Investigation of TiO_2 Nanotubes Formation on the Surface of Pure Ti and Ti6Al4V Alloy

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Abstract

Titanium and its alloys are known as the most suitable materials for biomedical applications due to their good corrosion resistance and biocompatibility. They owe their excellent corrosion resistance to the passivating oxide film that form on their surface at room temperature. Thanks to this oxide film, they are chemically inert in many media and they have biocompatibility which enable them to be used as a bio material. However, TiO_2 films in their native form, have poor mechanical properties. In recent years, different methods have been used for improving its mechanical properties and further enhancing their usability as a bio material. Anodization is a technique that is generally preferred for production of TiO_2 nanotubes. It is widely accepted as a rapid, simple and inexpensive process that forms strongly adherent TiO_2 layer on bulk and thin film Ti substrates.

The aim of this study is to form TiO_2 nanorods on commerically pure Ti (Cp-Ti) and Ti6Al4V surfaces in an ethylene glycol solution and to examine the electrochemical behavior of both metals in Ringer's solution. After anodic oxidation, surface morphology of the specimens were characterized by Field-Emission Scanning Electron Microscopy (FE-SEM). The electrochemical behavior of untreated Cp-Ti and Ti6Al4V were compared with anodically oxidized specimens in Ringer's solution using open-circuit potential measurement, potentiodynamic polarization and electrochemical impedance spectroscopy techniques.

Keywords: Cp-Ti, Ti6Al4V, anodic oxidation, TiO_2 nanotube, simulated body fluid.

Introduction

Ti and Ti-based alloys have been widely used in dental and orthopedic implants due to their superior mechanical properties, low elastic modulus, excellent corrosion resistance and good biocompatibility [1-3]. Ti owes its good corrosion resistance and biocompatibility to a thin, native oxide layer formed spontaneously on the surface when it is exposed to air at room temperature [2-4]. Despite their superior properties, untreated titanium surfaces fail to bond directly to bone due to their bio-inert nature. Besides, since body fluids are chloride-containing solutions, the physiological corrosion of Ti-based implants may occur, raising the possibility of release of metallic ions [2]. In order to overcome this problem and improve biocompatibility, various surface modification techniques have been developed [2,4,5]. Recently, TiO_2 nanotube films produced by anodization have gained considerable attention. Use of TiO_2 nanotube arrays provide greater control over film morphology. They can be easily prepared and have good adhesion to the substrate [2,3,4,6]. TiO_2 nanostructures with different size, shape and morphology can be achieved by controlling anodizing parameters such as the voltage, electrolyte composition and the treatment time [2]. The anodized nanotubular surfaces have been demonstrated to have better bio compatibility. These include enhanced osteoblast or bone-forming cell adhesion and function, improved growth of hydroxyapatite, and better cellular behavior and tissue integration [7,8].

For creating a nanostructured oxide layer simultaneous oxidation and dissolution of the oxide layer is essential. It was reported that anodization in fluoride containing electrolyte leads to a titanium fluoride complex and afterwards dissolution of the TiO_2 oxide layer occurs and owing to this phenomena a nanostructured oxide layer can be created [3,7,9]. The aim of the present work is to produce of titania nanotube arrays by anodization of Cp-Ti (commercially pure titanium) and Ti6Al4V in NH_4F/ethylene glycol/H_2O electrolyte and their morphological characterization. The oxide layers were analyzed by scanning electron microscopy. The electrochemical behaviors of Cp-Ti and Ti6Al4V alloy with nanotube on their surfaces were evaluated and compared in Ringer's solution which simulates the body fluid using open-circuit potential measurement, potentiodynamic polarization and electrochemical impedance spectroscopy techniques.

Experimental Procedure

Sample Preparation

10x10x1mm, Cp-Ti and Ti6Al4V (composition of 6.25 wt.% Al, 4.22 wt.% V, 0.17 wt.% Fe, 89.3 wt.% Ti) substrates were used in experimental studies. Specimens were grinded with 800, 1200, 2000 abrasive papers then cleaned with deionized water and ethanol before anodic oxidation.

Anodic Treatment

The anodization was performed using a two-electrode cell with sample as the working electrode and graphite plate as the counter electrode. During the process, 30 V DC potential was applied to specimen for 3 hours at room temperature. Ethylene glycol (EG) solution containing 0.25 wt% NH_4F and 90% vol. ethylene glycol and 10% vol. distilled water was used for the anodic oxidation [3]. The distance between the cathode and the anode (Ti plates) was kept constant (2 cm) for each treatment. The solution was stirred continuously using a magnetic stirrer during the anodization process.

Characterization

The surface morphology of the anodized samples was examined using a JEOL JSM 7000F Field Emission Scanning Electron Microscope (FESEM).

Electrochemical Tests

All electrochemical tests were conducted in a three electrode cell setup (Reference 1000 potentiostat/galvanostat, Gamry Instruments). The three electrodes of this setup were: working electrode as the specimens, a saturated calomel electrode as the references electrode and the graphite rods as counter electrodes. Since the chemical interaction between the metallic material and human body is crucial for evaluating the implant stability, the corrosion behavior of the specimens were investigated by electrochemical tests in Ringer's solution (6.0 g/L NaCl, 0.3 g/L $CaCl.2H_2O$, 4.0 g KCl, 3.0 g/L $C_3H_5NaO_3$) which has a similar composition to human blood plasma. In order to simulate human body temperature all electrochemical tests, open circuit potential (OCP) measurements, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) were carried out at 37 ^oC. In potentiodynamic tests, in order to cover both anodic and cathodic regions, 0.2 V below OCP point up to 2 V were scanned at a rate of 1 mV per second. In EIS analysis, data acquisition was performed by scanning a range of frequencies from 0.01 Hz to 100 kHz, with 10 points per decade, using a sine signal with an amplitude of 10 mV.

Results and Discussion

According to the SEM results, TiO_2 formed on the surface of Ti6Al4V represented a nanotubular structure. Figure 1 shows that the diameter of amorphous nanotubes on Ti6Al4V was approximately 150 nm.

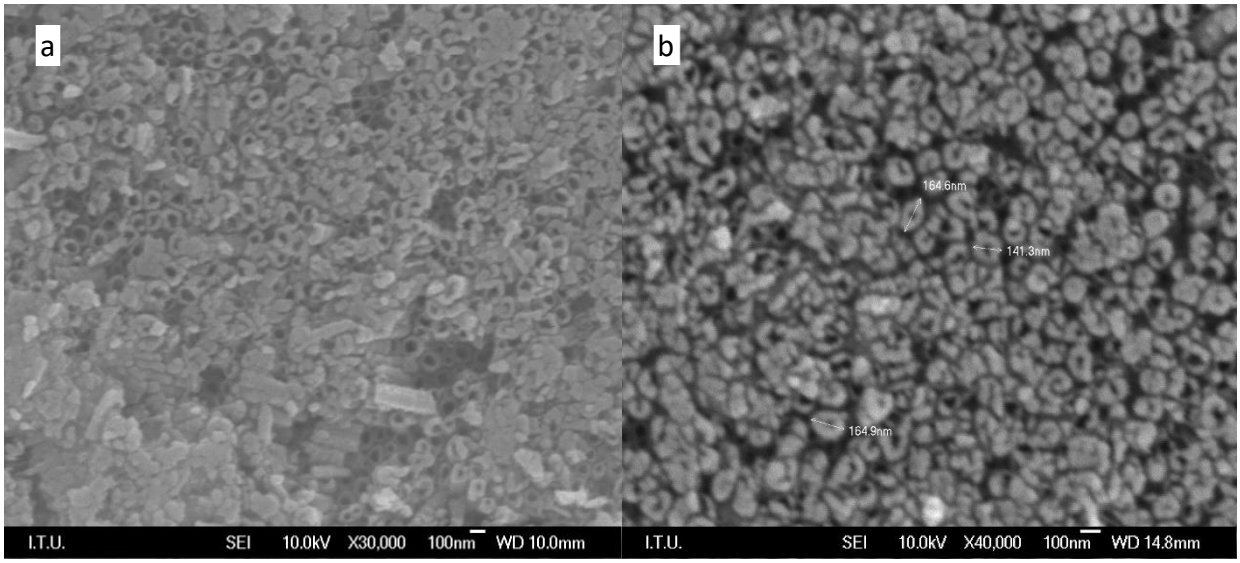

Figure 1. *Scanning electron microscopy image of nanotubular oxide structure formed on the surface of Ti6Al4V alloy at different magnifications a) X30000 b) X40000*

Table 1: *OCP values of untreated and anodized Cp-Ti and Ti6Al4V alloy.*

Sample		**OCP (mV)**
Cp-Ti	untreated	-282.2
	anodized	-226.8
Ti6Al4V	untreated	-462.6
	anodized	-485.0

OCP value is a good indication for observing the chemical activity of a metal in a specific solution. When untreated Cp-Ti and Ti6Al4V was compared according to OCP data, Ti6Al4V was more active than Cp-Ti. After anodic oxidation, OCP value for Cp-Ti slightly increased indicating the passivation of surface. On the contrary, after oxidation process, Ti6Al4V showed dissimilar properties (Table 1).

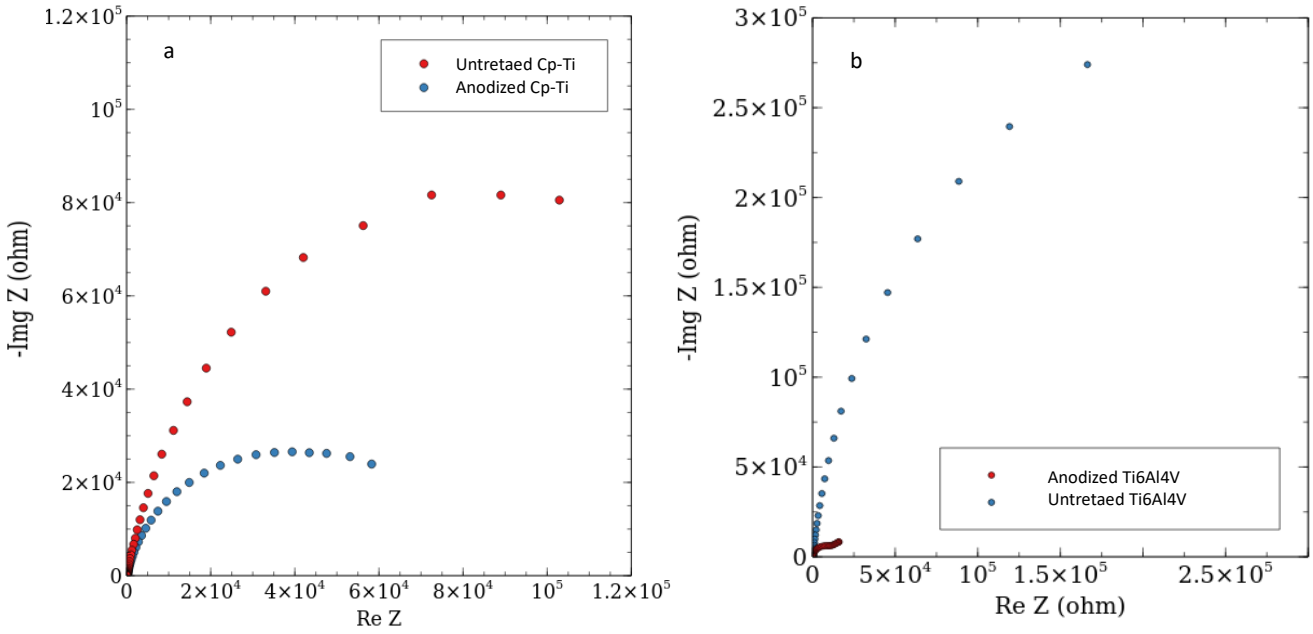

Figure 2. *Nyquist curves of the untreated and anodically oxidized surfaces of the a) Cp-Ti and b)Ti6Al4V samples in Ringer's solution.*

Figure 2 showed the Nyquist plot for untreated and anodically oxidized Cp-Ti and Ti6Al4V specimens. Both specimens depressed Nyquist semi-circle for anodically oxidized samples, revealing less protective oxide film structure. This result is associated with the nanotubular oxide growth as seen in Figure 2.

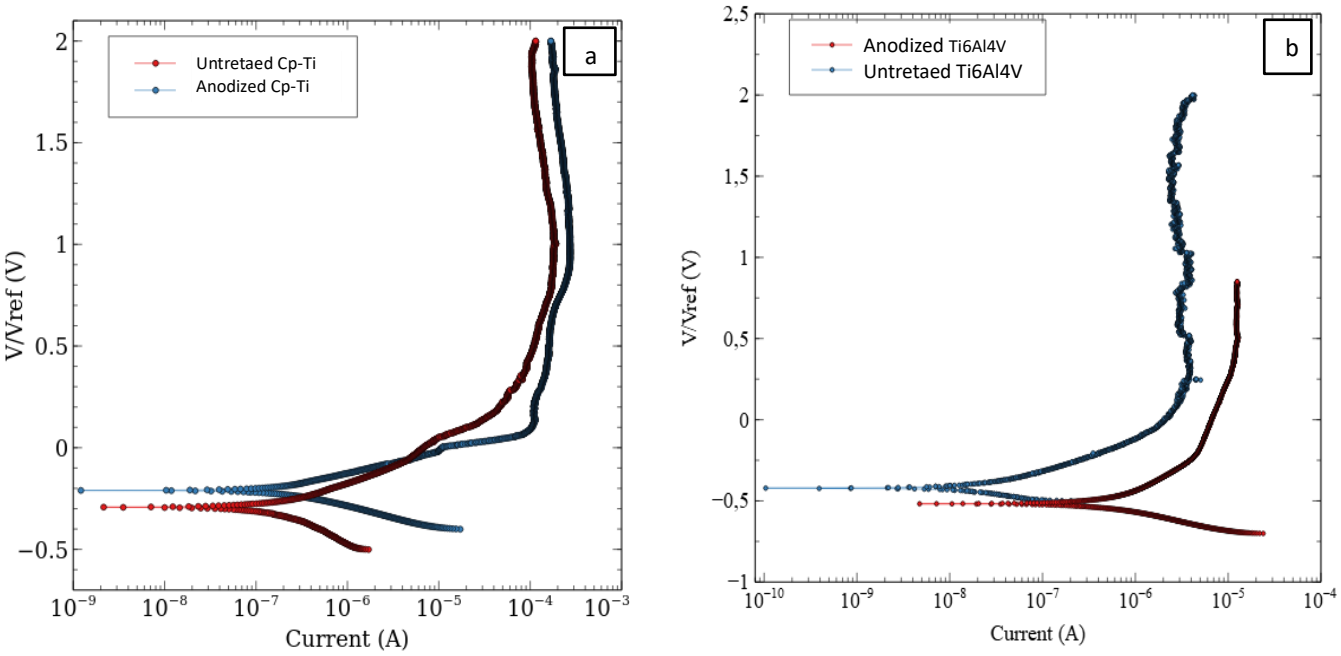

Figure 3. *Potentiodynamic polarization curves obtained for untreated and anodized a) Cp-Ti and b) Ti6Al4V surfaces in Ringer's solution at 37 ^{o}C.*

Potentiodynamic polarization curves corresponding to Cp-Ti and Ti6Al4V for both condition is presented as Figure 3. For Cp-Ti, anodically oxidation resulted an increase in V/V_{ref} indicating the passivation of the surface. This result is also consisted with OCP results. Similar findings for TiO_2 was also discussed in literature. Yu et al [10] indicates that TiO_2 nanotube layers fabricated by anodization in a 0.5 wt% HF solution at 20 V for 1 h suggest better corrosion resistance compared to the smooth Cp-Ti. However type of the oxide on the surface, such being barrier type or nanotubular, has significant impact on nature and protectiveness of the film. Robin et al [11] reported that TiO_2 in nanotube form had less corrosion resistant than untreated Cp-Ti in Ringer's solution at room temperature.

Conclusions

When untreated Cp-Ti and Ti6Al4V was compared by their OCP values, Ti6Al4V represented more active nature in Ringer's solution at room temperature. Nanotubular TiO_2 structures were obtained by anodization in NH_4F/ethylene glycol/H_2O solution at 30V DC potential for 3 hours at room temperature. The electrochemical behavior of oxide structures in Ringer's solution indicated that the surface with nanotubular oxides obtained in this study was not protective on both the Cp-Ti and Ti6Al4V alloy.

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