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Effect of anodization on the surface characteristics and electrochemical behaviour of zirconium in artificial saliva

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ABSTRACT

The paper is focused on elaboration of ZrO_2 films on pure zirconium *via* anodizing in phosphoric acid with and without fluoride at constant potentials of 30 V and 60 V. The structure and composition of the films were investigated using scanning electronic microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. The composition of the oxides formed at both potentials can be identified as monoclinic ZrO_2. In addition to Zr and O, the layers formed in phosphoric acid contain phosphorus originating from the phosphoric acid. When the phosphoric acid solution contains NaF, fluorine is also incorporated into the oxide layer. The oxides formed at a higher voltage have greater roughness than those formed at 30 V. Anodized samples exhibit smaller current densities during anodic polarization compared to the as-received zirconium covered with *native* oxide.

1. Introduction

The surface characterization of materials employed in orthopaedic surgery is a topic of great importance because the surface plays a key role in the interaction between the metal and the host tissue. Surface modification induced by anodization under the conditions presented in this work corresponds to a surface design criterion based on the modification of the chemical and topological features in the micrometric range with the aim of promoting the osseointegration of the zirconium as a permanent implant.

Zirconium is, as a valve metal, very stable in numerous aggressive media and has been extensively used in the nuclear industry owing to its low neutron absorption and in the microelectronic industry [1,2] due to its high dielectric constant. More recently, Zr was investigated for biomedical applications [3–5]. It is biocompatible and has a lower ion release than Ti in bioenvironments due to its native passive oxide, which acts as a protective layer, according to the results obtained in Hanks' physiological solution [6]. Despite the fact that self-passivation is an easy and practical solution for biomaterials used for permanent implants, it does not provide any possibility for the further functionalization of the surface. Modifying the surface *via* anodization in phosphoric acid media seems to be a convenient way to stimulate bone formation [7]. Furthermore, it was reported that Zr-containing Ti alloys are nontoxic, non-allergenic and have good mechanical properties, even more suitable for bioapplications than TiAlV [8–12]. In line with this approach, new ternary and binary alloys with titanium have been investigated (TiAlZr and TiZr with various Zr contents), elaborating a large variety of micro- and nanostructured TiO_2 and ZrO_2 oxides at voltages between 15 and 45 V in hybrid electrolytes [9–12]. Zirconium and titanium oxides can be tailored by controlling the anodization conditions, having structures from porous amorphous to crystalline layers. Their stability in bioenvironments and antibacterial properties can be correlated with their structure, denoting the relation between structure, properties and applications [13]. In a recent work, an atomic force microscopy (AFM) study of ZrO_2 fabricated in 0.1 mol/L ammonium oxalate at potentials between 0 V and 79 V showed a continuous decrease in roughness with the decreasing anodic potential [14].

In this manuscript, the electrochemical *in vitro* response of anodized zirconium was systematically studied to produce different surface topographies and to determine the effect of the surface modification process on the corrosion resistance of this metal. Although there have been many papers published about Ti and its alloys and Zr as an alloying element, the available literature on pure Zr is scarce, and, according to our knowledge, no reports in Afnor artificial saliva can be found [5–7,11,12,15–17]. This study presents the development of Zr oxides by anodization in phosphoric acid with and without the addition of fluoride ions for potential dental applications. F^- ions are known as strong modifiers of the structure of anodic oxides that may lead to structures from nanopores and nanotubes to microporosity depending on the anodic conditions [13,18,19].

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2. Experimental

2.1. Sample preparation and anodizing process

Flat samples of zirconium of 99.8% purity (Alfa Aesar) were cut into dimensions of 20 mm × 15 mm × 0.127 mm. The electrodes were anodized for 60 min in either 1 mol/L H_3PO_4 or a mixture of 1 mol/L H_3PO_4 and 0.15% w/v NaF using an electrophoresis power supply (Consort EV 231, Belgium). Before the anodization process, all of the samples were wet polished with 600 grit SiC paper, cleaned in ethylic alcohol for 10 min, washed with deionized water and dried at room temperature. Anodization was carried out in a two-electrode cell with the zirconium sample as the working electrode and a stainless steel mesh as the counter electrode, as described elsewhere [4].

The anodized samples were denoted as shown in Table 1.

2.2. Characterization of anodized samples

2.2.1. Surface characterization

The morphology and chemical composition of the oxide layers were studied by means of a scanning electron microscope (SEM, Quanta Inspect f, USA) equipped with an electron gun with field emission (FEG, field emission gun) and an energy dispersive X-ray spectrometer (EDS) with a resolution of 133 eV at Mn K.

X-ray photoelectron spectroscopy (XPS) was performed with a TFA Physical Electronics, Inc. spectrometer using non- and monochromatized Al K_α radiation (1486.6 eV) and a hemispherical analyser. The mono-chromatized radiation used for the high-resolution spectra yields a resolution of 0.6 eV, as measured on an Ag $3d_{5/2}$ peak. These spectra were used to differentiate between various species, while those obtained using non-monochromatized radiation were used to quantify the chemical composition. The take-off angle used, defined as the angle of emission relative to the surface, was 45°. The energy resolution was 0.5 eV. Survey scan spectra were recorded at a pass energy of 187.9 eV, and individual high-resolution spectra at a pass energy of 23.5 eV with an energy step of 0.1 eV. The diameter of the analysed spot was 400 μm. The values of the binding energies were aligned to the carbon peak C 1s at 284.8 eV. After taking the surface spectra, the depth profiling of the oxidized layers was performed. An Ar^+ ion beam, with an energy level of 3 keV and a raster of 3 mm × 3 mm (sputter rate 0.67 nm/min determined on a Ni/Cr multilayer standard), was used for sputtering.

The crystalline domains present in the anodic oxides were determined by Raman spectroscopy using an Invia Reflex confocal Raman microscope (Renishaw, UK). The Raman spectra were obtained using a 514 nm argon laser with a 50× objective lens. No thermal effects were observed on the samples during these measurements.

The topography of the anodized samples was analysed using an A100-SGS atomic force microscope (AFM) (A.P.E. Research Italy). AFM measurements were performed in contact mode. The calculated roughness values are basically the arithmetic average of the absolute values of the highest and lowest points of the samples, also taking in consideration the slopes of the surface (so it does not necessarily mean that the sample with the greatest height also has the highest roughness value). Roughness values were calculated after creating a baseline and levelling the image with the minimum amount of image preparation, as data may be lost during the processing.

Table 1
Denotation of the zirconium samples according to the conditions of the anodization process.

Sample denotation	Anodization condition
60P	60 V in phosphoric acid (1 mol/L)
30P	30 V in phosphoric acid (1 mol/L)
60PF	60 V in phosphoric acid (1 mol/L) + sodium fluoride (0.15% w/v)
30PF	30 V in phosphoric acid (1 mol/L) + sodium fluoride (0.15% w/v)

Table 2
Chemical composition of artificial saliva Afnor.

Compound	NaCl	KCl	Na_2HPO_4	$NaHCO_3$	KSCN	CH_4ON_2 (Urea)
Concentration (g/L)	0.7	1.2	0.26	1.5	0.33	1.3

2.2.2. Electrochemical characterization

After the anodizing process, the samples were electrochemically tested in Afnor artificial saliva (Table 2) [20]. All reagents were supplied by Sigma-Aldrich (analytical grade). Deionized water (18.2 MΩ cm, Millipore) was used throughout. Electrochemical tests were performed using a conventional three-electrode cell with a saturated calomel electrode (SCE, Radiometer Analytical, France) as reference and a platinum wire as counter electrode. Before each measurement, the potential was left to stabilize for 40 min at open circuit. Potentiodynamic polarization curves were measured from the open circuit potential to 1.0 V and backwards at a sweep rate of 0.002 V/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out with an amplitude of the perturbation signal of 10 mV rms, and the impedance was measured between 10^{-2} and 10^6 Hz. The impedance data were fitted to equivalent circuit models with Zplot for Windows software [21]. Electrochemical measurements were taken at 37 °C using a Vicking 4100 (Vicking Argentine) thermostatic bath.

3. Results and discussion

3.1. Anodization process

After the anodization process, the zirconium samples acquired different colours (Fig. 1). The obtained colours include the same shades as in previously reported data [4].

3.2. Surface characterization: morphology and elemental analysis

The morphology and the chemical composition of the samples were studied by SEM/EDS analysis. SEM images of anodized zirconium samples recorded at different magnifications are presented in Fig. 2.

The oxide layers formed for samples 60P and 30P present discontinuities distributed on the surface. Porosity is also observed for the 30PF and 60PF samples, together with a smoother surface. Although some authors found a nanotubular structure in anodic films formed in F-containing [18] aqueous electrolyte solutions, nanotubes were not

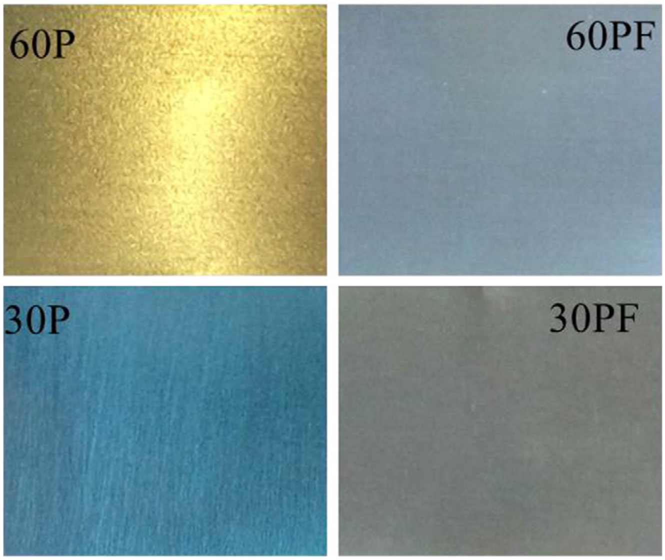

Fig. 1. Colour samples after anodization process in phosphoric acid (left) and in phosphoric acid and sodium fluoride (right).