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In situ corrosion monitoring of Ti–6Al–4V alloy in H_2SO_4/HCl mixed solution using electrochemical AFM

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ABSTRACT

Electrochemical atomic force microscope (ECAFM) was employed for in situ observation of corrosion of solution annealed and furnace cooled Ti–6Al–4V titanium alloy in 0.5 mol l^{-1} H_2SO_4 + 1 mol l^{-1} HCl mixed solution. A scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was also used for microstructure examination and chemical composition analysis. For solution annealed followed by furnace-cooled Ti–6Al–4V titanium alloy, selective corrosion of α phase and galvanic effect at α/β interface could be clearly observed at open circuit potential under ECAFM. A higher dissolution rate was also found in α phase than β phase on the bare Ti–6Al–4V titanium alloy. The effect of potential on the corrosion behavior was also explored. Negligible corrosion was found after potentiostatic etching at −0.5 and −0.85 V_{Pt} for 120 min. However, selective dissolution of α phase with respect to β phase occurred when the potential was controlled at −0.9 V_{Pt}. The polarity inversion during potentiostatic etching at −0.9 V_{Pt} was also found and discussed in this study.

1. Introduction

Titanium and its alloys exhibit excellent properties such as high strength, low density, super-plasticity, high biocompatibility, and high corrosion resistance which have resulted in them being used in many applications [1–6]. A compact and stable oxide mainly composed of TiO_2 can be naturally formed on the surface of Ti alloys, which provides satisfactory corrosion resistance against hostile environments. However, the oxide film formed in air or in other environments may be modified by incorporating the ions of alloying elements, which results in different corrosion performance [7–10].

Ti–6Al–4V, a duplex structured titanium alloy, which contains a hexagonal close packed (hcp) α phase and a body-centered cubic (bcc) β phase, has been widely used for biomedical, pipeline, sporting goods, marine and military applications. Ti–6Al–4V alloy exhibits a wide range of microstructures and is considered to be a heat treatable Ti alloy. Depending on heat treatment conditions, the α/β volume ratio and chemical composition of the respective constituent phases can be adjusted to yield different properties. It is known that the difference in chemical composition of the respective constituent phases in any dual-phase alloy, such as duplex stainless steels, can result in selective corrosion of one phase with respect to the other [8,11–14]. In addition, galvanic effect between the constituent phases in 2205 duplex stainless steel in H_2SO_4/HCl mixed solution has been reported in a most recent study [14]. Whether selective dissolution and/or galvanic effect occur in Ti alloy is of interest. In this investigation, an electrochemical atomic force microscope (ECAFM) was employed for in situ monitoring of the localized corrosion process at or near the phase boundary of the two constituent phases in Ti–6Al–4V alloy in 0.5 mol l^{-1} H_2SO_4 + 1 mol l^{-1} HCl mixed acid solution. The effect of applied potential on the occurrence of selective dissolution is investigated.

2. Experimental

2.1. Sample preparation

Ti–6Al–4V (Grade 5) alloy with dimensions of 50 mm × 20 mm × 3 mm was solution annealed (SA) at 1066 °C for 1 h and then furnace-cooled (FC). The heat treated alloy was cut into dimensions of 10 mm × 10 mm × 3 mm. The scale formed on the samples during heat treatment was removed by successive grinding with SiC papers, and they were polished with the slurry containing Al_2O_3 powders with an average particle size of 0.05 μm. After polishing, the samples were ultrasonically cleaned in deionized water for 30 min, rinsed in 95% ethanol and finally dried in air.

2.2. Microstructure examination and chemical analysis

The microstructures of the as-received and the heat-treated alloys were examined using a scanning electron microscope (SEM)

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under back-scattered electron (BSE) mode. The chemical composition of each constituent phase, before and after heat treatment, was analyzed by the energy dispersive spectrometer (EDS) attached to the SEM.

2.3. *In situ corrosion monitoring*

A Multi Mode ECAFM was used to monitor in situ the surface morphology change of the sample during etching at open circuit potential or under applied potential condition. The ECAFM used in this study consisted of a mini cell with a volume of 0.15 ml, which was similar to that reported in the literature [15]. In electrochemical tests, all potentials were measured with respect to a platinum reference electrode. An additional platinum wire was used as the counter electrode when potentiostatic etching was performed. For easy identification of the α/β phase boundary, the heat-treated alloy, which had a coarser grain size of β phase, was mainly used for ECAFM analysis in this study. After installing the polished sample into the electrochemical cell, the area consisting both α and β phases for ECAFM examination was pre-determined carefully in air. Then, the testing solution composed of $0.5\,\mathrm{mol\,l^{-1}}$ H_2SO_4 + $1\,\mathrm{mol\,l^{-1}}$ HCl mixed solution was injected into the cell. In situ corrosion monitoring either at open circuit potential or under potentiostatic condition (at −0.5, −0.85, or $-0.9\,V_{Pt}$) was conducted by contact mode ECAFM with a scanned area of 10 μm × 10 μm. The image of the surface was acquired every 10 min after the initial one was captured. The total period of ECAFM examination was 120 min for each test.

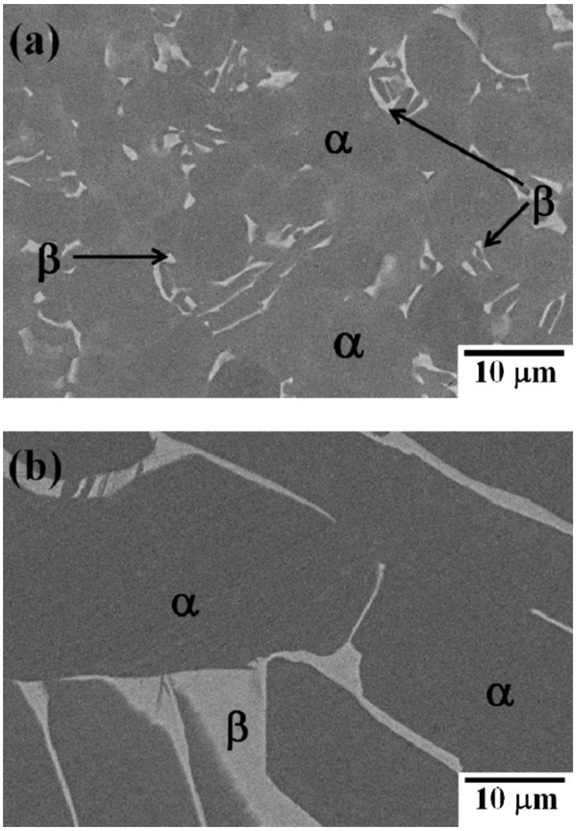

Fig. 1. Microstructure of Ti–6Al–4V alloy: (a) as-received and (b) solution annealed at 1066 °C/1 h + furnace cooling.

Table 1
Chemical composition of the as-received and heat-treated Ti–6Al–4V alloy analyzed by EDS (wt%).

Element (wt%)	[a]Heat treatment			
	As-received		Heat-treated	
	Phase α	Phase β	Phase α	Phase β
Ti	91.4	76.4	91.3	77.0
Al	6.2	2.7	6.3	4.2
V	2.4	20.9	2.4	18.8

[a] Heat treatment: solution annealed at 1066 °C for 1 h followed by furnace cooling.

3. Results and discussion

3.1. *Microstructure*

The SEM micrographs of the as-received Ti–6Al–4V alloy and the SA-FC alloy are shown in Fig. 1. The dark area is α phase and the bright area is β phase. For the as-received material, as shown in Fig. 1(a), the major phase was α while the β phase was about 10 vol.%. For the heat-treated alloy, though the size of β phase became coarser, as demonstrated in Fig. 1(b), the volume ratio between α and β phases did not change appreciably. According to the pseudo-binary phase diagram of Ti–6%Al with varying V content [16], β phase is the only phase stable at 1066 °C for Ti–6Al–4V. Cooling from 1066 °C to room temperature results in the precipitation of α phase and gives rise to the formation of dual phase microstructure. The pseudo-binary phase diagram also reveals that the solubility of V in α phase varies in a small range while that in β phase varies considerably as the solid solution annealed alloy is cooled to room temperature. For the as-received and heat-treated Ti–6Al–4V alloy used in this study, the results of EDS analysis for the two constituent phases are listed in Table 1. As shown in this table, the compositions of α and β phases in the as-received and the heat-treated alloys are almost the same. In both cases, Ti and Al are enriched in α phase. Though the volume content of β phase is much less than that of α phase, as revealed in Fig. 1, the V content in β phase is much higher than its average concentration in the alloy used. The results obtained are generally in agreement with those reported in the literature [17,18].

3.2. *In situ corrosion monitoring*

Fig. 2 demonstrates the results of in situ corrosion monitoring using ECAFM for the heat-treated alloy in $0.5\,\mathrm{mol\,l^{-1}}$ H_2SO_4 + $1\,\mathrm{mol\,l^{-1}}$ HCl solution at open circuit potential. The image obtained immediately after immersion in the testing solution is shown in Fig. 2(a). The phase boundary between α and β phases can barely be distinguished. After 80 min of immersion, the ECAFM image in Fig. 2(b) indicates that α phase dissolved at a faster rate than β phase, and a step between the two adjacent phases was established. By extending the immersion time to 140 and 200 min, the step resulting from the difference in corrosion rate between α and β phase became more pronounced as can be seen in Fig. 2(c) and (d), respectively. The selective dissolution of α phase with respect to β phase is mainly attributed to the considerable difference in chemical composition of the two constituent phases in Ti–6Al–4V alloy. The higher V content in β phase, as shown in Table 1, seems play more important role in increasing its resistance to dissolution.

The evolution of the depth with time between the adjacent α and β phase can be examined across any cross section, say the dashed diagonal line between p and q in Fig. 3(a). The magnitudes of the depth across the pq line measured using ECAFM at different times, resulting from selective dissolution, are depicted in Fig. 3(b). As pointed out above, the step height between α and β phases