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An electrochemical study on self-ordered nanoporous and nanotubular oxide on Ti–35Nb–5Ta–7Zr alloy for biomedical applications

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Abstract

Highly ordered nanoporous and nanotubular oxide layers were developed on low-rigidity β Ti–35Nb–5Ta–7Zr alloy by controlled DC anodization in electrolyte containing 1 M H_3PO_4 and 0.5 wt.% NaF at room temperature. The as-formed and crystallized nanotubes were characterized by electron microscopy, energy-dispersive X-ray spectrometry and X-ray diffraction. The electrochemical passivation behavior of the nanoporous and nanotubular oxide surfaces were investigated in Ringer's solution at 37 ± 1 °C employing a potentiodynamic polarization technique and impedance spectroscopy. The diameters of the as-formed nanotubes were in the range of 30–80 nm. The nanotubular surface exhibited passivation behavior similar to that of the nanoporous surface. However, the corrosion current density was considerably higher for the nanotubular alloy. The surface after nanotube formation seemed to favor an immediate and effective passivation. Electrochemical impedance spectra were simulated by equivalent circuits and the results were discussed with regard to biomedical applications.

Keywords: Nanotubes; Anodization; Ti–35Nb–5Ta–7Zr; Biomaterial; Corrosion

1. Introduction

Recently it has been shown that nanoscale porous as well as tubular oxide layers on titanium alloys can increase the bioactivity of an implant material [1–3]. Such titanium oxide tubular structures find potential applications in various other fields such as catalysis, sensors, solar energy conversion, etc., due to their peculiar semiconducting and photoelectrochemical properties [4,5]. In recent years, electrochemical anodization technique in F^- containing electrolytes was projected as an efficient and economic approach for the production of highly ordered porous structures on valve metals [6,7]. Depending on the metal substrate and electrochemical conditions, the anodic oxide film may exhibit a compact, porous or a tubular structure. Such nanostructure formations have been achieved electrochemically on Ti [8,9], Zr [10], Nb [11], and Ta [12]. Anodization of Ti and Zr resulted in distinctly separated hollow cylinder shaped nanotubes; however, porous oxide layers resulted in the case of Nb and Ta [13]. Nanotube growth has been reported on binary, ternary and quaternary titanium alloys such as TiNb [14], TiZr [15], Ti–6Al–7Nb [16], Ti–30Ta–XZr [17] and Ti–29Nb–13Ta–4Zr [18]. In the anodization of Ti, the dissolution is enhanced by fluoride containing electrolytes which form soluble complexes with titanium, resulting in pore or nanotube formation [13,19]. However, selective dissolution of less stable elements or different reaction rates of different alloy phases can hinder nanotube formation.

Quaternary β-titanium alloys of the system Ti–Nb–Ta–Zr are of current research interest due to their excellent mechanical properties such as very low elastic modulus, coupled with superior biocompatibility and corrosion resistance

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[20,21]. The aim of developing such low modulus titanium alloys was to decrease the elastic modulus difference between the bone (10–30 GPa) and the implant material, thereby promoting load sharing between them [22]. When insufficient load sharing occurs, natural bone resorption and loosening of the joint may occur [23]. Major quaternary alloys of this kind investigated include Ti–35Nb–5Ta–7Zr [20], Ti–4Nb–4Ta–15Zr [21], and Ti–29Nb–13Ta–4.6Zr [24]. Among these, Ti–35Nb–5Ta–7Zr alloy have the lowest elastic modulus (55 GPa) and can be considered as one of the best choices for orthopedic implants [25]. No reported information is available on nanotubular oxide formation on this alloy. Reported works on electrochemical corrosion behavior of porous oxide grown titanium alloys is limited [19]. Also, no comprehensive reported information is available on electrochemical corrosion behavior of titanium alloys after nanotubular oxide formation.

Hence in the present work, with a view to study the effect of nanoporous and nanotubular oxide layer formation on the electrochemical corrosion behavior of β Ti–35Nb–5Ta–7Zr alloy, highly ordered nanoporous and nanotubular oxide layers were produced on the alloy surface using controlled anodization in electrolyte containing 1 M H_3PO_4 and 0.5 wt.% NaF at room temperature. The nanotubes formed were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy/energy dispersive X-ray spectrometry (TEM/EDS). Electrochemical behavior of the nanoporous and nanotubular alloy was investigated using potentiodynamic polarization and impedance spectroscopy measurements in Ringer's solution at 37 ± 1 °C.

2. Experimental

Ti–35Nb–5Ta–7Zr alloy was fabricated by arc melting with non-consumable tungsten electrode and water-cooled copper hearth under ultra pure argon atmosphere. Commercially high-purity Ti, Nb, Ta and Zr were employed for the purpose. All the ingots were melted and inverted 10 times in order to homogenize the alloy chemical composition. To stabilize the β phase and to homogenize the microstructure, the casted alloy was heat-treated at 1000 °C for 2 h in Ar atmosphere, followed by water quenching. The phase structure and chemical composition of the heat-treated alloy were identified by X-ray diffraction (XRD, X'pert Pro, Philips, The Netherlands) using a Cu K_α radiation and EDS (JXA-8900M, Jeol, Japan) respectively. Chemical etching was performed using Keller's reagent ($HF + HCl + HNO_3 + H_2O$) and the microstructure was observed using optical microscopy (OM, Olympus BX 60MF, Japan) and SEM (FE-SEM Hitachi 4800, Japan). The chemical composition (wt.%) of the alloy as determined by EDS was Ti:Nb:Ta:Zr = 51.6:35.5:5.1:7.8.

A two-electrode system consisting of platinum as the counter electrode and the working electrode as the anode was used for anodization. A DC power source (Agilent E 3641 A) was employed. The sample was mounted on a cold mount epoxy resin. Before anodization, the sample was polished by standard ANSI silicon carbide papers of different grades ranging from 100 to 2000 and finally alumina (1 micron) polished, ultrasonically cleaned in deionized water and dried in flowing nitrogen. The area of the sample exposed was 1 cm^2. The electrolyte used was 1 M H_3PO_4 + 0.5 wt.% NaF. The anodization was performed by increasing the potential of the sample from 0 V to the desired potential with a scan rate of 100 $mV\,s^{-1}$, followed by holding the sample in the potential for a desired time. The anodized samples were rinsed in de-ionized water and dried in air. FE-SEM was used for observing the surface, lateral and bottom morphology of the nanotubes.

In order to study the crystallization behavior of the nanotubes, a heat treatment was carried out at 550 °C for 180 min in Ar atmosphere employing a tubular furnace. The heating rate used was 5 °C min^{-1}. The phase structure of the as-formed and the heat-treated nanotubular alloy was identified by XRD using a Cu-Kα radiation. Transmission electron microscopy (FE-TEM/EDS, JEM-2100F, JEOL, Japan) was employed to observe the nanotube structure more precisely as well as to study the compositional homogeneity of the nanotubes. A focused ion beam miller (FIB, SMI3050SE, Seiko Instruments, Japan) was used for specimen preparation for TEM studies.

Electrochemical potentiodynamic polarization and impedance spectroscopy studies were carried out in Ringer's solution (9 $g\,l^{-1}$ NaCl, 0.42 $g\,l^{-1}$ KCl, 0.48 $g\,l^{-1}$ $CaCl_2$, 0.2 $g\,l^{-1}$ $NaHCO_3$) at 37 ± 1 °C using a potentiostat/galvanostat (EG&G, 263A) and an electrochemical impedance spectrometer (EIS, EG&G, 1025). The salt concentration in Ringer's solution corresponded to that of body fluids. A conventional three-electrode system with high-density graphite as counter electrode and saturated calomel electrode (SCE) as reference was used. Preparation of the sample was as described above. The sample edges were carefully covered with epoxy to avoid the possible crevice attack. The electrolyte was de-aerated using high-purity Ar gas for 30 min before starting the experiment. De-aeration was continued at a uniform rate during the experiment. The scan rate used for potentiodynamic polarization was 1.667 $mV\,s^{-1}$. Tafel extrapolation was followed to determine the corrosion parameters; based on a software-based approximation.

EIS tests were conducted at the open circuit potential at the frequency range of 10^{-2} Hz to 10^5 Hz. A similar three electrode set-up was used for EIS studies. The amplitude of ac signal was 10 mV and 5 points per decade was used. An equivalent circuit was assigned for the acquired data and the data were curve fitted using ZSimpWin software.

3. Results and discussion

3.1. Phase and microstructure of Ti–35Nb–5Ta–7Zr alloy

Fig. 1 shows representative OM and SEM images of the quaternary alloy investigated after chemical etching. The micrographs revealed equiaxed β grains. The black spots

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