TITANIUM SURFACE MODIFICATION BY DOUBLE ANODIC OXIDATION

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Abstract. *The biocompatibility of titanium dental implants is related to the properties of the surface oxide layer in terms of the composition, roughness, and hydrophilicity. They are all parameters that may play a role in the interaction of implant–tissue. Rough surfaced implants favor both bone anchoring and biomechanical stability. Surface roughness can be divided into three levels from macro to nano-sized topologies. The macro scale is directly related to implant geometry, the micro scale is defined for surface roughness as being in the range of 1–10 µm. This range of roughness maximizes the interlocking between mineralized bone and the surface of the implant. Surface profiles in the nanometer range play an important role in the adsorption of proteins, adhesion of osteoblastic cells and thus the rate of osseointegration. Various methods have been developed in order to create a rough surface and improve the osseointegration of titanium dental implants. Among them, the anodic oxidation is considered an effective technique for modifying the thickness, structure, composition, and topography of titanium oxide. The anodization process depends on various parameters such as current density, process time, composition and concentration of electrolytes. Several works on the literature describes the anodic oxidation using* H_3PO_4 *or* H_2SO_4 *acids as electrolytes, each one with advantages and disadvantages. Our aim was to combine the effects of both electrolytes and produce an oxide layer with two levels of roughness, and evaluate its bioactivity, composition, crystallinity, wettability and roughness. Samples from Ti-cp (ASTM grade 2) were grinded with SiC#600, and then cleaned with acetone in an ultrasonic bath for 15 min, washed with deionized water and dried with hot air. The specimens were anodized at a constant voltage of 280 V in 1M* H_3PO_4 *during one minute, followed by 200V to 220 V in 1M* H_2SO_4 *with a Pt plate acting as the counter electrode. To test the bioactivity of oxide layers, the samples were soaked in simulated body fluid (SBF) with ion concentrations nearly equal to human blood plasma for 7 days. Anodized layers were characterized in terms of structure and morphology before and after bioactivity test by Scanning Electron Microscopy.*

Keywords: *Titanium, double anodic oxidation, bioactivity.*

1. INTRODUCTION

Almost every metal, when exposed to the atmosphere, undergoes a process of corrosion that leads to the buildup of a natural thin layer on its surface, which protects the surface from further changes. This layer is made of the oxides and hydroxides coming from the reaction of the metal itself with the oxygen and aqueous vapor present in the air (Diamanti et al. 2007) . When titanium reacts with oxygen at room temperature several kinds of oxides are formed. The most stable and abundant oxide is the TiO_2.

The use of titanium (Ti) and titanium alloys as materials for implants has been increasing in recent years because of their excellent mechanical strength, chemical stability and biocompatibility (Brunette et al. 2001). Several techniques have been developed for titanium to obtain a better biocompatible implant surface, such as the anodic oxidation. The technique of anodic oxidation is a electrochemical treatment that uses a combination of electric field and ionic diffusion with oxygen to increase the oxide layer, denser than that formed naturally in the atmosphere. Anodic oxidation is widely applied on pure titanium and titanium alloys to obtain a layer that increase the surface roughness and improve de biological perform for its use on dental and orthopedic implants (Sul et al. 2001-2002). Thick anodic films may be more homogenous compared to the air-formed films which would tend to reproduce the chemical heterogeneity of the multiphase underlying alloy (Ruzickova et al. 2005; Lausmaa and Electron 1996; Sittig et al. 1999) .

According to Liu et al. (Liu et al. 2005) the titanium and oxygen ions formed in the redox reactions, during the anodic oxidation, are driven through the oxide by the externally applied electric field resulting in the formation of the oxide film (Liu et al. 2005). During the oxidation process, the oxide formed on the titanium surface will drop the applied voltage. That happens with the growth of the film that creates a resistance for the flow of ions through the oxide layer. Liu also proposed that the final oxide thickness is almost linearly dependent on the applied voltage (Liu et al. 2005).

An important requirement for the selected electrolyte is that it should not be aggressive towards the growing oxide to avoid dissolution during the process. Sulfuric and phosphoric acids are the most used electrolyte in titanium anodizing (Pedeferri et al. 2005). The broad use of H_2SO_4 and H_3PO_4 in many biomaterials works is due to the deposition of sulfur and phosphorous ions at the samples surface, which induces bioactivity (Oh et al. 2008).

Different electrolytes require different voltages to make a layer with the same thickness, which means that some electrolytes create more resistance for the ions flow than others at the same or also in higher voltages. Many works that uses sulfuric acid as electrolyte usually uses a voltage between 150 and 180V and some works that uses phosphoric acid as electrolyte uses a voltage around 280V (Kuromoto et al. 2007). That’s because the anodic oxidation in a sulfuric acid electrolyte enable a higher current flow between the anode and the cathode, which reduces the voltage needed to form a thick film.

In this work an oxide layer was formed by anodic oxidation using an electrolyte followed by another one with different electrolyte and voltage/current conditions, making a double anodic oxidation. A double anodic oxidation breaks the first formed film to make a second one take its place, however some ions of the first film might stay in the second film and gives to the final film characteristics of both electrolytes used in each oxidation. The aim of this work is to study the double anodic oxidation technique and the phenomenon of the film breakdown and replacement as well as the morphology and bioactivity of the final layer.

2. MATERIALS AND METHODS

Commercially pure Ti (grade 2) was used for anodic oxidation. Specimens with 2-mm-thick and 9 mm of diameter were grinded with SiC #600, and then washed in an ultrasonic cleaner with pure acetone and deionized water.

Anodic oxidation was carried out in potentiostatic mode (constant voltage) at voltages of 280V to 320V for H_3PO_4 (1M) and 200V to 220V for H_2SO_4 (1M), and current density of 150 μA cm^{-2} for some cases of second oxidation. The purpose of the current density in this work was to find out the minimum voltage needed to start the first layer breakdown. It was also used to compare the formed layer in this process with the layer of a second oxidation obtained in potentiostatic mode at the same final voltage reached in current density mode but without a current limitation. The oxidation order was made following the “Tab. 1”.

Table 1. Anodic oxidation parameters.

First oxidation			**Second oxidation**		
Electrolyte	Mode	Voltage/ Density	Electrolyte	Mode	Voltage/ Density
H3PO4 (1M)	Potentiostatic	280V	H2SO4 (1M)	Current Density	150 μA cm^{-2}
H3PO4 (1M)	Potentiostatic	280V	H2SO4 (1M)	Potentiostatic	200V
H3PO4 (1M)	Potentiostatic	280V	H2SO4 (1M)	Potentiostatic	220V
H2SO4 (1M)	Potentiostatic	180V	H3PO4 (1M)	Current Density	150 μA cm^{-2}
H2SO4 (1M)	Potentiostatic	180V	H3PO4 (1M)	Potentiostatic	320V

Firstly, a sample was oxidized with phosphoric acid at a constant voltage of 280V and then oxidized with sulfuric acid at a current density of 150 μA cm^{-2} during a period of one minute. The constant current flow made the sulfuric acid's layer crop up all over the phosphoric acid's layer near the voltage of 200V. After the determination of the minimum voltage for the sulfuric acid electrolyte enable the flow of ions trough the phosphoric acid's layer, two voltages, near the minimum required voltage, were chosen for the oxidation in potentiostatic mode, which were 200V and 220V.

After oxidation using phosphoric and sulfuric acids respectively, the order of the used electrolytes was inverted following the same method describe above, however the voltage used for the sulfuric acid electrolyte, when it comes first, must be lower than the voltage used on the layer formed by the phosphoric electrolyte. For convenience the voltage used for the sulfuric acid electrolyte, when it comes first, was 180V. The phosphoric acid at a current density of 150 μA cm^{-2} didn't affect the layer formed by the sulfuric acid because of the resistance conferred by the first layer. A voltage of 320V was used as a try to break the sulfuric acid layer but it failed too. After each oxidation, the samples were washed with distilled-deionized water and then dried before the second oxidation with the other electrolyte. The voltage and current data were acquired with time using a digital oscilloscope (TDS2014B, Tektronix).

The surfaces were characterized by scanning electron microscopy (Jeol JSM6360-LV/EDS) and bioactivity "*in vitro*" tests in a modified SBF (Simulated Body Fluid) for a period of 7 days.

3. RESULTS AND DISCUSSION

3.1. Morphology of the anodic layers

The sample oxidized with H_3PO_4 (1M) – 280V and H_2SO_4 (1M) – 200V kept the phosphoric layer as a dominant morphology, which can be seen at "fig. 1". However the tonality of the H_3PO_4 film changed after the second oxidation, which means that there might had a change in the film.

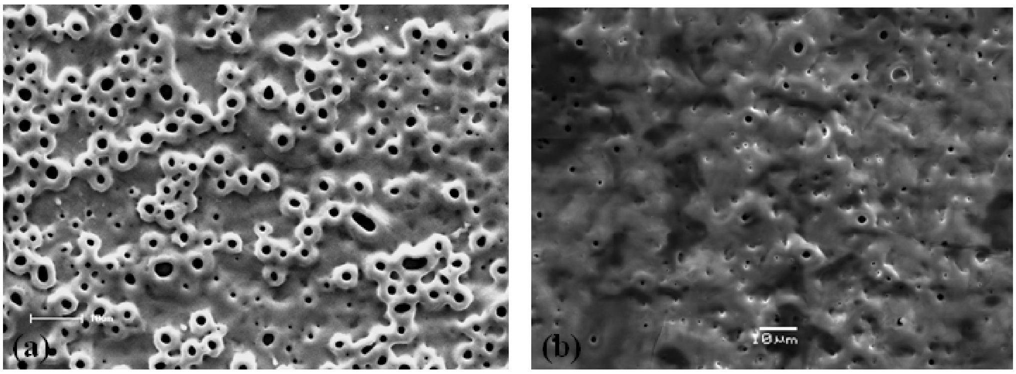

Figure 1. SEM surface morphology of: (a) Ti surface morphology of single oxidation with H_3PO_4 (1M) – 280V. (b) Ti surface morphology after double anodic oxidation using H_3PO_4 (1M) – 280V and H_2SO_4 (1M) – 200V.

Increasing the voltage of the second oxidation from 200V to 220V will form a layer which morphology is similar to the H_2SO_4 layer when oxidized directly on Ti substrate. The "fig. 2" shows a SEM surface morphology of a sample oxidized with H_3PO_4 (1M) – 280V and H_2SO_4 (1M) – 220V and a SEM of a sample single oxidized with H_2SO_4 (1M) – 180V for comparative purposes.

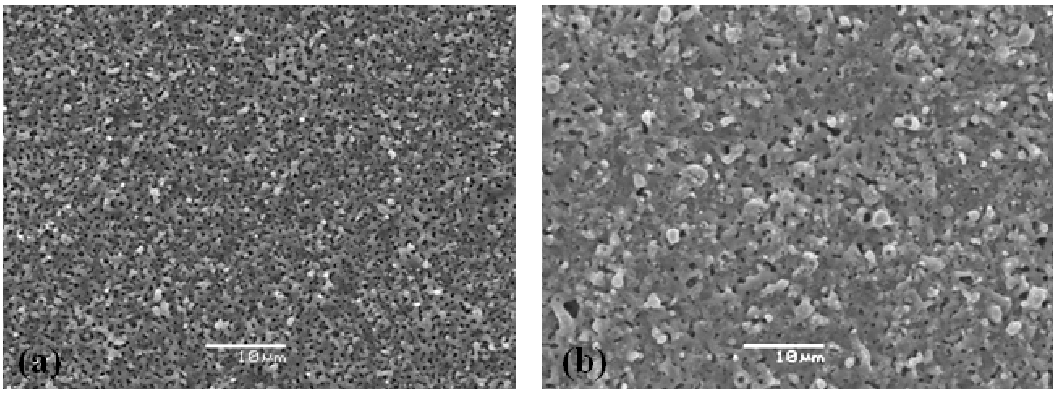

Figure 2. SEM surface morphology of: (a) H_2SO_4 (1M) – 180V single oxidized. (b) H_3PO_4 (1M) – 280V and H_2SO_4 (1M) – 220V.

The reason for the comparison between “fig. 2” (a) and (b) is to show the similarity of the maximum current flow that formed both films and the morphology similarities and differences. Comparing an oxidation in H_2SO_4 – 220V on a H_3PO_4 layer with a single oxidation of H_2SO_4 – 180V the current peaks of both reaches similar current values, as shown at “fig. 3”.

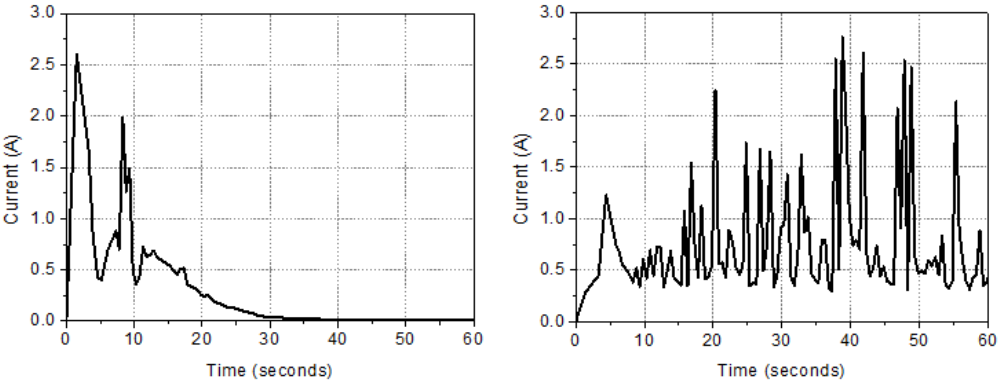

Figure 3. Current behavior during H_2SO_4 – 180V single oxidation (left) and H_2SO_4 – 220V oxidation on a H_3PO_4 layer (right).

During a single oxidation of the Ti substrate using H_2SO_4 the current curve behaves as the left graphic of “fig. 3”. The consecutive peaks of current represent the sparks that happens during the oxidation and the film stop its formation when current is equal zero. According to the left graphic of “fig. 3” the oxidation stops in 40 seconds and, consequently, the layer formation. However, the right graphic of “fig. 3” demonstrates that the oxidation would continue breaking the oxide layer formed by H_3PO_4 and forming the H_2SO_4 layer in its place.

3.2. Bioactivity test

The bioactivity of the films first oxidized by H_3PO_4 (1M) – 280V and then oxidized by H_2SO_4 (1M) – 200V and H_2SO_4 (1M) – 220V were tested in simulated body fluid (SBF) with ion concentrations nearly equal to human blood plasma for 7 days. The films morphology after the tests in SBF can be seen at “fig. 4”.

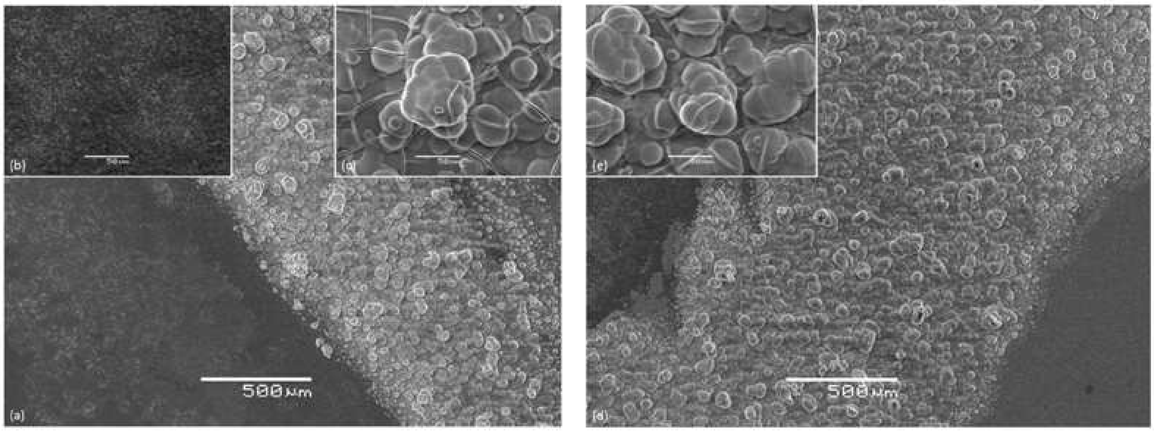

Figure 4. SEM images of Ti surface after double anodic oxidation and bioactivity tests. (a) Sample secondly oxidized with H_2SO_4 (1M) – 200V. (b) Characteristic morphology of H_3PO_4. (c) Deposited hidroxiapatite. (d) Sample secondly oxidized with H_2SO_4 (1M) – 220V. (e) Deposited hidroxiapatite.

An EDS of “fig. 4” (c) and (e) shown a high concentration of phosphorous and calcium, which can be seen at “fig. 5”. Both elements are hidroxiapatite (HAP) compounds, which indicate that a nucleation of HAP occurred on the samples film.

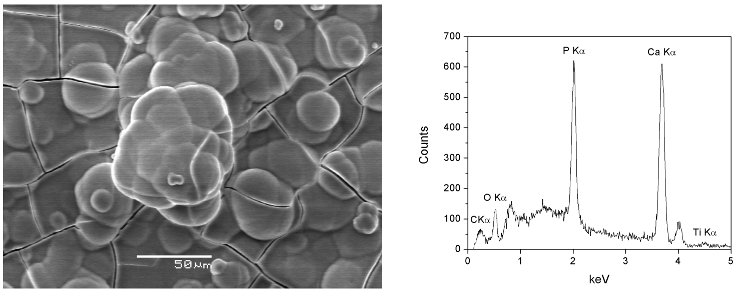

Figure 5. EDS of the SEM indicating the presence of phosphorous and calcium.

The nucleation of HAP on the samples occurred around the oxidized layer as shown by “fig. 4”, according to the literature (Kokubo and Takadama 2006). The possible causes of that partial HAP precipitation could be the short time the samples were immersed into SBF or the combination of two oxidations could have reduced the nucleation speed.

4. CONCLUSION

Anodic oxidation always breaks an oxide layer to form another one in its place, however the thicker the layer is, the greater its resistance to breakage and it will demand more time for the complete layer replacement. While oxidation occurs, time is the defining factor for the final film morphology. Double anodic oxidation could be an alternative way to obtain a higher roughness on Ti surface and larger pores as seen on “fig. 2”.

The higher current peak on bought graphics of “fig. 3” reaches a similar value, which means that the resistance of the natural oxide layer formed at atmosphere when using H_2SO_4 – 180V as electrolyte is similar to the resistance of the H_3PO_4 – 280V layer when using H_2SO_4 – 220V as electrolyte. However the time needed to replace the whole H_3PO_4 layer is higher than the time to replace the natural atmosphere layer.

The layers formed by H_2SO_4 – 180V as a first oxidation could not been broken by the voltages and the current density applied using H_3PO_4 as electrolyte, which means that the resistance of that film is too high and demand more energy to be broken.

After bioactivity tests in SBF of the double oxidized samples, they shown HAP nucleation on the oxide films which means that they might be bioactive and support bone regeneration.

5. REFERENCES

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