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Corrosion evaluation of Ti-48Al-2Cr-2Nb (at.%) in Ringer's solution

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Abstract

The corrosion behavior of Ti–48Al–2Cr–2Nb (at.%) in Ringer's solution was studied to evaluate its potential as a biocompatible material. Corrosion properties of Ti–6Al–4V were determined under the same conditions for comparison. Two electrochemical techniques, potentiodynamic anodic polarization and electrochemical impedance spectroscopy, were employed to test Ti–48Al–2Cr–2Nb and Ti–6Al–4V. Surface modifications to the samples were made by autoclaving and by oxidation in air at 500 °C and 800 °C. The results show excellent corrosion resistance for unmodified Ti–48Al–2Cr–2Nb, corroborated by the high values of polarization resistance and corrosion potential and low values of corrosion current and corrosion rate. Ti–48Al–2Cr–2Nb appears to possess corrosion characteristics similar to Ti–6Al–4V. Surface modification rendered the Ti–48Al–2Cr–2Nb material extremely corrosion resistant. © 2006 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Titanium alloy; Oxidation; Corrosion; Ringer's solution

1. Introduction

In general TiAl alloys possess low density, high strength-to-weight ratio, high stiffness and strength [1,2]. Gamma titanium aluminide (γ -TiAl) is being investigated and recommended for elevated temperature applications where weight reduction is a prime concern. However, the resistance of γ -TiAl to corrosion at room temperatures has not been investigated and there are no reports of electrochemical studies to this end in service environments. Ti-6Al-4V on the other hand has been used extensively for many years as an implant material, mainly in orthopedic applications. Many studies have been published recently on the corrosion of this titanium alloy [3-6]. Passivity as a result of film formation without breakdown was observed on Ti-6Al-4V surfaces over the potential range of -400 to +1400 mV vs. a standard calomel electrode (SCE) in Ringer's solution by Solar et al. [3]. In a study on corrosion of cast titanium in 1% NaCl solution [4], sandblasted surfaces showed a reduced passive region and a considerable increase in the passivation current density. In another study on orthopedic alloys [5], the corrosion behavior was examined in aerated Ringer's solution by anodic polarization from 0 mV up to +2200 mV (SCE), where passivity was observed for Ti-6Al-7Nb and Ti-6Al-4V with the primary passive current density at $\approx 10 \,\mu\text{A/cm}^2$. Low corrosion currents were measured for three non-V-containing Ti alloys (Ti-7Nb-6Al, Ti-13Nb-13Zr and Ti-15Zr-4Nb) used as biomaterials [6], indicating a passive state which is stable with time. This study showed slightly lower corrosion rates for non-V-containing alloys compared with Ti-6Al-4V. Despite the excellent corrosion resistance of Ti-6Al-4V in Ringer's solution, concern has developed over the issue of biocompatibility with respect to the dissolution of aluminum and vanadium ions and the possibility of consequential toxic effects [6-8]. For implant applications it is necessary to consider both biological and corrosion aspects. Other Ti-based alloys are also being investigated for implant applications. Recently, Ti-48Al-2Cr-2Nb (at.%) (33.35 wt.% Al, 2.68 wt.% Cr, 4.79 wt.%

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Nb, balance Ti) (hereafter referred to as γ -TiAl), a second generation gamma titanium aluminide, was evaluated as an implant material [9].

In this particular work, the corrosion behavior of γ -TiAl and Ti–6Al–4V in Ringer's solution, used to simulate human body fluids, is investigated for control, autoclaved, and samples oxidized at 500 °C and 800 °C. Two electrochemical techniques were used for this purpose: potentio-dynamic polarization and electrochemical impedance spectroscopy (EIS). Standard corrosion parameters such as corrosion current density ($i_{\rm corr}$), corrosion potential ($E_{\rm corr}$), polarization resistance ($R_{\rm p}$) and corrosion rate ($C_{\rm R}$) were calculated from these experiments.

2. Materials and methods

Both titanium alloys, γ -TiAl and Ti-6Al-4V, were received in the form of rods with a diameter of 25 mm. Disc-shaped specimens with approximate thickness of 2 mm and a diameter of 15 mm were obtained from the center of these rods using electric discharge machining. Prior to corrosion testing, each specimen was ground with 240 and 600 grit SiC paper and ultrasonically cleaned with alcohol, and then rinsed in distilled water. The corrosion measurements for each experimental condition were carried out using a potentiostat/galvanostat (Parstat 2263, Princeton Applied Research), a K-cell (Princeton Applied Research) and electrode holders. An SCE was used as the reference electrode and the counter electrode consisted of two graphite rods positioned symmetrically with respect to the working electrode. The surface area exposed to the electrolyte was 10 mm². The corrosion behavior of the Ti-based alloys was evaluated at room temperature using Ringer's solution which was not deaerated, with an approximate pH between 5 and 6.

The potentiodynamic anodic polarization curves for the Ti-based alloys were recorded for a potential scan from -1.0 V to 0.800 V vs. open circuit potential at a scan rate of 20 mV/s. The polarization curves were analyzed to determine $E_{\rm corr}$ (corrosion potential) and $i_{\rm corr}$ (corrosion current). The corrosion rate, $C_{\rm R}$ (rate of metal dissolution), in millimeters per year, was determined with the following standard equation:

$$C_{\rm R} = \frac{i_{\rm corr} * A_{\rm W}}{zF\rho}$$

where $A_{\rm W}$, z and ρ are characteristic properties of each sample (atomic weight, valence and density respectively) and F is the Faraday constant (96,500 As/mol). Equivalent weights based on standard equations were obtained to calculate the corrosion rate.

Electrochemical impedance spectroscopy was also used to evaluate the samples. This method was conducted according to the ASTM G-106 standard practice. Samples were left in contact with Ringer's solution at open circuit conditions for 1 h prior to carrying out the EIS tests. The alternating current (ac) impedance spectra for γ -TiAl and Ti-6Al-4V alloys were obtained at the open circuit potential, with a scan frequency range of 100 kHz to 1 mHz with amplitude of 10 mV to obtain 36 experimental points. Nyquist plots were obtained by curve fitting these data points using a commercial software package called Electrochemistry Power SuiteTM. These plots were analyzed to determine the solution resistance (R_{Ω}) , polarization resistance at the electrode/solution interface (R_p) , and the double layer capacitance at this interface (C_{DL}) . Bode plots were also plotted from the same data to analyze and understand better the corrosion phenomena occurring during the impedance tests.

All corrosion experiments were carried out for the Ti alloys used in this study for three different surface treatments: (a) autoclaved at 121 °C and 15 psi steam for 1 h, (b) oxidized in air at 500 °C and (c) oxidized in air at 800 °C, each of 1 h duration. The as-received sample in each alloy was used as control for comparison purposes. All corrosion testing was carried out at 25 °C. Four samples were tested for each experimental condition and the average of these results is reported. Outlier data was not included in these calculations.

3. Results and discussion

Micrographs of γ -TiAl and Ti-6Al-4V were obtained with electron backscattering using a scanning electron microscope (SEM) (JEOL JSM-5410 LVSEM). Fig. 1 shows the backscattered electron image for the two alloys being studied. γ -TiAl mainly consists of 80 vol.% lamella

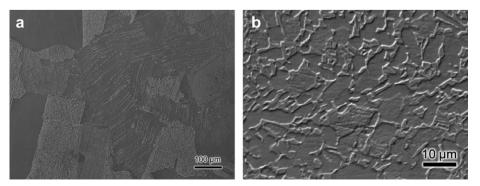


Fig. 1. Microstructure of (a) Ti-48Al-2Cr-2Nb and (b) Ti-6Al-4V. Backscattered SEM.

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