Materials Science and Engineering C 56 (2015) 532–537

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Corrosion behavior of Ti–39Nb alloy for dentistry

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ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form 10 June 2015
Accepted 13 July 2015
Available online 19 July 2015

Keywords:
Titanium alloy
Impedance
Surface analysis
Fluorides
Corrosion

ABSTRACT

To increase an orthopedic implant's lifetime, researchers are now concerned on the development of new titanium alloys with suitable mechanical properties (low elastic modulus–high fatigue strength), corrosion resistance and good workability. Corrosion resistance of the newly developed titanium alloys should be comparable with that of pure titanium. The effect of medical preparations containing fluoride ions represents a specific problem related to the use of titanium based materials in dentistry.

The aim of this study was to determine the corrosion behavior of β titanium alloy Ti–39Nb in physiological saline solution and in physiological solution containing fluoride ions. Corrosion behavior was studied using standard electrochemical techniques and X-ray photoelectron spectroscopy.

It was found that corrosion properties of the studied alloy were comparable with the properties of titanium grade 2. The passive layer was based on the oxides of titanium and niobium in several oxidation states. Alloying with niobium, which was the important part of the alloy passive layer, resulted in no significant changes of corrosion behavior. In the presence of fluoride ions, the corrosion resistance was higher than the resistance of titanium.

1. Introduction

Pure titanium and its widely commercialized α–β alloys, Ti–6Al–4V and Ti–6Al–4V ELI, are largely used as materials for orthopedic implants, particularly for their high fatigue strength, corrosion resistance, biological inactivity and biointegration ability [1]. Nevertheless, these materials suffer from a high degree of biomechanical incompatibility caused by their high elastic modulus (~105 GPa) compared to cortical bone (10–25 GPa) [2]. As per Wolff's law [3], the bone tissue cannot regenerate, and the mechanical bond between the bone and the implant can eventually be lost [4,5]. Furthermore, Vanadium and Aluminum have been proven to have negative immunological influence in humans [6–8].

Considering these facts, current materials research focuses on β-titanium alloys that have a lower elastic modulus (approximately 50–80 GPa) than the α and α–β alloys [2,9,10]. Because of their bioinertia, elements chosen for β-phase stabilization are predominantly Nb, Ta and Zr [11]. The elastic modulus of Ti–39Nb alloy varies between 40 GPa and 60 GPa [12,13]. Additionally, another substantial aspect to be considered is corrosion resistance of these elements. It has been determined that the resistance of the β-titanium alloys in the human body is equal to or even greater than that of Ti–6Al–4V and Ti grade 4 [14–22].

All materials used in dental implants face a specific problem as they come in contact with fluoride ions from the dental treatment products. Fluorides can cause destruction of the passive layer and substantially increase the corrosion rate of the implant. This topic has been thoroughly investigated for both titanium and Ti–6Al–4V [23–30] but not for β-titanium alloys. Robin and Meirelis studied the corrosion behavior of the Ti–6Al–4V and Ti–23Ta alloys in Fusayama artificial saliva of pH 2, 5 and 7, with various concentrations of F ions (0, 1000, 5000 and 10,000 ppm F), by the means of open circuit potential measurements, potentiodynamic polarization and electrochemical impedance spectroscopy. The results showed a decrease of corrosion resistance with increasing fluoride concentration and/or pH decrease [29]. The negative effect of fluoride ions was stated by Kwon et al. [31]. His work was focused on the mechanical properties of Ti–Mo wire and it was found that the combination of fluoride ions with decreased pH led to thinning of the wire and decreasing of its mechanical properties. The addition of 0.2% NaF into 0.9% NaCl resulted in a decrease of corrosion resistance to half in the case of Ti–30Nb–8.8Zr–0.8Fe alloy [32]. Watanabe and Watanabe studied the interaction between Ti–Mo and Ti–45Nb alloy wires with fluorides containing common medical preparations. They observed discoloration of the surface caused by corrosion of the material [33]. A decrease of corrosion resistance of Ti–Mo and Ti–45Nb alloys caused by the addition of fluoride ions into acidified artificial saliva solution was postulated by Bai et al. [34].

The goal of this work was to evaluate the corrosion properties of the newly developed alloy Ti–39Nb in the basic human body environment

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http://dx.doi.org/10.1016/j.msec.2015.07.029
0928-4931/

model. The effect of fluoride ions on the corrosion behavior was assessed, and the data obtained were compared with commercially available pure titanium grade 2.

2. Materials and methods

Titanium grade 2 (ASTM B265), Ti–39Nb and pure Nb (99.85 wt.%) were used for the corrosion resistance evaluation. The alloy was prepared by six-fold arc melting and subsequent annealing at 1200 °C/4 h/vacuum (homogenization) and hot forming at 1100 °C to 700 °C. During hot forming, the dynamic and post-dynamic recrystallization occurred and coarse cast grains were refined. The samples were then solution treated at 850 °C/0.5 h/water.

Prior to each measurement, the samples were water ground using FEPA (Federation of the European Producers of Abrasives) P1200 paper, degreased by ethanol in an ultrasonic bath and sterilized by saturated water vapor at 120 °C/20 min in an Ecosteri sterilizer (BMT).

The simplest model of the human body environment, a physiological saline solution containing 9 g/L NaCl, was chosen for corrosion resistance evaluation. The only aggressive components of this solution were the chloride ions. Any other phenomena that could make the interpretation of results difficult, such as phosphate precipitation on material surface from more sophisticated environments, were prevented. Two solutions were prepared: an unadjusted pH solution and a solution with pH adjusted to 4.2 using phthalate buffer [35]. The prophylactic treatment was modeled by introducing fluoride ions in the form of sodium fluoride. The fluoride concentration is equivalent to the lowest concentration used in medical preparations. The solution with decreased pH models the conditions found in inflammation. The abbreviated description of the used environments “environment/pH/fluoride ion concentration in ppm” (e.g., PS/4.2/200) is used throughout the text. The tests were performed at 37 °C in a polytetrafluoroethylene cell. The reference electrode (silver–silver chloride electrode/3 mol/L KCl, henceforth referred to as SSCE) was placed in a plastic salt bridge sealed by agar to prevent the fluoride ions from damaging the glass electrode. All potentials given in this work are related to this electrode.

After an eleven hour stabilization of the open circuit potential, the electrochemical impedance spectra and the potentiodynamic curves were measured (-0.05 V/E_{ocp} to 1 V/SSCE, 1 mV/s). The electrochemical impedance spectra were measured at the open circuit potential with a 10 mV amplitude of AC signal with a frequency range of 50 kHz to 1 mHz.

The surface of the samples was studied using an X-ray photoelectron spectrometer (XPS) ESCAprobe P (Omicron Nanotechnology Ltd.) equipped with an Al Kα ($\lambda = 1486.7$ eV) X-ray source. The spectra were measured with an energy step of 0.05 eV and normalized to the binding energy of C1s peak (285.0 eV). After 24 hours of immersion, the samples were thoroughly washed with distilled water, ethanol and acetone and transferred to the spectroscope. The data for the chemical state evaluation were obtained from the NIST X-ray Photoelectron Spectroscopy Database [36].

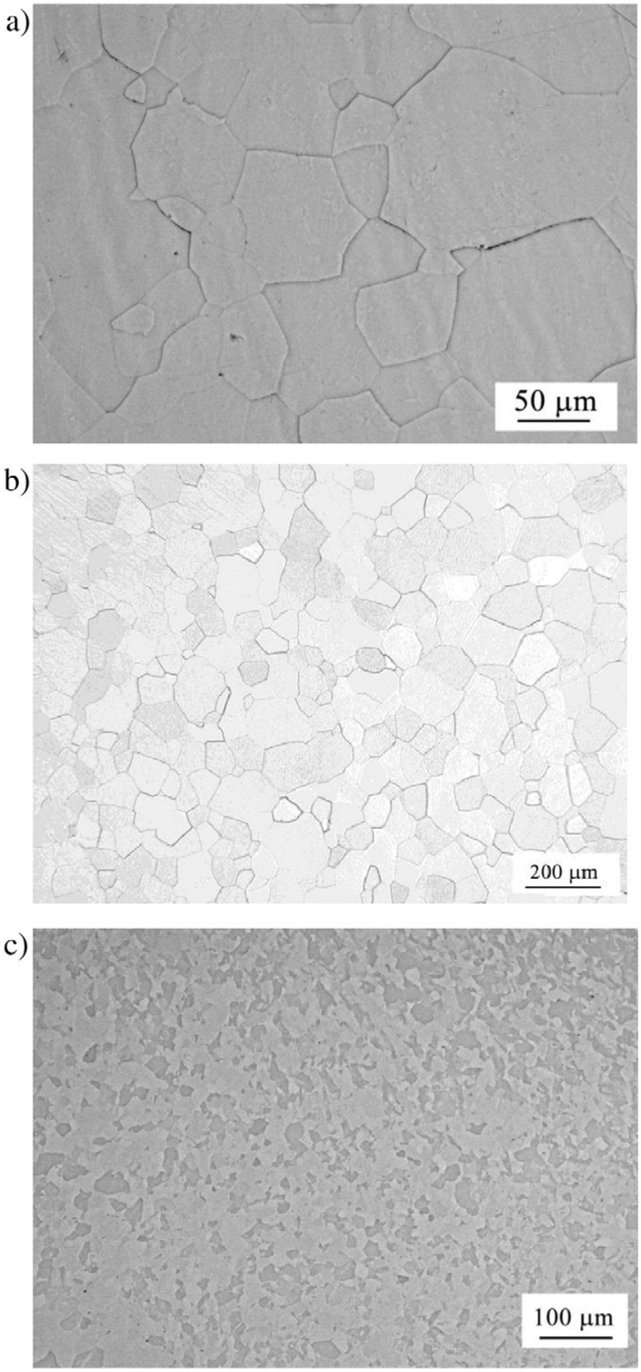

Fig. 1. Microstructure of Ti–39Nb alloy (a), Ti grade 2 (b) and Nb (c).

3. Results

The microstructure of the Ti–39Nb alloy consists of a β-matrix with fine particles of α-phase. Precipitation of the α-phase is predominantly visible on the grain boundaries (Fig. 1a). Microstructures of the titanium and niobium are shown in Fig. 1b and c respectively.

Fig. 2 depicts the open circuit potential time dependence of all studied materials during the 11 hour exposure. In the physiological solution with non-adjusted pH, the potential of all the materials was within the TiO_2 and Nb_2O_5 thermodynamic stability range [37]. A decrease of the pH value led to insignificant changes in open circuit time dependences. In the FR/4.2/200 media, the potential of pure titanium dropped rapidly to -1.02 V. This state corresponds to the active dissolution of titanium. In this case, its equilibrium potential is between -0.924 V to -1.104 V for Ti^{2+} concentration from 10^{-8} up to 10^{-2} mol/L [37]. Same behavior of titanium was observed also in works [23,38–40]. The subsequent increase of potential was most likely caused by the formation of less soluble corrosion products on the sample surface [25]. For niobium, the potential dropped to -0.45 V. This value corresponds to the border of the Nb_2O_5 and NbO_2 thermodynamic stability region.

The results of EIS spectra measurement are shown in Fig. 3 and summed up in Table 1. Fig. 4 shows the equivalent circuits used to evaluate the impedance spectra. In these circuits, the constant phase element (CPE) is used instead of a capacitor, which considers the non-ideal behavior of the system. The impedance of the constant phase element is defined as $Z = [C\,(j\omega)^{\alpha}]^{-1}$, where $\alpha \in \langle 0;1 \rangle$; if $\alpha = 1$, the CPE acts like a pure capacitor and if $\alpha = 0$, it acts as a pure resistor [41,42]. The components R2 and CPE2 correspond to the resistance of pore