Understanding Growth Mechanisms and Tribocorrosion Behaviour of Porous TiO₂ Anodic Films Containing Calcium, Phosphorous and Magnesium

Fernando G. Oliveira^{*1,2}, Ana R. Ribeiro^{2,3}, Geronimo Perez⁴, Bráulio S. Archanjo⁴, Cristol P. Gouvea⁴, Joyce R. Araújo⁴, Andrea P. C. Campos⁴, Alexei Kuznetsov⁴, Clara M. Almeida⁴, Márcia M. Maru⁴, Carlos A. Achete⁴, Pierre Ponthiaux⁵, Jean-Pierre Celis⁶, Luis A. Rocha^{1,2,7}

¹ Center MicroElectroMechanical Systems (MEMS-UMinho), Department of Mechanical Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

² IBTN/Br – Brazilian Branch of the Institute of Biomaterials, Tribocorrosion and Nanomedicine, Universidade Estadual Paulista – UNESP, Av. Eng. Luiz Edmundo Carrijo Coube, 17033-360 Bauru, São Paulo, Brazil

³ Diretoria de Metrologia Aplicada às Ciências da Vida, Grupo de Bioengenharia, Instituto Nacional de Metrologia, Qualidade e Tecnologia, Av. Nossa Senhora das Graças 50, 25250-020 Duque de Caxias, Rio de Janeiro, Brazil

⁴ Divisão de Metrologia de Materiais, Instituto Nacional de Metrologia, Qualidade e Tecnologia, Av. Nossa Senhora das Graças 50, 25250-020 Duque de Caxias, Rio de Janeiro, Brazil

⁵ Laboratoire Génie des Procédés et Matériaux, École Centrale de Paris, Grande Voie des Vignes, 92290 Chatenay-Malabry, France

⁶ Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium

⁷ Faculdade de Ciências, Departamento de Física, Universidade Estadual Paulista - UNESP, Av. Eng. Luiz Edmundo Carrijo Coube, 17033-360 Bauru, São Paulo, Brasil

*Corresponding author:

Fernando G. Oliveira

Center MicroElectroMechanical Systems (MEMS-UMinho)

University of Minho - Campus Azurém

4800-058 Guimarães

PORTUGAL

e-mail: fernando@dem.uminho.pt

Abstract

The growth of the dental implant market increases the concern regarding the quality, efficiency, and lifetime of dental implants. Titanium and its alloys are dominant materials in this field thanks to their high biocompatibility and corrosion resistance, but they possess a very low wear resistance. Besides problems related to osseointegration and bacterial infections, tribocorrosion phenomena being the simultaneous action between corrosion and wear, are likely to occur during the lifetime of the implant. Therefore, tribocorrosion resistant surfaces are needed to guarantee the preservation of dental implants.

This work focused on the incorporation of magnesium, together with calcium and phosphorous, in the structure of titanium oxide films produced by micro-arc oxidation (MAO). The characterization of morphology, chemical composition, and crystalline structure of the surfaces provided important insights leading to 1) a better understanding of the oxide film growth mechanisms during the MAO treatment; and 2) a better awareness on the degradation process during tribocorrosion tests. The addition of magnesium was shown to support the formation of rutile which improves the tribocorrosion properties of the surfaces.

Keywords: titanium; surface modification; micro-arc oxidation; dental implant; tribocorrosion

1. Introduction

Over the last decades, the worldwide dental implant market has been on the rise. This trend is expected to continue over the next years with a global yearly growth rate of 10 % from US\$ 3.4 billion in 2011, to reach values around US\$ 6.6 billion in 2018. [1] The driving force for this evolution has been the constant increase in life expectancy, as well as an increased concern over the oral hygiene. Also, the advances in dental technology are producing more attractive and efficient solutions to convince patients to opt for a dental implant.

Despite the high overall success rate of dental implants, some failures still occur. In a recent analysis by Hujuel et al. [2], failures of two dental implant brands were reported to range between 4.3 % (porous oxidized surface) and 8.2 % (chemically altered surface). Implant dentistry is a complex field, and the success/failure ratio will always be dependent on the patient host conditions, surgery procedures and material properties. [3, 4]

From the beginning of modern implantology by Branemark in the 1960's [5] to modern days,

titanium-based materials have been used for the production of dental implants, being in

commercial use nowadays. [6, 7] The evolution of dental implants went from the use of

simply machined titanium surfaces (still in use), to highly modified and functionalized surfaces, with a wide range of surface properties. [6, 8] However, most studies found in literature regarding surfaces for dental implants, only show concern about the osseointegration process, while other significant aspects, such as tribocorrosion have been left aside. [9]

Actually, titanium-based materials, represent the vast majority of the materials used in implant dentistry, due to their good mechanical properties, high corrosion resistance and excellent biocompatibility resulting from the spontaneous formation of a stable and inert oxide layer on its surface. [10] Nevertheless, tribological/tribocorrosive conditions may easily wear out this passive layer, leading to an increased corrosion, an accelerated wear and the ejection of wear debris to the surrounding environment, [11] with its deleterious effects reported in literature. [12, 13]

In fact, tribocorrosion (simultaneous wear and corrosion) is a concern in this kind of applications. Avoiding tribocorrosion damages is a target in today's dental implant practice, as the implants are submitted to tribological contacts with the bone during the implantation [14] and to physiological loads during mastication. [15] Also the complex biological environment accounts for intricate corrosion processes that synergistically enlarge and are enhanced by wear phenomena. [16, 17]

A possible way to overcome this problem is to modify the surface of titanium to create new tribocorrosion resistant surfaces, while maintaining/improving the adequate biological properties. Presumptions adopted in this work for the development of new surfaces were based on the abundant literature about surface properties and biological behavior of titanium alloys for biomedical implants. The performance of these devices is mainly driven by changes in either topography (roughness, porosity) or chemical composition (incorporation of bioactive elements). [8]

Surface modifications of titanium are widely reported in literature, can be achieved by using different techniques. [18-24] In this paper, micro-arc oxidation (MAO) was used to create thick, adherent, and porous titanium oxide films on titanium which are known to possess good biological properties. Regarding this technique, the work developed by Ishizawa and Ogino [25] is a major landmark. They successfully obtained a bioactive anodic titanium oxide film, containing bioactive elements with a Ca/P ratio similar to the one found in hydroxyapatite. The mechanism of titanium oxide growth under micro-arc oxidation conditions is well known and explained in previous works. [26-28] Briefly, the anodic polarization induces the growth of a titanium oxide film. At weak spots in the oxide (cracks, locals of high tension concentrations), highly energetic micro arcs start to appear, causing a localized melting of the oxide, and leaving a hole for each occurrence. The melted oxide, in contact with the electrolyte, solidifies rapidly, allowing some elements from the electrolyte to be incorporated in the new oxide structure. The high temperatures and pressures achieved during the process, contribute to the formation of crystalline phases, such as anatase and rutile, or even amorphous titania. Furthermore, the frequent micro arcs through the oxide, can have a calcination effect on the underlying layers, which become heated due to the low thermal conductivity of the oxide, and this facilitates the transformation of anatase into rutile. According to Wang et al. [28] this transformation becomes more noticeable at extended film growth duration in opposition to shorter times.

Recently, dos Santos et al. [29] produced and characterized porous titanium oxide anodic layers. Further analysis revealed an hydrophilic surface and the absence of cytotoxic effects during in vitro experiments.

The introduction of magnesium in bioactive coatings has been shown to increase osteoblast adhesion and differentiation through an integrin mediated mechanism, resulting in higher percentage of bone-to-implant contact. [30-32]

But, regardless of the amount of works on this subject, the tribocorrosion behavior and mechanisms are still not properly characterized. Regarding titanium without any specific surface treatment, Barril et al. [33] studied the fretting behaviour and the electrochemical responses of titanium as a passivating material. More recently, Doni et al. [34] have shown that the wear rate of Ti6Al4V alloy is about 45 times higher than for CoCrMo alloy (another material used in implantology, mainly in orthopaedics) under similar tribocorrosion conditions. Some authors [35-37] have tested the tribocorrosion behavior of titanium and titanium alloy in artificial saliva solutions of different pH's and fluoride contents. Souza et al. [38] were the first to investigate the role of biofilms in the tribocorrosion behavior of titanium surfaces. They concluded that biofilms are responsible for a reduction in the coefficient of friction, although a localized decreasing of the pH is responsible for a decrease in the corrosion resistance of the surface. Ramos-Saenz et al. [39] studied bone-implant contacts in thermally oxidized titanium alloys, which resulted in abrasion and adhesion wear mechanisms of these materials.

Some authors have already tried to characterize the tribocorrosion behavior of anodic titanium oxide films. E.g., Albayrak et al. [40] proposed a dual treatment consisting of nitriding followed by an anodizing to improve the tribocorrosion resistance of titanium, They showed that titanium nitride phases contributed for a better wear behavior, while duplex treated samples showed better corrosion properties thanks to the anodic TiO₂ layer. Alves et al. [41] studied several Plasma Electrolytic Oxidation (PEO) parameters and anodic film

characteristics, such as thickness and roughness, and their influence on the tribocorrosion of titanium surfaces. Garsivaz Jazi et al. [42] verified the improvement of tribocorrosion properties of anodic treated titanium alloy on using higher anodizing voltages. Yetim [43] used anodic oxidation in vacuum. He improved the wear behavior of titanium which was supposedly to be due to the lubricating properties of the oxide and the presence of rutile. In a previous work by Alves et al. [44], the important role of rutile in the improvement of tribocorrosion behavior was also referred.

This work attempts to achieve highly tribocorrosion resistant surfaces without compromising the biological properties. A detailed surface characterization was performed, and the discussion section emphasizes two important topics: firstly, the better understanding of the oxide film growth mechanism under MAO conditions, and secondly the better understanding of the degradation of these surfaces due to tribocorrosion.

2. Materials and Methods

2.1. Material

Commercially pure titanium (grade 2) sheet (Goodfellow) was cut into square shape 20x20x2 mm samples. Cleaning was performed in acetone during 5 min in ultrasonic bath. After drying, samples were chemically etched in highly concentrated acid solution containing HNO₃ and HF, for 5 s. Again, cleaning process was made by ultrasound in propanol (10 min) and water (5 min).

2.2. Surface modification

Micro-arc oxidation was performed in an aqueous electrolyte containing β -glycerol phosphate disodium salt pentahydrate (β -GP) (C₃H₇Na₂O₆P·5H₂O), calcium acetate monohydrate (CaA) (Ca(CH₃CO₂)₂·H₂O) and magnesium acetate tetrahydrate (MgA) ((CH₃COO)₂Mg·4H₂O) from Sigma-Aldrich. Concentrations of β -GP and CaA were established according to the experimental procedure followed in a previous work. [44]

Addition of magnesium was followed according to the concentration of Mg^{2+} and Ca^{2+} ions in the solution, based on some works referring the substitution role of magnesium for calcium in the Hydroxyapatite structure. [45-47] The ionic ratio $\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Ca}^{2+})$ in the electrolyte was controlled, varying from 0 to 12.5 %. Three different groups of MAO treated samples were tested, according to the molar concentration of magnesium acetate (MgA) in the electrolyte: 0 M (0MgA group), 0.01 M (0.01MgA group) and 0.1 M (0.1MgA group).

For the MAO treatment, a DC power supply (Agilent N5772A) was set at 300 V with a limiting current of 2.5 A. Samples (anode) were completely immersed in the electrolyte (surface area: 9.6 cm^2) and a platinum foil was used as cathode (surface area: 7.8 cm^2).

Distance between electrodes was fixed in 8 cm. The treatment was performed for 1 min at room temperature and under magnetic agitation.

2.3. Tribocorrosion experiments

Experimental design for the tribocorrosion tests was similar to the one presented in previous work by Alves et al. [44]

Samples were placed in an electrochemical cell and mounted on a pin-on-disk reciprocating sliding tribometer (CETR-UMT 2). Cp-Ti samples and anodized samples acted as working electrodes in a three electrode configuration completed with a saturated calomel electrode (SCE) ($\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{saturated KCl solution}$; $\text{SCE} = +244 \text{ mV/NHE}$) and a platinum electrode as reference and counter electrodes respectively. The electrolyte consisted of SBF solution [48] (NaCl 6,213 g/L; NaHCO_3 2.974 g/L; KCl 0.225 g/L; $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ 0.231 g/L; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.311 g/L; CaCl_2 0.292 g/L; Na_2SO_4 0.072 g/L; HCl $0.85 \times 10^{-3} \text{ M}$) used at 37°C to simulate oral environment.

Alumina balls ($\varnothing = 10 \text{ mm}$) were used as counterbody, sliding on the surface of the samples in a reciprocating way, with a displacement amplitude of 10 mm, a frequency of 2 Hz, and on applying a normal load of 1.5 N. Sliding time was 1,814 s corresponding to 7,256 contact events in each point of the wear track.

During the tribocorrosion tests, the variation of open circuit potential was measured before, during, and after the sliding using a Gamry Instruments potentiostat/galvanostat Reference 600.

Prior to sliding, samples were rested in the electrolyte for one hour to allow stabilization of OCP. At least three samples were tested for each set of testing conditions in order to guarantee the repeatability of the test.

2.4. Characterization

Surface morphology before and after the tribocorrosion tests was analyzed by scanning electron microscopy (SEM) with a FEI Quanta 200 equipped with a Genesis EDAX for energy dispersive spectroscopy (EDS) elemental analysis. Chemical composition of the oxide was measured in five different regions of each sample (2 samples per condition) using an acceleration voltage of 10 kV.

Roughness of the samples was assessed via 2D profilometry using a Dektak 6M profilometer from Veeco instruments (stylus radius = 0.7 μm). Wear profiles and topography of tribocorrosion tested surfaces were obtained by 3D profilometry with a Taylor Hobson profilometer (stylus radius = 2 μm) and the software TalyMapGold.

A WITec confocal AFM/Raman microscope with 532 nm wavelength laser light was used to perform combined AFM/Raman analyses. WSxM software was used for AFM image processing and analysis. [49]

X-ray diffraction to evaluate crystalline structures was performed with a Bruker D8 Focus diffractometer. Analyses were made with Co K α radiation (Fe filter) in the scan range 2θ from 10° to 60° , with step size of 0.02° and step time of 50 s. Data retrieved from diffractometer was treated with Rietveld refinement method using software Topas-Academic.

Cross-sections of the wear track area were observed in order to determine sub-surface deformation of the bulk material. Images were recorded using a Helios NanoLab 650 dual-

beam instrument with a gallium ion source for focused-ion beam (FIB) milling and a field emission gun scanning electron microscope for imaging.

Samples were prepared for transmission electron microscopy (TEM) analysis in the same dual-beam Helios Nanolab 650. TEM observation was made in a transmission electron microscope using a probe-corrected FEI TITAN 80-300 operated at 300 kV, equipped with a 2k×2k Gatan UltraScan 1000 CCD camera. Fast Fourier Transform was obtained from magnification-calibrated high resolution images with the Digital Micrograph software (Gatan Inc.).

Electrochemical behavior was evaluated with a Gamry Reference 600 Potentiostat by potentiodynamic polarizations in a similar three-electrode configuration as used in the tribocorrosion tests. Samples were immersed in SBF at 37 °C, for one hour to allow stabilization of corrosion potential and the polarization curves were acquired from cathodic to anodic domain at a scan rate of 1mV/s.

3. Results

3.1. Surface Characterization

The initial state of the cp-Ti reference samples was achieved by chemical etching of titanium as described in the experimental section. This treatment allowed the formation of a rough topography, evidencing the granular structure of titanium, while guaranteeing equal initial conditions for all samples, through the elimination of previous passive oxide films, and the growth of a new native oxide under controlled conditions. This initial surface state is shown in figure 1 (a), while the morphology of the anodized surface is shown in figure 1 (b).

The MAO treatment ended up in a porous anodic oxide film with similar structure, independently of the concentration of MgA added to the electrolyte. No differences in morphology or porosity (pore size, pore density, data not shown) were observed. Some cracks originated during the growth of the film are visible throughout the surface. Also the roughness values measured by profilometry were similar for all the MAO treatment conditions and

furthermore evidenced an increase in roughness from c.a. Ra 0.3 μm for Ti reference samples, to c.a. Ra 0.7 μm for MAO treated samples as perceived in the surface profiles of figure 1, for untreated titanium and MAO treated samples. The waved topography of the oxide layers are responsible for a large variation in thickness ranging from 3 to 6 μm in different zones of surfaces regardless of the processing conditions, as it will be discussed ahead.

The chemical composition analysis of the oxide film (figure 2) revealed that the amount of Mg incorporated in the film increased as the MgA concentration in the electrolyte rose from 0 M to 0.1 M. At the same time the amount of calcium and phosphorous present in the oxide, decreased. Therefore, the total incorporation of bioactive ions (Ca+P+Mg) in the anodic film was not significantly altered by the addition of MgA.

The titanium oxide created during the MAO treatment consisted of anatase and rutile, as revealed by the X-Ray Diffraction (XRD) spectra of figure 3. Peaks related to the bulk titanium also present in the graphic. Moreover, the addition of MgA to the electrolyte was responsible for an increase of rutile relative to anatase, despite anatase was still the dominant phase.

The quantitative analysis of the titanium oxide phases based on Rietveld refinement method, revealed an increase in the Rutile to Anatase ratio (R/A) at higher contents of MgA. The group with no addition of magnesium had R/A value of 0.25 (80 % anatase; 20 % rutile). In the samples 0.01MgA a slight increase in R/A value up to 0.28 (78 % anatase; 22 % rutile) was noticed. In samples 0.1MgA, the R/A value raised up to 0.75 (57 % anatase; 43 % rutile). Complementary to XRD experiments, coupled AFM-Raman analyses provided additional structural information at the microscopic scale that allowed one to infer about spatial distribution of anatase and rutile in the surface. As shown in figure 4(a), the samples containing higher amount of MgA present a more prominent Raman band corresponding to rutile at c.a. 450 cm^{-1} , confirming the XRD data. Figure 4(b) represents an AFM topographical analysis (30x30 μm) of the surface of a MAO treated sample, and figure 4(c)

presents a 3D view of that region. Figure 4(d) and 4(e) represent, respectively, the anatase and rutile distribution (bright areas) in the same region shown in figure 4(b). From the correlation of the four images (4(b), 4(c), 4(d) and 4(e)), one can conclude that anatase is evenly distributed through all the surface film, while rutile seems to be preferentially located in the higher zones around the major pores (“volcanoes”). Surface characteristics of the oxide layers did not allow for a proper measurement of the mechanical properties in different points of the oxide structure.

Figure 5(a) and 5(b) are Transmission Electron Microscopy (TEM) images of the cross section of the oxide film, and show two main regions concerning the structural arrangement of the oxide in a zone where the thickness was around 5 to 6 μm . This represented the highest value of oxide thickness recorded in different cross sections of MAO treated samples. Due to the irregular topography of the oxide, thickness was noted to vary from c.a. 3 to 6 μm , as already referred. The inner part of the oxide, is composed of a mixture of crystalline and amorphous material, while on top of the oxide, an amorphous region of varying thickness (200-500 nm) covers the entire surface of the oxide. The phase identification by HRTEM and Fast Fourier Transform (FFT) patterns of crystalline regions matched the findings obtained in the coupled AFM/Raman analysis. Small nanocrystals of rutile were observed near the top region of the oxide (figure 5(c)), in opposition to the bottom part of the film (figure 5(d)), where only anatase was found.

3.2. Electrochemical and Tribocorrosion behavior

Representative potentiodynamic polarizations curves in SBF solution are presented in figure 6, showing the variation of current density versus the applied potential for titanium and MAO treated samples. Two curves for each surface are presented, representing the range of variation of all the tests performed in each surface. All anodized samples presented good reproducibility in the cathodic domain and E_{corr} . Also, a well-defined passivation plateau is visible for all anodized samples with i_{pass} . However, for each condition, the range of variation

of the passive current density is of the order of half decade, with a relatively higher reproducibility observed for the samples not containing Mg. Anyway, when compared with pure titanium, MAO treatment caused a small increase in E_{corr} and significantly lower current densities in the passive domain.

Figure 7 shows representative curves of the evolution of the open circuit potential (OCP) before, during, and after tribocorrosion tests.

Before the start of the mechanical solicitations there is a distinctive behavior between MAO-treated samples and non-treated samples. In the absence of wear, the pure Ti has a lower OCP value, indicating a higher corrosion tendency, while all the MAO groups showed significantly higher OCP values (between c.a. 0 V/SCE and 0.2 V/SCE), due to the presence of a protective anodic film.

As soon as sliding starts, the OCP of the pure titanium samples undergo an abrupt decline, due to the destruction of the fragile passive film at the surface, therefore exposing bare titanium to the corrosive effects of the physiological solution. [17] For these samples, the OCP values during sliding stabilize around -1.3 V/SCE, presenting some oscillations usually attributed to the continuous mechanical depassivation and electrochemical repassivation, occurring simultaneously in the wear track. [50] After sliding, an uninterrupted repassivation process occurs in the wear track which eventually may lead to the complete recovery of the passive film and the return of the OCP values almost back to the level before the sliding test. [51]

For the MAO groups, two distinct behaviors are detected. Once sliding is started, a small and slow decrease in OCP values is noticed in the 0MgA and 0.01MgA groups. The ΔE being the difference in potential between the start up of sliding and the end of sliding, is approximately -0.4 V.

Also, all curves recorded for the 0.1MgA group reveal a slight linear decrease of OCP values throughout the entire sliding test. Nevertheless, the electrochemical behavior of all MAO

treated samples is undoubtedly better than the Ti group, from the point of view of both corrosion and tribocorrosion.

In figure 8, scanning electron microscopy (SEM) micrographs of the wear tracks of the four groups tested in this work illustrate the wear behavior of the surfaces. Wear tracks on reference Ti have well defined contours (detail in figure 8(a)), and reveal a high level of wear by abrasion and adhesion. In figure 8(a), the micrograph shows that the area inside the wear track has been mostly damaged by abrasion revealed by abrasion grooves caused by third body wear caused by detached particles. Despite the clearly visible abrasion mechanism, adhesion phenomena did also occur during the test, since a material transfer from the sample to the counterbody was observed after the sliding test.

For the three MAO treated groups, the same wear mechanisms took place independently of the treatment conditions. Figures 8(b), 8(c) and 8(d) show that only the outer part of the anodic film was damaged during sliding. Furthermore, the group with a higher content of MgA, presented the less damages at the surface.

In figure 9 the wear mechanisms of MAO treated groups submitted to tribocorrosion tests are considered. Despite the better behavior of 0.1MgA group, all the wear tracks presented the same characteristics; therefore it is reasonable to state that the same wear mechanisms were active on all treated groups.

Figures 8(b), 8(c), and 8(d) show that the sliding test only affected the top part of the anodic film. In figure 9(a) this assumption is confirmed since the top peaks of the film were erased, while the bottom part of the porous structure remained undamaged. Moreover, the material removed from the higher peaks of the rough surface remains entrapped in the recesses of the surface, filling up, and finally covering the porous structure as can be seen in figure 9(b). The inset image in 9(b) presents a cross section of the wear track area prepared and imaged by FIB, where the black arrows point to the wear debris deposited in the recesses of the porous structure and the white arrow signals some structural defects of the oxide (e.g. cracks).

Figures 9(c) and 9(d) reveal that the material erased from the top peaks can be sometimes smashed and pressed against the porous surface creating an accumulation of material that can be easily worn out. Furthermore, some sharp failures of the film are observed (figure 9(d)) which might be associated with the cracks referred to in figure 1(b) and the inset in figure 9(b). In some zones of the wear track (figure 9(c) and 9(d)), the counterbody caused a flattening of the wear track through the elimination of the higher peaks. This effect was also visible in the profilometry of the wear tracks on MAO treated sample (0MgA group) (see figure 10(a)) and etched titanium sample (Ti group) (see figure 10(b)).

The wear tracks on the reference Ti presented well defined contours and a significant depression after the tribocorrosion tests. The depth of the wear track reached a maximum of around 20 μm and its wear volume calculated by 3D profilometry was $96,5 \pm 2,1 \mu\text{m}^3$.

On the other hand, all groups of MAO treated samples presented wear profiles similar to figure 10(a). The wear track was barely visible so that the wear volume could not be calculated due to the high initial roughness of the anodic film. Anyway figure 10(a) shows that the counterbody interacted on the surface, and caused the leveling off of the higher peaks, and decreased the roughness inside the wear track area ($S_a = 1,15 \pm 0,05 \mu\text{m}$), when compared to the initial surface conditions, outside the wear track ($S_a = 1,55 \pm 0,10 \mu\text{m}$).

Recently, the study by Perret et al. [52] gathered some attention to the subsurface deformation of materials under tribocorrosion solicitations. Besides the synergism between wear and corrosion, the deformation of the subsurface material could affect both the mechanical properties and the electrochemical responses. In figure 11, cross sections of the wear tracks of untreated titanium and MAO treated sample (0.1MgA group) prepared and imaged by FIB are shown. The channeling effect, observed in FIB (Focused Ion Beam) images when collecting secondary electrons in crystalline samples, creates an orientation contrast, allowing an easy observation of grains at the microscale range. For untreated titanium (figure 11(a)), the deformation of near surface region is clearly visible, showing a gradient in the grain

deformation from the surface down to the bulk material. On the other hand, on MAO treated samples (figure 11(b)) the crystal structure of the bulk titanium remained unaltered, guaranteeing the mechanical integrity of the sample.

4. Discussion

This work aimed at the surface modification of titanium to produce highly wear/corrosion resistant surfaces for biomedical applications, without compromising the intrinsic biocompatibility of the material.. The understanding of growth mechanisms and the tribocorrosion behavior of the surfaces are the two main outputs of this work, and are addressed in the following subsections.

4.1. Growth mechanisms of titanium oxide films by MAO

MAO treated samples containing magnesium or not were produced and compared with acid etched surfaces, which provided an improved surface morphology comparable to the one on some commercial dental implants, and also allowing an increase in surface roughness, known to be suitable for cell adhesion. [53] Also the incorporation of bioactive elements such as calcium and phosphorous was achieved successfully. This incorporation has been reported to improve the biological performance of implant materials since they are elements natively present in bones. [54]

The study of the crystalline structure of the samples showed that anatase and rutile were present in the oxide, forming a nanocomposite. Their relative distribution varies as a function of film thickness and distance to surface, thus creating a graded structure. Based on the work of Wang et al. [28], the transformation of anatase to rutile is more prone to happen at longer processing durations. However, results presented here show that the addition of magnesium to the electrolyte can have the same effect, namely increasing the percentage of crystalline rutile. To explain this behavior, current vs. time plots during the MAO treatment were considered

(figure 12). Two main stages during the film growth can be identified. The first half of the graph shows a limiting current of 2.5 A ($\sim 0.26 \text{ A.cm}^{-2}$), meaning that in the first moments of the process, a high current contributes to the fast growth of the oxide film, and to a great extent of micro arcs appearing at the surface. As the oxide becomes thicker, its resistivity increases, therefore a more powerful driven voltage is needed to keep the high current. Eventually, the applied voltage reaches the equipment limit of 300 V (moment indicated by “ $t_{\text{gal/pot}}$ ” in the graph of figure 12) resulting in the decrease of current and reducing the number of micro arcs at the surface, even though the remaining sparks could be more energetic than the previous ones, and be the reason for the appearance of large sized pores.

In figure 12, the parameter $t_{\text{gal/pot}}$ corresponds to the time at which the current remains at its maximum value. Higher magnesium acetate additions cause $t_{\text{gal/pot}}$ to increase significantly (36 % increase from 0 MgA to 0.1 MgA. See Table 1), probably due to the increase in the conductivity of the electrolyte, causing a gradual increase in the rutile to anatase ratio, as higher currents remain for longer processing times. [28] This increase of the $t_{\text{gal/pot}}$ parameter is also related to an increase of the total charge ($Q = I \cdot t$) in the system, which is given by the integration of the curve seen in figure 12. Theoretically, this would influence the total amount of oxide formed during the process, with effects on the measured thickness and/or the compactness of the oxide layers. However, the increase of total charge did not account for a significant variation in the thickness of the oxide film as it ranges between 3 to 6 μm , independently of the different MAO treatment condition. Also, from the cross sections obtained in the samples from each group, it was not possible to conclude any visible effects in the compactness of the oxide.

The appearance of very high energetic discharges, could contribute to the formation of large and elongated pores, while the high temperatures and pressures generated by each spark could contribute to the preferential formation of rutile around these pores, in the higher zones of the oxide film as schematically shown in figure 13(a). The local melting of the oxide undergoes,

in contact with the electrolyte, an almost instantaneous re-solidification of the material at a very high cooling rate. The top part of the film is expected to re-solidify at first so quickly that an atomic rearrangement could not take place, what ends up in an amorphous layer. The cooling rate is expected to slow down as the distance from the interface film/electrolyte solution increases, meaning that conditions are created for the nucleation of small nanocrystals of anatase and rutile, as explained in figure 13(a), which end up in a nanocomposite gradient structure.

4.2. Tribocorrosion mechanisms in MAO treated surfaces

In the tribocorrosion tests, all MAO treated samples exhibit higher OCP values due to the protective effect of the oxide film. In the absence of wear an improved electrochemical behavior of MAO treated samples was confirmed by potentiodynamic polarizations (figure 6). According to recent works [55, 56], the analysis of these plots, and particularly the cathodic domains, can help on the interpretation of tribo-electrochemical results. It is known that the decrease of OCP during a tribocorrosion test is due to a galvanic coupling, established between the wear track (anodic) and the surrounding non-worn zone (cathodic area). Vieira et al. [55] highlighted two distinct situations: 1) galvanic coupling between the completely depassivated wear track and the surrounding area, or 2) a short range galvanic coupling between the depassivated areas and still passive zones (non-worn areas) within the wear track. Concerning the analysis of figures 8 and 9, one can conclude that etched titanium samples fall into the first category, while the MAO treated samples belong to the latter case. Papageorgiou [56] summarized the parameters influencing OCP evolution during tribo-electrochemical tests, as being: the evolution of anodic/cathodic areas; the amount of anodic current density (which is considered to be constant over time; and the kinetic properties of the test sample cathode (normally obtained by cathodic polarization of the sample in the absence of sliding). Therefore, the kinetic parameters of the cathodic areas during tribocorrosion tests, can be

deduced from the cathodic part of the plots presented in figure 6 through the calculation of Tafel constants and relation of anodic/cathodic areas. The plots for MAO treated samples, present a significant overlapping of the different curves in the cathodic domain, thus not allowing any direct inference on whether the cathodic kinetics are different for each group. Furthermore, the previous works by Vieira et al.[55], Papageorgiou [56] or Espallargas et al. [57] relied on several geometric correlations to estimate the evolution of the wear track area, considering a linear association between wear volume and sliding time, which is not applicable for the MAO treated samples studied in this work, as the graded composition of the oxide seen in figure 5, may account for different removal rates, according to the zone where the sliding is occurring.

As the electrochemical behavior was similar for all MAO treated conditions, the wear of the surface and the evolution of OCP decay during the tribocorrosion test can be related, to a great extent, to the mechanical properties of the oxide. For this assumption, the nanocrystalline gradient structure of the titanium oxide appears to be very important. From figures 7 and 8, one can conclude that rutile-rich oxides (0.1M MgA group) present a better tribocorrosion behavior, validated by either electrochemical measures or the evaluation of wear track damages. The good tribological properties of rutile-based titanium oxides was previously demonstrated in some works, [58, 59] and more recently applied to this same purpose. [43, 44]

The wear mechanisms on titanium oxides obtained by electrochemical methods were already reported. [43, 44] In the first moments of contact, the roughness of the oxide surface causes the contact to proceed only through the higher asperities. That generates elevated contact pressures due to the small contact area. This contact takes place at the amorphous superficial layer seen in figure 5(b), and schematically shown in figure 13(b). However these contact areas cannot withstand the high contact pressures, and are easily worn out, flattening of the contact, accommodating the opposing surfaces, increasing the contact area, and consequently

decreasing the contact pressure. Once this amorphous layer is worn out, the rutile preferentially located around the higher pores, in the form of a nanocomposite (rutile (harder and more resistant) + anatase (softer and more ductile) + amorphous), represents the first effective barrier against wear due to the better mechanical properties of the crystalline phase, specially the higher hardness of rutile. This rutile-rich layer slows down the degradation rate of the film, and contributes to the leveling off of the wear track profiles (figure 10). Besides the role of rutile, the presence of this nanocomposite layer can avoid the brittleness and cracking phenomena associated with harder materials (rutile) under loading conditions. During the wear of the upper rutile-rich layer, the inner zone of the oxide, containing amorphous and anatase phases can contribute to the accommodation of the stresses applied and preserve the mechanical stability of the film due to its softer nature caused by the decrease of rutile content in the inner zone. The excellent wear properties of the oxide can thus be linked not only to the presence of harder rutile, but also on the crystalline gradient structure, working as a cushion for the stresses applied during tribocorrosion tests.

Both bare titanium and MAO treated groups showed some signs of abrasive wear. However the contribution of this phenomenon was much more significant in the Ti group. Wear tracks on bare titanium samples presents very distinguishable grooves even at small magnification, originated by large third body particles detached from the surface. This effect is not so noticeable in the MAO treated groups mostly due to limited wear damages in the subsurface zones and also inside the porous structure.

The defects visible in figure 9(c) and (d), are still a concern due to the risk of detachment of micrometer-sized portions of material and brittle failure of the oxide, endangering the full integrity of the surface oxide. However, despite the increased brittleness associated with harder materials, significant wear improvements of rutile-rich titanium oxides are definitely worth to be considered in bio-tribocorrosion applications.

5. Conclusion

The addition of magnesium to titanium oxides containing calcium and phosphorous was successfully achieved using micro-arc oxidation. The mechanisms of film growth were addressed and explained in detail. The MAO treatment induced the formation of a nanocomposite gradient crystalline structure, and revealed a localized increase in rutile due to the addition of magnesium ions in the electrolyte.

Also, the presence of rutile and the shock absorbing properties of the nanocomposite gradient structure are thought to be determining factors for achieving an improved tribocorrosion behavior of the surfaces. Thus, guaranteeing good prospects for the application of MAO rutile-based titanium oxide coatings on dental implant surfaces.

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Figure Captions

Figure 1. SEM micrographs and surface profiles of etched titanium (a) and MAO treated surface (b). Microstructure of MAO treated sample (figure 1(b)) is representative of all three anodized conditions tested in this work.

Figure 2. Atomic percentage of bioactive ions incorporated into the anodic film measured by EDS.

Figure 3. XRD spectra of titanium oxides obtained by MAO treatment and reference to Rutile/Anatase ratio, measured by Rietveld method for each processing condition. Identification of crystalline phases: Ti) titanium; A) anatase; R) rutile

Figure 4. Raman spectra of MAO treated samples with indication of Anatase (A) and Rutile (R) raman bands (a); Topographical analysis of MAO treated sample by AFM (b); 3D view of area shown in b) (c); Anatase (d) and Rutile (e) distribution relative to the area shown in 4b

Figure 5. Bright field TEM images of a cross section of MAO treated sample (0.1MgA) showing two distinct structural regions along the thickness of the oxide film (a and b). HRTEM images of the region near the top of the oxide presenting a mixture of anatase and rutile (c) and near the interface with pure Ti, presenting only anatase (d). Insets in c and d show the FFT patterns of the respective images

Figure 6. Potentiodynamic plots of the variation of current density versus the applied potential for titanium and MAO treated samples.

Figure 7. Evolution of open circuit potential (OCP vs SCE) values before, during and after the tribocorrosion tests

Figure 8. Wear tracks of Ti group (inset shows a wider view of all wear track width, scale bar 500 μm) (a); and MAO treated groups: 0M MgA (b); 0.01M MgA (c); 0.1M MgA (d). All images at the same scale

Figure 9. Detailed SEM micrographs on wear mechanisms of MAO treated groups. Inset in figure 8(b) presents a cross section inside the wear track area prepared and imaged by FIB, with identification of wear debris (black arrows) and structural defects of the film (white arrow).

Figure 10. 2D profiles of the wear tracks of MAO treated surface (0MgA) (a) and etched titanium surface (b)

Figure 110. Subsurface deformation evaluated on cross sections of wear tracks prepared and imaged by FIB on untreated titanium (a) and MAO treated 0.1MgA (b).

Figure 12. Representative current vs. time curve from a micro arc oxidation process

Figure 13. a) Schematic illustration of the mechanisms involved in the growth of the porous layer. b) Tribocorrosion mechanism acting on the surface

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FIGURES

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Table 1. Electrochemical parameters of the MAO process for the different groups of samples

MgA concentration [M]	Tgal/pot [s]
0	27.54 ± 2.81
0.01	28.62 ± 2.38
0.1	37.41 ± 2.40