{constant} \quad (16)$$

When the energy gradient coefficient is constant, the constant in Equation (16) is the total amount of solute in the space region Ω , that is, the concentration is a conserved constant.

The concentration c of the binary alloy solution varies between c_L and c_S of the two components. To solve the phase mobility and solute diffusion mobility in the phase field chamber, the following equation can be given [43]:

$$M_\psi = (1 - c)M_\psi^A + cM_\psi^B \quad (17)$$

$$M_c = \frac{[1 - p(\psi)]D_S + p(\psi)D_L}{R'T} \quad (18)$$

where A and B are the two pure components of the alloy solution, D_S and D_L are the diffusion coefficients of the solid phase and the liquid phase, respectively, and R' is the gas constant.

Beckermann et al. [44] adopted the description of a regular solution to describe the solute field and provided a better method. In a two-dimensional space, considering the phase indicator equation $\psi(r, t)$, whose interface is described as ψ , the geometry is described as

$$\vec{n} = \frac{\nabla \psi}{|\nabla \psi|}, k = \nabla \cdot \vec{n} = \frac{1}{|\nabla \psi|} \left(\nabla^2 \psi - \frac{\nabla \psi \nabla |\nabla \psi|}{|\nabla \psi|} \right), v = -\frac{1}{|\nabla \psi|} \frac{\partial \psi}{\partial t} \quad (19)$$

where $\vec{n}$ is the normal direction on the ψ interface, k is the interface curvature, and v is the interface normal velocity.

According to Equation (7), the condition of the solid–liquid interface can be obtained as

$$\frac{v}{\mu_i} = T_M^i - T + m_L c_L - \frac{\sigma T_M^i}{L_i} k \quad (20)$$

where m_L is the liquidus slope, T_M^i is the equilibrium temperature (i is A, B), σ is the surface free energy, and L_i is the latent heat.

The change in the phase field parameter ψ on the interface along the normal direction can be expressed by the following equation:

$$\psi = \frac{1}{2} \left[1 + \tanh \left(\frac{n}{2\delta_m} \right) \right] \quad (21)$$

According to Equation (21), it can be obtained that

$$|\nabla \psi| = \frac{\partial \psi}{\partial n} = \frac{\psi(1 - \psi)}{\delta_m} \quad (22)$$

$$\frac{\nabla\psi\nabla|\nabla\psi|}{|\nabla\psi|} = \frac{\partial^2\psi}{\partial n^2} = \frac{\psi(1-\psi)(1-2\psi)}{\delta_m^2} \quad (23)$$

The relationship between the phase field parameter ψ in the normal direction and the interface thickness δ_m is obtained by Equations (22) and (23). By bringing Equations (21)–(23) into the interface equation, the phase field control equation can be obtained as follows:

$$\frac{1}{\mu_k} \frac{\partial\psi}{\partial t} = \Gamma \left[\nabla^2\psi - \frac{\psi(1-\psi)(1-2\psi)}{\delta_m^2} \right] + (T_M - T + m_L(c_L - c_0)) \left[\frac{\psi(1-\psi)}{\delta_m} \right] \quad (24)$$

where μ_k is the kinetic coefficient, T_M is the melting temperature of the alloy, δ_m is the interface thickness, Γ is the Gibbs–Thomson coefficient, and m_L is the liquidus slope of the alloy solution.

According to the heat transfer equation, the temperature field equation is

$$\frac{\partial\tilde{T}}{\partial t} = \alpha_T \nabla^2\tilde{T} + \frac{L_m}{C_p} \frac{\partial P(\psi)}{\partial t} \quad (25)$$

where α_T is the thermal diffusion coefficient, L_m is the latent heat, and C_p is the specific heat.

The law of solute diffusion is described by Fick's law, and the conservation equation for the solute field is derived by using the weighted value of the average concentration.

$$\frac{\partial c}{\partial t} = \nabla \cdot [(1-\psi)D_L\nabla c_L + \psi D_S\nabla c_S] \quad (26)$$

According to the mean concentration evolution equation, the liquid and solid concentration can be expressed as the mean concentration.

$$c_S = \frac{k_f c}{(1-\psi) + k_f \psi}, c_L = \frac{c}{(1-\psi) + k_f \psi} \quad (27)$$

where k_f [45] is the solute partition coefficient.

2.6. Anisotropy of Interfacial Growth

During the solidification process, the interfacial energy at the solid–liquid interface has anisotropy. The anisotropy is manifested as the preferred orientation of dendrite growth, which is always in the direction of the least energy at the interface. Therefore, the interface energy anisotropy has a very important influence on the dendrite morphology evolution and the interface stability [1]. The anisotropy ε of the interface depends on the direction of the normal vector outside the interface; the angle is expressed as

$$\theta = \frac{\nabla\psi}{|\nabla\psi|} = \arctan\left(\frac{\partial\psi/\partial y}{\partial\psi/\partial x}\right) \quad (28)$$

The anisotropic expression is

$$\varepsilon = \bar{\varepsilon}\eta(\theta) = \bar{\varepsilon}(1 + \delta \cos(k_\varepsilon(\theta - \theta_0))) \quad (29)$$

where $\bar{\varepsilon}$ is the average value of the anisotropic gradient energy coefficient; δ is the anisotropy intensity, generally between 0.02 and 0.1; k_ε is the anisotropic modulus, generally 4 or 6 because the material simulated in this paper is FCC (face-centered cubic structure), $k_\varepsilon = 4$; θ is the angle between the main dendrite arm and the interface normal vector; and θ_0 is the initial angle defined when the dendrite begins to grow.

2.7. Establishment of Quantitative Binary Alloy Phase Field Model

The phase field model for the binary alloy is derived according to Section 2.1, and the interface growth anisotropy was added. Thus, the governing equation for the phase field model of the binary alloy can be obtained as

$$\frac{1}{\mu_k} \frac{\partial \psi}{\partial t} = \Gamma \left[-\frac{\partial}{\partial x} \left(\varepsilon \frac{\partial \varepsilon}{\partial \theta} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\varepsilon \frac{\partial \varepsilon}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\varepsilon^2 \nabla \psi) \right] - \frac{\psi(1-\psi)(1-2\psi)}{\delta_m^2} + (T_M - T + m_L(c_L - c_0)) \left[\frac{\psi(1-\psi)}{\delta_m} \right] \quad (30)$$

By inputting the interface growth anisotropy $\varepsilon = \bar{\varepsilon}\eta(\theta)$ into Equation (30), we can expand it to obtain

$$\frac{1}{\mu_k \bar{\varepsilon}^2 \Gamma} \frac{\partial \psi}{\partial t} = \left[-\frac{\partial}{\partial x} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\eta^2 \nabla \psi) \right] - \frac{\psi(1-\psi)(1-2\psi)}{\bar{\varepsilon}^2 \delta_m^2} + \frac{1}{\bar{\varepsilon}^2 \Gamma} (T_M - T + m_L(c_L - c_0)) \left[\frac{\psi(1-\psi)}{\delta_m} \right] \quad (31)$$

Ranadip Acharya et al. [46] further modified Equation (31) to include the linear relationship between the interface temperature and the phase composition and melting temperature of the binary alloy, thus sorting out Equation (31).

$$\frac{1}{\mu_k \bar{\varepsilon}^2 \Gamma} \frac{\partial \psi}{\partial t} = \left[-\frac{\partial}{\partial x} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\eta^2 \nabla \psi) \right] + \frac{1}{\bar{\varepsilon}^2 \Gamma} \frac{2\Gamma}{\delta_m^2} \psi(1-\psi) \left[\psi - \frac{1}{2} + \frac{\delta_m}{2\Gamma} (T_M - T + m_L(c_L - c_0)) \right] \quad (32)$$

In the process of numerical calculation, to improve the convergence of the phase field equation, the linear function is replaced by a nonlinear bounded function as follows:

$$m(T) = \frac{\delta_m^2}{2\Gamma} (T_M - T + m_L(c_L - c_0)) = \frac{\alpha}{\pi} \arctan \left(\gamma \left[1 - \tilde{T} + \tilde{m}_L(c_L - c_0) \right] \right) \quad (33)$$

where $\tilde{T}$ is dimensionless temperature, $\tilde{T} = (T_L - T)/(T_L - T_S)$.

By $\tilde{t} = t/\tau$, $\tilde{l} = l/l_0$ means of dimensionless parameters, the phase field equation is dimensionless and can be written in the following form:

$$\frac{l_0^2}{\mu_k \bar{\varepsilon}^2 \Gamma \tau} \frac{\partial \psi}{\partial \tilde{t}} = \left[-\frac{\partial}{\partial x} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\eta^2 \nabla \psi) \right] + \frac{2l_0^2}{\bar{\varepsilon}^2 \delta_m^2} \psi(1-\psi) \left[\psi - \frac{1}{2} + \frac{\alpha}{\pi} \arctan \left(\gamma \left[1 - \tilde{T} + \tilde{m}_L(c_L - c_0) \right] \right) \right] \quad (34)$$

By introducing phase field interface parameters $\tilde{\varepsilon}_m^2 = \delta_m^2 \bar{\varepsilon}^2 / 2l_0^2$, $\tau_c = (l_0^2 \bar{\varepsilon}_m^2) / (\bar{\varepsilon}^2 \mu_k \Gamma \tau)$, the phase field equation can be expressed as

$$\frac{\tau_c}{\tilde{\varepsilon}_m^2} \frac{\partial \psi}{\partial \tilde{t}} = \left[-\frac{\partial}{\partial x} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \psi}{\partial x} \right) + \nabla \cdot (\eta^2 \nabla \psi) \right] + \frac{1}{\tilde{\varepsilon}_m^2} \psi(1-\psi) \left[\psi - \frac{1}{2} + \frac{\alpha}{\pi} \arctan \left(\gamma \left[1 - \tilde{T} + \tilde{m}_L(c_L - c_0) \right] \right) \right] \quad (35)$$

where $\tilde{\varepsilon}_m$ is the gradient coefficient of interfacial anisotropy, τ_c is the relaxation time parameter (which is a fitting parameter), α and γ are the interfacial coupling coefficients (both of which are constant), $\tilde{m}_L$ is the dimensionless liquidus slope, c_L is the average liquid phase concentration of secondary elements, and c_0 is the average concentration of secondary elements.

Due to the effect of austenite on coating properties during the laser cladding of 316L powder on 45 steel, the physical properties for the Fe-Ni binary solution were selected as the input parameters of the phase field model.

According to Equations (25) and (26), the governing equations for the temperature field and solute field in the solidification process of the binary alloy can be obtained as

$$\frac{\partial \tilde{T}}{\partial t} = \alpha_T \nabla^2 \tilde{T} + \frac{L_m}{C_p} \frac{\partial \psi}{\partial t} \quad (36)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot D_\psi \left[\nabla c + \frac{(1 - k_f)c}{(1 - \psi + k_f \psi)} \nabla \psi \right] \quad (37)$$

where D_ψ is the description of solute diffusion in the phase field variable, $D_\psi = D_S + (D_L - D_S)(1 - \psi)/(1 - \psi + k_f \psi)$.

3. Selection for Microscopic Boundary

3.1. Temperature Field Boundary Selection

The properties and quality of the cladding layer are affected by the temperature variation during the cladding process. The temperature distribution in the melt pool is an important factor determining the microstructure of the solidification. Therefore, it is of great significance to accurately grasp the temperature distribution of the cladding process for the accuracy of the microstructure simulation. This section analyzes the transient changes for temperature in the process of cladding and discusses the influence. The corresponding temperature distribution is shown in Figure 3.

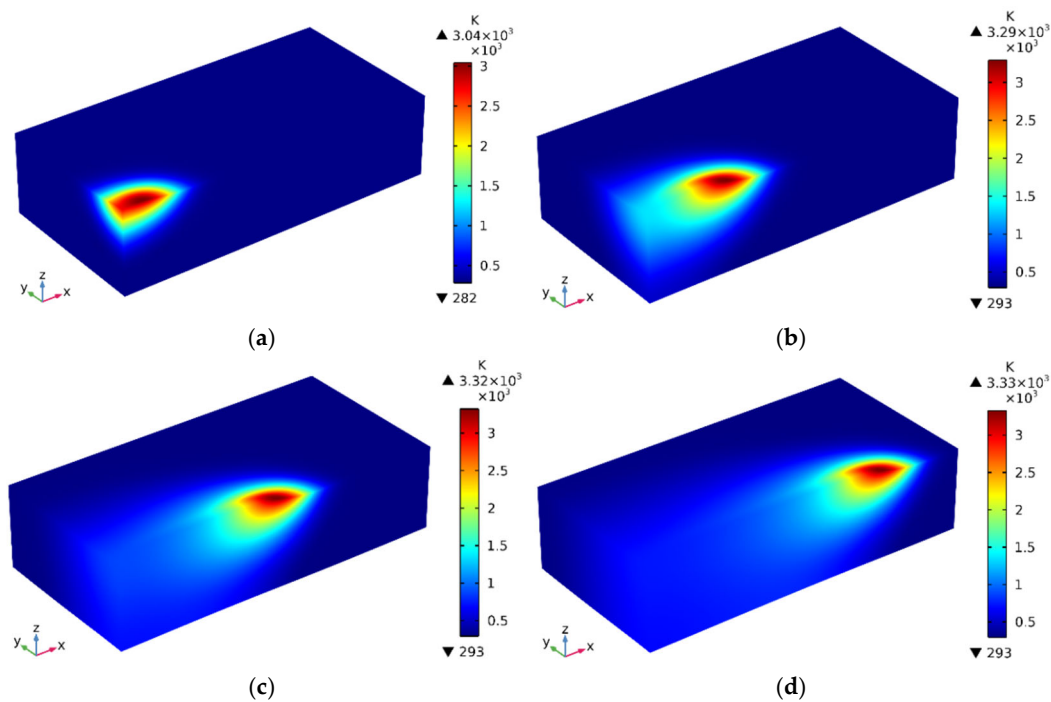


Figure 3. Cloud image for temperature field distribution at different moments of laser cladding 316L powder on 45 steel. (a) Temperature field distribution at 0.3 s; (b) temperature field distribution at 1.0 s; (c) temperature field distribution at 2.0 s; (d) temperature field distribution at 3.0 s.

According to the calculation method of phase diagram, the solid phase line temperature of 316L stainless steel and 45# carbon steel is 1602.26 K and 1656.15 K, respectively. As shown in Figure 3a, when the cladding is carried out for 0.3 s, the peak temperature of the cladding region reaches 2725 K, exceeding the melting point of the substrate and the cladding material. At this stage, because of the short laser irradiation time, the melt pool has not been completely formed. With continuous laser scanning, the melt pool temperature continues to rise, and the heat exchange between the melt pool and the substrate

causes heat accumulation in the melt pool. The width and depth of the melt pool gradually increases. At 1.0 s, the melt pool is fully formed and the maximum temperature at this moment rises to 2951 K, as shown in Figure 3b. As shown in Figure 3c,d, the temperature distribution in the melt pool tends to be stable at 2.0 s and 3.0 s as the heat absorption and diffusion after the melt pool is formed reach a state of equilibrium. The temperature in the melt pool center is the highest and the temperature gradient is large, while the temperature at the edge is relatively low and the temperature gradient is reduced. An obvious thermal diffusion layer was formed between the melt pool and the substrate, and the temperature distribution showed a unique “comet tail”.

To better simulate the microstructure evolution during the melt pool solidification process, the temperature distribution at the moment of 2.0 s was selected as the boundary condition for the simulation of dendrite growth behavior, as shown in Figure 3. Figure 4a shows that the paste region position at the bottom of the longitudinal section of the melt pool is selected as the boundary of the simulation. The temperature at mark 1 is still in the melting state at about 2000 K, and the temperature at mark 2 fluctuates around 1700 K, which is just in the position of the solid phase line and liquidus of the melt pool material. The temperature of the outer boundary at mark 2 was selected as the simulated boundary condition of the microstructure. As shown in Figure 4b, a cross-sectional temperature field at a distance from the center of the melt pool is selected. At the same time, according to the solid–liquidus temperature range of the cladding material, the temperature boundary at the cross-section is selected to draw an “ellipse” shape by the black line in Figure 4.

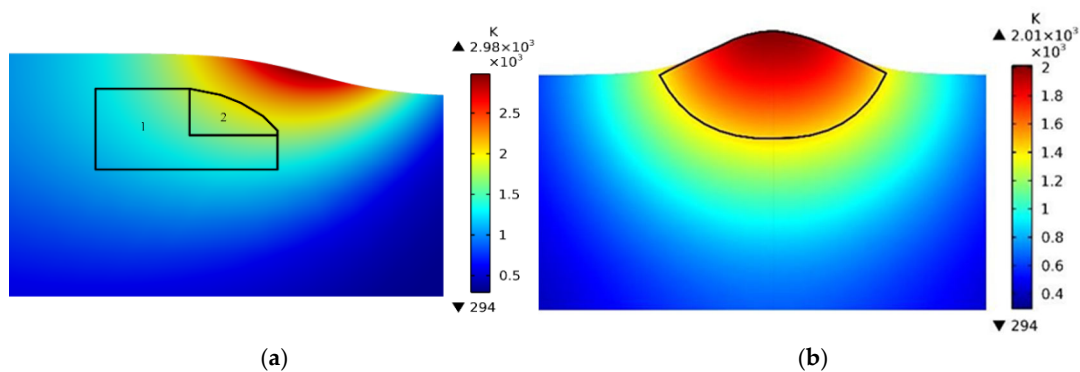


Figure 4. Temperature boundary selection in solidification microstructure simulation. (a) Temperature field boundary selection for longitudinal section; (b) temperature field boundary selection for cross-section.

3.2. Flow Field Boundary Extraction Under Silent Flow

Figure 5 shows the cloud image for the flow field distribution in the melt pool during laser cladding. At 0.3 s, the flow field in the melt pool has not completely formed, and a small circulation has formed. The maximum flow velocity is 0.23 m/s, as shown in Figure 5a. At 1 s, an obvious Marangoni convection had formed in the melt pool, and the flow field was completely formed and the maximum flow velocity is 0.34 m/s, as shown in Figure 5b. Compared with the flow field distribution in the melt pool at 1 s, the flow field distribution in the melt pool remained basically unchanged at 2.0 s and 3.0 s, and the maximum flow velocity changed slightly to 0.35 m/s, as shown in Figure 5b–d.

To better select the flow velocity size and direction for the static flow field simulation, the flow field distribution cloud image after stability at 2.0 s is selected, as shown in Figure 6. As shown in Figure 6a, melt flow is affected by surface tension, and the flow direction of the melt pool surface gradually spreads from the center of the spot to the periphery. Therefore, the flow velocity on the melt pool surface is characterized by a small center and a large edge. As shown in Figure 6b, there is an obvious Marangoni convection in the melt pool. Because of the effect of surface tension, two circulation structures are formed in front and behind the melt pool, and the circulation behind the melt pool is more significant. At

the same time, the maximum flow velocity appears on the surface of the melt pool and is 0.35 m/s. According to the numerical simulation results of the flow field, when analyzing the influence of melt pool flow velocity on dendrite growth, the flow velocity direction in the simulation is from left to right.

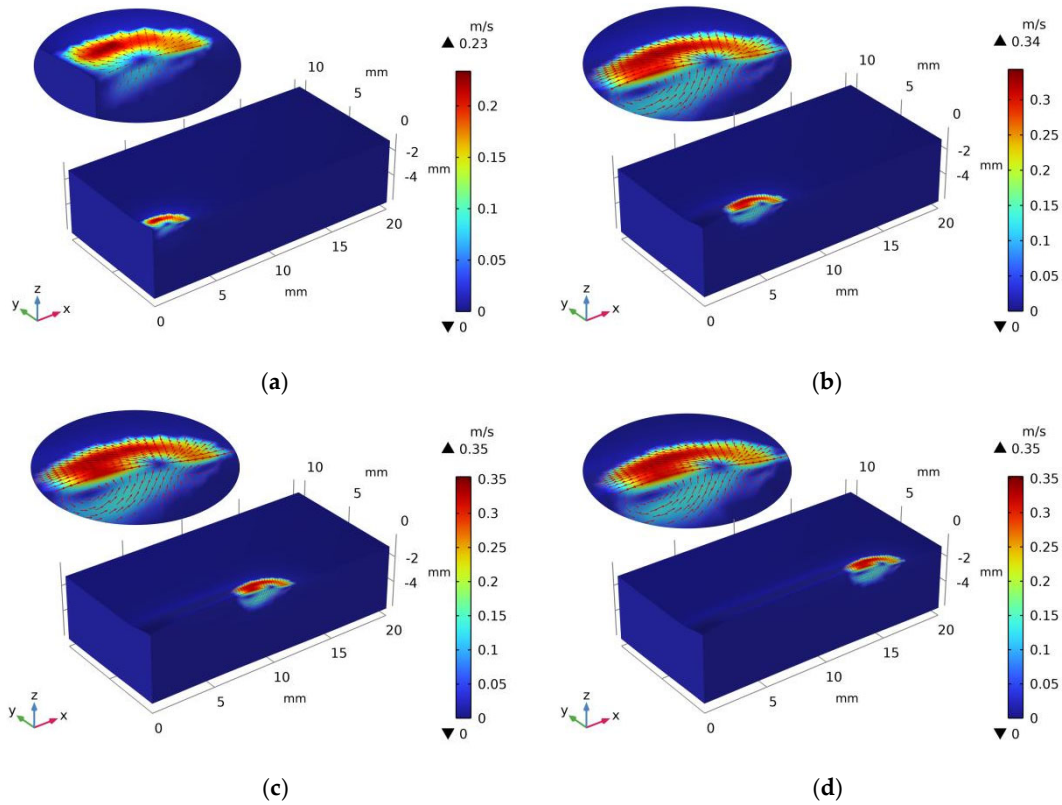


Figure 5. Velocity distribution cloud image at different times. (a) Velocity distribution at 0.3 s; (b) velocity distribution at 1.0 s; (c) velocity distribution at 2.0 s; (d) velocity distribution at 3.0 s.

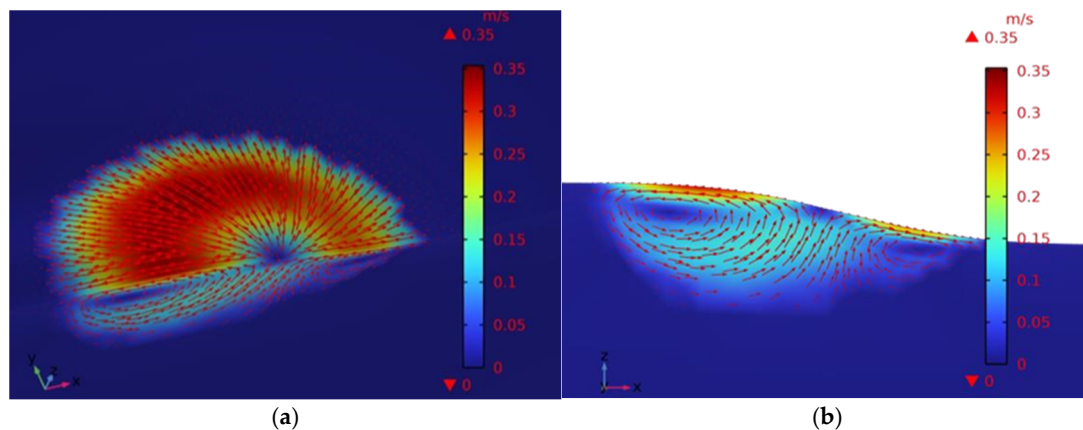


Figure 6. Distribution cloud image for the flow field in the melt pool at 2.0 s. (a) Temperature distribution on the surface of the melt pool; (b) temperature distribution inside the melt pool.

This section aims to deeply explore the evolution process of the microstructure in the laser cladding pool. Based on the macroscopic 3D numerical results, the downstream field simulation results at the time of 2.0 s are selected in this section. According to the simulation results of the temperature field, the solidification zone is mainly located in the back part of the melt pool. Therefore, the flow field data on the black scan line were adopted in this simulation, which was set as the input boundary condition of the static flow rate.

The direction of flow velocity flowing from the left side to the right side of the melt pool was selected, as shown in Figure 7. According to the flow field results at the time of 2.0 s, the static flow velocity can be obtained, as shown in Figure 8a. Dimensionless the actual flow velocity, and the result is shown in Figure 8b. Because microstructure solidification under actual flow is a complex process, the movement of dendrites under the action of the flow field (such as translation, etc.) was ignored in this section's numerical simulation, including the breakage of dendrites caused by flow shear force and the influence of gravity.

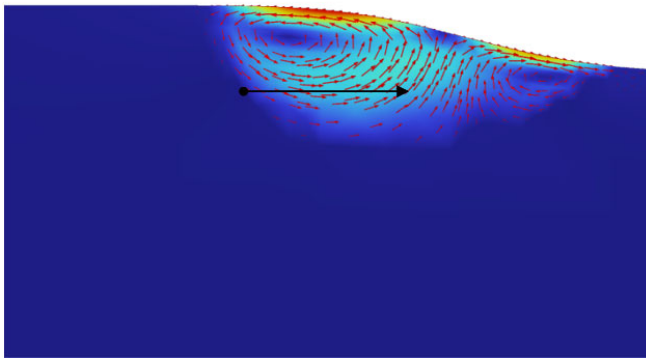


Figure 7. The position of the flow field collection line at 2.0 s.

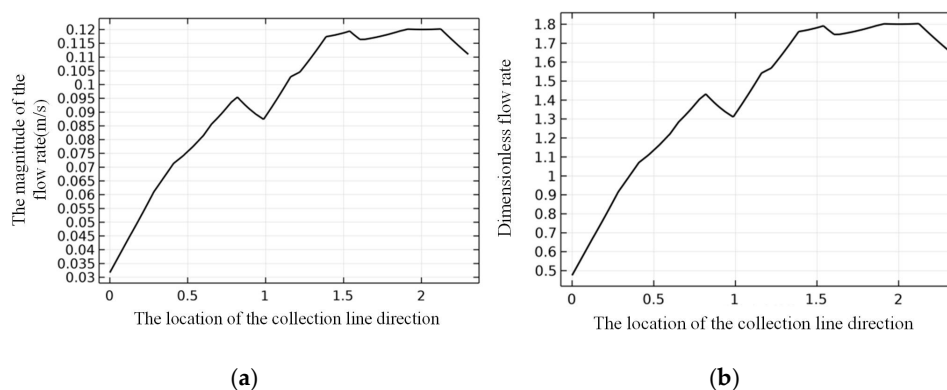


Figure 8. Static flow velocity and dimensionless flow velocity. (a) Velocity of static flow field; (b) dimensionless velocity of static flow field.

3.3. Flow Field Boundary Extraction Under Acoustic Flow

In this paper, acoustic flow action is introduced into the source term of the flow equation in the form of volume force. The flow field distribution cloud image under the action of ultrasonic acoustic flow was calculated, as shown in Figure 9. Figure 9 shows that under the action of acoustic streaming generated by ultrasonic vibration, the fluidity of the cladding process increases and the flow velocity on the surface and inside the melt pool increases. At 2.0 s, the circulation in the latter part of the melt pool significantly increases, which can promote the flow of solute elements during the solidification process, as shown in Figure 9b.

The direction of flow from the left side of the melt pool to the right side of the flow was selected, as shown in Figure 10. According to the flow field results at the time of 2.0 s, the static flow velocity under the action of acoustic flow is obtained, as shown in Figure 11a. Dimensionless the actual flow velocity, and the result is shown in Figure 11b. The acoustic streaming effect increases the flow velocity inside the melt pool, improves the flow state inside the melt pool, and promotes the flow of solute elements inside the melt pool to be more uniform.

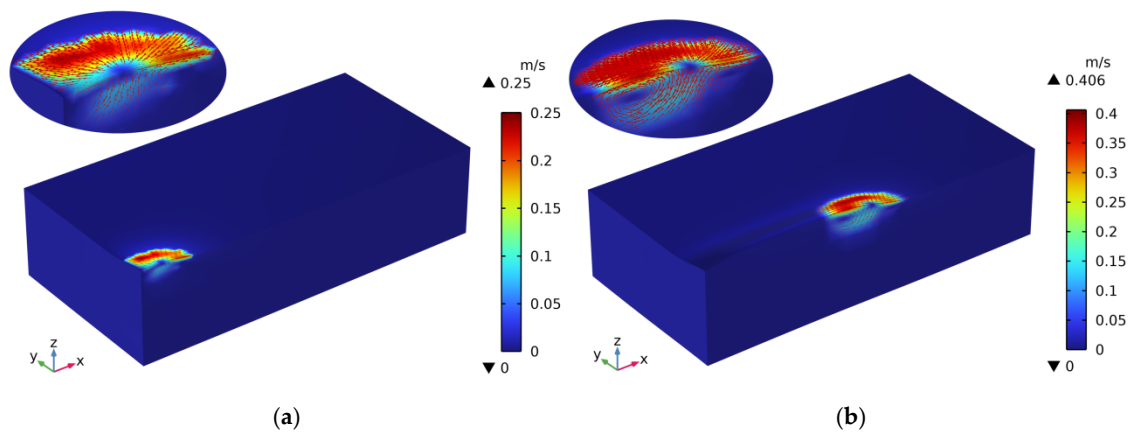


Figure 9. Flow field distribution cloud image under action of ultrasonic flow. (a) Velocity distribution at 0.3 s; (b) velocity distribution at 2.0 s.

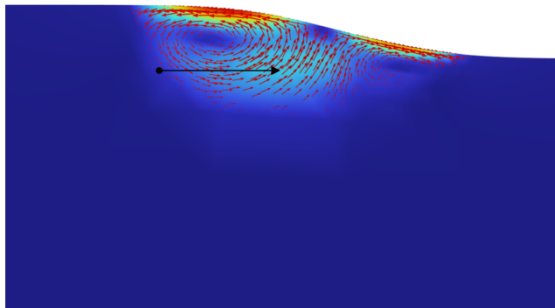


Figure 10. The acoustic flow field acquisition line position at 2.0 s.

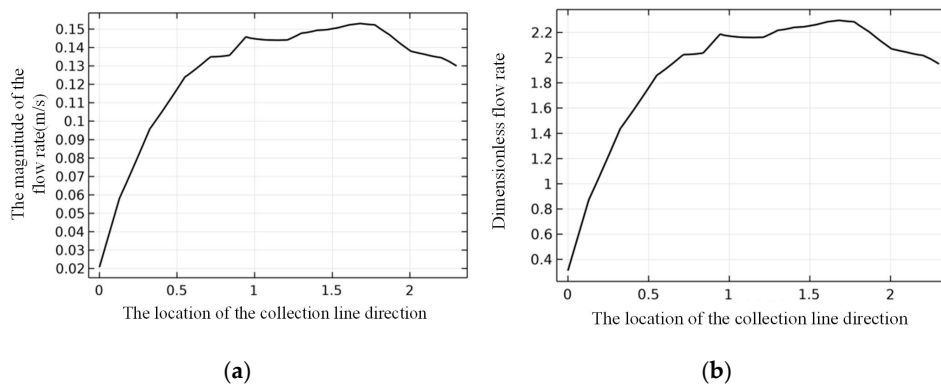


Figure 11. Static flow velocity and dimensionless flow velocity under action of acoustic streaming. (a) Velocity of sound flow field; (b) dimensionless velocity of acoustic flow field.

4. Results and Discussion

4.1. Dendrite Growth Behavior of Laser Cladding Without Flow Field

The finite element difference method is used to solve and analyze the numerical model. The normalized scale of the feature length is $l_0 = 25 \mu\text{m}$, and the mesh is divided by a free triangle mesh. The maximum cell size is $l_{\text{mesh}}/l_0 = 0.1$. The total number of units in the longitudinal section is 52,918, and the total number of units in the transverse section is 43,906. The phase field model parameters used in this paper are $\tau_c = 0.0003$, $\gamma = 10$, $\delta = 0.1$, $\alpha_T = 5.48 \times 10^{-6}$, $\mu_k = 0.05$, $k_f = 0.88$, $D_L = 4.8 \times 10^{-9} \text{ m}^2/\text{s}$, $D_S = 0.2 \times 10^{-12} \text{ m}^2/\text{s}$, $\tau = l_0^2/\alpha_T$, $\alpha_T = l_0^2/\tau = kT/(\rho C_p)$, and $\tilde{\epsilon}_m = 0.01$.

Figure 12 describes the microstructure evolution for the paste zone in the longitudinal section of the melt pool during laser cladding. According to the temperature distribution

boundary, crystal nuclei are set at boundaries 3, 4, and 5 on the longitudinal section. The temperature distribution is higher at boundaries 6 and 7, and the solidification process will not occur, as shown in Figure 12a. As shown in Figure 12b, the evolution process of the interface morphology at the bottom of the paste region is from plane to cellular. Due to the rapid heat dissipation to the outside of the joint at the bottom, the initial growth of the crystal nucleus appears as a plane crystal. With the solidification process, the direction of the temperature gradient in the melt pool is consistent with the preferred growth direction of the crystal. The initial plane interface gradually becomes uneven, thus transforming into cell growth. As shown in Figure 12c, dendrite growth accelerates at a faster rate due to the change in the crystal growth rate after plane interface instability compared to dendrite growth at 10 to 1000 Δt times. At the same time, there is obvious competitive growth among dendrites, and the winning crystal tip is obvious and the radius is larger; it continues to grow along the direction of the temperature gradient, and its shape is transformed into a columnar crystal. As shown in Figure 12d, at the time of 3500 Δt , the dendrites have fully grown, the growth rate of dendrites decreases, and the dendrite trunk begins to form secondary dendrite arms and tertiary dendrite arms. During the process of fierce competition, the dendrites that failed to grow formed elongated columnar crystals and elongated cellular crystals. It can be clearly seen at the left boundary that some dendrites that fail to grow fuse in the competition process to form larger cellular crystals.

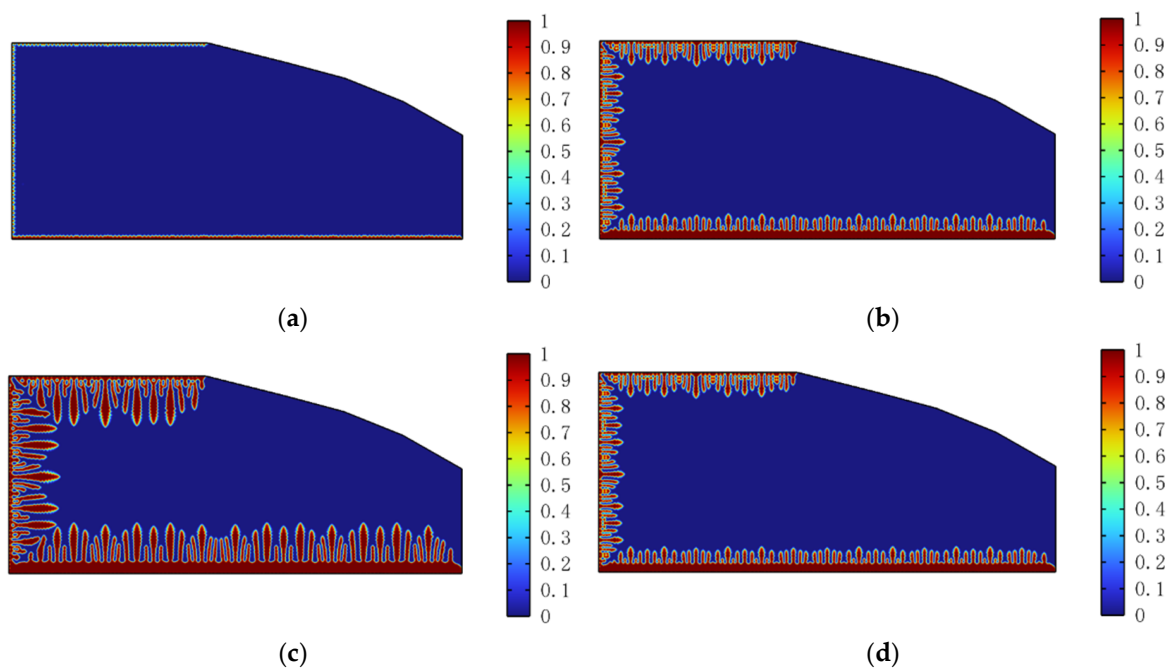


Figure 12. Dendrite growth process on laser cladding longitudinal section. (a) Dendrite morphology at 10 Δt ; (b) dendrite morphology at 1000 Δt ; (c) dendrite morphology at 2000 Δt ; (d) dendrite morphology at 3500 Δt .

The solute field morphology on the longitudinal section of the laser cladding pool is shown in Figure 13. As shown in Figure 13a, at 1000 Δt , the dendrites can be observed to have just begun to grow. At this time, the solute diffusion phenomenon at the dendrite growth boundary just appeared, but the change in the overall solute distribution was not obvious. With the solidification process, an obvious solute diffusion layer begins to form near the solid–liquid interface of the dendrites. Figure 13b shows that the solute field distribution on the longitudinal section of the melt pool is highly consistent with the dendrite morphology simulated by the phase field method. This indicates that the dynamic variation in the solute field is closely related to the morphological development of dendrites during dendrite growth.

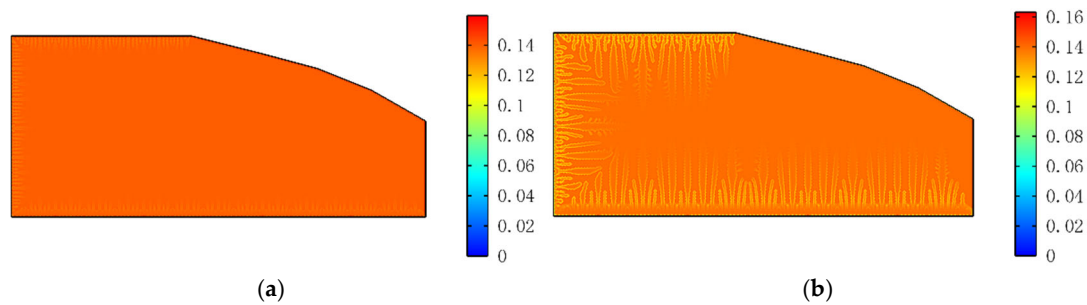


Figure 13. Solute field morphology on laser cladding longitudinal section. (a) Solute field morphology at $1000 \Delta t$; (b) solute field morphology at $3500 \Delta t$.

4.2. Growth Behavior of Convective Dendrites Under Silent Flow

Figure 14a shows the effect of flow velocity in the melt pool on dendrite growth at $2000 \Delta t$. The effect of flow on dendrite growth is not significant because of the low flow velocity in the melt pool. At the left boundary, dendrites grow in the same direction as the velocity (i.e., parallel to the flow), resulting in a slight shortening of the primary dendrite arm length of these dendrites, but the orientation remains the same. In contrast, the dendrite growth direction at the top and bottom of the melt pool is perpendicular to the velocity direction (i.e., shear flow), causing some of the primary dendrite arms to tilt slightly towards the onstream direction. Some of the dendrite arms have formed small protrusions on the onstream side.

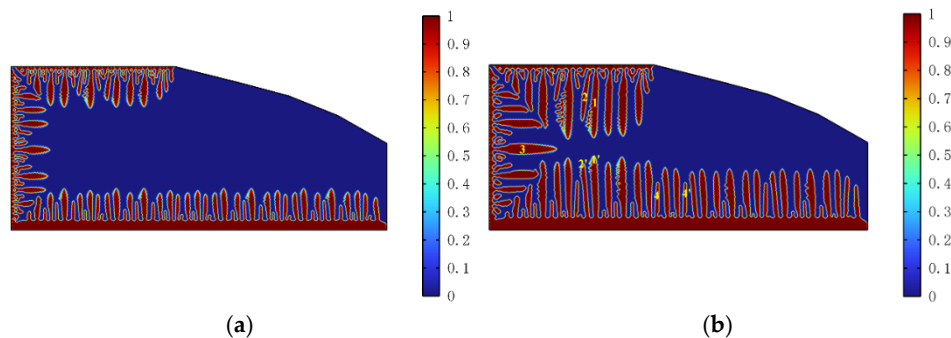


Figure 14. Dendrite morphology under static flow field. (a) Dendrite morphology at $2000 \Delta t$; (b) dendrite morphology at $3500 \Delta t$.

As shown in Figure 14b, the top and bottom dendrites are about to come in contact at $3500 \Delta t$; the dendrites are considered to be fully grown. At the left boundary, the dendrites at position 3 are not disturbed by the growth of other dendrites in the vertical direction, making it an ideal reference for analyzing the change in the growth rate of the last dendrite arm in the parallel downstream direction. Under the condition with no flow, the distance from the dendrite tip at position 3 to the left boundary is about $113.75 \mu\text{m}$. Under the condition of parallel concurrent flow, the distance from the dendrite tip at position 3 to the left boundary is about $103.15 \mu\text{m}$. Therefore, it can be seen that the parallel flow trend in the process of inhibiting dendrite growth is mainly manifested in inhibiting the emergence of secondary dendrite arms and the growth rate of primary dendrite arms. This is in agreement with the conclusions of most researchers.

Under the action of the flow field, because the flow direction of shear flow flows from left to right, the oncoming side is washed by the flow and the latent heat released by solidification can quickly dissipate. At the same time, part of the heat is carried from the oncoming side to the downstream side, resulting in an increase in the temperature of the downstream side, which is not conducive to diffusion. The solid–liquid boundary advances faster towards the oncoming side, and the growth rate of secondary dendrite arms on

the oncoming side accelerates and the number of secondary dendrite arms increases. On the contrary, the dendrite growth on the downstream side is inhibited and the dendrite morphology is “almost smooth”. The simulation results show that at both the top and bottom boundaries, dendrites that originally grew perpendicular to the boundary are now tilted in the direction of the oncoming flow. Specifically, the dendrite tilt at the boundary can be divided into three different cases. The first case shows the morphology of dendrites 1 and 1', and this branching crystal is not disturbed by neighboring dendrites during the growth process. Therefore, under the influence of shear flow, these dendrites tilt towards the oncoming flow, but the tilt angle is relatively small. The second case shows the morphology of dendrite 2 and dendrite 2'. During the growth of this branch crystal, due to the interference and limitation of the right dendrite, the tilt angle of this branch crystal which originally tilted to the left increases under the action of shear flow, and the tilt towards the oncoming flow is more significant. The third case shows the morphology of dendrite 4 and dendrite 4'. Due to the interference and limitation of the left dendrite, the branch crystal that originally tilted to the right is still tilted to the right under the action of shear flow, but the tilt angle decreases.

Figure 15a shows the solute field distribution morphology at $3500 \Delta t$ under the condition of pure diffusion. It can be seen that there is a uniform solute film at the interface of primary dendrite arms and secondary dendrite arms, and the distribution of solute elements has a good symmetry along the dendrite center. After the static flow field is introduced, the solute elements in the solidification process can be washed by the flow, and the distribution of the solute between the primary dendrite arms will spread along the flow direction. At the left boundary, the solute layer film thickens, and the solute concentration decreases at the dendrite tip parallel to the flow. At the top and bottom boundaries, the concentration of solute elements on the dendrite side increases, the solute gradient on the dendrite side increases, and the solute film becomes thinner. This promotes the advancement of the solid–liquid interface and the formation of secondary dendrite arms. However, the concentration of solute elements decreases, the solute layer films significantly increase, and the dendrite growth is inhibited, as shown in Figure 15b.

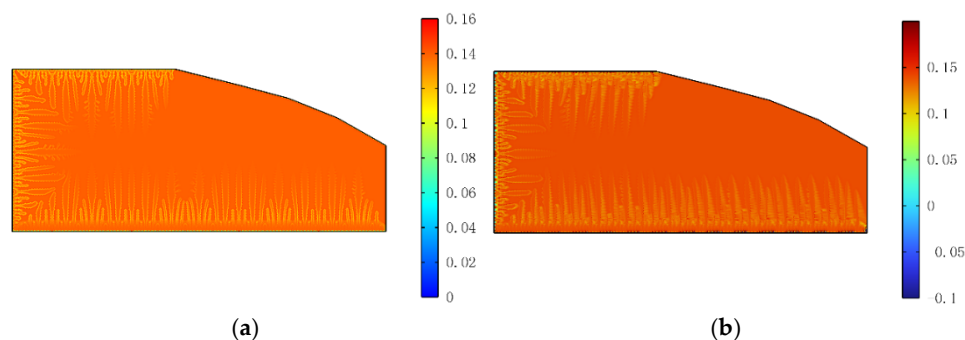


Figure 15. Solute distribution with and without flow field. (a) Morphology of solute field without flow field; (b) solute field morphology in static flow field.

4.3. Growth Behavior of Convective Dendrites Under Acoustic Flow

Figure 16a shows the dendrite morphology under the action of acoustic streaming at the time $2000 \Delta t$. The dendrite growth at the left boundary is basically the same as that at static flow velocity. Due to the effect of acoustic streaming, the flow velocity in the melt pool is accelerated and more stable. The number of secondary dendrite arms on the top and bottom side of the oncoming flow is increased, and the secondary dendrite arms are more developed. Figure 16b shows that the distance from the dendrite tip to the left boundary at position 3 in the static acoustic flow field is reduced to $98.25 \mu\text{m}$, indicating that the inhibition effect of flow on dendrite growth velocity is enhanced with the increase in parallel flow velocity.

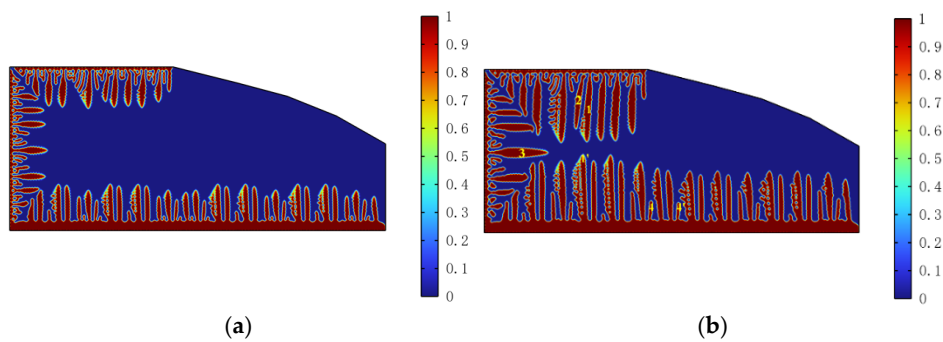


Figure 16. Dendrite morphology under static acoustic streaming field. (a) Dendrite morphology at $2000 \Delta t$; (b) dendrite morphology at $3500 \Delta t$.

The acoustic streaming effect of ultrasonic vibration enhances the fluidity and makes the flow more uniform during the solidification process. It leads to an increase in the temperature gradient and solute gradient on the dendrite onstream side, accelerates the advancing velocity of the solid–liquid interface on the onstream side, and promotes the formation and growth of secondary dendrite arms. Therefore, on the top and bottom dendrite onstream sides, secondary dendrite arm growth is observed to be more significant. The dendrite morphology of the downstream side is “smooth”. In the process of dendrite growth under the static acoustic flow field, three different states of dendrite tilt at the top and bottom boundaries are also observed. It can be seen that under the static acoustic streaming field, the number of dendrites with inclined morphology 1 and 1' significantly increases, while the number of dendrites with inclined morphology 2 significantly decreases. This is because the inclined angle of dendrite 1 increases and the growth of secondary dendrite arms on the oncoming side is more developed, which limits the growth of tilted dendrites on the left side. The dendrites with reduced shape 2 failed to grow. In addition, the number of dendrites with inclined morphologies 4 and 4' is also reduced because the growth of these branches is affected by the restriction of the right dendrites and the inhibition of parallel flow. As shown in Figure 17, the dendrite tilt angle under the flow field is 2.27° and the dendrite tilt angle under the acoustic streaming field is 3.05° .

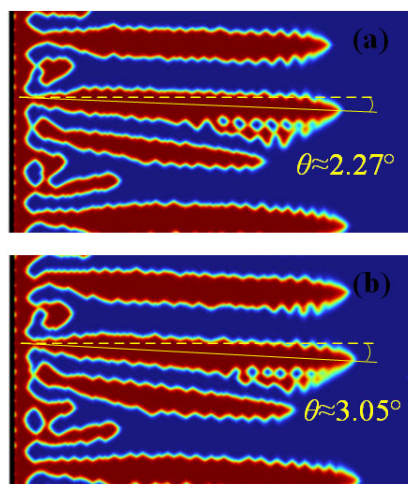


Figure 17. Dendrite tilt angle under the action of flow field. (a) Dendrite tilt angle under static flow field; (b) dendrite tilt angle under static acoustic flow field.

To verify the validity of the numerical simulation results, laser cladding experiments were carried out. The experiment selected a TruDisk4002 laser produced by TRUMPF, Ditzingen, Germany. The laser power was 1600 W, the minimum fiber diameter was 0.2 mm, and the laser wavelength was 1030 nm. The substrate material and powder of cladding

were 45 steel and 316L, respectively. The specimen was cut lengthwise along the vertical scanning direction and the section was polished and corroded with a 4% nitrate alcohol solution. The metallographic experiment was carried out with an optical microscope to observe the microstructure of the coating layer. Figure 18 shows that the secondary dendrite arms of labeled columnar crystals 1, 2, and 3 grow significantly on the oncoming side, while the wall of the main shaft arm on the downstream side presents a relatively “smooth” feature. At the same time, the dendrites are inclined in the direction of the oncoming flow. The comparison shows that the numerical simulation results are consistent with the experimental results, which verifies the validity of the model.

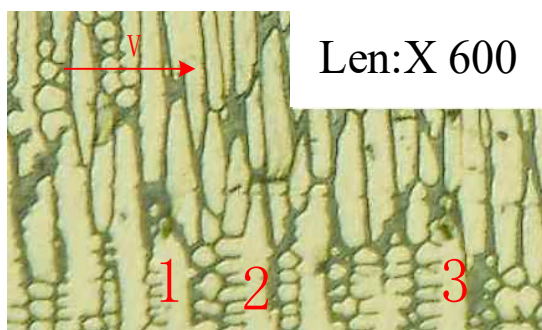


Figure 18. Cladding layer microstructure.

The cladding layer produced by the laser cladding of 316L powder is mainly composed of an austenite phase. The experimental results of Gao Jingxiang show that the 316L laser cladding assisted by ultrasonic vibration does not change the phase structure but significantly improves the performance of the cladding layer. Therefore, it can be concluded that ultrasonic vibration has the effect of strengthening the austenite phase. Considering that Fe and Ni are the main components of the austenite phase, the Ni element expands the austenite and stabilizes the austenite structure. The strength of the austenitic phase is determined by the dissolution and precipitation of Ni during the solidification of the Fe-Ni alloy. Figure 19 shows the precipitation and distribution of Ni as a solute when dendrites grow in the melt pool under the flow field and sound flow field. As shown in Figure 19a, due to the small and uneven fluidity of the static flow field, the area near the dendrite root on the oncoming side exhibits solute element enrichment and segregation. In Figure 19b, under the action of acoustic streaming, the fluidity of the supercooled melt is enhanced, the flow is more uniform, and the solute segregation between the dendrites is significantly reduced. The decrease in Ni segregation indicates the increase in its solubility in an Fe base, which enhances the strength of the austenite phase and provides the possibility for obtaining a cladding coating with better performance.

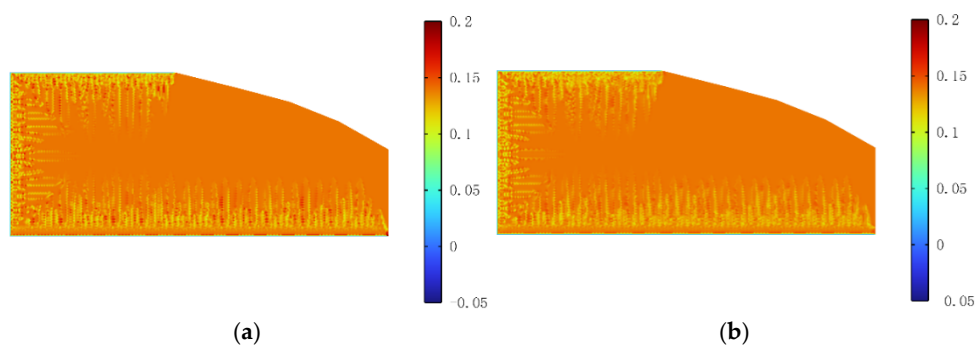


Figure 19. Solute segregation and enrichment under static and acoustic flow fields. (a) Solute precipitation in flow field; (b) solute precipitation in acoustic flow field.

5. Conclusions

- (1) The numerical simulation results of coupling a static flow field and a sound flow field show that melt flow changes the heat and mass transfer behavior at the solidification interface and also changes the growth morphology of dendrites. The dendrite growth is inhibited under parallel concurrent flow, and the dendrite at the original vertical interface under shear flow inclines to the oncoming side. The dendrite tilt in the flow field is as follows: influenced by convection, the dendrite tilts to the oncoming side, and the tilt angle is small. Due to the influence of convection and the orientation of oncoming dendrites (the dendrites that are inclined to the oncoming side due to competitive growth), the dendrites are inclined to the oncoming side, and the inclination angle is large. Influenced by convection and consequent dendrite orientation (the dendrites that grow inclined to the consequent side due to competitive growth), the dendrites grow inclined to the consequent side, and the inclination angle is large.
- (2) Acoustic flow increases the flow velocity of the melt pool, increases the dendrite tilt angle to the onstream side, and promotes the growth of secondary dendrite arms on the onstream side. At the same time, the melt flow is more uniform, the solute distribution of dendrite growth is improved, and the enrichment and segregation of secondary elements between dendrites are reduced.

Author Contributions: X.H. and H.Z. acquired the grant and revised the paper; C.L. and X.W. performed modeling and wrote the paper; S.L. and J.L. extracted and analyzed the data; Q.S. and F.K. checked the grammar. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Applied Basic Research Program of Liaoning Province (2023JH2/101300226), Liaoning Supported by the Fundamental Research Funds for the Liaoning Universities (LJ222410146021), Liaoning Province Metallurgical equipment and process control key laboratory open project (2024KFKT-01), Project for Graduate Education Reform and Technological Innovation and Entrepreneurship of the University of Science and Technology Liaoning (2023YJSCX02).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that supports the findings of this study are available within the article.

Conflicts of Interest: The authors declare no potential conflicts of interest in the research, authorship, and/or publication of this article.

References

1. Valente, C.; Morgado, T.; Sharma, N. LASER cladding—A post processing technique for coating, repair and re-manufacturing. In *Materials Forming, Machining and Post Processing*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 231–249. [CrossRef]
2. Zhu, L.; Xue, P.; Lan, Q.; Meng, G.; Ren, Y.; Yang, Z.; Xu, P.; Liu, Z. Recent research and development status of laser cladding: A review. *Opt. Laser Technol.* **2021**, *138*, 106915. [CrossRef]
3. Siddiqui, A.A.; Dubey, A.K. Recent trends in laser cladding and surface alloying. *Opt. Laser Technol.* **2021**, *134*, 106619. [CrossRef]
4. Qi, K.; Yang, Y.; Sun, R.; Hu, G.; Lu, X.; Li, J.; Liang, W.; Jin, K.; Xiong, L. Effect of magnetic field on crack control of Co-based alloy laser cladding. *Opt. Laser Technol.* **2021**, *141*, 107129. [CrossRef]
5. Campbell, J. Effects of vibration during solidification. *Int. Met. Rev.* **1981**, *26*, 71–108. [CrossRef]
6. Ji, F.; Qin, X.; Hu, Z.; Xiong, X.; Ni, M.; Wu, M. Influence of ultrasonic vibration on molten pool behavior and deposition layer forming morphology for wire and arc additive manufacturing. *Int. Commun. Heat Mass Transf.* **2022**, *130*, 105789. [CrossRef]
7. Wei, X.; Li, X.; Zhang, L.; Lv, Q. Effect of in-situ ultrasonic impact treatment on flow and solidification behavior of laser metal deposition: By finite element simulation. *Int. J. Heat Mass Transf.* **2022**, *192*, 122914. [CrossRef]
8. Wang, Z.; Jiang, F.; Guo, C.; Xing, X.; Yang, Z.; Li, H.; Liu, C.; Xu, D.; Jiang, G.; Konovalov, S. Effects of ultrasonic vibration on microstructure and mechanical properties of 1Cr12Ni3MoVN alloy fabricated by directed energy deposition. *Ultrasonics* **2023**, *132*, 106989. [CrossRef]
9. Zhuang, D.-D.; Du, B.; Zhang, S.-H.; Tao, W.-W.; Wang, Q.; Shen, H.-B. Effect and action mechanism of ultrasonic assistance on microstructure and mechanical performance of laser cladding 316L stainless steel coating. *Surf. Coat. Technol.* **2022**, *433*, 128122. [CrossRef]

10. Song, H.; Jiang, F.; Guo, C.; Sun, Q.; Li, H.; Yang, Z.; Li, L.; Diao, M.; Zhang, Z. Effect of ultrasonic vibration on the microstructure and microhardness of laser cladding Fe-based crystalline/amorphous composite coatings. *Mater. Lett.* **2023**, *335*, 133780. [CrossRef]
11. Ma, G.; Yan, S.; Wu, D.; Miao, Q.; Liu, M.; Niu, F. Microstructure evolution and mechanical properties of ultrasonic assisted laser clad yttria stabilized zirconia coating. *Ceram. Int.* **2017**, *43*, 9622–9629. [CrossRef]
12. Geng, R.W.; Du, J.; Wei, Z.Y.; Zhao, G.X. An adaptive-domain-growth method for phase field simulation of dendrite growth in arc preheated fused-coating additive manufacturing. *J. Phys. Conf. Ser.* **2018**, *1063*, 012077. [CrossRef]
13. Wu, L.; Zhang, J. Phase field simulation of dendritic solidification of Ti-6Al-4V during additive manufacturing process. *Jom* **2018**, *70*, 2392–2399. [CrossRef]
14. Zhang, Y.; Jung, Y.-G.; Zhang, J. Phase field modeling of microstructure evolution in selective laser melting-manufactured titanium alloy. In *Multiscale Modeling of Additively Manufactured Metals*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 141–154. [CrossRef]
15. Sun, D.; Liu, J.; Li, Q. Phase-field method simulation of microstructure evolution at the bottom of melt pool in coaxial laser cladding. *Zhongguo Jiguang (Chin. J. Lasers)* **2013**, *40*, 0403005-6. [CrossRef]
16. Li, A.; Wang, Z.; Sun, Z. Effect of Ultrasonic Vibration on Microstructure and Fluidity of Aluminum Alloy. *Materials* **2023**, *16*, 4110. [CrossRef] [PubMed]
17. Lian, G.; Yue, K.; Zeng, J.; Feng, M.; Lan, R.; Kong, L. Microstructures and Properties of NbC-Reinforced Ni-Based Coatings Synthesized In Situ by Ultrasonic Vibration-Assisted Laser Cladding. *Materials* **2023**, *16*, 1704. [CrossRef] [PubMed]
18. Lv, J.; Zhou, J.; Zhang, T.; Meng, X.; Li, P.; Huang, S. Microstructure and Wear Properties of IN718/WC Composite Coating Fabricated by Ultrasonic Vibration-Assisted Laser Cladding. *Coatings* **2022**, *12*, 412. [CrossRef]
19. Han, X.; Li, C.; Chen, X.; Jia, S. Numerical simulation and experimental study on the composite process of submerged arc cladding and laser cladding. *Surf. Coat. Technol.* **2022**, *439*, 128432. [CrossRef]
20. Lugscheider, E.; Bolender, H.; Krappitz, H. Laser cladding of paste bound hardfacing alloys. *Surf. Eng.* **1991**, *7*, 341–344. [CrossRef]
21. Fellowes, F.; Steen, W.; Coley, K. Ceramic coatings for high temperature corrosion resistance by laser processing. *Key Eng. Mater.* **1990**, *46*, 435–446. [CrossRef]
22. Zhou, J. *Stress Evolution and Control in Laser Deposition Manufacturing*; Shenyang University of Aeronautics and Astronautics: Shenyang, China, 2016; pp. 15–20.
23. Kumar, S.; Wu, C.; Padhy, G.; Ding, W. Application of ultrasonic vibrations in welding and metal processing: A status review. *J. Manuf. Process.* **2017**, *26*, 295–322. [CrossRef]
24. Humphrey, V.F. Ultrasound and matter—Physical interactions. *Prog. Biophys. Mol. Biol.* **2007**, *93*, 195–211. [CrossRef] [PubMed]
25. Yao, Y.; Pan, Y.; Liu, S. Power ultrasound and its applications: A state-of-the-art review. *Ultrason. Sonochemistry* **2020**, *62*, 104722. [CrossRef] [PubMed]
26. Khavari, M.; Priyadarshi, A.; Hurrell, A.; Pericleous, K.; Eskin, D.; Tzanakis, I. Characterization of shock waves in power ultrasound. *J. Fluid Mech.* **2021**, *915*, R3. [CrossRef]
27. Wells, P.N.T. Physics of ultrasound. In *Ultrasonic Exosimetry*; CRC Press: Boca Raton, FL, USA, 2020; pp. 9–45.
28. Čáp, I.; Čápková, K.; Smetana, M.; Borik, Š. Mechanical Waves. *Electromagn. Acoust. Waves Bioeng. Appl.* **2021**, *57*. [CrossRef]
29. Li, Y.; Chen, C.; Yi, R. Recent development of ultrasonic brazing. *Int. J. Adv. Manuf. Technol.* **2021**, *114*, 27–62. [CrossRef]
30. Sui, D.; Han, Q. Ultrasound-assisted cast-on method: Obtaining high-quality metallurgical bonds between a bare steel insert and A354 aluminum alloy within a composite casting. *J. Mater. Process. Technol.* **2023**, *311*, 117783. [CrossRef]
31. Sonia, P.; Jain, J.K.; Saxena, K.K. Influence of ultrasonic vibration assistance in manufacturing processes: A Review. *Mater. Manuf. Process.* **2021**, *36*, 1451–1475. [CrossRef]
32. Li, Q.; Jiang, W.; Xu, Y.; Yu, L.; Niu, Y.; Fan, Z. Development of prominent bonding strength in Al/Mg bimetal composites prepared by ultrasonic vibration-assisted compound casting: Effects of ultrasonic powers. *J. Mater. Sci. Technol.* **2024**, *197*, 78–93. [CrossRef]
33. Kardyś, W.; Milewski, A.; Kogut, P.; Kluk, P. Universal ultrasonic generator for welding. *Acta Phys. Pol. A* **2013**, *124*, 456–458. [CrossRef]
34. Faraday, M. On a peculiar class of acoustical figures; and on certain forms assumed by groups of particles upon vibrating elastic surfaces. *Abstr. Pap. Print. Philos. Trans. R. Soc. Lond.* **1837**, *3*, 49–51. [CrossRef]
35. Liu, F. *Numerical Study of Acoustic Flow Effects Based on Weakly Compressible Equations*; Huazhong University of Science and Technology: Wuhan, China, 2017; Available online: https://kns.cnki.net/kcms2/article/abstract?v=k15566fjT2nTsAZ-sqgee1b4BNxqOltVHx21XJoEUw7bNtCOqYzYSWGERnYH1MGfAoo32d2CVyVqb7TdCmWltSUN93VzIXQj1lYU5uVmM_Hzi9kZCJIF38DF6folUvNOKTZCHIcld6KhkMLOxU5seiLSTLBDGvQ0_pZHIW84BOl_hRDi7iviXVxPNsbtKYh492Im8E5NtMg=&uniplatform=NZKPT&language=CHS (accessed on 27 September 2024).
36. Rayleigh, J.W.S.B. *The Theory of Sound*; Macmillan: New York, NY, USA, 1896.
37. Eckart, C. Vortices and streams caused by sound waves. *Phys. Rev.* **1948**, *73*, 68. [CrossRef]
38. Pierce, A.D. Mathematical theory of wave propagation. In *Handbook of Acoustics*; Springer: Berlin/Heidelberg, Germany, 1998; pp. 21–37.

39. Schuster, G. Basic Principles of Wave Propagation. 2011. Available online: <http://csim.kaust.edu.sa/files/Short.Courses/BasicSeismology.pdf> (accessed on 27 September 2024).
40. Muller, P.B.; Barnkob, R.; Jensen, M.J.H.; Bruus, H. A numerical study of microparticle acoustophoresis driven by acoustic radiation forces and streaming-induced drag forces. *Lab Chip* **2012**, *12*, 4617–4627. [CrossRef] [PubMed]
41. Qian, Z. *Nonlinear Acoustics*; Science Press: New York, NY, USA, 2009.
42. Hou, C. *Simulation of NiCu Alloys by Phase Field Method and Study of Related Models*; North Central University: Minneapolis, MN, USA, 2016. Available online: https://kns.cnki.net/kcms2/article/abstract?v=k15566fjT2m4VwbB8a1o4IdKakPlMIzF8joXRahBIhL_5XhhSFPkad11WvqKa_FJezOgySqm4QsXJcE79ykPa_At_Ug7gIaCbQ_eP9U7oaWdVF8dLQp3yUzpGDkroGPvsOBwK_1o5SaUJLGIZwa8dHdRoCedj99BYXvDzw2bW6f3wvG-dzzijx1bv8Rye7RoBnBpraSmSh4=&uniplatform=NZKPT&language=CHS (accessed on 27 September 2024).
43. Boettinger, W.J.; Warren, J.A.; Beckermann, C.; Karma, A. Phase-field simulation of solidification. *Annu. Rev. Mater. Res.* **2002**, *32*, 163–194. [CrossRef]
44. Beckermann, C.; Diepers, H.-J.; Steinbach, I.; Karma, A.; Tong, X. Modeling melt convection in phase-field simulations of solidification. *J. Comput. Phys.* **1999**, *154*, 468–496. [CrossRef]
45. Alexiades, V. *Mathematical Modeling of Melting and Freezing Processes*; Routledge: London, UK, 2018. [CrossRef]
46. Acharya, R.; Sharon, J.A.; Staroselsky, A. Prediction of microstructure in laser powder bed fusion process. *Acta Mater.* **2017**, *124*, 360–371. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

MDPI AG
Grosspeteranlage 5
4052 Basel
Switzerland
Tel.: +41 61 683 77 34

Coatings Editorial Office
E-mail: coatings@mdpi.com
www.mdpi.com/journal/coatings



Disclaimer/Publisher's Note: The title and front matter of this reprint are at the discretion of the Guest Editor. The publisher is not responsible for their content or any associated concerns. The statements, opinions and data contained in all individual articles are solely those of the individual Editor and contributors and not of MDPI. MDPI disclaims responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



Academic Open
Access Publishing

mdpi.com

ISBN 978-3-7258-4304-6