XVIII IMEKO WORLD CONGRESS
Metrology for a Sustainable Development
September, 17 – 22, 2006, Rio de Janeiro, Brazil

TITANIUM OXIDE FILMS PRODUCED BY MICRO-ARC OXIDATION FOR HIGH PERFORMANCE TITANIUM IMPLANTS

J.T. Filho[1,2*], *L.R. Lidízio*[1], *L.A. Sena*[1], *J.C. Damasceno*[1] *and C.A. Achete*[1,2]

[1] Materials Metrology Division, National Institute of Metrology, Standardization and Industrial Quality, RJ, Brazil
[2] Department of Metallurgy and Materials Engineering, Federal University of Rio de Janeiro, RJ, Brazil
*jtfilho@inmetro.gov.br

Abstract: The growth of titanium oxide layer on titanium surface by the micro-arc oxidation technique was investigated. $Ca(CH_3COO)_2$ (0.3M), Na_2CO_3 (0.6M) and Na_2HPO_4 (0.1M) solutions were employed as electrolytes. SEM and EDS microanalysis were used for morphology, composition characterization and low-angle X-ray diffraction to describe titanium oxide crystallographic orientation. TiO_2 films formed by using 0.3M $Ca(CH_3COO)_2$ and 0.1M Na_2HPO_4 solutions showed a porous, homogeneous surface structure, with presence of phosphorous and after an hydrothermical treatment using a $Ca(OH)_2$ suspension during 24h at 60ºC was observed phosphorous and calcium.

Keywords: titanium oxide, micro-arc oxidation, titanium implants.

1. INTRODUCTION

Titanium and titanium alloys are currently used as base materials for surgical implants in biomedicine as for example in artificial joint replacements, maxillofacial reconstruction, audiological applications or dental implants. Success has been related to their good mechanical properties and excellent biocompatibility [1]. However, alternative approaches to produce bioactive, porous and nano-crystallized titanium implant surfaces are being studied [2]. An attractive option is to induce the growth of a natural, bio-inert titanium oxide film [3]. The micro-arc oxidation (MAO) is a particular interesting process to produce such oxide layers due its versatility and cost-effectivity [4]. This technique can electrochemically produce porous and uniformly coated oxides on metal surfaces.

In order to produce high performance implants it is very important to measure some film properties such as thickness, chemical composition and surface morphology. The morphology and pore configuration of titanium oxide films seems to be related to its biological performance [5]. The presence of the allotropic phase anatase in the oxide structure is also important because it is responsible for the biocompatibility of the material [6]. However, the anatase is a meta-stable phase, so that the synthesis conditions must be carefully controlled.

Production of implants with adequate surface finishing is extremely important for biocompatibility and osseointegration, contributing for a high quality product. In addition, the development of reference substrates that induce specific cellular responses bridge the gap between fundamental knowledge and the product development needs in industry, specially in developing measurement methodologies and reference materials to asses interactions in complex systems of living cells with synthetic materials.

In this work, pure titanium samples were coated using MAO to produce TiO_2 layers. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectrometry (EDS) microanalysis were used respectively for morphology and composition characterization. X-ray diffraction was used for crystallographic characterization of titanium oxide.

2. MATERIALS AND METHODS

Pure titanium (ASTM grade 2) samples of 1 x 1 cm^2 and 5 x 3 cm^2 were carefully grounded in SiC paper, polished and submitted to the electrochemical treatment using two configurations of the MAO process to produce porous TiO_2 layers. In the first experimental setup, a very simple 60Hz, AC power supply was used to apply 140 V between the sample and a pure Pt electrode during approximately 3 minutes for each sample. $Ca(CH_3COO)_2$ (0.3M) and Na_2CO_3 (0.6M) solutions were used separately as electrolytes.

In another MAO experimental setup a 60Hz, pulsed DC power supply was used to apply 110 V between the sample and a stainless steel cube during approximately 10 minutes for each sample. In this case, a Na_2HPO_4 (0.1M) solution was used as electrolyte and a stainless steel cube as counter-electrode. Generation of sparks was observed in all experiments.

An hydrothermical treatment using a $Ca(OH)_2$ suspension during 24h at 60ºC was employed on samples anodized with phosphate solution to produce a surface rich in calcium and phosphorous. The presence of calcium and phosphorous on sample surface can provide biologic advantages for surgical and odontological applications [7].

SEM and EDS microanalysis were employed for morphology and composition characterization, respectively.

Crystallographic characterization of the oxide phases was done by X-ray diffraction analysis.

3. RESULTS

Figure 1a shows a SEM micrograph of the film surface produced with the $Ca(CH_3COO)_2$ solution. As can be seen, the film surface presents a porous structure, with pore sizes of approximately 1 µm, homogeneously distributed on the surface. On the other hand, the surface of the film produced with Na_2CO_3 solution showed a porous but very irregular surface with a great quantity of delaminated areas (Figure 1b). This suggests that the conditions of ionic conductivity and/or applied potential used for the 0.6M Na_2CO_3 solution were too aggressive, causing delamination of the oxide layer during the process of titanium oxide film growing.

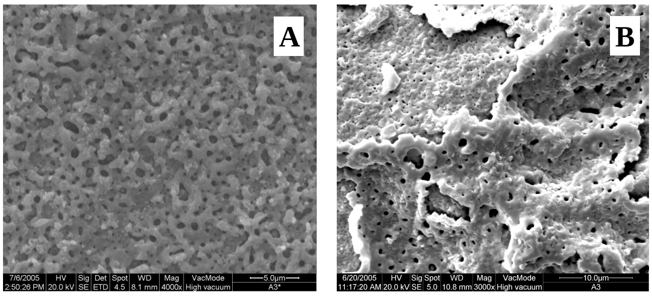

Fig. 1. SEM micrographs of TiO_2 layers produced with: a) 0.3M $Ca(CH_3COO)_2$ solution (Magnification = 4000x) Bar = 5 µm and b) 0.6M Na_2CO_3 solution (Magnification = 3000x) as electrolytes. Bar = 10 µm.

EDS microanalysis of the oxide surface produced with the $Ca(CH_3COO)_2$ solution for the same region of Figure 1a shows the presence of calcium, as can be seen on Figure 2.

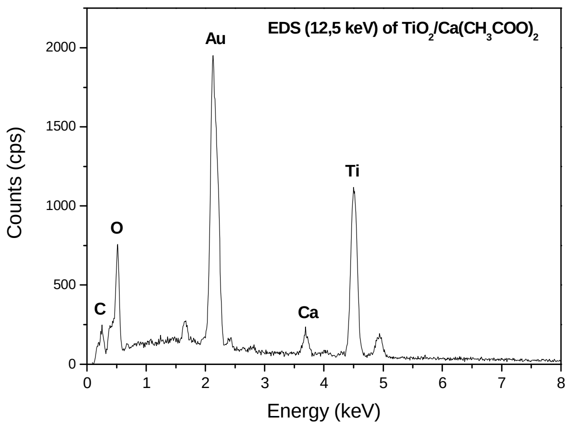

Fig. 2. EDS spectrum of TiO_2 layer produced with 0.3M $Ca(CH_3COO)_2$ solution as electrolyte.

Figure 3b shows the calcium mapping of the oxide surface for the same sample, where the black dots indicate the presence of Ca. This figure corresponds to the same area of the micrograph shown in Figure 3a. It can be observed that the calcium is homogeneously distributed on the titanium oxide surface. Incorporation of calcium to the oxide structure is very beneficial to the bioactivity of the surface as results found in the literature show that it helps the growth of osteoblast cells [8]. This can be related with the acceleration of the bone-like apatite layer formed on its surface.

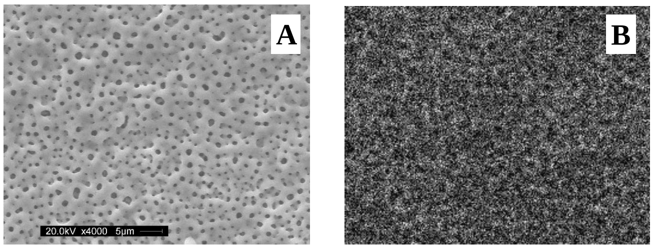

Figure 3. Images of TiO_2 layer produced with 0.3M $Ca(CH_3COO)_2$ solution as electrolyte: a) SEM micrograph and b) calcium mapping (white dots) by EDS microanalysis. Magnification = 4000x. Bar = 5 µm.

Figure 4a shows a SEM micrograph of the porous and homogeneous oxide surface produced by MAO using sodium phosphate (Na_2HPO_4) solution as electrolyte. EDS microanalysis of the same region of Figure 4a (see Figure 4b) shows the presence of phosphorous.

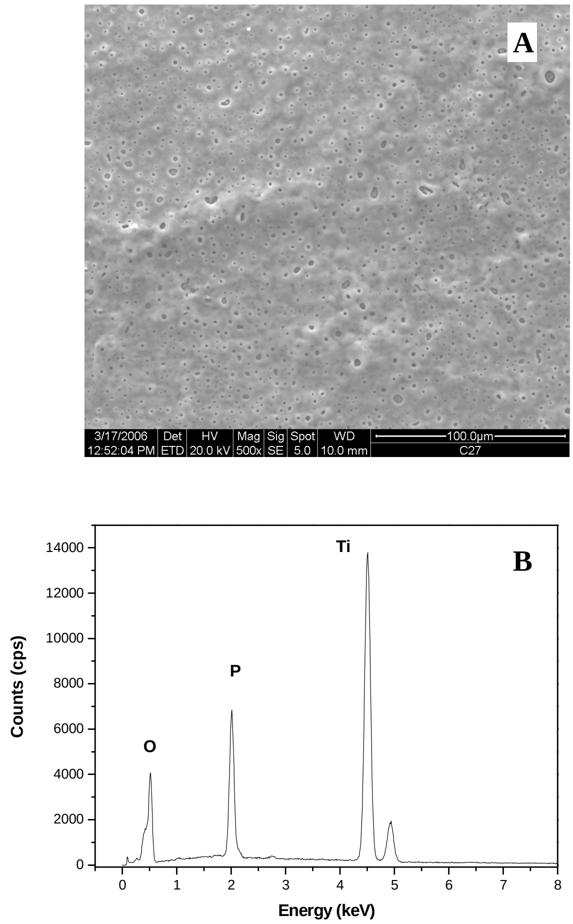

Fig. 4. Images of TiO_2 layer produced with 0.1M Na_2HPO_4 solution as electrolyte: a) SEM micrograph and b) EDS microanalysis. Magnification = 500x.

Figures 5a and 5b show: a SEM micrograph of the morphology after hydrothermical treatment and EDS microanalysis of the same region. As can be seen, the surface becomes more porous and presents a less defined structure. Presence of Ca and P on the oxide surface was observed in this case. Further studies must be done to verify if the calcium and phosphorous presence accelerates the bioactivity in relation to each one individually.

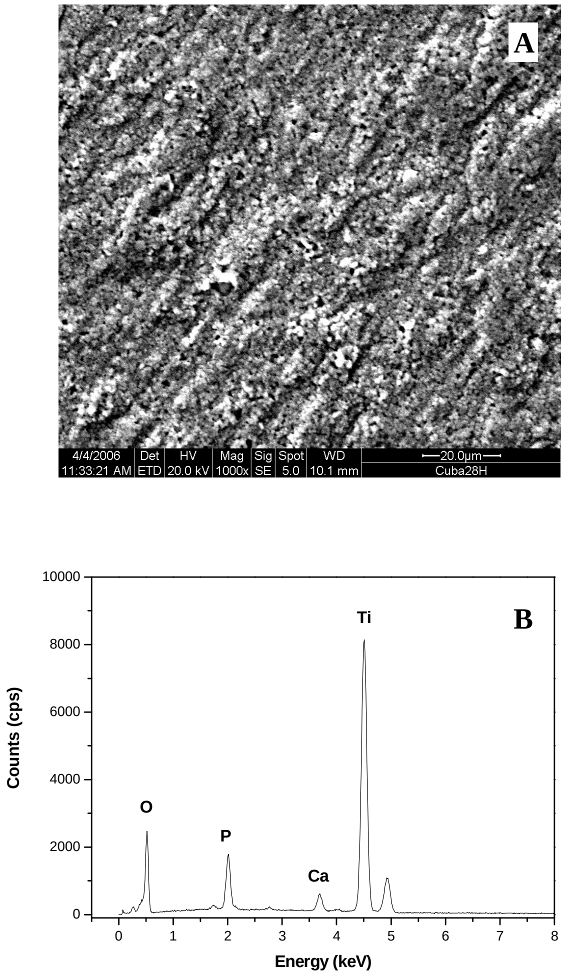

Fig. 5. Images of TiO_2 layer produced with 0.1M Na_2HPO_4 solution as electrolyte after the hydrothermical treatment with suspension of $Ca(OH)_2$ during 24h at 60ºC: a) SEM micrograph and b) EDS microanalysis. Magnification = 1000x.

Figure 6a shows a micrograph of the hydrothermically treated titanium oxide and Figures 6b and 6c show EDS mappings of the same region for calcium and phosphorous elements respectively. As one can observe, P and Ca are homogeneously distributed on the surface.

Low-angle X-ray diffraction analysis was performed for all surfaces showing the presence of anatase as the main allotropic titanium oxide phase. The spectrum obtained for the film produced with Na_2HPO_4 (0.1M) is shown in Figure 7. Titanium oxide layers with this structural configuration are known to be more bioactive than others surfaces that present a mixture between rutile and anatase phases. However, an in vitro evaluation of the cellular behavior for this set of layers is needed to confirm this issue.

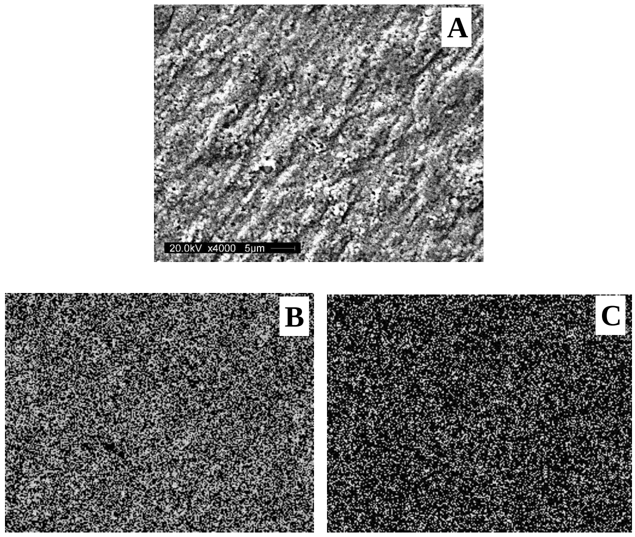

Fig. 6. SEM micrograph and microanalysis of TiO_2 layer: a) SEM micrograph, b) phosphorous and c) calcium mapping from EDS microanalysis produced with hydrothermical treatment. Magnification = 4000x. Bar = 5 µm.

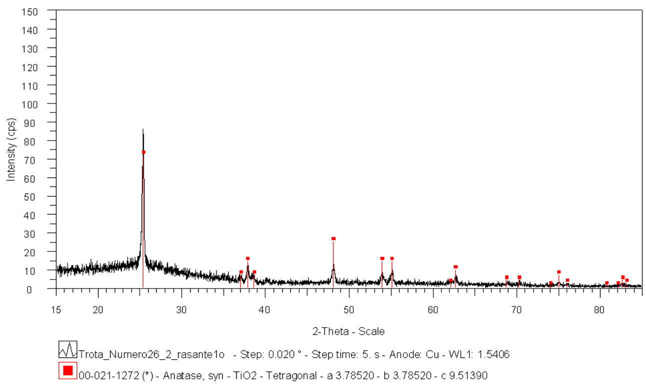

Figure 7. X-ray pattern of titanium oxide film that was produced by micro-arc oxidation using 0.1M Na_2HPO_4 solution as electrolyte.

4. CONCLUSION

Titanium oxide layers were produced onto pure titanium surface by micro-arc oxidation using a very simple AC power supply and a pulsed DC supply. The oxide layers produced with $Ca(CH_3COO)_2$ (0.3M), Na_2CO_3 (0.6M) and Na_2HPO_4 (0.1M) solutions showed a porous and homogeneous surface topography. Layers produced with $Ca(CH_3COO)_2$ (0.3M) showed the presence of calcium on the surface, while the ones produced with Na_2HPO_4 (0.1M) showed the presence of phosphorous. In the last case, a further hydrothermical treatment using a $Ca(OH)_2$ suspension was able to produce a surface rich in phosphorous and calcium, as observed by EDS microanalysis. It is known that the presence of these elements on the surface can be extremely beneficial to the growth of osteoblast cells and osseointegration, enhancing the bioactivity of the layer. Further investigation on this matter will be done to asses the cellular behavior over these surfaces. In addition, the presence of homogeneously distributed calcium on the titanium oxide surface can increase its biocompatibility properties. Low-angle X-ray diffraction revealed anatase-rich crystallographic structure for all the titanium oxide layers, which is known to stimulate osseointegration.

ACKNOWLEDGMENTS

The authors would like thank Prof. Renata Simão for providing helpful suggestions. This work was financially supported by CNPq/PROMETRO and FINEP.

REFERENCES

[1] D.M. Brunette, P. Tengvall, M. Textor, P. Thomsen, et al., Titanium in Medicine: Material Science, Surface Science, Engineering, Biological Responses and Medical Applications, Springer, 1st ed. (January 15, 2001).

[2] X. Liu, P.K. Chu and C. Ding, Materials Science and Engineering R, 47 (2004) 49-121.

[3] A.L. Yerokhin, X. Nie, A. Leyland and A. Matthews, Surface and Coatings Technology, 130 (2000) 195-206.

[4] Yong Han, Seong-Hyeon Hong and Kewei Xu, Surface and Coatings Technology, 168 (2003) 249-258.

[5] Y.-T. Sul, C.B. Johansson, Y. Jeong *et al.*, Clinical Oral Implants Research 13 (2002) 252-259.

[6] B. Yang, M. Uchida, H.-M. Kim et al., Biomaterials, 25 (2003) 1003-1010.

[7] R. Rodriguez, K. Kim, J.L. Ong, J. Biomed. Mater. Res. A., 65 3 (2003) 352–358.

[8] Y.-T. Sul, C. Johansson, E. Byon and T. Albrektsson, Biomaterials, 26 (2005) 6720–6730.