EFFECT OF PHOSPHORIC ACID CONCENTRATION AND ANODIZING TIME ON THE PROPERTIES OF ANODIC FILMS ON TITANIUM

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Abstract

In this study, it was investigated the influence of electrolyte concentration and anodizing time on the electrochemical behaviour and morphology of anodic films formed on commercially pure Ti. Electrochemical methods and surface analyses were used to characterize the films. It was found that the electrolyte concentration and anodizing time affect the growth and protective characteristics of films in a physiologic medium. It was possible to observe their non-uniformity on Ti substrates under the tested conditions. In potentiodynamic profiles, it was observed that passivation current values are affected by an anodizing time increase. Variations in impedance spectra were associated with an increase of defects within the film.

Keywords: Titanium, Anodizing, Anodic films, Chloride medium, Biomedical implants.

1. Introduction

There has been an increasingly strong demand for implanting materials every year due to loss of body functions caused by aging and accidents. In the latest 20 years, Ti and its alloys have been utilized for this purpose, which is proper for their high corrosion resistance and biocompatibility [1]. However, their implantation directly into the bone for a long period may lead to ion release to an adjacent tissue to the implant and damaging implications for the organism [2-4], as it is a bioinert metal. A passive Ti condition is attributed to a thin and adherent film presence formed spontaneously on its surface. For its application to be successful as a biomedical

material, some new processes of surface treatment have been developed in order to obtain oxide films which are denser and stable in a physiologic medium.

Ti anodic films with nano-porous structures are desirable because of their large superficial area and high compatibility as medical implant material. Depending on nature and electrolyte concentration, these films may have different structures and morphologies that act as a barrier which protects the metal substrate against corrosion [5]. Considering that metal corrosion of biomedical application occurs by interactions between the surface and the physiologic environment, the effective surface area determined by porosity and roughness has an important role in electrochemical measurements of corrosion. Several studies have been conducted with the purpose of obtaining films with higher surface area to promote cell adhesion and components deposition with chemical composition that are similar to a bone, leading to a more rapid osseointegration and implant stability within the body [6-8].

Bibliographic research on using the anodizing process as a method of modifying titanium surfaces shows that this topic has been extensively studied, since there are countless possibilities of varying inherent parameters in the anodizing process (applied potential, type and concentration of the electrolyte, temperature, time, etc.) in order to change the morphology and structure of titanium oxide films. In addition to these possibilities, there are many processes of surface pre-treatment to be anodized (mechanical polishing, electropolishing, immersion in acids or bases, etc.), as well as heat treatments after the anodization to modify the surface texture of titanium [9-17]. It is highlighted that not all combinations of pre and post-treatment were assessed to finally investigate its effect on tissue response to bone implant. In order to contribute with knowledge on anodizing titanium, the aim of this study is investigating the electrochemical behaviour of anodic films formed on different anodizing times and H_3PO_4 concentrations. Surface analysis techniques were also used to supplement the electrochemical results.
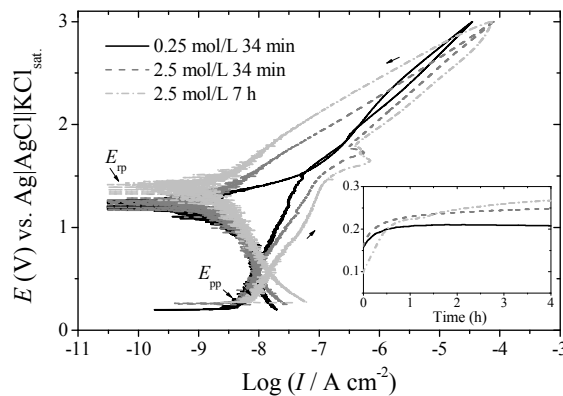
2. Experimental

Thin plates of Ti with dimensions of 30×70 mm were used as anodes in an electrolytic cell. The films were obtained by anodization in 0.25 and 2.5 mol L^{-1} H_3PO_4 solutions, applying a 10 mA cm^{-2} DC density for 34 minutes and 7 hours. The current density value remained constant during these periods. Samples used for the anodizing were prepared by mechanical polishing. The scanning electron microscopy (SEM) ZEISS DSM 940 and the atomic force microscopy (AFM) were used to morphologically characterize the films. AFM images were taken at a temperature of 18 $^{\circ}$C, with scanning regions of (30×30) μm^2, in contact mode with Si_3N_4 cantilevers with elastic constant of 0.6 Nm^{-1}. Measurements of open circuit potential (OCP), cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS) were carried out in 0.9% NaCl, which contains a chloride ion concentration which is similar to that found in blood plasma [18]. The utilized equipment was the Autolab potentiostat/galvanostat. For each type of assay, there were two replicate measures. It was used a conventional cell with three electrodes, and each anodized sheet was the working electrode. A Pt electrode was used as auxiliary and all potentials were recorded against a saturated Ag/AgCl electrode. The CP measurements were registered at a scan rate of 1.0 mV s^{-1} from the OCP at

steady state. EIS diagrams were recorded at OCP by applying a 10 mV sinusoidal potential through a frequency domain of 100 kHz to 10 mHz.

3. Results and Discussion

OCP curves obtained for the anodized samples in three experimental conditions are showed in Fig. 1. According to these graphics, it was observed a progressive increase of potential during the first immersion minutes, suggesting relative film stability in a chloride medium. Increasingly positive values of potential were obtained for conditions which led to thicker films. The direct scan in CP curves revealed a well-defined passive region up to 1.5 V, with current density values that are lower than 0,1 $\mu A\ cm^{-2}$ (Fig. 1). In this potential range, passive current density values are higher with increasing H_3PO_4 solution concentration and anodizing time. When the anodizing was carried out in a 2.5 mol L^{-1} H_3PO_4 solution, a complex oxidation peak at ~1.6 V was observed in CP curves, which had been previously attributed to new phase formation [19]. At more positive potentials, the current density increases more rapidly. Despite E_{pp} and E_{rp} [20] (primary passivation and re-passivation potentials, respectively) being similar in these three conditions, negative hysteresis loops were significantly different.

Fig. 1. OCP and CP curves obtained in a 0.9% NaCl solution for anodized Ti in different experimental conditions.

In Fig. 2, it is shown EIS spectra for the three anodizing conditions evaluated in Bode format. All EIS measurements represent electrodes in a passive state with different compactness degrees of formed films, in agreement with other authors [5, 21], with impedance values that are higher than 1 MΩ cm^2, determined by log ($|Z|_{\lim f\to 0}$). There are fewer impedance modules as the film becomes thicker, i.e., if Ti is anodized in a more concentrated medium during longer anodizing time. This variation is consistent with the one registered for passivation current density values at CP curves by comparing the three evaluated conditions. Steeper phase angles near -90° at intermediate frequencies and slopes which are very close to -1 in impedance module plots were recorded in accordance with previous works [22-24] and attributed to an

ideally capacitive character. Although these characteristics are common to all obtained spectra, it was observed that the broad peak of the phase angle is more evident for the sample that was anodized in a more dilute solution. For this reason, greater uniformity of the formed film is attributed to this condition. In literature [25, 26], a large phase angle peak can be an indicative of interaction of at least two time constants.
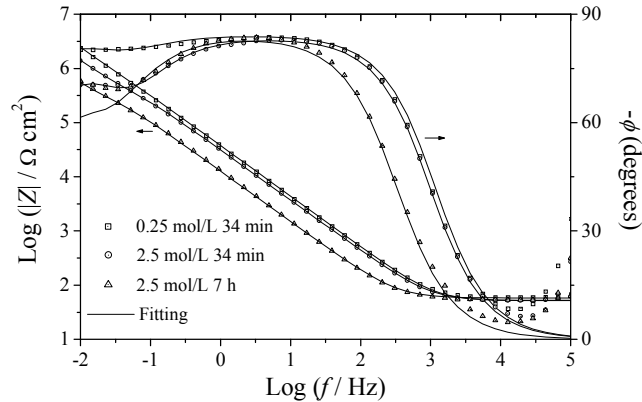
Fig. 2. EIS spectra obtained in a 0.9% NaCl solution for anodized Ti in different experimental conditions.
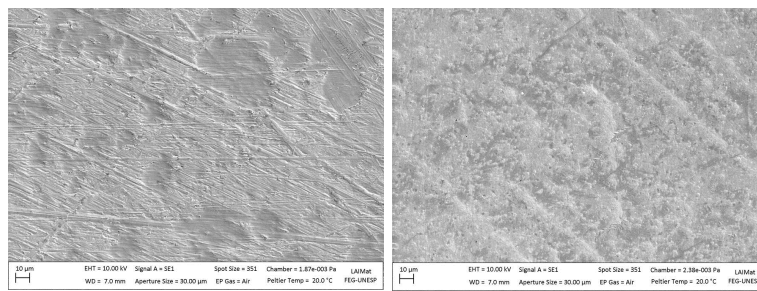
According to Poznyak et al. [21], the films thickness increase can be evidenced by the appearance of a second component in the impedance spectra. In fact, the relaxation time between the first and the second component onset becomes more evident as the film becomes thicker, as it can be observed by changes in phase angles maximums. The thickness increase should lead to loss in uniformity and compactness, due to their larger number of defects and porosities. An interpretation of these diagrams was obtained using a fitting procedure with equivalent electrical circuit software. A better fitting was obtained utilizing the model with two time constants, $R_\Omega(Q_1R_1)(Q_2R_2)$, based on a two-layer structure, composed by an inner barrier layer and an outer porous one in accordance with previous investigations [21, 26]. In this model, R_Ω is the uncompensated ohmic resistance, Q_1R_1 represents the outer porous layer and Q_2R_2 corresponds to the inner barrier layer. Q_1 and Q_2 are the constant phase elements [5, 21-22] used in the fitting instead of capacitance C, and are related to non-uniform current distribution due to surface roughness or inhomogeneity. Data in Table 1 show that Q_1 and Q_2 were significantly higher for longer anodizing time, while little difference was observed when comparing the two concentrations of the solution, keeping the time of 34 min. An analysis of fitting results also indicates that $R_2 > R_1$ for evaluated conditions.

Due to difficulty in evidencing film presence using SEM, it was carried out an anodizing for 7 h in a more concentrated medium in order to form a thicker film (~3.7 μm calculated by Faraday's law). In Fig. 3, it is shown SEM images obtained for polished and anodized surfaces. It is possible to observe a non-uniformity of the anodic film (light gray region) and pores of different sizes (black points) on Ti substrate (dark gray region). AFM images obtained for

polished and anodized Ti surfaces are shown in Fig. 4. The anodic film grows on an irregular surface. Ti dioxide growth often involves preferential development on specific crystallographic planes. After 7 h of anodizing, the film presents some isolated crystals and clusters, as well as pores. Thus, the metal texture as well as the thickness, heterogeneity and discontinuity of the film have a significant effect on its electrochemical behaviour.

Table 1. Fitting results of the EIS spectra obtained for anodized Ti in different experimental conditions.

Anodizing Time	H_3PO_4 Solutions (mol/L)	R_Ω Ω cm^2	R_1 $k\Omega$ cm^2	Q_1 $[Y_0(j\omega)^n]$ $S\,s^{-n}\,cm^2$	n_1	R_2 $M\Omega$ cm^2	Q_2 $[Y_0(j\omega)^n]$ $S\,s^{-n}\,cm^{-2}$	n_2
34 min	0.25	51.5	113	28.3×10^{-6}	0.89	54.4	5.66×10^{-6}	0.94
	2.5	52.2	167	14.1×10^{-6}	0.91	9.29	9.29×10^{-6}	0.93
7 h		57.9	61.5	44.2×10^{-6}	0.89	2.27	34.0×10^{-6}	0.97

Fig. 3. SEM images obtained for Ti surfaces: left-polished and right-anodized for 7 h in a 2.5 mol L^{-1} H$_3$PO$_4$ solution.
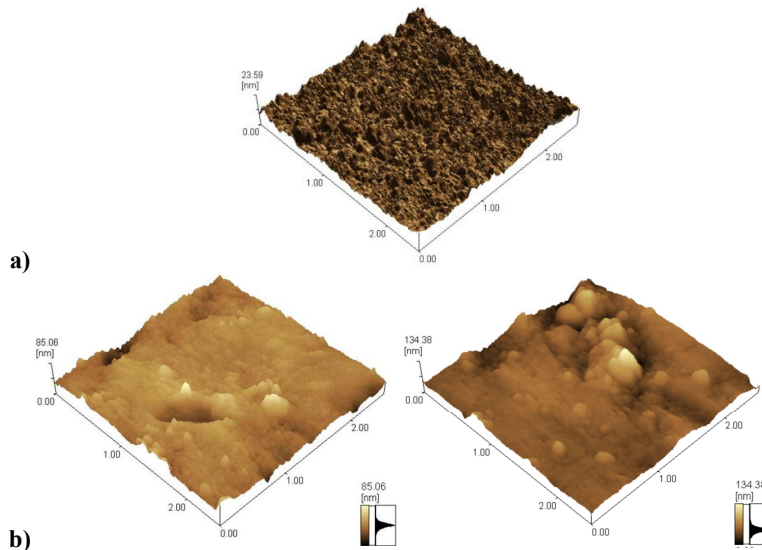
Fig. 4. AFM images obtained for Ti surfaces: a) polished and b) anodized for 7 h in a 2.5 mol L^{-1} H$_3$PO$_4$ solution.

4. Conclusions

The morphology and stability of anodic films in a 0.9% NaCl solution was correlated using metallographic and electrochemical techniques. It was found that a higher corrosion resistance was associated with the film being formed in a more dilute solution. Films formed in more concentrated H_3PO_4 solutions and greater anodizing times are less protective, which is probably due to a higher degree of heterogeneity and discontinuity. Passive films were analysed in terms of a dual layer constituted of an inner barrier and an outer porous layer.

Acknowledgments

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