Surface characterization of anodized zirconium for biomedical applications

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ABSTRACT

Mechanical properties and corrosion resistance of zirconium make this material suitable for biomedical implants. Its good *in vivo* performance is mainly due to the presence of a protective oxide layer that minimizes corrosion rate, diminishes the amount of metallic ions released to the biological media and facilitates the osseointegration process.

Since the implant surface is the region in contact with living tissues, the characteristics of the surface film are of great interest. Surface modification is a route to enhance both biocompatibility and corrosion resistance of permanent implant materials. Anodizing is presented as an interesting process to modify metal surfaces with good reproducibility and independence of the geometry.

In this work the surface of zirconium before and after anodizing in 1 mol/L phosphoric acid solution at a fixed potential between 3 and 30 V, was characterized by means of several surface techniques.

It was found that during anodization the surface oxide grows with an inhomogeneous coverage on zirconium surface, modifying the topography. The incorporation of P from the electrolyte to the surface oxide during the anodizing process changes the surface chemistry. After 30 days of immersion in Simulated Body Fluid (SBF) solution, Ca-P rich compounds were present on anodized zirconium.

1. Introduction

Zirconium is a valve metal with excellent corrosion resistance in a wide range of conditions including aggressive organic solutions, different acids and alkalis. The main application of zirconium is in the nuclear industry, because of its low neutron absorption coefficient but, its electrochemical resistance, together with its mechanical properties makes it to be considered as a potential biomaterial [1]. Although the biocompatibility of zirconium has been proved in a few *in vivo* studies, this material has not been systematically studied yet [2–5]. Zirconium and its alloys promote the osseointegration and its citotoxicity is very low and, in some cases, lower than the reported for titanium alloys [6,7]. Okazaki and Gotoh determined by inductively coupled plasma–mass spectrometry the ions released to different solutions after static immersion. In their study they determined less metallic ions released for the Ti–15Zr–4Nb–4Ta alloy than for classic Ti–6Al–4V alloy or the V free Ti–6Al–7Nb alloy. The amount of (Zr + Nb + Ta) was considerably less than (Al–Nb) or (Al + V) of the respective alloys. Moreover, in the Ti alloys containing Zr as alloying element, the

quantity of Ti ions released to the solutions was smaller than in the other Ti alloys [8]. The good *in vivo* performance of zirconium is mainly due to the presence of a protective oxide layer formed in air or in oxygenated electrolytes. This film diminishes the corrosion rate, minimizing the metal ion release to the biological media and facilitating osseointegration [9–11]. Zirconium knee implants with surface oxide films thickness of 2–5 μm are being commercially used due to the good wear resistance of zirconia [12–14].

The surface characterization of materials employed in orthopedic surgery is a topic of main importance since the surface plays a key role in the living tissue response to the metal presence. There are several aspects of the biomaterials surface–living media interactions that are still not solved. This topic has been extensively studied in titanium and its alloys [15–18]. In these materials, it was found that both the topography and the chemical surface composition have a strong influence in the early stages of the osseointegration process. The surface–biological media interactions is a multiscale problem, with a broad range from a few microns, where the surface topography changes the effective contact area between the implant and the surrounding bone [15,16] to tens of nanometers, where the influence of chemical species present on the surface can modify the nucleation and growth of Ca–P compounds that precede the formation of hydroxyapatite [17,18].

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Table 1
Amount of the principal impurities present in Zr (as part per million).

Element	p.p.m.
C	90
Fe + Cr	<700
H	<3
Hf	70
N	30
O	900

The "native" zirconium oxide film thickness reported from different authors varies between 2 and 5 nm [19–21]. The thickening of the film may improve the barrier effect against corrosion, and may also change the surface topography of zirconium. Anodizing is a simple and economic process to obtain a uniform surface oxide film despite the geometry of the specimen. The anodic oxide thickness can be controlled by controlling the processing parameters such as current density, anodizing potential, or electrolyte and the resulting oxide surface film attain strong bonding and adherence with the underlying metal substrate [19–24]. This technique has been extensively used with the aim of improving the performance of implants of pure titanium and also of titanium alloys [25–29]. Phosphoric acid is an interesting electrolyte because during the anodizing treatment phosphate ions may be incorporated into the growing film. The anodic film thus formed would increase the corrosion resistance while improve the tissue compatibility with the environment [30].

This work presents the study of the topological and chemical evolution of zirconium surface when anodizing at a fixed potential between 3 and 30 V. It is also determined the surface changes that occur when the modified surfaces are immersed in a simulated body fluid solution, in a typical *in vitro* test.

2. Experimental

2.1. Materials and surface modification treatment

Specimens of 20 mm × 15 mm × 0.127 mm of commercially pure zirconium (99.5%) sheets were used. The amounts of the principal impurities present (as part per million) are shown in Table 1. An electrical contact, conveniently isolated from electrolyte was mounted on each zirconium sample.

Anodizing treatment was carried out in a two-electrode cell. The auxiliary electrode was a stainless steel mesh that acts simultaneously as a reference electrode. Bardwell et al. [21] used stainless steel as counter electrode in their study of anodic zirconium oxide films and found no differences in experimental results when platinum counter electrodes were used. The specimens were anodized in 1 mol/L H_3PO_4 solution at a constant potential between 3 and 30 V with respect to the reference electrode for 60 min. Phosphoric acid was selected as the anodizing electrolyte with the aim of promoting the incorporation of P to the oxide film. The anodizing solution was prepared by diluting concentrated H_3PO_4 (Aldrich) in deionized water (18.2 MΩ cm, Millipore).

Before and after each test the samples were cleaned with acetone, dried in air and stored in a dryer.

2.2. Colors of anodic oxide films

The colors of anodic oxide films are the result of interference phenomenon of incident light on surface films. The coloration of thin films may be described by the multiple beam interference theory (Fig. 1). When white light (beam 1) makes contact with the film, the reflected beam, which is formed by the interfering beams (2, 5, 8, 11, . . .) will be colored [31]. While anodic oxide colors are principally related to the thickness of the films (d), there are several
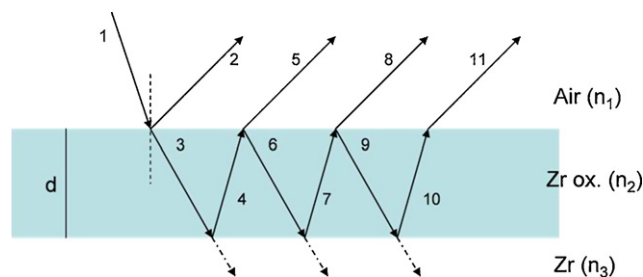

Fig. 1. Scheme describing the multiple beam interference theory. d: thickness of the film, n_1, n_2 and n_3: refractive index of air, oxide film and metal substrate respectively.

factors that influence the resulting color observed at each anodizing condition, and that may alter the sequence of colors respect to the theoretical succession (yellow, brown, dark blue, sky blue, green, yellow). The main of them are: substrate roughness, non-uniform film thickness over the entire sample, the surface oxide stoichiometry, defects or impurities present [31]. For this reason the colors reported for different authors are different, even when the same potential (and therefore the same thickness) is expected. The variation in colors is notorious when different electrolytes are used, or even when different concentrations of the same electrolyte vary. These differences are evident in studies of anodic oxides of titanium, when the reported colors differ from one author to the other [26,32]. However, when starting conditions are maintained (i.e. substrate characteristics and electrolyte), the colors of oxide films can be used for a quick identification purpose of the resultant oxide thickness in association with the anodic forming voltage [26].

In order to characterize the colors observed on different samples with an accurate and systematic manner to facilitate the study of reproducibility, and to further relate with the film thickness, a computer program was developed by the Image Analysis Laboratory of the Electronic Department at the Faculty of Engineering of the National University of Mar del Plata. This software quantified the contribution of the primary colors red, green and blue (RGB), according to the scale widely used in commercial programs for image analysis, on each pixel of high resolution images of the samples. This program assigns a value between 0 and 255 for each primary colors contribution, and finally determines the average for each color on the entire sample.

2.3. Surface characterization

The overall surface morphology of the specimens corresponding to all the anodizing conditions was observed by scanning electron microcopy (SEM) (JEOL JSM-6460LV) at 15 kV. Surface elemental analysis was simultaneously determined by energy dispersive X-ray spectroscopy (EDS) (EDAX Genesis XM4-Sys 60). The EDS analysis was carried out at least in two different regions per sample, and a mapping of selected regions as well as punctual analysis of different morphologies of interest was included.

The surface topography was characterized by atomic force microscopy (AFM) using an AFM Agilent 550 in contact mode. Image analysis was performed with Gwyddeon free software. The roughness average (Ra) and root mean square roughness (RMS) parameters were determined on square regions with side lengths of 40 μm × 40 μm. The roughness parameters determined were calculated from the entire sample image (40 μm × 40 μm), with a previous mask of the drifted lines (in all samples those lines were below 3% of the image data). This analysis was repeated on at least 5 images of each sample, and at least in 2 samples for each anodizing condition, verifying the variation of the roughness parameters for each condition (<10%)