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EFFECTS OF CURRENT DENSITY ON THE FORMATION OF TITANIUM OXIDE CONTANING Ca AND P OBTAINED BY ANODIC OXIDATION

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Abstract. *In the past 20 years, pure titanium and its alloys have been used as dental and orthopedic implants due to its good mechanical properties, corrosion resistance and biocompatibility. However, the titanium is a bioinert material that cannot bond properly with the living bone. Several surface modifications techniques have been studied aiming to improve the bioactive bone bonding ability of titanium metal. Among them, surface properties such as surface roughness and chemical composition have been considered the most important parameters for altering cell activity. The anodic oxidation method is a traditional method for surface modification. It can modify the structures and chemical properties of the oxide layer by modifications on electrolyte composition or concentration, applied potential or current, temperature, among others. The anodic oxidation has also emerged as a unique method for processing an oxide film containing Ca and P on titanium. This oxide film containing Ca and P alone can enhance Hydroxiapatite precipitation in a simulated body fluid (SBF) and improve the osseointergration of titanium implants. This work describe the effects of high current density (400 to 1200 mA/cm^2) on the formation of titanium oxide containing Ca and P, and its characterization regarding crystalline structure, surface morphology, chemical composition, roughness, surface wettability and "in-vitro" bioactivity test in SBF.*

Keywords*: Anodic Oxidation, Titanium, Implants, Wettability, Bioactivity*

1. INTRODUCTION

In the past 20 years, pure titanium and its alloys have been used as dental and orthopedic implants due to their good mechanical properties, corrosion resistance and biocompatibility. However, the titanium is a bioinert material so it cannot bond properly with the living bone. Several surface modifications on titanium surface have been studied aiming to improve the bioactive bone bonding ability of titanium metal. Among the surface properties, morphology, roughness and chemical composition have been considered the most important parameters for altering the cell activity.

The Micro-arc Oxidation MAO (also named Plasma Electrolytic Oxidation or Anodic Spark Oxidation) is a traditional technique that can be used to easily control surface properties such as the crystalline structure, chemical properties, oxide layer thickness, pore size and roughness. The MAO could produce a uniform oxide layer over complex geometries like dental or orthopedic implants (Kung et al., 2010).

The oxide characteristics are affected by the electrolyte solution (composition and concentration), electrical potential applied between the anode and cathode and the current density imposed to reach that value of potential difference (Diamanti and Pedeferri, 2007).

The most commonly used electrolyte on titanium MAO are phosphoric and sulfuric acids, at different degrees of concentration (Zhu et al., 2001). In the last years, electrolytes containing ions of calcium and phosphorous have been used aiming to produce an oxide layer on titanium containing these ions, in order to improve the bioactivity, especially on dental implants.

Electrolytes using calcium glycerophosphate and calcium acetate, are used with success on formation on oxide layer containing Ca and P (Park et al., 2007, Liu et al., 2005, Suh et al., 2003). In all these works the quantity of Ca and P ions on the oxide layer can be controlled by changes on electrolyte concentration or changes in the electric variables (potential difference / current density).

The MAO process with constant current density (galvanostatic mode) is the widely used mode for anodic oxidation in titanium. The current density varies normally from 4 to 300 mA/cm^2 and for times ranging from 30 to 540 seconds. The titanium oxide layers formed present both amorphous and crystalline structures, depending on the process parameters. Crystalline oxides, mostly anatase and rutile show great hydrophilicity and biocompatibility properties.

To evaluate the biocompatibility and bond to bone of an artificial material we could implant in a body environment or soak the material on Simulated Body Fluid (SBF). The formation of a bone-like apatite layer on its surface indicates the biocompatibility and bone-bond abilities as shown on previous works (Cui et al., 2009).

The objective of this study was to evaluate the modifications of titanium surface using MAO with high current density from 400 to 1200 mA/cm^2 on aqueous electrolyte containing Ca and P. This study includes a crystal structure analysis, surface morphology, chemical composition, roughness, surface wettability and in vitro bioactivity.

2. MATERIALS AND METHODS

Substrates of commercially pure Titanium (ASTM F67 Grade: 2) with 12,7 mm diameter and 2 mm in thickness, were mechanically grinded with silicon carbide paper #320 / 500 / 800, then polished with diamond paste 9 μm and colloidal silicon. Then, the samples were washed in ultrasonic bath with ethanol and distilled water for 15 min each process.

The MAO was performed under galvanostatic mode (constant current) using an electrolyte composed by 0.02 mol/L of Calcium Glycerophosphate and 0.15 mol/L of Calcium Acetate diluted in deionized water. The current density applied on the anodic oxidation were 400, 700, 1000 and 1200 mA/cm² for 15 s. The galvanostatic polarization was obtained using a DC power supply (Chroma). A Pt plate was used as a counter electrode and a magnetic stirrer was used to avoid bubble formation on the samples surface.

After the anodic oxidation the samples were rinsed with distilled water and then sterilized in autoclave at temperature of 134 C^o and pressure of 2,10Bar for 15 min.

After the sterilization process the samples were soaked in 30 mL of simulated body fluid (SBF) with ion concentration nearly equal to human blood plasma for 15 days at 36.5 °C.

The phase and microstructure of the specimens were evaluated by X-ray diffraction (XRD - Shimadzu, DRX-700) and scanning electron microscopy (SEM - Jeol JSM6360LV). The composition of the surface layer was analyzed by energy dispersive spectroscopy (EDS - Thermo). The Roughness average (Ra) using a bench profilometer (Taylor-Hobson Series 2) and contact angle with a goniometer (Easy-Drop, Kruss), using deionized water as the liquid.

3. RESULTS AND DISCUSSION

The SEM images of the surface samples show a homogeneous titania layer with a 3D oxide structure consisting of numerous open pores in all samples. The size and quantity of the pores change with the current density (Fig. 1). For 1200 mA/cm², the surface of the sample show some regions with melted titanium, possibly formed due to the intense arcing formed on the surface due to a high tension reached. This effect is noted on the EDS and XRD analysis of this sample, as observed the decrease on the elements concentration and cristallinity.

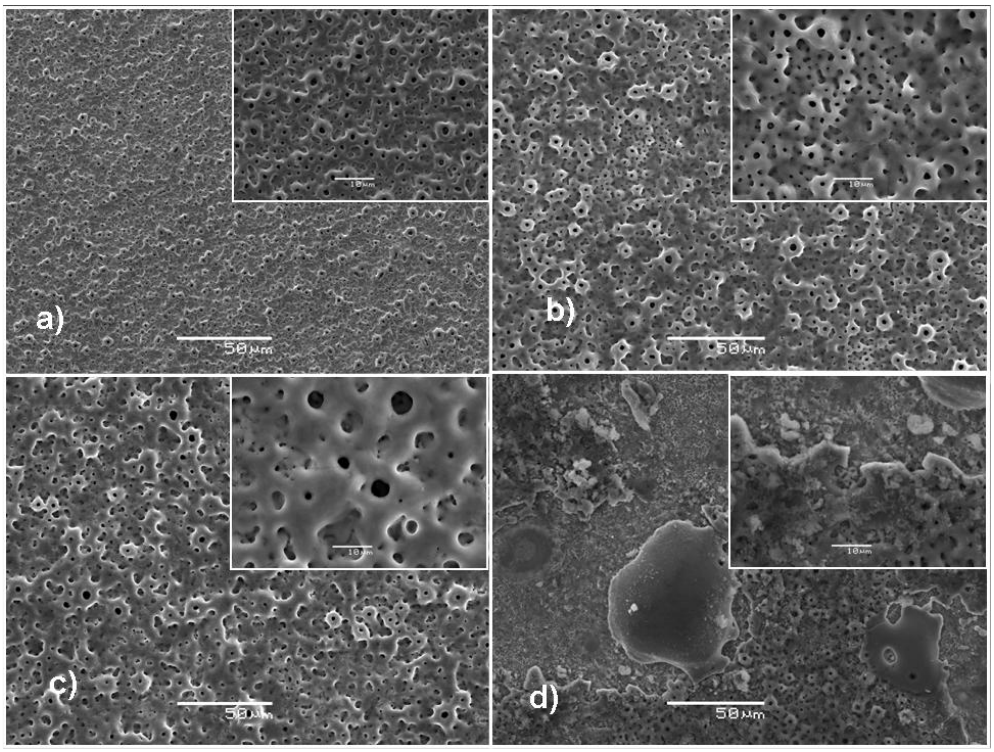

Figure 1. SEM images of the samples after the anodic oxidation: (a) 400, (b) 700, (c) 1000 and (d) 1200 mA/cm^2.

EDS results are shown on table 1. We observe that the calcium concentration on the oxide layer increase from 6.3% on the sample oxidized with 400 mA/cm^2, to 19.8 % on sample oxidized with 1000 mA/cm^2. On the sample oxidized with 1200 mA/cm^2 the concentration of Ca drops to 12.2%. The phosphorous concentration changed from 4.3 to 5.9 %.

Table 1. Concentration of the elements (% wt).

Element	400 mA/cm^2	700 mA/cm^2	1000 mA/cm^2	1200 mA/cm^2
O	34.9 ± 2.8	35.5 ± 2.3	31.1 ± 6.3	29.6 ± 2.5
P	4.3 ± 0.3	4.2 ± 0.6	5.9 ± 0.9	4.9 ± 0.5
Ca	6.3 ± 0.3	10.9 ± 1.0	19.8 ± 2.3	12.2 ± 0.6
Ti	54.5 ± 0.9	49.4 ± 1.9	43.1 ± 3.7	53.2 ± 2.0

Figure 2 shows the variation of the Ca / P ratio with current density. We observe that the Ca/P ratio increase until 1000 mA/cm^2, decreasing for the sample oxidized with 1200 mA/cm^2.

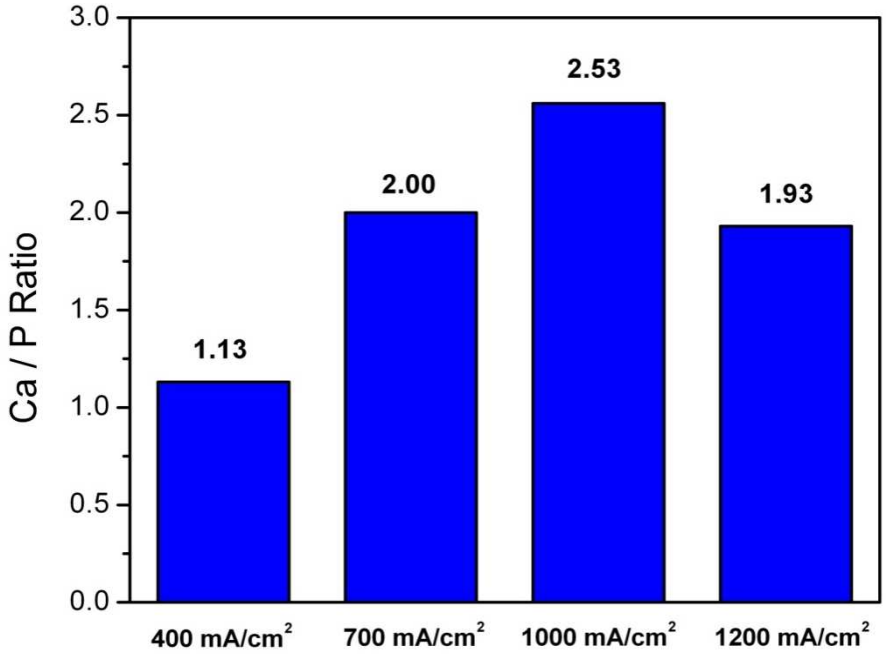

Figure 2. Graphic showing the Ca/P relation with variation of current density

The XRD patterns showed that anatase and rutile phases are formed in all samples. However, new rutile peaks appears with the increase of the current density (28° and 35°), but with a current density of 1200 mA/cm² the rutile peaks intensity decreases (Fig. 3). It is interesting to note that for the current density of 1000 mA/cm², there is an intense peak of the anatase phase (74°). Figure 4 shows that the average roughness (Ra) increases linearly with current density.

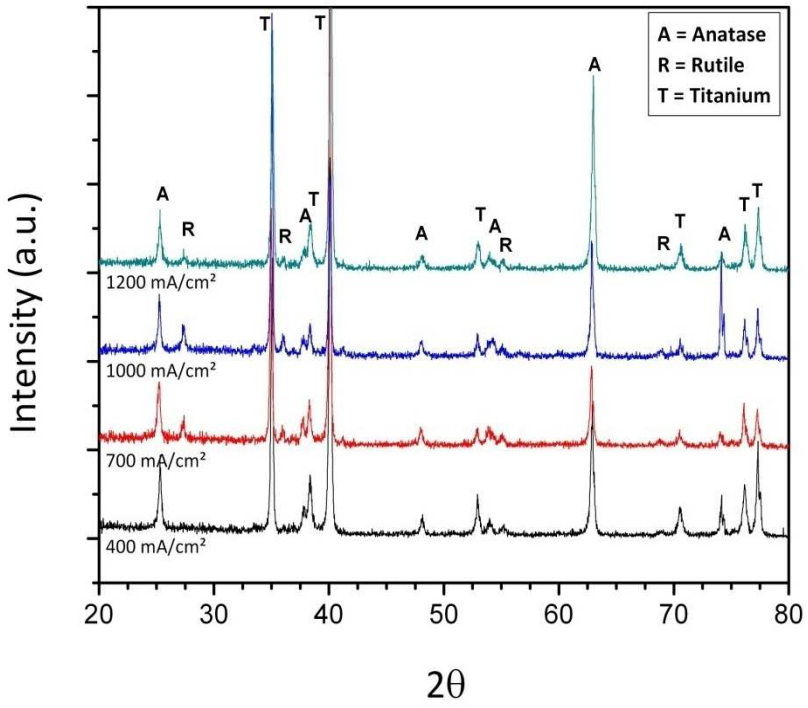

Figure 3. XRD patterns of the surfaces oxidized anodically with current densities of 400, 700, 1000 and 1200 mA/cm^2.

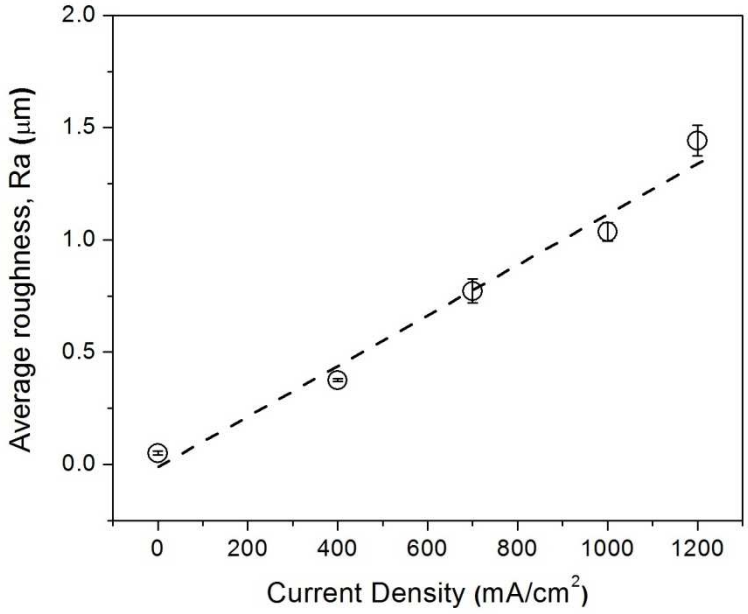

Figure 4. Graphic showing the variation of the average roughness (Ra) with current density.

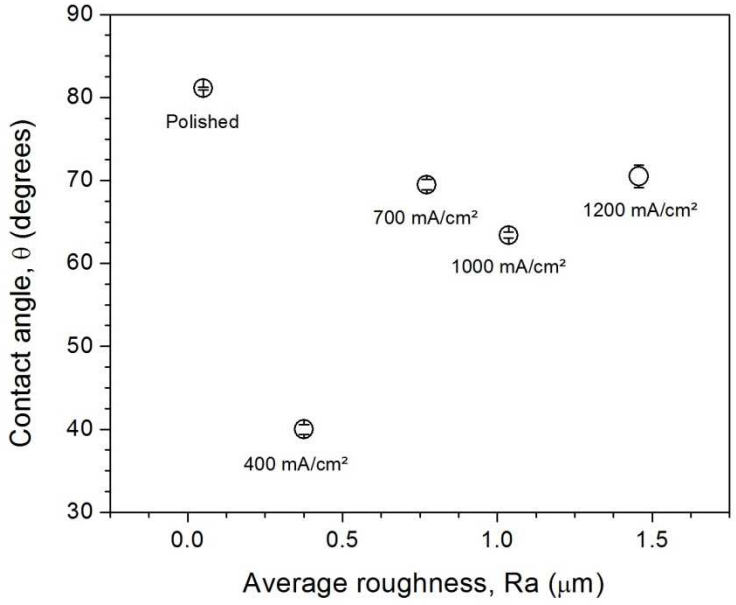

Figure 5. Contact angle variation with average roughness.

In comparison with the polished control, the sample oxidized with 400 mA/cm^2 show the better wettability as the contact angle is about 40°. In the samples oxidized with current density of 700, 1000 and 1200 mA/cm^2 the contact angle increases and is still minor than the control sample (Fig 5).

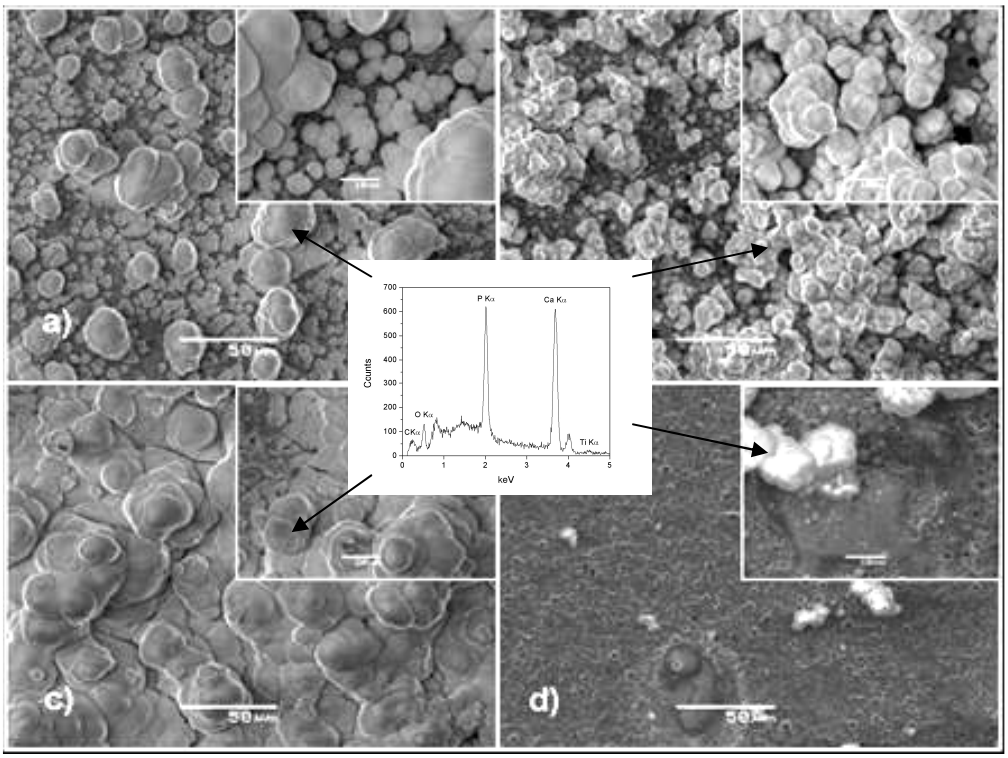

Figure 6. SEM images of the samples after bioactivity test on SBF for 15 days. (a) 400, (b) 700, (c) 1000 and (d) 1200 mA/cm^2. At the center, a representative EDS curve for the HAP.

The figure 6 shows the SEM images of the samples after the bioactivity test after 15 days of immersion in SBF at 36.5 °C. We can observe that the samples anodically oxidized with 1000 mA/cm^2 are completely covered by HAP. The samples of 400 and 700 show some regions covered by HAP, but not completed covered as the 1000 mA/cm^2 sample. The sample oxidized with 1200 mA/cm^2 showed only few and localized points on the surface with HAP. EDS results

confirm the presence of Ca and P elements. According to Tang et al. (2004), the anatase phase shows an enhanced ability to induce bonelike apatite as compared to rutile phase, which is corroborated by our XRD and SEM results.

Actually there are many techniques for improving the titanium biocompatibility. These techniques often promote changes on the structure, morphology, and chemical composition by depositing a coating on the surface of titanium. The MAO is capable to produce a porous and uniform oxide coating and with chemical and morphological properties which can improve biocompatibility.

In the present study, the MAO using high current density produces oxide coatings with the same characteristics as shown on previous studies using low current density values. The morphology of the oxide coating is very similar as encountered by Suh et al. (2003), which use the same electrolyte but with current density of 7 mA/cm^2 but oxidizing time of 30 minutes.

3. CONCLUSIONS

For all samples anodically oxidized, the ones produced with current density of 1000 mA/cm^2 showed the best results regarding "*in-vitro*" bioactivity, roughness average, and Ca / P ion concentration, except for the wettability results. The presence of anatase phase may have influenced the precipitation of HAP after bioactivity test.

4. ACKNOWLEDGEMENTS

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5. RESPONSABILITY NOTICE

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