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Research paper

Tribo-mechanical characterization of rough, porous and bioactive Ti anodic layers

Gelson B. de Souza[a,*], *Gabriel G. de Lima*[b], *Neide K. Kuromoto*[b], *Paulo Soares*[c], *Carlos M. Lepienski*[b], *Carlos E. Foerster*[d], *Alexandre Mikowski*[b,e]

[a] *Sciences Department, Universidade Estadual de Maringá, 87020-900, Maringá, PR, Brazil*
[b] *Physics Department, Universidade Federal do Paraná, 81531-990, Curitiba, PR, Brazil*
[c] *Mechanical Engineering Department, Pontifícia Universidade Católica do Paraná, 80215-901, Curitiba, PR, Brazil*
[d] *Physics Department, Universidade Estadual de Ponta Grossa, 84030-900, Ponta Grossa, PR, Brazil*
[e] *Mobility Engineering Center, Universidade Federal de Santa Catarina, 89219-905, Joinville, SC, Brazil*

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ABSTRACT

Rough and porous titanium oxide layers, which are important features for improving the osseointegration of Ti implants with bone tissues, are obtained through the technique of anodic oxidation. The thicknesses of such coatings are typically in the order of micrometers, and their mechanical characterization can be assessed by instrumented indentation, provided that the composite nature of the surface is considered. Titania anodic layers were produced on Ti under galvanostatic mode using Ca–P-based electrolytes (a mixture of $(CH_3COO)_2Ca{\cdot}H_2O$ and $NaH_2PO_4{\cdot}2H_2O$), employing current densities (J) of 150 mA/cm^2 and 300 mA/cm^2. The structure and morphology were characterized by X-ray diffraction (XRD), scanning electron microscopy with electron dispersive X-ray spectroscopy (SEM/EDS), and profilometry, and the chemical features were characterized by X-ray photoelectron spectroscopy (XPS). TiO_2 layers presented the crystalline phases rutile and anatase, and incorporation of Ca and P presented as a calcium phosphate compound. The porosity, roughness, and thickness increased with J. Analytical methods were employed to obtain the modified layers' elastic modulus and hardness from instrumented indentation data, deducting the substrate and roughness effects. The elastic moduli were about 40 GPa for both values of J, which are similar to the values for human bones (10–40 GPa). The hardness decreased with indentation load, varying from 5 GPa at the near surface to 1 GPa at the layer–substrate interface. Such hardness behavior is a consequence of the surface brittleness under normal loading. Additional scratch tests using an acute tip indicated that the layer integrity under shear forces was 220 mN ($J = 150$ mA/cm^2) and 280 mN ($J = 300$ mA/cm^2). TiO_2 layers produced with both current densities presented good results for *in vitro* bioactivity tests using simulated body fluid (SBF) solution, which can be attributed to a combined effect of the microstructure, layer porosity, and hydroxyl radicals in plenty at the near surface.

* *Corresponding author.* Tel.: +55 44 3522 1851.
E-mail addresses: gbsouza@uem.br, gelbsou@yahoo.com.br (G.B. de Souza).

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1. Introduction

Among several methods that have been studied to improve titanium osseointegration with living tissues (Chu et al., 2002; de Jonge et al., 2008; Liu et al., 2004), the production of titania coatings by anodic oxidation processes offers some interesting features. Porous layers can be produced using different electrolytes, such as H_2SO_4, H_3PO_4 and Ca–P-based solutions, and setting up the oxidation parameters (voltage, current density, and time) to allow the dielectric rupture of the layer (Sul et al., 2002). Besides the improved adhesion with the substrate, the porous structure of such anodic oxide layers favours cell adhesion, and, in the presence of body fluids, nucleates hydroxyapatite on their surfaces (Fini et al., 1999; Frauchiger et al., 2004; Kuromoto et al., 2007; Li et al., 2004; Liu et al., 2004; Yang et al., 2004; Zhu et al., 2001). The hydroxyapatite nucleated on the biomaterial surface can work as the means to a direct implant–bone connection, without intermediate fibrous tissues, as verified by Nishiguchi et al. (1999, 2001) using *in vivo* tests. According to the literature, these conditions promote a better fixation strength, which can be achieved in earlier periods of *in vivo* implantation (Liu et al., 2004; Nishiguchi et al., 1999, 2001; Paital and Dahotre, 2009). The hydroxyapatite nucleation is mostly attributed to the large number of hydroxyl radicals at the oxide layer, produced during the dielectric rupture regime, which triggers interactions between calcium and phosphates from the body fluid with the surface (Liu et al., 2004; Chen et al., 2006).

In addition to the osseointegration capability, the mechanical properties of anodic layers are also important features to ensure long implant lifetime (Liu et al., 2004; Mändl and Rauschenbach, 2002). The recovery of a bone that has been damaged by fracture or surgical processes is influenced by the mechanical stress on it. Stress shielding, i.e., the reduction or absence of mechanical stress in the bone, causes atrophy or absorption of the bone tissue. Such a detrimental effect can also occur in artificial prosthesis, even if the implant site is under regular loading conditions by the patient. In this situation, stress shielding is due to large differences between the elastic moduli of the bones and the implant, which make the load transfer from the body to the prosthesis difficult. A reduction in the mechanical stresses occurs around the implant, inducing bone resorption, osseous atrophy, and even prosthesis release (Niinomi et al., 2004). Among the metals used as biomaterials, titanium and its alloys (such as Ti–6Al–4V) present the lowest elastic modulus (∼100 GPa), which is considered a biomechanical benefit to prevent stress shielding (Liu et al., 2004; Niinomi, 2008). However, this elastic modulus is still five times larger than that of cortical human bone (∼20 GPa). Studies have been conducted in order to obtain novel Ti alloys with stiffness closer to that of bone tissues (Niinomi, 2003). On the other hand, the load transference can be improved by tailoring the implant surface properties, since mechanical interactions are critical at the interface between artificial material and living tissues.

Instrumented indentation is an appropriate method to mechanically characterize thin coatings and modified surfaces (Oliver and Pharr, 2004), and it has been used in the study of bioactive layers (Santos Jr. et al., 2007; Soares et al., 2008). However, the determination of the elastic modulus (*E*) and hardness (*H*) of the porous anodic layers is not simple. Substrate effects influence the values measured by instrumented indentation (Saha and Nix, 2002), and roughness and porosity cause inaccuracies in the *E* and *H* profiles (de Souza et al., 2010a).

Another situation concerning the implant surfaces also demands special attention. During fixation or normal use, the implants are submitted to wear mechanisms by shear forces. There is a (small) chance that the released ionic Ti will combine with biomolecules to cause cytotoxicity, allergy, and other biological influences (Hanawa, 2004). Notwithstanding, the detachment of coatings and debris generation are highly undesirable, since fragments can cause reactions and the necessity of prosthesis replacement (Korkusuz and Korkusuz, 2004).

In this work, commercially pure Ti was anodically oxidized using Ca- and P-based electrolytes. The surface morphology, structural, and chemical features were evaluated, as well as the *in vitro* bioactivity. The layers' tribo-mechanical behavior was studied by using an instrumented indentation device. Analytical methods were employed to obtain the elastic modulus and hardness of the modified layers from indentation data, by taking into account the substrate and roughness effects on the measured values.

2. Materials and methods

Mechanical characterization at the nanoscale (elastic modulus and hardness calculated from the instrumented indentation data) is strongly affected by the presence of asperities (de Souza et al., 2006, 2010a). Therefore, in order to minimize the roughness effects on the mechanical property results, the Ti samples were prepared to a mirror-like finish, thereby limiting the surface texture to the one produced by the anodic oxidation process. Commercially pure titanium (grade 2) samples were grounded using #600 SiC paper, followed by polishing with 9 μm diamond paste and colloidal silica suspension.

The plates were successively washed with acetone, isopropyl alcohol, and distilled water in an ultrasonic cleaner. Samples were then galvanostatically anodized at room temperature in an electrolytic 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. Two different current densities were applied for 100 s: 150 and 300 mA/cm^2. From this point on, the samples will be denominated by their respective current densities.

The morphology of the layers was analyzed using scanning electron microscopy (SEM) with electron dispersive X-ray spectroscopy (EDS). Structural changes were characterized by X-ray diffraction (XRD) in θ–2θ geometry, using Cu Kα radiation and scan velocity 0.24°/min. The diffraction peaks were indexed using the Inorganic Crystal Structure Database (FIZ, 2008). The average roughness (R_a) and layer thickness were determined using a stylus profilometer. The surface profile was integrated by the ensemble of 2000 data points assembled across the scan length of 1000 μm, in ten different surface sites. The value of R_a was calculated according to the literature (Bhushan, 2001).