

Article

Corrosion Properties of Wrought Ti-6Al-4V and SLMed Ti-6Al-4V in 0.05 mol/L H₂SO₄: A Comparison Investigation

Huiling Zhou, Lei Dong, Xiaoru Zhuo, Sheng Lu * and Yanxin Qiao * 

School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212100, China; zhouhl@just.edu.cn (H.Z.)

* Correspondence: lusheng_ktz@just.edu.cn (S.L.); yxqiao@just.edu.cn (Y.Q.)

Abstract

Although the corrosion properties of Ti-6Al-4V have been widely studied, the differences in passive film evolution and corrosion mechanism between wrought and SLMed Ti-6Al-4V in acidic service environments are still unclear. In this work, the corrosion behaviors of wrought and selective laser melting (SLMed) Ti-6Al-4V alloys in 0.05 mol/L H₂SO₄ solution were systematically investigated using electrochemical impedance spectroscopy, potentiodynamic polarization curves, Mott–Schottky analysis and XPS depth profiling. Wrought and SLM-fabricated Ti-6Al-4V were selected to reveal the effects of typical forming processes on corrosion resistance, considering their wide applications and distinct microstructures. Electrochemical results demonstrate that the wrought alloy exhibits a higher polarization resistance, a thicker passive film, and a lower corrosion current density, corresponding to superior corrosion resistance. Mott–Schottky analysis reveals that the passive films formed on both alloys show n-type semiconductor characteristics, while the wrought alloy possesses a lower carrier concentration, fewer defects, and a more compact film structure. XPS depth analysis indicates that the content of TiO₂ in the passive films decreases with increasing etching depth, accompanied by an increase in TiOOH, TiO, and metallic Ti.

Keywords: selective laser melting (SLM); Ti-6Al-4V alloy; corrosion; electrochemical behavior; passive

1. Introduction

Titanium alloys have been widely applied in biomedical engineering, marine engineering, aerospace, and other fields, owing to their outstanding properties including high strength, low density, and excellent corrosion resistance [1–6]. With the increasing complexity and diversification of application requirements, selective laser melting (SLM) has emerged as a major research focus in materials science due to its high flexibility and capability to fabricate components with complex structures [7]. Edwards et al. [8] investigated the fatigue properties of SLMed Ti-6Al-4V and found that its fatigue resistance was significantly inferior to that of the wrought alloy, mainly owing to the unavoidable formation of pores and residual stresses during manufacturing. Leuders et al. [9] investigated the crack propagation and fatigue behavior of SLMed Ti-6Al-4V and similarly observed poor fatigue resistance caused by defects such as porosity.

To date, most domestic and international studies have concentrated on the mechanical properties of SLMed titanium alloys, while differences in corrosion resistance between



Academic Editors: Eric Hug and Tomáš Prošek

Received: 13 February 2026

Revised: 24 March 2026

Accepted: 1 April 2026

Published: 3 April 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

SLMed and conventionally wrought titanium alloys have also been recognized. Thermodynamically, titanium is a relatively reactive metal. Previous studies [7,10–12] have verified that the excellent corrosion resistance of titanium alloys arises mainly from the dense passive film formed on the surface, which blocks the transfer of electrons and ions. Numerous researchers have confirmed that the primary component of this passive film is TiO_2 [4,13–16], which behaves as a wide-bandgap semiconductor with high resistivity and thus effectively protects the substrate. However, the formation of the TiO_2 passive film can be hindered in specific environments such as those containing high concentrations of halide ions. Jesus et al. [17] investigated the corrosion behavior of titanium alloys under acidic conditions and found that the passive film was damaged by the aggressive action of anions such as Cl^- and SO_4^{2-} . Macdonald et al. [18,19] developed a model for passivation and passivity breakdown based on the point defect model (PDM), assuming that cation migration from the oxide–electrolyte interface to the metal–oxide interface gives rise to mass transport, and simulating how anions like Cl^- can affect vacancy diffusion. Lebea et al. [20] studied the corrosion resistance of SLMed titanium alloys for dental applications in 3.65 wt% NaCl solution and Ringer’s solution, revealing that the weight loss of SLMed titanium alloys was much higher in Ringer’s solution (containing KCl, NaCl, CaCl_2 , etc.) than in 3.65 wt% NaCl solution due to varying degrees of pitting corrosion. Li et al. [4] examined the corrosion behavior of TA15 titanium alloy in HCl solution and illustrated the effect of Cl^- adsorption on pitting initiation. They reported that wrought TA15 exhibited better corrosion resistance than SLMed TA15 in 1 mol/L HCl solution. Both alloys suffered pitting corrosion, but larger and deeper pits appeared on the SLMed TA15 samples, whereas the wrought TA15 showed shallower and more uniform pits, indicating more severe corrosion in the SLMed alloy.

At present, research on the corrosion behavior of titanium alloys is primarily focused on chloride-containing media. However, in practical conditions such as polluted marine environments and petroleum extraction, corrosive components like sulfuric acid are often present. In such sulfate-containing media, titanium alloys typically exhibit characteristic uniform corrosion, and the influence mechanisms of different alloying elements on their corrosion kinetics also show significant variations. There are relatively few studies focusing on the effects of sulfate ions on the corrosion behavior of titanium alloys in acidic, polluted marine environments. In this work, wrought Ti-6Al-4V and SLMed Ti-6Al-4V alloys were used as research materials. Their corrosion and passivation behaviors in 0.05 mol/L H_2SO_4 solution were systematically investigated. The microstructures were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Potentiodynamic polarization and Mott–Schottky measurements were performed to analyze the corrosion behavior. The composition and chemical states of the passive films were examined using X-ray photoelectron spectroscopy (XPS).

2. Experimental Procedures

The materials employed in this study were wrought Ti-6Al-4V alloy and SLM-produced Ti-6Al-4V alloy. Their main chemical compositions are listed in Table 1. The SLMed-TC4 titanium alloy was fabricated on a commercial Concept Laser M2 powder bed fusion apparatus, which has a maximum laser output power of 400 W and a maximum laser scanning speed of 1000 mm/s. The processing parameters of SLM were set as follows: layer thickness of 30 μm , laser power of 280 W, laser scanning speed of 1000 mm/s, and the protective atmosphere was high-purity argon (99.99%). The wrought Ti-6Al-4V samples were prepared as rectangular sheets with dimensions of 10 × 5 × 2 mm, while the SLM samples were cylindrical with a diameter of $\phi 14$ mm and a thickness of 2 mm.

Table 1. Chemical compositions of the two tested Ti-6Al-4V alloys.

	Al	V	Fe	O	Ti
wrought	5.98	4.03	0.33	0.08	Bal
SLMed	6.12	4.20	0.06	0.15	Bal

The corrosion behavior was characterized in 0.05 mol/L H₂SO₄ solution under thermo-static conditions at 25 °C. In this experiment, the test solution was used without deaeration. All samples were ground with SiC abrasive papers to remove surface oxide scales, then soaked in anhydrous ethanol for 5 min to eliminate surface contaminants. The sample thickness was maintained at no less than 2 mm. For electrochemical measurements, each sample was mounted in epoxy resin, exposing a working area of 0.5 cm² for the wrought alloy and 1.54 cm² for the SLM alloy. After the resin was fully cured, the encapsulated samples were removed and successively ground with SiC papers. The surfaces were then polished with alumina suspension, followed by ultrasonic cleaning in anhydrous ethanol for 5 min to remove residual contaminants. Kroll's reagent (3 vol% HF + 9 vol% HNO₃) was used to etch the sample surfaces for microstructural observation [21].

X-ray diffraction analysis was conducted using a Rigaku D/Max 2400 X-ray diffractometer (Rigaku, Tokyo, Japan) over a 2 θ range of 30–80° at a scanning rate of 6°/min. Microstructural characterization was performed using a Zeiss Merlin Compact field-emission scanning electron microscope (SEM) (Zeiss, Oberkochen, Germany). Corrosion performance was evaluated using a Gamry 1010E electrochemical workstation (Gamry, Warminster, PA, USA). The experiment was carried out using a platinum sheet electrode as the counter electrode and a saturated calomel electrode as the reference electrode, with measurements including electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and Mott–Schottky analysis. An open circuit potential test was performed for 3600 s in 0.05 mol/L H₂SO₄ solution before each electrochemical test to stabilize the material surface. The EIS measurements were performed at open circuit potential with a 10 mV sinusoidal AC perturbation over the frequency range from 10^{−2} Hz to 10⁵ Hz. Mott–Schottky analysis was performed at a frequency of 1000 Hz with an AC signal amplitude of 10 mV. After testing, the current density of the material stabilized following 3600 s of potentiostatic polarization. Therefore, prior to the measurement, the working electrode was polarized at a passivation potential of 0.9 V for 3600 s to form a stable passive film. A minimum of three parallel samples were tested to ensure the reliability of the experimental results. All experiments were conducted in accordance with the standard GB/T 24196-2009 [22]. The composition and depth distribution of the passive films were characterized by a Thermo Scientific Nexsa X-ray photoelectron spectrometer (XPS) (Thermo Fisher Scientific, Waltham, MA, USA). Before the test, all specimens were subjected to potentiostatic polarization at 0.9 V for 3600 s.

3. Results and Discussion

3.1. Microstructural Analysis

Figure 1 presents the XRD patterns of the two Ti-6Al-4V alloys. The diffraction peaks of the forged alloy can be well indexed to the characteristic peaks of the α phase and β phase, indicating a typical $\alpha + \beta$ duplex structure. The diffraction intensity of the α phase is significantly higher than that of the β phase, suggesting a higher volume fraction of the α phase. The SLM-produced Ti-6Al-4V alloy shows similar diffraction peaks to the forged alloy, also corresponding to an $\alpha + \beta$ duplex titanium alloy [15,23].

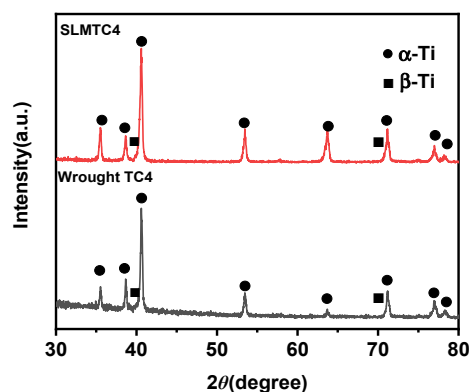


Figure 1. XRD results of Ti-6Al-4V alloy prepared by wrought and SLM.

As observed from the microstructural morphologies of the two Ti-6Al-4V alloys in Figure 2, distinct microstructural features are present between the two materials. The forged alloy consists of equiaxed α -Ti grains and lamellar β -Ti, with the β phase homogeneously dispersed. In contrast, the SLM-fabricated alloy exhibits an acicular microstructure. This is attributed to the extremely high laser energy density and small molten pool size during SLM processing, which enables rapid heat conduction through the solidified layer and substrate, leading to an ultrafast solidification rate. Such rapid cooling suppresses the equilibrium phase transformation and promotes the formation of non-equilibrium acicular α' martensite [24,25].

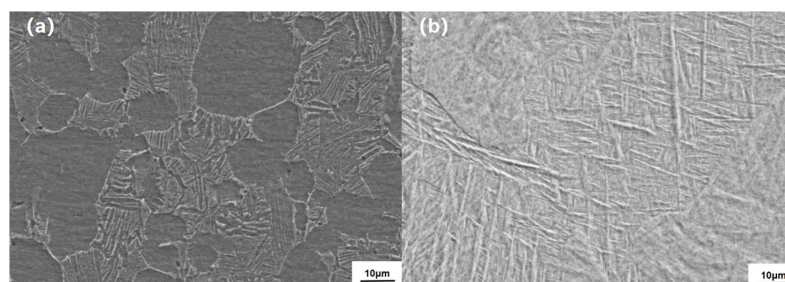


Figure 2. SEM of the two tested Ti-6Al-4V alloys: (a) wrought Ti-6Al-4V, (b) SLM Ti-6Al-4V.

3.2. Electrochemical Studies

Figure 3 shows the electrochemical impedance spectroscopy (EIS) of two tested Ti-6Al-4V alloys in 0.05 mol/L H_2SO_4 solution. As shown in Figure 3a, the Nyquist plots exhibit an incomplete single capacitive loop, which arises from the charge-transfer process occurring at the electrolyte/electrode interface [26,27]. The radius of the capacitive loop is indicative of the charge-transfer resistance associated with the reaction at the electrode/electrolyte interface. The larger radius corresponds to a higher charge-transfer resistance, greater kinetic hindrance to interfacial electron transfer, and a lower corrosion rate, thereby signifying superior corrosion resistance of the material [28]. The capacitive loop radius of the wrought Ti-6Al-4V is distinctly larger than that of the SLM Ti-6Al-4V, demonstrating that the wrought Ti-6Al-4V has superior corrosion resistance in 0.05 mol/L H_2SO_4 solution.

The Bode plots of the two Ti-6Al-4V alloys are presented in Figure 3b. The impedance modulus $|Z|$ at a frequency of 10^5 Hz represents the solution resistance of the corrosive medium, whereas that at a frequency of 10^{-2} Hz corresponds to the polarization resistance of the material [29]. The low-frequency impedance moduli $|Z|_{0.01}$ of wrought and SLM Ti-6Al-4V are $1.28 \times 10^6 \Omega \cdot \text{cm}^2$ and $4.09 \times 10^5 \Omega \cdot \text{cm}^2$, respectively. The wrought alloy exhibits a higher value, which can be attributed to differences in the properties of the passive film. The phase angle profiles in the Bode plots reveal that both Ti-6Al-4V alloys display a single time constant. As reported in the literature [28–30], the maximum phase

angle at low frequency originates from the formation of a passive film, while that at high frequency is related to the formation of the electric double layer [29]. Compared with the SLM Ti-6Al-4V, the wrought Ti-6Al-4V shows a maximum phase angle closer to 90° , indicating a higher interfacial charge-transfer resistance/polarization resistance and a more protective passive film on the substrate.

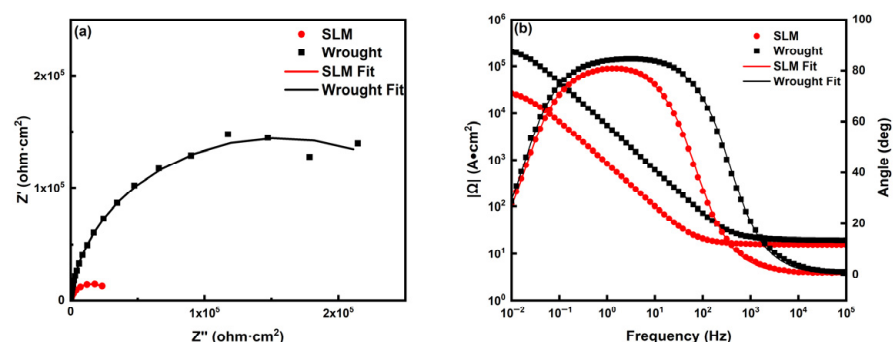


Figure 3. EIS of the two tested Ti-6Al-4V alloys in 0.05 mol/L H_2SO_4 solution: (a) Nyquist plot, (b) Bode plot.

The EIS data were fitted using the equivalent circuit depicted in Figure 4, and the corresponding fitting parameters for the two Ti-6Al-4V alloys are listed in Table 2, where R_s is the resistance of 0.05 mol/L H_2SO_4 , R_f is the film resistance, CPE is the constant phase element, CPE_{dl} is the constant phase element of the double layer, n is the CPE exponent and R_{ct} is the charge transfer resistance. In corrosion electrochemical measurements, surface inhomogeneity of the electrode generally gives rise to a relaxation effect, which makes it necessary to employ the CPE instead of an ideal capacitor to fit the EIS [28,30,31]. In general, a higher R_f implies greater resistance to interfacial charge transfer, stronger protective ability of the passive film, and better corrosion resistance of the material [30]. As shown in the table, the R_f values of wrought and SLM Ti-6Al-4V are $4.36 \times 10^5 \Omega \cdot \text{cm}^2$ and $3.49 \times 10^4 \Omega \cdot \text{cm}^2$, respectively. The R_f of the wrought alloy is approximately 3.22 times that of the SLM Ti-6Al-4V, indicating that the passive film formed on the SLM Ti-6Al-4V provides relatively weak protection to the substrate [4].

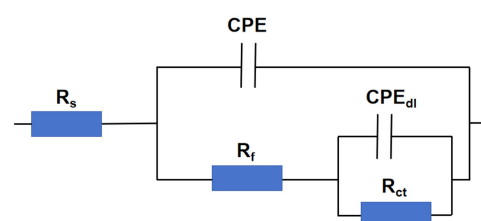


Figure 4. An equivalent circuit is used for the quantitative evaluation of the EIS.

Table 2. The fitted 4 EIS data of wrought and SLM Ti-6Al-4V alloys.

	R_s ($\Omega \cdot \text{cm}^2$)	R_f ($\Omega \cdot \text{cm}^2$)	CPE ($\Omega^{-1} \cdot \text{S}^n \cdot \text{cm}^{-2}$)	n	CPE_{dl} ($\Omega^{-1} \cdot \text{S}^n \cdot \text{cm}^{-2}$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	n_2	$d_{ox}/(\text{nm})$
wrought	21.65	4.36×10^5	2.61×10^{-5}	0.99	3.41×10^{-6}	3.12×10^5	1	20.32
SLM	15.75	3.49×10^4	6.9×10^{-4}	0.94	1.52×10^{-7}	3.17×10^4	0.89	7.69

When estimating the passive film thickness using the parallel-plate capacitor model based on EIS data, it is assumed that the passive film is a homogeneous, compact, and defect-free single oxide layer behaving as an ideal parallel-plate capacitor, and the capacitive response is predominantly contributed by the outer passive film while the influence of the

double layer is neglected. The thickness of the passive film can be determined from EIS using Equation (1) [32]:

$$d_{\text{ox}} = \frac{\varepsilon \varepsilon_0 A}{C} \quad (1)$$

where d_{ox} is the thickness of the passive film, C could be determined from EIS data following constant potential polarization measurements. A is the surface area of the sample, and ε is the dielectric constant (the main component of the passive film is TiO_2 , and a value of 60 is generally adopted) [33,34]. ε_0 is the permittivity of vacuum (8.85×10^{-14} F/cm). The calculated results are summarized in Table 2. It can be observed in Table 3 that the passive film thicknesses of wrought and SLM Ti-6Al-4V alloys are 20.32 nm and 7.69 nm, respectively. The passive film formed on the wrought Ti-6Al-4V is slightly thicker than that on the SLM.

Figure 5 presents the potentiodynamic polarization curves of wrought and SLM Ti-6Al-4V alloys in 0.05 mol/L H_2SO_4 solution. The potentiodynamic polarization measurement was conducted over a potential range from $-1.5 \text{ V}_{\text{SCE}}$ to 2 V_{SCE} . Both alloys exhibit distinct cathodic and anodic regions in the potentiodynamic polarization curves. The cathodic region generally reflects the difficulty of the hydrogen evolution reaction. The SLMed alloy is located at the upper right of the wrought alloy, indicating a higher hydrogen evolution rate. The anodic region characterizes the corrosion and passivation behavior of the materials, and both alloys show obvious passivation behavior. The potentiodynamic polarization curves were fitted using the Tafel extrapolation method [35], and the corresponding fitting results are listed in Table 3. E_{corr} is the corrosion potential, i_{corr} is the corrosion current density, and i_p is the passivation current density. It can be concluded from the fitting data that the E_{corr} of the two alloys is close. However, a remarkable difference is observed in their corrosion current densities i_{corr} : the E_{corr} value of SLM Ti-6Al-4V is approximately 3.94 times that of the wrought alloy, indicating superior corrosion resistance of Ti-6Al-4V [4]. In the passive region, the passive current densities i_p of the wrought and SLM alloys are $(2.14 \pm 0.13) \times 10^{-6} \text{ A/cm}^2$ and $(6.78 \pm 0.16) \times 10^{-6} \text{ A/cm}^2$, respectively. The lower i_p of the wrought Ti-6Al-4V alloy demonstrates that its passive film provides stronger protection to the substrate. When the potential exceeds $0.75 \text{ V}_{\text{SCE}}$, the passive current densities of both alloys increase significantly, indicating that the passive film is damaged and the anodic dissolution takes place again. The appearance of secondary passivation occurs for both alloys at an applied potential of $1.27 \text{ V}_{\text{SCE}}$. It demonstrates that the passive film on the titanium alloy has moderate self-healing ability.

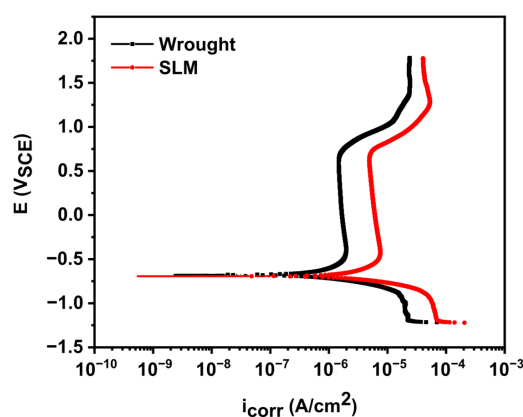
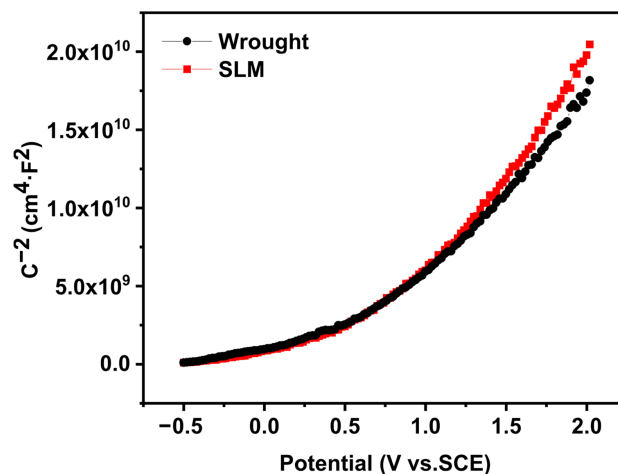


Figure 5. Potentiodynamic polarization curves of the two tested Ti-6Al-4V alloys in 0.05 mol/L H_2SO_4 solution.

Table 3. Electrochemical parameters derived from Figure 6.

	E_{corr} (V _{SCE})	i_{corr} (A/cm ²)	i_p (A/cm ²)
wrought	−0.68~−0.66	1.57×10^{-6} ~ 1.85×10^{-6}	2.01×10^{-6} ~ 2.27×10^{-6}
SLM	−0.72~−0.66	6.57×10^{-6} ~ 6.89×10^{-6}	6.76×10^{-6} ~ 6.80×10^{-6}

**Figure 6.** Mott-Schottky plots of two tested Ti-6Al-4V alloys in 0.05 mol/L H₂SO₄ solution.

3.3. Mott-Schottky Analysis

To further investigate the characteristic differences between the passive films formed on the two alloys, Mott-Schottky measurements were conducted in H₂SO₄ solution. Figure 6 displays the Mott-Schottky curves of the two Ti-6Al-4V alloys in 0.05 mol/L H₂SO₄ solution. Both curves exhibit a positive slope, indicating that the passive films on both alloys exhibit an n-type semiconductor [36]. This feature is mainly attributed to donor-type defects such as oxygen vacancies and interstitial titanium ions present in the oxide layer. A larger slope in the Mott-Schottky plot corresponds to a lower carrier density, implying a lower defect density and a more compact structure of the passive film, thus leading to superior corrosion resistance [37]. The carrier density (N_D) can be calculated using Equations (2) and (3) [4,38]:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{\text{FB}} - \frac{kT}{e} \right) \quad (2)$$

$$N_D = \frac{2}{ke\epsilon\epsilon_0} \quad (3)$$

where C is the space-charge capacitance, N_D is the carrier density, e is the elementary charge (1.6029×10^{-19} C), k is the Boltzmann constant (1.389×10^{-23} J/K), E is the electrode potential, E_{FB} is the flat-band potential, and T is the absolute temperature. The main component of the passive film is TiO₂, and its dielectric constant ϵ is 60 [4]. For an n-type semiconductor, $1/C^2$ is proportional to E and inversely proportional to N_D .

The slope of the curve for wrought Ti-6Al-4V is lower than that of the SLM Ti-6Al-4V. The corresponding results are listed in Table 4. As can be seen from the table, the carrier densities N_D of the wrought and SLM alloys are 5.45×10^{19} cm^{−3} and 7.07×10^{19} cm^{−3}, respectively. The defects in the passive film of titanium alloys are oxygen vacancies and interstitial metal cations [39]. Generally, a higher carrier density corresponds to lower protective ability of the passive film and poorer corrosion resistance [7,40]. The lower carrier density of wrought Ti-6Al-4V further confirms its superior corrosion resistance compared with the SLM alloy.

Table 4. The donor density for passive films on two tested Ti-6Al-4V alloys in 0.05 mol/L H₂SO₄ solution.

	Wrought	SLM
N_D (cm ⁻³)	5.45×10^{19}	7.07×10^{19}

3.4. XPS Analysis of Passive Film

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and depth distribution of passive films formed on Ti-6Al-4V in 0.05 mol/L H₂SO₄ solution. Figure 7 shows the XPS of the passive film formed on wrought Ti-6Al-4V. The XPS reveals that the film is mainly composed of C 1s, Ti 2p, O 1s, and V 2p. The characteristic peaks of these elements vary to different degrees with increasing sputtering time (etching depth). In addition, no Ti LMM Auger peak is observed on the outermost surface within the high binding energy region, whereas this peak becomes distinct after sputtering. Meanwhile, the intensity of the O KLL Auger peak first increases markedly and then decreases gradually.

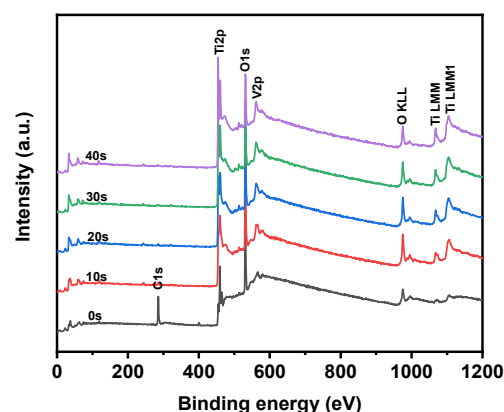
**Figure 7.** XPS of the surface passive film formed on wrought Ti-6Al-4V alloy in 0.05 mol/L H₂SO₄ solution.

Figure 8 shows the atomic percentages of each element obtained from XPS. The relative atomic percentage of Ti increases continuously with sputtering time, while those of V and Al show only a slight increase. By contrast, the relative atomic percentage of O decreases gradually, which is attributed to the gradual removal of surface oxides during prolonged sputtering. Since the chemical state of Ti is mainly reflected by the Ti 2p peak, peak fitting was performed on the Ti 2p spectra to identify the specific chemical forms of Ti in the passive film [21].

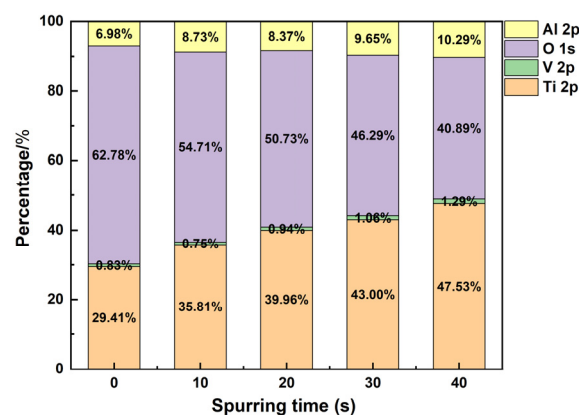
**Figure 8.** The atomic concentrations of elements in the passive film on wrought Ti-6Al-4V in 0.05 mol/L H₂SO₄.

Figure 9 presents the peak-fitting results of the Ti 2p XPS spectra for the passive film on wrought Ti-6Al-4V at different depths. The outermost layer contains 74.34% TiO_2 and 9.50% Ti_2O_3 , indicating that the surface film is dominated by TiO_2 . As a wide-bandgap semiconductor, TiO_2 possesses a large bandgap, requiring high energy for electron transition from the valence band to the conduction band, which endows the passive film with excellent protectiveness. Generally, a higher TiO_2 content corresponds to a larger charge-transfer resistance and stronger protection [41].

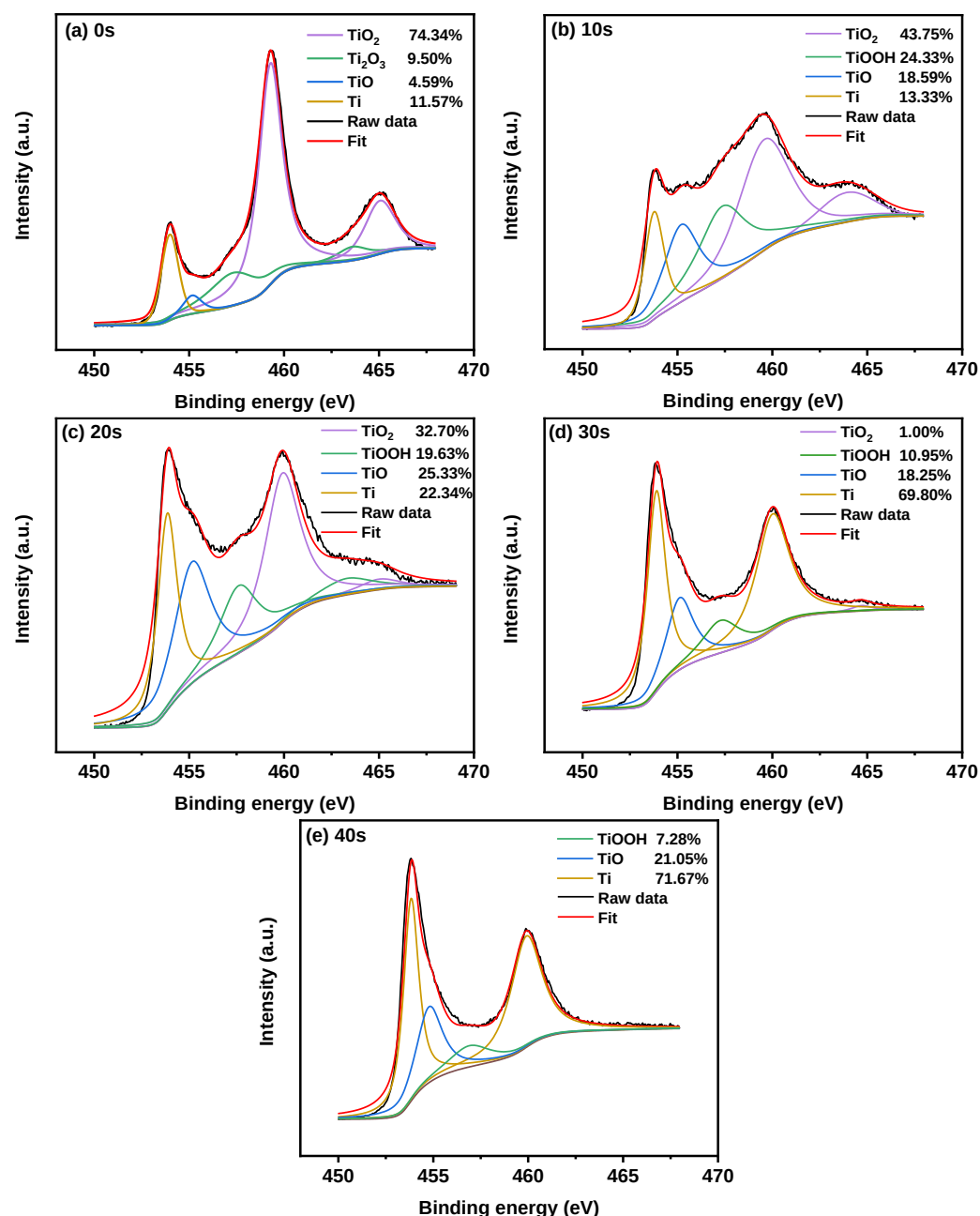


Figure 9. The chemical state of element Ti in the passivation film of wrought Ti-6Al-4V alloy and its variation with sputtering time.

With increasing sputtering time, the TiO_2 fraction decreases sharply, dropping to 43.75% after 10 s of sputtering. At this depth, TiOOH (24.33%) and TiO (18.59%) are detected. After 20 s of sputtering, the TiO_2 content continues to decrease (32.70%). When the sputtering time reaches 30 s, TiO_2 almost disappears (only 1.00%), and the fractions of TiOOH and TiO decrease to 10.59% and 18.25%, respectively. Meanwhile, the content of

metallic Ti increases significantly, reaching 69.80% and 71.67% at sputtering times of 30 s and 40 s, respectively.

Figure 10 shows the full XPS survey spectrum of the passive film on SLM Ti-6Al-4V. Characteristic peaks of C 1s, Ti 2p, O 1s, and V 2p are also detected, and their evolution with sputtering time is consistent with that observed for the wrought alloy.

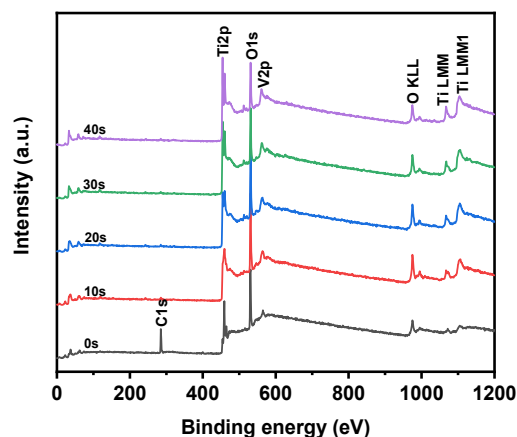


Figure 10. XPS spectra of the surface passive film formed on SLM Ti-6Al-4V alloy in 0.05 mol/L H_2SO_4 solution.

Figure 11 shows the atomic percentages of elements in the passive film of the SLM alloy. The relative atomic percentage of Ti increases continuously with sputtering time, whereas those of V and Al increase slightly, and the O percentage decreases gradually.

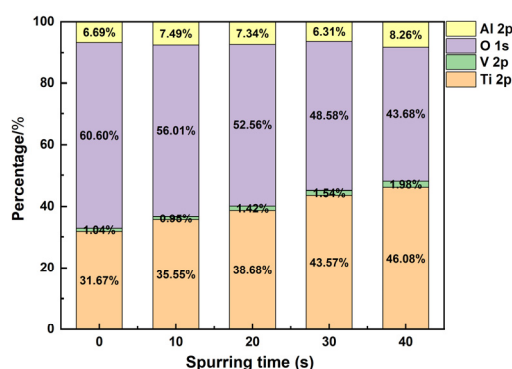


Figure 11. The atomic concentrations of elements in the passive film on SLMed Ti-6Al-4V in 0.05 mol/L H_2SO_4 .

Peak-fitting results of the Ti 2p spectra at different depths for the SLM Ti-6Al-4V are displayed in Figure 12. The outermost passive film contains 71.26% TiO_2 , slightly lower than that of the wrought counterpart, and 10.41% Ti_2O_3 , slightly higher than that of the wrought counterpart. After 10 s of sputtering, the TiO_2 content drops rapidly to 28.45%, Ti_2O_3 disappears, and TiOOH (34.66%) and TiO (23.74%) appear. The TiOOH fraction is approximately 1.42 times that in the wrought alloy. After 20 s, the TiO_2 content in the SLM alloy is only 9.66%, about 30% of that in the wrought counterpart at the same sputtering time. After 30 s, TiO_2 disappears in the SLM alloy, while 1.00% TiO_2 remains in the wrought alloy. At 40 s, TiO_2 completely disappears, and the fraction of metallic Ti increases to 78.56%.

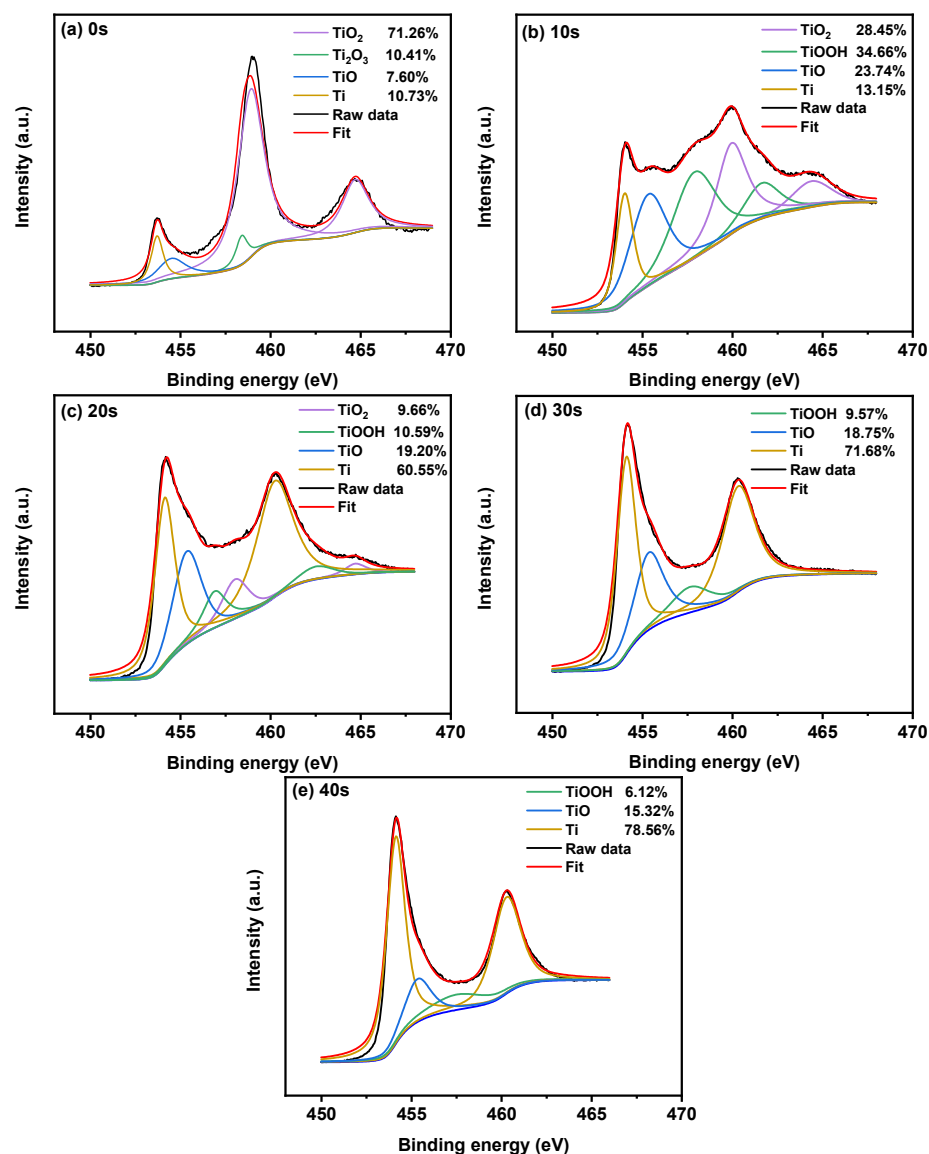


Figure 12. The chemical state of element Ti in the passivation film of Ti-6Al-4V alloy prepared by SLM technology and its variation with sputtering time.

Compared with the wrought counterpart, the TiO₂ content in the passive film of the SLMed alloy is considerably lower, indicating that the passive film formed on SLMed Ti-6Al-4V is thinner compared with the wrought counterpart. This is consistent with the passive film thickness calculated earlier.

4. Conclusions

- (1) The corrosion behaviors of forged and SLM-formed Ti-6Al-4V alloys in 0.05 mol/L H₂SO₄ solution were characterized using electrochemical impedance spectroscopy and potentiodynamic polarization curves. The results show that the forged alloy exhibits a larger polarization resistance, a thicker passive film, and a lower corrosion current density, indicating that its overall corrosion resistance is superior to that of the SLM-formed alloy.
- (2) Mott-Schottky analysis reveals that the passive films on the surfaces of the alloys fabricated by both processes exhibit n-type semiconductor characteristics. Among them, the forged alloy shows a larger slope and lower carrier concentration, suggesting

fewer defects, a more compact structure, and stronger protective ability of its surface passive film.

- (3) XPS depth profiling results demonstrate that with increasing sputtering time, the TiO₂ content in the passive films of both alloys gradually decreases until it disappears, while the contents of TiOOH and TiO increase progressively. Ti is barely detected on the surface but increases significantly with etching depth and eventually becomes the main component.
- (4) The electrochemical tests, Mott–Schottky analysis and XPS characterization results mutually verify that the forged Ti-6Al-4V alloy possesses overall better corrosion resistance than the SLM-formed alloy in a 0.05 mol/L H₂SO₄ environment.

Author Contributions: Conceptualization, H.Z., L.D. and Y.Q.; Writing—Original Draft Preparation, H.Z., L.D., X.Z., S.L. and Y.Q.; Writing—Review and Editing, H.Z., L.D., X.Z., S.L. and Y.Q.; Supervision, S.L.; Funding Acquisition, H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. U25A20201).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Zhou, H.L.; Li, J.; Zhang, S.G.; Yang, B.; Gui, Y.B.; Li, X.B.; Zhang, H.X.; Zhuo, X.R.; Lu, S.; Qiao, Y.X. Research progress on the microstructure, mechanical properties, and corrosion behavior of TC4 alloy fabricated by Selective Laser Melting. *Metals* **2026**, *16*, 284. [\[CrossRef\]](#)
- Gai, X.; Bai, Y.; Li, J.; Li, S.; Hou, W.; Hao, Y.; Zhang, X.; Yang, R.; Misra, R.D.K. Electrochemical behaviour of passive film formed on the surface of Ti-6Al-4V alloys fabricated by electron beam melting. *Corros. Sci.* **2018**, *145*, 80–89. [\[CrossRef\]](#)
- Pirro, G.; Martucci, A.; Morri, A.; Lombardi, M.; Ceschini, L. A novel solution treatment and aging for powder bed fusion-laser beam Ti-6Al-2Sn-4Zr-6Mo alloy: Microstructural and mechanical characterization. *Int. J. Miner. Metall. Mater.* **2025**, *32*, 414–424.
- Li, X.X.; Chen, L.Y.; Hu, W.B.; Wan, S.; Song, L.F.; Wang, Y.P.; Liao, B.K.; Guo, X.P. Corrosion and passive behavior of SLM and wrought TA15 titanium alloys in hydrochloric acid solutions. *J. Iron Steel Res. Int.* **2024**, *32*, 1356–1370. [\[CrossRef\]](#)
- Su, B.; Luo, L.; Wang, B.; Su, Y.; Wang, L.; Ritchie, R.O.; Guo, E.; Li, T.; Yang, H.; Huang, H.; et al. Annealed microstructure dependent corrosion behavior of Ti-6Al-3Nb-2Zr-1Mo alloy. *J. Mater. Sci. Technol.* **2021**, *62*, 234–248. [\[CrossRef\]](#)
- Sun, J.Z.; Pan, Y.; Liu, Y.J.; Kuang, F.; Lu, R.P.; Lu, X. Strength–ductility synergy strategy of Ti₆Al₄V alloy fabricated by metal injection molding. *Int. J. Miner. Metall. Mater.* **2025**, *32*, 1641–1654. [\[CrossRef\]](#)
- Qin, P.; Chen, L.Y.; Liu, Y.J.; Jia, Z.; Liang, S.X.; Zhao, C.H.; Sun, H.; Zhang, L.C. Corrosion and passivation behavior of laser powder bed fusion produced Ti-6Al-4V in static/dynamic NaCl solutions with different concentrations. *Corros. Sci.* **2021**, *191*, 109728.
- Edwards, P.; Ramulu, M. Fatigue performance evaluation of selective laser melted Ti-6Al-4V. *Mater. Sci. Eng. A* **2014**, *598*, 327–337. [\[CrossRef\]](#)
- Leuders, S.; Thöne, M.; Riemer, A.; Niendorf, T.; Tröster, T.; Richard, H.A.; Maier, H.J. On the mechanical behaviour of titanium alloy TiAl6V4 manufactured by selective laser melting: Fatigue resistance and crack growth performance. *Int. J. Fatigue* **2013**, *48*, 300–307. [\[CrossRef\]](#)
- Liu, D.; Yang, H.; Li, J.; Li, J.; Dong, Y.; Yang, C.; Jin, Y.; Yassir, L.; Li, Z.; Hernandez, D.; et al. Electron transfer mediator PCN secreted by aerobic marine *Pseudomonas aeruginosa* accelerates microbiologically influenced corrosion of TC4 titanium alloy. *J. Mater. Sci. Technol.* **2021**, *79*, 101–108. [\[CrossRef\]](#)
- Qin, T.; Lin, X.; Yu, J.; Wang, M.; Guo, P.; Li, J.; Zhang, Y.; Liu, J.; Zhang, S.; Huang, W. Performance of different microstructure on electrochemical behaviors of laser solid formed Ti-6Al-4V alloy in NaCl solution. *Corros. Sci.* **2021**, *185*, 109392. [\[CrossRef\]](#)
- Li, N.; Wang, L.; Zhou, Z.; Jiang, X.; Yu, H.; Sun, D. The interaction mechanism of titanium alloy TC4 between passive film and sulfate reducing bacteria biofilm in marine environment. *Appl. Surf. Sci.* **2025**, *690*, 162620. [\[CrossRef\]](#)

13. Chu, Y.H.; Chen, L.Y.; Qin, B.Y.; Gao, W.; Shang, F.; Yang, H.Y.; Zhang, L.; Qin, P.; Zhang, L.C. Unveiling the contribution of lactic acid to the passivation behavior of Ti–6Al–4V fabricated by laser powder bed fusion in Hank’s solution. *Acta Metall. Sin. (Engl. Lett.)* **2023**, *37*, 102–118. [[CrossRef](#)]
14. Cui, Y.W.; Chen, L.Y.; Chu, Y.H.; Zhang, L.; Li, R.; Lu, S.; Wang, L.; Zhang, L.C. Metastable pitting corrosion behavior and characteristics of passive film of laser powder bed fusion produced Ti–6Al–4V in NaCl solutions with different concentrations. *Corros. Sci.* **2023**, *215*, 111017. [[CrossRef](#)]
15. Leban, M.B.; Kosec, T.; Finšgar, M. Corrosion characterization and ion release in SLM-manufactured and wrought Ti6Al4V alloy in an oral environment. *Corros. Sci.* **2022**, *209*, 110716. [[CrossRef](#)]
16. Li, X.; Wang, L.; Fan, L.; Cui, Z.; Sun, M. Effect of temperature and dissolved oxygen on the passivation behavior of Ti–6Al–3Nb–2Zr–1Mo alloy in artificial seawater. *J. Mater. Res. Technol.* **2022**, *17*, 374–391. [[CrossRef](#)]
17. Jáquez-Muñoz, J.M.; Gaona-Tiburcio, C.; Mendez-Ramirez, C.T.; Carrera-Ramirez, M.G.; Baltazar-Zamora, M.A.; Santiago-Hurtado, G.; Lara-Banda, M.; Estupiñán-Lopez, F.; Nieves-Mendoza, D.; Almeraya-Calderon, F. Corrosion of anodized titanium alloys. *Coatings* **2024**, *14*, 809. [[CrossRef](#)]
18. Macdonald, D.D. The point defect model for the passive state. *J. Electrochem. Soc.* **2019**, *139*, 3434–3449. [[CrossRef](#)]
19. Macdonald, D.D. Review of mechanistic analysis by electrochemical impedance spectroscopy. *Electrochim. Acta* **1990**, *35*, 1509–1525. [[CrossRef](#)]
20. Lebea, L.; Ngwangwa, H.M.; Desai, D.A.; Nemavhola, F.; Carniel, E.L. Corrosion resistance of 3D-printed titanium alloy Ti64-ELI parts for dental application. *Appl. Bionics Biomech.* **2022**, *2022*, 1804417. [[CrossRef](#)]
21. Qiao, Y.X.; Xu, D.K.; Wang, S.; Ma, Y.J.; Chen, J.; Wang, Y.X.; Zhou, H.L. Effect of hydrogen charging on microstructural evolution and corrosion behavior of Ti–4Al–2V–1Mo–1Fe alloy. *J. Mater. Sci. Technol.* **2021**, *60*, 168–176. [[CrossRef](#)]
22. GB/T 24196-2009; Corrosion of Metals and Alloys—Electrochemical Test Methods—Guidelines for Potentiostatic and Potentiodynamic Polarization Measurements. China Standards Press: Beijing, China, 2009.
23. Qin, H.Z.; Wang, C.S.; Lei, Y.; Li, C.L. Effect of cyclic heat treatment on microstructure and tensile property of a laser powder-bed fusion-manufactured Ti–6Al–2Zr–1Mo–1V alloy. *J. Mater. Res. Technol.* **2023**, *27*, 4032–4042. [[CrossRef](#)]
24. Murr, L.E.; Quinones, S.A.; Gaytan, S.M.; Lopez, M.I.; Rodela, A.; Martinez, E.Y.; Hernandez, D.H.; Martinez, E.; Medina, F.; Wicker, R.B. Microstructure and mechanical behavior of Ti–6Al–4V produced by rapid-layer manufacturing, for biomedical applications. *J. Mech. Behav. Biomed. Mater.* **2009**, *2*, 20–32. [[CrossRef](#)] [[PubMed](#)]
25. Tao, P.; Li, H.X.; Huang, B.Y.; Hu, Q.D.; Gong, S.L.; Xu, Q.Y. Tensile behavior of Ti–6Al–4V alloy fabricated by selective laser melting: Effects of microstructures and as-built surface quality. *China Foundry* **2018**, *15*, 243–252. [[CrossRef](#)]
26. Zhou, H.L.; Liu, H.Q.; Li, J.; Li, C.T.; Yang, H.K.; Qiao, Y.X. Effect of Carbon addition on mechanical and corrosion properties of CoCrFeNiMn High Entropy Alloy. *Metals* **2026**, *16*, 50.
27. Wang, T.Y.; Zhang, S.G.; Etim, I.I.N.; Li, C.T.; Zhou, H.L.; Chen, Z.L.; Qiao, Y.X.; Zhang, Y.H.; Zhang, L.L.; Xu, Y.Z. Corrosion behavior of pure copper as a material for high-level radioactive waste in simulated groundwater environments. *J. Mater. Res. Technol.* **2026**, *41*, 2989–3000. [[CrossRef](#)]
28. Zhu, Y.S.; Yu, S.J.; Chen, S.; Hu, B.W.; Wang, C.M.; Xu, Y.Z.; Huang, Y.; Wang, M.Y. Electrochemical behavior of FeCoNiAl_{0.75}Cr_{1.25} high-entropy alloy in Na₂SO₄ solution with acidic pH. *J. Iron Steel Res. Int.* **2025**, *32*, 1151–1162. [[CrossRef](#)]
29. Sun, C.; Wang, Y.; McMurtrey, M.D.; Jerred, N.D.; Liou, F.; Li, J. Additive manufacturing for energy: A review. *Appl. Energy* **2021**, *282*, 116041. [[CrossRef](#)]
30. Zhang, X.Q.; Qiang, S.H.; Fan, J.X.; Zhou, H.L.; Yang, L.L.; Tang, Y.B.; Liu, Z.H.; Lu, D.H. Annealing treatment on corrosion resistance deterioration of LPBF 316L SS in 0.1 mol/L HCl solution. *J. Iron Steel Res. Int.* **2025**, *32*, 1286–1301. [[CrossRef](#)]
31. Liao, X.Y.; Zheng, Z.B.; Liu, T.L.; Long, J.; Wang, S.; Zhang, H.Y.; Zheng, K.H. Achieving high impact–abrasion–corrosion resistance of high–chromium wear–resistant steel via vanadium additions. *J. Mater. Res. Technol.* **2024**, *29*, 2425–2436.
32. Fu, Y.; Luo, H.; Chen, X.R.; Prabhakar, J.M.; Wang, X.F.; Cheng, H.X.; Du, C.W.; Hu, S.Q.; Li, X.G. The corrosion behavior and passive film properties of the cast and annealed AlCoCrFeNi_{2.1} eutectic high-entropy alloy in sulfuric acid solution. *Corros. Sci.* **2024**, *240*, 112456. [[CrossRef](#)]
33. Moayed, M.H.; Newman, R.C. Evolution of current transients and morphology of metastable and stable pitting on stainless steel near the critical pitting temperature. *Corros. Sci.* **2006**, *48*, 1004–1018. [[CrossRef](#)]
34. Yin, L.; Liu, Y.; Dai, N.; Qian, S.; Wan, Y.; Wu, J.; Li, J.; Jiang, Y. Effect of hydrogen charging conditions on hydrogen blisters and pitting susceptibility of 445J1M ferritic stainless steel. *J. Electrochem. Soc.* **2018**, *165*, C1007–C1016. [[CrossRef](#)]
35. Amin, M.A.; Khaled, K.F.; Fadl-Allah, S.A. Testing validity of the Tafel extrapolation method for monitoring corrosion of cold rolled steel in HCl solutions—Experimental and theoretical studies. *Corros. Sci.* **2010**, *52*, 140–151.
36. Fattah-alhosseini, A.; Soltani, F.; Shirsalimi, F.; Ezadi, B.; Attarzadeh, N. The semiconducting properties of passive films formed on AISI 316 L and AISI 321 stainless steels: A test of the point defect model (PDM). *Corros. Sci.* **2011**, *53*, 3186–3192. [[CrossRef](#)]
37. Niu, Y.; Li, M. Application of thermohydrogen processing for formation of ultrafine equiaxed grains in near α Ti600 alloy. *Metall. Mater. Trans. A* **2009**, *40*, 3009–3015. [[CrossRef](#)]

38. Zhu, H.J.; Han, J.Y.; Fang, K.W.; Zheng, Z.I.; Zhou, H.I.; Yang, L.L.; Qiao, Y.X.; Chen, J.; Cui, J.; Wang, Q. Corrosion behavior of CoCrCu_{0.1}FeMoNi high entropy alloy in 0.5 mol/L NaOH solution. *J. Iron Steel Res. Int.* **2025**, *32*, 1163–1175. [[CrossRef](#)]
39. Liu, M.; Huang, F.; Lai, Z.; Chen, S.; Li, J.; Wang, Y.; Fan, L.; Ma, L.; Jin, Y. Atomic-scale de-passivation mechanisms of anatase TiO₂ induced by corrosive halides based on density-functional theory. *Appl. Surf. Sci.* **2023**, *621*, 156859. [[CrossRef](#)]
40. Alves, V.A.; Reis, R.Q.; Santos, I.C.B.; Souza, D.G.; Gonçalves, T.d.F.; Pereira-da-Silva, M.A.; Rossi, A.; da Silva, L.A. In situ impedance spectroscopy study of the electrochemical corrosion of Ti and Ti–6Al–4V in simulated body fluid at 25 °C and 37 °C. *Corros. Sci.* **2009**, *51*, 2473–2482.
41. Osarinmwian, C.; Mellor, I.M.; Roberts, E.P.L. Electro-deoxidation modelling of titanium dioxide to titanium. *Electrochim. Acta* **2016**, *209*, 95–101. [[CrossRef](#)]

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