

Article

The Study on Corrosion Resistance of Ti-6Al-4V ELI Alloy with Varying Surface Roughness in Hydrofluoric Acid Solution

Han Wang ^{1,*}, Quanshi Cheng ², Zhuo Chang ^{3,*}, Kedi Wang ¹, Xuemin Gao ² and Xueling Fan ¹

¹ Xi'an Key Laboratory of Extreme Environmental and Protection Technology, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an 710049, China

² Henan Key Laboratory of Fastening Connection Technology, Henan Aerospace Precision Machining Co., Ltd., Xinyang 464000, China

³ Laboratory for Multiscale Mechanics and Medical Science, State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an 710049, China

* Correspondence: wishhappy@foxmail.com (H.W.); zhuochang@xjtu.edu.cn (Z.C.)

Abstract: The corrosion resistance of titanium alloy poses a crucial challenge, significantly affecting its prospect for service and application. The present study aimed to investigate the corrosion resistance of Ti-6Al-4V ELI alloys with varying surface roughness in hydrofluoric acid solution, in order to assess the influence of roughness on their corrosion resistance performance. The weight loss percentage, surface morphology evolution, and roughness variation of Ti-6Al-4V ELI alloys before and after exposure to hydrofluoric acid corrosion were characterized. While the weight loss and weight loss percentage of the Ti-6Al-4V ELI alloy increased with prolonged corrosion, the overall weight loss rate decreased. The accumulation of TiF₃ phases and depletion of the Ti-6Al-4V ELI matrix mutually led to the alterations of the surface roughness. Due to the inability to prevent fluoride ions from contacting with the Ti-6Al-4V ELI alloy, continuous corrosion occurred in hydrofluoric acid. Based on these experimental results and analysis, the corrosion mechanism of the Ti-6Al-4V ELI alloy corroded by hydrofluoric acid solution was elucidated. Furthermore, an analysis was conducted to explore the influence of corrosion time on mechanical properties by analyzing the decay in compressive properties of the Ti-6Al-4V ELI titanium alloy after hydrofluoric acid corrosion treatment. The bearing capacity of the Ti-6Al-4V ELI alloy deteriorated over the corrosion time.



Citation: Wang, H.; Cheng, Q.; Chang, Z.; Wang, K.; Gao, X.; Fan, X. The Study on Corrosion Resistance of Ti-6Al-4V ELI Alloy with Varying Surface Roughness in Hydrofluoric Acid Solution. *Metals* **2024**, *14*, 364. <https://doi.org/10.3390/met14030364>

Academic Editor: Caterina Zanella

Received: 17 February 2024

Revised: 13 March 2024

Accepted: 18 March 2024

Published: 20 March 2024



Copyright: © 2024 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) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: Ti-6Al-4V ELI; corrosion resistance; surface morphology; surface roughness; mechanical property recession

1. Introduction

Titanium and its alloys are characterized by their low density, high specific strength/stiffness, and biocompatibility, as well as excellent corrosion and heat resistance [1–5]. The aforementioned characteristics render titanium alloy highly promising in the domains of aerospace engineering, marine engineering, and biomedical engineering [6–9]. Furthermore, the utilization of titanium alloys as raw materials for additive manufacturing is highly commendable [10–14]. In the extensive application scenarios of titanium alloy, the service performance of titanium alloy is contingent upon its corrosion resistance [15], a critical property that has attracted considerable interest from researchers and engineers.

The physicochemical properties of titanium and its alloys have also demonstrated desirable characteristics [12,16]. Under normal conditions, titanium alloys typically exhibit high resistance to corrosion by most strong acids due to the formation of a stable oxide film on their surfaces [17]. However, the corrosion resistance to hydrofluoric acid (HF) is generally insufficient. In the fields of aerospace and biological engineering [18,19], it is often imperative to employ hydrofluoric acid for pretreatment or corrosion of titanium alloys, which inevitably impacts their properties. For example, titanium alloys used as dental implants in the oral cavity are frequently exposed to fluoride ions from toothpaste

or tap water. It has been demonstrated that implants can often benefit from optimal surface roughness and microstructural features [14,20,21].

In order to alter the performances of titanium alloys, the surface topography of titanium and its alloys can be altered through various methods such as mechanical and chemical approaches. In terms of solution etching techniques, titanium and its alloys can be modified by H_2SO_4 [2], HCl [20], $NaCl$ [22], H_3PO_4 [23], HF [24], or their combination. Ti-6Al-4V alloy is nowadays extensively employed as one of the most commonly utilized titanium alloys, consisting of $\alpha + \beta$ phases [3,22]. The Ti-6Al-4V extra low interstitial (ELI) alloy [12,25] has been developed as a modification of the Ti-6Al-4V alloy by reducing the content of carbon, oxygen, nitrogen, and iron elements with the aim of enhancing its physicochemical and mechanical properties. For example, the surface topography of Ti-6Al-4V ELI alloy can be modified using the hydrofluoric acid etch technique [26,27], and such fluoride modification on Ti-6Al-4V ELI alloy is beneficial to its biomedical applications [28]. In the field of biomedical engineering, fluoride modification of titanium alloy is advantageous for promoting bone growth around the implant [18,29]. Consequently, this method enhances the physical interlocking and bonding strength between bone and titanium implant [24]. However, there is still a lack of understanding of the corrosion issues of hydrofluoric acid and how the surface roughness associates with the corrosion resistance of Ti-6Al-4V ELI alloy to hydrofluoric acid. Researchers and engineers should pay close attention to a series of corrosion issues arising from hydrofluoric acid and explain the influence of surface roughness on the corrosion resistance of Ti-6Al-4V ELI alloy to hydrofluoric acid. Additionally, the degradation behavior of mechanical properties in Ti-6Al-4V ELI alloy after exposure to hydrofluoric acid corrosion has not been fully investigated. Addressing these challenges and developing effective treatment methods are crucial for advancing the application of Ti-6Al-4V ELI alloy in the fields of aerospace and biological engineering.

Aiming at exploring the impact of surface roughness on corrosion resistance, in the present study, we investigated the corrosion resistance property of Ti-6Al-4V ELI alloys with varying surface roughness to hydrofluoric acid solution. Specifically, the weight loss percentage, evolution of surface morphology, and changes in roughness before and after exposure to hydrofluoric acid corrosion were assessed. Next, based on the experimental findings, we elucidated the corrosion mechanism of the Ti-6Al-4V ELI alloy when subjected to hydrofluoric acid solution. Finally, we evaluated the influence of the corrosion time on the mechanical properties of the Ti-6Al-4V ELI alloy through an analysis of the degradation in mechanical properties after the hydrofluoric acid corrosion treatment.

2. Materials and Methods

2.1. Corrosion Experiment

The Ti-6Al-4V ELI alloy was developed by reducing the content of C, O, N, and Fe elements, and the element composition is summarized in Table 1. Initial cylindrical specimens with a diameter of 4.0 mm and a height of 3.0 mm were fabricated from machined Ti-6Al-4V ELI alloy bars (M state).

Table 1. The element composition of Ti-6Al-4V ELI alloy/wt.%.

Element	Ti	Al	V	Fe	C	N	O	Other
wt.%	Bal.	6.15	4.28	0.20	0.009	0.010	0.112	<0.30

To achieve varying surface roughness, the surface of the specimen was ground to achieve different levels of roughness (raw machined surface, 400[#] and 240[#]) by different sandpapers. The 2% HF solution was prepared by diluting a 40% HF solution with deionized water. The specimens were all cleaned using an ultrasonic cleaner and weighed using an analytical balance. Subsequently, the specimens were immersed in 2% HF solutions (Figure 1) for varying corrosion times (5, 30, 60, and 90 min) at room temperature with-

out agitation. In this study, the corrosion experiment was repeated at least three times under different conditions, and the average values were obtained by three results. For the Ti-6Al-4V ELI specimens, a sufficient amount of 2% HF solution was prepared for corrosion [28,30,31]. Following the corrosion experiment, the specimens were meticulously cleaned using an anhydrous ethanol, dried in air and weighed again using an analytical balance [32]. The weight loss (W), weight loss percentage (P), and weight loss rate (C) were calculated utilizing Equations (1)–(3):

$$W = m_0 - m_1, \quad (1)$$

$$P = \frac{m_0 - m_1}{m_0} \times 100\%, \quad (2)$$

$$C = \frac{m_0 - m_1}{T} \quad (3)$$

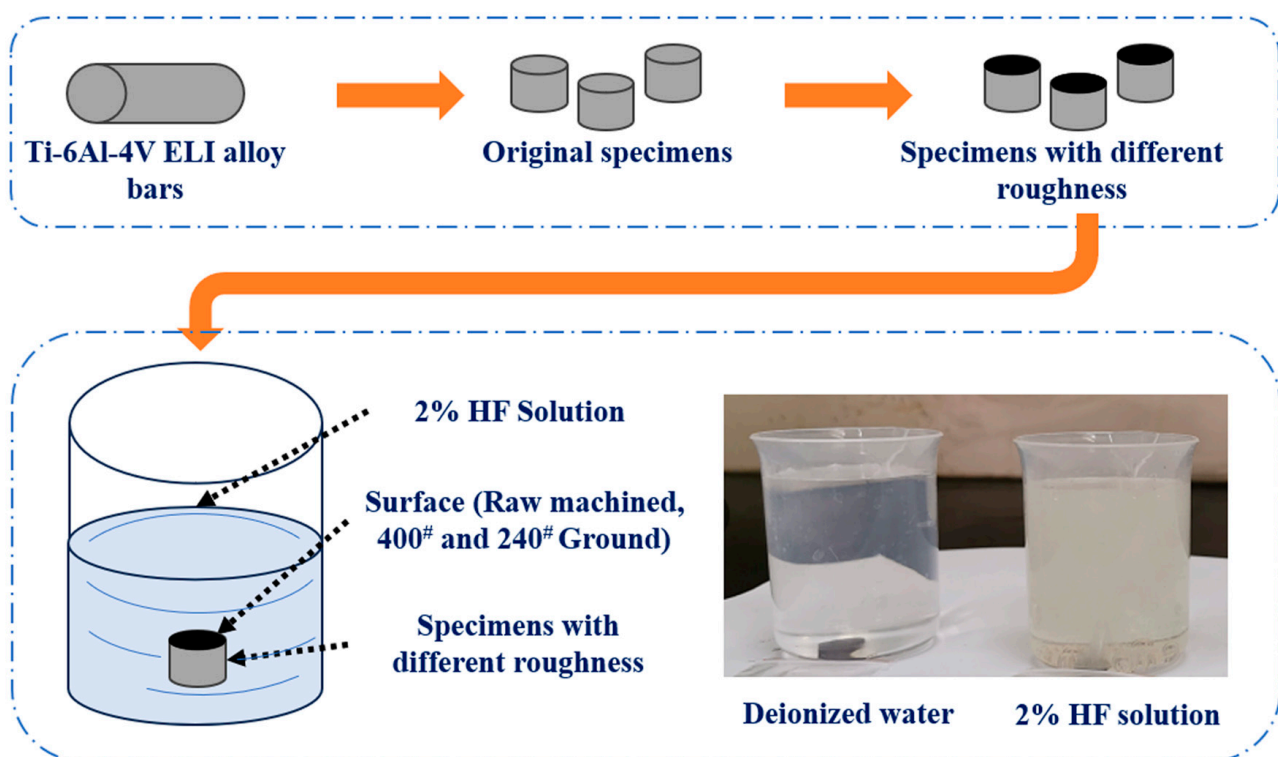


Figure 1. The illustration of the corrosion experiment and specimens of Ti-6Al-4V ELI alloy with different surface roughness.

The weights of the specimens before and after the corrosion experiment are denoted as m_0 and m_1 , respectively. T represents the duration of the corrosion process. The detailed parameters for the corrosion experiments and samples are summarized in Table 2. The surface labels (R_0 , R_1 , R_2) represent the specimens with different surface states. R_0 represents the raw machined surface. R_1 and R_2 represent the surfaces ground to different levels of roughness, 400# and 240#, respectively.

2.2. Characterization

The surface morphologies of specimens, both before and after corrosion, were observed using a scanning electron microscope (SEM, EVO 10, Jena, Germany) equipped with an energy dispersive spectroscope (EDS, Oxford Xmax 50, Borehamwood, UK). The phase composition was analyzed using an X-ray diffraction (XRD, Bruker D8 ADVANCE, Karlsruhe, Germany) with Cu-K α radiation. The surface morphologies and roughness were characterized by an atomic force microscope (AFM, MFP-3D Infinity, Santa Barbara,

CA, USA) and a white light interferometer (WLI, Profilm 3D, Unterhaching, Germany). Compression tests were carried out at an initial strain rate of 10^{-3} s^{-1} on a universal mechanical testing machine (MTS, C45.105, Eden Prairie, MN, USA) to characterize the recession in compressive properties. To ensure data stability and repeatability, at least three compressive specimens were tested for each condition at room temperature.

Table 2. The detailed parameters of the corrosion experiments and specimens.

Number	Surface Label	Surface State	Etching Time/min
1	R ₀	Raw machined surface	0
2	R ₀	Raw machined surface	5
3	R ₀	Raw machined surface	30
4	R ₀	Raw machined surface	60
5	R ₀	Raw machined surface	90
6	R ₁	400 [#] ground	0
7	R ₁	400 [#] ground	5
8	R ₁	400 [#] ground	30
9	R ₁	400 [#] ground	60
10	R ₁	400 [#] ground	90
11	R ₂	240 [#] ground	0
12	R ₂	240 [#] ground	5
13	R ₂	240 [#] ground	30
14	R ₂	240 [#] ground	60
15	R ₂	240 [#] ground	90

3. Results and Discussion

3.1. Weight Loss of Ti-6Al-4V ELI Alloy Subjected to Hydrofluoric Acid Corrosion

The results of the weight loss (W), weight loss percentage (P), and weight loss rate (C) calculated by Equations (1)–(3) are presented in Figure 2. The repetitive measurements were performed, and the standard deviations were calculated. The average values and the standard deviations of the weight loss (W), weight loss percentage (P), and weight loss rate (C) are summarized in Table 3. It was observed that both the weight loss and weight loss percentage increased as the corrosion time prolonged. Initially, the specimens with different surface states (R_0 , R_1 , R_2) exhibited similar levels of weight loss and weight loss percentage. These findings indicated that in the initial corrosion stage (during the first 30 min), the surface roughness had a limited impact on the weight loss and weight loss percentage of the Ti-6Al-4V ELI alloy (Figure 2a,b). As the corrosion time exceeded 30 min, the average values of the weight loss and weight loss percentage (Ave. of W and P in Table 3) for specimens with different surface states (R_0 , R_1 , and R_2) showed tiny differences. Considering the standard deviation (Std. of W and P in Table 3), the effect of surface roughness on the weight loss and weight loss percentage was not significant. Although the weight loss and weight loss percentage increased with the prolongation of corrosion times, a distinct reduction in the weight loss rate was noticed (Figure 2c). Specially, when the corrosion time exceeded 30 min, it was observed that the average values of the weight loss rate (Ave. of C in Table 3) for specimens with R_0 surface became a little higher than those with R_1 and R_2 surfaces. From the difference in curves in the Figure 2, it can be seen that the influence of the surface roughness on the curves of weight loss rate was greater compared with the curves of weight loss and weight loss percentage. Considering the standard deviation (Std. of C in Table 3), however, the effect of the surface roughness on the weight loss rate was still not significant. These findings highlighted that the weight loss, weight loss percentage, and weight loss rate varied significantly with corrosion progression, while their sensitivity to the influence of surface roughness was limited.

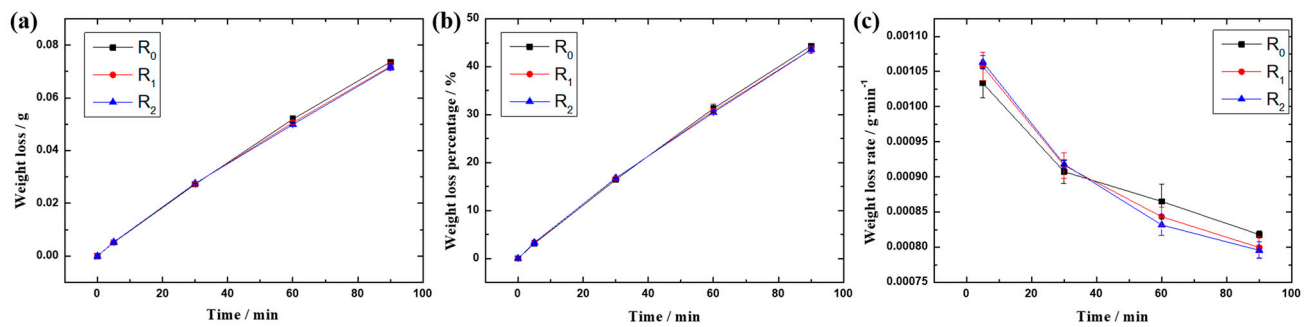


Figure 2. (a) Weight loss, (b) weight loss percentage, and (c) weight loss rate of specimens with different surface states at various HF solution corrosion times.

Table 3. The average value (Ave.) and the standard deviation (Std.) of the weight loss (W , g), weight loss percentage (P , %), and weight loss rate (C , $\text{g} \cdot \text{min}^{-1}$).

	Time	R ₀		R ₁		R ₂	
		Ave.	Std.	Ave.	Std.	Ave.	Std.
W	5	0.00517	0.00010	0.00529	0.00010	0.00532	0.00005
	30	0.02722	0.00050	0.02749	0.00055	0.02754	0.00016
	60	0.05192	0.00145	0.05061	0.00079	0.04990	0.00087
	90	0.07363	0.00045	0.07198	0.00136	0.07161	0.00106
P	5	3.11366	0.06365	3.33350	0.03117	3.25631	0.04789
	30	16.42258	0.29857	16.69526	0.35188	16.77791	0.07577
	60	31.30024	0.83020	30.76174	0.51683	30.47066	0.41385
	90	44.35515	0.20741	43.59825	0.76163	43.58085	0.67050
C	5	0.001030	0.000021	0.001060	0.000020	0.001060	0.000010
	30	0.000907	0.000017	0.000916	0.000018	0.000918	0.000005
	60	0.000865	0.000024	0.000844	0.000013	0.000832	0.000015
	90	0.000818	0.000005	0.000800	0.000015	0.000796	0.000012

3.2. Surface Roughness of Ti-6Al-4V ELI Alloy before and after Corrosion

The changes in the surface roughness indexes (indicated by Sa and Sq [26,30]) of the Ti-6Al-4V ELI alloy before and after corrosion were investigated, as illustrated in Figure 3. Sa (arithmetical mean height) is the extension of Ra (arithmetical mean height of a line) to a surface. Sq (root mean square height) represents the root mean square value of ordinate values within the definition area. It is equivalent to the standard deviation of heights. It was observed that the specimens with R_0 surfaces exhibited a lower initial surface roughness compared with specimens with R_1 and R_2 surfaces (R_0 : 0.209, R_1 : 0.582, R_2 : 0.728 for Sa , R_0 : 0.269, R_1 : 0.764, R_2 : 0.933 for Sq). Interestingly, it was found that with an increase in the corrosion time, the surface roughness of specimen with R_0 continuously rose; however, the specimens R_1 and R_2 demonstrated a distinct trend in contrast to the former case. It was observed that there was a consistent reduction in the surface roughness of specimens with R_1 and R_2 to a minimum value (~ 0.2) before experiencing a subsequent increase (~ 0.3). The surface roughness variations between the initial state (0 min) and the final state (90 min) are shown in Table 4. It was found that the surface roughness variation was different for different surface states (Sa and $Sq > 0$ for R_0 , Sa and $Sq < 0$ for R_1 and R_2). The results were different from the investigation findings of Bezuidenhout et al. [33]. The results of their research showed that the surface roughness tended to decrease as the duration of the corrosion increased. In our study, however, there were increasing stages of surface roughness, depending on the initial roughness values and whether the minimum roughness was reached. Furthermore, it is worth noting that in this study the 0.2% HF solution corrosion imposed a limitation on the surface roughness, approximately at the level of 0.2 μm .

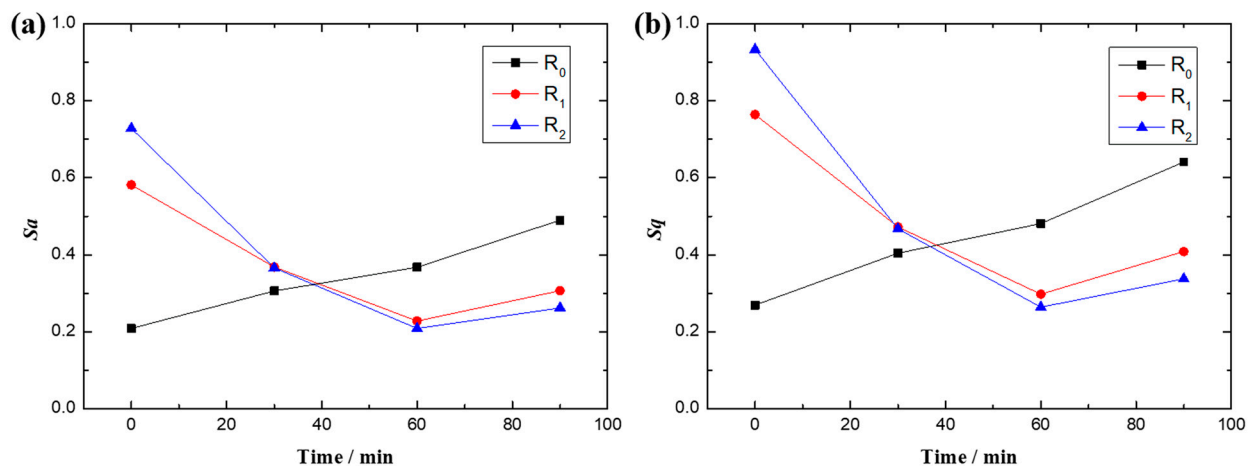


Figure 3. The surface roughness indexes (a) Sa and (b) Sq of Ti-6Al-4V ELI alloy before and after corrosion.

Table 4. The surface roughness variation between initial state (0 min) and final state (90 min).

	Surface Label	Initial State	Final State	Variation
Sa	R ₀	0.209	0.490	0.281
	R ₁	0.582	0.307	−0.275
	R ₂	0.728	0.262	−0.466
Sq	R ₀	0.269	0.641	0.372
	R ₁	0.764	0.409	−0.355
	R ₂	0.933	0.338	−0.595

Further, the evolution of surface morphology under different corrosion periods on Ti-6Al-4V ELI alloy before and after corrosion with the increasing corrosion time was explored as illustrated in Figure 4. Initially, during the first 30 min of corrosion, the surface morphology of the specimen exhibited a distinctive pattern of strip groove with varying altitudes, attributed to the utilization of abrasive paper with different mesh grades. Then it was noticed that subsequent corrosion by the HF solution induced substantial changes in the surface morphology of the specimen, leading to the disappearance of the strip groove pattern (initial surface morphology of R₀, R₁, R₂ at 0 min in Figure 4) and the emergence of a columnar peak and valley morphology instead (surface morphology of R₀, R₁, R₂ at 5, 30, 60, 90 min in Figure 4). Moreover, it was found that noticeable changes occurred in the altitudes of these peaks and valleys with the increasing corrosion time. These results demonstrated that the HF solution corrosion had markable impacts not only on the surface roughness but also on alterations in the overall surface morphology.

3.3. Microstructure of Ti-6Al-4V ELI Alloy before and after Corrosion

Subsequently, the alterations on the phase and microstructure of the Ti-6Al-4V ELI specimens at different corrosion stages are examined. As shown in Figure 5, a consistent XRD diffraction pattern after the corrosion on Ti-6Al-4V ELI alloy was found [33]. Particularly, the positions of diffraction peaks remained consistent after corrosion, while there was a slight increase in the intensity of diffraction as the corrosion time increased. Importantly, it was noted that there was a distinct strength on the diffraction peaks of the TiF₃ phase at the first 5 min of corrosion. The diffraction peaks of the TiF₃ phase were observed to strengthen with the increase in the corrosion time. It is speculated that the formation of the TiF₃ phase was on the specimen surface initially. In the hydrofluoric acid solution, the passivation film on the surface of the titanium alloy was destroyed and removed, leading to direct contact between fluorine ions and titanium. Consequently, it was observed that

a gradual accumulation of TiF_3 phase occurred on the specimen surface along with the generation of hydrogen.

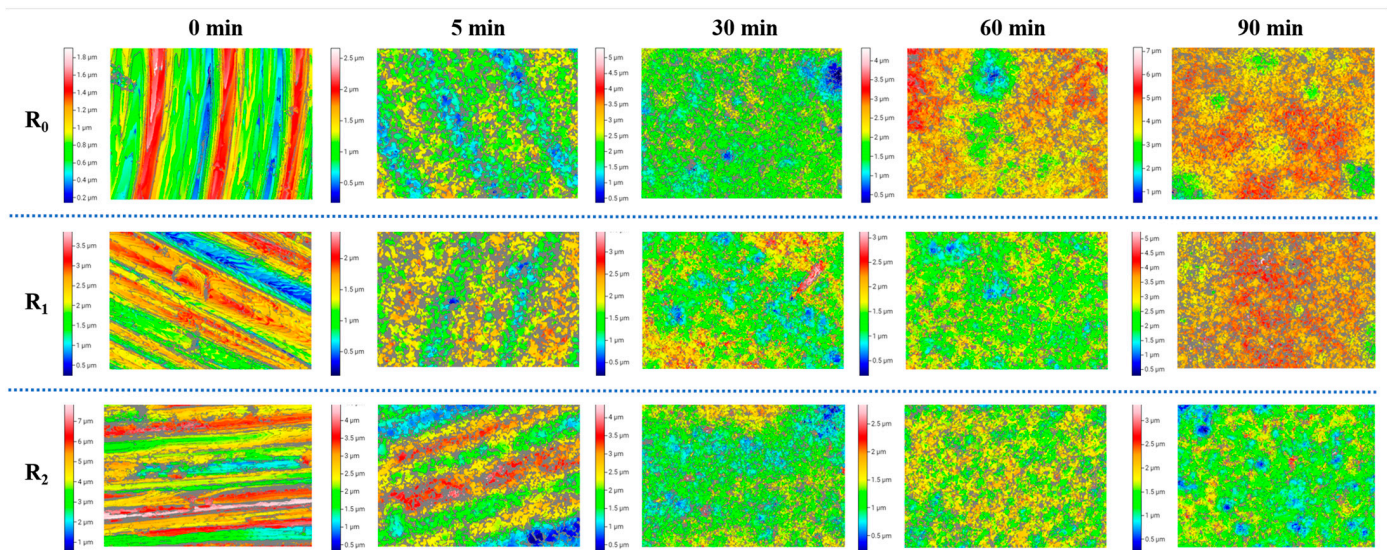


Figure 4. The surface morphology of Ti-6Al-4V ELI alloy before and after corrosion observed by WLI.

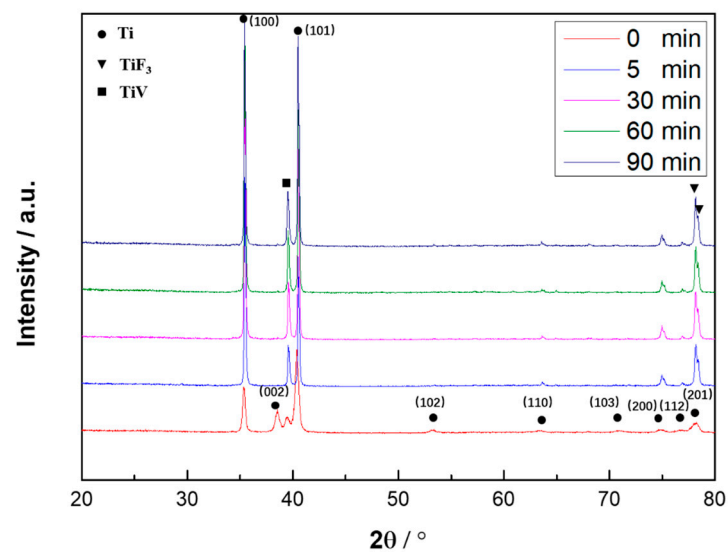


Figure 5. The XRD pattern of the Ti-6Al-4V ELI alloy specimens before and after HF solution corrosion.

In order to assess the changes in the microstructure of sample surfaces, the microstructural characteristics among specimens with different degrees of corrosion were compared. Figure 6 presents the SEM images of the Ti-6Al-4V ELI alloy specimens before and after 2% HF solution corrosion. It is observed that the specimen surface exhibited black regions and white phases. Random distribution regions formed on all the sample surfaces after corrosion. Specifically, the white phases appeared as polygonal particles dispersed within the black region. According to the further element analysis results obtained by EDS, it was revealed that the black regions consisted of Ti-6Al-4V ELI alloy, while the white phases were composed of TiF_3 particles. We believe that the development of T6Al4V/ TiF_3 in two phases was mainly due to the dynamic equilibrium of corrosion/formation of different compositions. To be specific, the HF solution reacted with the Ti-6Al-4V ELI alloy, leading to the formation of the TiF_3 phase on the specimen surface. Simultaneously, there was a continuous consumption of the Ti-6Al-4V ELI alloy as the matrix, which progressively developed a notched substrate. TiF_3 phases gradually deposited on the rough Ti-6Al-4V ELI

substrate. The accumulation of TiF_3 phases and depletion of the Ti-6Al-4V ELI matrix resulted in the alterations of surface characteristics including surface roughness, morphology, and compositions.

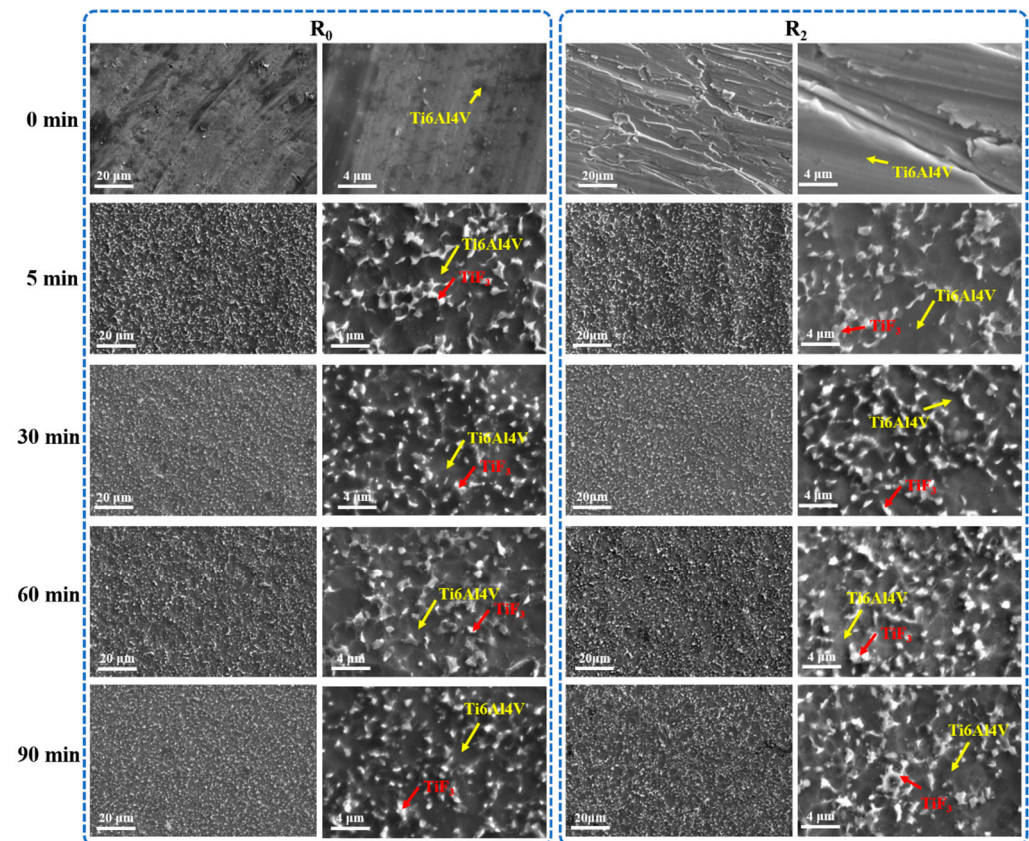


Figure 6. The surface microstructure and morphology of Ti-6Al-4V ELI alloy specimens before and after corrosion observed by SEM.

In addition, the microstructural changes with corrosion were studied by AFM. The AFM images in Figure 7 illustrate the surface topography of the Ti-6Al-4V ELI alloy specimens before and after exposure to a 2% HF solution for corrosion testing. The colors on the AFM images correspond to different elevations, indicating variations in the specimen surface topography. Notably, significant alterations were observed in the surface morphology of specimens with R_0 and R_2 with the increasing corrosion time. The strip groove patterns disappeared, and the peak/valley morphologies emerged, proving that the different microstructure characterization methods of surface morphology evolution by WLI, SEM, and AFM presented consistent and correct results.

Given the findings in how the surface morphology and compositions changed, the corrosion mechanism of the Ti-6Al-4V ELI alloy corroded by 0.2% HF solution is illustrated in Figure 8. Due to the inability to prevent fluoride ions from coming into contact with the titanium alloy, continuous corrosion occurs in hydrofluoric acid. For specimens with R_0 surfaces, with the initially lower roughness (raw machined surface), it is believed that the application of hydrofluoric acid could result in a coarsening effect. Then, the fluoride ions reacted quickly with titanium, leading to the rapid accumulation of the TiF_3 phase on the surface of specimen. This, in turn, led to the gradual formation of bulges on the surface. In the case of a specimen with an R_2 surface characterized by an initially higher roughness, there was a quick reaction on the peaks, while a slower reaction occurred in the valleys, resulting in a gradual polishing effect on the surface of the specimen [33]. The continuous depletion of the Ti-6Al-4V ELI alloy along with the gradual accumulation of the TiF_3 phase contributed to the changes in the surface roughness.

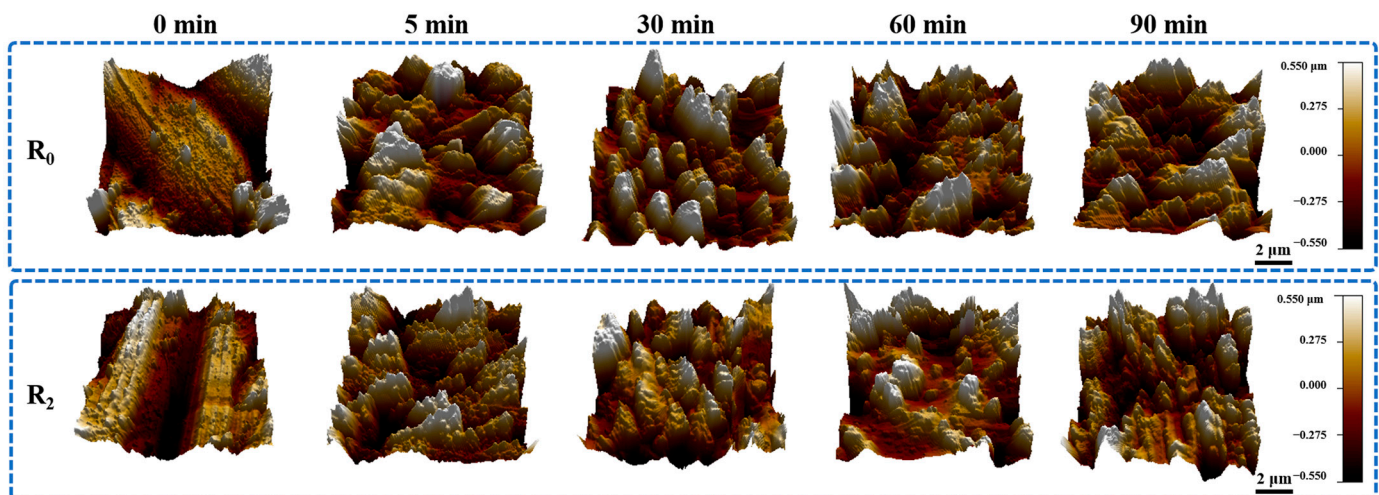


Figure 7. The surface microstructure and morphology of Ti-6Al-4V ELI alloy specimens before and after corrosion observed by AFM.

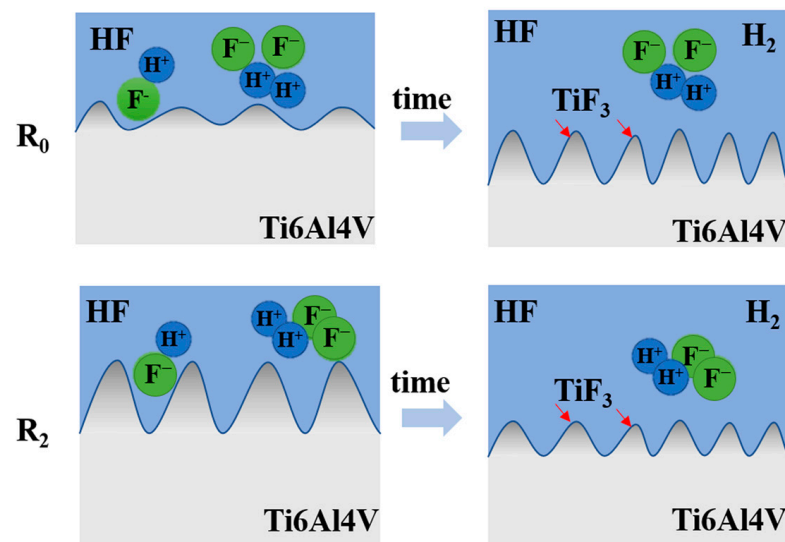


Figure 8. The depiction of corrosion mechanism of Ti-6Al-4V ELI alloy when exposed to an HF solution.

3.4. Recession Behavior of Mechanical Properties after HF Solution Corrosion

Last, the alterations in the compressive mechanical behaviors [13] of the Ti-6Al-4V ELI specimens after corrosion were investigated. Figure 9a shows the force–displacement curves of the Ti-6Al-4V ELI alloy subjected to 2% HF solution corrosion over varying durations. It was observed that with the increasing compression displacement, the compressive force increased. Initially, it was found that there was a linear elastic stage, followed by yielding and plastic deformation stages. Ultimately, when it reached its ultimate compression limit, the Ti-6Al-4V ELI alloy specimen fractured abruptly, resulting in a rapid drop in the compression force. The stress–strain curves of the Ti-6Al-4V ELI alloy subjected to 2% HF solution corrosion with different times are shown in Figure 9b. The trend of the corresponding curve was similar to that of the force–displacement curve. It is worth noting that the stress–strain curves were closer because the effect of changes in specimen cross-section size before/after corrosion was excluded. These results proved that the stress level of the Ti-6Al-4V ELI alloy with different corrosion times remained almost unchanged; however, the maximum compressive force decreased.

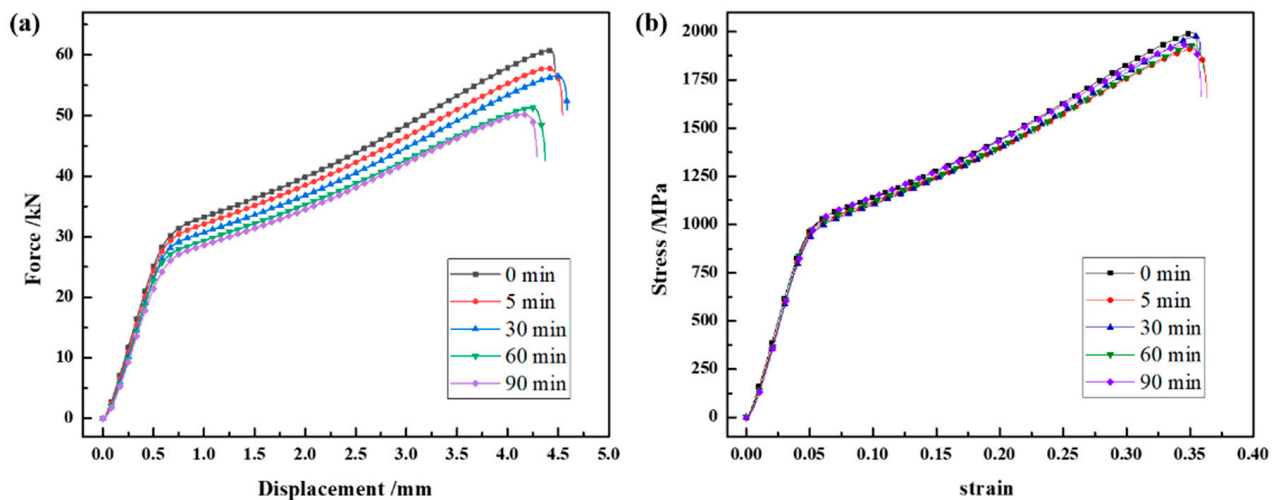


Figure 9. (a) The compression force–displacement curves and (b) the stress–strain curves of Ti-6Al-4V ELI alloy before and after corrosion.

The Ti-6Al-4V ELI alloy specimen without corrosion exhibited the highest bearing capacity throughout the entire compression process compared with specimens with corrosion. Figure 10a shows the quasi-static compression processes of the Ti-6Al-4V ELI alloy before and after corrosion (corrosion times of 0, 5, and 90 min). It was evident that the compression deformation process of the specimen before and after corrosion was similar, indicating that the surface corrosion carried out in this study had little effect on the deformation process of the complete sample. However, as the corrosion time increased, there was a gradual decrease in the bearing force of the Ti-6Al-4V ELI alloy specimen. This decrease was attributed to the corrosion experienced by the specimens when exposed to hydrofluoric acid solution, resulting in the surface erosion. Moreover, it was noticed that the surface of the Ti-6Al-4V ELI alloy was continuously consumed by hydrofluoric acid, leading to a gradual reduction in the specimen diameter as shown in Figure 10b. The reduction in the bearing area subsequently led to a gradual decline in the compressive load with the increasing corrosion time. Therefore, the bearing capacity of the Ti-6Al-4V ELI alloy specimen deteriorated over time when exposed to HF solution. The diameters (D , mm), the bearing area (S , mm²), the maximum compressive force (F_{max} , kN), and the compressive stress (σ_c , MPa) of the specimens are listed in Table 5. By this quantitative comparison, we demonstrated that the diameters, the bearing area, and the maximum compressive force decreased with the increase in the corrosion time. This underscored the importance of considering such corrosion-driven mechanical property changes when utilizing Ti-6Al-4V ELI alloy as crucial engineering materials.

Table 5. The diameters (D , mm), the bearing area (S , mm²), the maximum compressive force (F_{max} , kN), and the compressive stress (σ_c , MPa) of specimens.

Time	D	S	F_{max}	σ_c
0	6.233	30.50	60.74	1993.61
5	6.207	30.24	57.80	1909.26
30	6.080	29.02	56.51	1976.48
60	5.903	27.35	51.30	1930.71
90	5.753	25.98	50.21	1934.46

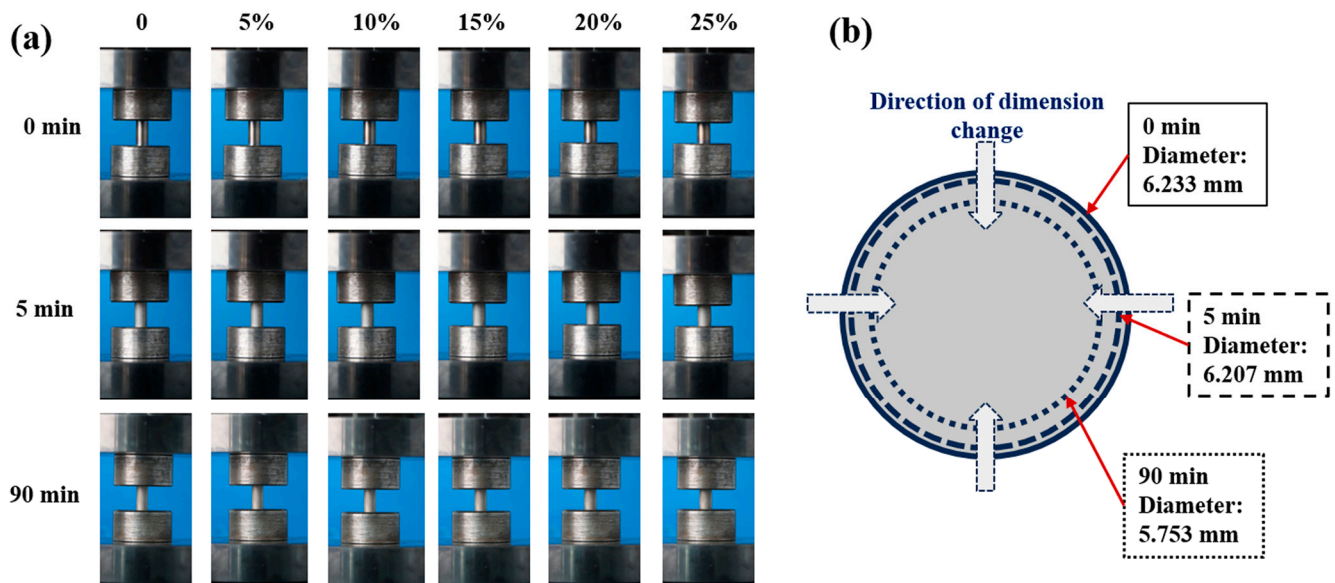


Figure 10. (a) The quasi-static compression processes and (b) the specimen diameter variation of Ti-6Al-4V ELI alloy before and after corrosion.

4. Conclusions

In this study, we investigated the corrosion resistance property of Ti-6Al-4V ELI alloys with varying surface roughness to hydrofluoric acid solution. The main conclusions are summarized as follows:

- The weight loss and weight loss percentage of the Ti-6Al-4V ELI alloy increased with longer corrosion times, while the weight loss rate decreased. Compared with the weight loss and weight loss percentage, the influence of the surface roughness on the weight loss rate was greater. The weight loss, weight loss percentage, and weight loss rate varied significantly with corrosion progression, while their sensitivity to the influence of surface roughness was limited.
- HF solution corrosion imposed a limitation on the surface roughness at approximately $0.2\ \mu\text{m}$. Furthermore, it not only affected the surface roughness but also induced alterations in the surface morphology, transitioning from the strip groove pattern to a columnar peak and valley morphology instead.
- The microstructure of the specimen surface exhibited two distinct phases: the black regions and white phases after corrosion. We believed that the HF solution reacted with the Ti-6Al-4V ELI alloy, leading to the formation of TiF_3 phases. The accumulation of TiF_3 phases and the depletion of the Ti-6Al-4V ELI matrix collaboratively altered the surface roughness. The continuous corrosion occurring in hydrofluoric acid solution was mainly caused by the titanium alloy's inability to prevent fluoride ions from coming into contact with it.
- As the corrosion time increased, the surface of the Ti-6Al-4V ELI alloy was continuously consumed by hydrofluoric acid, leading to a gradual reduction in the bearing area. Hence, the bearing capacity of the Ti-6Al-4V ELI alloy specimen deteriorated over time.

These findings underscore the importance of considering corrosion resistance and surface properties when utilizing Ti-6Al-4V ELI alloy in various applications, particularly in the presence of hydrofluoric acid.

Author Contributions: Conceptualization, H.W. and Z.C.; data curation, Q.C., Z.C., K.W. and X.G.; formal analysis, H.W.; funding acquisition, H.W. and X.F.; investigation, H.W.; methodology, H.W. and Z.C.; project administration, X.F.; resources, X.G. and X.F.; software, H.W.; validation, Q.C. and X.G.; visualization, H.W., Q.C., Z.C. and K.W.; writing—original draft, H.W.; writing—review and editing, H.W., Z.C., K.W. and X.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Science and Technology Major Project (J2019-IV-0003-0070), the National Natural Science Foundation of China (12102335), and the China Postdoctoral Science Foundation (2021M702604).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: Authors Quanshi Cheng and Xuemin Gao was employed by the company Henan Aerospace Precision Machining Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Zhao, Q.; Sun, Q.; Xin, S.; Chen, Y.; Wu, C.; Wang, H.; Xu, J.; Wan, M.; Zeng, W.; Zhao, Y. High-strength titanium alloys for aerospace engineering applications: A review on melting-forging process. *Mater. Sci. Eng. A* **2022**, *845*, 143260. [\[CrossRef\]](#)
2. Gurrappa, I.; Reddy, D.V. Characterisation of titanium alloy, IMI-834 for corrosion resistance under different environmental conditions. *J. Alloys Compd.* **2005**, *390*, 270–274. [\[CrossRef\]](#)
3. Deng, T.; Zhong, X.; Zhong, M.; Lai, Y.; Zhu, Z.; Zhang, L.; Ojo, O.A. Effect of scandium on microstructure and corrosion resistance of Ti64 alloy in NaCl solution. *Mater. Charact.* **2023**, *197*, 112671. [\[CrossRef\]](#)
4. Hong, C.L.X.P. Investigation of Corrosion Processing for Ti-6Al-4V in Hydrofluoric-Nitric Acid System. In Proceedings of the ASME 2011 International Manufacturing Science and Engineering Conference, Corvallis, OR, USA, 13–17 June 2011.
5. Fu, Y.; Xu, Y.; Wang, Y.; Bai, Y.; Hao, H.; Zhu, X. Microstructures and mechanical properties of (TiBw+Ti5Si3)/TC11 composites fabricated by hot isostatic pressing and subjected to 2D forging. *J. Alloys Compd.* **2023**, *966*, 171523. [\[CrossRef\]](#)
6. Zheng, X.; Xu, C.; Cai, Y.; Zhang, B. Effect of Plastic Deformation and Acidic Solution on the Corrosion Behavior of Ti-6Al-4V ELI Titanium Alloy. *Metals* **2023**, *13*, 1740. [\[CrossRef\]](#)
7. Semenova, I.; Polyakov, A.; Gareev, A.; Makarov, V.; Kazakov, I.; Pesin, M. Machinability Features of Ti-6Al-4V Alloy with Ultrafine-Grained Structure. *Metals* **2023**, *13*, 1721. [\[CrossRef\]](#)
8. Hsu, C.; Lin, C.; Chen, J. Wear and Corrosion Performance of Ti-6Al-4V Alloy Arc-Coated TiN/CrN Nano-Multilayer Film. *Metals* **2023**, *13*, 907. [\[CrossRef\]](#)
9. Harun, S.; Burhanuddin, Y.; Ibrahim, G.A. The Effect of Cutting Parameters on Surface Roughness and Morphology of Ti-6Al-4V ELI Titanium Alloy during Turning with Actively Driven Rotary Tools. *J. Manuf. Mater. Process.* **2022**, *6*, 105. [\[CrossRef\]](#)
10. Lopez-Heredia, M.A.; Sohier, J.; Gaillard, C.; Quillard, S.; Dorget, M.; Layrolle, P. Rapid prototyped porous titanium coated with calcium phosphate as a scaffold for bone tissue engineering. *Biomaterials* **2008**, *29*, 2608–2615. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Polley, C.; Radlof, W.; Hauschulz, F.; Benz, C.; Sander, M.; Seitz, H. Morphological and mechanical characterisation of three-dimensional gyroid structures fabricated by electron beam melting for the use as a porous biomaterial. *J. Mech. Behav. Biomed. Mater.* **2022**, *125*, 104882. [\[CrossRef\]](#)
12. Suresh, S.; Sun, C.; Tekumalla, S.; Rosa, V.; Nai, S.M.L.; Wong, R.C.W. Mechanical properties and in vitro cytocompatibility of dense and porous Ti-6Al-4V ELI manufactured by selective laser melting technology for biomedical applications. *J. Mech. Behav. Biomed. Mater.* **2021**, *123*, 104712. [\[CrossRef\]](#)
13. Hameed, P.; Liu, C.; Ummethala, R.; Singh, N.; Huang, H.; Manivasagam, G.; Prashanth, K.G. Biomimetic porous Ti6Al4V gyroid scaffolds for bone implant applications fabricated by selective laser melting. *Prog. Addit. Manuf.* **2021**, *6*, 455–469. [\[CrossRef\]](#)
14. Santos, P.B.; de Castro, V.V.; Baldin, E.K.; Aguzzoli, C.; Longhitano, G.A.; Jardini, A.L.; Lopes, É.S.N.; de Andrade, A.M.H.; de Fraga Malfatti, C. Wear Resistance of Plasma Electrolytic Oxidation Coatings on Ti-6Al-4V Eli Alloy Processed by Additive Manufacturing. *Metals* **2022**, *12*, 1070. [\[CrossRef\]](#)
15. Shao, S.A.; Xi, H.Z.; Chang, Y.P. Study on the Salt Spray Corrosion and Erosion Behavior of TC4 Titanium Alloy. *Adv. Mater. Res.* **2011**, *233–235*, 2409–2412. [\[CrossRef\]](#)
16. Singh, G.; Sharma, N.; Kumar, D.; Hegab, H. Design, development and tribological characterization of Ti-6Al-4V/hydroxyapatite composite for bio-implant applications. *Mater. Chem. Phys.* **2020**, *243*, 122662. [\[CrossRef\]](#)
17. Guo, W.Y.; Sun, J.; Wu, J.S. Electrochemical and XPS studies of corrosion behavior of Ti-23Nb-0.7Ta-2Zr-O alloy in Ringer's solution. *Mater. Chem. Phys.* **2009**, *113*, 816–820. [\[CrossRef\]](#)
18. Lamolle, S.F.; Monjo, M.; Rubert, M.; Haugen, H.J.; Lyngstadaas, S.P.; Ellingsen, J.E. The effect of hydrofluoric acid treatment of titanium surface on nanostructural and chemical changes and the growth of MC3T3-E1 cells. *Biomaterials* **2009**, *30*, 736–742. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Pyka, G.; Burakowski, A.; Kerckhofs, G.; Moesen, M.; Van Bael, S.; Schrooten, J.; Wevers, M. Surface Modification of Ti6Al4V Open Porous Structures Produced by Additive Manufacturing. *Adv. Eng. Mater.* **2012**, *14*, 363–370. [\[CrossRef\]](#)
20. Lim, P.Y.; She, P.L.; Shih, H.C. Microstructure effect on microtopography of chemically etched $\alpha + \beta$ Ti alloys. *Appl. Surf. Sci.* **2006**, *253*, 449–458. [\[CrossRef\]](#)
21. Costa, A.I.; Sousa, L.; Alves, A.C.; Toptan, F. Tribocorrosion behaviour of bio-functionalized porous Ti surfaces obtained by two-step anodic treatment. *Corros. Sci.* **2020**, *166*, 108467. [\[CrossRef\]](#)

22. Atapour, M.; Pilchak, A.L.; Shamanian, M.; Fathi, M.H. Corrosion behavior of Ti–8Al–1Mo–1V alloy compared to Ti–6Al–4V. *Mater. Des.* **2011**, *32*, 1692–1696. [\[CrossRef\]](#)
23. Park, J.; Kim, Y.; Jang, J.; Kwon, T.; Bae, Y.; Suh, J. Effects of phosphoric acid treatment of titanium surfaces on surface properties, osteoblast response and removal of torque forces. *Acta Biomater.* **2010**, *6*, 1661–1670. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Keller, J.C.; Schneider, G.B.; Stanford, C.M.; Kellogg, B. Effects of Implant Microtopography on Osteoblast Cell Attachment. *Implant Dent.* **2003**, *12*, 175–181. [\[CrossRef\]](#)
25. Lee, J.; Lee, M.; Yeon, S.M.; Yoon, J.; Lee, H.; Jun, T. Unravelling anisotropic deformation behaviour of Ti-6Al-4V ELI fabricated by powder bed fusion additive manufacturing. *Mater. Charact.* **2023**, *202*, 113017. [\[CrossRef\]](#)
26. Zahran, R.; Rosales Leal, J.I.; Rodríguez Valverde, M.A.; Cabrerizo Vélchez, M.A. Effect of Hydrofluoric Acid Etching Time on Titanium Topography, Chemistry, Wettability, and Cell Adhesion. *PLoS ONE* **2016**, *11*, e0165296. [\[CrossRef\]](#)
27. Wang, D.; He, G.; Tian, Y.; Ren, N.; Liu, W.; Zhang, X. Dual effects of acid etching on cell responses and mechanical properties of porous titanium with controllable open-porous structure. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2020**, *108*, 2386–2395. [\[CrossRef\]](#)
28. Pham, M.H.; Landin, M.A.; Tiainen, H.; Reseland, J.E.; Ellingsen, J.E.; Haugen, H.J. The effect of hydrofluoric acid treatment of titanium and titanium dioxide surface on primary human osteoblasts. *Clin. Oral Implant. Res.* **2014**, *25*, 385–394. [\[CrossRef\]](#)
29. Pham, M.H.; Haugen, H.J.; Rinna, A.; Ellingsen, J.E.; Reseland, J.E. Hydrofluoric acid treatment of titanium surfaces enhances the proliferation of human gingival fibroblasts. *J. Tissue Eng.* **2019**, *10*, 204173141982895. [\[CrossRef\]](#)
30. Monetta, T.; Bellucci, F. The effect of sand-blasting and hydrofluoric acid etching on Ti CP2 and Ti CP4 surface topography. *Open J. Regen. Med.* **2012**, *1*, 41–50. [\[CrossRef\]](#)
31. Alla, R.K.; Ginjupalli, K.; Upadhya, N.; Shammash, M.; Ravi, R.K.; Sekhar, R. Surface roughness of implants: A review. *Trends Biomater. Artif. Organs* **2011**, *25*, 112.
32. Sefer, B.; Dobryden, I.; Almqvist, N.; Pederson, R.; Antti, M. Chemical Milling of Cast Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo Alloys in Hydrofluoric-Nitric Acid Solutions. *Corrosion* **2017**, *73*, 394–407. [\[CrossRef\]](#)
33. Bezuidenhout, M.; Haar, G.T.; Becker, T.; Rudolph, S.; Damm, O.; Sacks, N. The effect of HF-HNO₃ chemical polishing on the surface roughness and fatigue life of laser powder bed fusion produced Ti6Al4V. *Mater. Today Commun.* **2020**, *25*, 101396. [\[CrossRef\]](#)

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.