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Research Paper

Mechanical properties of anodic titanium films containing ions of Ca and P submitted to heat and hydrothermal treatment

Gabriel G. de Lima[a], *Gelson B. de Souza*[b], *Carlos M. Lepienski*[c], *Neide K. Kuromoto*[c,*]

[a]*Materials Research Institute, Athlone Institute of Technology, Athlone, Ireland*
[b]*Department of Physics, Universidade Estadual de Ponta Grossa – UEPG, Ponta Grossa, PR, 84030-900 Brazil*
[c]*Department of Physics, Universidade Federal do Paraná – UFPR, CP 19044, PR, 81531-990 Brazil*

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ABSTRACT

Anodic oxidation is a technique widely used to improve the bioactivity of Ti surface. In this study, micro-arc oxidation (MAO) was used to obtain an anodic film incorporating Ca and P ions to evaluate the effect of heat and hydrothermal treatment on the mechanical and *in vitro* bioactivity properties of these new layers. The MAO process was carried out using $(CH_3COO)_2Ca \cdot H_2O$ and $NaH_2PO_4 \cdot 2H_2O$ electrolytes under galvanostatic mode (150 mA/cm^2). The thermal treatments were made at 400 °C and 600 °C in air atmosphere while hydrothermal treatment was made in an alkaline water solution at 130 °C. These surfaces presented desired mechanical properties for biomedical applications owing to the rutile and anatase phases in the anodic film that are more crystalline after thermal treatments; which provided an increase in hardness values and lower elastic modulus. The dry sliding wear resistance increased by performing thermal treatments on the surfaces with one condition still maintaining the film after the test. Bioactivity was investigated by immersion in simulated body fluid during 21 days and hydroxyapatite was formed on all samples. Finally, lower values of contact angle were obtained for heat treated samples.

1. Introduction

The aging of worldwide populations is expanding faster than the last decade (Flaherty et al., 2007; Jin et al., 2015; Peine et al., 2015) and are significantly related to the increasing numbers of osteoporosis incidents. Fragility fractures owing to osteoporosis are one of the causes of mortality that implies social and economic burdens (Cummings and Melton, 2002; Serrano and Blasco, 2007). For these reasons, the substitution

*Corresponding author.
E-mail address:
kuromoto@fisica.ufpr.br (N.K. Kuromoto).

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and regeneration of bone tissue take up important place in tissue engineering field.

Titanium (Ti) and its alloys are widely used in implants for presenting good mechanical properties and excellent biocompatibility. The main factor of using titanium as a biomaterial from biocompatible metals is its low elastic modulus (~ 100 GPa) and, therefore, closer to the bone (10–40 GPa) (Niinomi, 2008). In addition, titanium has a layer of native oxide film which grows spontaneously on the surface on exposure to air (Kasemo, 1983) and determines the surface properties of a titanium implant. However, the concentration of hydroxyl groups in the oxide on the pure metal is very low. Thus, titanium surface modifications are necessary to make it bioactive. Surface modification can have different morphologies and varied properties of the substrate targeting specific applications (Liu et al., 2004; D. Wei et al., 2007).

Anodic oxidation, as surface modification for titanium oxide, has the advantage to produce an oxide layer with tailored properties, such as chemical and mechanical properties (Li et al., 2008). However, the oxide layer formed by the anodic oxidation presents bioactivity only if it is formed under dielectric breakdown (Yang et al., 2004). At voltages above the dielectric breakdown threshold, sparks occurs and the formed layer is more porous and less uniform. This process is known as micro-arc oxidation (MAO) or Plasma electrolytic oxidation (PEO). Using this technique, the best qualities of coatings can be synthesized with high hardness, adhesion strength and wear resistance than those obtained by the standard procedure (Yang et al., 2004). The coatings features can be controlled by adjusting the electrolyte parameters, such as temperature, composition, voltage, current, and time (Liu et al., 2004).

The literature has shown that the incorporation of ions in the oxide layer is beneficial for the nucleation kinetics of the hydroxyapatite (HA). Anodic films containing Ca and/or P ions induce new bone tissue and become bioactive (Laurindo et al., 2014; Liu et al., 2011; J. Wei et al., 2007). The bioactivity of oxide layers containing Ca and P depends on the existence of hydroxyl radicals and the release of Ca ions in the body fluid, raising the pH and the ionic activity factor. These features together favor the nucleation of hydroxyapatite (Chen et al., 2006). Anodic layers rich in Ca and P produced on Ti by MAO process also presents a significant improvement on corrosion resistance (Park et al., 2007).

de Souza et al. (2011) showed that anodic layers grown on titanium using electrolyte containing Ca–P present soft Ca–P rich areas, whereas the oxide layer itself had an elastic modulus close to the bone (~70 GPa). However, such Ca–P containing layer presented brittleness in scratch tests, which is removed under lower charge forces. The instability of the coating affects the stability of the prosthesis, since the generated particles cause inflammation at the implant site (Korkusuz and Korkusuz, 2004). In addition, recent studies show that due to heat or hydrothermal treatments on MAO films there is an improvement of the bioactivity of the films since the Ca ions incorporated in the oxidation process greatly affect the cellular response (Ryu et al., 2008; Yang et al., 2014). However, these studies with respect to anodic film obtained by MAO technique and subsequent thermal or hydrothermal treatment on surfaces containing Ca and P ions do not address important characteristics such as mechanical properties and corrosion resistance. These questions are relevant when the layers demand that is both bioactive and with needs to have good mechanical properties. Therefore, in the current study TiO_2 films were produced by anodic oxidation using Ca- and P-electrolytes based on the work carried out by de Souza et al. (2011) with posterior thermal and hydrothermal treatments to induce an improvement in the mechanical properties and bioactivity of these films.

2. Experimental

2.1. Sample preparation

Commercially pure titanium (grade 2, supplied by Ti Brazil – ASTM F67) samples were grounded using 400 and 600 SiC papers, followed by polishing with 6 μm diamond paste and colloidal silica suspension. The samples were successively washed with acetone, isopropyl alcohol, and distilled water in an ultrasonic cleaner for 30 min each step. The final dimension of the substrate was 10 mm × 10 mm × 1.0 mm.

The MAO process was made galvanostatically at room temperature in an electrolyte solution containing 0.14 mol/l calcium acetate monohydrate ($(CH_3COO)_2Ca \cdot H_2O$) and 0.06 mol/l sodium biphosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) in deionized water. The current density was 150 mA/cm^2 for 100 s. The voltage was recorded during the test and it increases from zero to about 400 V. Micro arcs were observed during anodization process when voltage increases to higher values.

2.2. Heat treatment and hydrothermal treatment

The thermal and hydrothermal treatments were used in order to induce structural changes in the anodic layers and evaluate the effects of heating on the mechanical properties of Ti anodic film. The thermal treatment was done using a muffle furnace. Samples were divided into two groups and labeled appropriately:

Sample were heated at 5 °C/min up to 400° and 600 °C staying at these temperatures for 1 h and allowed to cool in the oven. Such temperatures were chosen for presenting the best results in accordance with the literature in terms of bioactivity (Tao et al., 2009; D. Wei et al., 2007). Hydrothermal treatment was performed in a conventional autoclave at 130 °C and P_{MAX} of 80 kPa. The samples were immersed in 50 ml falcon tubes with deionized water and addition of NaOH addition to adjust the pH value between 10–11, then the tubes were immersed in deionized water contained in an autoclave for 5 h (Alsaran et al., 2011; Vangolu et al., 2011).

Samples codes in this research paper are defined as AO – Anodic oxidation; AO+HT – Anodic oxidation with hydrothermal treatment; AO+TT400 °C – Anodic oxidation with thermal treatment at 400 °C; AO+TT600 °C – Anodic oxidation with thermal treatment at 600 °C.