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An Overview on 3D Printing of Ceramics Using Binder Jetting Process †

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Abstract: Binder jetting is a promising 3D printing technology that employs a liquid binder to selectively attach the particles of a pulverised material to form three-dimensional objects. It is also a popular technique for fabricating ceramics, as it permits the creation of intricate geometries and customised shapes that would be hard or impossible to achieve using conventional ceramic manufacturing techniques. This study focuses on the capabilities of some of the most essential ceramic materials, such as alumina, SiC, and calcium phosphate, to construct complicated geometries with a high level of accuracy and precision when using a process called binder jetting. These ceramic components find widespread usage in a broad variety of applications, including those relating to aircraft, biomedical, and industry.

Keywords: binder jetting; 3D printing; ceramics; calcium phosphate; alumina; SiC

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1. Introduction

Additive manufacturing, often known as 3D printing, is a technique for fabricating three-dimensional solid items by adding them together in successive layers. In accordance with the ASTM standard [1] the great majority of additive manufacturing (AM) or 3D printing technologies can be sorted into one of seven groups. Binder jetting (BJ) is one of the latest AM processes. ASTM describes binder jetting as an "additive manufacturing processes where powder materials are joined by selectively depositing a liquid bonding agent". In the late 1980s, the Massachusetts Institute of Technology (MIT) was the first institution to develop binder jetting [2,3]. Other major 3D printing industries then went on to commercialize the technology [4].

BJ is made up of a succession of distinct steps, which are as follows: In the first step of the process, which is known as "Design Preparation", a 3D digital model of the object that is going to be printed is created. The computer-aided design (CAD) programme that is commonly used to produce this model is one among several that are currently available. The second stage is called "powder bed preparation", and powdered metal, ceramic, or polymer is evenly distributed across a build platform to create a smooth surface for 3D printing [5]. Each layer's thickness can be adjusted to obtain the appropriate resolution and object characteristics. In the third step, print heads or nozzles are used to deposit a liquid binder in precise patterns onto the powdered material. The binder adheres the particles together to form the 3D model's desired shape. Subsequently, an additional layer of powdered material is applied atop the previously printed layer, thereby facilitating the continuation of the aforementioned procedure. To secure the fresh layer to the old one, the binder is applied strategically. This deposition process continues until the final object is complete. When printing overhanging or otherwise complex geometries, it may be necessary to incorporate additional supports or structures to ensure their structural integrity. After the printing process is complete, infiltration may be performed on the green (unfired) portion [6]. The printed object is submerged in a liquid, which penetrates the porous structure and gives the finished part additional strength or the desired qualities. After printing and infiltrating, the object undergoes post-processing. This includes eliminating surplus powder, curing the binder, and removing supporting structures. The material and end use determine the post-processing procedures.

For processing ceramic materials, BJ is one of the most promising AM technologies because of its great degree of design freedom, lack of explicitly needed supporting structures, ability to print a wide range of materials, and scalability [5]. Furthermore, binder jetting of ceramics has several advantages over conventional ceramic production methods. When using conventional manufacturing methods, tooling may account for as much as 80% of the total cost of producing complicated ceramic components. BJ is a quick and cost-effective method for manufacturing complex shapes, and it can be used to produce highly precise and accurate parts, as shown in Figure 1. Additionally, BJ may be used to simultaneously print multiple components, which can reduce production time and costs. For instance, every year, millions of people choose to have artificial joints implanted. Ceramics are an excellent option for joint implants because of their high hardness and biocompatibility, excellent wear and corrosion resistance, and low cost compared to other implant materials. However, they are not widely used because of the high cost of fabrication using traditional manufacturing technologies.

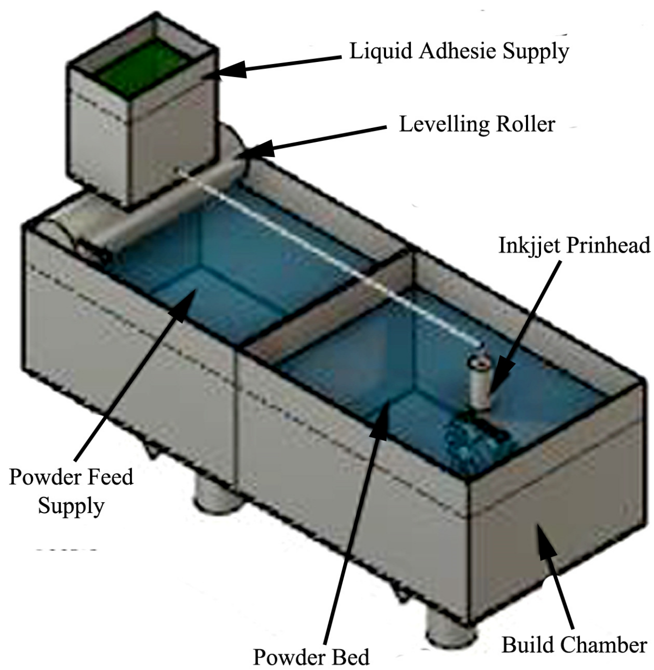

Figure 1. Process flow diagram for 3D printing with binder jetting.

2. Different Ceramics

2.1. Alumina Ceramics

Alumina is a popular ceramic material that has extensive uses in refractory, grinding, dental implants, joint replacements, and other medical equipment because of its high melting point, great biocompatibility, strong thermal and mechanical capabilities, and resistance to corrosion and wear [7]. The impact of uneven particle size of aluminium powder on the qualities of binder jetted parts that may be utilised as electrical components was studied by Joanna Marczyk et al. [8]. Coarse-to-fine powder mixes (73:27 wt.%) and fine-to-coarse powder blends (27:73 wt.%) were studied, as were powders of varying particle sizes. The layers were printed at a thickness of 120 μm, the rollers rotated at 10 mm/s, and 80% binder saturation was maintained throughout the printing process. The final findings, as shown in Figure 2, show that 3D parts successfully manufactured utilising BJ technology are suitable for usage as electronic components like transistor parts and heat sinks.

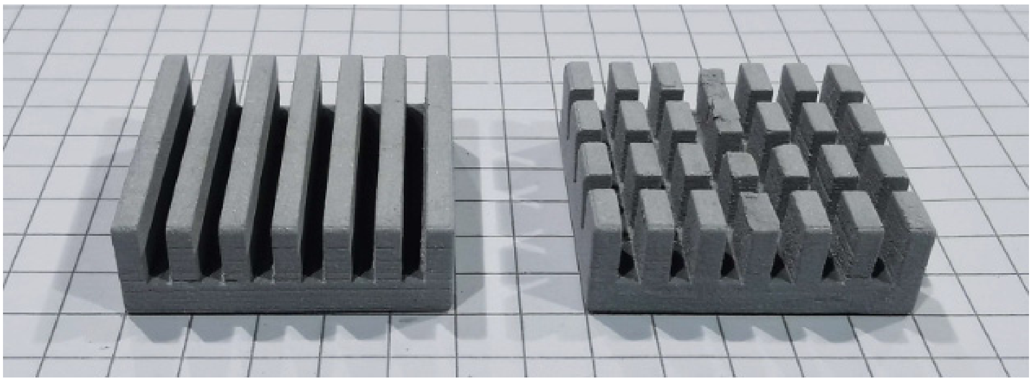

Figure 2. Utilizing a 50 μm:20 μm aluminium powder combination, heat sinks manufactured with binder jetting technology [8].

In this study, Marco Mariani et al. [9] examined binder jetting 3D printing of alumina (α-Al_2O_3) components. The results demonstrate that excellent powder size distribution has generated highly dense green bodies (61.2%) and the greatest final sintered density (75.4%) using BJ's pressureless traditional sintering technique of alumina. Software simulations, the LS algorithm, and the DEM model predict powder behaviour. Ceramic alumina made via photosensitive binder jetting was studied by Supalak Manotham et al. [10] for its shrinkage, porosity, density, microstructures, mechanical characteristics, and printing patterns. For the entire printing sample, there was an 11% shrinkage, a 39% density decrease, a 1.04 MPa flexural strength, and a 1.78 MPa compressive strength. Powder formulations were created by Solis et al. [11] and made up of stearic acid-coated aluminium (Al) powder and dextrin-coated aluminium oxide (Al_2O_3) powder, applied via binder jetting, and then processed using reaction-bonding aluminium oxide (RBAO) in order to quickly manufacture alumina ceramic powders for the standard binder jetting technique. Understanding the effect of powder quality and processing settings is discussed by Chen et al. [12], who also provide some fundamental guidelines.

2.2. Silicon Carbide Ceramics

Silicon carbide ceramics have been widely used in the nuclear and petrochemical industries, metallurgical machinery, electronic devices, aerospace, and other fields due to their better physicochemical properties, such as high chemical stability and thermal conductivity, high corrosion and wear resistance, low thermal expansion coefficient, and good mechanical properties [13]. Two cycles of binder jet 3D printing with SiC powders produced the greatest density, Young's modulus, flexural strength, and thermal conductivity. This was followed by many cycles of phenolic infiltration and pyrolysis, and a final silicon reactive melt infiltration procedure [14]. A commercial binder jetting technique produced bimodal powder feedstocks using modelling and experiments, as reported by Du et al. [15]. The model accurately predicted bimodal powder tap density. Bimodal powder prints had greater green densities than unimodal ones. Using binder jetting and subsequent densification by phenolic-binder impregnation and liquid Si infiltration, Thomas et al. [16] showed a technique for printing a silicon-carbide ceramic counter-flow heat exchanger (HX) with integrated headers. In addition, as shown in Figure 3, the thick SiC ceramics HX body with channels has been effectively prototyped via binder-jetting printing, demonstrating the possibility of replacing conventional metal HXs with these devices. The investigation of silicon nitride ceramics by Rabinskiy et al. [17] using the BJ procedure and pressureless sintering with the application of the suggested epoxy-based binder demonstrates sufficiently good mechanical characteristics without any extra approaches for the post-processing of the samples.

Figure 3. The prototype binder-jetting printed SiC ceramic heat exchanger's green body [16].

2.3. Calcium Phosphate Ceramics

In recent years, calcium phosphate, or CaP, has become an intriguing material in geology, chemistry, biology, and medicine [18]. This is primarily due to the fact that CaP is widespread in the natural environment and is present in every single living thing. Because of its great biocompatibility and osteoinductive properties, CaP is an important inorganic component. These features make CaP useful in a variety of environments, including bone tissue engineering and medication delivery [19]. To improve the binder jetting 3D printing of HA powder, Zhou et al. [20] explored several water-soluble adhesives. Maltodextrin and polyvinyl alcohol (PVOH) of varying molecular weights (10–30 wt.%) were combined with HA. Fabricated samples using a variety of adhesives and mixing ratios attained or exceeded 85% geometrical precision and showed an exceptional green compressive strength of 5.63 ± 0.27 MPa, which is 500% more than the regular BJ powder. Using a BJ 3D printer, Ryohei et al. [21] studied the mechanical anisotropy and fracture mechanism of calcium sulphate moulds manufactured in a variety of orientations. The findings showed that the amount of dihydrate precipitated during the hemihydrate hydration hardening process was regulated by the ink/volume ratio. By adjusting the resolution and nozzle pattern of the print head, they discovered that they could modify the mechanical anisotropy and fracture mode of the printed mouldings. Dongxu et al. [22] produced porous scaffolds made of tricalcium phosphate (TCP) and MgO/ZnO-TCP using a unique binder-jet 3D printing technology. These scaffolds were then sintered at a temperature of 1250 °C. These results show that the TCP surface area rose from 1.17 ± 0.02 m^2/g to 2.64 ± 0.03 m^2/g in the presence of MgO and ZnO, the bulk den-sity increased from 37.90 ± 0.82% to 50.82 ± 1.10%, and the compressive strength in-creased from 17.93 ± 1.66 MPa to 27.46 ± 2.64 MPa. In addition to this study, existed welding and joining technologies which were applied for various materials are resulted in numerous challenges [23–38], and are solved by systematic studies to obtain the required properties [39–46].

3. Conclusions

The ceramic binder jetting method of 3D printing offers a number of distinct benefits. The binder jetting 3D printing technique is discussed in this study, along with its capacity to produce complex geometries with a high degree of precision and accuracy out of some of the most important ceramic materials such as alumina, SiC, and calcium phosphate. These ceramic components are used in aerospace, biomedical, and industrial applications.

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References

1. *ISO/ASTM 52900:2015*; Additive Manufacturing—General Principles—Terminology. ASTM International: West Conshohocken, PA, USA, 2015.
2. Sachs, E.M.; Haggerty, J.S.; Cima, M.J.; Williams, P.A. Three-Dimensional Printing Techniques. U.S. Patent US5340656A, 1993.
3. Cima, M.J.; Sachs, E.; Fan, T.; Michaels, S.P.; Khanuja, S.; Lauder, A.; Lee, S.-J.J.; Brancazio, D.; Curodeau, A.; Tuerck, H. Three-Dimensional Printing Techniques. U.S. Patent US5387380A, 1993.
4. ExOne. History | ExOne. Available online: https://www.exone.com/About-ExOne/History (accessed on 9 February 2019).
5. Mostafaei, A.; Elliott, A.M.; Barnes, J.E.; Li, F.; Tan, W.; Cramer, C.L.; Nandwana, P.; Chmielus, M. Binder jet 3D printing—Process parameters, materials, properties, modeling, and challenges. *Prog. Mater. Sci.* **2021**, *119*, 100707. [CrossRef]
6. Sarila, V.K.; Moinuddin, S.Q.; Cheepu, M.; Rajendran, H.; Kantumuchu, V.C. Characterization of Microstructural Anisotropy in 17–4 PH Stainless Steel Fabricated by DMLS Additive Manufacturing and Laser Shot Peening. *Trans. Indian Inst. Met.* **2023**, *76*, 403–410. [CrossRef]
7. Mavrič, A.; Valant, M.; Cui, C.; Wang, Z.M. Advanced applications of amorphous alumina: From nano to bulk. *J. Non. Cryst. Solids* **2019**, *521*, 119493. [CrossRef]
8. Marczyk, J.; Hebda, M. Effect of the Particle Size Distribution of Irregular Al Powder on Properties of Parts for Electronics Fabricated by Binder Jetting. *Electron* **2023**, *12*, 2733. [CrossRef]
9. Mariani, M.; Beltrami, R.; Brusa, P.; Galassi, C.; Ardito, R.; Lecis, N. 3D printing of fine alumina powders by binder jetting. *J. Eur. Ceram. Soc.* **2021**, *41*, 5307–5315. [CrossRef]
10. Manotham, S.; Channasanon, S.; Nanthananon, P.; Tanodekaew, S.; Tesavibul, P. Photosensitive binder jetting technique for the fabrication of alumina ceramic. *J. Manuf.* **2021**, *62*, 313–322. [CrossRef]
11. Solis, D.M.; Silva, A.V.; Volpato, N.; Berti, L.F. Reaction-bonding of aluminum oxide processed by binder jetting. *J. Manuf.* **2019**, *41*, 267–272. [CrossRef]
12. Chen, Q.; Juste, E.; Lasgorceix, M.; Petit, F.; Leriche, A. Binder jetting process with ceramic powders: Influence of powder properties and printing parameters. *Open Ceram.* **2022**, *9*, 100218. [CrossRef]
13. Yamada, K.; Mohri, M. Properties and Applications of Silicon Carbide Ceramics. In *Silicon Carbide Ceramics—1*; Sömiya, S., Inomata, Y., Eds.; Springer: Dordrecht, The Netherlands, 1991; pp. 13–44.
14. Cramer, C.L.; Elliott, A.M.; Lara-Curzio, E.; Flores-Betancourt, A.; Lance, M.J.; Han, L.; Blacker, J.; Trofimov, A.A.; Wang, H.; Cakmak, E.; et al. Properties of SiC-Si made via binder jet 3D printing of SiC powder, carbon addition, and silicon melt infiltration. *J. Am. Ceram. Soc.* **2021**, *104*, 5467–5478. [CrossRef]
15. Du, W.; Singh, M.; Singh, D. Binder jetting additive manufacturing of silicon carbide ceramics: Development of bimodal powder feedstocks by modeling and experimental methods. *Ceram. Int.* **2020**, *46*, 19701–19707. [CrossRef]
16. Thomas, J.; Banda, M.; Du, W.; Yu, W.; Chuang, A.; France, D.M.; Singh, D. Development of a silicon carbide ceramic based counter-flow heat exchanger by binder jetting and liquid silicon infiltration for concentrating solar power. *Ceram. Int.* **2022**, *48*, 22975–22984. [CrossRef]
17. Rabinskiy, L.N.; Sitnikov, S.A.; Pogodin, V.A.; Ripetskiy, A.A.; Solyaev, Y.O. Binder Jetting of Si3N4 Ceramics with Different Porosity. *Solid State Phenom.* **2017**, *269*, 37–50. [CrossRef]
18. Canillas, M.; Pena, P.; de Aza, A.H.; Rodríguez, M.A. Calcium phosphates for biomedical applications. *Boletín De La Soc. Española De Cerámica Y Vidr.* **2017**, *56*, 91–112. [CrossRef]

19. Sun, H.; Hu, C.; Zhou, C.; Wu, L.; Sun, J.; Zhou, X.; Xing, F.; Long, C.; Kong, Q.; Liang, J.; et al. 3D printing of calcium phosphate scaffolds with controlled release of antibacterial functions for jaw bone repair. *Mater. Des.* **2020**, *189*, 08540. [CrossRef]
20. Zhou, Z.; Lennon, A.; Buchanan, F.; McCarthy, H.O.; Dunne, N. Binder jetting additive manufacturing of hydroxyapatite powders: Effects of adhesives on geometrical accuracy and green compressive strength. *Addit. Manuf.* **2020**, *36*, 101645. [CrossRef]
21. Hamano, R.; Nakagawa, Y.; Irawan, V.; Ikoma, T. Mechanical anisotropy and fracture mode of binder jetting 3D printed calcium sulfate moldings. *Appl. Mater. Today* **2021**, *25*, 101160. [CrossRef]
22. Ke, D.; Bose, S. Effects of pore distribution and chemistry on physical, mechanical, and biological properties of tricalcium phosphate scaffolds by binder-jet 3D printing. *Addit. Manuf.* **2018**, *22*, 111–117. [CrossRef]
23. Muralimohan, C.H.; Haribabu, S.; Hariprasada Reddy, Y.; Muthupandi, V.; Sivaprasad, K. Evaluation of microstructures and mechanical properties of dissimilar materials by friction welding. *Procedia Mater. Sci.* **2014**, *5*, 1107–1113. [CrossRef]
24. Bandi, A.; Cheepu, M.; Bakshi, S.R. Unveiling heat-affected zone softening in dissimilar AZ31B and WE43 alloy welds. *Mater. Sci. Technol.* **2024**, 02670836231212289. [CrossRef]
25. Sonar, T.; Ivanov, M.; Sambath, S.; Rajendran, C.; Ramachandran, N.; Kumar, P.S.; Cheepu, M.; Xu, J. Effect of gas metal arc and cold metal transfer arc welding processes on microstructure and mechanical properties of AA8011-H18 alloy joints. *Mater. Test.* **2023**, *66*, 129–136. [CrossRef]
26. Cheepu, M.; Baek, H.J.; Kim, Y.S.; Cho, S.M. Melting characteristics of C-type filler metal in GTAW. *Weld. J.* **2023**, *102*, 201–216. [CrossRef]
27. Kumar, G.P.; Balasubramanian, K.R.; Cheepu, M.; Kottala, R.K. Characterization of corrosion behavior of inconel 617 welded joints using cmt-gmaw multi-control welding. *Surf. Rev. Lett.* **2023**, 2450023. [CrossRef]
28. Chigilipalli, B.K.; Karri, T.; Chetti, S.N.; Bhiogade, G.; Kottala, R.K.; Cheepu, M. A Review on Recent Trends and Applications of IoT in Additive Manufacturing. *Appl. Syst. Innov.* **2023**, *6*, 50. [CrossRef]
29. Kocharla, R.P.B.; Kolli, M.; Cheepu, M. Real-Time Detection of Faults in Rotating Blades Using Frequency Response Function Analysis. *Appl. Mech.* **2023**, *4*, 356–370. [CrossRef]
30. Pramod Kumar, G.; Balasubramanian, K.R.; Phani Prabhakar, K.V.; Cheepu, M. Investigation of microstructure, mechanical, and corrosion properties of Inconel 617 joints welded by laser–MIG hybrid welding. *Proc. Inst. Mech. Eng. Part L: J. Mater. Des. Appl.* **2023**, 14644207231161992. [CrossRef]
31. Moinuddin, S.Q.; Machireddy, V.V.; Raghavender, V.; Kaniganti, T.B.; Sarila, V.; Ponnappan, S.M.; Shanmugam, R.; Cheepu, M. Analysis on Bonding Interface during Solid State Additive Manufacturing between 18Cr-8Ni and 42CrMo4 High Performance Alloys. *Metals* **2023**, *13*, 488. [CrossRef]
32. Xian, G.; Cheepu, M.; Yu, J.; Cho, S.M.; Yeom, J.-T.; Choi, Y.S.; Kang, N. Enhancing Tensile Properties of Wire-Arc Additively Manufactured Ti-6Al-4 V Deposits Via Cryogenic Vaporised Ar Shielding/Cooling. *Met. Mater. Int.* **2022**, *29*, 501–514. [CrossRef]
33. Lee, J.M.; Cheepu, M.; Chung, H. Experiment-based distortion prediction model for wire-based additive manufactured parts. *J. Mech. Sci. Technol.* **2022**, *36*, 6227–6237. [CrossRef]
34. Xian, G.; Yu, J.; Cheepu, M.; Cho, S.M.; Kang, N. Effect of Welding Speed on Microstructure and Anisotropic Properties of Wire-Arc Additive-Manufactured Ti-6Al-4V alloy. *Trans. Indian Inst. Met.* **2022**, *76*, 483–489. [CrossRef]
35. Cheepu, M.; Venkateswarlu, D.; Rao, P.N.; Muthupandi, V.; Sivaprasad, K.; Che, W.S. Microstructure characterization of superalloy 718 during dissimilar rotary friction welding. In *Materials Science Forum*; Trans Tech Publications Ltd.: Bäch, Switzerland, 2019; Volume 969, pp. 211–217.
36. Anuradha, M.; Das Vemulapalli, C.; Cheepu, M. Effect of filler materials on dissimilar TIG welding of Inconel 718 to high strength steel. *Mater. Today Proc.* **2021**, *52*, 1314–1320.
37. Karpagaraj, A.; Kumar, N.R.; Thiyaneshwaran, N.; Shanmugam, N.S.; Cheepu, M.; Sarala, R. Experimental and numerical studies on gas tungsten arc welding of Ti–6Al–4V tailor-welded blank. *J. Braz. Soc. Mech. Sci. Eng.* **2020**, *42*, 1–11. [CrossRef]
38. Cheepu, M. Machine Learning Approach for the Prediction of Defect Characteristics in Wire Arc Additive Manufacturing. *Trans. Indian Inst. Met.* **2022**, *76*, 447–455. [CrossRef]
39. Cheepu, M.; Society, A.W.; Baek, H.J.; Kim, Y.S.; Cho, S.M. Penetration Estimation of GTAW with C-Type Filler by Net Heat Input Ratio. *Weld. J.* **2022**, *101*, 240s–248s. [CrossRef]
40. Cheepu, M.; Che, W.S. Characterization of Interfacial Microstructure in Friction Welds Between Inconel 718 and SM45C Steel. *Trans. Indian Inst. Met.* **2020**, *73*, 1567–1571. [CrossRef]
41. Shanmugam, R.; Ramoni, M.; Gnanavel, B.K. A Review on Additive Manufacturing for Aerospace Application. *Mater. Res. Express* **2024**, *11*, 022001. [CrossRef]
42. Raja, R.; Shanmugam, R.; Jannet, S.; Kumar, G.V.; Venkateshwaran, N.; Naresh, K.; Ramoni, M. Development of Al-Mg2Si Alloy Hybrid Surface Composites by Friction Stir Processing: Mechanical, Wear, and Microstructure Evaluation. *Materials* **2023**, *16*, 4131. [CrossRef]
43. Shanmugam, R.; Bee, S.H.; Manikandan, C.; Sreehariharan, K.K.; Manikanta, K.V. A study on fly ash, M− Sand and bottom ash incorporated ecological geo polymer blocks with banana fiber. *Mater. Today Proc.* **2023**. [CrossRef]
44. Salunkhe, S.; Murali, A.P.; Mohammed Abdel Moneam, H.; Naranje, V.; Shanmugam, R. 3D printing of plant fiber reinforced polymer composites (PFRC's): An insight into methods, challenges and opportunities. *Polym. -Plast. Technol. Mater.* **2023**, *62*, 816–838. [CrossRef]

45. Kang, S.; Lee, J. Wear Properties of High-Hardness Tool Steel by Directed Energy Deposition Based Additive Manufacturing. *J. Weld. Join.* **2023**, *41*, 169–174.
46. Muralimohan, C.H.V.; Muthupandi, V.; Sivaprasad, K. The influence of aluminium intermediate layer in dissimilar friction welds, Inter. *J. Mater. Res.* **2014**, *105*, 350–357.