Corrosion behavior of nanotubular oxide layer anodically formed in the Ti6Al7Nb alloy

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Abstract

The purpose of this work is to investigate the corrosion behavior of self-organized nanotubular oxides on Ti6Al7Nb alloy. The alloy was fabricated by arc melting with no consumable tungsten electrode and water cooled copper hearth under argon atmosphere. The anodization was performed using fluoride solution and cell potential of 20V. After anodization, the samples were rinsed in de-ionized water and dried in nitrogen atmosphere. Due to nanotubular oxide amorphous characteristics, they were annealed at 650°C in air atmosphere for 2 hours and then, cooled back to room temperature in a box furnace. In the current study, the corrosion behavior of titanium with nanotubes oxide layers was studied in naturally aerated NaCl solutions (0.1 mol L^{-1}) and Na₂SO₄ solutions (0.1 mol L^{-1}) using open circuit potentials (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests.

Introduction

The fabrication of ordered oxide nanotube arrays on Ti and Ti alloys has been investigated extensively in recent decades for application in water purification, photocatalysis, photoelectrolysis, gas sensors and orthopedic implants, due to their high photocatalytic activity and self-cleaning properties, good corrosion resistance and high strength, enhanced biocompatibility, and hemocompatibility the area photocatalysis, [1]. In of photoelectrocatalysis and sensors, the nanotubular structures of TiO₂ provide a high surface area that increases photocurrent conversion efficiency considerably, making these processes more efficient and resulting in reduced dimensions of the electrodes. In order to investigate the characteristics of these nanotubular oxides growth on Ti6Al7Nb alloy during photoelectrocatalysis treatment, the corrosion behavior was studied.

Experimental

Ti-6Al-7Nb were prepared in the form of ingots from high purity Ti sheets (99.8%), Al (99.8%) and Nb samples (99.99%), according to nominal compositions, by arc melting with non-consumable tungsten electrode and water cooled copper hearth under argon atmosphere. The Ti alloy was machined into 11.2 mm diameter x 80 mm long cylinders. The chemical composition of the alloys was determined by X-ray fluorescence (XRF). The specimens were cut into 6-mm-thick cylinders. The ordered semiconductor oxide nanotubes were grown by anodization in an electrochemical cell using Pt foil as the counter electrode and Ti alloy as working electrodes. The samples were pressed against an O-ring-sealed into an opening in the wall of the electrochemical cell, leaving 1 cm² exposed to the electrolyte. A steel rod was attached to the samples to capture anodizing current data. The samples were polished with 220, 400, 800, 1000 and 2000 grit water sandpaper prior to anodization, after which they were sonicated in isopropyl alcohol (5 min) and deionized water (5 min), and dried in a nitrogen stream.

Anodization was carried out under an applied voltage of 20 V during 2 hours, at a sweep rate of 2 V/min in the first 10 min, using an Autolab PGSTAT30 potentiostat/galvanostat coupled to an ET 2042C voltage multiplier. Aqueous solution containing 0.1 vol.% HF stirred at 750 rpm and anode to cathode distance of 2.5 cm were applied to produce nanotubes with 104.5 (\pm 13.5) nm of external diameter and 67.5 (\pm 10.5) nm of internal diameter. The samples were

then rinsed with deionized water and dried under a N_2 stream. The structural characterization of the anodized layers was performed with a field emission scanning electron microscope (SEM, JEOL JSM 6360LV). After anodization, the samples were rinsed in de-ionized water and dried in nitrogen atmosphere. Due to nanotubular oxide amorphous characteristics, they were annealed at 650°C in air atmosphere for 2 hours and then, cooled back to room temperature in a box furnace.

The corrosion resistance of Ti6Al7Nb alloy anodized was evaluated by means of electrochemical measurements carried out in 60 mL of naturally aerated and unstirred 0.1 mol L⁻¹ NaCl and Na₂SO₄ solution. All the electrochemical tests were carried out using a classical three electrodes cell with Ag/AgCl/KClsat and a platinum grid as reference and counter electrode, respectively, which were always positioned at the same distance relatively to the working electrode. The working electrode was mounted with an exposing area of 1 cm^2 to the solution. All the electrochemical measurements were carried out within a Faraday cage in order to minimize external interference on the system studied. Open-circuit potential (Eoc vs. time) and electrochemical impedance spectroscopy (EIS) measurements were performed in a EG&G potentiostat/galvanostat model 273A and a Solartron[®] 1255B frequency response analyzer. The measurements were performed in 10^5 kHz to 10^{-2} Hz frequency range, with an acquisition rate of 10 points per frequency decade after 1 h of immersion in test solution. The ac signal amplitude was 10 mV. All the experiments were performed at the open circuit potential (OCP), which was recorded prior to the measurement in order to verify the stationary condition. Polarization curves were recorded for all samples in a potential range from -0.25 to + 1.60 V versus $E_{oc}/Ag/AgCl/KCl_{sat}$ at a scan rate of 1.0 mV/s.

Results and Discussion

The results of EIS are shown in the form of Nyquist diagram in Figure 1(a) and in the form of the Bode diagram, $\theta \ge \log f$ (Fig. 1b), and $|Z| \ge \log f$ (Fig. 1c). In Fig.1a it is observed that the diameter of the capacitive arcs is higher for the Ti6Al7Nb alloy anodized. In Figure 1b shows that there are at least two time constants for the alloy Ti6Al7Nb anodized. The one at high frequencies is related to the barrier effect of the film resistance of a passive layer and that at low frequencies to see if the charge transfer at the interface substrate / electrolyte. The alloy has an anodized Ti6Al7Nb phase angle $\theta = 75^{\circ}$ for a frequency range higher than for the alloy Ti6Al7Nb. In Figure 1c shows that both at low frequencies, the anodizing of the alloy Ti6Al7Nb is protecting it, since the values of |Z| are larger compared to pure alloy. The alloys Ti6Al7Nb in Na₂SO₄ are much lower when compared in the NaCl.



Figure 1- EIS result with Nyquist (a) and Bode (b) and (c) for the pure Ti, Ti6Al7Nb alloy and anodized alloy Ti6Al7Nb obtained after 1 hour of immersion in NaCl 0.1 mol.L⁻¹.

Figure 2 (a) and (b) show the potentiodynamic polarization curves for Ti6Al7Nb alloys and pure Ti and anodized alloy to the different electrolytes. It is observed for the alloy Ti6Al7Nb a corrosion potential (Ecorr) around -0.288 V and -0.275 V, for the case of pure Ti. Immediately after the corrosion potential, is a zone of activation in a subsequent passivation potential range of 0 V to 1.5 V. This potential is a slight increase of current density due to the two possibilities, oxidation of TiO and Ti₂O₃ or growth of TiO₂ film [2]. Following this increase in current returns the process to stabilize, and this fact shows the presence of an oxide film on the surface of the alloy Ti6Al7Nb. The alloy anodized Ti6Al7Nb when analyzed in the middle Na₂SO₄ also proved to be stronger (more positive anodic potential, Figure 2 (b) when compared with pure alloy, but was not much more efficient in this electrolyte. Anodic curves showed further the vicinity of the efficiency of the alloys, since the response current density appear to be very similar.



Figure 2- Polarization curves for pure Ti, pure alloy Ti6Al7Nb and Ti6Al7Nb alloy anodized in different electrolytes: (a) NaCl 0.1 mol L^{-1} and (b) Na₂SO₄ 0.1 mol L^{-1} .

However, it is also observed that the corrosion potential of the alloy anodized Ti6Al7Nb is more positive than the potential for the pure Ti and alloy, indicating that the alloy anodized Ti6Al7Nb protects more effectively, due to the presence of the nanotubes arranged. When analyzing the anodic polarization, it is noted that the responses in current density are lower for the alloy anodized Ti6Al7Nb compared with pure alloy Ti6Al7Nb and Ti, thereby indicating the protection provided by the nanotubes formed in this alloy.

Conclusions

The electrochemical experiments carried out in the Ti6Al7Nb alloy showed some interesting points about the behavior in a medium of NaCl 0.1 mol L^{-1} and Na₂SO₄ 0.1 mol L^{-1} . Preliminary results of the measures EIS revealed that the alloy anodized has a barrier effect more efficient because of the nanotubes developed on the surface and more resistant when measured in the NaCl solution. The polarization curves showed that the alloy anodized Ti6Al7Nb has high corrosion resistance even when compared in the presence of NaCl medium.

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