



Structure of the oxide film on Ti–6Ta alloy after immersion test in 8 mol/L boiling nitric acid medium



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ABSTRACT

By using X-ray photoelectron spectroscopy (XPS), X-ray diffractometer (XRD) and scanning electron microscopy (SEM), we investigate the corrosion behavior and the structure of the oxide film of Ti–6Ta alloy that is subjected to the immersion corrosion test in 8 mol/L boiling nitric acid for 432 h. Based on the phase constitution identified by depth profile XPS, the oxide film could be divided into three sub-layers along its thickness direction: the chemical stable TiO_2 and Ta_2O_5 are present in layer I; the sub-oxide Ti_2O_3 and TaO are present in the layer II and layer III, and the high valence oxide evolves from their sub-oxide gradually. Owing to the shielding effect of Ta_2O_5 , the corrosion rate of the Ti–6Ta alloy decreases from 0.051 mm/y to 0.014 mm/y with increasing immersion time, showing an excellent corrosion resistance in 8 mol/L boiling nitric acid.

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1. Introduction

The demand on the performance of the nuclear materials is becoming stricter, because the safety of nuclear is a matter of concern to the entire world since the late 1950s [1,2]. The reprocessing of the spent fuel of a nuclear reactor involves a series of complex chemical processes in complicated equipment, in which some systems incorporate as dissolvers where hot or boiling nitric acid is used [3]. The conventional stainless steel, served as the structural material, frequently suffers from the severe intergranular and general attack in the above media. As a result, many cases of failures about the equipment made of stainless steels related to the intergranular corrosion are reported [4]. With a corrosion rate of 0.1 mm/y, the corrosion resistance of titanium in the boiling nitric acid is superior to that of stainless steel owing to the formation of stable titanium oxide film [4,5]. However, the nitric acid solution used in the nuclear industry often contains powerful oxidizers, such as Cr^{6+} , and the corrosion rate of titanium increases in such corrosion media [6].

One strategy is the alloying titanium with refractory metals like Ta and Nb which possess similar metallic ion sizes like titanium and low solubility in nitric acid [4,6]. Comparing with the titanium, the improved corrosion resistance of the Ti–5Ta and Ti–5Ta–1.8Nb alloy for nuclear application could be attributed to the structure variation of the oxide film [7,8]. It is reported that the oxide film

on Ti–5Ta–1.8Nb alloy contains not only the titanium oxide (TiO_2) but also the oxide of these refractory metals (Ta_2O_5 and Nb_2O_5) [9,10]. In addition, the oxide film is protective, stable, adherent and continuous [11].

The corrosion rate of Ti–5Ta and Ti–5Ta–1.8Nb alloy in nitric acid could be influenced by many factors such as the concentration of the nitric acid, the oxidizing ions, the irradiation effects and the microstructure of the alloy. In fact, the corrosion rate of titanium alloy is strongly influenced by oxide film because the metal is isolated by the corrosion media once the oxide film forms. It is understandable that the structural and compositional character of the oxide film may vary as the corrosion condition differs. However, little information is available on the structure and the formation mechanism of the oxide film, which strongly influence the corrosion behavior of titanium alloy in nitric acid.

In this work, we select the binary Ti–6Ta alloy and investigate the structure of the oxide film after immersion corrosion test in the 8 mol/L boiling nitric acid for 432 h. By using X-ray photoelectron spectroscopy (XPS) equipped with the Ar^+ bombardment, we investigate the structure of the oxide film layer-by-layer. The objective of our work is to investigate the formation mechanism of the oxide film and the evolution of the chemical stable oxide inside, trying to explain the reinforced corrosion resistance of Ti–6Ta alloy in the view of its oxide film.

2. Materials and methods

2.1. Sample preparation

The Ti–6Ta (in wt%) ingot, with the composition of 6.2 wt% Ta, 0.03 wt% Fe, 0.05 wt% O, 0.003 wt% H, and balance Ti, was prepared

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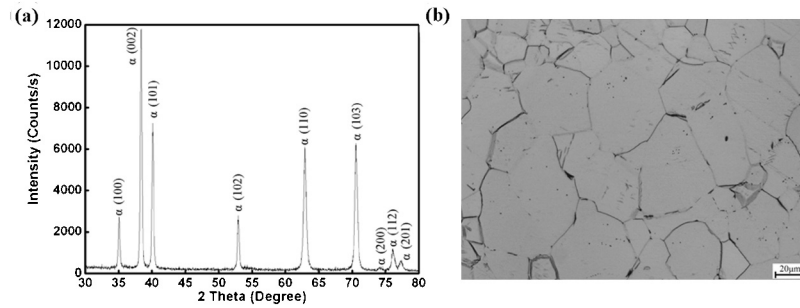


Fig. 1. Phase constitution and microstructure of initial Ti-6Ta specimen, (a) XRD pattern and (b) metallographic photograph.

by twice-melting in a vacuum arc furnace. The ingot was first forged in the β field at 1180 °C to break up the original coarse β grain boundary and then forged in the α + β field at 830 °C to refine the grain size. The billet was cold rolled to 3 mm sheet, following 650 °C annealing for 2 h in vacuum. The metallographic samples were prepared by grinding and polishing techniques, followed by etching for 10 s in 2% HF, 8% HNO₃, 90% H₂O (Kroll's reagent). The corrosion specimen with the dimension of 50 mm × 25 mm × 3 mm was machined from the Ti-6Ta alloy sheet and then grinded up to 1200 grit emery paper before the immersion test.

2.2. Corrosion test

The glass set up of the corrosion test in the present study was described in elsewhere [12]. The sample was exposed in the 8 mol/L boiling nitric acid for a total period of 432 h, during which the solution was renewed in every 48 h. For every 24 h, the weight loss of the sample was recorded with the precision of 0.1 mg, and the corrosion rate was calculated by the weight loss method by [13].

$$Y = \frac{365 \Delta W}{\rho s t} \quad (1)$$

where ΔW (g) is the weight loss after corrosion, ρ (g/mm³) is the density of Ta-6Ta alloy, s (mm²) is the surface area of the corrosion sample and t (day) is the immersion time.

2.3. Surface characterization

After immersion corrosion test, the Ti-6Ta specimen was ultrasonically cleaned with acetone and distilled water. JSM-6700 SEM equipped with the EDS detector was used to observe the microstructure of the alloy and the surface morphology of the corroded specimen. The XRD was performed on Rigaku-Dmax/2500 diffractometer with a Cu K α source in θ -2 θ model. ESCALAB-250 XPS equipped with a monochromatized Al K α X-ray was used to obtain the Ti2p, Ta4f and O1s core level high resolution spectra. The scanning area is 500 μ m × 500 μ m, and the XPS data were recorded as a function of Ar⁺ etching time until 3120 s. The Shirley background was used in the peak fitting of the XPS spectra.

3. Results

3.1. Initial structure

Before the corrosion test, the XRD pattern of the Ti-6Ta sheet specimen is shown in Fig. 1(a). It is found that the phase constitution of the alloy is the α -Ti and the sheet exhibits the [001] _{α} texture due to the observation of the strong and sharp (002) _{α} reflection. Fig. 1(b) presents the metallography of Ti-6Ta alloy. The average dimension of the equiaxial α grain is about 40 μ m, in which distributes a low volume fraction of the dark particles. The precipitation should be the bcc β phase, because its Ta concentration

measured by EDS is about 7 wt%, which is higher than the nominal Ta concentration of the alloy. Although Ta is a weak β stabilizer, it is understandable that a small volume fraction of the bcc β phase could form in Ti-6Ta alloy after annealing, and the volume fraction of the β phase should be lower than 5% because the reflections of the bcc β -Ti could not be detected in the XRD pattern. Our observation is consistent with the previous work on Ti-5Ta-1.8Nb alloy, in which the β precipitation has also been found inside the equiaxial α grain [4,10].

3.2. Corrosion rate and surface morphology

As shown in Fig. 2, the corrosion rate of Ti-6Ta alloy is fitted as a function of the immersion time. It is found that the corrosion rate decreases exponentially from 0.051 mm/y in the first period (48 h) to 0.014 mm/y in the last period (432 h).

The SEM micrographs of Ti-6Ta alloy exposed to 8 mol/L boiling nitric acid are shown in Fig. 3. In Fig. 3(a) and (b), the flat region (dark contrast), porosity (light contrast) and pits (light contrast) could be observed, suggesting that the surface of the immersed specimen is inhomogeneously corroded. As presented in Fig. 3(c), the detail morphology of the flat region is the agglomerate of the oxide cluster, in which the porosity could be observed.

3.3. Phase identification of the oxide film

Fig. 4 shows the XRD pattern of the corroded specimen. Compared with the XRD pattern of the initial alloy (Fig. 1), a broad diffraction peak from 20° to 30° is detected, and such diffraction peak should belong to the oxide cluster observed in SEM. In the XRD spectra, the sharp diffraction peaks of the α -Ti also appear,

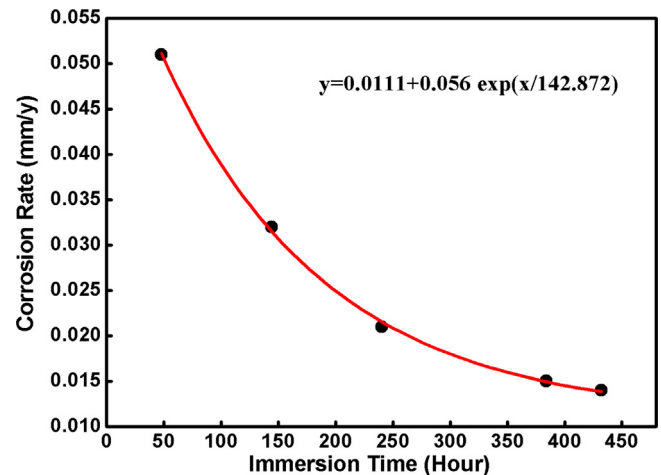


Fig. 2. Corrosion rate of Ta-6Ta alloy as a function of immersion time in the 8 mol/L boiling nitric acid.

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