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Niobium treated by Plasma Electrolytic Oxidation with calcium and phosphorus electrolytes

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ABSTRACT

Niobium plates were electrochemically treated by Plasma Electrolytic Oxidation (PEO) with electrolytes containing phosphorous and/or calcium. Three different electrolyte and experimental parameters were used forming three different surfaces. Film morphology, thickness, and chemical composition were analyzed by scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). A profilometer and the sessile drop technique measured the average surfaces roughness (Ra) and contact angles respectively. X-ray diffraction technique (XRD) analyzed the oxide crystallinity, and scratch tests evaluated the film adhesion. All oxidized surfaces presented pores, without observed cracks. Comparing the different experimental conditions, films obtained with phosphoric acid (P100) show superficial pores, phosphorus incorporation, high hydrophilicity, non-crystalline oxide formation, and good scratch resistance. Films treated with calcium acetate electrolyte (Ca100), compared to P100 exhibit smaller size pores and film thickness, smaller hydrophilicity, and lower scratch resistance. They also demonstrated higher oxide crystallinity, calcium incorporation, and pores interconnections. When the PEO was executed with a blended electrolyte containing calcium acetate and phosphoric acid (Ca50P50) the formed films presented the highest thickness, high phosphorus incorporation, and the lowest contact angle compared with other films. In addition, the pores size, the scratch resistance, calcium incorporation, and oxide crystallinity present intermediate values compared to P100 and Ca100 films. Film crystallinity seems to be influenced by calcium incorporation, whereas, hydrophilicity is phosphorus amount dependent. The pores amount and their interconnections reduced the scratch resistance. Surface features obtained in this work are largely mentioned as positive characteristics for osseointegration processes.

1. Introduction

Niobium and niobium alloys exhibit a wide range of applications in science, technology, and industrial areas. The niobium versatility is consequence of physical, mechanical, chemical and biological properties combination, such as: high melting and boiling point, moderate density, good ductility and fabricability, low vapor pressure, low thermal-neutron absorption cross section (Sankar et al., 2009), high corrosion resistance (Matsuno et al., 2001), superconductivity (Eisenstein, 1954). When added to titanium it is possible to form biomaterials with low elastic modulus (Abdel-Hady Gepreel and Niinomi, 2013; Niinomi, 2008, 2002), non-toxic behavior (Dsouki et al., 2014; Zuldesmi et al., 2014), good biocompatibility (Eisenbarth et al., 2006; Matsuno et al., 2001), and osteoconductivity (Matsuno et al., 2001).

Biocompatibility and corrosion resistance properties are not directly related to Nb bulk. They are attributed to the superficial protective compact barrier-type oxide layer (mostly niobium pentoxide) (Mazur et al., 2015) that rapidly and tightly covers the entire niobium surface when the metal are exposed in environments containing oxygen (Sowa et al., 2013). In other words, the key for the possible niobium implant biological success is to modify properly niobium pentoxide layer. If surface topography (Anselme, 2000; Gupta et al., 2014), porosity (Kuboki et al., 1998), wettability (Bacakova et al., 2011; Park et al., 2012), and bioactivity (Yan et al., 1997) are in good suitable ranges, a bone-bonding mechanism between bone-implant can occur (osseointegration) (Kokubo and Takadama, 2006).

A way to reach suitable osseointegration features is to modify the oxide layer employing an appropriate surface treatment. Plasma Electrolytic Oxidation (PEO) is an electrochemical process that produces oxide layers over the metals, enabling to grow a thick oxide layer,

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that can be rough, porous, crystalline or amorphous or crystalline/amorphous (Cimenoglu et al., 2011; Galvis et al., 2015; Iván et al., 2015; Pereira et al., 2014; Yang, 2004). This treatment may be considered an intermediate process between low voltage anodizing and dry high plasma energy coating (Lukiyanchuk et al., 2014; Walsh et al., 2009). The simplest PEO experimental configuration consists of two electrodes connected to a voltage source immersed in an electrolyte. Under relatively low voltages, the anodizing phenomenon follows Faraday's Law and Ohm's Law (Walsh et al., 2009). When applied voltage exceeds the dielectric rupture limit of the oxide will initiate the PEO process and the electric current promotes an event series characterized by arc-plasma formation (Liu et al., 2010, 2004; Wang et al., 2015; Yerokhin et al., 1999). PEO treatment is regarded as low safety hazard process, quick, easy (Curran and Clyne, 2006), inexpensive (Sowa et al., 2016) and suitable for coating of complex geometries (Dorozhkin, 2015). Chemical species, such as calcium and phosphorus from the electrolyte can be incorporated into the layer, which may increase biocompatibility and provide bioactivity (Lugovskoy and Lugovskoy, 2014; Sowa et al., 2015).

There are some studies of PEO technique applied to niobium (Sowa et al., 2013, 2016; Stojadinović et al., 2015), however, this treatment applied to niobium in biomaterial research area is rare (Sowa et al., 2016). Thus, in the present paper, niobium plates were oxidized by PEO with electrolytes containing Ca and P and the experimental parameters were regulated to attain favorably: film formation, morphology, thickness, chemical composition, crystalline systems, wettability, and film adhesion for application as biomaterial.

2. Materials and methods

Nb samples of (20 × 15) mm were obtained from 99,8% (wt%) niobium sheet with 1.0 mm thickness. Samples were dry-sanded using successive SiC sandpaper (grit #300, #400 and #600), ultrasonically cleaned for 15 min in propanone, ethanol, distilled water and dried at 40 °C for 24 h.

2.1. Surface treatment-PEO

All oxidations were carried out using Nb as the counter-electrode under potentiostatic mode (constant voltage and free electrical current), electrolyte agitation, at room temperature, and during 60 s.

A programmable DC power supply Chroma 62000P provided constant voltage. A magnetic agitator kept the electrolyte under constant agitation into the electrolytic cell (acrylic box). The contact of the sample with the electrolyte is provided by a hole of defined area on the lateral wall of the acrylic box. The samples (anode) were pressed against a Viton O-ring, at the wall hole of electrolytic cell to stanch it. In this manner, the electrode area in contact with the electrolyte is constant for all measurements.

Several previous tests assisted the choose of the experimental parameters and PEO occurred under three different conditions:

1. **Code P100:** niobium sample was oxidized under 350 V during 60 s in phosphoric acid electrolyte plus hydrogen peroxide: *0.8 mol l^{-1} H_3PO_4 + 3 mol l^{-1} H_2O_2.*

2. **Code Ca100:** niobium sample was oxidized under 170 V during 60 s in calcium acetate electrolyte*: 0.5 mol l^{-1} Ca $(CH_3CO_2)_2 \cdot H_2O$, 170 V/60 s (code = Ca100).*

3. **Code Ca50P50:** niobium sample was oxidized under 350 V during 60 s in the electrolytes mixture *(% in volume): 50% 0.5 mol l^{-1} Ca $(CH_3CO_2)_2 \cdot H_2O$ + 50% 0.8 mol l^{-1} H_3PO_4 + 3 mol l^{-1} H_2O_2. This mixture produces a suspension containing calcium phosphates with white color.*

2.2. Morphology, crystallinity, chemical composition, roughness, wettability, and cross-sectional images

Oxidized surfaces, film thickness, and scratch groove morphologies were analyzed by scanning electronic microscopy (SEM – Jeol JSM-6360LV and TESCAN VEGA3 LMU trademarks). Chemical compositions were obtained using electron dispersive X-ray spectroscopy (EDS, a system coupled to the TESCAN SEM), running at 15 kV to analyze the anodic film and at 8 kV in line mode along the groove produced by nanoscratch test. Crystalline phases were identified by X-ray diffraction (XRD) in Bragg–Brentano geometry using a Shimadzu XRD-7000 equipment. XRD measurements were collected with Cu Kα radiation (λ = 1.54 Å), operating at 40 kV and 20 mA in a range between 20° and 80°, with a copper monochromator coupled and scan speed of 0.8°/minute. Average surface roughness (Ra) was measured by a Dektak 150 Profilometer, applying 6.86 × 10^{-2} mN of constant force and crossing a distance of 500 μm during 30 s. Contact angle measurements were performed with a goniometer (*Krüss Easy Drop*) by Sessile Drop technique, using 1 μL of distilled water. Cross-sectional SEM images were obtained of samples inlay into a plastic resin.

2.3. Nanoscratch tests

Nanoscratch tests with a Nanoindenter XP-MTS, using a Berkovich tip, evaluated the mechanical behavior and film adhesion. The tests were performed applying a linearly increasing load in the range from 0 to 400 mN, covering a distance of 600 μm on the oxidized layer.

The Fig. 2.3.1 shows an example of profiles produced by the scratch test. Firstly, a low load is applied on the surface without producing modifications (solid line). Secondly, a ramping load (dash line) is applied modifying the surface (dot line – more spaced), and finally, also a low load applied through the tip verifies the surface changes (dot line).

3. Analysis and discussion

3.1. Morphology and chemical composition

Figs. 3.1.1–3.1.3 show the Nb surface morphologies and EDS spectra after PEO treatments. A porous film with spherical pores formed uniformly dispersed in P100 and Ca100 sample surfaces. Ca50P50 porous layer is a combination of rounded pores and elongated pores. P100 diameter pores can achieve larger diameters than 5 μm. Ca100 surface morphology has smaller pores (the diameter may measure as far as 1.5 μm), whereas Ca50P50 has an intermediate pore size. Visible at the SEM resolution, cracks were not observed over oxidized samples. Open pores obtained by PEO treatment increase surface area contact, mimics

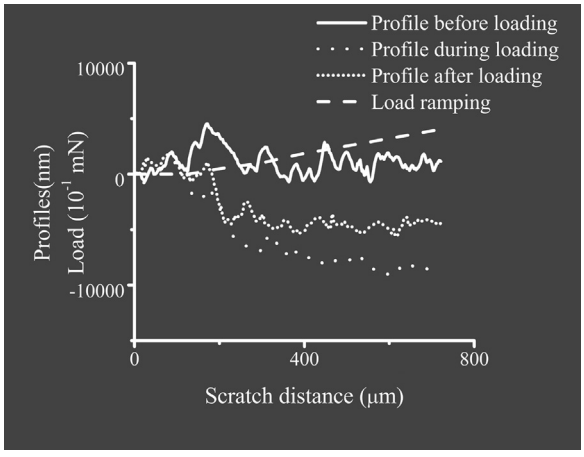

Fig. 2.3.1. Profiles obtained by nanoscratch tests: before loading, during loading, after loading, and the load ramping.