



## Corrosion behavior of $\beta$ titanium alloys for biomedical applications

M. Atapour<sup>a,b</sup>, A.L. Pilchak<sup>a,c,d</sup>, G.S. Frankel<sup>a,\*</sup>, J.C. Williams<sup>a</sup>

<sup>a</sup> Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, United States

<sup>b</sup> Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

<sup>c</sup> Air Force Research Laboratory, Materials and Manufacturing Directorate/RXLM, Wright Patterson Air Force Base, OH 45433, United States

<sup>d</sup> Universal Technology Corporation, Dayton OH 45432, United States

### ARTICLE INFO

#### Article history:

Received 23 September 2010

Received in revised form 7 December 2010

Accepted 12 February 2011

Available online 18 February 2011

#### Keywords:

Ti alloys

Corrosion

### ABSTRACT

The corrosion behavior of biocompatible  $\beta$  titanium alloys Ti–13Mo–7Zr–3Fe (TMZF) and Ti–35Nb–7Zr–5Ta (TiOsteum) was investigated in 0.9% NaCl and 5 M HCl solutions. Extra-low-interstitial Ti–6Al–4V, which is also a candidate material for biomedical applications, was studied for comparison. The as-received TiOsteum and TMZF alloys exhibited single-phase  $\beta$  and  $\alpha + \beta$  microstructures, respectively, so the latter was also investigated in the solutionized and quenched condition. In 0.9% NaCl solution, all three alloys exhibited spontaneous passivity and very low corrosion rates. Ti–6Al–4V and the as-received TMZF exhibited active-passive transitions in 5 M HCl whereas TiOsteum and TMZF in the metastable  $\beta$  condition showed spontaneous passivity. Potentiodynamic polarization tests, weight loss and immersion tests revealed that TiOsteum exhibited the best corrosion resistance in 5 M HCl. Analysis of surfaces of the corroded specimens indicated that the  $\alpha/\beta$  phase boundaries were preferential sites for corrosion in Ti–6Al–4V while the  $\beta$  phase was preferentially attacked in the two-phase TMZF. The performance of the alloys in corrosive environment was discussed in terms of the volume fraction of the constituent phases and partitioning of alloying elements between these phases.

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### 1. Introduction

Titanium (Ti) and its alloys are widely used for biomedical and dental applications because of their unique combination of high specific strength, high corrosion resistance and good biocompatibility [1,2]. They are used for artificial hip and knee joints, bone plates, dental crowns, and dental bridges, among other things. In all of these applications, there is an interaction between the metallic implant and the biological environment, and therefore the service life of the component is strongly dependent on the corrosion behavior of the alloy. In air, Ti alloys spontaneously form a passive film consisting mainly of TiO<sub>2</sub> that protects these alloys in environments of varying aggressiveness [3].

It is well known that the corrosion properties of Ti alloys are dependent on several factors such as composition and microstructure [4–6]. Ti undergoes an allotropic transformation, changing from the high temperature  $\beta$  phase (body-centered cubic structure) to  $\alpha$  phase (hexagonal close-packed structure) upon cooling. Alloying elements are classified as  $\alpha$  or  $\beta$  stabilizers depending on their effect on the transformation temperature, or  $\beta$  transus. Al is the most commonly used element to stabilize the  $\alpha$  phase to higher temperatures, although it also has significant solubility in the  $\beta$  phase. V, Mo, and Nb are  $\beta$

stabilizers that form an isomorphous system with Ti. Fe is also a  $\beta$  stabilizer, but it forms a eutectic system with titanium. Depending on the phases that can be retained at room temperature, Ti alloys are classified into three categories:  $\alpha$ ,  $\alpha + \beta$ , and metastable  $\beta$  alloys [4].

The  $\alpha + \beta$  alloy Ti–6Al–4V is the most frequently used Ti alloy for biomedical [1,5] and structural applications [4]. Ti–6Al–4V can be thermomechanically processed to produce a wide range of microstructures with varying spatial distributions and morphologies of the  $\alpha$  and  $\beta$  phases, allowing for a wide range of properties to be achieved. Recently, however, there have been concerns that V is potentially toxic [6] and that Al can contribute to the development of Alzheimer's disease [7], especially with long-term implantation. Furthermore, the elastic modulus of Ti also tends to increase with increasing Al content and increasing volume fraction of the  $\alpha$  phase [8]. Ti–6Al–4V, for example, has a modulus of approximately 110 GPa, which is significantly higher than human bone, which has a modulus in the range of 10 to 40 GPa [2]. When joined to bone, either adhesively or mechanically, such large mismatches in elastic moduli result in the formation of large stresses at the bone/implant interface, which can lead to crack nucleation and early fracture. This large difference might also cause some health problems in long-term applications [9]. Alloys containing primarily  $\beta$  phase tend to exhibit significantly lower elastic modulus values than near- $\alpha$  and  $\alpha + \beta$  alloys [8], making them more favorable for mating with bone.

Considering the potentially harmful effects of Al and V, combined with the high stiffness of Ti–6Al–4V, recent efforts have focused on

\* Corresponding author. Tel.: +1 614 688 4128.

E-mail address: [frankel.10@osu.edu](mailto:frankel.10@osu.edu) (G.S. Frankel).

developing new titanium alloys specifically for biomedical applications [7,10]. These alloys include Ti–35Nb–7Zr–5Ta (known commercially as TiOsteum®, ATI Allvac, Monroe, NC) [11] and Ti–13Mo–7Zr–3Fe, (known commercially as TMZF®, ATI Allvac, Monroe, NC) [8,12,13], where alloying elements like Nb, Ta, Zr and Fe have improved biocompatibility. In addition, besides Zr which is neutral, these elements stabilize the  $\beta$  phase, resulting in lower elastic moduli, approximately 65 GPa for TiOsteum [12] and between approximately 75 GPa and 85 GPa for TMZF [13].

While a few studies have reported on the microstructure and mechanical properties of the TiOsteum [14] and TMZF [8,15] alloys, there have been no systematic investigations regarding the corrosion behavior of these alloys. Thus, in the present work, the corrosion behavior of TiOsteum and TMZF was explored and compared to Ti–6Al–4V ELI, which is another biomedical grade alloy.

## 2. Experimental procedure

Ti–6Al–4V ELI, an  $\alpha + \beta$  alloy, and two low modulus metastable  $\beta$  titanium alloys, Ti–13Mo–7Zr–3Fe (TMZF), and Ti–35Nb–7Zr–5Ta (TiOsteum), were acquired as bar stock. The as-received bars were sectioned so that longitudinal sections could be prepared for metallographic observation. The specimens were mounted in conductive Bakelite and prepared by standard metallographic techniques including grinding through 1200 grit with progressively finer SiC paper and subsequently polishing to a mirror finish with 0.05  $\mu\text{m}$  non-crystallizing colloidal silica in a vibratory polisher. The specimens were ultrasonically cleaned using deionized water and methanol before evaluation via scanning electron microscopy (SEM). The samples were imaged in a field emission source scanning electron microscope at an accelerating voltage of 20 kV with a probe current of approximately 2.5 nA at a working distance of 5 mm. Preliminary investigations showed that the as-received TMZF was in the two-phase,  $\alpha + \beta$ , condition. Thus, a disc approximately 20 mm in diameter and 7 mm thick was encapsulated in a quartz tube under Ar and subsequently heat treated at 800 °C for 30 min followed by rapid water quenching to retain the single-phase  $\beta$  microstructure, which was confirmed by SEM and optical microscopy.

Electrochemical tests were conducted in 0.9% NaCl at 37 °C  $\pm$  1 °C to simulate an environment and temperature representative of what a biomedical component would experience [16]. Additionally, it has been reported that in some cases, such as crevices or other occluded cells, the pH of the implant-physiologic system shifts to more acidic conditions [17]. Thus, the corrosion behavior of the alloys was also studied in reducing 5 M HCl to simulate a more aggressive environment.

Open circuit potential (OCP), potentiodynamic polarization and immersion tests were performed to assess the corrosion behavior of the various alloys. All electrochemical tests were carried out using a VoltaLab PGP-201 potentiostat. Longitudinal samples were cut from the as-received bar, mounted in cold-setting epoxy resin and then polished to a mirror finish as described above, followed by cleaning with acetone and distilled water. The edges between the specimen and epoxy mold were sealed with MICCROstop acrylic lacquer (Tolber Chemical Division, Hope, AK) to prevent crevice corrosion. No evidence of crevice corrosion was observed in any of the experiments.

Solutions were deaerated with nitrogen for 1 h prior to and also during the electrochemical tests. A conventional three electrode cell with a saturated calomel reference electrode (SCE) and a platinum counter electrode were used. The surface area exposed to the electrolyte was 1, 1.2, 0.6 and 1  $\text{cm}^2$  for Ti–6Al–4V, TiOsteum, TMZF ( $\alpha + \beta$ ) and TMZF (metastable  $\beta$ ), respectively. Anodic and cathodic polarization tests were performed separately over potential ranges relative to the open circuit potential (OCP) of –50 mV to 1500 mV and 30 mV to –250 mV, respectively. The scan rate was 0.5 mV/s. In the NaCl solution the polarization tests were started after 2 h at OCP. In the HCl solution, polarization was initiated following observation of a sharp decrease in OCP associated with activation of the surface.

The polarization tests were repeated at least three times for each condition.

Corrosion resistance was also evaluated by performing weight loss experiments in 5 M HCl at 37 °C. Three 0.5 cm  $\times$  0.5 cm  $\times$  0.5 cm samples of each alloy were cut from the as-received bars. After grinding all sides to 1200 grit SiC, the samples were ultrasonically cleaned in deionized water and acetone. During the weight loss experiments, the samples were removed every 2 days over a 10 day period, ultrasonically cleaned in deionized water for 5 min, dried, weighed, and then placed in freshly prepared solution for the next time period.

Immersion tests were performed to study the morphology of the as-corroded surfaces. Longitudinal samples were cut from the bar, mounted and polished to 0.05  $\mu\text{m}$  alumina, and then ultrasonically cleaned with acetone and deionized water. The samples were exposed to 5 M HCl for 50 h in a bath at 37 °C  $\pm$  1 °C, after which the surface morphology was studied by SEM.

## 3. Results

### 3.1. Microstructure

Backscattered SEM images of longitudinal sections of the microstructures of the as-received bars are shown in Fig. 1. Although the exact thermomechanical histories of the alloys were unknown, the microstructures provided an indication of the processing routes. The as-received TMZF exhibited a structure that was formed by recrystallization above the  $\beta$  transus (Fig. 1a) followed, perhaps, by slow cooling and aging. The prior  $\beta$  grains were nominally equiaxed, having low curvature boundaries that were decorated by continuous layers of grain boundary  $\alpha$ . Fine, acicular intergranular  $\alpha$  phase was present within most of the grains in Fig. 1b. However, there were regions adjacent to some grain boundaries without substantial  $\alpha$  phase precipitation suggesting that there were occasionally differences in alloy composition near the grain boundaries compared to the center of the grain. The as-received TiOsteum was in the metastable condition consisting of single-phase  $\beta$  with no  $\alpha$  phase precipitation detected (Fig. 1c). It had elongated bands that were between 20  $\mu\text{m}$  and 30  $\mu\text{m}$  wide, but the individual bands were made of up small ( $\sim$ 2  $\mu\text{m}$ ) equiaxed subgrains. The elongated features were parallel to the bar axis suggesting they were formed by the rolling and rapid cooling. The microstructure of the Ti–6Al–4V alloy (Fig. 1d) was typical of a mill annealed structure, exhibiting elongated, unrecrystallized bands of  $\alpha$  phase with some acicular transformed  $\beta$  between them probably formed by rolling at a moderate temperature in the  $\alpha + \beta$  phase field. An optical micrograph of the solutionized and quenched TMZF alloy is shown in Fig. 2. Optical microscopy was used to show the microstructure because the lack of elemental partitioning in the single-phase condition resulted in a lack of phase contrast in the backscattered SEM images. The solutionized and quenched TMZF alloy exhibited equiaxed  $\beta$  grains approximately 50  $\mu\text{m}$  in diameter. An aggressive etch was used to reveal the grain boundaries, which resulted in the formation of some pits inside the grains, but no  $\alpha$  phase was detected via backscattered electron imaging in the SEM.

### 3.2. Electrochemical measurements

Open circuit potential measurements for each alloy in 0.9% NaCl exhibited similar behavior as shown in Fig. 3. The OCP plots of each alloy in 0.9% NaCl show a fast increase in potential during the first 0.1 h of exposure followed by a more gradual change towards more positive potentials. This behavior is consistent with spontaneous passivation during OCP exposure in NaCl solution. Fig. 3 also shows that TiOsteum had the most positive values, while Ti–6Al–4V ELI exhibited the most negative values.

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