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Voltammetric stability of anodic films on the Ti6Al4V alloy in chloride medium

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Abstract

The biocompatibility and mechanical integrity of Ti and Ti6Al4V alloy can be affected by corrosion processes. This paper presents studies on the stability of anodic oxide films on Ti6Al4V and Ti in chloride medium. The oxides were grown potentiodynamically up to 8.0 V in the phosphate buffer saline (PBS) solution (pH 6.8) at 25 and 37 °C. The morphology of the obtained anodic oxides and the type of corrosion that occurred were analyzed by SEM–EDS. The Ti6Al4V alloy presented less corrosion resistance than pure Ti. Elemental analyses showed that the decrease of the alloy corrosion resistance is due mainly to the corrosion of Al.

Keywords: Ti6Al4V alloy; Titanium; Corrosion resistance; Anodic films; SEM

1. Introduction

Titanium and its alloy Ti6Al4V are widely used in surgical and odontological applications due to their excellent biocompatibility characteristics such as chemical stability, mechanical resistance and absence of toxicity. The corrosion of metallic implants is a critical process since it can adversely affect the biocompatibility and mechanical integrity of the biomaterial. Corrosion and surface film dissolution of the implants are two of the most important mechanisms for the introduction of foreign ions into the body, which can result in adverse biological reactions [1,2]. The high corrosion resistance of titanium is due to the spontaneous formation of a protective oxide film of 1–4 nm thickness [3] on its surface at open circuit conditions. However, body fluids contain chloride ions which can induce the breakdown of the oxide films on titanium prostheses [4–6]. Chloride readily destroys the passive film on several biomaterials, so it is necessary to study the stability of these oxide films in biological media.

In order to improve not only the corrosion behavior of metallic biomaterials, but also their biocompatibility and mechanical properties, numerous surface modification treatments have been studied [7–9]. Studies made in isotonic NaCl or Ringer solutions showed that titanium alloys are also passive over a wide range of potentials [10,11].

Titanium presents a hexagonal-close-packed structure (α-titanium phase) stable up to 882 °C, which is transformed into a face-centered cubic structure (β-titanium phase) above this temperature. Below 882 °C this β phase can only be stabilized by the addition of specific alloying elements, resulting in the β and α + β phases [12]. In the Ti6Al4V alloy, aluminum stabilizes the α phase and vanadium stabilizes the β phase, increasing the mechanical properties of titanium [1,13,14]. The difference between the chemical compositions of the surface oxides on the Ti6Al4V alloy and on Ti might influence the tissue response to the implant surface; in particular, the amount of metal ions released from the surface oxide layer could hinder the osteointegration process [2]. In vivo animal testing of the alloy has demonstrated the presence of high levels of aluminum in the bone surrounding the implant [15]. In this work, an electrochemical study on the stability of anodic films grown on the Ti6Al4V alloy and on Ti is carried out in a chloride medium (the PBS solution). The oxide morphology and the type of corrosion are characterized by scanning electron

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microscopy (SEM) analyses and microanalyses of elements by an energy-dispersive spectrometry detector (SEM–EDS).

2. Experimental

A conventional 250-mL three-electrode electrochemical cell was used. The working electrodes were made from rods of pure titanium and Ti6Al4V alloy (from Titanium Industries, USA) embedded in epoxy resin and sealed into glass cylinders, with a geometrical area of 1.33 cm^2 exposed to the electrolytic solution. Before each experiment, the electrodes were mechanically polished with 600-grit silicon carbide paper and washed with bidistilled water. A platinum sheet was used as a counter electrode; all potentials were measured against a saturated calomel electrode (SCE).

The electrolyte, that contains Cl^- ions in a concentration of 0.14 mol L^{-1}, was a phosphate buffer saline (PBS) solution of a pH of 6.8 (8.77 g L^{-1} NaCl, 3.58 g L^{-1} Na_2HPO_4, 1.36 g L^{-1} KH_2PO_4).

The anodic oxides were obtained potentiodynamically at 50 mV s^{-1}. The initial (E_i) and final (E_f) potentials for the oxide growth were $E_i = -1.0$ V and $E_f = 1.0$ V up to 8.0 V (versus SCE). Before being used, the PBS solution, kept at room (25 °C) or body (37 °C) temperature, was deaerated with nitrogen for 30 min. All electrochemical measurements were carried out with an Ecochemie/Autolab PGSTAT 20 electrochemical system.

The microstructures of Ti and Ti6Al4V alloy were investigated by means of optical microscopy using an Olympus BX-60M microscope. The surface morphology and the elemental analysis of the Ti6Al4V/oxide electrodes were investigated using a Zeiss DSM 960 scanning electron microscope.

3. Results and discussion

3.1. Microstructural analysis

The microstructures of the Ti6Al4V alloy and Ti electrodes were analyzed after mirror polishing and etching their surfaces with a Kroll solution (6:1:1000, v/v/v, HNO_3:HF:H_2O) for approximately 15 s. A micrograph of a typical monophasic titanium microstructure (α phase at room temperature) is shown in Fig. 1a. It is possible to unambiguously observe the grain boundaries and the homogeneous distribution of grain sizes, while clear and dark areas are related to different orientations of the grain crystallographic planes [12]. On the other hand, Fig. 1b shows two phases for the Ti–6Al–4V alloy, which has smaller-sized grains; the clear and dark areas refer to the α and β phases, respectively. These micrographic results clearly show that the addition of the alloying elements to titanium leads to a refinement of the grain sizes, thus conferring better mechanical resistance to the material, as pointed out in the literature [12,16].

The formation and stability of phases depend mainly on their crystalline structure and elemental nature; while the microstructure of the Ti6Al4V alloy indicates a better mechanical resistance, it does not reveal much on the alloy corrosion resistance. Therefore, the electrochemical results shown hereinafter help to elucidate the alloy corrosion resistance compared to that of pure titanium.

3.2. Stability of the anodic oxides

Studies on the stability of passive films on titanium alloys have been carried out due to their importance from the point of view of corrosion [17,18]. Corrosion and dissolution of the surface oxide film are processes that lead to the introduction of foreign ions into the body, in the case of implants [18]. The corrosion resistance conferred to Ti and its alloys by the relative stability of their oxide films on dental and orthopedic implants was investigated by other authors [11,17–22], who obtained these barrier oxides in various electrolytes by different methods.

Voltammetric profiles obtained during the anodization of the Ti6Al4V alloy in PBS solution at room and body temperatures are shown in Fig. 2. As can be seen, these profiles resemble those presented by other valve metals, and by titanium in particular [3]. The anodic peak at about −0.6 V corresponds to the onset of oxide film formation on the alloy, which has been shown to be essentially TiO_2 [11,19–22]. It should be pointed out that a thin surface film of basically TiO_2 is formed on the Ti6Al4V alloy upon its exposition to air [16,22,23]. The oxide growth on the Ti6Al4V alloy in PBS solution at room temperature was found to proceed up to limiting anodic potentials slightly higher than 6.0 V, presenting a very stable behavior, i.e. a wide potential range of corrosion absence. The oxide growth profile was similar at body temperature, though the stability region decreased to a limiting anodic potential smaller than 6.0 V. This limiting potential in the PBS solution is ca. 2.0 V greater than the one presented by the Ti6Al4V alloy in the so-called Hank's physiological solution, as reported by Milosev et al. [22].

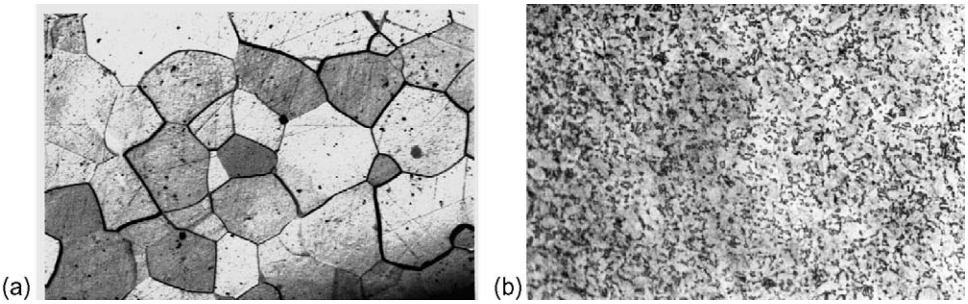

Fig. 1. Photomicrographs of the Ti (a) and Ti6Al4V alloy (b) surfaces etched with a Kroll reagent (200×).