Porous TiO$_2$-ZrO$_2$ thin film formed by electrochemical technique to improve the biocompatibility of titanium alloy in physiological environment

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Abstract. Porous Ti and Ti alloys have received increasing research interest for bone tissue engineering, especially for dental and orthopaedic implants because they provide cell ingrowths and vascularization, improving of adhesion and osseointegration. The tribocorrosion process is encountered in orthopaedic and dentistry applications, since it is known that the implants are often exposed to simultaneous chemical/electrochemical and mechanical stresses. The purpose of this study was to carry out a systematic investigation of the tribo-electrochemical performance of porous TiO$_2$–ZrO$_2$ thin film formed by anodization of Ti–10Zr alloy surface in an artificial saliva solution and to compare the resulted performance with that of the untreated Ti–10Zr alloy surface in order to be applied for biomedical use. The in situ electrochemical technique used for investigation of tribo-electrochemical degradation was the open circuit potential (OCP) measurement performed before, during and after sliding tests. The results presented herein show that controlled anodic oxidation method can significantly improve the tribocorrosion and friction performances of Ti–10Zr alloy surface intended for biomedical applications.

1. Introduction

The use of commercially pure titanium (c.p. Ti) and its alloys as biomaterials, especially for orthopaedic prostheses and dental implants is increasing due to their superior biocompatibility, high mechanical strength and corrosion resistance [1-2].

Since the mechanical/tensile strength of c.p. Ti is not high enough for some implanted devices (artificial hip joint, pin, or dental screw), many titanium alloys have been developed for this purpose [3]. In the biomedical field titanium alloys have developed of to create materials with improved properties (strength and castability) compared to unalloyed Ti, for use as implants for a long period of time. Taking into account the binary alloys, Ti-Zr with different quantities of Zr have been developed and considered for applications in dental and medical fields: Ti–xZr alloys (with Zr contents ranging from 5 to 20 wt. %) [4], Ti–10Zr [5], Ti–xZr (with a zirconium content of 13–17%) [6] and Ti–50Zr [7].

The excellent corrosion resistance of Ti and Ti alloys is attributable mainly to the formation of a stable titanium oxide (TiO$_2$) layer that forms naturally on the surface of titanium metal on exposure to...
air or water. The thickness of this natural oxide film is typically ranging between 4-6 nm [8-9]. Although the native oxide film considerably reduces the corrosion of Ti and its alloy, this one can be damaged easily by mechanical stress that may lead to accelerated corrosion. Moreover, the native TiO$_2$ film is not bioactive enough to form a direct bonding with bone. Therefore, porous structures are necessary to improve the cell adhesion and osseointegration properties [10]. Consequently, many assays were carried out to grow a thicker oxide layer on titanium or its alloys which can reduce the passivity current and hinder the ion release of titanium and its alloyed elements into physiological fluids. Anodic oxidation of titanium and its alloys might be employed for increasing the thickness of the TiO$_2$ native film and can build up rough and porous surfaces suitable for osseointegration [10-11]. This electrochemical method is increasingly applied for surface treatment on titanium and its alloys and can improve the shear strength and the wear resistance properties of these materials by obtaining nanotube or nanopore structures at the surface [9,12].

The tribocorrosion process finds applications in orthopaedic and dentistry fields, since it is known that the implants are often exposed to simultaneous chemical/electrochemical and mechanical stresses. Tribocorrosion phenomena can affect living systems, as it can cause damage to restorative dentistry, prostheses and other devices, which in turn can affect life quality and overall health. Taking notice of the past studies [4,7] which have presented only the physical properties and corrosion behaviour of Ti–Zr binary alloys, the purpose of this study was to evaluate the tribocorrosion behaviour of porous TiO$_2$–ZrO$_2$ layer obtained by controlled anodic oxidation treatment compared to untreated Ti-10Zr alloy. To our knowledge there are no studies in the literature about the effect of the anodic oxidation treatment on the tribocorrosion properties of oxide films grown on Ti-10Zr alloy.

2. Materials and methods

2.1. Formation and growth of the porous oxide films
Previously to the growth of the porous oxide films by controlled anodic oxidation method, the Ti–10Zr anode electrode (cylinder) was embedded in epoxy resin, cut and polished into disks (with exposed geometric area of about 2.5 cm$^2$) to a mirror finish using silicon carbide paper with grit from 320 to 4000 µm, diamond paste (3 and 1 µm size) and a suspension of silica (0.04 µm size of particles). Samples were ultrasonically cleaned with ethanol for 5 minutes and dried using dry, cold air. Anodic oxidation was carried out at room temperature in a two-electrode electrochemical cell with Ti-10Zr samples as anode and Ti-6Al-4V alloy plate (2.4 x 2.4 cm) as cathode. As anodizing electrolyte to grow the oxide films was used 1 M H$_2$SO$_4$. The growth of the oxide films was carried out using a programmable DC power supply with digital multimeter (Genesys – GEN 300-8) by applying 200 V for 2 minutes. During all anodic oxidation processes, the electrolyte was stirred using magnetic stirrer in order to speed up the escape of gas resulted in the electrochemical reaction from the surface of the Ti-10Zr alloy substrate and keep the homogeneity of the electrolyte. After anodization the specimens were washed thoroughly with distilled water in an ultrasonic bath for 10 min and finally dried with hot air.

2.2. Material characterization
The surface morphology of obtained porous structures was determined by using scanning electron microscopy (SEM, FEI Quanta 200 FEG). Moreover, the energy dispersive X-ray spectrometer (EDX) equipped on the SEM system was used to detect the elemental composition of the sample surfaces.

The tribocorrosion performance of the materials was evaluated with a unidirectional pin-on-disc tribometer coupled with a Solartron 1287 electrochemical interface and a Solartron 1255 frequency response analyser. The three electrodes configuration were utilized, with the samples as work electrode (WE), Ag/AgCl (saturated KCl solution, E=200 mV vs. standard hydrogen electrode - SHE) as reference electrode (RE), and a circular Pt-Rh grid as auxiliary electrode (AE). In figure 1 is schematically presented the experimental setup for tribocorrosion experiments.
The tribocorrosion experiments were performed at room temperature (23°C) in Fusayama Mayer artificial saliva solution having a pH=4.8 [10]. During tribocorrosion tests an alumina pin cylinder (7 mm diameter with 100 mm radius spherical tip) slides against the sample specimen fully immersed in electrolyte. The pins cylinder made of Al₂O₃ (an electrically non-conductive material with high hardness and wear resistance) were degreased with ethanol prior to sliding tests. The tribocorrosion method used consisted of three sequences: (1) stabilization of the system under open circuit potential (OCP) for 30 min (in absence of sliding) to achieve a stable passive surface; (2) sliding under OCP for 5000 cycles, and finally, (3) re-stabilization of the system under OCP (after sliding was stopped) for 30 min. All sliding tests were carried out at a constant rotation speed of 120 rpm, by applying a normal force of 5 N for 5000 cycles.

3. Results and discussion

3.1. Morphological and elemental characterization
A simple and feasible method to construct rough and porous oxide films at ambient temperature with bioactive composition and which is able to realize a direct bonding with bone of implant surface is controlled anodic oxidation method. figure 2 (a) shows the surface morphology obtained after anodic oxidation of Ti-10Zr alloy and figure 2 (b) the corresponding elemental composition.
The main oxidation reactions at the interface of the titanium anode and electrolyte are [13]:

\[ \text{Ti} \leftrightarrow \text{Ti}^{4+} + 4e^- \]  
\[ \text{Ti}^{4+} + 2O^{2-} \leftrightarrow \text{TiO}_2 \]  

Regarding the formation of anodic TiO$_2$-ZrO$_2$ film, the following reactions may occur:

\[ \text{Zr} \leftrightarrow \text{Zr}^{4+} + 4e^- \]  
\[ \text{Zr}^{4+} + 2O^{2-} \leftrightarrow \text{ZrO}_2 \]  
\[ \text{Ti}^{4+} + \text{Zr}^{4+} + 4O^{2-} \leftrightarrow \text{TiO}_2 + \text{ZrO}_2 \]

Zirconium element is a better reducing agent and therefore competes with titanium during anodic oxidation and will oxidize first under the same condition as Minagar et al. [13] have affirmed.

The occurrence of pores represents a positive characteristic of the materials intended for implantation, since it is well know that porous surfaces interact better with tissue, favoring the osseointegration properties.

3.2. Tribocorrosion behaviour tests

The open circuit potential measurements recorded in Saliva Fusayama Meyer artificial saliva before the onset of sliding, during sliding and after the sliding motion is stopped, corresponding to untreated Ti–10Zr alloy surface and anodic porous TiO$_2$–ZrO$_2$ surface are shown in figure 3.

![Figure 3](image)

**Figure 3.** Variation of the open circuit potential of: (1) untreated Ti–10Zr alloy and (2) anodic porous TiO$_2$–ZrO$_2$ surface immersed in Fusayama–Mayer saliva before, during and after sliding tests by applying \( F_n = 5 \) N, for 5000 cycles, at a constant rotation speed of 120 rpm.

Before starting the sliding tests, an increase of the OCP corresponding to untreated Ti-10Zr alloy is noticed. This behaviour indicates that a stable passive surface state is achieved due to growth of a passive film on the electrode. The extent shift of potential associate to untreated Ti-10Zr alloy in the active direction at the end of 30 min. was to +0.234 V value vs. Ag/AgCl, from the immersion value of +0.106 V vs. Ag/AgCl. The OCP of anodic porous TiO$_2$–ZrO$_2$ surface has evolved at the end of 30 min. to 0.095 V vs. Ag/AgCl from the immersion value of +0.219 V vs. Ag/AgCl.

With the onset of sliding, a sudden drop of the OCP in the cathodic domain takes place for untreated Ti-10Zr alloy. Similar observations have been made earlier for untreated Ti–6Al–4V alloy.
surface in phosphate buffer saline solution [14] and also for untreated Ti–6Al–4V alloy surface in Fusayama–Mayer saliva solution [10]. The sudden cathodic shift in OCP of untreated Ti–10Zr alloy indicate the removal of the passive layer with the onset of sliding therefore increase its corrosion susceptibility. In contradistinction to untreated Ti–10Zr alloy, anodic porous TiO$_2$–ZrO$_2$ surface did not reveal a sudden shift in OCP with the onset of sliding; rather it is progressive until the sliding motion is stopped. Similar observation has been made also by Kumar et al. [17] for thermally oxidized CP-Ti tested in Ringer’s solution [15]. This progressive shift in OCP of anodic porous TiO$_2$–ZrO$_2$ surface indicates that the grown anodic oxide film is not totally removed with the onset of sliding, being gradually destroyed. This behavior of anodic porous TiO$_2$–ZrO$_2$ film reveals its enhanced tribocorrosion properties.

Finally on unloading of the Al$_2$O$_3$ counterbody from the samples, the OCP of both surfaces untreated Ti–10Zr alloy and anodic porous TiO$_2$–ZrO$_2$ film starts to increase. This behavior indicates the re-establishment of passive state (repassivation) on their surfaces in the wear track area. Both tested surfaces fails to reach the initial steady state value in the given duration of time after the sliding motion is stopped.

In figure 4 is presented the evolution of friction coefficient versus sliding cycles corresponding to untreated Ti–10Zr alloy and anodic porous TiO$_2$–ZrO$_2$ film. According to figure 4 it could be noticed that the lowest friction coefficient is obtained by anodic porous TiO$_2$–ZrO$_2$ surface with a mean value of 0.20 compared with untreated Ti–10Zr alloy surface which reveal a mean value of 0.40.

![Figure 4. Friction coefficients versus sliding cycles obtained in Fusayama–Mayer saliva during sliding tests by applying $F_n = 5$ N at a constant rotation speed of 120 rpm: (1) untreated Ti–10Zr alloy and (2) anodic porous TiO$_2$–ZrO$_2$ surface.](image)

The decreasing of friction coefficient on anodic porous TiO$_2$–ZrO$_2$ surface could be explained by diminishing the shear strength of the contacting interfaces. Nasab and his collaborators [16] explained that a low wear resistance or high coefficient of friction results in implant loosening. In the present work controlled anodic oxidation to form porous oxide film, reduces the friction coefficient of Ti–10Zr alloy surface. This demonstrate that anodic oxidation treatment extend the lifetime of a biomedical implant using Ti–10Zr alloy. Anodic porous TiO$_2$–ZrO$_2$ surface did not reveal a sudden shift in OCP with the onset of sliding, rather it is progressive until the sliding motion is stopped. The lowest friction coefficient is obtained by anodic porous TiO$_2$–ZrO$_2$ surface compared with untreated Ti–10Zr alloy surface.
4. Conclusions
The evolution of open circuit potential shown that at the moment when the sliding start, untreated Ti–10Zr alloy surface expose a sudden cathodic shift caused by the mechanical destruction and removal of the native passive oxide film induced by sliding. This behavior confirms its increase in susceptibility for corrosion. Anodic porous TiO$_2$–ZrO$_2$ surface did not reveal a sudden shift in OCP with the onset of sliding, rather it is progressive until the sliding motion is stopped. The lowest friction coefficient is obtained by anodic porous TiO$_2$–ZrO$_2$ surface compared with untreated Ti–10Zr alloy surface.

Tribocorrosion properties in simulated physiological fluid (Fusayama Mayer saliva) revealed that in their native form, TiO$_2$ layers have poor tribological properties and are easily fractured under tribocorrosion conditions. The tribocorrosion performance of anodic formed porous TiO$_2$–ZrO$_2$ surface is higher compared with that of untreated Ti–10Zr alloy surface under similar experimental conditions.

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