Corrosion Science 83 (2014) 245–254

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Composition and processing effects on the electrochemical characteristics of biomedical titanium alloys

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ARTICLE INFO

Article history:
Received 4 November 2013
Accepted 8 February 2014
Available online 14 February 2014

Keywords:
A. Titanium
A. Alloys
B. XRD
C. Passive films
B. Polarization
B. EIS

ABSTRACT

The electrochemical behaviour of the Ti–13Nb–13Zr and Ti–6Al–4V ELI alloys with martensitic microstructures was investigated by polarization and electrochemical impedance spectroscopy (EIS) in Ringer's solution. The impedance spectra were interpreted by a two time-constants equivalent circuit. Both investigated alloys showed high corrosion resistance, but the thin and uniform passive film on the Ti–6Al–4V ELI alloy surface was more protective. The inner barrier and outer porous layer were highly resistant and capacitive. However, thicker and more porous passive film on the Ti–13Nb–13Zr alloy surface may be beneficial for osteointegration. The suitable thermomechanical processing improved the corrosion resistance of Ti–13Nb–13Zr alloy.

1. Introduction

The Ti–6Al–4V ELI (extra low impurity) alloy (chemical composition in this paper is given in mass%) is widely employed in manufacture of artificial hip joints and dental roots, due to its high mechanical biocompatibility [1–3]. A low Young's modulus (120–136 GPa [1,3–5]), which plays the main role in inhibiting bone absorption after implantation, is an important advantage of this metallic biomaterial for surgical implants that replaces hard tissues [1–4,6–8]. Namely, the Young's modulus of Ti–6Al–4V ELI alloy is closer to that of human bone (10–30 GPa [1–3,7,8]) as compared to Co–Cr-based alloys and stainless steels. However, it is desirable to further reduce the Young's moduli of titanium alloys used in bone surgery.

One possible way to drastically reduce the Young's modulus is designing new types of biomedical titanium alloys. Thus, a novel Ti–Nb–Zr (TNZ) and Ti–Nb–Zr–Ta (TNZT) system alloys have been developed [1,2,9–12]. In addition to better mechanical biocompatibility, vanadium and aluminium, which can generate cytotoxic reactions and neuron damage, have been eliminated and replaced by niobium, zirconium or tantalum considered as non-toxic elements [1,9,10,13–19]. Among these alloys, Ti–13Nb–13Zr alloy is the most promising biomedical material whose Young's modulus is in a range of 56–82 GPa [5,20,21]. The lowest value for this alloy is reported when the alloy is hot rolled in the $(\alpha+\beta)$ phase field and subsequently water quenched from the β phase field to produce the martensitic microstructure [5].

However, such improved titanium alloy should also exhibit a high corrosion resistance in physiological fluids, since the implant corrosion may adversely affect its mechanical properties leading to implant failure [22–24]. Furthermore, the generated corrosion products can cause serious inflammatory reactions and periprothetic bone loss [22,24]. Therefore, the investigation of implant corrosion behaviour is of major importance. Many corrosion studies have been conducted on Ti–6Al–4V ELI and Ti–13Nb–13Zr alloys, revealing that both alloys offer the excellent corrosion resistance in various environments [2,14,24–29]. The passive oxide film formed on the implant surface is responsible for their high resistance to corrosion in simulated physiological fluids. According to literature [14,16,30–33], high corrosion resistance is mainly due to a dense inner layer, containing a thermodynamically stable TiO_2. Namely, there is evidence that formed oxide film exhibits a duplex structure composed of an inner compact layer and an outer porous layer. The inner layer acts as a barrier against the ion dissolution [16,31,34], so that the corrosion resistance increases with its thickness. The outer layer is of lower resistance, but the incorporation of environmental components into its pores favours osteointegration [17,29,30,35,36].

Although the formation rate and characteristics of the passive oxide film determine the alloy corrosion resistance, these data referring to Ti–13Nb–13Zr alloy thermomechanically treated to

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http://dx.doi.org/10.1016/j.corsci.2014.02.017
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exhibit super biomechanical compatibility are not available. There are only few studies on its corrosion resistance carried out by open-circuit potential (E_{oc}) measurements as a function of time and potentiodynamic polarization. Thus, Geetha et al. [24] investigated the heat treatment effect on the corrosion behaviour of hot-rolled Ti–13Nb–13Zr alloy in deaerated Ringer's solution at 37 °C. It was found that the E_{oc} of samples water quenched from the β phase field shifts towards active direction with time (−350 to −467 mV(SCE)). Same authors noticed that for these samples the lowest passive current density was recorded in comparison to the other samples cooled from the β phase field. More recently, Cvijović-Alagić et al. [37] compared the corrosion behaviour of martensitic Ti–13Nb–13Zr alloy in cold rolled condition and the heat treated Ti–6Al–4V ELI alloy with different microstructures. The obtained results revealed that in spite of the similar corrosion resistance in naturally aerated Ringer's solution at body temperature, the martensitic Ti–6Al–4V ELI alloy exhibits better anodic polarization properties than the cold-rolled Ti–13Nb–13Zr alloy with martensitic microstructure. On the other hand, the corrosion resistance of the martensitic Ti–13Nb–13Zr alloy is improved compared to the Ti–6Al–4V ELI alloy with equiaxed microstructure. This is in agreement with the fact that the alloying elements and their partitioning between phases affect the passive oxide film formation. Therefore, it is of particular interest to investigate the properties of an oxide film passivating the surfaces of the hot-rolled Ti–13Nb–13Zr alloy with martensitic microstructure attaining the lowest Young's modulus.

The aim of the present study was to investigate the effect of martensitic microstructure on the electrochemical characteristics of Ti–13Nb–13Zr alloy subjected to different thermomechanical treatments. As the nature of passive oxide film formed on recently developed Ti–13Nb–13Zr alloy with Young's modulus resembling those of the human bone, when compared to other titanium alloys, has not been systematically analyzed, we attempted to determine the composition, thickness and structure of such passivating film. The corrosion tests were carried out in electrolyte simulating the physiological fluid using polarization and electrochemical impedance spectroscopy (EIS) methods. Electrochemical data were correlated to passive oxide film composition. Comparison of these results with those obtained under the same experimental conditions for the conventional Ti–6Al–4V ELI alloy heat treated to develop martensitic microstructure was also performed.

2. Experimental procedure

The dog-bone-shaped ingots of Ti–13Nb–13Zr alloy were laboratory produced from pure (99.9%) titanium, niobium and zirconium (A.D. Mackay Inc., Denver, USA) by arc melting in a water-cooled copper hearth in argon atmosphere using a non-consumable electrode. To ensure chemical homogeneity, the 8-mm-thick ingots of 50 g were remelted several times. The ingots were then solution treated in the β phase field (β ST) at 900 °C for 30 min, water quenched (WQ) and subsequently deformed by cold rolling (CR) or by hot rolling (HR) in the ($\alpha + \beta$) phase field at 680 °C to obtain the 6-mm-thick plates. The hot-rolled plates were afterwards solution treated in the β phase field at 760 °C for 1 h, followed by water quenching. The Ti–6Al–4V ELI alloy, in a form of 38-mm-diameter bars, was supplied by Krupp VDM GmbH, Germany. The alloy bars were solution treated in the β phase field at 1000 °C for 1 h and water quenched. All heat treatment procedures were performed in the argon atmosphere.

The microstructures of cold-rolled and heat-treated alloys were investigated by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). The specimens for SEM examinations were prepared by standard metallographic techniques and then etched with Kroll's reagent (10 vol.% HF and 5 vol.% HNO_3 in water). The identification of present phases was performed by XRD. The XRD patterns were obtained from the mechanically polished specimens using Cu Kα radiation. They were recorded in the 2θ range from 0° to 100° with a scanning rate of 0.02°/s, while DIFFRACplus EVA v7.0.0.1 softwere was used for the phase identification and data analysis. The lattice parameters of identified phases were calculated using the standard Wincell v1.1 program.

Electrochemical tests were performed in the naturally aerated Ringer's solution (6.5 g/l NaCl, 0.14 g/l KCl, 0.12 g/l $CaCl_2$, 0.2 g/l $NaHCO_3$ and 0.4 g/l glucose) at room temperature (≈25 °C). A number of electrochemical tests, used to evaluate the corrosion behaviour of biocompatible titanium alloys, have been carried out at 25 °C [19,26,29,34,38–43]. Several authors [34,42,43] studied the effect of temperature on the electrochemical behaviour of titanium and its alloys. It was observed that the temperature can influence the results, but the intensity of the corrosion damage was similar for both 25 °C and 37 °C. Alves et al. [34] reported that the formation of the porous layer on the titanium and Ti–6Al–4V alloy in Hank's solution is more pronounced at body temperature. Based on this, the present data can be used to predict what would happen at 37 °C. The potentiodynamic polarization and EIS measurements were conducted in a three-electrode cell using Gamry Reference 600 Potentiostat/Galvanostat/ZRA equipment. Prior to each measurement the specimens, which served as a working electrode with the exposed surface of 1 cm^2, were mechanically polished and then ultrasonically cleaned. The working electrode potential was recorded against a saturated calomel electrode (SCE) (=+0.242 V *vs.* SHE), whereas a platinum grid was used as a counter electrode. After stabilization of the open-circuit potential (E_{oc}), the polarization measurements were conducted in the potential range from −0.75 V(SCE) or −0.35 V(SCE) to 4.0 V(SCE) with a scan rate of 1.0 mV/s, which is in accordance with other investigations [7,16–18,30,35,44]. Namely, the adopted scan rates in the literatures vary from 0.1 to 10 mV/s [45–47]. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were determined using the Tafel extrapolation method. The linear polarization measurements were applied for a range of ±250 mV(SCE) around the E_{oc}, which reaches a stable value after 60 min. The potential was started at the E_{oc} and increased with a rate of 1 mV/s to cathodic and, independently, to anodic side. The Tafel slopes were derived using the tangent line method.

All electrochemical tests were conducted in triplicate to verify the reproducibility of the results.

EIS measurements were conducted at the open-circuit potentials with potential perturbation amplitude of 10 mV (rms – root mean square). The impedance spectra presented as Nyquist and Bode diagrams were measured in the frequency range from 100 kHz to 10 mHz. The impedance data were analyzed using Gamry Instruments Echem Analyst version 5.50 software. To model the EIS spectra, different equivalent electrical circuits (EEC) were used. A best fitting of the experimental data was obtained using an EEC with two time-constants, *i.e.* a two-layer oxide film as illustrated in Fig. 1a. In this model, shown in Fig. 1b, R_{Ω}, R_b and R_p represent the resistance of the electrolyte, inner barrier layer and porous outer layer, respectively. On the other hand, CPE_b and CPE_p are constant phase elements (CPE) related to the pseudocapacitive behaviour of the inner barrier layer and porous outer layer, respectively. Based on the fitting of the impedance spectra, the numerical values of impedance parameters were estimated. The quality of fitting with the proposed EEC was judged by the values of the "Goodness of Fit" parameter, which is similar to Boukamp's Chi-squared and is represented by the relation (Chi-squared)/(number of points).

The corroded surfaces were examined using a XRD analysis outlined above.