Original Article

Effect of roughness on electrochemical and pitting corrosion of Ti-6Al-4V alloy in 12 wt.% HCl solution at 35 °C

Guangfang Chi\textsuperscript{a,b}, Danqing Yi\textsuperscript{a,b,e}, Huiqun Liu\textsuperscript{a,b}

\textsuperscript{a} School of Materials Science and Engineering, Central South University, Changsha 410083, China
\textsuperscript{b} Key Laboratory for Nonferrous Materials Science and Engineering, Education Ministry, Central South University, Changsha 410083, China

**A R T I C L E  I N F O**

Article history:
Received 5 July 2019
Accepted 16 November 2019
Available online 13 December 2019

Keywords:
Ti–6Al–4V alloy
Surface roughness
Polarization
Electrochemical impedance spectroscopy
Pitting corrosion

**A B S T R A C T**

This study experimentally investigated the electrochemical corrosion and pitting corrosion of Ti–6Al–4V alloy samples with different roughness in 12 wt.% HCl solution at 35 °C. The corrosion behavior of these alloy samples was studied by potentiostatic and potentiodynamic polarization. Both the corrosion rate and pitting sensitivity of the sample increased with increasing surface roughness. Moreover, the effect of surface roughness on the corrosion of Ti–6Al–4V alloy could be characterized by the aspect ratio ($w/d$) of the peak-valley morphology on the surface, where $w$ and $d$ are the width of the valley and relative depth of the peak. The $w/d$ and true surface areas influenced the pitting corrosion of the alloy. Polishing the surface of the Ti–6Al–4V alloy can enhance the corrosion resistance of the working surface, rendering the material suitable for use in the oil and gas industries.

© 2019 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

In recent years, the exploration of oil and gas has gradually shifted to region with harsh environment and complicated geological conditions [1]. The exploration and extraction of petroleum and gas from sea bottoms and deep wells are becoming increasingly difficult because of the high-temperature, high-pressure, and highly corrosive conditions of these source locations [2]. The metal oil casings lining the wells are often exposed to harsh environments where wear and corrosion are common [3]. Thus, the choice of materials used in the petrochemical industry is a more important issue. In most environments, the traditional duplex stainless steels are more resistant to corrosion than carbon steel [2]; however, they are prone to active corrosion in some environments such as in 10–28 wt.% HCl (i.e., matrix acidizing conditions) because their protective oxide film dissolves [3]. Hence, titanium alloys have been used as petroleum tubes in oil and gas exploration, because they offer high specific strength, good corrosion resistance, low modulus of elasticity, easy cold forming, seawater erosion resistance, and other excellent characteristics [4,5]. However, pitting corrosion, an extremely localized form of corrosion, can occur in a range of aggressive environments...
containing Cl− ions and H2S [6,7]. This process generates small pits or holes, invisible to the naked eye, which consequently grow inside the alloy and damage the passivation layer [8]. In particular, pitting corrosion provides initiation points for stress corrosion crack propagation or corrosion fatigue, both of which reduce the useful lifetime of the material [9–11]. Hence, accurate assessment of such corrosion processes is required to mitigate damage to alloy components [12,13]. Of the various electrochemical testing methods used for studying corrosion mechanisms, potentiodynamic polarization curves can provide information regarding the pitting susceptibility via pitting potential (Epit) measurement [14,15], but these potentials do not give information about the number of pits or their relative sizes [14,16–18]. Therefore, in order to analyze current transients caused by the occurrence of metastable pits [16,19,20], a potentiostatic polarization method was developed to produce corrosion pits [21–24]. The evolution of the transients over time provides information on the initiation, propagation, and re-passivation of metastable pits.

In general, the initial stages of corrosion are highly dependent on the surface roughness [25–27], because dense oxide films on the metal/alloy surface protecting the alloy from the corrosive medium can be more easily damaged (e.g., during abrasion) at higher surface roughness. However, with different machining methods and machining accuracies, the workpiece surfaces of Ti–6Al–4V differ in surface roughness. The specific surface conditions of titanium alloys and other metals [28] are often different from those of the subsurface bulk metals because the surface is inevitably subjected to heavy wear during component fabrication (such as rolling, machining, and grinding) and during use, such as the exploration and extraction of petroleum and gas [28,29]. Previous studies have verified the relationship between surface roughness and pitting corrosion in steel, aluminum alloys, and titanium alloys [6,25,26]. For instance, Burstein et al. [30] showed that rougher stainless steel surfaces had a lower susceptibility to metastable pitting in a chloride (Cl−)-containing solution; however, once pitting occurred, metastable pits were more likely to achieve stable pit growth than those on a smoother surface. Pradhan et al. [31] found that a larger available surface area can increase the corrosion rate, and the surface area increased with increasing surface roughness. Li et al. [32,33] reports the same conclusion as Pradhan et al.; in addition, they reported that the average surface electron work function (EWF) reduced and the fluctuation in the local EWF increased. This promoted the formation of microelectrodes, thereby accelerating corrosion. However, to the best of our knowledge, there are few reports of deformation of the surface layer of Ti–6Al–4V alloys due to wear and related corrosive behavior.

The corrosion behavior of titanium alloys in accelerated corrosion environments has been extensively studied. However, the influence of surface roughness on pitting has not yet been thoroughly evaluated or quantified. In addition, in order to restore or increase the permeability of petroleum and gas reservoirs and enhance petroleum and gas recovery, the matrix acidizing technique of petroleum and gas reservoirs is widely used. At present, the most frequently used acidizing solutions are inorganic acid systems (e.g. HCl and HCl/HF mixtures) and organic acid systems (e.g. formic acid and acetic acid); in acidizing, high concentrations of these solutions are injected into the well [34,35]. Some studies investigated the effect of surface roughness on the corrosion behavior of engineering components [3,9–11]. However, very few reports have addressed the effects of surface roughness on the resistance of titanium alloys to metastable and stable pitting. Thus, this study investigates the metastable and stable pitting of Ti–6Al–4V alloy samples with different roughness in a 12 wt.% HCl solution at 35 °C. Samples of Ti–6Al–4V alloy with different surface roughness were produced by manually abrading the surfaces with different sandpaper or polished. The surface morphologies were analyzed using an optical surface profiler system. In addition, the effect of surface roughness on the corrosion characteristics of Ti–6Al–4V alloy was studied by electrochemical techniques, such as potentiodynamic method, electrochemical impedance spectroscopy (EIS), and potentiostatic method. This study aimed to examine the effect of the electrochemical corrosion and pitting mechanisms on titanium alloys with different surface roughness, and we believe that the results would contribute to the development of titanium alloys for oil and gas exploitation applications.

### 2. Experiments

#### 2.1. Materials and surface treatment

In this work, we chose Ti–6Al–4V alloy as the experimental material. The chemical composition of samples is shown in Table 1. The samples for the electrochemical measurements were cut from titanium alloy plate of 10 mm in thickness and coated with epoxy resin with an insulated copper line contact by conductive adhesive. A test area of 1 cm² was left uncoated to allow exposure to the electrolyte in the electrochemical tests. Before the electrochemical tests, the samples were successively ground with 80, 400, and 800-grit SiC paper and polished using a 0.06-μm colloidal silica suspension. After polishing, some electrode samples (exposed area of 10 x 10 mm²) were then unidirectionally ground again using SiC paper of up to 80, 400, or 800 grit. The sample types are henceforth referred to as “80-grit abraded,” “400-grit abraded,” “800-grit abraded,” and “polished.” Then, the electrodes were cleaned with alcohol, followed by deionized water, and then dried with cold air. The surface morphologies were analyzed parallel to the grinding direction using scanning electron microscopy (SEM, Quanta-200, USA) at a 20 kV accelerating voltage and a 10 mm working distance. The surface texture and surface roughness (Rq) of all samples were measured using an optical surface profiler system (Wyko NT9100, USA) with a measurement area of 1.3 x 0.95 mm². All tests were carried out three times.

<p>| Table 1 – Chemical composition (wt.%) of Ti–6Al–4V alloy. |</p>
<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>V</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contents</td>
<td>5.82</td>
<td>3.61</td>
<td>balance</td>
</tr>
</tbody>
</table>

2.2. Electrochemical measurements

All electrochemical tests were performed in 12 wt.% HCl in a water bath at 35 °C with a potentiostat workstation (Multi Autolab M204, Holland). A standard three-electrode cell was used. The reference electrode was a saturated calomel electrode (SCE), the working electrode was the titanium alloy specimens, and the counter-electrode was a platinum plate. The potentiodynamic polarization of the samples was performed from −0.80 V_SCE at a scanning rate of 1 mV/s after 2 h of immersion in 12 wt. % HCl at 35 °C. EIS tests were performed in the frequency range of 100000-0.01 Hz at the open circuit potential (OCP) with the application of sinusoidal potentials of amplitude 10 mV. The experimental impedance data were fitted by an appropriate electrochemical equivalent circuit (EEC) and analyzed using ZSimpWin software [36]. In this work, all potentials obtained were relative to the SCE (V_SCE). All tests were carried out at least three times.

2.3. Pitting corrosion measurements

In order to obtain measurable current transients, Ti–6Al–4 V alloy electrode samples with an active diameter of 1 mm were polarized potentiostatically for 1000s. However, in order to obtain a large number of stable pits introduced by the potentiostatic polarization, electrodes with an exposed area of 1 cm² were used at 1.20 V_SCE. In order to effectively generate metastable pitting, we applied potentials 50 mV below the respective E_corr with a polarization time of 1000s. We defined the generation of pits as a transient event lasting at least 1.5 s [14], with a peak current of at least twice the respective background.

To obtain a stable pitting current with the sample, it was necessary to apply potentiostatic polarization for 3600 s. The current signals were collected at applied potentials lower than E_corr to avoid producing stable pits at the beginning of the measurements. Therefore, for comparison, the current fluctuations for all samples were collected at 1.20 V_SCE, which was slightly lower than E_corr for the 80-grit abraded sample. Observation of the morphology of stable pits on the sample surfaces was performed using SEM and a Keyence VHX-5000 three-dimensional video microscope. Prior to the analysis of the pit microstructure, the surface layer of corrosion products was cleaned with dilute HNO₃ in an ultrasonic bath for 10 min [18]. All tests were repeated at least three times until repeatable values were observed.

3. Results

3.1. Surface morphology and surface roughness

The surface topographies of the Ti–6Al–4 V alloys after the three different surface preparation steps are presented in Fig. 1. The sample ground with emery paper showed many prominent deep scratches along the grinding direction that are approximately parallel to each other, along with asperities arranged regularly on the sample surfaces (Fig. 1(a), (b)). The wear traces of the 80-grit abraded sample are narrower and deeper than those of the 800-grit abraded sample; the polished sample shows no obvious wear traces at the magnification analyzed.

Fig. 2 shows the surface roughness and corresponding profiles of the alloy samples prepared using different grinding parameters. Each roughness curve was obtained along the pink line to reveal the two-dimensional sample surface topographies, showing groove height distribution. With increasing grit size of the SiC emery paper, the surface roughness of the samples markedly decreased. After grinding with 80-grit emery paper, distinct elongated ridges and parallel valleys are observed along the scratch direction (Fig. 2(a)), with an average depth and width of 4 and 90 μm, respectively. As the grit number increased from 80 to 800, the grinding marks become increasingly shallow, and the sample surface becomes smoother (Fig. 2(b), (c)). On the polished sample (Fig. 2(d)), no obvious grinding marks are observed at the microscale resolution of the instrument. As expected, the average surface roughness (R_a) decreased from 2.31 μm to 0.21 μm as the grit of the sandpaper increased from 80 grit to 800 grit. The polished alloy has the lowest surface roughness (0.03 μm).

3.2. Polarization behavior

Potentiodynamic polarization curves for the alloy samples with various surface finishes in 12 wt.% HCl solution at 35 °C are illustrated in Fig. 3; a passive region can be distinctly observed in all curves, indicating similar typical passivation behaviors [37,38]. Table 2 shows the potential of corrosion (E_corr), corrosion current density (I_corr), passivation current density (I_pass), and E_corr. E_corr and I_corr were obtained using the Tafel extrapolation method [39,40]. With increasing grit number, E_corr and E_corr of the samples become positive, indicating that a smoother surface exhibits lower pitting susceptibility and has less active sites than the rougher surface. Moreover, the increase in E_corr with increasing grit number is larger than that of E_corr. However, the passivation current decreased, indicating that the stability of the passivity film on the surface of the titanium alloy increased with decreasing roughness.

3.3. Impedance spectra

The Nyquist and Bode diagrams for the Ti–6Al–4 V alloys are presented in Fig. 4 and used to effectively evaluate the electrode reaction processes. The three samples show similar impedance characteristics, indicating similar corrosion processes. The Nyquist plots of all Ti–6Al–4 V samples (Fig. 4(a)) show two capacitive loops related to two time constants. The low-frequency loop is probably associated with pitting corrosion processes (metastable and stable), whereas the high-frequency loop is related to film defects [41]. Because many microcracks exist on the sample surface, the aggressive solution could reach the alloy through these microcracks and form active zones at the interface region. Such pitting dominated the corrosion process [42]. The capacitive arc for the polished sample is the largest among the four tested samples, suggesting that its oxide film provides the highest electrochemical resistance. The Bode phase angles of the Ti–6Al–4 V alloys with different roughness reach a maximum phase angle of ~80° over a wide frequency range (100–10 Hz), as depicted in Fig. 4(b). The highest phase angle of the polished sample
confirms that its oxide film offers the highest electrochemical resistance.

To quantitatively estimate the corrosion of Ti–6Al–4 V with different surface roughness, the EIS spectra were fitted using the EEC shown in Fig. 4(c), and the parameters obtained from the fitting are shown in Table 3. The $R(QR(QR))$-type equivalent circuit provided the best fit to the test data, where $R_T$ and $Q_f$ correspond to the pore resistance and the capacitance of the film, respectively, $R_s$ refers to the solution resistance, and $R_w$ and $Q_w$ indicate the charge transfer resistance and capacitance of the double layer, respectively [54,55]. Here, $Q_f$ and $Q_w$ are both constant phase elements (CPEs), which are used instead of the pure capacitance response because of the differences in the surface roughness [43]. As expected, the fitted values of $R_T$ increase with decreasing roughness, while $Y_0$ decreases, indicating that the density and stability of the protective oxide film both increased with increasing smoothness.

The wider semicircle on Nyquist plot of the polished sample confirms the higher resistance of oxide layer compared to that of Ti–6Al–4 V with a surface roughness of $R_s > 0.03 \mu m$. The results show that the fitting results are in good agreement with the potentiodynamic polarization curve data. The polished sample exhibits better corrosion resistance than the 80-grit, 400-grit, and 800-grit abraded samples. Therefore, the surface roughness significantly affects the integrity of the passivation film, which further affects the corrosion performance of Ti–6Al–4 V alloy.

3.4. Metastable pitting current transients

Fig. 5 shows the potentiostatic polarization plots. The base current signals of all samples are similar. A relatively slow growth before repassivation is indicated by sharp increases and subsequent decreases in the current at the same rate. Such
Fig. 2 – (a, c, e, g) 2D surface topographies and (b, d, f, h) curves of Ti–6Al–4 V alloy ground with (a, b) #80 grit, (c, d) #400 grit, (e, f) #800 grit sandpaper, and (g, h) polished by 0.06-μm colloidal silica suspension.

Table 3 – Parameters obtained from fitting EIS data for Ti–6Al–4 V alloys with different surface finishes measured in 12 wt.% HCl solution at 35 °C with the EEC model described in Fig. 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω·cm$^2$)</th>
<th>$Q_f$ (F·cm$^{-2}$)</th>
<th>$n$</th>
<th>$R_f$ (Ω·cm$^2$)</th>
<th>$Q_{ct}$ (F·cm$^{-2}$)</th>
<th>$n$</th>
<th>$R_c$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-grit abraded</td>
<td>0.7</td>
<td>$1.1 \times 10^{-3}$</td>
<td>0.96</td>
<td>260.8</td>
<td>$3.0 \times 10^{-2}$</td>
<td>0.78</td>
<td>360.5</td>
</tr>
<tr>
<td>400-grit abraded</td>
<td>0.9</td>
<td>$6.1 \times 10^{-4}$</td>
<td>0.96</td>
<td>389.4</td>
<td>$2.3 \times 10^{-2}$</td>
<td>0.79</td>
<td>546.7</td>
</tr>
<tr>
<td>800-grit abraded</td>
<td>1.9</td>
<td>$4.9 \times 10^{-4}$</td>
<td>0.94</td>
<td>560.8</td>
<td>$3.2 \times 10^{-2}$</td>
<td>0.91</td>
<td>574.5</td>
</tr>
<tr>
<td>Polished</td>
<td>0.95</td>
<td>$1.8 \times 10^{-4}$</td>
<td>0.95</td>
<td>668.8</td>
<td>$6.2 \times 10^{-3}$</td>
<td>0.31</td>
<td>3571</td>
</tr>
</tbody>
</table>
current transients are widely observed for passive materials [16,41,42]. Moreover, with increasing roughness, the frequency and intensity of the current transients of the metastable pitting current are generally increased. Multiple current peaks may be caused by the simultaneous activation of multiple metastable pits or changes in the anolyte chemistry in one pit [42–45]. By integrating the transient current of a single metastable pit, the dissolution volume of the corresponding metastable pit can be obtained. The high nucleation rate of pits at the surface results in a high formation rate of metastable pits. Hence, once a metastable pitting event occurs, pitting tends to continue at or near the same site. This phenomenon is used to describe the synergistic behavior of metastable pitting and pitting events and the increase in local corrosion. In addition, because of the 2-mm-diameter sample produces the relatively high base current, therefore, only relatively large current transients are detected here.

The frequency of metastable pitting events is assessed from the current–time (I–t) data collected over 1000s at 50 mV below $E_{pit}$ in 12 wt.% HCl solution at 35 °C. The number of metastable pitting transients decreases significantly with decreasing roughness, suggesting that the frequency of metastable pitting corrosion decreases with

---

**Fig. 3** – Potentiodynamic polarization curves of Ti–6Al–4 V alloy samples with four different surface finishes in 12 wt.% HCl solution at 35 °C.

**Fig. 4** – (a) Nyquist plots, (b) Bode plots, and (c) equivalent circuit used in EIS analysis of Ti–6Al–4 V alloys with different surface finishes in 12 wt.% HCl solution at 35 °C.

**Fig. 5** – Current curves obtained from 2-mm-diameter samples of Ti–6Al–4 V alloy with the four different surface finishes during potentiostatic polarization at 50 mV below $E_{pit}$ in 12 wt.% HCl solution at 35 °C.
The morphology of the stable pits formed on the sample surface after three surface treatments is shown in Fig. 7. The most severe pitting corrosion is observed for the alloy with the largest surface roughness. The pits are seen to propagate along the grinding direction and combine with nearby pits to form localized corrosion, especially on the roughest surface. Moreover, the average pit depth determined from three-dimensional microscopy images are shown in Fig. 8. The pit depths are 109.61 μm, 93.56 μm, 84.29 μm, and 60.29 μm for the 80-grit, 400-grit, 800-grit, and polished samples, respectively. The roughest surface has the highest pit depth, consistent with the scanning results.

Statistical analysis of the corrosion areas is performed for each sample type, as shown by the area distribution histograms of stable pits shown in Fig. 9. Pits are less likely to occur on the smoother surface; the number and surface areas of all pits are increased with increasing roughness. Furthermore, larger and less regular pits are formed on the rougher surfaces, demonstrating that these pits are formed by dissolving the product generated by local accumulation. Multiple micro-pits tend to aggregate, indicating that after the re-passivation of a metastable pit, the region around the metastable pit remains active for the nucleation of metastable pits. Hence, even if no stable pitting occurs in the surface alloy, small current fluctuations may result in cumulative pitting damage and local dissolution. The total numbers of pits observed on the 80-grit, 400-grit, 800-grit, and polished samples are 2600, 1994, 1288, and 527, respectively, while the total pit surface area is 9586, 6972, 3084, and 1209 μm², respectively. The average areas of the pit mouths tend to decrease with increasing roughness, indicating that stable pits are less likely to form and propagate more slowly on smoother surfaces. Thus, smoother surfaces exhibit better pitting corrosion resistance than rougher surfaces.

4. Discussion

4.1. Pitting mechanism

The mechanism of pitting corrosion and local corrosion of Ti-6Al-4V alloy in 12 wt.% HCl solution at 35 °C over time is described in the schematic in Fig. 10. Initially, pitting corrosion causes defects on the surface, as shown in Fig. 10 (a) and Fig. 10 (b). In general, pitting corrosion occurs in three stages: passivity breakdown, pit initiation, and pit propagation [46–48]. To date, several different corrosion mechanisms have been proposed, but three main mechanisms, i.e., the penetration, the passive film breakdown mechanism, and the absorption mechanism have been supported by most authors [49–51]. The penetration mechanism is shown by Fig. 10 (a), where aggressive Cl⁻ ions can pass through the passive layer on the alloy surface and participate in the local dissolution of the alloy/passive layer interface [52–55]. In contrast, the passive film breakdown mechanism suggests that the passive film on rougher surfaces contains defects and that the adsorption of aggressive Cl⁻ ions reduces the surface tension of the passive film, causing cracks that allow anions to reach the alloy surface [56,57]. Meanwhile, according to the adsorption mechanisms, the aggressive anions are adsorbed on the oxide surface, which

---

**Table 4 – Statistical parameters of the current transients generated on 2-mm-diameter samples with the four surface finishes during potentiostatic polarization in 12 wt.% HCl solution at 35 °C.**

<table>
<thead>
<tr>
<th>Surface Finish</th>
<th>N</th>
<th>Δi (μA)</th>
<th>Δt (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-grit abraded</td>
<td>159 ± 24</td>
<td>11.65 ± 6.28</td>
<td>38 ± 17</td>
</tr>
<tr>
<td>400-grit abraded</td>
<td>131 ± 18</td>
<td>8.65 ± 3.28</td>
<td>25 ± 6</td>
</tr>
<tr>
<td>800-grit abraded</td>
<td>129 ± 12</td>
<td>3.35 ± 1.56</td>
<td>18 ± 11</td>
</tr>
<tr>
<td>Polished</td>
<td>69</td>
<td>1.25 ± 0.87</td>
<td>9 ± 5</td>
</tr>
</tbody>
</table>

N is the number of current transients; Δi is the average peak current; and Δt is the lifetime of the current transient.

---

Fig. 6 – Potentiostatic polarization curves for 1-cm² samples with different surface finishes measured at 1.7 V SCE in 12 wt.% HCl solution at 35 °C.
catalyzes and enhances the transfer of metal cations from the oxide to the electrolyte; there, they form a surface complexes with titanium oxide. This effect results in thinning of the passivation film, and eventually, parts of the passivation film are completely removed [58–60]. HCl is a completely dissociated acid, where continuous electrolysis involving H⁺ and Cl⁻ ions maintains at low-pH pit (Fig. 10(b)). During propagation of the pit, localized acidification occurs, which concentrates Cl⁻ and Ti⁴⁺ ions following the initial stage of pit formation, as shown in Fig. 10(b). In addition, the hydrolysis of the anolyte inside the pit with the dissolved metal cations can also cause local acidification. The diffusion of corrosion products controls the propagation of pits, resulting in the accumulation of alloy cations and Cl⁻ ions, as well as significant local acidification [61]. This localized acidification is capable of sustaining further pit growth via autocatalytic reactions [62–64]. Simul-

Fig. 7 – Morphologies of stable pits on 1-cm² samples with (a, b) 80 grit, (c, d) 400 grit, (e, f) 800 grit and (g, h) polished surface finishes after 3600 s at 170 V_{SCE} in 12 wt.% HCl solution at 35 °C.
Fig. 8 – (a, c, e) 2D images of representative pits formed in 12 wt.% HCl solution at 35 °C, and (b, d, f) cross-sectional profiles of the alloy samples with (a, b) 80 grit, (c, d) 400 grit, (e, f) 800 grit and (g, h) polished surfaces.

taneously, the anodic reaction takes place in the pit and the supporting cathode reaction takes place on the alloy surface near the pit. A propagating pit introduces a potential drop and causes localized chemical changes that can increase the probability of pit initiation; pits are thus more likely to occur near the original pit propagating along a groove. With the propaga-
Fig. 9 – Number of stable pits on 1-cm² samples with the four different surface finishes after treatment at 1.70 V_SCE in 12 wt.% HCl solution at 35 °. Insets: Magnifications of areas outlined in blue dashes.

Fig. 10 – Schematics of the pitting initiation and development mechanisms on the alloy surface during potentiodynamic polarization in 12 wt.% HCl solution at 35 °. (a) pit initiation, (b) pit propagation, (c) pit combination, and (d) local corrosion.

4.2. Effect of roughness on electrochemical and pitting corrosion

The results of the potentiodynamic polarization showed that the smoother samples had higher $E_{corr}$ values and lower $I_{pass}$ values, indicating lower corrosion reactivities and lower dissolution rates of the films during passivation, thus yielding fewer
surface defects. The lower \( I_{\text{pass}} \) indicated that the oxide films on the surface of alloy were stable and intact. \( E_{\text{p}} \) decreased with increasing surface roughness, indicating that a higher surface roughness increased pitting sensitivity. Furthermore, the smoothest sample showed the highest impedance during EIS measurements, indicating a better corrosion resistance than the rougher samples. The larger high-frequency capacitive loop corresponding to film defects suggested that the smoother sample had a higher pitting resistance than the rougher ones owing to the continuous passive film. Generally, an increasing \( R_{\text{ct}} \) demonstrates increasing corrosion resistance [65].

It is well known that different surface roughnesses can be induced during the production and use of alloy pieces, which determine the size of the opening of surface grooves and the real surface areas. Because the growth of deep pits is controlled by diffusion [66], the surface grooves are defined by the peak-to-trough depth \( d \), longest side length of the feature \( L \), and peak-to-peak width of the grooves \( w \), as shown in Fig. 11. For each 80-grit, 400-grit, and 800-grit sample, 20 surface grooves were measured, and their \( w/d \) ratios were calculated to be 5.57 ± 2.50, 10.18 ± 5.83 and 24.87 ± 9.93, respectively. No obvious scratches exist on the surface of the polished sample, so the \( w/d \) value approaches infinity. The \( w, d, L \), and \( w/d \) values all obviously decrease with decreasing roughness. This indicates that relatively narrow and deep grooves on the rough samples result in deeper diffusion barriers, which limit ion diffusion, while more severe acidification occurs form hydrolysis [43,67,68]. Because the width of the surface grooves changes the diffusion conditions, it significantly affects the pitting corrosion of alloys under diffusion control [69]. The fitted results of the EIS data measured in this study showed that \( Y_0 \) decreased and \( R_{\text{ct}} \) increased with the decreasing surface roughness of the samples, which suggested that a more complete, denser oxide layer formed on the smoother samples. This passive film can prevent localized corrosion [72]. These results agreed with the stable pitting revealed in Fig. 7. Meanwhile, the increasing \( R_{\text{ct}} \) represented increasing the corrosion resistance. Thus, surface roughness obviously influences the characteristics of the passive film, which provides the alloy with corrosion resistance.

In addition, the true surface area is determined by the surface roughness and can strongly affect the number of available pitting sites. Stable pits can only be initiated when the current is proportional to the actual surface area; hence, the sample with three roughnesses resulted in distinctly different base currents (see Fig. 6). We assumed that \( L \) increased with increasing roughness. Although the real surface areas were not quantified, we observed different critical \( I_{\text{pass}} \) value from the potentiodynamic polarization curves for the three surface finishes. This implied that the surface areas of the three samples differed [37], and indicated that the number of available pit sites increased with increasing the real surface area on the rougher samples.

Furthermore, surface defects and the EWF of an alloy surface can affect the corrosion. The roughness increases the dislocation density in the surface layer of the alloy. Metal atom concentrations enhanced by dislocation diffusion, which can be explained by considering the short-circuit paths provided by the dislocations [71]. Because these discontinuities have higher energies and correspondingly larger base potentials, anodic dissolution may occur preferentially at these locations. In addition, because pitting progresses along the scratch direction, the cyclically alternating peak–valley morphology can provide short-circuit paths that contribute to the diffusion of metal atoms. Further, EWF, the minimum energy for electrons to detach from surface, has been reported to decrease with increasing roughness [32,71–73]. Therefore, electrons are more easily released from rougher surfaces with higher densities of defects, leading to higher corrosion rates.

5. Conclusions

Our findings clearly showed that the surface roughness was important to affecting the electrochemical and pitting corrosion of the Ti–6Al–4V alloy in 12 wt.% HCl solution at 35 °C. The electrochemical results suggested that the passivation tendency increased with decreasing surface roughness and caused increased pitting susceptibility. The increasing \( R_{\text{ct}} \) implied that the corrosion resistance increased with the increasingly smoother surface. The peak current, frequency, and lifetime of metastable pits clearly decreased, and the numbers and sizes of stable pits were remarking decreased with decreasing roughness. The larger \( w/d \) of the grooves and higher true surface areas of the rougher surfaces promoted the initiation and growth of both stable and metastable pits. We demonstrated that Ti–6Al–4V alloy with a polished finish shown lower pit growth rate and pitting corrosion susceptibility than rougher samples. Therefore, the corrosion resistance of Ti–6Al–4V alloy for oil and gas exploration applications can be enhanced using parts with a polished finish.

Conflict of interest

We declared that we have no conflicts of interest to this work.

Uncited references

[70].

Acknowledgements

This work was carried out with the financial support from Tubular Goods Research Institute of CNPC, in Xi’an, Shanxi,
China. This work was also supported by "the Project supported by State Key Laboratory of Powder Metallurgy", Central South University, Changsha, China.

References


[70] Wei L, Liu Y, Li Q, Cheng YF. Effect of roughness on general corrosion and pitting of (FeCoCrNi)0.89(WC)0.11 high-entropy alloy composite in 3.5 wt.% NaCl solution. Corros Sci 2019;146:44–57.

