

Review

Research Advances in the Corrosion Behavior and Underlying Mechanisms of Additively Manufactured Titanium Alloys

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Abstract

Titanium alloys are irreplaceable in aerospace, biomedical and marine industries due to their low density, high specific strength and excellent biocompatibility. Conventional manufacturing methods suffer from low material utilization and difficulty in fabricating complex components, while additive manufacturing (AM) realizes near-net-shape forming of customized structures but introduces unique non-equilibrium microstructures and defects, which significantly alter the corrosion behavior and limit the long-term service reliability of additively manufactured (AMed) titanium alloys. This work systematically analyzes the corrosion behavior of titanium alloys fabricated by four mainstream AM processes: LPBF (laser powder bed fusion)/SLM (selective laser melting), EBM (electron beam melting), DED (directed energy deposition) and WAAM (wire arc additive manufacturing). It quantitatively summarizes the key electrochemical parameters and discusses the regulatory effects of matrix composition, post-treatment and service environment on their corrosion behaviors. The universal corrosion mechanisms—namely, passive film breakdown, micro-galvanic corrosion, and defect-induced localized corrosion—as well as process-specific corrosion mechanisms inherent to AMed titanium alloys are systematically elucidated. This study offers theoretical foundations for optimizing corrosion resistance and ensuring the reliable engineering implementation of AMed titanium alloys.

Keywords: titanium and its alloys; additive manufacturing; corrosion resistance



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1. Introduction

Titanium alloys, owing to their exceptional combination of low density, high specific strength, excellent biocompatibility, and corrosion resistance [1,2], have emerged as indispensable structural and functional materials across multiple critical industrial sectors [3]. As shown in Figure 1a,b, in the aerospace field, titanium alloys are extensively employed to fabricate key aero-engine components, airframe structures, and spacecraft parts, serving as the core materials that enable equipment lightweighting and high-temperature service performance [4,5]. As depicted in Figure 1c–e, in the biomedical engineering domain, their favorable osseointegration capacity and biological non-toxicity render them essential materials for orthopedic implants, dental restorations, and cardiovascular stents [6,7]. Furthermore, titanium alloys possess outstanding resistance to chloride-induced corrosion, which has facilitated their widespread adoption in marine engineering applications including ship hulls, offshore platforms, and seawater desalination facilities [8], as illustrated in Figure 1f,g.

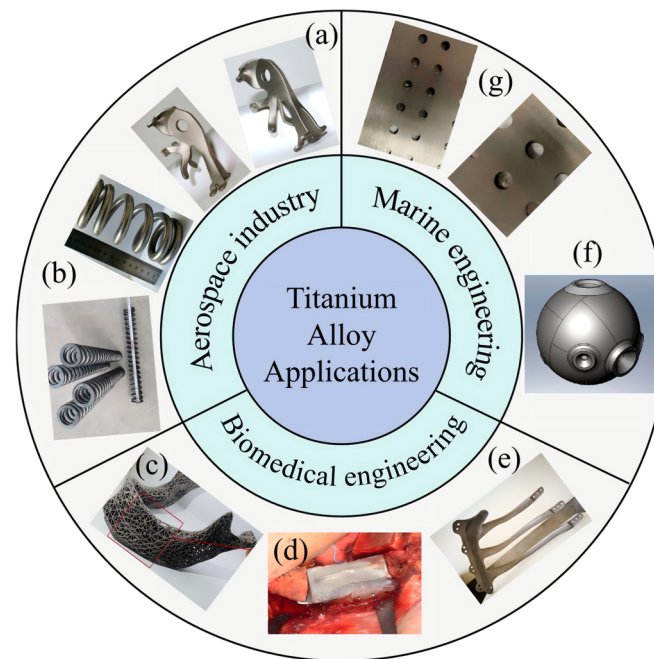


Figure 1. Summary diagram of application domains of titanium alloys: (a) aircraft bracket [9]; (b) springs [10]; (c) 3D mesh mandibular prosthesis scaffold [11]; (d) implants [12]; (e) 3D-printed sternum [13]; (f) Schematic of "Jiaolong" pressure hull [14]; (g) Titanium alloy sheets [15].

Conventional manufacturing techniques for titanium alloys mainly include casting, forging, and machining, which suffer from numerous inherent limitations: generally low material utilization rates, tedious post-processing procedures, and difficulty in fabricating components with complex geometric features or customized structures [16]. In contrast, AM technology, based on the principle of “layer-wise discretization and sequential accumulation”, has revolutionized the production paradigm of titanium alloy components [17]. AM enables a near-net-shape forming of complex customized structures, significantly improving material utilization [18], remarkably shortening production cycles, and reducing manufacturing costs [19].

Despite the numerous technical advantages of AMed titanium alloys, their corrosion behavior and mechanisms of corrosion-caused failures remain the core factors restricting their long-term service reliability and safety. Unlike conventional cast and wrought titanium alloys, the AM process involves extreme non-equilibrium metallurgical conditions, including ultra-fast cooling rates of up to 10^8 K/s (for the laser powder bed fusion (LPBF) process), complex thermal cycling processes, and directional solidification characteristics [20,21]. These unique process characteristics lead to the microstructures, phase compositions, and metallurgical defects (such as porosity, lack-of-fusion defects, and residual stresses) of AMed titanium alloys that are distinctly different from those produced by conventional manufacturing techniques, thereby significantly altering their corrosion behavior and failure mechanisms.

To date, extensive research has been conducted worldwide on the corrosion performance of AMed titanium alloys under various service environments, and the influences of matrix composition, process parameters, post-processing methods and corrosive media on electrochemical corrosion behavior have been preliminarily clarified. Nevertheless, three notable deficiencies remain in the current research system, which constitute the core focus of the present work.

First, most existing studies are confined to a single AM process or specific material system. A systematic cross-process comparative framework covering the four mainstream processes, laser powder bed fusion (LPBF; synonym: selective laser melting, SLM), electron

beam melting (EBM), directed energy deposition (DED), and wire arc additive manufacturing (WAAM), has not yet been established, and there is a lack of unified compilation and quantitative benchmarking of electrochemical corrosion parameters across different processes. The correlations among process characteristics, microstructure and corrosion performance are mostly scattered in single-process studies, without forming a complete logical chain of analysis.

Second, although common corrosion mechanisms such as passive film breakdown, micro-galvanic corrosion and defect-induced localized corrosion have been widely recognized, there remains a lack of clear cross-process discrimination regarding how the differentiated microstructural features—arising from variations in heat source mode, cooling rate and thermal cycle characteristics among different AM processes—specifically modulate the corrosion process and give rise to process-specific corrosion patterns. The boundary between universal mechanisms and process-specific mechanisms is ambiguous, and relevant discussions suffer from considerable repetition and confusion.

Third, current conclusions regarding the regulatory effects of matrix composition, post-treatment regimes and service environments are mostly drawn under specific process conditions. There is a shortage of cross-process universal summaries and differentiated comparisons, making it difficult to directly provide systematic theoretical references for AM process selection, post-treatment scheme design and service adaptability evaluation in engineering applications.

Against this background, this work systematically analyzes the corrosion behavior of titanium alloys fabricated by four mainstream AM processes, quantitatively summarizes the key electrochemical parameters under various conditions, and sorts out the regulatory effects of composition, post-treatment and service environment on corrosion performance. Furthermore, the common corrosion mechanisms and process-specific corrosion features of AMed titanium alloys are elucidated, in order to provide theoretical foundations for optimizing corrosion resistance and ensuring reliable engineering implementation of AMed titanium alloys.

2. Classification and Operational Principles of AM Technologies

Among the diverse array of additive manufacturing technologies developed for titanium alloys, four processes have emerged as the most technologically mature and industrially relevant: LPBF/SLM, EBM, DED and WAAM. We systematically elaborate on the fundamental forming principles, process parameter control, and technical features of these four processes and clarify the differences in their metallurgical evolution behaviors, so as to establish a critical process-based framework for the subsequent analysis of corrosion performance and underlying mechanisms of AMed titanium alloys. A composite schematic diagram illustrating the four processes is provided in Figure 2, and the technical details of each process are described in the following subsections.

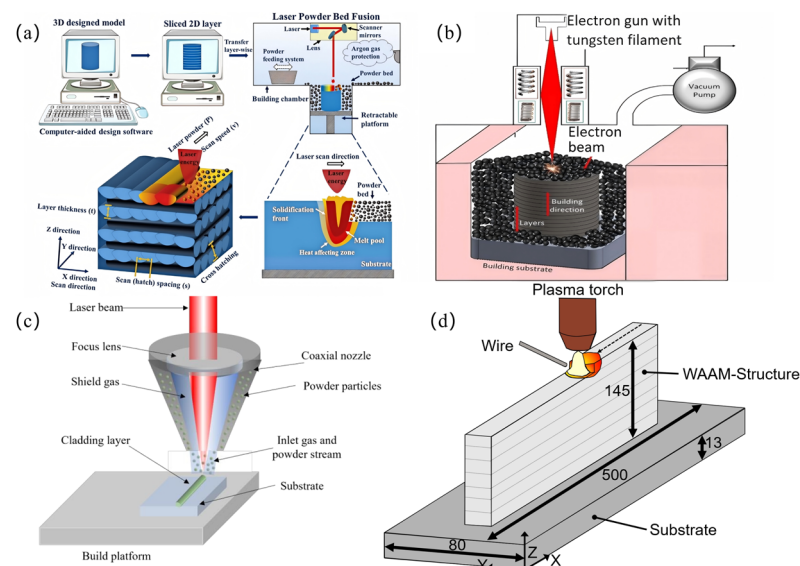


Figure 2. Schematic illustration of four mainstream AM processes for titanium alloys: (a) LPBF/SLM [22]; (b) EBM [23]; (c) DED [24]; (d) WAAM [25].

2.1. LPBF/SLM

LPBF, also known as SLM, is the most widely applied powder bed fusion process in the field of metal AM. The two terms differ only in commercial nomenclature and some subtle details of scanning strategies, while their core forming and metallurgical principles are completely identical [26,27].

As shown in Figure 2a, this technology employs a focused laser with high-energy-density as the heat source and achieves layer-by-layer near-net-shape forming of metallic components based on the discrete-stacking principle under a high-purity argon atmosphere. The core process flow is as follows: first, the 3D model of the component is sliced into layers and the scanning path is planned; then, the component is fabricated layer by layer through the cyclic process of “powder spreading—selective laser scanning and melting—ultra-high-speed solidification of the molten pool (10^3 – 10^8 K/s)”. The fluid flow within the molten pool ensures excellent metallurgical bonding between powder particles as well as between the deposited layers and the substrate [28].

The linear energy density can be regulated by key parameters such as laser power and scanning speed, enabling precise control over the relative density, grain size and residual stress of the fabricated components. This technology breaks through the geometric limitations of traditional casting and forging processes, allowing fabrication of complex customized structures and precise tailoring of material properties. It has become the dominant manufacturing technology for biomedical titanium alloy implant devices at present [29].

2.2. EBM

EBM, also known as electron beam powder bed fusion, is one of the core powder bed fusion-based metal AM processes [30]. As shown in Figure 2b, this technology achieves layer-by-layer fabrication of metallic components in a hermetically sealed building chamber through the cyclic process of “powder spreading—selective scanning and melting by an electron beam along predefined paths—solidification and forming of the molten pool”. Upon solidification, the molten pool forms a robust metallurgical bond with the underlying substrate, and this iterative process continues until the complete three-dimensional component is formed [31].

Distinguished from other mainstream AM processes, EBM technology possesses two core characteristics. First, high-temperature preheating of the powder bed prior to melting can significantly reduce thermal gradients, thereby minimizing residual stress and the risk of deformation and cracking in the fabricated components. Second, the high-vacuum operating environment prevents high-temperature oxidation of titanium alloys, ensuring the uniformity of the chemical composition and microstructure throughout the components. Currently, this technology has been widely adopted for the precision fabrication of customized biomedical titanium alloy implants [32].

2.3. DED

The processes described in this section all belong to the DED family, mainly including laser cladding deposition (LCD), laser solid forming (LSF), and laser metal deposition (LMD) [33–35].

As shown in Figure 2c, these laser-based DED processes employ a high-power laser as the heat source to form a micrometer-scale molten pool on the surface of the metallic substrate. Powder is delivered through a nozzle coaxial with the laser beam in either synchronous or pre-placed modes, and the powder particles rapidly melt in the molten pool and form a robust metallurgical bond with the substrate. Driven by a computer numerical control system, the laser then moves along predefined paths, and the molten pool travels synchronously and solidifies rapidly to form a continuous single-track cladding layer. Ultimately, the desired three-dimensional metallic component is fabricated through multiple transverse overlapping tracks and vertical layer-by-layer deposition.

During the fabrication process, argon is used as both shielding and carrier gas to prevent high-temperature oxidation of the molten metal. Key process parameters such as laser power, scanning speed, and powder feeding rate can regulate the thermal behavior and solidification rate of the molten pool, thereby determining the microstructure and various service properties of the fabricated components [33].

2.4. WAAM

WAAM is an additive manufacturing technology that employs an electric arc as the melting heat source and metal wire as the feedstock, fabricating metallic components via layer-by-layer cladding and deposition. It has now emerged as one of the dominant processes for the low-cost, high-efficiency near-net-shape fabrication of large-scale titanium alloy components [36].

As shown in Figure 2d, its core working principle follows the fundamental “discrete-deposition” logic of AM. The key process flow is as follows: First, the 3D digital model of the target component is discretized using slicing software, and the scanning paths for layer-by-layer deposition are planned. Subsequently, an electric arc generated by an arc welding power source is used as the heat source [1]. Under a protective atmosphere of 99.99% high-purity argon, the synchronously fed titanium alloy wire is continuously melted to form a stable molten pool on the substrate. The welding torch is driven by a multi-axis industrial robot or a computer-controlled worktable to travel along predefined paths. After the heat source moves away, the molten metal in the molten pool rapidly cools and solidifies to form a single deposited bead [37]. This melting–solidification cycle is repeated on the previously solidified metal layer. Through continuous multilayer and multi-track deposition, the near-net-shape forming of three-dimensional bulk titanium alloy components is ultimately achieved.

The core thermophysical characteristics, microstructural features and corrosion-related attributes of the four AM processes show significant differences due to their distinct heat input modes and solidification conditions. Table 1 systematically summarizes the key

indicators of each process, establishing a clear comparative basis for the subsequent analysis of corrosion behavior and mechanisms.

Table 1. Comparison of process characteristics and corrosion-related features of four AM processes.

Process	Heat Source	Cooling Rate	Residual Stress	Typical Defects	As-Built (AB) Microstructure	Key Corrosion Features
LPBF/SLM	High-energy laser	10^3 – 10^8 K/s	High	Microporosity, lack of fusion	Acicular α' martensite; textured fine columnar grains	High-defect passive film; strong corrosion anisotropy; corrosion evolution governed by α' decomposition
EBM	Electron beam (vacuum)	10^2 – 10^3 K/s	Low (preheated powder bed)	High surface roughness; low internal porosity	Lamellar $\alpha + \beta$ Widmanstätten structure; coarse epitaxial β grains	Combined action of α/β micro-galvanic corrosion and surface-occluded cell effect
DED	High-power laser (coaxial feeding)	10^2 – 10^4 K/s	Medium	Large irregular pores; pronounced HAZ inhomogeneity	Mixed $\alpha' + \beta$ Widmanstätten $\alpha + \beta$; distinct fusion boundary	Amplified micro-galvanic effect; severe occluded cell corrosion from large defects
WAAM	Electric arc (wire feedstock)	10 – 10^2 K/s	High, non-uniform	Interlayer HAZs; interlayer bonding defects	Coarse textured columnar $\alpha + \beta$ Widmanstätten structure	Strong texture-induced anisotropy; selective corrosion at interlayer HAZs

3. Corrosion Behavior of AMed Titanium Alloys

3.1. LPBF/SLM

LPBF, also widely termed selective laser melting (SLM), shares identical core metallurgical principles with SLM, differing only in commercial nomenclature and minor scanning strategy details. The microstructure, metallurgical defects, and residual stress features arising from their ultra-fast non-equilibrium solidification process fundamentally govern the intrinsic corrosion behavior of as-deposited titanium alloy components. To systematically and quantitatively summarize the variation trends of corrosion performance under diverse conditions, key electrochemical corrosion parameters (corrosion potential (E_{corr}), corrosion current density (I_{corr}), and polarization resistance (R_p)) from LPBF-fabricated (LPBFed) titanium alloys are compiled in Table 2, and additional datasets from SLM-fabricated (SLMed) titanium alloys are summarized in Table 3. The following subsections collectively analyze the regulatory effects of matrix composition, post-treatment and service environment on the corrosion resistance of LPBFed/SLMed titanium alloys.

Table 2. Corrosion parameters of LPBFed titanium alloy under different test conditions.

Matrix	Post-Treatment Methods	Sample States	Corrosion Mediums	Reference Electrode	E_{corr} (V)	I_{corr} (A/m ²)	R_p (Ω·m ²)	Ref.
TC4	LSM	LPBF WR	SBF	Ag/AgCl	-0.468 ± 0.041 -0.489 ± 0.023	$(5.3 \pm 2.2) \times 10^{-4}$ $(2.0 \pm 0.8) \times 10^{-4}$	- -	[38]
TC4	LSM	LSM-LPBF LSM-WR	SBF	Ag/AgCl	-0.110 ± 0.008 -0.157 ± 0.002	$(3.2 \pm 0.49) \times 10^{-3}$ $(1.1 \pm 0.13) \times 10^{-3}$	- -	[39]
TC4	SB: F100 WFA/5 bar/2 min AE: Modified Kroll's reagent	WR AB AB-SB AB-AE	SBF	Ag/AgCl	-0.13 ± 0.06 -0.50 ± 0.08 -0.10 ± 0.07 -0.37 ± 0.165	$(1.83 \pm 0.5) \times 10^{-2}$ 0.3397 ± 0.084 $(1.52 \pm 4.3) \times 10^{-2}$ 0.3539 ± 0.143	1.8518 ± 0.00403 0.1563 ± 0.00575 3.8292 ± 0.0481 0.2065 ± 0.00826	[40]
TC4	850 °C/2 h/FC/Ar	AB HT	0.9 wt% NaCl	Ag/AgCl	-0.389 ± 0.007 -0.158 ± 0.11	8.46×10^{-4} 3.5×10^{-4}	271 ± 132 782 ± 204	[41]
TC4	800 °C/2 h/FC	PBF HAM	3.5 wt% NaCl	Ag/AgCl	-0.3713 -0.3067	9.9×10^{-3} 1.12×10^{-2}	- -	[42]
TC4	HT: 850 ± 2 °C/2 h/FC HIP: 899 ± 14 °C/1034 ± 34 bar/2 h/WQ	HT-H HIP-H HT-V HIP-V	3.5 wt% NaCl	Ag/AgCl	-0.085 -0.069 -0.058 -0.085	1.53×10^{-3} 2.15×10^{-3} 1.98×10^{-3} 2.62×10^{-3}	- - - -	[43]
TC4	800 °C/2 h/FC/Ar	WR AB HT	3.5 wt% NaCl	SCE	-0.318 ± 0.010 -0.494 ± 0.016 -0.337 ± 0.011	$1.15 \times 10^{-3} \pm 4.0 \times 10^{-5}$ $1.82 \times 10^{-2} \pm 5.9 \times 10^{-4}$ $1.51 \times 10^{-3} \pm 6 \times 10^{-5}$	- - -	[44]
TC4	-	Top-S1 Middle-S2 Bottom-S3	20 °C/3.5 wt% NaCl	SCE	-0.45 ± 0.029 -0.43 ± 0.069 -0.39 ± 0.016	85 ± 130 110 ± 170 190 ± 290	199 ± 16 158 ± 29 94 ± 111	[45]
TC4	-	Cast AB	1 mol/L HCl	SCE	-0.341 ± 0.018 -0.389 ± 0.046	$9.2 \times 10^{-3} \pm 6.0 \times 10^{-4}$ $1.11 \times 10^{-2} \pm 2.4 \times 10^{-3}$	- -	[46]
TC4	-	ST DT	ST DT	SCE	-0.548 ± 0.016 -0.627 ± 0.019	$8.0 \times 10^{-5} \pm 4.0 \times 10^{-5}$ $3.0 \times 10^{-4} \pm 3.0 \times 10^{-5}$	- -	[47]
TC4	-	1 h 100 h	RS	Ag/AgCl	-0.172 -0.329	4.0×10^{-4} 3.6×10^{-3}	- -	[48]
TC4	400/600/800 °C/1 h/FC/Ar	AB 400–800 °C	AS + 5% NaF	SCE	-1.2623 -1.2012 -1.2534	2.84 0.586 3.66	- - -	[49]
TC4	700 °C/2 h/FC 700 °C/2 h/AC	AB FC AC	HBSS	Ag/AgCl	-0.376 ± 0.015 -0.228 ± 0.017 -0.517 ± 0.034	$1.28 \times 10^{-3} \pm 1.1 \times 10^{-4}$ $2.12 \times 10^{-3} \pm 1.8 \times 10^{-4}$ $1.12 \times 10^{-3} \pm 8.0 \times 10^{-5}$	- - -	[29]
TMZF	900 °C/1 h/WQ	AB ST	SBF	SCE	-0.44 -0.41 ± 0.03	$3.5 \times 10^{-3} \pm 2 \times 10^{-4}$ $1.16 \times 10^{-2} \pm 1 \times 10^{-4}$	26 7	[50]
NiTi SMAs	-	200 W 80 W 300 W	3.5 wt% NaCl	SCE	-0.320 ± 0.012 -0.430 ± 0.014 -0.340 ± 0.013	$(5.34 \pm 0.42) \times 10^{-4}$ $(1.321 \pm 0.035) \times 10^{-3}$ $(1.845 \pm 0.037) \times 10^{-3}$	- - -	[51]
Ti-12Ni	-	67 J/mm ³ 133 J/mm ³ 267 J/mm ³	3.5 wt% NaCl	SCE	-0.25 ± 0.05 -0.29 ± 0.06 -0.30 ± 0.02	$(4.55 \pm 1.3) \times 10^{-5}$ $(4.839 \pm 0.97) \times 10^{-4}$ $(1.754 \pm 0.24) \times 10^{-4}$	- - -	[52]
Ti-xCu	-	0–8	AS	SCE	-	$(1.16\text{--}5.38) \times 10^{-4}$	-	[53]
TNZ	900 °C/1 h/IQ 660 °C/1 h/WQ	WR AB IQ WQ	PBS	SCE	-0.355 ± 0.022 -0.348 ± 0.016 -0.425 ± 0.048 -0.462 ± 0.077	$8.6 \times 10^{-4} \pm 3.2 \times 10^{-4}$ $5.1 \times 10^{-4} \pm 2.2 \times 10^{-4}$ $3.0 \times 10^{-4} \pm 2.9 \times 10^{-4}$ $4.6 \times 10^{-4} \pm 1.9 \times 10^{-4}$	- - - -	[54]

Table 2. Cont.

Matrix	Post-Treatment Methods	Sample States	Corrosion Mediums	Reference Electrode	E _{corr} (V)	I _{corr} (A/m ²)	R _p (Ω·m ²)	Ref.
TC4	-	TC4			−0.47 ± 0.01	$4.6 \times 10^{-3} \pm 7.0 \times 10^{-4}$	-	
TNzT	-	TNzT	PBS	SCE	−0.47 ± 0.02	$3.5 \times 10^{-3} \pm 8.0 \times 10^{-4}$	-	[55]
TNzTS	1200 °C/30 min/IQ	TNzTS			−0.52 ± 0.06	$2.8 \times 10^{-3} \pm 1.0 \times 10^{-3}$	-	
Ti-12Cr-3Sn	-	Ti-12Cr + Ti-12Cr-3Sn	PBS	Ag/AgCl	−0.381	4×10^{-4}	-	[56]

Additional electrochemical corrosion parameters from SLMed studies are listed in Table 3.

Table 3. Corrosion parameters of SLMed titanium alloy under different test conditions.

Matrix	Post-Treatment Method	Sample States	Corrosion Mediums	Reference Electrode	E _{corr} (V)	I _{corr} (A/m ²)	R _p (Ω·m ²)	Ref.
HDH-Ti GA-Ti	-	HDH-Ti GA-Ti	3.5 wt% NaCl	SCE	−0.28751 −0.25241	1.96×10^{-2} 3.07×10^{-2}	- -	[57]
Cp-Ti	PO:750 °C/4 h	F F-PO AB AB-PO	SBF	Ag/AgCl	−0.114 ± 0.00548 −0.0789 ± 0.00552 −0.232 ± 0.01856 −0.0996 ± 0.00727	$1.15 \pm 3.45 \times 10^{-2}$ $0.399 \pm 2.39 \times 10^{-2}$ $1.18 \pm 8.26 \times 10^{-2}$ $0.297 \pm 2.08 \times 10^{-2}$	- - - -	[26]
TC4	-	400–700 μm	SBF	-	−0.972–−0.508	$(4.78–18.07) \times 10^{-3}$	-	[58]
TC4	-	AB WR	SBF	SCE	−0.10 −0.10	- -	- -	[59]
TC4	-	160–240 W	SBF	Ag/AgCl	−0.462–−0.352	$(1.176–3.395) \times 10^{-3}$	11.3–31.13	[60]
TC4	-	WR AB-H AB-V	RDF	SCE	−1.22 −1.23 −1.29	1.76×10^{-4} 8.325×10^{-4} 3.428×10^{-3}	- - -	[61]
TC4	800 °C/2 h + 500 °C/0.5 h/FC (VA)	WR AB-HT	RS	Ag/AgCl	−0.333 ± 0.04 −0.388 ± 0.015	$1.2 \times 10^{-3} \pm 3 \times 10^{-5}$ $6.0 \times 10^{-4} \pm 5 \times 10^{-5}$	- -	[62]
TC4	-	WR XOZ XOY	AS/37 ± 1 °C	Ag/AgCl	−0.55 ± 0.02 −0.55 ± 0.03 −0.54 ± 0.02	2.08×10^{-2} 1.98×10^{-2} 1.75×10^{-2}	2.08 ± 0.05 2.58 ± 0.06 2.78 ± 0.05	[11]
TC4	800/940 °C/4 h/WQ	800 °C 940 °C	SSW	SCE	−0.204 −0.161	0.3438 0.5379	-	[63]
TC4	-	600– 1200 mm/s	0.9 wt% NaCl	Ag/AgCl	−0.664–−0.57	$(1.4–4.67) \times 10^{-3}$	-	[27]
TC4	APEP:10 wt.% OA/30 min + EP/20 min	AB APEP20	3.5 wt% NaCl	SCE	−0.078 −0.009	2.42×10^{-2} 1.25×10^{-3}	- -	[64]
TC4	HT: 650 °C/3 h (VA) HIP: 925 ± 14 °C/100 MPa/3 h/Ar	WR HT HIP	3.5 wt% NaCl	SCE	−0.4883 −0.4178 −0.3243	1.9×10^{-4} 1.97×10^{-3} 8.5×10^{-4}	- - -	[65]
TC4	PN: 485– 545 °C/300 Pa/1 h	AB PN-(485–545)	3.5 wt% NaCl	SCE	−0.401 −0.455–−0.314	2.168×10^{-2} $(1.021–303.9) \times 10^{-4}$	2094 1663–12190	[66]
TC4	Aa + HT 600 °C/1 h Aa + Ca/Ag/24 h + HT 600 °C/1 h	AB AB-Na AB-Na-9.9 Ca/0.1 Ag	3.5 wt% NaCl	Ag/AgCl	−0.257 −0.170 −0.207	$1 \times 10^{-4} \pm 1 \times 10^{-5}$ $6 \times 10^{-5} \pm 2 \times 10^{-2}$ $2 \times 10^{-5} \pm 3 \times 10^{-2}$	- - -	[67]
TC4	800 °C/2 h/FC hydrogen charging	F-HC HT-XY HT-XY-HC	3.5 wt% NaCl	SCE	0.095 −0.258 0.195	1.40×10^{-4} 2.28×10^{-5} 7.19×10^{-5}	- - -	[68]
TC4	MAO	0–15 min	3.5 wt% NaCl	SCE	−0.334–−0.13	0.1532–0.6212	-	[32]
TC4	HT: 900 °C/2 h/FC + 200 °C/AC (VA) HIP: 900 °C/120 MPa/2 h	AB HT HIP	1 M NaCl	SCE	−0.92 ± 0.03 −0.68 ± 0.04 −0.57 ± 0.03	8.3×10^{-2} 4.5×10^{-2} 1.5×10^{-3}	- - -	[69]
TC4	800 °C/2 h + 500 °C/0.5 h/FC (VA)	F AB-HT	20 wt.% HCl	Ag/AgCl	−0.63 −0.61	0.813 0.847	0.04278 0.03908	[70]
TC4	-	XY-YZ XY-XZ	1 M HCl	SCE	0.3152 −0.1788	7.66×10^{-3} 1.90×10^{-2}	6.39 3.84	[71]
TC4	-	AB Cast	6 M 95 °C HNO ₃ -OI	SCE	1.06 1.019	8.30×10^{-2} 0.4203	0.352 0.125	[72]
TC4-3Cu	760/820/875 °C/ 2 h/WQ/Ar	AB 760–875 °C	0.9 wt% NaCl	SCE	−0.37 −0.423–−0.344	6.965×10^{-4} $(3.92–49.2) \times 10^{-4}$	26.25 8.632–34.57	[73]

Table 3. Cont.

Matrix	Post-Treatment Method	Sample States	Corrosion Mediums	Reference Electrode	E_{corr} (V)	I_{corr} (A/m ²)	R_p ($\Omega \cdot \text{m}^2$)	Ref.
TC4-3Cu	750 °C/2 h/AC	Cast	0.9 wt% NaCl	SCE	-0.322 ± 0.021	2.15×10^{-3}	23.152 ± 2.594	[74]
		Pre-alloyed			-0.389 ± 0.010	6.66×10^{-4}	37.167 ± 10.360	
		Mixed			-0.354 ± 0.042	8.42×10^{-4}	35.417 ± 14.178	
Ti ₂ AlN/ TC4 (IPCs)	-	TC4	3.5 wt% NaCl	SCE	-0.551	9.3×10^{-3}	-	[75]
		Ceramic			-0.527	2.0×10^{-4}	-	
		NSS			-0.532	3.4×10^{-3}	-	
		DSS			-0.554	9.8×10^{-3}	-	
		35% Ti ₂ AlN			-0.458	4.6×10^{-3}	-	[76]
Ti-55531	-	SLM-H	3.5 wt% NaCl	SCE	-0.194 ± 0.009	$4.16 \times 10^{-3} \pm 1.6 \times 10^{-4}$	-	[77]
		SLM-V			-0.275 ± 0.032	$5.19 \times 10^{-3} \pm 2.8 \times 10^{-4}$	-	
Ti-55531	ST: 790 °C/1.5 h/AC + 600 °C/6 h/AC HT: 870 °C/1.5 h/AC + 750 °C/1 h/AC + 600 °C/6 h/AC	STA-H	3.5 wt% NaCl	SCE	-0.3956 ± 0.019	$3.52 \times 10^{-3} \pm 2.8 \times 10^{-4}$	-	[78]
		STA-V			-0.4386 ± 0.027	$3.75 \times 10^{-3} \pm 3.3 \times 10^{-4}$	-	
		HT-H			-0.6145 ± 0.017	$4.76 \times 10^{-3} \pm 2.1 \times 10^{-4}$	-	
		HT-V			-0.6462 ± 0.030	$5.35 \times 10^{-3} \pm 3.8 \times 10^{-4}$	-	
Zr/TC4	-	0–4%Zr	HBSS	SCE	-0.641 – -0.504	$(3.106$ – $4.915) \times 10^{-3}$	-	[79]
TNZT	-	SLM-45°	PBS	Ag/AgCl	-0.04	2.3×10^{-3}	2.48	[80]
		SPS			-0.02	3.15×10^{-2}	1.99	

It should be noted that the literature's conclusions regarding the role of metastable α' martensite in passive film stability are not fully consistent. Most studies on TC4 alloy indicate that supersaturated V in α' increases the defect density of the passive film and deteriorates corrosion resistance. However, studies on near- β titanium alloys (e.g., TNZ, Ti-12Ni) show that fine α' microstructures can provide more nucleation sites for passivation, even yielding better corrosion resistance than wrought counterparts. These divergences are mainly attributed to differences in alloy composition, process-induced defect levels and sample surface states across studies, and the net effect of the α' phase depends on the combination of these factors.

3.1.1. Influence of Matrix Composition on Corrosion Properties

Under identical corrosion environments and post-treatment conditions, LPBFed titanium alloys with different matrix compositions exhibit pronounced disparities in corrosion performance. In 3.5 wt% NaCl solution, the I_{corr} of LPBFed Ti-12Ni alloy fabricated at the optimal volumetric energy density 67 J/mm^3 is merely $4.55 \times 10^{-5} \text{ A/m}^2$, which is two orders of magnitude lower than that of TC4 alloy ($9.9 \times 10^{-3} \text{ A/m}^2$) under the same conditions, demonstrating exceptionally superior passivation capability [52]. The corresponding potentiodynamic polarization (PDP) curves are presented in Figure 3a.

In PBS at 37 °C, the I_{corr} of Si-containing TNZTS alloy is $2.8 \times 10^{-3} \text{ A/m}^2$, which is slightly lower than that of TC4 ($4.6 \times 10^{-3} \text{ A/m}^2$) and also outperforms the Si-free TNZT alloy. This observation indicates that the incorporation of Si element is beneficial for further enhancing the corrosion resistance of this alloy system [55]. The PDP behavior of LPBFed TC4, TNZT, and heat-treated TNZTS alloys in PBS solution is illustrated in Figure 3b, with the inset showing a magnified view near the E_{corr} .

For the biomedical TNZ alloy, the AB state exhibits an I_{corr} of $5.1 \times 10^{-4} \text{ A/m}^2$, which is even lower than that of the wrought alloy of the same composition ($8.6 \times 10^{-4} \text{ A/m}^2$). This finding highlights that this alloy can achieve superior corrosion resistance via AM compared to conventional processing routes, even in the AB state [54]. The PDP curves for as-cast and LPBFed TNZ alloys in PBS solution at 37.5 °C are depicted in Figure 3c, where the inset provides a magnification of the potential range around E_{corr} .

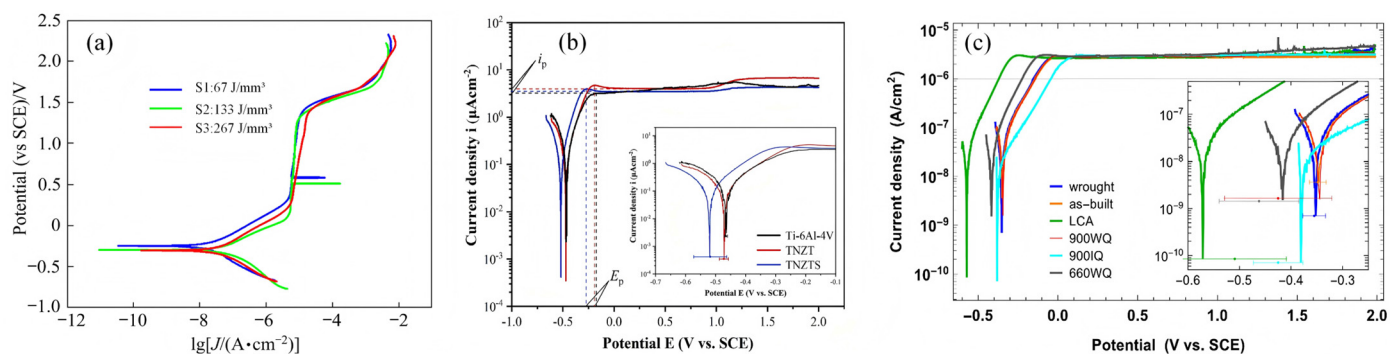


Figure 3. Electrochemical corrosion of various titanium alloys. (a) LPBF Ti-12Ni in 3.5 wt.% NaCl [52]. (b) LPBF TC4, TNZT and heat-treated TNZTS in PBS at 37 °C. Inset: E_{corr} region; error bars show E_{corr} standard deviation [55]. (c) As-cast and LPBF TNZ in PBS at 37.5 °C. Inset: E_{corr} region; error bars show E_{corr} standard deviation [54].

3.1.2. Effects of Post-Treatment Methods on Corrosion Behavior

Post-treatment is a core approach to regulating the corrosion properties of LPBFed titanium alloys. Different treatment processes can significantly affect corrosion behavior by altering the microstructure, residual stress and surface state of the alloys. For TC4 alloy in 0.9 wt% NaCl solution, the I_{corr} of the AB sample is $8.46 \times 10^{-4} A/m^2$, with a R_p of $271 \Omega \cdot m^2$. After annealing at 850 °C, the I_{corr} decreases to $3.5 \times 10^{-4} A/m^2$, and the R_p increases to $782 \Omega \cdot m^2$. These results confirm that annealing effectively eliminates the residual stress generated during the LPBF process and optimizes the stability of the passive film [41].

In terms of surface modification, sandblasting treatment exhibits a remarkable optimization effect on corrosion resistance. In SBF environment, the AB LPBFed TC4 specimen presents the I_{corr} as high as $0.0397 A/m^2$. After F100 WFA sandblasting treatment, this value decreases to $1.52 \times 10^{-2} A/m^2$, and the R_p increases from $0.1563 \Omega \cdot m^2$ to $3.8292 \Omega \cdot m^2$, surpassing that of the wrought control specimen. In contrast, acid etching treatment deteriorates the corrosion performance: the I_{corr} of the acid-etched specimen rises to $0.3539 A/m^2$, which is slightly higher than that of the untreated specimen. This phenomenon is attributed to the surface active sites introduced by acid etching [40].

In addition, different cooling methods after heat treatment also lead to differences in corrosion performance. In HBSS, the I_{corr} of the sample annealed at 700 °C followed by air cooling (AC700) is $1.12 \times 10^{-3} A/m^2$, lower than that of the sample with furnace cooling (FC700, $2.12 \times 10^{-3} A/m^2$), along with a lower corrosion rate. This indicates that a faster cooling rate is conducive to retaining a more uniform microstructure and improving corrosion resistance [29]. However, LSM shows a negative effect in the study: after LSM treatment, the I_{corr} of the sample increases from $5.3 \times 10^{-4} A/m^2$ of the original LPBF state to $3.2 \times 10^{-3} A/m^2$, and the corrosion rate also rises accordingly, which may be related to the new micro-defects introduced during the remelting process [38,39].

Consistent regulatory patterns of post-processing are also verified in SLMed titanium alloy systems.

Heat treatment and surface modification effectively compensate for SLM-induced performance defects by adjusting microstructures or creating protective surface layers. Various post-processing approaches exhibit different regulatory effects.

For the TC4-3Cu alloy in 0.9 wt.% NaCl solution, after water quenching heat treatment at 760 °C, the E_{corr} of the AB SLM specimen shifts positively from $-0.370 V$ to $-0.344 V$ (vs. SCE), the I_{corr} decreases from $6.965 \times 10^{-4} A/m^2$ to $3.92 \times 10^{-4} A/m^2$, and the R_p increases from $26.25 \Omega \cdot m^2$ to $34.57 \Omega \cdot m^2$. However, when the heat treatment temperature rises to 875 °C, the corrosion performance deteriorates significantly, verifying that low-temperature

heat treatment in the sub- β transition range is more suitable for improving the corrosion performance of SLMed TC4-3Cu [73]. The inverse pole figures and grain size distribution of SLMed TC4-3Cu are displayed in Figure 4a,b, while those after 760 WQ are shown in Figure 4c,d, directly reflecting the grain refinement effect of appropriate low-temperature heat treatment.

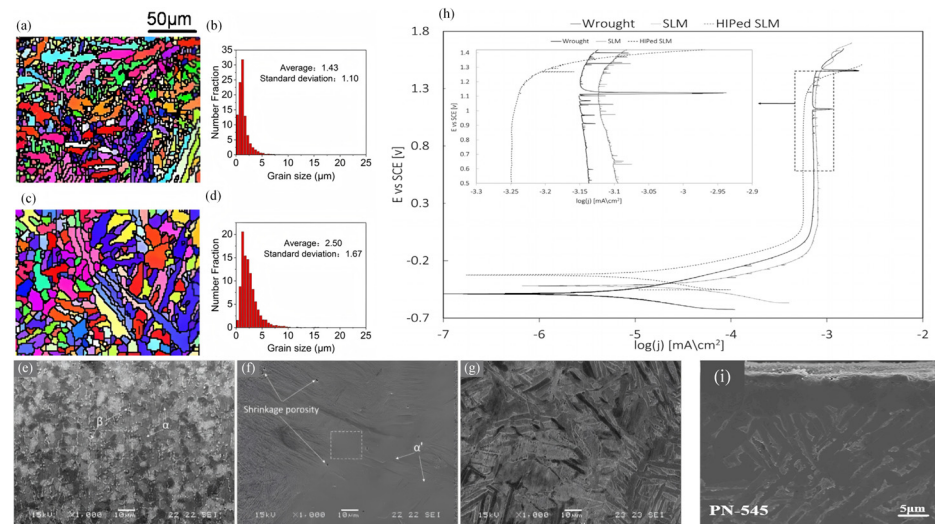


Figure 4. Microstructure and electrochemical corrosion behavior of titanium alloys. (a–d) IPF maps and grain size distributions for (a,b) AB and (c,d) 760 WQ SLM samples [73]. (e–g) Cross-sectional SEM micrographs of (e) wrought, (f) SLM, (g) HIPed SLM [65]. (h) PDP curves of wrought, SLM, and HIPed SLM alloys in 3.5 wt.% NaCl solution [65]. (i) SEM micrograph of PN-545 [66].

Surface modification techniques fundamentally block the acceleration effect of SLM-induced pores and defects on the corrosion process by constructing a protective surface barrier. After PO treatment at 750 °C for 4 h, the AB SLM Cp-Ti exhibits a positively shifted E_{corr} from -0.232 V to -0.0996 V (vs. Ag/AgCl) and a sharply reduced I_{corr} from 1.18 A/m² to 0.297 A/m². Its corrosion performance even surpasses that of the untreated as-forged specimen, which is mainly attributed to the dense TiO₂ ceramic coating formed via PO, which effectively hinders the penetration of corrosive ions into the substrate [26].

Other surface modification techniques and HIP post-processing also exhibit excellent modulation effects. After HIP treatment, the specimen presents a positively shifted E_{corr} from -0.4178 V to -0.3243 V (vs. SCE) and a reduced I_{corr} from 1.97×10^{-3} A/m² to 8.5×10^{-4} A/m². The transverse cross-sectional microstructures of wrought TC4, SLMed TC4 and HIP SLMed TC4 are presented in Figure 4e–g, respectively, and the PDP curves of these three samples in 3.5% NaCl solution are shown in Figure 4h, proving that HIP can eliminate SLM-induced shrinkage porosity and optimize corrosion performance. Various post-processing techniques achieve effective improvement in the corrosion performance of SLMed titanium alloys from both microstructure tailoring and surface barrier construction [65]. After PN at 545 °C, the I_{corr} of SLMed TC4 decreases from 2.168×10^{-2} A/m² to 1.021×10^{-4} A/m², and the R_p increases from $2094 \Omega \cdot \text{m}^2$ to $10,920 \Omega \cdot \text{m}^2$ [66]; the cross-sectional SEM micrograph of the PN-545 sample is shown in Figure 4i.

3.1.3. Influence of Corrosion Environment on Corrosion Failure Modes

The medium composition and service conditions of the corrosion environment are primary determinants of the corrosion behavior and failure modes exhibited by LPBFed titanium alloys. For LPBFed TC4 alloy immersed in HS, the I_{corr} is only 8.0×10^{-5} A/m² under static conditions; however, under dynamic flow conditions in the same solution, the I_{corr} increases to 3.0×10^{-4} A/m². This observation indicates that fluid scouring

disrupts the dynamic repair equilibrium of the passive film, thereby accelerating the corrosion process [47]. The corresponding PDP curves for samples tested in static Hank's solution (ST) and dynamic Hank's solution (DT) at 37 °C are presented in Figure 5a, where E_{pp} denotes the pitting potential, i.e., the critical breakdown potential of the protective passive film.

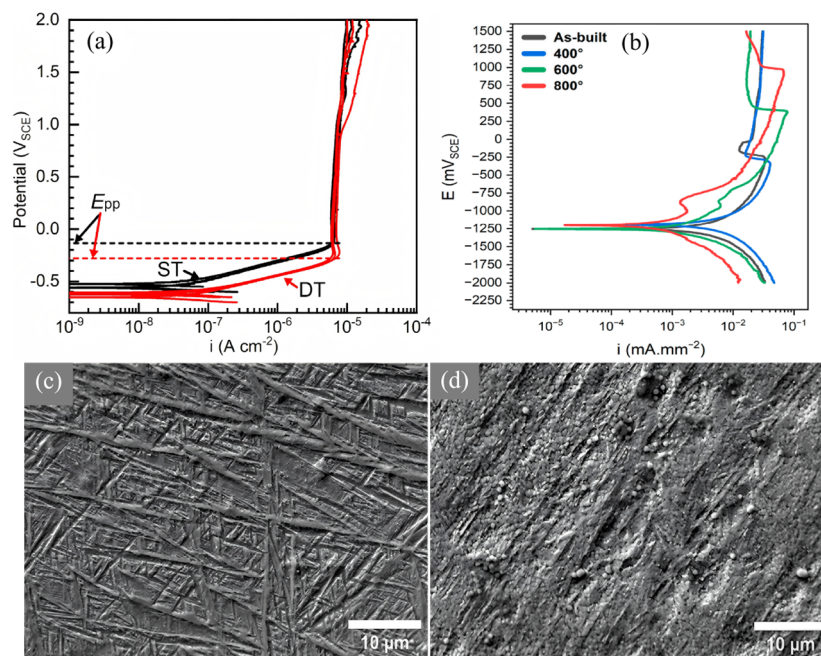


Figure 5. Electrochemical corrosion results of titanium alloys. (a) PDP curves of ST and DT samples in HS at 37 °C [47]. (b) PDP curves of AB and heat-treated specimens in AS + 5% NaF under tensile stress [49]. (c,d) Corrosion morphologies of (c) AB and (d) 800 °C heat-treated specimens after tensile testing in AS + 5% NaF [49].

In fluorine-containing artificial saliva, the E_{corr} of the alloy shifts significantly in the negative direction, reaching a minimum value of -1.2623 V (vs. SCE), and the I_{corr} is substantially higher than that observed in conventional physiological environments. This degradation in corrosion resistance arises from the ability of fluoride ions to chemically attack and destroy the protective TiO_2 passive film on the titanium alloy surface, leading to a marked reduction in passivation capability. Even after annealing at 800 °C, the I_{corr} in this aggressive environment remains as high as 0.586 A/m², which is orders of magnitude greater than that of the same alloy in SBF [38,49]. Figure 5b shows the PDP behavior of the alloy under tensile stress corresponding to the 0.2% proof stress in saliva solution containing artificial saliva (AS) + 5% NaF. Electron microscopy analysis of the corrosion morphologies for the AB and 800 °C-annealed specimens after tensile straining in the fluorine-containing solution is provided in Figure 5c,d, respectively.

Furthermore, immersion duration exerts a pronounced effect on the corrosion behavior of LPBFed titanium alloys. In Ringer's solution, the I_{corr} of LPBF TC4 is 4.0×10^{-4} A/m² after 1 h of immersion but increases to 3.6×10^{-3} A/m² after 100 h of immersion. This trend demonstrates that the stability of the passive film gradually deteriorates with prolonged exposure, resulting in an accelerated corrosion rate [48].

3.2. EBM

The corrosion behavior of EBM-fabricated (EBMed) titanium alloys is a critical performance indicator that determines their engineering applications in key fields such as biomedicine and marine engineering. The corrosion resistance of these alloys is synergis-

tically regulated by multiple factors, including matrix composition, fabrication process, post-processing regimes, and service environments, and thus exhibits significant differences under various processing and service conditions.

To systematically elucidate the controlling mechanisms of the key factors on the corrosion resistance of EBMed titanium alloys, this section systematically analyzes the electrochemical test results under different working conditions. Table 4 summarizes the core electrochemical characterization data of EBMed titanium alloys and their corresponding control specimens in various corrosion environments, which provides quantitative experimental evidence and data support for the subsequent analysis of the corrosion performance of EBMed titanium alloys from two core dimensions: matrix metal composition and post-processing processes.

Table 4. Corrosion parameters of EBMed titanium alloy under different test conditions.

Matrix	Post-Treatment Method	Sample States	Corrosion Mediums	Reference Electrode	E_{corr} (V)	I_{corr} (A/m ²)	R_p ($\Omega \cdot \text{m}^2$)	Ref.
TC4	-	XX-YZ XX-XZ XX-XY	1 M HCl	SCE	-0.6938 0.1962 -0.7492	0.22 0.01885 0.163	0.237 5.25 0.33	[71]
TC4	PN	AB AB-PN	3.5 wt% NaCl	SCE	- -	2.75×10^{-3} 3.39×10^{-4}	- -	[81]
TC4	MAO	AB MAO-5 min MAO-10 min MAO-15 min	3.5 wt% NaCl	SCE	-0.249 -0.141 -0.130 -0.118	0.504 0.176 0.4528 1.138	- - - -	[32]
TC4	HT1:600 °C/1 h/FC HT2:800 °C/1 h/FC HT3:920 °C/1 h/WQ	AB HT1 HT2 HT3	3.5 wt% NaCl	SCE	-0.461 ± 0.025 -0.335 ± 0.018 -0.507 ± 0.027 -0.331 ± 0.034	1.09×10^{-3} 2.45×10^{-3} 2.20×10^{-4} 2.02×10^{-3}	5.4152 1.2278 36.779 3.2647	[30]
TC4	-	EBM WR	SBF	SCE	-0.18 -0.10	- -	- -	[59]
TC4	Feed rate: 0.1 mm/r Cryogenic: LN ₂ /0.9 kg/min	WR-C-0.1 AM-C-0.1	SPC	SCE	-0.43 -0.35	2.00×10^{-4} 1.00×10^{-4}	- -	[82]
TC4	-	EBM-H EBM-V F	RDF	SCE	-1.18 -1.24 -1.22	1.127×10^{-4} 3.112×10^{-4} 1.76×10^{-4}	- - -	[61]
TC4	-	1 h 100 h	RS	Ag/AgCl	-0.279 -0.165	8.0×10^{-4} 8.7×10^{-3}	- -	[48]
TC4	-	WR EBM	RS	Ag/AgCl	-0.25 ± 0.01 -0.16 ± 0.02	$(7 \pm 0.5) \times 10^{-3}$ $(2.7 \pm 0.6) \times 10^{-3}$	- -	[83]
TC4	- SiC polishing: P400/P800/P1200	WR EBM EBM-MP	HBSS	SCE	-0.48 0.04 -0.49	- - -	- - -	[84]
TC4	-	0.166 mV/s 0.05 mV/s	HBSS	SCE	-0.353743 -0.379018	1.507×10^{-2} 4.335×10^{-3}	- -	[85]
TC4	SB: Al ₂ O ₃ /30 bar/30 s Machined: Ra $\approx$ 1.66 μm HIP: 910 °C/2 h/ 1500 bar/Ar	AB AB-SB AB-M HIP-M	HBSS	SCE	- - - -	$(6.144 \pm 3.773) \times 10^{-2}$ $(2.516 \pm 2.308) \times 10^{-2}$ $(3.1 \pm 1.5) \times 10^{-4}$ $(3.2 \pm 2.1) \times 10^{-4}$	1.99 ± 1.55 4.38 ± 2.56 111.69 ± 8.11 106.47 ± 19.21	[86]
Ti536	-	TC4 Ti536	SBF	Ag/AgCl	-0.03 ± 0.01 -0.09 ± 0.03	$(1.90 \pm 0.10) \times 10^{-4}$ $(5.60 \pm 0.20) \times 10^{-4}$	132 24.2	[87]

Table 4. Cont.

Matrix	Post-Treatment Method	Sample States	Corrosion Mediums	Reference Electrode	E _{corr} (V)	I _{corr} (A/m ²)	R _p (Ω·m ²)	Ref.
Ti536	-	TC4-2 h	0.9 wt% NaCl	Ag/AgCl	−0.025 ± 0.138	$(4.2 \pm 0.4) \times 10^{-4}$	4.453 ± 0.02	[88]
		Ti536-2 h			−0.035 ± 0.015	$(2.6 \pm 0.2) \times 10^{-4}$	1.994 ± 0.02	
		TC4-2 h	0.9% NaCl + H ₂ O ₂		0.165 ± 0.013	$(3.1 \pm 0.3) \times 10^{-4}$	0.588 ± 0.01	
		Ti536-2 h			0.203 ± 0.174	$(4.4 \pm 0.4) \times 10^{-4}$	0.203 ± 0.03	
Ti4822	-	TC4	0.9 wt% NaCl	Ag/AgCl	−0.41 ± 0.23	$(3.4 \pm 1.2) \times 10^{-4}$	276 ± 37	[89]
		Ti4822			−0.46 ± 0.11	$(9.2 \pm 3.8) \times 10^{-4}$	149 ± 72	
Ti-42Nb	-	Ti-42Nb	SBF	SCE	−0.225 ± 0.002	$(3.84 \pm 0.02) \times 10^{-5}$	2091 ± 94	[90]

3.2.1. Influence of Matrix Composition on the Corrosion Performance of EBMed Titanium Alloys

As revealed by the horizontal comparison of the test data in Table 3, the matrix alloy composition is the core intrinsic factor determining the corrosion performance of EBMed titanium alloys, and their corrosion resistance exhibits remarkably different characteristics with the variation in the type and content of alloying elements as well as the service environment. In the conventional neutral chloride-containing environment of 0.9 wt% NaCl solution, the initial free I_{corr} of the Ti536 matrix is 2.6×10^{-4} A/m², which is lower than that of the TC4 matrix (4.2×10^{-4} A/m²) under the same environment. This indicates that the alloying design with low Cu content slightly improves the initial uniform corrosion resistance of the alloy [88], and the corresponding PDP curves of samples after 2 h of immersion in 0.9% NaCl solution are shown in Figure 6a. In the 0.9 wt% NaCl solution with H₂O₂ addition simulating the inflammatory environment, the I_{corr} of the Ti536 matrix rises to 4.4×10^{-4} A/m², which is higher than that of the TC4 matrix (3.1×10^{-4} A/m²). This result suggests that Cu element exerts an adverse effect on the initial corrosion resistance of the alloy in the complex physiological environment containing reactive oxygen species [88], and the corresponding PDP curves are shown in Figure 6b. In the 0.9 wt% NaCl solution, the γ -TiAl matrix presents an I_{corr} of 9.2×10^{-4} A/m² and a R_p of $149 \pm 72 \Omega \cdot \text{m}^2$, with significantly inferior corrosion resistance to the TC4 matrix (I_{corr} : 3.4×10^{-4} A/m², R_p : $276 \pm 37 \Omega \cdot \text{m}^2$), demonstrating that the high Al content alloying design markedly deteriorates the corrosion resistance of EBMed titanium alloys [89]. The PDP curves of EB-PBF-produced TC4 and γ -TiAl alloy for 1 h in 0.9% NaCl solution are presented in Figure 6c.

In the physiological service environment of SBF, the TC4 matrix exhibits superior long-term corrosion resistance, with an I_{corr} of 1.9×10^{-4} A/m² and an R_p up to $132 \Omega \cdot \text{m}^2$, which is significantly better than that of the Ti536 matrix (I_{corr} : 5.6×10^{-4} A/m², R_p : $24.2 \Omega \cdot \text{m}^2$) [87]. The Ti-42Nb matrix achieves exceptional corrosion resistance in this environment, with an I_{corr} as low as 3.84×10^{-5} A/m² and an R_p as high as $2091 \pm 94 \Omega \cdot \text{m}^2$, realizing an order-of-magnitude leap in corrosion resistance compared with EBMed titanium alloys with other matrices [90]. The Tafel plot of Ti-42Nb alloy in SBF is shown in Figure 6d.

Overall, Nb alloying can substantially optimize the corrosion resistance of EBMed titanium alloys. The influence of Cu element on the corrosion resistance of the alloy is highly coupled with the service environment, while the TiAl matrix with high Al content significantly impairs the corrosion resistance of the alloy. The conventional TC4 matrix maintains stable corrosion performance in most chloride-containing and physiological

environments, and its corrosion properties can be further optimized through the regulation of post-treatment processes and building orientation.

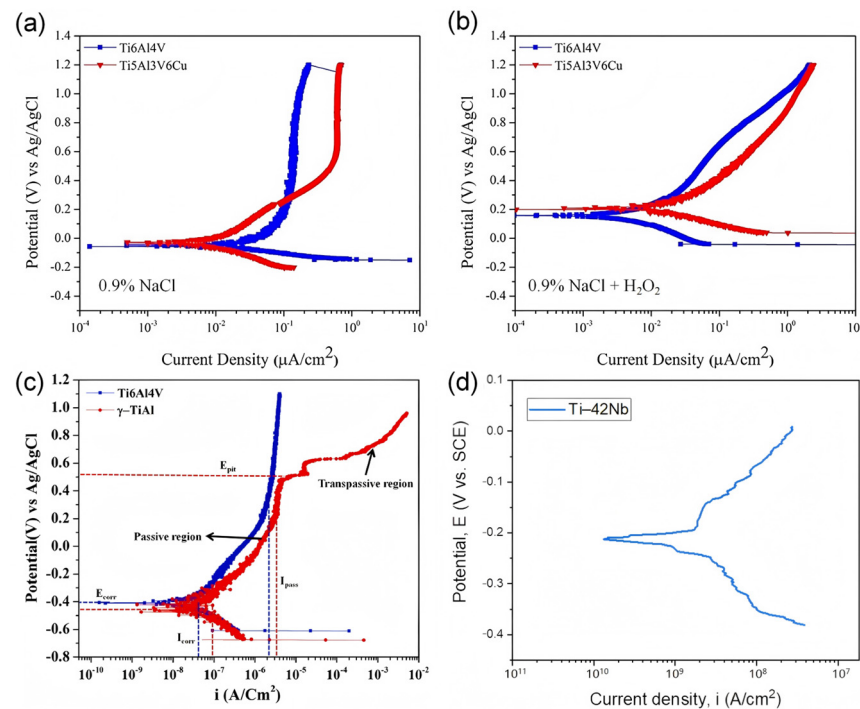


Figure 6. Polarization curves of titanium alloys in simulated physiological solutions. (a) PDP curves of TC4 and Ti5Al3V6Cu in 0.9 wt.% NaCl. (b) PDP curves in 0.9 wt.% NaCl + H₂O₂ [88]. (c) PDP curves of EBM TC4 and γ-TiAl in 0.9 wt.% NaCl [89]. (d) Tafel plot of Ti-42Nb in SBF [90].

3.2.2. Modulating Effects of Various Post-Treatment Processes on the Corrosion Performance of EBMed Titanium Alloys

Various post-treatment processes exhibit significantly different modulating effects on the corrosion performance of EBMed titanium alloys, and their influencing laws are highly coupled with the process type, parameter settings and service environment. The AB EBMed titanium alloy without post-treatment, whose corrosion performance is significantly affected by the building orientation, matrix composition and service environment, serves as the benchmark for the performance comparison of various post-treatment processes. Its corrosion resistance deteriorates apparently with increasing immersion time and environmental corrosivity [71,83].

Among the heat treatment processes, the HT800 annealing (holding at 800 °C for 1 h followed by furnace cooling) leads to the best corrosion resistance of EBMed TC4 in a 3.5 wt% NaCl environment. This treatment reduces the I_{corr} of the specimen to 2.20×10^{-4} A/m² and increases the R_p to 36.779 Ω·m², achieving an order-of-magnitude improvement in corrosion resistance compared with the control specimen. In contrast, both the HT600 stress relief annealing (holding at 600 °C for 1 h followed by furnace cooling) and HT920 solution treatment with water quenching (holding at 920 °C for 1 h followed by water quenching) exert adverse effects on its corrosion performance [30].

Machining and hybrid post-treatments are the core approaches to regulating the corrosion performance of EBMed titanium alloys in physiological environments. Machining treatment drastically reduces the I_{corr} of EBMed TC4 in HBSS to 3.1×10^{-4} A/m² and increases the R_p to 111.69 ± 8.11 Ω·m², realizing an order-of-magnitude leap in corrosion resistance. Hybrid treatment combined with HIP can further stabilize its high corrosion resistance, whereas sandblasting treatment significantly deteriorates the corrosion resistance of the specimen [86]. Cryogenic cutting treatment further reduces the I_{corr} of EBM

specimens in the simulated physiological environment to 1.00×10^{-4} A/m², which further improves the corrosion resistance compared with dry/wet cutting processes [82]. SiC polishing treatment significantly alters the electrochemical behavior of EBMed TC4 in HBSS, making its E_{corr} characteristics consistent with those of wrought specimens [84].

3.3. DED

The corrosion performance of DED-fabricated (DEDed) titanium alloys is highly dependent on the microstructural features determined by their fabrication processes. This section systematically compiles the corrosion thermodynamic tendencies and kinetic behaviors of titanium alloys under diverse process conditions, with all key electrochemical test results summarized in Table 5. Subsequently, a cross-sectional comparison will be performed to investigate the regulatory effects of different manufacturing routes and critical process parameters on the corrosion resistance of DEDed titanium alloys, providing a robust quantitative data foundation for the subsequent elucidation of the underlying corrosion mechanisms.

Table 5. Corrosion parameters of DEDed titanium alloy under different test conditions.

Matrix	AM Method	Post-Treatment Method	Sample States	Corrosion Medium	Reference Electrode	E_{corr} (V)	I_{corr} (A/m ²)	R_p ($\Omega \cdot \text{m}^2$)	Ref.
TC4	LWAM-V	-	F LWAM-V	3.5 wt% NaCl	Ag/AgCl	-0.1967 -0.1638	7.852×10^{-3} 1.607×10^{-2}	4.335 2.408	[91]
TC4	DED HAM	800 °C/2 h/FC	DED HAM	3.5 wt% NaCl	Ag/AgCl	-0.4384 -0.3067	7.1×10^{-3} 1.12×10^{-2}	- -	[42]
TC4	DED	-	WR DED WR DED WR DED	HBSS 0.9 wt% NaCl AS	Ag/AgCl	-0.319 ± 0.086 -0.094 ± 0.076 -0.334 ± 0.025 -0.074 ± 0.032 -0.337 ± 0.030 -0.039 ± 0.066	$(1.2 \pm 0.2) \times 10^{-4}$ $(1.5 \pm 0.7) \times 10^{-4}$ $(1.4 \pm 0.3) \times 10^{-4}$ $(5.3 \pm 1.2) \times 10^{-4}$ $(1.5 \pm 0.5) \times 10^{-4}$ $(5.9 \pm 3.4) \times 10^{-4}$	570 323 809 154 880 64	[92]
TC4	LSF	HT: 650 °C/1 h/FC	LSF-HT F	15 wt% NaCl	SCE	-0.224 ± 0.0012 -0.230 ± 0.0010	$(1.559 \pm 0.268) \times 10^{-2}$ $(6.064 \pm 1.754) \times 10^{-2}$	- -	[35]
TC4	LSF	-	LSF F	15 wt% NaCl	SCE	-0.255 ± 0.0015 -0.230 ± 0.0010	$(7.862 \pm 3.508) \times 10^{-2}$ $(6.064 \pm 1.754) \times 10^{-2}$	- -	[93]
TC4	LCD	-	3.5 wt% 10 wt% 15 wt%	3.5/10/15 wt% NaCl	SCE	-0.204 ± 0.001 -0.280 ± 0.003 -0.356 ± 0.009	$(3.36 \pm 0.04) \times 10^{-3}$ $(1.11 \pm 0.08) \times 10^{-3}$ $(1.02 \pm 0.26) \times 10^{-3}$	- - -	[94]
TC4	LC-CPF	-	LC-CPF F	SBF	SCE	-0.22 ± 0.00585 -0.11 ± 0.00529	$(2.53 \pm 0.0692) \times 10^{-2}$ $(2.93 \pm 0.17) \times 10^{-3}$	0.473 0.583	[95]
TC4	LMD	-	WR One-way Cross	AS	SCE	-0.249 ± 0.005 -0.281 ± 0.003 -0.334 ± 0.003	$(5.11 \pm 0.48) \times 10^{-5}$ $(9.33 \pm 0.20) \times 10^{-5}$ $(14.03 \pm 0.16) \times 10^{-5}$	- - -	[96]
TC4	LMD	SFPB: Al ₂ O ₃ /1.5 MPa/ 60 s	LMD LMD-SFPB	3.5 wt% NaCl	SCE	-0.362 -0.347	7.05×10^{-3} 1.1802×10^{-3}	- -	[97]
TC4	LENS	P-PHT: 950 °C/30 min/ 10 ⁻² mbar/ FC HIP: 950 °C/30 min/ 300 MPa/FC/Ar	LENS P-PHT HIP	0.9 wt% NaCl	Ag/AgCl	-0.021 -0.034 -0.074	3.1×10^{-3} 3.6×10^{-3} 7.7×10^{-4}	- - -	[98]
TC11 TC11-10Mo	LMD	-	TC11 TC11-10Mo	3.5 wt% NaCl	-	-0.702 -0.411	8.89×10^{-3} 4.18×10^{-4}	- -	[99]

Table 5. Cont.

Matrix	AM Method	Post-Treatment Method	Sample States	Corrosion Medium	Reference Electrode	E_{corr} (V)	I_{corr} (A/m ²)	R_p ($\Omega \cdot \text{m}^2$)	Ref.
Ti-2Fe-0.1B	LMD	-	Cast	HBSS	Ag/AgCl	-0.168 ± 0.01	$(7.144 \pm 1.40) \times 10^{-4}$	-	[100]
			F			-0.176 ± 0.02	$(5.727 \pm 1.10) \times 10^{-4}$	-	
			LMD			-0.128 ± 0.03	$(4.689 \pm 0.99) \times 10^{-4}$	-	
Ti-Al-xSi-xCu	LMD	-	TC4	3.5 wt% NaCl	-	-0.245	5.58×10^{-3}	4.607	[34]
			Ti-Al-12Si-2Cu			-0.465	0.0196	0.1313	
			Ti-Al-7Si-4Cu			-0.388	3.86×10^{-3}	6.658	
Ti-Zr	LCD	-	Ti-40Zr	1 mol/L HCl	SCE	0.062819	1.035×10^{-3}	-	[33]
Ti-17Nb-6Ta	LCD	-	Ti-17Nb-6Ta	RS	SCE	-0.3	2.26×10^{-3}	-	[101]
Ti-15Mo	DED	-	DLD-H	SBF	SCE	-0.472	2.99×10^{-2}	0.419	[102]
			DLD-V			-0.667	7.70×10^{-2}	0.238	

Horizontal Comparison of Corrosion Performance Across Fabrication Routes

From the perspective of fabrication route, the process category, key process parameters, building orientation, and post-treatment process of AM all exert significant effects on the corrosion performance of titanium alloys, serving as the core regulatory approaches for the corrosion resistance of AMed titanium alloys.

Among the key parameters of the LMD process, laser power exhibits a clear linear correlation with the corrosion performance of TC4 alloy. As the laser power increases from 0.8 kW to 3.0 kW, the I_{corr} of the samples decreases continuously, accompanied by a synchronous reduction in corrosion rate. The sample fabricated at 0.8 kW presents the highest I_{corr} and the weakest corrosion resistance, while the sample built at 3.0 kW achieves the optimal corrosion resistance, which is even superior to that of the TC4 matrix. This variation is attributed to the fact that higher laser power reduces pore defects in the AB parts, facilitating the formation of a denser microstructure and a more stable passive film on the surface [103].

The effect of building orientation on corrosion performance is particularly prominent in DEDed Ti-15Mo alloy. The I_{corr} of the horizontally built sample is only 38.8% of that of the vertically built counterpart, and its R_p is 1.76 times that of the vertically built sample, corresponding to a 75% improvement in corrosion resistance. The core mechanism is that the horizontally built sample has lower surface roughness and can form a double-layer passive barrier, while the high roughness and unmelted particles on the surfaces of the vertically built sample increase the number of defect sites on the passive film and reduce corrosion resistance [102].

3.4. WAAM

To clarify the inherent laws of the corrosion behavior of titanium alloys fabricated via WAAM (WAAMed) and quantitatively evaluate the regulatory effects of matrix composition, AM process, post-treatment method, and corrosive media on their corrosion properties, this section systematically collates the core electrochemical corrosion parameters and corrosion rate indicators of WAAMed titanium alloys under different service conditions. The relevant data are organized into Table 6, which provides quantitative data support for the subsequent multi-dimensional analyses of the differences in corrosion performance of WAAMed titanium alloys.

Table 6. Corrosion parameters of WAAMed titanium alloy under different test conditions.

Matrix	AM Method	Post-Treatment Method	Sample States	Corrosion Mediums	Reference Electrode	E _{corr} (V)	I _{corr} (A/m ²)	R _p (Ω·m ²)	Ref.
Cp-Ti	WDED	-	1N HCl 6N HCl	1N/6N HCl	SCE	0.5292 0.7018	0.3985 11.59	-	[104]
Ti-6Al-xV	WAAM	-	Ti-6Al	3.5 wt% NaCl	SCE	-0.108 ± 0.015	(4.2 ± 1.2) × 10 ⁻³	-	[105]
			Ti-6Al-2V			-0.097 ± 0.023	(6.7 ± 2.5) × 10 ⁻³	-	
			TC4	1 M LA + AS		-0.109 ± 0.026	(3.9 ± 1.0) × 10 ⁻³	-	
			Ti-6Al			-0.057 ± 0.022	(1.6 ± 0.3) × 10 ⁻³	-	
			Ti-6Al-2V			-0.156 ± 0.015	(7.0 ± 1.0) × 10 ⁻⁴	-	
TC4	CMTAM	-	Cast 100%Ar 100%He 50%Ar + 50%He	3.5 wt% NaCl	SCE	-0.48 -0.59 -0.44 -0.34	9.53 × 10 ⁻⁴ 2.06 × 10 ⁻³ 9.17 × 10 ⁻⁴ 5.47 × 10 ⁻⁴	184.9 24.7 105.4 212.3	[106]
TC4	WAAM	HT: 950 °C/ 1 h/AC + 600 °C/4 h/AC	BR HT-BR	3.5 wt% NaCl	SCE	-0.47 -0.47	9.87 × 10 ⁻³ 4.37 × 10 ⁻³	- -	[107]
TC4	WAAM	-	C-WAAM + TSG P-WAAM P-WAAM + TSG	3.5 wt% NaCl	SCE	-0.52 -0.47 -0.5	8.46 × 10 ⁻³ 8.52 × 10 ⁻³ 8.50 × 10 ⁻³	- - -	[108]
TC4	WAAM	-	WAAM Rolling	3.5 wt% NaCl	SCE	- -	- -	5.14 7.84	[109]
TC4	WAAM	850/1050 °C/2 h/FC/Ar	WR AM AM-850 AM-1050	0.5 M H ₂ SO ₄ + 5 ppm F ⁻ /70 °C/O ₂	Ag/AgCl	-0.831 ± 0.009 -0.794 ± 0.011 -0.803 ± 0.009 -0.833 ± 0.008	0.892 ± 0.033 0.779 ± 0.012 0.619 ± 0.008 0.54 ± 0.0125	0.01802 0.02104 0.02617 0.02844	[110]
TC4-7.3% Cu	WPC-AM	S1: 630 W/<850 °C S2: 690 W/850–1000 °C S3: 810 W/1000–1200 °C	AB	3.5 wt% NaCl	SCE	-0.243	420	-	[111]
			S1			-0.176	320	-	
			S2			-0.048	50	-	
			S3			-0.162	190	-	
TMN	WAAM	STA: 850/FC + 650 °C/2 h HT: 650 °C/FC	AB	3.5% NaCl (pH = 2)	SCE	-0.337	(2.73 ± 0.3) × 10 ⁻³	-	[112]
			STA			-0.401	(4.03 ± 0.4) × 10 ⁻³	-	
			HT	3.5 wt% NaCl + 0.005 M F ⁻		-0.388	(5.65 ± 0.3) × 10 ⁻³	-	
			AB			-0.473	0.178 ± 0.004	-	
			STA			-0.518	0.177 ± 0.006	-	
HT	-0.485	0.207 ± 0.004	-						
TC11	MWAAM	-	360A 380A 400A	3.5 wt% NaCl	SCE	-0.311 -0.315 -0.329	1.23 × 10 ⁻⁴ 2.34 × 10 ⁻⁴ 3.36 × 10 ⁻⁴	- - -	[37]
Ti6321	WAAM	-	Rolling DED-BD DED-TD	3.5 wt% NaCl	SCE	-0.403846 -0.456391 -0.315705	8.7 × 10 ⁻⁵ 4.8 × 10 ⁻⁵ 2.9 × 10 ⁻⁵	- - -	[113]
Ni-Ti	MPAM	-	Ni45Ti55 Ni50Ti50 Ni55Ti45	3.5 wt% NaCl	SCE	-0.26 -0.29 -0.37	2.81 × 10 ⁻² 4.15 × 10 ⁻² 5.47 × 10 ⁻²	- - -	[114]
Ni-Ti	MPAM	-	Ni45Ti55	HBSS	SCE	-0.28 ± 0.01	(4.8 ± 0.3) × 10 ⁻³	0.12	[115]
TC4-5Cr TC4-2.5Cr2.5Ni TC4-5Ni	μ-PAPAM	-	TC4-5Cr	3.5 wt% NaCl	Ag/AgCl	-0.302	1.95 × 10 ⁻³	51.66	[116]
			TC4-			-0.348	2.37 × 10 ⁻³	46.17	
			2.5Cr2.5Ni			-0.412	2.94 × 10 ⁻³	37.47	
			TC4-5Ni TC4			-0.473	3.49 × 10 ⁻³	19.78	

Regulatory Effect of Post-Processing Methods on the Corrosion Performance of WAAMed Titanium Alloys

Different post-processing processes present diverse regulatory effects on the corrosion performance of WAAMed titanium alloys, which are highly correlated with the base metal composition and corrosive environment. For TC4 alloy immersed in 3.5 wt.% NaCl aqueous solution, the binding region (BR) specimens subjected to solution treatment at 950 °C for 1 h followed by aging treatment at 600 °C for 4 h exhibited a reduction in I_{corr} from 9.87×10^{-3} A/m² to 4.37×10^{-3} A/m², which yields an obvious improvement in corrosion resistance [107]. In the strong anodic corrosion environment of a proton exchange membrane water electrolyzer with 0.5 M H₂SO₄ + 5 ppm F⁻ at 70 °C, the as-deposited WAAM TC4 has an I_{corr} of 0.779 A/m². After heat treatment at 850 °C for 2 h followed by furnace cooling, the I_{corr} decreases to 0.619 A/m², and it further drops

to 0.54 A/m^2 after heat treatment at $1050 \text{ }^\circ\text{C}$ for 2 h with furnace cooling, while the R_p increases from $0.02104 \text{ }\Omega\cdot\text{m}^2$ to $0.02844 \text{ }\Omega\cdot\text{m}^2$. This indicates that the increase in heat treatment temperature can gradually optimize its corrosion resistance in strongly acidic fluorine-containing environments [110]. For TC4-7.3% Cu alloy, laser quenching exhibits extremely strong corrosion resistance improving capability. After laser quenching at 690 W, the E_{corr} of the specimen shifts positively from -0.243 V (vs. SCE) in the as-fabricated state to -0.048 V (vs. SCE), and the I_{corr} decreases from 420 A/m^2 to 50 A/m^2 , which is the most optimized parameters among all post-processing processes [111]. In contrast, for the TMN alloy, aging treatment exerts a negative effect on its corrosion resistance. In 3.5 wt.% NaCl solution at pH = 2, after two-stage aging at $850 \text{ }^\circ\text{C} + 650 \text{ }^\circ\text{C}$ and single-stage aging at $650 \text{ }^\circ\text{C}$, the I_{corr} of the specimen increases from $2.73 \times 10^{-3} \text{ A/m}^2$ in the as-deposited state to $4.03 \times 10^{-3} \text{ A/m}^2$ and $5.65 \times 10^{-3} \text{ A/m}^2$, respectively. In 3.5 wt.% NaCl solution containing F^- , aging treatment has no significant effect on its corrosion resistance [112].

4. Corrosion Mechanisms of AMed Titanium Alloys

The corrosion mechanisms of AMed titanium alloys are rigorously divided into two hierarchical tiers: (1) universal corrosion phenomena shared by all AM processes, which distinguish AMed alloys from conventional cast/wrought counterparts; (2) process-specific vulnerabilities derived from unique thermal histories and microstructural features, which determine distinct dominant corrosion pathways.

On the microkinetic scale, local passivation behavior is governed by crystallographic texture, grain boundary characteristics, and defect/pore morphology. These factors directly alter passive film nucleation, uniformity and stability, and dominate the initiation of localized corrosion. The following sections first elaborate the universal mechanistic framework and then delineate process-specific modulation patterns.

4.1. Universal Corrosion Mechanisms of AMed Titanium Alloys

4.1.1. Passive Film Formation and Failure Mechanism

The corrosion resistance of titanium alloys relies on a spontaneously formed n-type semiconductor passive film dominated by rutile TiO_2 , with minor contributions from oxides of alloying elements. According to the point defect model, aggressive anions (Cl^- , Br^-) adsorb on oxygen vacancies in the film, promote inward migration of cation vacancies, and trigger localized film rupture at the metal/film interface once vacancies accumulate to a critical concentration, acting as the precursor of pitting initiation [48,103,108,110].

The non-equilibrium AM process degrades passive film protection from three dimensions: supersaturated V increases film porosity and ionic conductivity; Al^{3+} substitution for Ti^{4+} generates extra oxygen vacancies and reduces film compactness. In contrast, Mo, Nb and Zr form stable oxides to fill film defects and hinder aggressive ion penetration. Overall, passive films on all AMed titanium alloys exhibit higher defect density and donor concentration than conventional alloys, with greater risk of localized rupture [78,99].

4.1.2. Micro-Galvanic Corrosion and Phase-Selective Dissolution

Micro-galvanic corrosion is the intrinsic driving force for corrosion of $\alpha + \beta$ titanium alloys, originating from the potential difference between Al-rich α phase (anode, preferential dissolution) and V/Mo/Nb-rich β phase (cathode). α/β phase interfaces are the preferential initiation sites for corrosion reactions [49,78,99].

The rapid non-equilibrium solidification of AM amplifies this effect: elemental micro-segregation widens the potential gap between phases and exacerbates phase-selective dissolution. Precipitated intermetallics (e.g., Ti_2Cu) from Cu alloying form additional micro-galvanic couples with the matrix. Crystal defects including martensite lath boundaries

and dislocation accumulation regions also act as preferential dissolution sites, exerting a synergistic acceleration effect [49].

4.1.3. Multi-Scale Microstructural Modulation of Local Passivation and Localized Corrosion

Titanium alloy passivation follows typical nucleation-growth kinetics. Spatial heterogeneities in surface energy and atomic activity across crystallographic texture, grain boundaries and defect morphologies directly create disparities in local passivation behavior and further dominate the initiation and propagation of localized corrosion.

(1) Crystallographic texture and orientation-dependent corrosion anisotropy

Directional solidification under steep thermal gradients induces pronounced crystallographic texture in all AM processes. For the HCP α phase, the close-packed (0001) basal plane has the lowest surface energy and slowest anodic dissolution rate, while prismatic/pyramidal planes exhibit higher surface energy and faster dissolution kinetics. High-index planes reduce the critical nucleation Gibbs free energy of TiO_2 , leading to faster initial passivation but higher passive film defect density and lower breakdown potential. In contrast, low-index basal planes form more compact and stable passive films despite slower nucleation.

For microstructures with the c-axis preferentially oriented along the building direction, the top surface (perpendicular to building direction) is dominated by basal planes with better corrosion resistance, while the side surface exposes more high-index planes with poorer long-term film stability. This orientation-dependent passivation kinetics is the intrinsic origin of corrosion anisotropy, and its magnitude is positively correlated with texture intensity.

(2) Grain boundary characteristics and intergranular corrosion susceptibility

Grain boundary misorientation dominates intergranular passivation heterogeneity. High-angle grain boundaries (HAGBs, $>15^\circ$ misorientation) with high interfacial energy accelerate initial passivation by providing abundant nucleation sites, but the formed passive films have poor structural continuity and high defect density, making them preferential sites for aggressive ion penetration. Low-angle grain boundaries (LAGBs, $<15^\circ$ misorientation) with moderate lattice distortion enable more continuous and stable passive films.

AM processes with different cooling rates produce distinct grain boundary distributions: ultra-fast cooling (LPBF/SLM) forms abundant fine martensite laths and LAGBs, while slow cooling (WAAM, EBM) generates more HAGBs and coarse grain boundaries, directly leading to different intergranular corrosion susceptibility.

(3) Defect/pore morphology: from passivation kinetics to localized corrosion propagation

Metallurgical defects (porosity, lack of fusion, melt pool boundaries) are the critical triggers for localized corrosion, and their effects run through both microscopic passivation kinetics and macroscopic corrosion evolution.

At the microkinetic level, defect morphology controls interfacial passivation behavior via geometric constraint and stress concentration. Irregular defects with sharp edges induce high local stress and atomic activity, lowering the critical breakdown potential of passive films. The concave geometry restricts mass transport of dissolved oxygen and passivating ions, and the repassivation rate decreases exponentially with increasing defect aspect ratio, making deep/narrow defects difficult to repassivate after film rupture. Spherical gas pores with smooth walls cause weaker disturbance to passivation kinetics, while irregular lack-of-fusion defects with sharp corners are the most dangerous initiation sites for localized corrosion.

At the macroscopic scale, defects further accelerate corrosion propagation via two pathways. First, irregular defects induce a typical occluded cell effect: restricted electrolyte

convection leads to internal acidification and continuous Cl^- enrichment, accelerating matrix dissolution and promoting the transition from metastable pitting to stable pitting/crevice corrosion [26,39]. In cyclic polarization tests, metastable pitting occurring in AMed titanium alloys originates from the repeated rupture and repassivation of the passive film at these manufacturing defects. Even if most metastable pits do not develop into stable pits, they will significantly increase the passive current density of the alloy and reduce the long-term stability of the passive film [39]. Second, high residual tensile stresses concentrated at defect boundaries and dislocation accumulation regions reduce the passive film rupture energy, promote dislocation slip and generate surface active sites, forming a synergistic “stress-corrosion” acceleration effect [45,49]. High-density dislocations and LAGBs also act as preferential diffusion channels to further accelerate corrosion propagation.

4.2. Process-Specific Corrosion Vulnerabilities

As shown in Figure 7, while the corrosion behavior of AMed titanium alloys adheres to the aforementioned general core mechanisms, the fundamental differences in heat input modes, cooling rates, thermal cycle characteristics, and forming environments across different processes lead to the formation of markedly distinct microstructures and defect features, which in turn give rise to significant process-dependent variations in dominant corrosion mechanisms, localized corrosion susceptibility, and passive film evolution behavior.

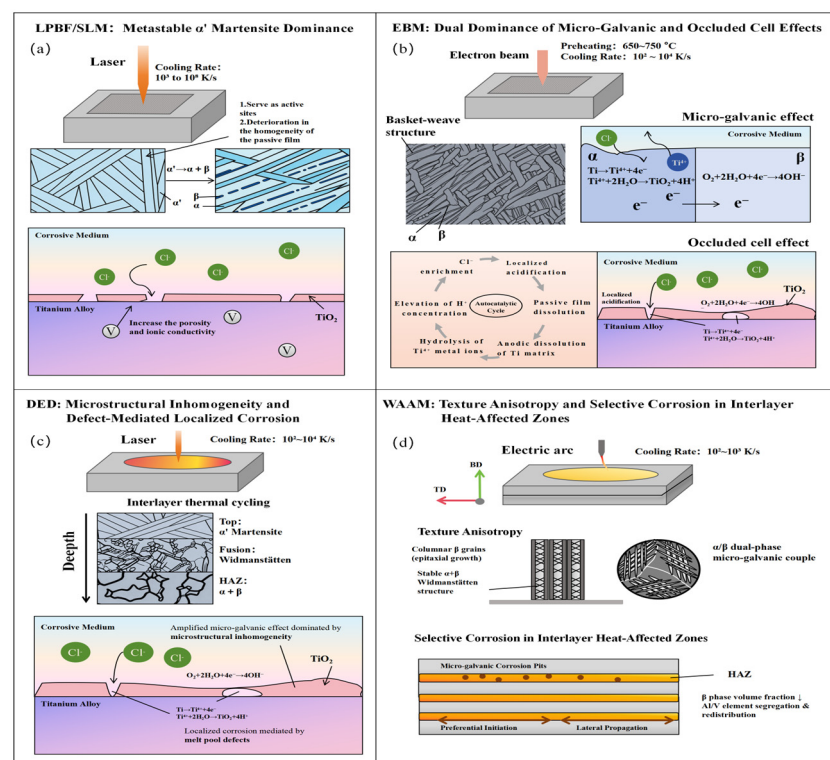


Figure 7. Specificity of corrosion mechanisms for different AM processes: (a) LPBF/SLM; (b) EBM; (c) DED; (d) WAAM.

4.2.1. LPBF/SLM: Vulnerabilities from Metastable α' Martensite and High Residual Stress

The core corrosion vulnerabilities of LPBF and SLM are inherently determined by their ultra-high cooling rate of 10^3 to 10^8 K/s, which gives rise to two process-specific features: a single-phase microstructure dominated by metastable acicular α' martensite and high residual tensile stress induced by the steep thermal gradient. These two characteristics are

unique to high-energy laser powder bed fusion processes and constitute the root causes of their distinct corrosion behavior.

The ultra-high cooling rate suppresses the diffusion of alloying elements and the $\beta \rightarrow \alpha$ phase transformation, resulting in a supersaturated solid solution of vanadium in the α' martensite phase. While the high lattice distortion and dislocation density of α' martensite provide more active sites for passive film nucleation, they also lead to a significant decrease in the uniformity of the passive film. Vanadium in supersaturated solid solution makes it difficult to form stable protective oxides in the passive film, and its dissolution further increases the porosity and ionic conductivity of the film, resulting in a much higher defect density than that of conventional cast and wrought alloys [49,78].

When the heat treatment temperature exceeds 600 °C, the metastable α' martensite begins to decompose into stable α phase and V-rich β phase, forming corrosion galvanic couples at the α/β phase interfaces, and phase-selective dissolution becomes the main driving force for corrosion. At 800 °C, α' martensite is completely decomposed into a coarsened $\alpha + \beta$ microstructure. The increased number of phase boundaries and aggravated elemental segregation further amplify the micro-galvanic effect, leading to the deterioration of corrosion resistance [49].

4.2.2. EBM: Vulnerabilities from High Surface Roughness and Dual-Phase Lamellar Microstructure

EBM is formed in a high-vacuum environment with the characteristic of high-temperature preheating of the powder bed at 650 to 750 °C, and its cooling rate is much lower than that of LPBF/SLM. Its corrosion mechanism is characterized by the bi-model dominance of the micro-galvanic effect of the stable dual-phase microstructure and the occluded cell effect induced by high surface roughness.

No metastable α' martensite is formed in EBMed titanium alloys, which directly develop a lamellar $\alpha + \beta$ microstructure dominated by Widmanstätten/basket-weave structures. Therefore, corrosion is dominated by α/β dual-phase micro-galvanic corrosion from the initial stage of forming, and there is no mechanism transformation caused by metastable phase decomposition [32,83]. The dense α/β lamellar interfaces and the epitaxially grown β grains along the building orientation provide rapid diffusion channels for Cl^- , leading to the preferential propagation of corrosion along grain boundaries and phase interfaces [83]. Meanwhile, the surface roughness of EBMed parts is much higher than that of LPBF/SLMed specimens. The strong occluded cell effect induced by unmelted powders, stair-stepping effect and irregular pits is the foremost cause of the deterioration of corrosion resistance for AB EBM alloys [84,86].

Post-processing exerts the most significant regulatory effect on the corrosion mechanism of EBMed titanium alloys. Machining could completely eliminate surface defects and inhibit the occluded cell effect, reducing the I_{corr} by two orders of magnitude. HIP can close internal pores, improve the homogeneity of the dual-phase microstructure, and transform the corrosion mechanism from localized pitting to uniform dissolution of the passive film. Surface modification processes such as MAO and PN can completely change the dominant corrosion mechanism by constructing dense protective coatings [32,86].

4.2.3. DED: Vulnerabilities from Fusion Zone Heterogeneity and Large-Size Irregular Defects

DED is centered on coaxial powder/wire feeding laser cladding, with a lower cooling rate than LPBF/SLM and the molten pool undergoing complex and repeated thermal cycles. Its unique corrosion vulnerabilities lie in the pronounced microstructural inhomogeneity between the fusion zone and heat-affected zone (HAZ), as well as the large-size, irregularly shaped metallurgical defects introduced by the coaxial powder feeding mode.

A large amount of metastable α' martensite tends to form during DED fabrication, resulting in high corrosion susceptibility [117]. Meanwhile, repeated interlayer thermal cycles cause significant microstructural inhomogeneity in the fusion zone and HAZ, such as coarsened Widmanstätten structures near the fusion line, which aggravates the local micro-galvanic effect and becomes the preferential initiation site for corrosion [34]. Compared with LPBF/SLM, DED has a larger laser spot and a wider HAZ, so the influence of microstructural inhomogeneity on corrosion behavior is more prominent. In addition, the DED process is more prone to generating lack-of-fusion and porosity defects with larger sizes and more irregular morphologies, leading to a more significant occluded cell effect. Laser power is the fundamental parameter regulating the defect content, and both excessively low and high laser power will form preferential corrosion sites [103].

The flexibility of DED in alloying design and coating preparation makes its corrosion mechanism prominently manifested as the modification effect of alloying elements on the passive film. The addition of elements such as Mo, Nb and Si can directly optimize the composition and compactness of the passive film and inhibit the initiation and propagation of pitting corrosion. This modification mechanism has been widely applied in DED systems [99].

4.2.4. WAAM: Vulnerabilities from Interlayer HAZ Variations and Strong Columnar Grain Texture

WAAM uses an electric arc as the melting heat source, with a significantly lower cooling rate than powder bed fusion processes, and no α' martensite is formed during the forming process. Therefore, its corrosion mechanism is fundamentally different from that of powder bed processes [106,113], with characteristics of texture-mediated corrosion anisotropy and selective corrosion in interlayer HAZs.

WAAMed titanium alloys are mainly composed of a stable $\alpha + \beta$ dual-phase Widmanstätten structure. The core driving force for corrosion is the micro-galvanic corrosion between α and β phases, as well as the microstructural and textural inhomogeneity generated during the arc melting–solidification process [110]. The strong thermal gradient along the deposition direction induces the epitaxial growth of β grains, forming a columnar grain structure with strong texture, which imparts extremely strong anisotropy to the corrosion behavior of the alloy [13,113].

Selective corrosion in interlayer HAZs is a unique weak point of WAAMed titanium alloys. During the layer-by-layer deposition process, the thermal effect of the newly deposited bead on the underlying substrate forms repeatedly distributed multilayer HAZs. After multiple thermal cycles, the α phase in the HAZs is coarsened, the volume fraction of β phase is reduced, and elemental segregation occurs. These changes create an electrochemical potential difference between the HAZs and the deposited layer matrix, inducing local micro-galvanic corrosion. Corrosion preferentially initiates in the interlayer HAZs and propagates laterally along the interlayer interfaces, eventually leading to interlayer delamination failure of the components [1,109]. In addition, the complex cyclic thermal history of WAAMed components results in non-uniform residual stress distribution, and the synergistic acceleration effect of stress and corrosion is more prominent than that of other processes [108,110].

To further clarify the process-specific corrosion rules and provide targeted guidance for performance optimization, the dominant corrosion mechanisms, characteristic microstructures and most effective improvement strategies of the four AM processes are systematically compared in Table 7.

Table 7. Comparison of dominant corrosion mechanisms and improvement strategies for different AM processes.

Process	Dominant Mechanism	Characteristic Microstructure	Effective Improvement Strategies
LPBF/SLM	α' martensite-mediated passive film breakdown; α/β micro-galvanic corrosion; defect-induced localized corrosion	Fine acicular α' martensite; textured columnar grains; high dislocation density	Sub-transus annealing; HIP; surface modification (SB/PO)
EBM	α/β micro-galvanic corrosion; surface-occluded cell effect; intergranular corrosion propagation	Lamellar $\alpha + \beta$ Widmanstätten structure; epitaxial β grains; high surface roughness	Machining/polishing; HIP; protective surface coating (MAO/PN)
DED	Micro-galvanic effect amplified by microstructural inhomogeneity; localized corrosion from large defects; alloying-modified passive film	Distinct fusion zone and HAZ; mixed-size microstructure; large irregular defects	Process parameter optimization; stress relief annealing; Mo/Nb/Zr alloying
WAAM	Texture-induced corrosion anisotropy; selective corrosion at interlayer HAZs; interlayer micro-galvanic effect	Coarse textured columnar grains; multi-thermal-cycle interlayer HAZs	Solution + aging treatment; interlayer rolling; laser surface quenching

5. Conclusions and Outlook

5.1. Conclusions

This review systematically analyzes the corrosion behavior and underlying mechanisms of titanium alloys fabricated by four mainstream AM processes (LPBF/SLM, EBM, DED, WAAM), revealing their universal corrosion mechanisms and process-specific characteristics. All AMed titanium alloys share three common mechanisms: passive film failure following the point defect model, α/β phase micro-galvanic corrosion amplified by non-equilibrium solidification, and localized corrosion induced by metallurgical defects. Their passive films generally have higher defect densities than conventional cast/wrought alloys, resulting in inferior localized corrosion resistance.

Different AM processes exhibit distinct dominating mechanisms: LPBF/SLM is dominated by metastable α' martensite-mediated passive film failure; EBM by dual effects of micro-galvanic corrosion and occluded cell effect; DED by microstructural inhomogeneity and large-size defect-induced corrosion; WAAM by texture anisotropy and interlayer HAZ selective corrosion. The corrosion resistance is synergistically regulated by matrix composition, post-treatment and service environment, and the combination of process optimization and post-treatment is the prevailing enhancement strategy.

5.2. Outlook

Despite extensive research on the corrosion behavior of AMed titanium alloys, the current literature database has notable inherent limitations that restrict cross-study comparability and reliable engineering translation. First, corrosion testing procedures lack universal standardization. Variations in sample surface preparation, electrochemical test parameters (e.g., scan rate, reference electrode type, pre-immersion time) and environmental conditions introduce systematic deviations, making direct quantitative comparison of results across studies extremely difficult. Second, the high heterogeneity of AM processing parameters (energy input, scanning strategy, powder quality, etc.) leads to divergent microstructures and defect characteristics, while most studies focus on narrow process windows and fail to establish a unified process–microstructure–corrosion mapping relationship. Third, current evaluations rely heavily on short-term laboratory accelerated tests, and long-term corrosion degradation data under realistic service environments, especially

multi-field coupled conditions, are severely insufficient, which hinders accurate prediction of full-life corrosion durability.

Targeting the above limitations, future research should focus on the following frontier directions to promote the reliable long-term engineering application of AMed titanium alloys.

First, advanced in situ monitoring and characterization methods should be applied to reveal the dynamic evolution mechanism of corrosion processes. Most existing studies depend on ex situ post-test characterization, which cannot capture transient processes such as passive film nucleation, metastable pitting initiation and localized corrosion propagation. Multi-scale in situ techniques including in situ electrochemical atomic force microscopy, in situ Raman spectroscopy and embedded fiber-optic electrochemical sensors will enable real-time dynamic characterization of corrosion behavior from nanoscale to component scale, clarifying the critical conditions for stable pitting initiation and the synergistic damage mechanism of stress and corrosion at defect sites.

Second, artificial intelligence and machine learning tools should be deeply integrated to realize intelligent prediction and precise regulation of corrosion durability. On the one hand, data-driven long-term corrosion degradation models can be constructed based on accumulated experimental data. By integrating process parameters, microstructural features, environmental factors and electrochemical data, machine learning algorithms can establish high-precision quantitative mapping between multiple influencing factors and long-term corrosion degradation behavior, bridging the gap between laboratory accelerated tests and actual long-term service performance. On the other hand, machine learning enables integrated optimization of process–microstructure–corrosion performance. By constructing a multi-scale correlation database, reverse optimization of AM process parameters oriented to target corrosion resistance can be achieved, greatly reducing trial-and-error costs. In the long term, combined with digital twin technology, full-lifecycle corrosion digital twins of AMed titanium alloy components can be built to support real-time corrosion state assessment and remaining life prediction.

Third, novel titanium alloy compositions explicitly tailored for AM processing should be designed to achieve intrinsically excellent corrosion resistance. Currently widely used titanium alloys (e.g., TC4) were originally developed for conventional casting and forging processes, and their composition design does not match the non-equilibrium solidification characteristics of AM, resulting in element segregation, metastable phase formation and poor passive film stability in the as-built state. Future alloy design should target the unique metallurgical environment of AM: by rationally regulating the type and content of alloying elements, the segregation tendency during rapid solidification can be reduced, the composition and compactness of the passive film can be optimized, and the formation of harmful intermetallic phases can be suppressed. AM-oriented metastable β -titanium alloys or multi-element functional alloys containing Nb, Mo and Zr can achieve superior and stable intrinsic corrosion resistance, reducing the dependence on subsequent post-treatment processes.

In addition, in-depth research on multi-field coupled corrosion mechanisms, engineering promotion of high-efficiency surface modification technologies, and establishment of standardized full-lifecycle corrosion evaluation systems are also important development directions for the future.

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Abbreviations

The following abbreviations are used in this manuscript:

Abbreviation	Full Term	Abbreviation	Full Term
Aa	Alkali activation	NiTi SMAs	NiTi shape memory alloys
AB	As-built	NSS	Network structure surface
AC	Air cooling	OA	Oxalic acid
AE	Acid etching	OI	Oxidizing ions
			Phosphate-buffered saline (1 L of deionized water: 8.18 g NaCl, 0.22 g KCl, 1.13 g Na ₂ HPO ₄ ·2H ₂ O, 0.56 g NaH ₂ PO ₄ ·2H ₂ O, adjusted to pH 7.4 with dilute sodium hydroxide solution at 37 °C.)
AM	Additive manufacturing	PBS	
	Artificial saliva (1 L of deionized water: 0.400 g NaCl, 0.400 g KCl, 0.795 g CaCl ₂ ·2H ₂ O, 0.690 g NaH ₂ PO ₄ ·2H ₂ O, 0.005 g Na ₂ S·9H ₂ O, 1.000 g urea, adjusted to pH 5.3 with lactic acid at 37 °C)	PDP	Potentiodynamic polarization
AS		PN	Plasma nitriding
BD	Building direction	PO	Plasma oxidation
BR	Bonding region	P-P HT	Pressure-free annealing
Cp-Ti	Commercially pure titanium	P-WAAM	Pulsed wire arc additive manufacturing
C-WAAM	Conventional wire arc additive manufacturing	RDF	Runway deicing fluid
DED	Directed energy deposition	Rp	Polarization resistance
DLD	Direct laser deposition		Ringer's solution (1 L of bidistilled water: 8.500 g NaCl, 0.300 g KCl, 0.330 g anhydrous CaCl ₂ , 0.200 g NaHCO ₃ , and a pH of 7.4 at 37 °C)
DSS	Dispersed structure surface	RS	
	Dynamic Hank's solution (1 L of distilled water: 8.000 g NaCl, 0.350 g NaHCO ₃ , 0.400 g KCl, 0.060 g KH ₂ PO ₄ , 0.048 g Na ₂ HPO ₄ , 0.140 g CaCl ₂ , 0.098 g MgSO ₄ , 1.000 g D-glucose, 0.011 g phenol red sodium salt, and a pH of 7.35 adjusted by diluted HCl and NaOH at 37 ± 0.5 °C)	SB	Sand blasting
DT			Simulated body fluid (1 L of bidistilled water: 7.996 g NaCl, 0.350 g NaHCO ₃ , 0.224 g KCl, 0.228g K ₂ HPO ₄ ·3H ₂ O, 0.305 g MgCl ₂ ·6H ₂ O, 40 mL 1 mol/L HCl, 0.278 g CaCl ₂ , 0.071 g Na ₂ SO ₄ , 6.057 0 NH ₂ C(CH ₂ OH) ₃ , and a pH of 7.4 at 37 °C)
EBM	Electron beam melting	SBF	

Ecorr	Corrosion potential		
EP	Electropolishing	SFPB	Supersonic fine particle bombardment
F	Forging	SLM	Selective laser melting
FC	Furnace cooling	SPC	Simulated physiological conditions
GA-Ti	Gas atomized titanium	SPS	Spark plasma sintering
			Synthetic seawater
H	Horizontal	SSW	(1 L of deionized water: 26.72 g NaCl, 0.72 g KCl, 1.15 g CaCl ₂ , 2.26 g MgCl ₂ , 3.25 g MgSO ₄ , 0.20 g NaHCO ₃)
HAM	PBF-DED hybrid		Static Hank's solution
			(1 L of distilled water: 8.000 g NaCl, 0.350 g NaHCO ₃ , 0.400 g KCl, 0.060 g KH ₂ PO ₄ , 0.048 g Na ₂ HPO ₄ , 0.140 g CaCl ₂ , 0.098 g MgSO ₄ , 1.000 g D-glucose, 0.011 g phenol red sodium salt, and a pH of 7.35 adjusted by diluted HCl and NaOH at 37 ± 0.5 °C)
HAZ	Heat-affected zone	ST	
	Hank's balanced salt solution		
	(1 L of deionized water: 8.000 g NaCl, 0.408 g KCl, 0.142 g CaCl ₂ , 0.105 g MgSO ₄ ·7H ₂ O, 0.111 g MgCl ₂ ·6H ₂ O, 0.065 g Na ₂ HPO ₄ ·2H ₂ O, 0.063 g KH ₂ PO ₄ , 1.000 g D-Glucose, 0.353 g NaHCO ₃ , tested at 25 °C)		
HBSS		STA	Solution treatment and aging heat treatment
HC	Hydrogen charging	TC4	Ti-6Al-4V
HDLH-Ti	Hydrogenation-dehydrogenation titanium	TC11	Ti-6.5Al-3.5Mo-1.5Zr-0.3Si
HIP	Hot isostatic pressing	TD	Transverse direction
HS	Hank's solution	Ti4822	Ti-48Al-2Cr-2Nb
HT	Heat treatment	Ti536	Ti5Al3V6Cu
Icorr	Corrosion current density	Ti-55531	Ti-5Al-5Mo-5V-3Cr-1Zr
IPCs	Interpenetrating phase composites	Ti6321	Ti-6Al-3Nb-2Zr-1Mo
IQ	Ice cooling	TMN	Ti-0.3Mo-0.8Ni
LA	Lactic acid	TMZF	Ti-12Mo-6Zr-2Fe
LC-CPF	Laser cladding with coaxial powder feeding	TNZ	Ti-13Nb-13Zr
LCD	Laser cladding deposition	TNZT	Ti-35Nb-7Zr-5Ta
LENS	Laser-engineered net shaping	TNZTS	Ti-34.5Nb-6.9Zr-4.9Ta-1.4Si
LMD	Laser metal deposition	TSG	Trailing shielding gas
LPBF	Laser powder bed fusion	V	Vertical
LSF	Laser solid forming	VA	Vacuum annealing
LSM	Laser surface melting	WAAM	Wire arc additive manufacturing
LWAM-V	Laser wire additive manufacturing—vacuum	WPC-AM	Wire-powder collaborative arc additive manufacturing
MAO	Micro-arc oxidation	WQ	Water quenching
MKR	Modified Kroll's reagent	WR	Wrought
MPAM	Micro-plasma arc additive manufacturing	μ-PAPAM	Micro-plasma arc powder additive manufacturing
MWAAM	Multi-wire arc additive manufacturing		

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