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CORROSION BEHAVIOR AND BIO-WETTABILITY OF THERMALLY OXIDIZED TITANIUM ALLOY SURFACE FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Thermal oxidation (TO) of a titanium (Ti) surface was carried out at diverse conditions of temperature and time. The major goal of this paper is to study the influence of the TO treatment on the bio-wettability and corrosion behavior of investigated Ti alloy in simulated body fluid (SBF). The results revealed a substantial improvement is obtained in the bio-wettability and corrosion resistance of Ti alloy samples after TO compared to an untreated sample. Also, the optimal contact angle and corrosion resistance were observed for the sample treated at 850^{o}C for 8 h.

KEYWORDS

Biomedical applications; Bio-wettability; β-titanium; Corrosion; Thermal oxidation.

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1. INTRODUCTION

Ti and its alloys are extensively utilized for various medical systems because of their excellent physical, mechanical, and electrochemical characteristics (Mohammed et al., 2014a). The most commercial Ti biomaterials, widely employed in different medical applications, are pure Ti (CP-Ti) and Ti-6Al-4V alloy. However, CP-Ti uses in limited purposes owing to its poor strength and wear resistance (Oliveira et al., 1998 and Mohammed et al., 2013). On the other hand, Ti-6Al-4V has aluminum and vanadium in its composition which could induce some harmful outcomes to human body like neurological troubles and toxicity (Balazic et al., 2007). In addition, these Ti materials have greater values of elastic modulus compared to cortical bone (Niinomi and Boehlert, 2015), which may cause the phenomenon of stress shielding and thus the final failure of implant during the service (Li et al., 2014). Therefore, it has become very important to find alternatives to these two Ti materials with high technologies and distinctive properties in order to simulate different medical applications. In recent years, great consideration has been paid to the improvement of various surface technologies to develop the surface of Ti. The surface has a vital role as it directly affects some of the important properties of the implant, especially wear and corrosion resistances. It is well identified that Ti is one of the metals that have a strong ability to form a spontaneous passive layer onto their surface; this states the reason why Ti has outstanding biocompatibility (Liu et al., 2004 & Mohammed et al., 2014b). Nevertheless, this native surface layer may be broken as a result of any low shear stress (Lilley et al., 1992). Consequently, the development of Ti surface properties has become a very imperative issue. To achieve this purpose, a number of surface modification techniques is developed. Among them, TO is one of the most important surface methods, as it is capable to create a hard oxide surface layer with the lowest cost. Previous studies have shown that the TO process is an exceptional manner to create protective oxide film on Ti surface with great bio-performance (Zhang et al., 2011; Mohamed et al., 2022). It is important to mention here that we have already investigated in a previous work the influence of TO on the morphology of TZN alloy and some its characteristics like hardness, roughness, and wear resistance (Mohammed et al., 2019). However, the present research is concerned with the study of bio-wettability and corrosion resistance of Ti alloy after oxidation procedure, since these properties and their biological effects are an essential factor that cannot be ignored. The major goal is to alter the surface structure of investigated Ti alloy and then improve its bio-wettability and corrosion resistance.

2. METHDOLOGY

In this work, as-cast Ti-15Zr-12Nb (TZN) samples (10-mm x 10-mm x 3-mm) were utilized as major substrates for TO. The production steps of this alloy were mentioned elsewhere (Mohammed, 2017). Firstly, the surface of investigated TZN samples has been prepared for TO process using standard grinding and polishing procedures. Afterward, ultrasonically cleaning was applied for 15 min using a solution of distilled water and acetone followed by air drying. The major parameters of temperature and time for TO were selected to be 450◦C for 24 h, 650◦C for 16 h and 850◦C for 8 h (TO treated TZN samples are henceforth denoted as TO-1, TO-2 and TO-3, respectively). Note, TO process was done using a heating rate of 5◦C/min. The time of the TO was designed to be less with increasing temperature. It was pointed out that the performing of TO at high temperature for long time may cause a debonding to oxidized layer (Kumar et al., 2010a). Also, the cooling in air was accomplished for all treated TZN samples except those oxidized at 850^{o}C which were cooled in furnace to prevent high thermal stresses. Field emission scanning electron microscope was utilized to study the surface morphology of treated TZN samples (TESCAN MIRA3, FESEM). Bio-wettability of the investigated TZN substrates was estimated by calculating water contact angles using optical contact angle and interface tension meter (model: SL200KS). The test was performed at 25^{o}C by deposition three drops of deionized water at different areas of investigated sample. The corrosion resistance of the investigated samples was investigated via three-electrode cell potentiostat. During the test, a potential range from -750 to 2500 mV(Ag/AgCl) was applied on a surface area of 0.126 cm^2 at a scan rate of 0.166 mV/s. To simulate the physiological fluid, a solution of 0.9% NaCl at 7.4 pH and 37 ± 1^{o}C was utilized. Open circuit potential (OCP), corrosion current density (I_{corr}), and corrosion rate were determined from the polarization curves as main measurements for corrosion test.

3. RESULTS AND DISCUSSION

Fig. 1 shows the surface morphology of TZN samples after performing TO process at various temperatures and times. This figure obviously reveals the development of oxide layers over the treated surfaces. Also, the flaking and spallation are not noticed. For TO-1, a thin oxide layer is developed over the entire surface with outward growth of oxide grains (Fig. 1a). However, in case of TO-1, a large external oxidation with agglomeration is existing in the oxide owing to the long time (24 h). Hence, this result can be considered as a discontinuity or incoherence of the oxide grains (Kumar et al., 2010a). In case of TO-2, the surface has been entirely covered with fine, compact and adherent oxide particles along with higher amount of the porosity (Fig. 1b) compared to TO-1 (Fig. 1a). However, the morphology of TO-3 surface exhibited specific formation of distinct and homogeneous oxide crystals by the mechanism of the nucleation and then the growth of finer grains on the TO layer (Fig.1c). Thus, it is expected that this morphology under high temperature (850^{o}C) and suitable time (8 h) produced in situ ceramic layer, essentially composed of greatly crystalline rutile phase with considerable thickness, along with the oxygen dissolution beneath it (Kumar et al., 2010b).

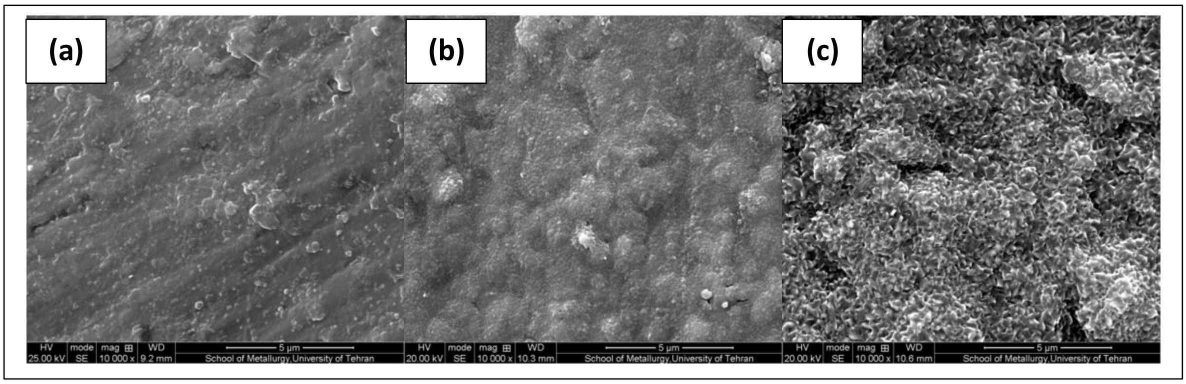

Fig. 1. SEM of the morphology of TZN surface: (a) TO-1, (b) TO-2, and (c) TO-3.

It is well identified that hydrophilicity is highly connected to the surface energy of the material and has a significant effect on the implant's osseointegration (Le Gu_ehennec et al., 2007). Many biological aspects can be attained with hydrophilic surface especially higher cell adhesion (Sertan et al., 2015) together with considerable interaction of the treated surface with physiological fluid, especially with proteins and bacteria (Anselme et al., 2000). It is worth noting here that the surface is considered hydrophilic if the contact angle made between the surface and the water drop is < 90º, otherwise the surface is considered hydrophobic (Barbosa et al., 2017). The bio-wettability results of the investigated TZN substrates are shown in Fig. 2. As can be seen, the untreated surface had the highest contact angle, 85º ±2 as compared to TO treated samples. Also, the TO-3 sample presented greater hydrophilicity, with a contact angle of 48º ±3.5, followed by TO-1 (73º ±1.5) and TO-2 (55º ±3). Therefore, in this work, all investigated samples, i.e. untreated and TO treated TZN samples, displayed a hydrophilic behavior because of the forming of the oxide phase through TO. However, the optimum contact angle was observed for the sample treated at 850^{o}C for 8 h.

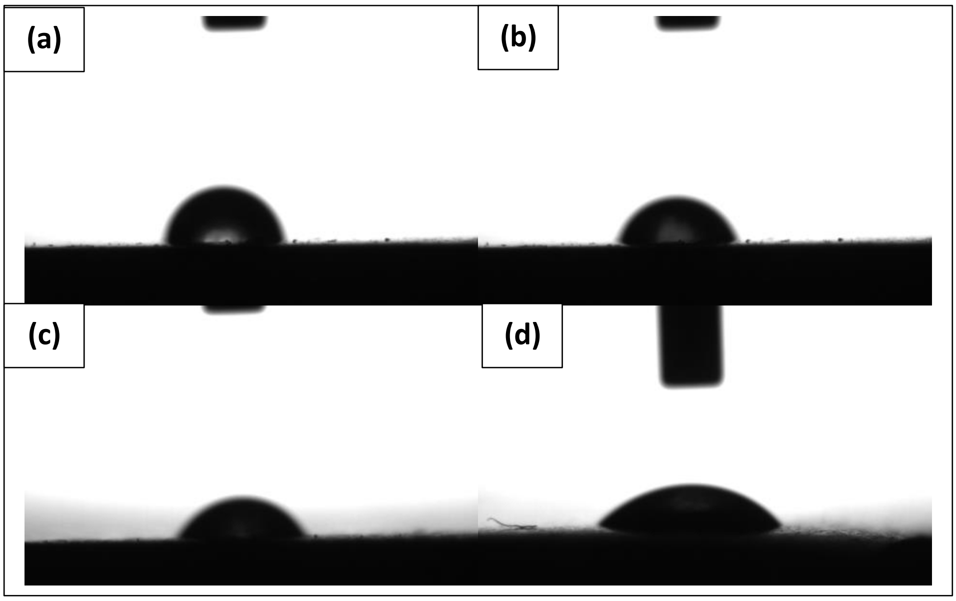

Fig. 2. Contact angles of investigated TZN alloy samples: (a) untreated, (b) TO-1, (c) TO-2 and (d) TO-3.

Fig. 3 demonstrates the variation of OCP of the investigated TZN substrates with time; the test was accomplished until steady state. This figure proves that the thermally oxidized TZN samples exhibit nobler character (higher OCP) in contact with a 0.9% NaCl compared to untreated sample (lower OCP). On the other hand, among all oxidized TZN samples, TO-3 sample shows the highest value of OCP which indicates the nobler electrochemical characteristics. Moreover, both TO-2 and TO-3 samples displayed the strongest tendency to move in the direction of noble behavior owing to the development of strong and constant oxide layers on their surface.

Fig. 4 shows Tafel curves of the investigated TZN samples in 0.9% NaCl solution. Higher anodic potential (+2500 mV vs. saturated calomel electrode) was chosen to identify the influence of TO on the passivity characteristics as a result of forming an oxide layer with protective properties. Potentiodynamic anodic polarization plots in Fig. 4 disclose that all investigated TZN samples have a typical active–passive representation. The corrosion behavior shifts directly into the passive part after constant rise of the current with the potential. This indicates that the oxide layers formed after TO had a protective nature for improving the corrosion resistance of TZN (Carolina et al., 2020). Also, the passive current densities for investigated TZN substrates continued constant with expanding potential because of the increased thickness of their passive layers (Ikeda et al., 2002; Mohammed et al., 2015). However, polarization plots of TO TZN samples illustrated an altering in the active region towards inferior I_{corr}. This clearly specifies the enhancing of the electrochemical characteristics after carrying out TO.

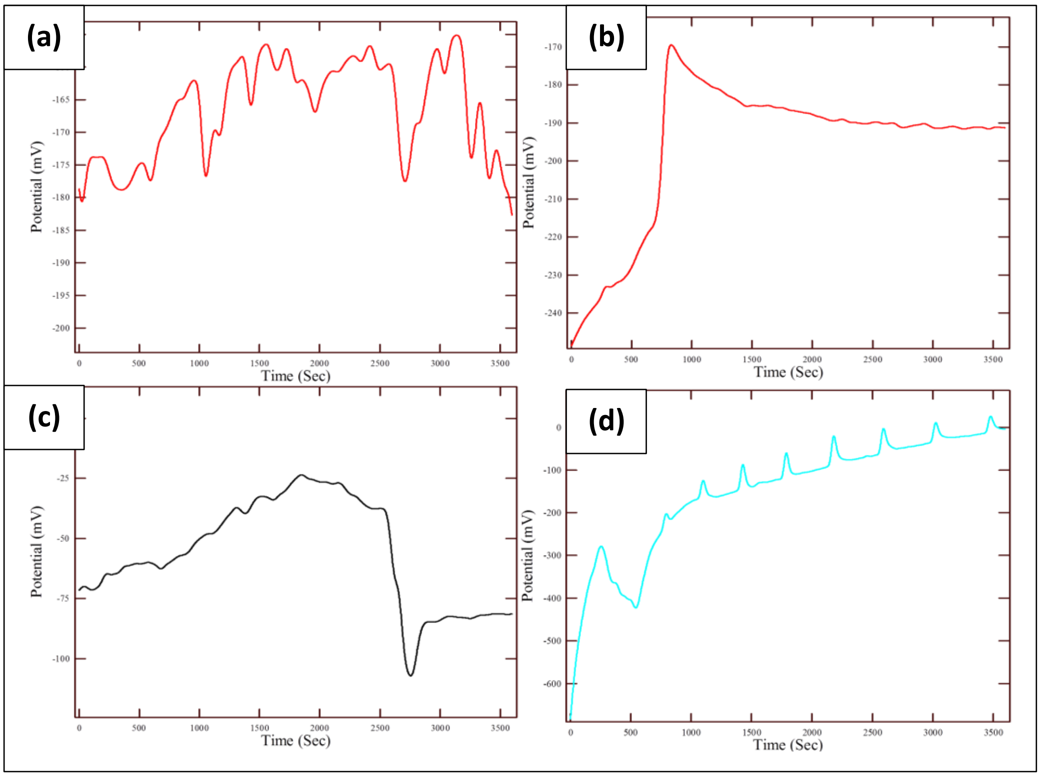

Fig. 3. Variation of OCP with time: (a) untreated, (b) TO-1, (c) TO-2, and (d) TO-3.

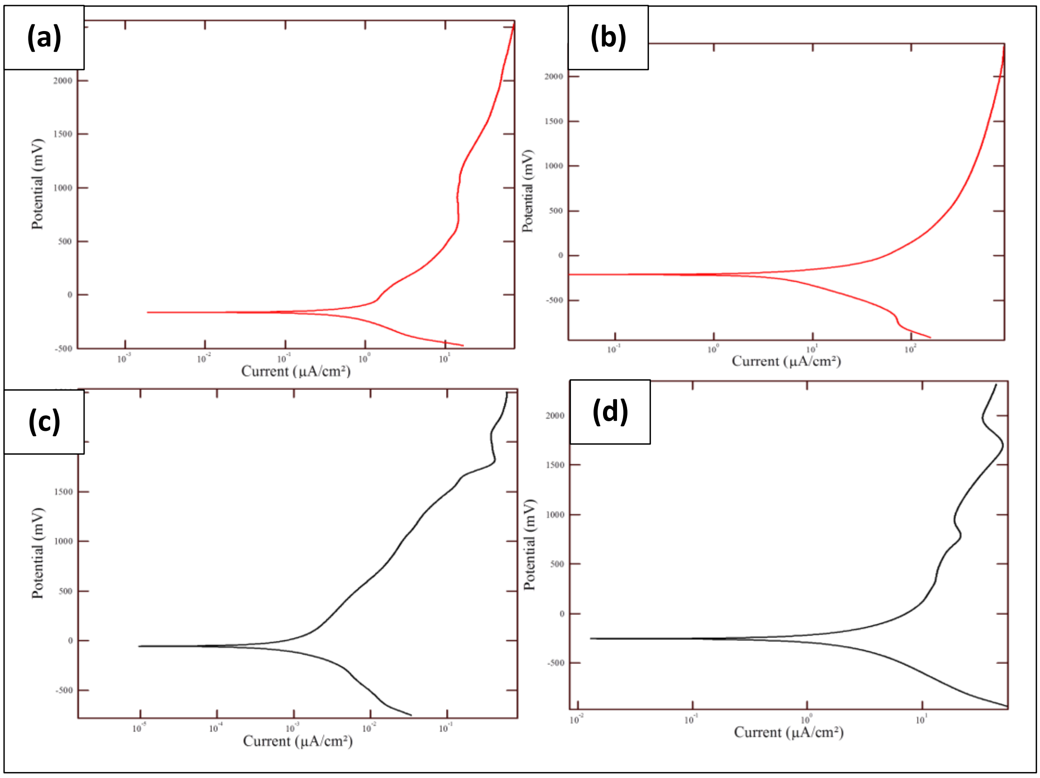

Fig. 4 Plots of potentiodynamic anodic polarization: (a) untreated, (b) TO-1, (c) TO-2, and (d) TO-3.

The average values of E_{corr} were obtained from the polarization curves as -208.54, -249.81, -255.27, -162.75 and -55.071 mV (vs. SCE) for untreated, TO-1, TO-2 and TO-3 substrates, respectively. As can be observed, the oxidized substrates display a move in E_{corr} towards the nobler behavior (from -208.54 to -55.3071 mV vs. SCE). Furthermore, Fig. 4 evidently specifies that the TO-1 and TO-2 samples have more reducing in E_{corr} compared to that of the TO-3 samples. The corresponding corrosion data of the oxidized substrates, i.e. mean I_{corr} and corrosion rate, were attained via Tafel extrapolation analysis (see Table 2). A substantial decrease in I_{corr} (from 12.5137 to 6.409 x 10^{-6} μA/cm^2) and corrosion rate (from 9.7942 to 0.0050162 mils/yr) was found in case of treated substrates compared to an untreated sample. This is owing to the increase of the oxidation temperature from 450 to 850°C. This verifies that the oxidized layer created on TO-3 samples is denser and protecting owing to the high thickness of this oxide layer, which may act as an obstacle in front of passing higher current for further chemical reactions of TZN in the bioelectrolyte. Hence, the I_{corr} of TO-3 samples is very much lower in comparison to that of untreated sample.

Table 2. Corrosion test results of the investigated TZN substrates.

Sample No.	B_a (mV)	B_c (mV)	E_{corr} (mV)	I_{corr} (μA/cm^2)	Corrosion rate (mils/yr)
Untreated	114.89	285.45	-208.54	12.5137	9.7942
TO-1	208.98	199.09	-255.27	0.9896	0.7745668
TO-2	92.853	101.47	-162.75	0.5268	0.2219162
TO-3	122.48	114.5	-55.071	0.00641	0.0050162

Many investigations have proved the superior electrochemical characteristics of various thermally oxidized medical Ti materials in SBF (Kumar et al., 2010a; Arslan et al., 2010; Jamesh et al., 2013; Wen et al., 2014). Additional verification is attained during this work in order to develop the corrosion behavior of TZN samples using TO process. Based on this work, the improvements of the corrosion resistance of the untreated and oxidized TZN substrates can be ordered as follows: TO-3 > TO-2 > TO-1 > untreated.

4. CONCLUSIONS

The influence of TO treatment accomplished at different temperatures and times on the bio-wettability and corrosion resistance of the medical TZN alloy was investigated. The major conclusions of this study can be written as follows:

- Oxide layers without flaking or spallation were effectively deposited on the surface of TZN by performing TO at various temperature and times.
- The morphology of the TZN surface oxidized at 850^{o}C for 8 h displayed homogeneous crystals with porous structure of fine grains.
- Compared to untreated sample, all TO treated TZN samples showed higher hydrophilicity owing to the forming of the oxide layer via TO. However, the best value of contact angle was achieved for the sample treated at 850^{o}C for 8 h.
- The development of the compact and protecting oxide layer on the surface of the studied TZN alloy substantially enhances the corrosion resistance in SBF, especially when the TO treatment performed at 850°C for 8 h.

5. ACKNOWLEDGEMENT

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