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The Effect of Normal Force on Tribocorrosion Behaviour of Ti-10Zr Alloy and Porous TiO$_2$–ZrO$_2$ Thin Film Electrochemical Formed

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Abstract. The tribocorrosion behaviour of Ti-10Zr alloy and porous TiO$_2$–ZrO$_2$ thin film electrochemical formed on Ti-10Zr alloy was evaluated in Fusayama-Mayer artificial saliva solution. Tribocorrosion experiments were performed using a unidirectional pin-on-disc experimental set-up which was mechanically and electrochemically instrumented, under various solicitation conditions. The effect of applied normal force on tribocorrosion performance of the tested materials was determined. Open circuit potential (OCP) measurements performed before, during and after sliding tests were applied in order to determine the tribocorrosion degradation. The applied normal force was found to greatly affect the potential during tribocorrosion experiments, an increase in the normal force inducing a decrease in potential accelerating the depassivation of the materials studied. The results show a decrease in friction coefficient with gradually increasing the normal load. It was proved that the porous TiO$_2$–ZrO$_2$ thin film electrochemical formed on Ti-10Zr alloy lead to an improvement of tribocorrosion resistance compared to non-anodized Ti-10Zr alloy intended for biomedical applications.

1. Introduction

Commercially pure Ti and its alloys are mainly used for biomedical applications as implantable materials due to their good properties such as high strength, low density, moderate elastic modulus and excellent corrosion resistance, compared to other metallic biomaterials. The highly corrosion resistance of Ti based materials is due to the stable and adhesive passive oxide film (TiO$_2$) formation on their surface, in the presence of oxygen. This TiO$_2$ film protects material and provides chemical inertness in different media and is generally around 5 nm thick [1-2]. Nevertheless, the native TiO$_2$ film is not entirely stable under certain conditions such as mechanical stress, when this one can be easily damaged leading to an accelerated corrosion. Consequently, a strong destructive attack may occur on the surface of Ti based material due to its reaction with hostile environment. This instability of TiO$_2$ film will affect the biocompatibility of metallic implant, leading to the implant failure [3].

To overcome this problem, surface modification methods are often performed in order to enhance the mechanical, biological and chemical properties of Ti and its alloys. Anodic oxidation treatment is one of the simplest among the different techniques employed to form rough, porous and uniform films across which oxygen ions can diffuse and oxidize the substrate, increasing the thickness of the film.
By anodic oxidation process the ion release is decreases and the corrosion and tribocorrosion resistance of Ti and its alloys is enhances.

The tribocorrosion process has applications in biomedical fields, since it is known that the material implants are often exposed to simultaneous chemical/electrochemical and mechanical stresses [3-4]. The previous studies from the literature focused on the importance of Ti-xZr binary alloy as implant material [5-6] only in terms of corrosion performance of this alloy. Consequently, the main goal of this paper was to bring in a great contribution to the applicability of Ti-10Zr binary alloy as biomaterial. Therefore in this work was study the tribocorrosion performance of treated and untreated Ti-10Zr alloy in Fusayama-Mayer artificial saliva, under various solicitation conditions.

2. Materials and Methods

2.1. Anodic oxidation treatment

The fabrication method of porous TiO$_2$-ZrO$_2$ thin film on Ti-10Zr alloy consisted in anodic oxidation. The chemical composition of Ti-10Zr alloy is shown in table 1. Before anodic oxidation, samples of the Ti-10Zr alloy in the form of rods were cut into cylinders, embedded in epoxy resin, exposing a geometrical area of about 2.5 cm$^2$. Then the samples were ground using successively finer SiC abrasive papers (320 - 4000 μm), diamond paste (3 and 1 μm) and a suspension of SiO$_2$ solution (0.04 μm size of particles), finally achieving a mirror finish. Subsequently, the polished samples were cleaned with ethanol in an ultrasonic bath for 5 min and dried using dry, cold air.

| Element | Ti  | Zr  | Fe  | Ni  | Cu  |
|---------|-----|-----|-----|-----|-----|
| Chemical composition [wt %] | 88.23 | 10.89 | 0.39 | 0.28 | 0.21 |

The electrochemical setup for the growth of the porous oxide films by controlled anodic oxidation method consisted of a two-electrode configuration, with Ti–10Zr specimens previously prepared worked as anode and a Ti–6Al–4V alloy sample (in a size of 5.7 cm$^3$) used as counter electrode. The anodization was performed in a glass cell containing a 1M H$_2$SO$_4$ solution, by applying a DC voltage of 200 V, for 2 min. under magnetic stirring. During the anodic oxidation, 1M H$_2$SO$_4$ solution was stirred (300 rpm) in order to maintain the homogeneity of electrolyte and to accelerate the escape of gas produced in the electrochemical reaction from the surface of the Ti–10Zr substrate.

2.2. Materials characterization

The porous surface morphology of Ti–10Zr alloy specimens after anodic oxidation treatment was examined by scanning electron microscopy (SEM–EDX, FEI Quanta 200 FEG) and the chemical composition was evaluated with an energy dispersive X-ray spectroscopy (EDX) device attached to the SEM.

Tribocorrosion tests were performed using a unidirectional pin–on–disc tribometer permitting to carry out experiments in corrosive aqueous media under controlled electrochemical conditions. For electrochemical measurements was used a three–electrode arrangement which was controlled by a 1287 potentiostat and a 1255 frequency response analyser Solartron. The working electrode (WE) consisted of untreated Ti–10Zr alloy surface and porous TiO$_2$–ZrO$_2$ film formed by anodic oxidation. A circular Pt-Rh grid was used as a counter electrode (CE) whereas the reference one an Ag/AgCl electrode with KCl saturated solution (E = 200 mV vs. standard hydrogen electrode – SHE). The schematic set–up of electrochemical cell used in tribocorrosion experiment is shown in figure 1.

The electrolyte utilized in tribocorrosion tests was the Fusayama-Mayer artificial saliva [3], with the pH equal to 4.8. Alumina pin cylinder (7 mm diameter with 100 mm radius spherical tip) was used as counterpart in the sliding tests due to its high hardness, high wear resistance, chemical inertness and
electrical insulating properties. The alumina pin was rotated under continuous sliding conditions drawing a circular wear track on the test sample. Prior to any sliding test, the counterbodies were degreased with ethanol. The sliding tests were carried out at a constant rotation speed of 120 rotation min$^{-1}$, by applying two normal force of 2N and 5 N for 5000 cycles.

3. Results and discussions

3.1. Materials characterization

Figure 2 (a) shows the surface morphology obtained after anodic oxidation treatment of Ti-10Zr alloy and figure 2 (b) the corresponding elemental composition.

Figure 2 (a) shows that the oxide coating formed by anodic oxidation exhibits rough and porous surface with pores distributed randomly over the surface. Also it can be seen that the anodic film
reveal irregular and in some regions large pores. This porous structure is able to form biological adhesive interface between bone and implant.

From figure 2 (b) which shows the wt. % of anodic porous TiO$_2$–ZrO$_2$ surface it can be seen that the wt. % corresponding to Zr element almost doubles compared to those of untreated Ti–10Zr alloy (Table 1). This can be explained by the fact that Zr element which is a better reducing agent, competes with Ti during anodization, and will oxidize first under the same electrochemical conditions.

3.2. Tribocorrosion behaviour

In figure 3 (a) and (b) are shown the evolutions of open circuit potential (OCP) as a function of the normal force applied, corresponding to treated and untreated Ti-10Zr alloy immersed in artificial saliva before (30 min.), during (5000 sliding cycles) and after (30 min.) sliding tests, at a constant rotation speed of 120 rotation min$^{-1}$.

![Figure 3](attachment:image.png)

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

From figure 3 (a) it is observed that the OCP recorded before sliding ($E_{oc}^1$) of untreated Ti–10Zr alloy showed a shift of potential in the active direction and also that by the end of 30 min. a steady state potential is attained for this surfaces. From the same figure 3 (a) it can be clearly seen that with the onset of sliding a sudden decrease of the OCP occurs for both normal forces applied. The cathodic shift potential increases with increasing the normal load. This sudden drop in potential is associated with the damage of native passive film by its partial or complete removal [7]. The sudden drop in OCP observed for untreated Ti–10Zr alloy surface induces its susceptibility for corrosion. In the period of sliding motion some oscillations in the OCP for were reported, these being attributed to the periodic removal caused by the contact with counter body (depassivation) and growth caused by contact with the electrolyte (repassivation) of the passive film in the sliding zone [8–9]. After unloading, the OCP of untreated Ti–10Zr alloy reveal an anodic shift caused by repassivation of the substrate forming immediately a protective thin film. Both tested surfaces fail to reach the initial steady state value in the given duration of time after the sliding is stopped.

From figure 3 (b) it is observed that the OCP recorded before sliding ($E_{oc}^1$) of anodic porous TiO$_2$–ZrO$_2$ surface remained nearly constant, confirming that the samples are in the passivated state. By applying the normal force of 2 N, the anodic porous TiO$_2$–ZrO$_2$ surface did not exhibit a sudden cathodic drop in OCP, being rather gradual until the sliding motion is stopped. With the onset of sliding under the normal force of 5 N, the anodic porous TiO$_2$–ZrO$_2$ surface presents a very small drop of the OCP in the cathodic domain. Also for this surface it can be said that the cathodic shift potential increases with increasing the normal load. The lack or the insignificant of such a sudden drop in OCP
for anodic porous TiO$_2$–ZrO$_2$ layer surface suggest that the hard and thick oxide film is not totally removed with the onset of sliding. The potential fluctuations observed during sliding are more pronounced for untreated Ti–10Zr alloy surface compared to anodic porous TiO$_2$–ZrO$_2$ film surface. This behaviour of anodic porous TiO$_2$–ZrO$_2$ film reveals its enhanced tribocorrosion properties.

The effect of normal loads (2 and 5 N) on the evolution of friction coefficient for treated and untreated Ti–10Zr alloy recorded for 5000 sliding cycles, at a constant rotation speed of 120 rotation min$^{-1}$ in artificial saliva is observed in figure 4.

![Figure 4](image-url)

**Figure 4.** Friction coefficients versus sliding cycles obtained in Fusayama–Mayer saliva for: (a) untreated Ti–10Zr alloy and (b) anodic porous TiO$_2$–ZrO$_2$ surface by applying (1) - $F_n = 2$ N and (2) - $F_n = 5$ N, for 5000 cycles, at a constant rotation speed of 120 rotation min$^{-1}$.

Figure 4 (a) and (b) reveals a decrease in the coefficient of friction with increasing normal force at constant rotation speed and constant number of cycles, on the same type of sample. This behaviour can be explained by the smoothening of the surface under high load and diminishing the shear strength of the contacting interfaces.

Comparing the coefficients of friction of the untreated Ti–10Zr alloy surface (figure 4 (a)) with those of anodic porous TiO$_2$–ZrO$_2$ film surface (figure 4 (b)), it can be noticed that the lowest coefficients of friction are obtained for the last type of surface. These results highlight once again that anodic oxidation treatment extend the lifetime of a biomedical implant made of Ti–10Zr alloy.

4. Conclusions

The tribocorrosion behaviour of untreated Ti–10Zr alloy surface and anodic porous TiO$_2$–ZrO$_2$ surface sliding against Al$_2$O$_3$ pin in an artificial saliva solution was investigated in a pin–on–disc contact configuration combined with in situ electrochemical measurements (OCP).

Applied normal forces were found to greatly affect the potential of untreated Ti–10Zr alloy during tribocorrosion experiments. An increase in the normal force induces a decrease in potential accelerating the depassivation process, due to the removal of the native passive oxide film induced by sliding, confirming its increase in susceptibility for corrosion.

The lack or the insignificant shift in OCP for anodic porous TiO$_2$–ZrO$_2$ layer surface with the onset of sliding suggests that the hard and thick oxide film is not totally removed. This behaviour of anodic porous TiO$_2$–ZrO$_2$ film reveals its enhanced tribocorrosion properties.

Applied normal forces greatly affect also the coefficients of friction. The coefficient of friction decreases with increasing normal force under constant rotation speed and constant number of sliding cycles, on the same type of tested material. Lower friction coefficients were obtained by anodic porous TiO$_2$–ZrO$_2$ surface compared with untreated Ti–10Zr alloy surface.
All experimental results have proved that porous TiO$_2$–ZrO$_2$ film surface formed by anodic oxidation reveal higher tribocorrosion performances as compared with untreated Ti–10Zr alloy, under lubricated conditions.

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