CATHODIC BEHAVIOUR OF ANODIZED TITANIUM IN SIMULATED PHYSIOLOGICAL CONDITIONS

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Abstract — **In the present work, anodic oxide films on titanium specimens were formed in physiological solution under potentiostatic condition. The immediate- to short-term changes in the oxide film were studied by open-circuit potential measurements and cyclic voltammetry. The results show that the intensity of the cathodic current peak related to oxygen reduction at around –0.7 Vsce, decreased and disappeared after 30 minutes of finishing the anodic oxidation. For titanium without anodization (non-coated titanium), the cyclic voltammograms show an anodic current in the range that begins at -0.9 Vsce and continues to more positive potentials (vs SCE), related to the hydrogen oxidation reaction. For anodically polarized titanium (coated titanium), in the anodic direction of the cyclic voltammograms an anodic current in the range that begins at -0.9 Vsce and continues to more positive potentials (vs SCE) was observed. In this case, the oxidation process is related to previous cathodic processes: the hydrogen formation and the cathodic transformation of titanium oxides before the oxygen reduction potential region.**

Keywords — **Cathodic Behaviour, Cyclic Voltammetry, Anodized Titanium, Titanium Oxide.**

I. INTRODUCTION

Titanium, one of the most important materials used for many years as biomedical and dental implant applications, has an excellent corrosion resistance in many aqueous environments because of its oxide film, which has been shown to be highly stable and fairly non-reactive. Due to its excellent corrosion resistance, titanium is often included as a benchmark in the corrosion studies of biomedical alloys. Many investigations have shown that this type of natural surface film is normally a few nm thick and essentially formed by a thin layer of amorphous TiO_2, however, different oxides (TiO, TiO_2, Ti_2O_3, Ti_3O_5, TiO_3) may also be present (Frauchiger *et al.*, 1997; Lausmaa *et al.*, 1990; Pan *et al.*, 1996).

Among other factors, the oxidation state of titanium in the oxide and, consequently, its stoichiometry and its surface characteristics are dependent on the final positive potential and on the electrolyte used for the oxide growth (Frauchiger *et al.*, 1997; Kuromoto *et al.*, 2007; Marino *et al.*, 2001; Pan *et al.*, 1996). Blackwood *et al.* (1988) found that the oxide film undergoes uniform dissolution and its stability depends strongly on the rate at which it has been formed. These authors also reported that the growth rate has a marked influence on the properties of anodic oxide film on titanium (Blackwood and Peter, 1989).

There are a few possible explanations for the origin of cathodic peaks between 0.0 and -1.0 Vsce. For example, the formation of lower valence states such as Ti^{3+} in the anodic oxide film of TiO_2 may be associated with such a cathodic reaction (Baez *et al.*, 1992; Kim *et al.*, 2003). Baez *et al.* (1992) explained the cathodic current peak in terms of the formation of Ti^{3+} at the uppermost monolayer (or multi-layers) of the oxide film. The formation of titanium hydroxide may also be related to such a redox reaction, which forms the outermost layer of the oxide film (Kim *et al.*, 2003). Another possible explanation is the reduction of H^+ ion, which is adsorbed on and absorbed in the film at the underpotential deposition region (Yoon and Pyun, 1995). Azumi and Seo (2001) found a transformation of TiO_2 to unstable titanium peroxides such as TiO_3 above 3 Vsce. These compounds are reduced below 0.5 Vsce and showed a characteristic cathode current peak. In a previous work, the authors (Pelaez-Abellan *et al.*, 2007) found a cathodic peak around –0.4 Vsce in aerated simulated physiological solution due to the reduction of titanium peroxides such as TiO_3.

The reduction of oxygen may occur at negative potential also. Parkinson *et al.* (1980) reported only one wave at a rather negative potential. In contrast, two other authors (Clechet *et al.*, 1979; Danzfuss and Stimming, 1984) have reported a well defined reduction wave at less negative potential and evidence was presented that hydrogen peroxide was formed. There are clearly several disparities between conclusions drawn from these studies, due to differences in experimental conditions. Baez *et al.* (1992) proved that the reduction of oxygen could occur at a more negative potential than the reduction reaction of titanium oxide and they suggested that this surface redox process take place at most in a few monolayers of titanium oxides. In all materials, the potential for oxygen reduction appears to coincide with the potential range where the cyclic voltammetry in the absence of O_2 would indicate the reduction of the titanium oxide.

Very few studies have been conducted, as far as the authors are aware, on the changes in the passive titanium oxide film under cathodic polarization. The processes which could occur under the cathodic polarization are: various stages of oxide reduction up to its dissolution, the adsorption and absorption of hydrogen, hydrogen evolution, and oxygen reduction. Regardless of the fact that some publications have been directed to the study of these cathodic processes (Baez *et al.*, 1992; Kim *et al.*, 2003; Yoon and Pyun, 1995), there is not enough knowledge of the phenomena caused by a cathodic polarization on the anodic titanium oxide film. The knowledge of the role of these processes is important in order to develop a methodology for covering of titanium with hydroxyapatite by a cathodic electrolytic method with the aim of increasing the biocompatibility of titanium implants. The purpose of this investigation is to study the behaviour at open circuit potential of the titanium oxides formed in simulated physiological solution and the influence of a cathodic polarization on the changes of the surface and the electrochemical properties of this passive film to enlarge the knowledge of the interaction between the Ti-implant and the human body fluid.

II. MATERIALS AND METHODS

In this study was used ASTM F 67 95 Grade II cp (chemically pure) titanium specimens (20 mm x 20 mm x 3 mm). Prior to each measurement, the electrodes were abraded with emery paper #80, rinsed with water, cleaned in an ultrasonic water bath for 10 minutes and dried in air more than 2 days[*]. Chemicals were of analytical grade and doubly distilled water was used in the preparation of the solutions. An aerated simulated physiological solution (ASPhS) consisting of (g.L^{-1}): 8.74 NaCl; 0.35 NaHCO$_3$; 0.06 Na$_2$HPO$_4$; 0.06 NaH$_2$PO$_4$ at pH 7.0 was employed for measurements at room temperature. A platinum wire electrode as counter electrode and a saturated calomel reference electrode (SCE) was employed in a special three-electrode configuration (mini-cell system) (Müller and Ibendorf, 1994). The active area of the electrode was 0.008 cm^2. The electrode potentials were referred to SCE (0.224 V vs. NHE[**]). Measurements were started approximately 5 s after the tip of the mini-cell system touched the specimen.

Anodic oxidation of cp titanium specimens was carried out under potentiostatic condition at 0.7; 1.0; 1.5 or 5 V vs SCE (Vsce) during 5 or 15 minutes. The immediate- to short-term changes in the oxide film were studied by open-circuit potential measurements and cyclic voltammetry (CV) in negative-going direction from 0.3 to -1.0 Vsce and in positive-going direction from –1.5; -1.0; or –0.6 Vsce to 2.5 Vsce. In some experiments, the electrode was polarized at the initial negative potential for 10 minutes before the potentiodynamic sweep was

started. To define the picks better in the CV, all experiments were performed with a potential scan rate of 30 mVs^{-1} using a Solartron SI 1287 potentiostat, computer controlled with CorrWare and experimental data were processed with CorrView version 2.80 software.

III. RESULTS AND DISCUSSION

To investigate the behaviour of the titanium oxides formed in the ASPhS solution at potential above 3 Vsce by at 5 Vsce an open circuit potential of cp titanium was measured. The E-t curve for cp titanium after polarization at 5 Vsce during 15 minutes (Fig. 1) has an unusual behaviour, because it does not have a maximum or a minimum at short times, characteristic of these systems.

In this case, the potential shifted with time to the cathodic region in an almost linear relation and at around 30 minutes the slope changed and the potential shift was slower. As this phenomenon could be related to the transformation of unstable titanium peroxides (Azumi and Seo, 2001; Pelaez-Abellan *et al.*, 2007), cp titanium oxidized at 5 Vsce during 15 minutes was kept at the open circuit potential for different times and later cyclic voltammograms between 0.3 and –1.0 Vsce were recorded.

The results show (Fig. 2) that the cathodic peak around –0.7 Vsce decreased as the time at the open circuit potential increased and after 30 minutes the peak completely disappeared. For a polarization of 5 minutes at the open circuit potential (Fig. 2, curve 1), it can show a shoulder around -0.4 Vsce, which is characteristic of TiO$_3$ reduction. This shoulder disappeared when the time at open circuit potential (OCP) is larger due to the high instability of Ti peroxide (Azumi and Seo, 2001; Pelaez-Abellan *et al.*, 2007). The results obtained from Fig. 1 and Fig. 2, coincided perfectly and could be explained as follows: when the polarization at 5 Vsce is finished, the concentration of dissolved oxygen in the solution near the electrode was very large (saturated concentration) because the oxygen evolution occurs simultaneously with the anodic oxidation of Ti surface and it can reduce at negative potential.
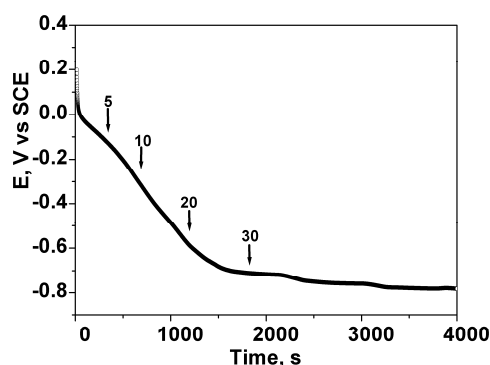

Figure 1 Open Circuit Potential vs. time in aerated simulated physiological solution of cp Ti anodically polarized at 5 Vsce during 15 minutes. The arrows signal different times in minutes.

In the cathodic potentiodynamic scan a current peak appeared around –0.7 Vsce due to a reduction process
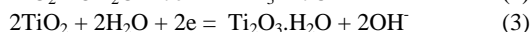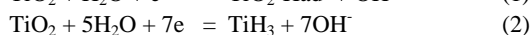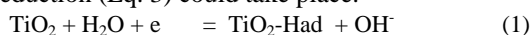
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[*] The authors used here similar conditions than in the pretreatment of Ti before hydroxyapatite deposition.

[**] Normal Hydrogen Electrode.

where the oxygen and titanium oxide reductions can take place jointly (Blackwood and Peter, 1989; Pelaez-Abellan *et al.*, 2007). When the oxidized cp titanium was kept at the open circuit potential during different times, the large oxygen concentration in the solution near the electrode, owing to the oxygen evolution reaction, decreased with time due to its diffusion to the bulk of the solution and the establishment of the equilibrium conditions. During this time, the open circuit potential shifted to the cathodic region with a high slope and the charge associated to the peak around –0.7 Vsce decreased, because the oxygen concentration decreases near the electrode. After 30 minutes, the oxygen concentration in the solution reached the equilibrium state and the E-t curve changed in slope, so the potential shift was slower and the peak around –0.7 Vsce disappeared.

To investigate the influence of the hydrogen evolution reaction, the effect of the reduction peak of TiO_3 around -0.4 Vsce (Azumi and Seo, 2001; Pelaez-Abellan *et al.*, 2007) should be eliminated. Therefore, the electrode was kept at a positive potential less than 3 Vsce and then cyclic voltammograms started from this positive potential to -1.0 Vsce were recorded. The results show (Fig. 3) that the cathodic region starts at a potential around -0.65 Vsce, that is, in this case the instable TiO_3 peroxide was not formed during the anodic polarization. In the opposite scan, the anodic current appeared at around -0.9 Vsce. Some authors (Blackwood and Peter, 1989; Kim *et al.*, 2003; Marino *et al.*, 2001; Pelaez-Abellan *et al.*, 2007) have suggested that the process that occurred in this potential region could be related to some oxidation reaction of a compound formed during the previous negative potential scan as the deactivation (reduction) or dehydration of titanium oxides or the hydrogen evolution reaction.

Cyclic voltammograms started at potentials (Ec) more negative than -0.6 Vsec with or without anodic polarization of cp titanium at 5 Vsce during 15 minutes were obtained. The results show (Fig. 4 and Fig. 5) that the behaviour is different for these different titanium surfaces. For an Ec value of -0.6 Vsce, anodic currents at any negative potential is practically negligible for both surfaces, anodically polarized or not. But for Ec values of –1.0 or –1.5 Vsce an anodic current at negative potential around 5 and 13 $\mu A/cm^2$ could be observed, respectively. This means that in the cathodic region before –0.6 Vsce the processes above mentioned could not occur, but when the Ec values are more negative than –0.6 Vsce, it is possible that hydrogen sorption (equation 1) or formation of hydride (Eq. 2) or some oxide reduction (Eq. 3) could take place.

$$TiO_2 + H_2O + e = TiO_2\text{-Had} + OH^- \quad (1)$$
$$TiO_2 + 5H_2O + 7e = TiH_3 + 7OH^- \quad (2)$$
$$2TiO_2 + 2H_2O + 2e = Ti_2O_3.H_2O + 2OH^- \quad (3)$$

For cp titanium without anodic polarization (Fig. 4), a plateau with a limiting current of some $\mu A/cm^2$ is always present (curve 1). When the initial potential was more negative, the limiting current was higher. Thus, for a Ec value of –1.5 Vsce the limiting current was

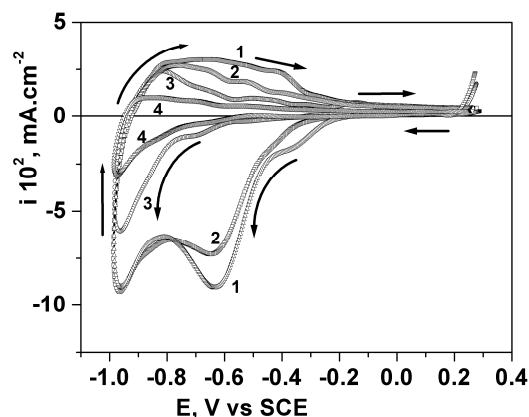around 10 $\mu A/cm^2$. The behaviour was different for anodically polarized cp titanium (Fig. 5). In this case, a

Figure 2 Cyclic voltammograms from 0.3 Vsce to –1.0 Vsce in aerated simulated physiological solution of cp Ti anodically polarized at 5 Vsce during 15 minutes and later kept on the open circuit potential during different times: 5 (curve 1), 10 (curve 2), 20 (curve 3) and 30 minutes (curve 4). Sweep rate was 30 mVs^{-1}.
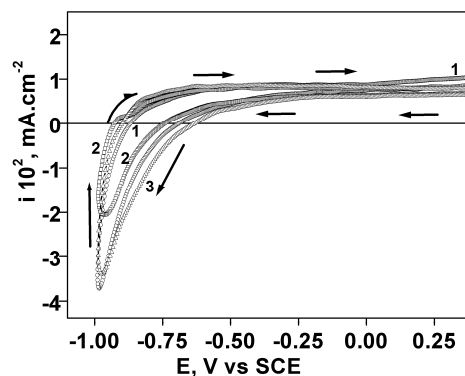

Figure 3 Negative potential region of the cyclic voltammograms from initial variable Ea to –1.0 Vsce in aerated simulated physiological solution. Ti was anodically polarized at initial variable Ea: 0.7 (curve 1), 1.0 (curve 2), and 1.5 Vsce (curve 3) during 5 minutes. Sweep rate was 30 mVs^{-1}.
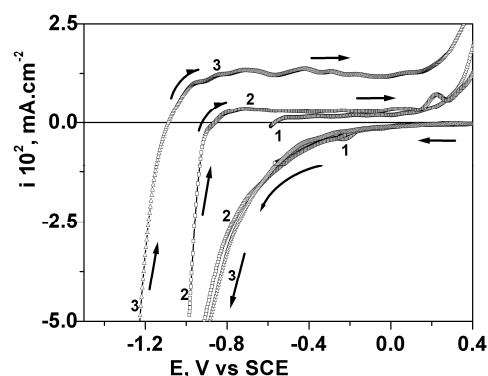

Figure 4 Negative potential region of the cyclic voltammograms in aerated simulated physiological solution of cp Ti at variable Ec to 2.5 Vsce. Ec values: -0.6 Vsce (curve 1), -1.0 Vsce (curve 2) and -1.5 Vsce (curve 3). Sweep rate was 30 mVs^{-1}.
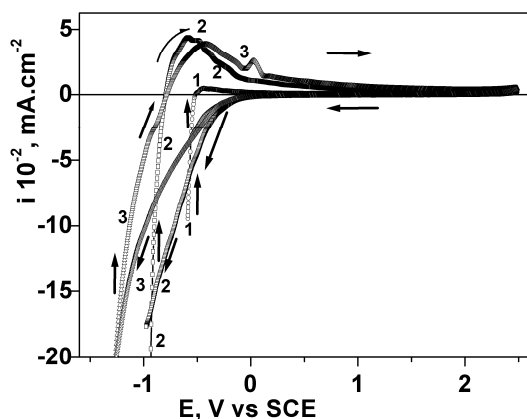
Figure 5 Cyclic voltammograms from variable Ec to 2.5 Vsce in aerated simulated physiological solution. Ti was anodically polarized at 5 Vsce during 15 minutes. Ec values: -0.6 Vsce (curve 1), -1.0 Vsce (curve 2) and -1.5 Vsce (curve 3). Sweep rate was 30 mVs⁻¹.

Figure 6. Cyclic voltammograms from variable Ec to 2.5 Vsce in aerated simulated physiological solution. Ti was anodically polarized at 5 Vsce during 15 minutes and kept 10 minutes at Ec values: -0.6 Vsce (curve 1), -1.0 Vsce (curve 2) and -1.5 Vsce (curve 3). Sweep rate was 30 mVs⁻¹.

wide peak was observed at around –0.7 Vsce with a peak current that increased as the negative potential increased.

The differences in behaviour are related to the main process that could occur depending on electrode surface condition. For cp titanium without anodic polarization it is impossible that the reduction of titanium oxides could be the main reaction. Thus the anodic current is due to the oxidation of hydrogen (Eq. 4) that could have been adsorbed on or absorbed in the titanium or a titanium hydride was formed during the cathodic process (Eq. 3).

$$TiO_2\text{-Had} \ + \ OH^- \ = \ TiO_2 + H_2O + e \qquad (4)$$

According to this assumption, if Ec value is more negative, the hydrogen evolution reaction will be faster and then the anodic peak will be higher. For an anodically polarized cp Ti, the main reaction is related, as mentioned before, to the transformation of titanium oxides that could occur alone or with the reduction of oxygen according to the mechanism proposed by Baez *et al.* (1992). Kim *et al.* (2003) found in the negative potential region a reversible transformation reaction from TiO_2 to $TiO_{2-x}(OH)_x$. Marino *et al.* (2001) suggested that this behaviour is due to oxide transformation during the cathodic polarization and named the anodic reaction as "oxide activation".

To confirm the stability of titanium oxides, cp titanium was polarized anodically at 5 Vsce during 15 minutes, kept at variable Ec during 10 minutes and then cyclic voltammograms from the selected Ec value to 2.5 Vsce were recorded. Results (Fig. 6) show an anodic current peak near an Ec value that increased, as Ec value was more negative. This fact could be explained as follows: as the Ec value was more negative, the oxidation process took place at positive potential less than -0.6 Vsce and the anodic current increased quickly. The anodic current peak at negative potential is related, as mentioned before, to the transformation of titanium oxides that could occur alone or simultaneously with oxygen reduction.
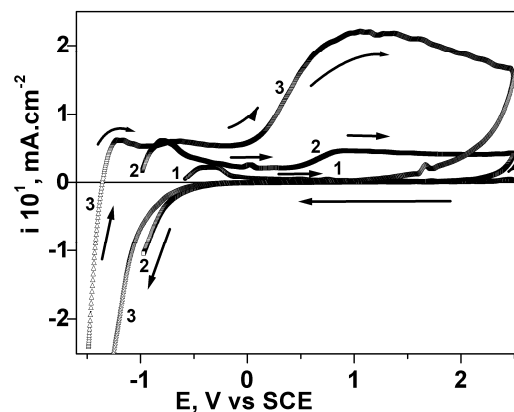
The curve shape at positive potential indicates a strong oxidation process of cp Ti. Then, the following assumption is possible: under potentiostatic condition and at high negative potential not only a transformation such as dehydration, oxide or hydroxide partial reduction occurred, but also the dissolution of titanium oxides could take place. In this way, the layer thickness could decrease, as the Ec value is more negative. This could happen because the oxide dissolution is related to the sub-oxide formation that increased as the Ec value was more negative. Blackwood *et al.* (1988) found that the oxide film underwent uniform reduction and their stability depended strongly on the conditions under which they had been formed. In our conditions, the sub-oxide formation during cathodic polarization increases the layer dissolution. On the other hand, Torresi *et al.* (1987a; b) found that the hydrogen absorbed in the oxide film in the hydrogen evolution potential region considerably affected the oxide film stability. In aqueous alkaline solutions Bonilla and Zimila (1998) found a similar behaviour and considered that it is due to the dissolution of the partially reduced titanium oxides in the negative potential region where the evolution of hydrogen took place. Moreover, Müller *et al.* (1992) found different dissolution processes, one of which is a potential independent chemical dissolution that could be possible in this case too.

IV. CONCLUSIONS

An unusual behaviour of potential-time curve for cp titanium polarized at 5 Vsce during 15 minutes was related to the dissolved oxygen near the electrode. For this condition, the oxygen concentration only reached the same concentration that in the bulk of the electrolyte after 30 min., the potential-time curve changed in slope and the cathodic peak around –0.7 Vsce disappeared in the voltammogram.

The cyclic voltammograms for cp titanium without anodic polarization showed at the hydrogen evolution region an anodic current at negative potential (between -

0.6 and -1.5 Vsce), which is related to the oxidation of the hydrogen adsorbed or absorbed during the cathodic process. For an anodically polarized cp Ti, the anodic reaction at potentials less negative than -0.9 V is related to the inverse process to the cathodic transformation of titanium oxides that took place in the cathodic scan simultaneously with the reduction of oxygen.

The stability studies of titanium oxides after cathodic polarization showed an oxidation process at higher positive potential with an anodic current (Fig. 6) that increased as the Ec value was more negative. This behaviour is observed under potentiostatic conditions and this is not only due to a slight transformation such as dehydration, oxide or hydroxide partial reduction, but rather it can also happen the dissolution of titanium oxide. This process can take place only at high negative potential because it is favored with the sub-oxide formation.

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