

## Article

# Low-Cycle Corrosion Fatigue Deformation Mechanism for an $\alpha+\beta$ Ti-6Al-4V-0.55Fe Alloy

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**Abstract:** Titanium alloys with high strength and good corrosion resistance have become one of the critical bearing structural materials in marine engineering. But in service, corrosion fatigue would occur under the synergetic action of cyclic external load and corrosion environment, threatening the safety of components. In this study, compared with low-cycle fatigue in laboratory air, the low-cycle corrosion fatigue deformation mechanism and fracture characteristic of the Ti-6Al-4V-0.55Fe alloy were investigated in 3.5% NaCl corrosion solution under selected stress amplitudes. The results showed that under low stress amplitude, corrosion fatigue was determined by fatigue damage and corrosion damage, causing a reduction in fatigue life. The local stress concentration caused by corrosion pits and dislocations pile-up accelerated the initiation of fatigue cracks, and other corrosion behavior including crevice corrosion promoted fatigue crack propagation; the corrosion solution increased the surface damage. While under high stress amplitude, due to the short contact time between the sample and solution and higher applied stress, the fatigue life is determined by fatigue damage caused by multiple slips.

**Keywords:** Ti-6Al-4V-0.55Fe alloy; low-cycle fatigue; corrosion fatigue; corrosion damage; deformation mechanism; fatigue crack propagation



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## 1. Introduction

Titanium and titanium alloys are widely applied in marine engineering equipment due to their excellent mechanical properties, such as high specific strength and excellent corrosion resistance [1,2]. However, titanium alloy components are always used in high loading conditions, which causes low-cycle fatigue (LCF) damage. In addition to the conventional fatigue mentioned above, these components are inevitably subjected to the corrosive effect of seawater containing chloride under stress. Corrosion fatigue was first mentioned in 1917 by Haigh [3] and was identified as a combination of electrochemical and mechanical phenomena [4]. Under the synergetic action of cyclic load and corrosive environment, corrosion fatigue with the significantly accelerated initiation and propagation of fatigue cracks is induced in titanium components, causing structural instability and premature failure [5]. Therefore, it is essential to investigate the corrosion fatigue properties of titanium alloys in seawater to clarify the failure mechanisms and to ensure their long-term durability.

It was reported that in an oxygen-containing or corrosive ion environment, a continuous and dense passive film can easily and rapidly form on the surface of titanium alloys, which reduces the surface-active dissolution areas and improves corrosion resistance for titanium alloys by hindering the transmission of reactive particles [6–8]. But in a marine environment, the huge cyclic load on the titanium alloy can inevitably damage the integrity of the passive film and result in a decrease in its corrosion resistance because chloride ions easily destroy and pass through the passive film on the surface, making contact with the matrix [9].

Recently, research on the effect of the corrosive environment on the fatigue crack growth of titanium alloys has been carried out. Zhao et al. [10] proved that the corrosion fatigue crack growth rate (CFCGR) of the Ti6Al4V alloy was strongly dependent on the microstructure, where compared to equiaxed and bimodal microstructures, the CFCGR of the lamellar microstructure was far higher in simulated body fluid due to the  $\alpha/\beta$  phase interface and  $\beta$  grain boundary with a high corrosion sensitivity to the corrosive environment. Ahn et al. [11] suggested that the microstructure-sensitive cracking of the Ti6Al4V alloy was more sensitive to the NaCl solution. Jesus et al. [12] studied the effect of corrosion potential on the fatigue crack growth of Ti-6Al-4V caused by selective laser melting and concluded that the fatigue crack growth rate in a 3.5%wt NaCl solution is 3.3 times higher than that in an inert ambient environment. Zheng et al. [5] also found that the CFCGR of the Ti6Al4V ELI alloy was accelerated by 3.5%NaCl solution and a high stress ratio ( $R = 0.5$ ). The higher the concentration of NaCl in the solution, the higher the fatigue crack growth rate.

The fatigue properties of titanium alloy are also closely related to its service environment. Nie et al. [13] studied the LCF behavior of the TC21 alloy with a bi-lamellar basketweave microstructure in an ambient air environment and found fatigue cracks initiated at the lamellar  $\alpha/\beta$  interface and the slip bands on the surface. Singh et al. [14] undertook research on the cyclic stress response and LCF behavior of the high-temperature titanium alloy IMI 834 at room temperature. Okazaki et al. [15] compared the corrosion fatigue strength of titanium alloys in physiological saline solution and proposed conditions for corrosion fatigue occurrence. Zavanelli et al. [16] studied the corrosion fatigue of CP-Ti and Ti6Al4V in different storage environments and found that the fatigue life of both alloys in a corrosion solution was significantly reduced due to the production of corrosion pits. Fleck et al. [17] found that under low stress amplitude ( $<500$  MPa), there is a distinct reduction in the fatigue life of CP-Ti tested in Ringer's solution compared to CP-Ti tested in a laboratory air environment. Shi et al. [18] reported that the fatigue property of the TC11 alloy under a maximum load of 450 MPa was further reduced in pre-hot salt corrosion due to the appearance of fatigue cracks accelerated by both the local stress concentrations caused by corrosion pits and the promoted fatigue crack propagation caused by the hydrogen and hydride phases. Cremasco et al. [19] evaluated the corrosion fatigue properties of the Ti-35Nb alloy in 0.9% NaCl solution under stresses ranging from 150 to 450 MPa and found that compared to tests in air, the fatigue strength of this alloy in solution declined from 225 MPa to 150 MPa. Baragetti et al. [20] analyzed the chemical and mechanical driving forces during corrosion fatigue tests of the Ti6Al4V alloy. But the results in Bache's research [21] showed that the LCF properties, including the crack growth behavior of the Ti10V2Fe3Al alloy under an applied stress of 300 MPa, were essentially insensitive to the test environments of air and salt fog. However, few studies have paid attention to the characteristics of the low-cycle corrosion fatigue (LCCF) of titanium alloys under corrosive environment.

In previous studies, a novel low-cost titanium alloy, Ti6Al4V-0.55Fe, with a good combination of strength–plasticity and a high level of toughness was prepared [22,23]. This alloy also has a better LCF life than that of Ti6Al4V alloy [24], showing promising application potential for deep-sea equipment manufacturing. It is well known that titanium equipment in deep-sea service is subjected to greater fatigue loading and more severe corrosive environments. Accordingly, fatigue damage increases the corrosion of titanium alloys, and corrosion damage to titanium alloy also accelerates fatigue crack growth [25], both of which interact with each other, posing a huge challenge for TC4-F alloy used in deep-sea equipment manufacturing. But considering the actual service conditions, the effects of the corrosion environment on the LCF property and the failure mechanisms of the TC4-F alloy have not yet been determined. Therefore, in this paper, the LCF and LCCF properties, fracture characteristics, and dislocation structures of the TC4-F alloy under different stress levels in both the corrosion solution and the air environment are examined in order to explore fatigue and corrosion mechanisms.

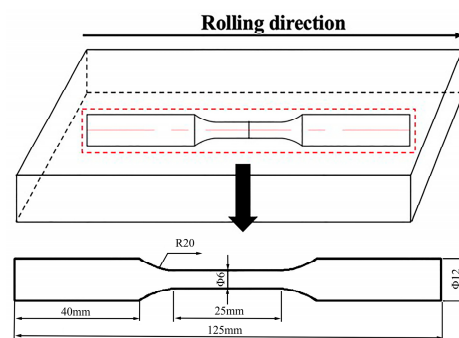
## 2. Materials and Methods

### 2.1. Material

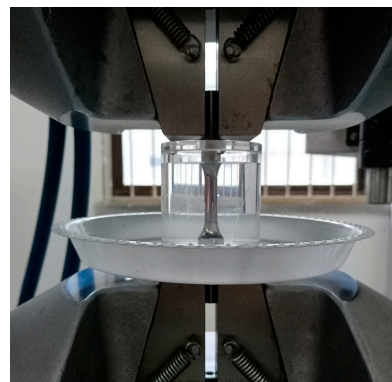
The experiment material used in this work is rolled Ti-6Al-4V-0.55Fe alloy (referred to as TC4-F hereafter), which was produced by vacuum arc remelting (VAR) and then hot-forged and rolled to a plate with a thickness of 42 mm. The chemical compositions of the alloy are Al-6.20, V-4.14, Fe-0.537, C-0.020, O-0.13, N-0.02, H-0.001, Si-0.016 and Ti-balance (wt.%). The  $\beta$ -transus temperature of TC4-F alloy was measured as  $975 \pm 5$  °C via the metallographic method. In order to keep a favorable balance between high strength and high plasticity, the duplex microstructure for this alloy was obtained by the heat treatment consisting of a solid solution at 940 °C for 1.5 h with air cooling to room temperature, and aging at 580 °C for 4 h with air cooling, based on determined  $\beta$ -transus temperatures.

### 2.2. Low-Cycle and Corrosion Fatigue Tests

The cylindrical fatigue sample of 25 mm gauge length with 6 mm gauge diameter, prepared from the plate along the rolling direction, is illustrated in Figure 1. According to the Chinese Standard GB/T 3075-2021 (ISO 1099-2017) [26], the low-cycle fatigue (LCF) in laboratory air (LA) and low-cycle corrosion fatigue (LCCF) tests in 3.5% NaCl corrosion solution (CS) (SHANGJI Co., Nanjing, China) were carried out on the MTS 810 servo hydraulic machines (MTS Co., Shanghai, China) under the stress control with a triangular waveform, a stress ratio of  $R = -1$ , and a frequency of  $f = 0.5$  Hz. Based on the tensile stress–strain curve, the stress amplitudes ( $\Delta\sigma_t/2$ ) including 650 MPa, 690 MPa, 750 MPa, 880 MPa and 910 MPa were selected for fatigue tests. For LCCF tests, the PH value of the used 3.5% NaCl solution was determined as 8.6 by a pH meter (DEYI Co, Shenzhen, China). According to the actual operation and requirements of this experiment, a solution container and device used in LCCF tests are shown in Figure 2. Three parallel samples were used in LCF tests in LA and CS under each stress amplitude. All fatigue tests were conducted at room temperature (about 25 °C).



**Figure 1.** The shape and dimension of samples for LCF and LCCF used in LA and CS in accordance with GB/T 3075-2021 (ISO 1099-2017). Adapted from Ref. [26].



**Figure 2.** The solution container and device used in the LCCF test.

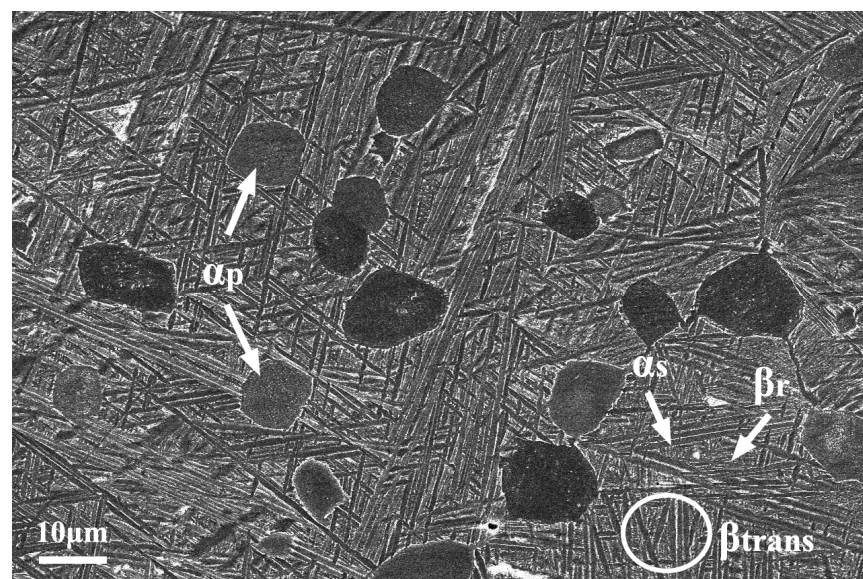
### 2.3. Microstructure and Morphology Characterization

The microstructure of the heat-treated sample and the fracture surface morphology of fatigue samples were observed using scanning electron microscopy (SEM, JSM-6510, JOEL Co., Beijing, China). The chemical composition of several typical points on the fracture surface was analyzed qualitatively and quantitatively using an energy spectrometer matched with the SEM. A transmission electron microscope (TEM, JEM-2100 F, JOEL Co., Beijing, China) was used for dislocation observation of fractured samples after LCCF.

## 3. Results

### 3.1. Initial Microstructure

The duplex microstructure obtained by the heat treatment above is shown with a SEM image in Figure 3. It is composed of primary equiaxed  $\alpha$  phase ( $\alpha_p$ , size  $\sim 6.43\text{--}14.89\ \mu\text{m}$ ), transformed  $\beta$  matrix ( $\beta_{\text{trans}}$ ) consisting of secondary  $\alpha$  ( $\alpha_s$ ) with a thickness of  $\sim 0.50\text{--}1.16\ \mu\text{m}$  and a thin residual  $\beta$  phase ( $\beta_r$ ).

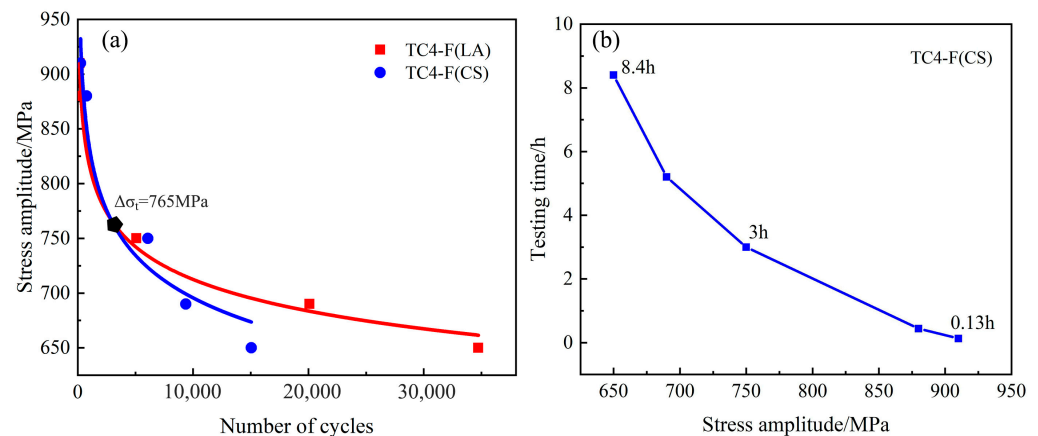


**Figure 3.** SEM image of the duplex microstructure for TC4-F alloy.

### 3.2. Fatigue Life

The variation in fatigue life for TC4-F alloy samples tested in LA and CS under different stress amplitudes is shown in Figure 4a. Under high stress amplitude, there is no significant change in fatigue life for both conditions. However, under low stress amplitude, it is seen that a wide variation in fatigue life between LA and CS is observed. With the decrease in stress amplitude, the fatigue life of TC4-F alloy in CS increases to 15,074 cycles under low stress amplitude of 650 MPa, which is 56% lower than that in LA. The testing time for TC4-F alloy in CS is given in Figure 4b, which shows that at high stress amplitude of 910 MPa, the contacting time between the fatigue sample and the 3.5% NaCl corrosion solution is only 0.13 h, while the contacting time at low stress amplitude of 650 MPa is up to about 8.4 h. It follows that the LCCF deformation mechanisms of TC4-F alloy in CS under low stress amplitudes are totally different from that under high stress amplitude, which is consistent with the results of other titanium alloys tested in laboratory air and a corrosive medium [17,25].

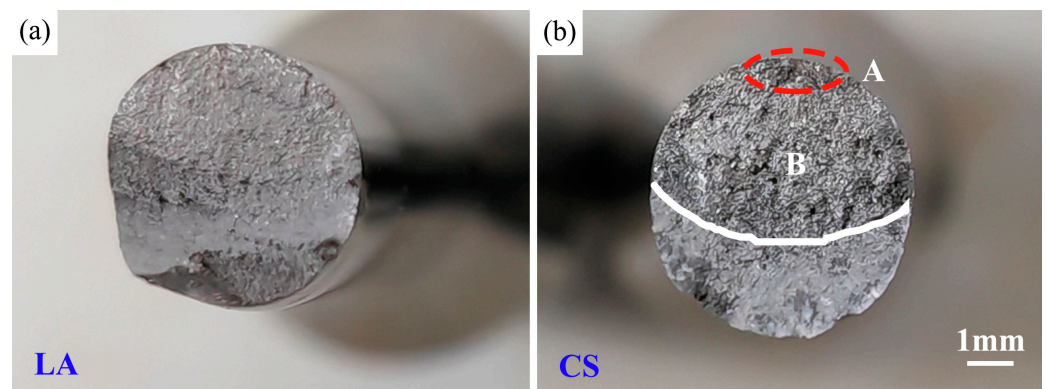




**Figure 4.** Stress amplitude vs. number of cycles for TC4-F alloy in LA and CS (a); testing time for TC4-F alloy in CS (b).

### 3.3. Fracture Characteristics

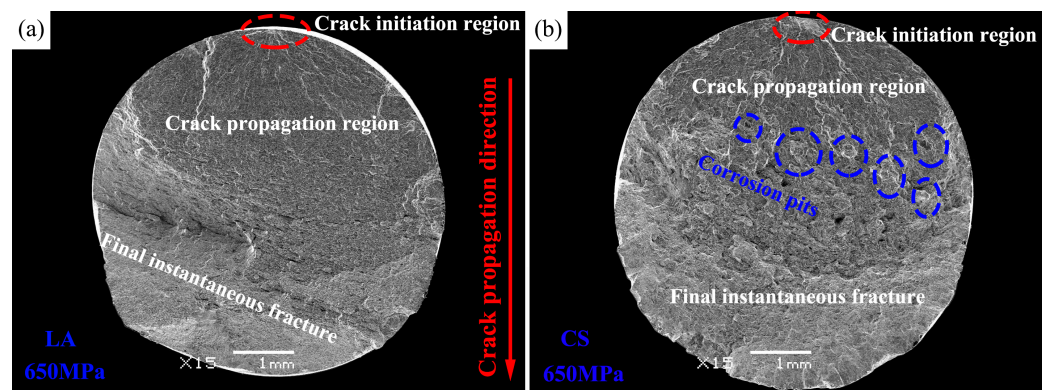
In order to reveal the difference in fracture behavior of TC4-F alloy between LA and CS, the macro-fracture morphologies of the fractured samples in LA and CS under stress amplitude of 650 MPa were detected with the camera, respectively. As shown in Figure 5, an obvious corrosion phenomenon could be observed on the fracture surface of TC4-F alloy in CS. It exhibits that the fatigue crack initiation region (A) and crack propagation region (B) show dark and rough morphological features with some small-scale pits (Figure 5b). The fracture surface in LA is bright and flat (Figure 5a). In contrast, it is preliminarily judged that the corrosion behavior during the LCCF test mainly occurs in fatigue crack initiation and propagation regions.



**Figure 5.** Fracture observation images of TC4-F alloy under the stress amplitude of 650 MPa: (a) in LA; (b) in CS. A (the region marked by red circle) and B represent the fatigue crack initiation region and crack propagation region, respectively.

Figure 6 shows SEM images of the macro view of uncorroded and corroded fracture surface in LA and CS under a low stress amplitude of 650 MPa. The crack initiation region (marked with a red circle), crack propagation region and final instantaneous fracture region on the fracture surface in LA and CS can be distinguished without clear dividing lines. It is seen that for both LA and CS, fatigue cracks initiate from the surface of fatigue samples and propagate radially toward the center. While there are obvious differences in crack propagation region of fracture surfaces between LA and CS, as Figure 6b shows, several corrosion pits (CPs) are observed on the rougher surface with tear edges around [27], which indicates that initiation and propagation of micro-cracks occur at the boundary of CPs. The sizes of CPs are close to that of the equiaxial  $\alpha_p$  phase. It was reported that  $\alpha_p$  dominates the plastic deformation [28]. It determines that  $\alpha_p$  gives priority to

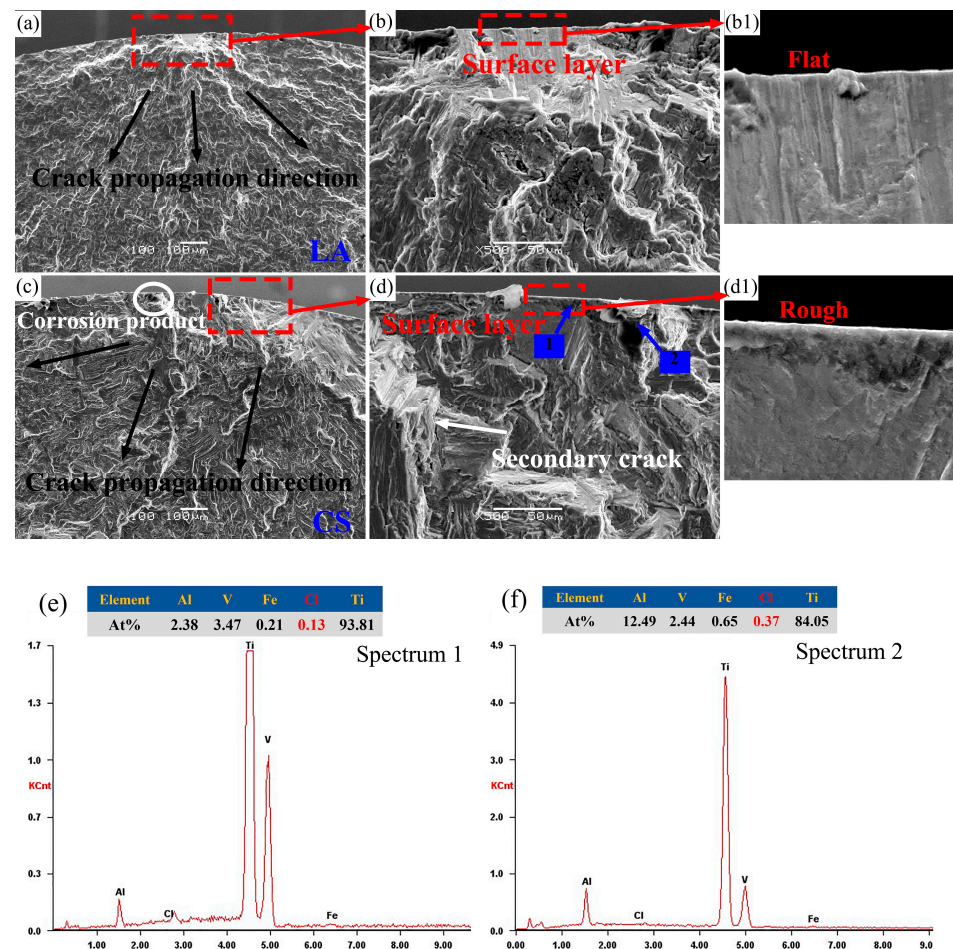
participating in plastic deformation of internal damage, which intensifies the corrosion potential difference between  $\alpha_p$  and  $\beta$  phases. The formation of the primary battery at the interface of  $\alpha_p/\beta$  phases causes corrosion at grain boundary, resulting in pitting corrosion [29], which makes corrosion behavior develop along the grain boundary and eventually form intergranular corrosion, becoming a favorable position for fatigue crack initiation. Under the interaction of cyclic load and corrosion damage, pitting corrosion at  $\alpha_p$  grain boundary develops into CPs. This process above accelerates the propagation rate of fatigue cracks in the crack propagation region.



**Figure 6.** SEM images of fracture morphology for TC4-F alloy under the stress amplitude of 650 MPa: (a) in LA; (b) in CS.

Moreover, the final instantaneous fracture regions of this alloy in LA and CS are not flat, showing a typical shear fracture characteristic [30]. It is attributed to the increased shear stress offered by the applied loading during the final instantaneous fracture period, resulting in the occurrence of final failure at an approximate  $45^\circ$  angle [31]. Although the differences in final instantaneous fracture region are observed in LA and CS, their effect on fatigue life in LA and CS could be negligible due to the short-lasting time.

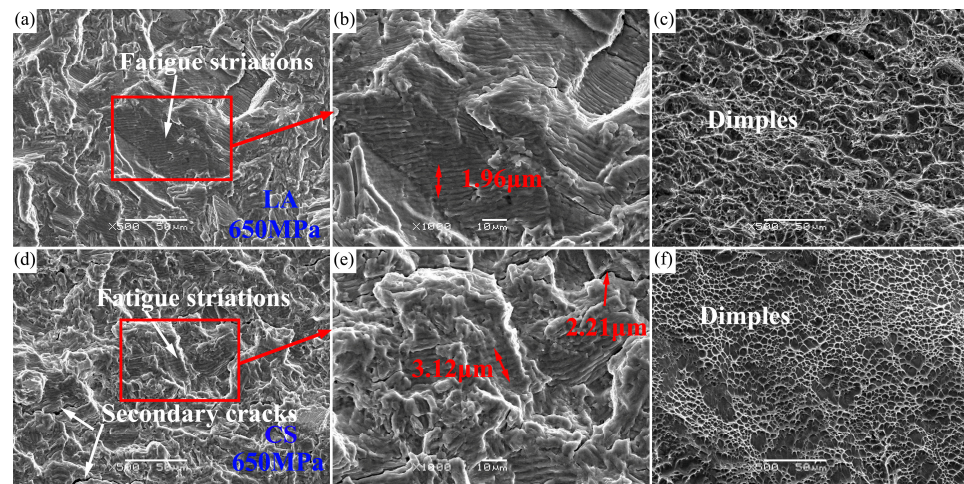
It is certain that the distinctive mechanisms of fatigue crack initiation and propagation behavior lead to the different features on the fracture surface of TC4-F alloy in LA and CS. Figure 7 exhibits the fatigue crack initiation regions of samples in LA and CS at a high magnification region. For the sample in LA, only one fatigue crack initiation site is observed in Figure 7a, and the fatigue crack initiates from the sample surface with crystal facets associated with slip bands (Figure 7a,b) due to the activation of slip bands on the sample surface caused by applied cyclic reversal load. Usually, the size of the grain where the crack initiation occurs is larger than the average grain size [32]. For the sample in CS, the observation in fractography shows the corrosion product and characteristics of multiple crack sites (Figure 7c), which indicates that the superimposed effect of fatigue and corrosion accelerates fatigue crack initiation. In addition, compared with the flat layer in LA (Figure 7b1), the surface layer of the fatigued sample in CS turns out to be rough and forms a corrosion layer (Figure 7d1). As shown in Figure 7e,f, EDS analysis for the chemical composition of Spectrum 1 and Spectrum 2 detects the presence of elemental Cl in the crack initiation site and CPs. During cyclic load, tiny CPs at the surface corrosion scale induce the stress concentration, which causes serious corrosion damage, promotes the fatigue crack initiation, and finally shortens fatigue life [18].



**Figure 7.** Microscopic fracture morphology of the crack initiation region for TC4-F alloy under the stress amplitude of 650 MPa: (a,b) LA; (c,d) CS; (b1) and (d1) the partially enlarged view of the sample surface in (b) and (d), respectively; (e,f) the element composition at the positions of 1 and 2 in (d), respectively.

Figure 8 shows the crack propagation and final instantaneous fracture region of the TC4-F alloy in LA and CS. In contrast, obvious fatigue striations and secondary cracks are observed as the main features in the crack propagation process for the sample in CS. On one hand, the fatigue striation spacing of 3.12 μm in CS is wider than that of the sample in LS (1.96 μm). It indicates that the corrosion environment decreases the crack closure effect and promotes the increase in fatigue crack propagation rate [33,34]. On the other hand, the secondary crack with a width of 2.21 μm observed in Figure 8e is closely related to crevice corrosion [4], which increases the dissolution rate of the fatigue crack front, promoting the initiation and propagation of the fatigue crack. In terms of the final instantaneous fracture region, the main feature of samples in LA and CS is dominated by dimples. The dimples in CS turn out to be smaller in size and depth, which manifests in a fracture region in a corrosive environment that shows poor plasticity, further shortening the fatigue life. In fact, the cycles occupied by fracture region are quite short, so the effect of corrosion damage in fracture region on fatigue life could be ignored.





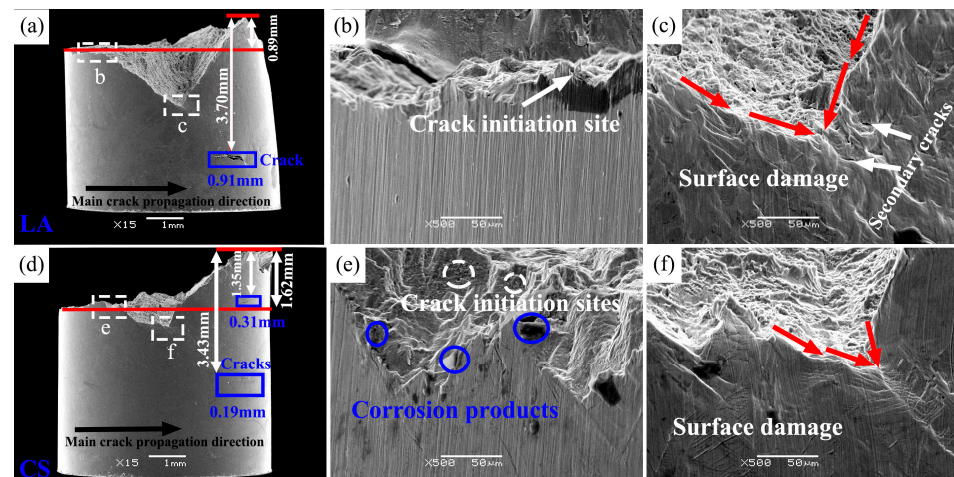
**Figure 8.** Microscopic fracture morphology for TC4-F alloy under the stress amplitude of 650 MPa: (a,b) crack propagation region in LA; (c) final instantaneous fracture region in LA; (d,e) crack propagation region in CS; (f) final instantaneous fracture region in CS.

Figure 9 shows the side morphology of fatigue samples under a stress amplitude of 650 MPa in LA and CS. As shown in Figure 9a,d, the fatigue step in CS reaches 1.62 mm, which is nearly twice the height of that in LA (about 0.89 mm). It is because the corrosion damage accelerates the crack propagation rate, reduces the crack closure effect, and increases the plastic zone of the crack tip, which makes cracks deflect at a large angle during crack propagation. In LA, only one crack with a length of about 0.91 mm is found at 3.7 mm from the cross-section. In CS, multiple cracks could be observed. For example, one crack of 0.31 mm appears at 1.35 mm from the section, and several parallel cracks with a maximum length of about 0.19 mm are also found at a distance of 3.43 mm. It means that the corrosion environment promotes the initiation and propagation of surface cracks, increasing the surface damage of samples. Furthermore, an obvious difference in the crack propagation path of TC4-F alloy tested in LA and CS could be observed in Figure 9a,d. In LA, the driving force for crack propagation is only the low applied stress, which may be unable to break through the barrier of grain boundary to crack propagation, making the crack propagate along the grain boundary and deflect with a large angle. In CS, the driving force for crack propagation turns out to be a synergy of applied stress and corrosion. The degradation of the surface microstructure and the weakening or destruction of grain and phase boundaries could be caused by corrosion behavior [18], which makes cracks propagate across the grain boundary and deflect with a low angle.

During the crack propagation region (Figure 9b,e), samples in LA and CS present a mixed fracture mode of transgranular and intergranular fracture. But in CS, some corrosion products are observed on the surface of the sample near the crack propagation path, which provides more favorable sites for crack initiation, resulting in more fatigue crack initiation and propagation at the interface between corrosion products and the matrix. In addition, there are obvious corrosion phenomena on the fracture.

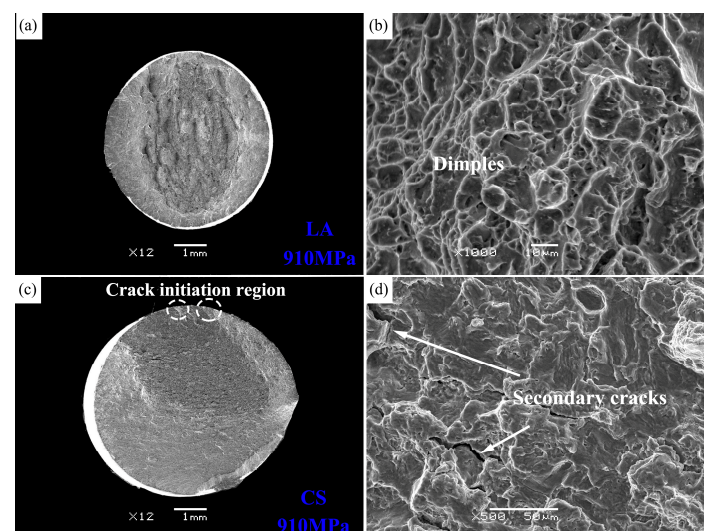
Figure 9c,f give the surface damage area at the junction of the crack propagation region and instantaneous fracture region. Surface damage morphologies of samples in LA and CS show obvious characteristics of plastic deformation at the crack tip and cracking along the slip. Secondary cracks are observed on the surface in LA. In this process, the stress intensity factor range  $\Delta K$  [35] of the TC4-F alloy sample in CS is high with the corresponding high crack growth rate, causing the short fatigue life and loading time, which makes cyclic plastic deformation play a dominant role. In addition, this area in the fracture surface of this alloy in LA and CS shows sudden static failure with appreciable plastic deformation [36].





**Figure 9.** The side fracture morphology of TC4-F alloy under the stress amplitude of 650 MPa: (a) the overall morphology in LA, (b) morphology near the crack propagation region in LA, (c) surface damage in LA; (d) the overall morphology in CS, (e) morphology near the crack propagation region in CS, (f) surface damage in CS.

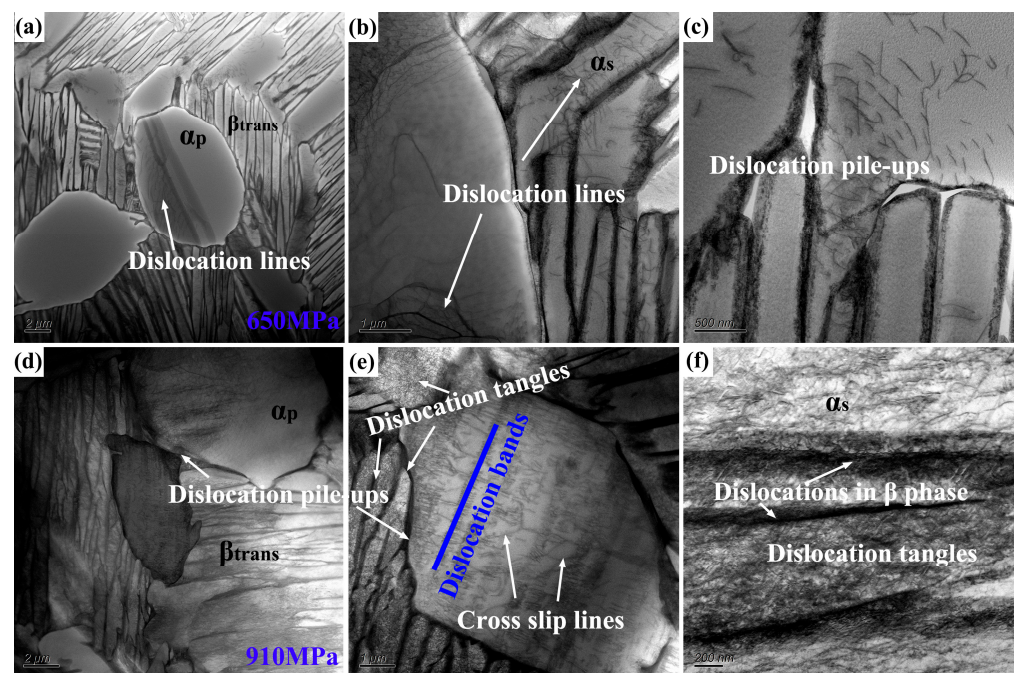
The SEM micrographs in Figure 10 present the fracture morphology of TC4-F alloy under a high stress amplitude of 910 MPa in LA and CS. In LA, the fatigue fracture morphology shows quasistatic fracture characteristics due to the obvious necking phenomenon without clear crack initiation and propagation regions (Figure 10a). The fracture morphology of this alloy in LA is composed of interconnected dimples (Figure 10b). In CS, the fracture with visible crack initiation, propagation, and instantaneous fracture regions still presents typical characteristics of fatigue fracture. Multiple fatigue crack initiation regions, where fatigue cracks initiate from the sample surface, are also observed. Due to the high crack propagation rate, there are several secondary cracks instead of fatigue striations in the crack propagation region. The different fracture morphologies of the samples between LA and CS could be attributed to that 3.5% NaCl solution can effectively carry away the heat generated by fatigue sampling during the cyclic deformation within a short time, which is beneficial to fatigue life. However, the fatigue failure under high stress amplitude of 910 MPa is determined by the accumulation of fatigue damage, which makes the alleviating effect from CS on the fatigue life dispensable.



**Figure 10.** Fracture morphology of TC4-F alloy under the stress amplitude of 910 MPa (a,b) in LA; (c,d) in CS.

### 3.4. Dislocation Structures in Fatigued Samples in CS

The dislocation characteristics of TC4-F alloy samples after cyclic deformation in CS under stress amplitudes of 650 MPa and 910 MPa examined by TEM are given in Figure 11. It can be seen that cyclic deformation mainly occurs in  $\alpha_p$  grains because they have a softer phase than  $\beta_{trans}$  [37]. Under a low stress amplitude of 650 MPa, dislocation structures are dominated by simple short dislocation lines mainly activated in  $\alpha_p$  grains with preferential orientation, and few are detected in the  $\alpha_s$  phase (Figure 11a,b). Short dislocation lines pile up in  $\alpha/\beta$  interfaces (Figure 11c), which means that dislocation interaction occurs in the vicinity of  $\alpha/\beta$  interfaces. Due to the low applied stress close to the elastic region, no significant macro plastic deformation occurs in the deformed sample. Then, only micro yielding takes place by dislocation interaction [38]. Under a high stress amplitude of 910 MPa, more complex dislocation structures with high dislocation density are activated to accommodate the cyclic plastic deformation, which indicates that multiple slip systems occur in a deformed sample. Dislocation tangles are observed in both the  $\alpha_p$  grain and the  $\alpha_s$  phase (Figure 11e,f), caused by the dislocation pile-ups and dislocation interaction in  $\alpha/\beta$  interfaces. Furthermore, a dislocation band and cross slip lines form inside the  $\alpha_p$  grain (Figure 11e). It was reported that the dislocation band is strongly related to the prismatic slip [39], while crossing slip lines are dominated by prismatic  $\langle a \rangle$  slips and pyramidal  $\langle c + a \rangle$  slips [40]. Additionally, dislocations are detected clearly in the  $\beta$  phase (Figure 11f). Also, a large number of dislocations easily activated inside  $\alpha_p$  grain would pile up in  $\alpha/\beta$  interface due to high plastic strain. As a result, the main deformation mechanisms of this alloy in CS are cross slips and dislocation tangles.



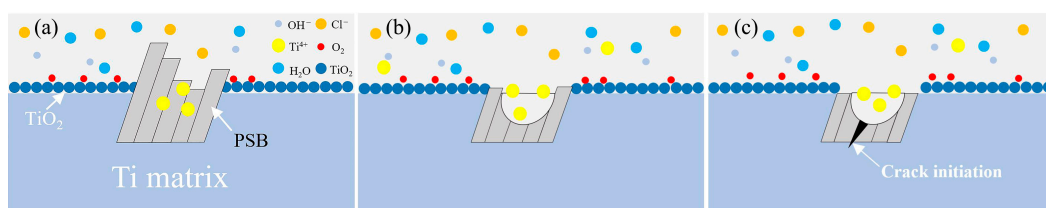
**Figure 11.** Dislocation structures observed in TC4-F alloy fatigued in CS using TEM under the amplitude of 650 MPa (a–c) and 910 MPa (d–f).

Similarly in both stress amplitudes, dislocation pile-ups in  $\alpha/\beta$  interface induce local stress concentration and plastic strain localization, causing  $\alpha/\beta$  interface to be preferential nucleation sites of fatigue cracks in this alloy [28].

### 4. Discussion

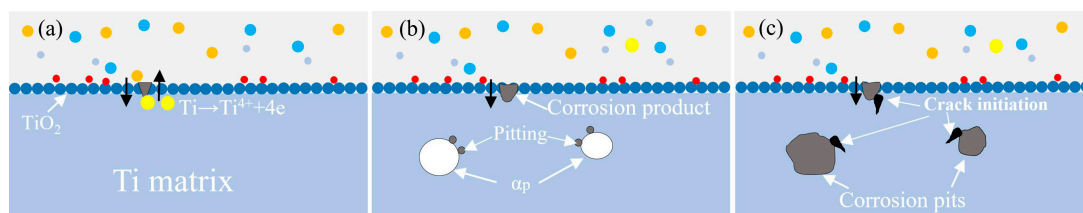
Under high stress amplitude, the mechanism of corrosion fatigue for TC4-F alloy is determined by fatigue damage, as shown in Figure 12. The high applied stress makes the surface of this alloy sample prone to slip deformation, which generates a persistent

slip band (PSB) [13,41]. Then, it breaks the integrity of the passive film on the surface of the titanium matrix, which exposes the fresh titanium matrix completely to a corrosive medium and makes the electrochemical reaction occur. But corrosion products or CPs cannot form on the surface of the sample due to the quite short contacting time between the sample and corrosive medium. Finally, the local stress concentration induced by PSB contributes to the fatigue crack initiation at the interface between the slip band and the matrix. According to dislocation structures in Figure 11d–f, cross slips and dislocation tangles induce the accumulation of irreversible plastic deformation, resulting in huge fatigue damage. Compared with fatigue damage, the influence of the corrosive medium on the fatigue life of this alloy is very limited. Under high stress amplitude, the accumulation of fatigue damage caused by cyclic loading radically results in fatigue failure. Therefore, under high stress amplitudes, there is no significant change in fatigue life for samples testing in LA and CS.



**Figure 12.** Schematic illustration of corrosion fatigue damage mechanism for TC4-F alloy under high stress amplitude: (a) PSB caused by high applied stress; (b) the passivation film was destroyed by slip, and anodic dissolution in the matrix occurs [42]; (c) fatigue crack initiation occurs on the surface of sample due to stress concentration.

Under low stress amplitude, the mechanism of corrosion fatigue for TC4-F alloy is determined by fatigue damage and corrosion damage. The schematic illustration for corrosion damage under 650 MPa is shown in Figure 13. Due to the low applied stress, slips on the sample surface are not easy to activate. With the synergy of cyclic loading and corrosive medium for a long time, the passive film on the sample surface is finely broken in the local area. Chloride ions (Cl<sup>-</sup>) could pass through the broken passive film and make electrochemical corrosion occur with the exposed titanium matrix [27,43], where they could form an anodic dissolution [42] and produce corrosion products. Then, the passive film is further destroyed and is unable to be repaired in time [6,44], which exposes a fresher titanium matrix to the corrosive medium. The CPs and corrosion products gathering near the passive film easily promote local stress concentration on the surface of the sample under the axial tension–compression loading, inducing the initiation of fatigue cracks on the surface. In the crack propagation stage, high Gibbs free energy in the interface and a potential difference between the  $\alpha_p$  phase and  $\beta$  phase easily lead to forming micro battery at  $\alpha_p/\beta$  interface, which provides a potential point for corrosion. Finally, fatigue cracks initiate in these points and propagate along the  $\alpha_p/\beta$  interface, resulting in intergranular corrosion (Figure 6b) and accelerating the fatigue crack.



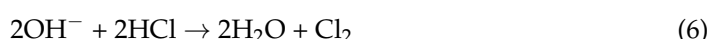
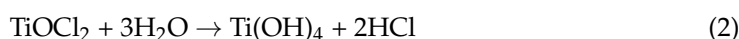
**Figure 13.** Schematic illustration of corrosion fatigue damage mechanism for TC4-F alloy under low stress amplitude: (a) Cl<sup>-</sup> pass through the broken passive film (black arrows); (b) corrosion products form on the surface and pitting corrosion occurs; (c) fatigue initiation is accelerated, and corrosion pits form.



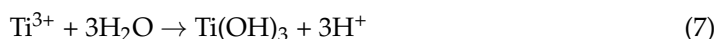
In addition, once a crack initiates, its propagation rate will be accelerated by anodic dissolution, resulting in cracking on the surface of the sample. In the narrow gap, due to the low internal oxygen content, micro batteries form in these areas with large differences in internal and external oxygen concentration, making the damaged passive film not be repaired by oxygen inhalation and activated titanium matrix inside the gap. It means the concentration of titanium ions would increase, and a hydrolysis reaction occurs with the aggregation of  $H^+$ , resulting in the acidification of the solution in the gap and the inward migration of  $Cl^-$  outside the gap, which further promotes the dissolution of the titanium matrix in the gap, and brings out crevice corrosion damage [4].

Meanwhile, activated dislocations in  $\alpha_p$  grains pile up in  $\alpha/\beta$  interface during cyclic deformation would cause stress concentration and plastic strain localization. Finally, it induces fatigue crack initiation and propagation in this alloy. Therefore, under low stress amplitude, the fatigue life of the TC4-F alloy in CS is determined by the superposition effects from fatigue damage and corrosion damage, which contributes to lower fatigue than that of the TC4-F alloy in LA (Figure 4a).

The electrochemical reaction equations [45] involved in the corrosion process are as follows:



The hydrolysis reaction equation [9] involved in gap corrosion is as follows:



In a word, the research results fill in the research on the comparison between low-cycle and corrosion fatigue to some extent and provide a theoretical basis for understanding the corrosion fatigue failure mechanism of TC4-F alloy in applications. But more importantly, the fatigue life of the TC4-F alloy decreased by approximately 56% in CS ( $N_f = 15,074$ ) under a low stress amplitude compared with that in LA ( $N_f = 34,734$ ), expanding the mechanical database for life evaluation and design of TC4-F alloy components in marine service environments.

## 5. Conclusions

In this work, the mechanisms of low-cycle fatigue in laboratory air and low-cycle corrosion fatigue in a 3.5% NaCl corrosion solution of an  $\alpha+\beta$  Ti-6Al-4V-0.55Fe alloy under control of stress amplitudes were systematically investigated via SEM and TEM techniques. The main findings can be summarized as follows:

- (1) Under a low stress amplitude of 650 MPa, the corrosion fatigue mechanism of this alloy in 3.5% NaCl corrosion solution is determined by the superposition effects from fatigue damage and corrosion damage, shortening the fatigue life; under a high stress amplitude of 910 MPa, the corrosion fatigue of this alloy with a similar fatigue life is mainly dependent on the fatigue damage.
- (2) Under a low stress amplitude, together with the dislocation pile-ups, corrosion products and pitting induce the local stress concentration, accelerating fatigue crack initiation. Intergranular corrosion and crevice corrosion promote fatigue crack propagation.
- (3) Under a high stress amplitude, a broken passive film on the surface cannot be repaired in time. The local stress concentration induced by slips contributes to the fatigue crack initiation at the interface.

- (4) The corrosion solution also brings out more surface damage under a low stress amplitude, improving fatigue cracks.

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## References

- Sun, C.; Li, Y.; Xu, K.; Xu, B. Effects of intermittent loading time and stress ratio on dwell fatigue behavior of titanium alloy Ti-6Al-4V ELI used in deep-sea submersibles. *J. Mater. Sci. Technol.* **2021**, *77*, 223–236. [\[CrossRef\]](#)
- Boyer, R.R.; Briggs, R.D. The use of  $\beta$  titanium alloys in the aerospace industry. *J. Mater. Eng. Perform.* **2013**, *22*, 2916–2920. [\[CrossRef\]](#)
- Haigh, B.P. Experiments on the fatigue of brasses. *J. Inst. Met.* **1917**, *18*, 55–77.
- Behvar, A.; Haghshenas, M. A critical review on very high cycle corrosion fatigue: Mechanisms, methods, materials, and models. *J. Space Saf. Eng.* **2023**, *10*, 284–323. [\[CrossRef\]](#)
- Zheng, X.; Xu, C.; Zhang, B.; Cai, Y.; Zhou, X. Effect of corrosive environment and stress ratio on the fatigue crack growth behavior of titanium alloy. *Mater. Today Commun.* **2024**, *39*, 108732. [\[CrossRef\]](#)
- Yang, J.; Song, Y.; Dong, K.; Han, E. Research progress on the corrosion behavior of titanium alloys. *Corros. Rev.* **2023**, *41*, 5–20. [\[CrossRef\]](#)
- Pazhanivel, B.; Sathiya, P.; Muthuraman, K.; Sozhan, G. Influence of NaCl environment on stress corrosion cracking of additive manufactured Ti-6Al-4V alloy. *Eng. Fail. Anal.* **2021**, *127*, 105515. [\[CrossRef\]](#)
- Voiculescu, I.; Brito-Garcia, S.J.; González-Díaz, Ó.M.; Mirza-Rosca, J. Mechanical characteristics and corrosion behavior of two new titanium alloys. *Metals* **2023**, *13*, 1729. [\[CrossRef\]](#)
- Wang, X.; Zhu, S.; Yang, Z.; Wang, C.; Wang, N.; Zhang, Y.; Yu, F. Corrosion-resistance mechanism of TC4 titanium alloy under different stress-loading conditions. *Materials* **2022**, *15*, 4381. [\[CrossRef\]](#)
- Zhao, X.; Song, X.; Wang, R.; Wang, L.; Liu, Y.; Hu, J. Microstructure-dependent corrosion fatigue crack growth behavior of Ti-6Al-4V alloy in simulated body fluid. *Eng. Fail. Anal.* **2023**, *148*, 107184. [\[CrossRef\]](#)
- Ahn, S.; Jeong, D.; Kwon, Y.; Goto, M.; Sung, H.; Kim, S. Environmental fatigue crack propagation behavior of  $\beta$ -annealed Ti-6Al-4V alloy in NaCl solution under controlled potentials. *Int. J. Fatigue* **2018**, *111*, 186–195. [\[CrossRef\]](#)
- Jesus, J.S.; Borrego, L.P.; Ferreira, J.A.M.; Costa, J.D.; Capela, C. Fatigue crack growth under corrosive environments of Ti-6Al-4V specimens produced by SLM. *Eng. Fail. Anal.* **2020**, *118*, 104852. [\[CrossRef\]](#)
- Nie, B.; Song, Y.; Huang, X.; Qi, H.; Zhao, Z.; Chen, D. Low cycle fatigue behavior of TC21 titanium alloy with bi-lamellar basketweave microstructure. *Crystals* **2022**, *12*, 796. [\[CrossRef\]](#)
- Singh, N.; Gouthama; Singh, V. Low cycle fatigue behavior of Ti alloy IMI 834 at room temperature. *Mater. Sci. Eng. A* **2002**, *325*, 324–332. [\[CrossRef\]](#)
- Okazaki, Y.; Ito, Y.; Kyo, K.; Tateishi, T. Corrosion resistance and corrosion fatigue strength of new titanium alloys for medical implants without V and Al. *Mater. Sci. Eng. A* **1996**, *213*, 138–147. [\[CrossRef\]](#)
- Zavanelli, R.A.; Pessanha Henriques, G.E.; Ferreira, I.; de Almeida Rollo, J.M.D. Corrosion-fatigue life of commercially pure titanium and Ti-6Al-4V alloys in different storage environments. *J. Prosthet. Dent.* **2000**, *84*, 274–279. [\[CrossRef\]](#) [\[PubMed\]](#)
- Fleck, C.; Eifler, D. Corrosion, fatigue and corrosion fatigue behaviour of metal implant materials, especially titanium alloys. *Int. J. Fatigue* **2010**, *32*, 929–935. [\[CrossRef\]](#)
- Shi, H.; Liu, D.; Zhang, X.; Jia, T.; Zhao, W. Effect of pre-hot salt corrosion on hot salt corrosion fatigue behavior of the TC11 titanium alloy at 500 °C. *Int. J. Fatigue* **2022**, *163*, 107055. [\[CrossRef\]](#)
- Cremasco, A.; Lopes, E.S.N.; Cardoso, F.F.; Contieri, R.J.; Ferreira, I.; Caram, R. Effects of the microstructural characteristics of a metastable  $\beta$  Ti alloy on its corrosion fatigue properties. *Int. J. Fatigue* **2013**, *54*, 32–37. [\[CrossRef\]](#)

20. Baragetti, S.; Arcieri, E.V. Corrosion fatigue behavior of Ti-6Al-4 V: Chemical and mechanical driving forces. *Int. J. Fatigue* **2018**, *112*, 301–307. [\[CrossRef\]](#)
21. Bache, M. Fatigue and Fracture Evaluations in Ti-10V-2Fe-3Al (Ti 10-2-3). *Metals* **2023**, *13*, 1986. [\[CrossRef\]](#)
22. Li, X.; Zhu, Q.; Liu, S.; Wang, C.; Li, F.; Chen, F.; Feng, L.; Wang, H.; Cheng, J.; Chang, H. Phase transformation behaviours and mechanical properties of Ti6Al4V-0.55Fe alloy during continuous cooling. *Mater. Sci. Technol.* **2022**, *38*, 1543–1553. [\[CrossRef\]](#)
23. Chen, F.; Gu, Y.; Xu, G.; Cui, Y.; Chang, H.; Zhou, L. Improved fracture toughness by microalloying of Fe in Ti-6Al-4V. *Mater. Des.* **2020**, *185*, 108251. [\[CrossRef\]](#)
24. Sun, Y.; Alexandrov, I.V.; Dong, Y.; Valiev, R.Z.; Chang, H.; Zhou, L. Optimized low-cycle fatigue behavior and fracture characteristics of Ti-6Al-4V alloy by Fe microalloying. *J. Mater. Res. Technol.* **2021**, *15*, 5277–5287. [\[CrossRef\]](#)
25. Zhao, Y.; Yu, P.; Wu, L.; Zhang, X.; Wei, P.; Zhao, J. Corrosion-induced deceleration-to-acceleration of fatigue crack growth for deep-sea Ti6Al4V ELI titanium alloy. *Eng. Fract. Mech.* **2023**, *281*, 109160. [\[CrossRef\]](#)
26. GB/T 3075-2021; Metallic Materials—Fatigue Testing—Axial Force-Controlled Method. Standards Press of China: Beijing, China, 2021.
27. Ali, N.; Fulazzaky, M.A.; Mustapa, M.S.; Ghazali, M.I.; Ridha, M.; Sujitno, T. Assessment of fatigue and corrosion fatigue behaviours of the nitrogen ion implanted CpTi. *Int. J. Fatigue* **2014**, *61*, 184–190. [\[CrossRef\]](#)
28. Tan, C.; Li, X.; Sun, Q.; Xiao, L.; Zhao, Y.; Sun, J. Effect of  $\alpha$ -phase morphology on low-cycle fatigue behavior of TC21 alloy. *Int. J. Fatigue* **2015**, *75*, 1–9. [\[CrossRef\]](#)
29. Ma, J.; Zhang, B.; Wang, J.; Wang, G.; Han, E.-H.; Ke, W. Anisotropic 3D growth of corrosion pits initiated at MnS inclusions for A537 steel during corrosion fatigue. *Corros. Sci.* **2010**, *52*, 2867–2877. [\[CrossRef\]](#)
30. Wu, G.Q.; Shi, C.L.; Sha, W.; Sha, A.X.; Jiang, H.R. Microstructure and high cycle fatigue fracture surface of a Ti-5Al-5Mo-5V-1Cr-1Fe titanium alloy. *Mater. Sci. Eng. A* **2013**, *575*, 111–118. [\[CrossRef\]](#)
31. Sterling, A.J.; Torries, B.; Shamsaei, N.; Thompson, S.M.; Seely, D.W. Fatigue behavior and failure mechanisms of direct laser deposited Ti-6Al-4V. *Mater. Sci. Eng. A* **2016**, *655*, 100–112. [\[CrossRef\]](#)
32. Jiang, R.; Karpasitis, N.; Gao, N.; Reed, P.A.S. Effects of microstructures on fatigue crack initiation and short crack propagation at room temperature in an advanced disc superalloy. *Mater. Sci. Eng. A* **2015**, *641*, 148–159. [\[CrossRef\]](#)
33. Lee, H.; Mall, S.; Allen, W.Y. Fretting fatigue behavior of shot-peened Ti-6Al-4V under seawater environment. *Mater. Sci. Eng. A* **2006**, *420*, 72–78. [\[CrossRef\]](#)
34. Niinomi, M.; Saga, A.; Fukunaga, K.-I. Long crack growth behavior of implant material Ti-5Al-2.5Fe in air and simulated body environment related to microstructure. *Int. J. Fatigue* **2000**, *22*, 887–897. [\[CrossRef\]](#)
35. Nakai, Y.; Kikuchi, S.; Osaki, K.; Kawabata, M.O.; Ameyama, K. Effects of rolling reduction and direction on fatigue crack propagation in commercially pure titanium with harmonic structure. *Int. J. Fatigue* **2021**, *143*, 106018. [\[CrossRef\]](#)
36. Bologna, O.; Cecchel, S.; Cornacchia, G.; Avanzini, A.; Sepe, R.; Berto, F.; Razavi, N. Investigating post-processing impact on fatigue performance of LPBF Ti6Al4V with heat treatment, high pressure heat treatment, and dry electropolishing strategies. *Int. J. Fatigue* **2024**, *185*, 108365. [\[CrossRef\]](#)
37. Huang, C.; Zhao, Y.; Xin, S.; Zhou, W.; Li, Q.; Zeng, W. Effect of microstructure on torsion properties of Ti-5Al-5Mo-5V-3Cr-1Zr alloy. *Mater. Sci. Eng. A* **2017**, *682*, 202–210. [\[CrossRef\]](#)
38. Sen, M.; Suman, S.; Mukherjee, S.; Banerjee, T.; Sivaprasad, S.; Tarafder, S.; Bhattacharjee, A.; Kumar Kar, S. Low cycle fatigue behavior and deformation mechanism of different microstructures in Ti-5Al-5Mo-5V-3Cr alloy. *Int. J. Fatigue* **2021**, *148*, 106238. [\[CrossRef\]](#)
39. Wang, Q.; Ren, J.Q.; Xin, C.; Jiang, P.; Zhang, L.; Liu, Q.T.; Wu, J.P. Low cycle fatigue behavior of near-alpha titanium alloys used in deep-driving submersible: Ti-6Al-3Nb-2Zr-1Mo vs. Ti-6Al-4V ELI. *J. Alloys Compd.* **2023**, *934*, 167856. [\[CrossRef\]](#)
40. Xu, Z.; Huang, C.; Wan, M.; Tan, C.; Zhao, Y.; Ji, S.; Zeng, W. Influence of microstructure on strain controlled low cycle fatigue crack initiation and propagation of Ti-55531 alloy. *Int. J. Fatigue* **2022**, *156*, 106678. [\[CrossRef\]](#)
41. Shi, H.; Liu, D.; Zhang, X.; Zhao, W.; Liu, Z.; Li, M.; He, Y. Effect of plasma electrolytic oxidation on the hot salt corrosion fatigue behavior of the TC17 titanium alloy. *Mater. Corros.* **2022**, *73*, 558–572. [\[CrossRef\]](#)
42. Chen, Q.; Xu, Y.; Ma, A.; Zhang, L.; Zheng, Y. Study of the passivation and repassivation behavior of pure titanium in 3.5 wt% NaCl solution and 6 M HNO<sub>3</sub> solution. *Corros. Sci.* **2023**, *224*, 111538. [\[CrossRef\]](#)
43. Long, J.; Li, X.; Guo, B.; Wang, L.; Zhang, N. Catalytic delignification of sugarcane bagasse in the presence of acidic ionic liquids. *Catal. Today* **2013**, *200*, 99–105. [\[CrossRef\]](#)
44. Li, Z.; Wang, J.; Dong, Y.; Xu, D.; Zhang, X.; Wu, J.; Gu, T.; Wang, F. Synergistic effect of chloride ion and *Shewanella* algae accelerates the corrosion of Ti-6Al-4V alloy. *J. Mater. Sci. Technol.* **2021**, *71*, 177–185. [\[CrossRef\]](#)
45. Sato, N. Basics of corrosion chemistry. *Green Corros. Chem. Eng. Oppor. Chall.* **2011**. [\[CrossRef\]](#)

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