Corrosion resistance of ultrafine-grained pure titanium in simulated sea water

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Abstract. Corrosion resistance of ultrafine-grained Ti processed by equal channel angular pressing with 3 passes was investigated. Results indicated that corrosion rate of ultrafine-grained Ti significantly reduced in comparison with coarse grain Ti. Furthermore, corrosion resistance of 3 passes ECAP sample had an obvious distinguish for different extraction planes; normal plane has shown a best corrosion resistance than transversal and extrusion plane, which could be attributed to higher fraction of low angle grain boundary.

1. Introduction

Ti and Ti alloy are widely used in the field of petrochemical, biomedical and marine engineering due to their high specific strength and excellent corrosion resistance [1]. Severe plastic deformation (SPD) could achieve unique mechanical and service properties due to the grain refinement of materials, which has received extensive attention in recent years [2]. Among them, ECAP is one of the most popular methods to obtain bulk ultrafine-grained (UFG) materials with a uniform structure by the introduction of large plastic deformation without changing the material size [3].

In comparison with the extensive researches on strength, fatigue and biocompatibility behaviors of UFG-Ti alloy fabricated by SPD, the study on corrosion resistance is relatively limited and controversial. Balyanov et.al [4] studied the corrosion resistance of UFG-Ti processed by ECAP in different concentrations of HCl and H\textsubscript{2}SO\textsubscript{4} solutions, the results indicated that UFG-Ti has better corrosion resistance than coarse-grained Ti (CG-Ti), which is mainly because of the rapid growth of a passivation film in UFG-Ti. The same conclusions have been also achieved in other studies [5, 6] in various corrosive environments. As we all know, the grain boundary characteristics distribution (GBCD) plays a key role in the formation of the properties of UFG materials, as well as corrosion resistance. However, in the related literature on the corrosion of UFG materials, most studies were focused on the variation of grain size, and the role of grain boundary in corrosion behavior were less related. Low angle grain boundaries (LAGBs) have very good corrosion behavior due to the low interfacial energy and impurity segregation [7]. Since a large volume fraction of high angle grain

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boundaries (HAGBs) could be generated by ECAP, it is interesting to investigate the relationship between the grain size and the corrosion resistance with the analysis of GBCD.

2. Materials and methods

Pure Ti was used in the present studies. 3 passes of ECAP at 400 °C in route C were used to obtain UFG-Ti. Different extraction planes of the sample after 3 ECAP passes were selected for the investigation; figure 1 shows a schematic diagram of different extraction planes.

![Figure 1. Schematic diagram of different extraction planes.](image)

Microstructure of the samples were observed and quantitatively characterized by EBSD. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) test were used to characterize the corrosion behavior of the samples in 3.5 wt.% NaCl by CHI660E electrochemical workstation. The details can be found in the other published paper of authors [8].

3. Results and discussion

3.1. Microstructural characterization

Fig. 2 shows EBSD figures of the samples with different extraction planes. As shown in figure 2a, as-received Ti exhibits an equiaxed microstructure with an average grain size of ~ 143 μm. After ECAP, the grain size decreased to 620 nm, 653 nm, and 683 nm for the NP, EP, and TP, respectively.

![Figure 2. EBSD figures of as-received (a) and 3 passes ECAP samples of NP (b), EP (c), TP (d), respectively.](image)

Figure 3 displays the misorientation distribution of CG-Ti and UFG-Ti. The results indicate that GBCDs change obviously after ECAP, accompanied by refining of the grain size. It shows that a fraction of HAGBs is high to 87.6% for CG-Ti, after ECAP process, the fraction of HAGBs decreased dramatically. The fraction of HAGBs is distinguished from each other for different extraction planes of the sample after 3 passes ECAP, the lowest fraction of HAGBs is NP, which could get 50.9%. Meanwhile, the fraction of HAGBs increased to 59.8% for EP. Furthermore, the fractions of HAGBs exceeding 90° reached to 30% for EP, which is differential from the others.
3.2. Corrosion behavior

Polarization curves of the samples in 3.5 wt.% NaCl are shown in figure 4a. All polarization curves of the tested samples are analogous, which indicate that grain size refining cannot influence the corrosive mechanism. High Cl\(^-\) in simulated seawater could penetrate the passive film to substrate of Ti, which led to pitting corrosion. The corrosion current density (\(i_{\text{corr}}\)) and corrosion potential (\(E_{\text{corr}}\)) can be obtained by linear fitting of Tafel region. The fitting results are shown in table 1.

![Figure 4. Polarization curves (a) and EIS (b, c) of CG-Ti and UFG-Ti in 3.5 wt.% NaCl.](image)

### Table 1. Electrochemical properties and equivalent circuit fitting parameters of CG-Ti and UFG-Ti.

| Sample   | \(E_{\text{corr}}\) V | \(E_{\text{pit}}\) V | \(i_{\text{pass}}\) \(\mu\text{A/cm}^2\) | \(i_{\text{corr}}\) \(\mu\text{A/cm}^2\) | \(R_s\) \(\Omega\text{-cm}^2\) | \(CPE\) \(10^{-5}\) \(S\cdot\text{s}^{-1}\text{-cm}^2\) | \(n\) | \(R_p\) \(10^5\) \(\Omega\text{-cm}^2\) | Chi-squared |
|----------|---------------------|---------------------|------------------|-----------------|----------------|----------------|-----|----------------|-------------|
| CG-Ti    | -0.271              | 0.006               | 0.898            | 0.8927          | 4.787          | 3.575          | 0.8721 | 5.219          | 0.00053     |
| 3P NP    | -0.259              | 0.112               | 0.100            | 0.0941          | 5.154          | 2.577          | 0.8932 | 42.520         | 0.00915     |
| 3P EP    | -0.195              | 0.033               | 0.667            | 0.4746          | 4.936          | 2.919          | 0.8824 | 7.256          | 0.00511     |
| 3P TP    | -0.286              | 0.135               | 0.158            | 0.1358          | 4.976          | 2.173          | 0.9094 | 13.940         | 0.00874     |

As shown in table 1, \(E_{\text{corr}}\) did not change obviously. However, it can be found that \(E_{\text{pit}}\) of UFG-Ti is generally higher than CG-Ti, and \(i_{\text{pass}}\) is much lower than CG-Ti, which indicates that the pitting resistance was enhanced for UFG-Ti. The corrosion resistance of the materials can be directly reflected by \(i_{\text{corr}}\). It shows that the corrosion resistance from strong to weak is NP > TP > EP > CG-Ti.

The Nyquist diagram composed of semicircular arcs is illustrated in figure 4b, which was obtained from the test under a stable OCP. Generally speaking, the corrosion resistance increases as the radius of the arc increases [8, 9]. In order to get the corrosion behavior of the material, the experimental data were fitted by the ZSimDemo software. The used equivalent circuit is shown in figure 4b. Among them, \(R_s\) is the solution resistance; CPE is the capacitance; \(R_p\) is the polarization resistance, which can reflect the corrosion resistance of materials intuitively, i.e. the larger \(R_p\) value, the better corrosion resistance. The fitting results are listed in table 1. Obviously, \(R_p\) value of the samples is NP > TP > EP > CG-Ti. A little difference of \(n\) values indicates that uniformity of the passivation film on the surface of all samples is not much different. Figure 4c shows the bode plot of CG-Ti and UFG-Ti in 3.5 wt.% NaCl solution. It indicates that the frequency is lower than \(10^3\) Hz, the spectra displays a linear slope of about −1, which shows the characteristic response of a capacitive behavior of the passive film [10]. UFG-Ti exhibits a higher impedance and phase angle than the CG-Ti at low frequencies. It indicates that the corrosion resistance of the samples is NP > TP > EP > CG-Ti.

As we all know, Ti and Ti alloys surfaces are easy to form a dense oxide film, it can hinder the direct contact between the substrate of metal and the corrosive medium, then improves corrosion resistance of the materials effectively. Exactly speaking, the corrosion behavior of Ti is more concerned with the state of the surface oxide film.
As shown in table 1, \( E_{\text{pitt}} \) of UFG-Ti is higher than CG-Ti, which indicates that the occurrence of the pitting corrosion is difficult due to a higher potential. On the other hand, \( i_{\text{pass}} \) of UFG-Ti is lower than CG-Ti, which indicates that UFG-Ti is easier to form passivation on the surface. In comparison with CG-Ti, the grain size decreased with the process of ECAP and high stored energy can be formed in the dislocations and grain boundaries of the material, which is beneficial to the formation of the passivation film and increase self-repairing ability of the passivation film. On the other side, not only grain refinement, but the improvement activity of electrons near the grain boundaries also can promote the formation of passivation film of metals [11]. It is worthy to note that the ECAP processing can introduce a large number of dislocations at grain boundaries and grain interior simultaneously, which is benefits to the uniformity of nucleation of the passivation film and improve the density of the passivation film, then can hinder the penetration of chloride ions via the passivation film to the substrate effectively.

As mentioned above, the corrosion resistance of the sample after 3 ECAP passes with a different extraction plane is significantly different, although the grain size seems similar. GBCD plays an important role in the corrosion resistance of UFG materials, and LAGBs have a very good corrosion resistance due to the low interfacial energy and the impurity segregation. In the present study, the fraction of LAGBs of NP reached to 49.1%, which is higher than TP (equal to 42.9%) and EP (equal to 40.2%). From the perspective of grain boundary engineering, if corrosion occurred at a high-angle segment of a grain boundary and extended, it could be encountered by arrested LAGBs, then the intergranular corrosion was arrested [12]. The EP has the lowest fraction of LAGBs, as well as the concentration of HAGB exceeds 90°, which is probably the reason to cause the worst corrosion resistance of all the deformed planes.

4. Conclusions
The corrosion resistance of UFG-Ti processed by ECAP was investigated by potentiodynamic polarization and EIS in 3.5 wt.% NaCl solution. Electrochemical results indicated that the corrosion resistance of UFG-Ti was improved obviously in comparison with CG-Ti Ti. Furthermore, NP of the sample after 3 ECAP passes has shown a better corrosion resistance than TP and EP, which could be attributed to the higher fraction of LAGBs.

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References
[1] Wang X et al. 2017 Journal of Alloys and Compounds 728 709
[2] Hoseini M, Shahryari A, Omanovic S and Szpunara J A 2009 Corrosion Science 51 3064
[3] Valiev R Z and Langdon T G 2006 Progress in Materials Science 51 881
[4] Balyanov A et al. 2004 Scripta Materialia 51 225
[5] Gurao N P et al. 2013 Metallurgical & Materials Transactions A 44 5602
[6] Chuvil'deev V N et al. 2017 Journal of Alloys and Compounds 723 354
[7] Zhao Y, Cheng I C, Kassner M E and Hodge A M 2014 Acta Materialia 67 181-188
[8] Li X et al. 2019 Acta Metallurgica Sinica 55 967
[9] Yang D S et al. 2018 Materials and Corrosion 69 1455
[10] Hodgson A W E et al. 2002 Electrochimica Acta 47 1913
[11] Nikfahm A, Danaee I, Ashrafi A and Toroghejad M R 2013 16 1379
[12] Hu C, Xia S, Li H, Liu T, Zhou B, Chen W and Wang N 2011 Corrosion Science 53 1880