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Anodic oxidation of zirconium in silicate solutions

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ABSTRACT

Herein, a study of the surface modification of zirconium by anodic oxidation is reported. The oxidation process was carried out in a solution containing K_2SiO_3 and KOH. The anodization was conducted at voltages of 100, 200 and 400 V. It was found that the morphology of the surface did not change during the oxidation of the zirconium at 100 and 200 V. The application of 400 V resulted in the incorporation of silicon into the formed oxide layer and a significant modification of the surface morphology. The obtained coatings are typical of coating produced during an electrolytic plasma oxidation process and contain a considerable amount of silicon. The anodic oxidation of zirconium leads to a significant improvement in the corrosion resistance of the material in the presence of Ringer's physiological solution.

1. Introduction

Implants made of metals or alloys are widely used in medicine. These materials cannot be introduced into the human body without a proper surface treatment. A modification must be performed to provide the appropriate functional properties on the surface of the implants. Biologically active or non-active surfaces can be formed by electrochemical methods that are often used during metal biomaterials production. The electrochemical processes used in implant production include: electrolytic etching, electrolytic polishing, anodic oxidation, electrophoretic deposition and cathodic deposition. The electrolytic polishing process is used for the production of very smooth and tension-free surfaces. Moreover, it results in an increase in the corrosion resistance of treated elements [1]. The effects obtained in the process can be improved by the application of a magnetic field [2,3]. Electrophoretic and cathodic depositions are used for the formation of layers, e.g., apatite layers on titanium implants that increase their bioactivity [4,5]. The anodic oxidation process is commonly used for the treatment of biomaterials made of titanium and its alloys, as well magnesium, niobium, tantalum and zirconium [6,7]. It also can be used for the formation of thin oxide layers that considerably improve the corrosion resistance of the implants [8–10]. A particular type of process is the so-called plasma electrolytic oxidation (PEO) or micro-arc oxidation (MAO), which proceed above the oxide layer breakdown potential [11]. A number of physical and chemical phenomena occur during this type of oxidation. These phenomena make it possible to obtain a treated surface coating of a ceramic that is enriched in the components present in the anodizing solution [12–15]. The coatings exhibit very good tribological properties, good corrosion resistance and improve the osseointegration of the coated biomaterials [16].

Commercially pure Ti and Ti–6Al–4V extra low interstitial (ELI) are the most commonly used titanium materials for implant applications. Although Ti–6Al–4V was originally developed for aerospace applications, its high corrosion resistance and excellent biocompatibility led to its entry into the biomedical industry [17]. Although titanium and its alloys, mainly Ti–6Al–4V, have excellent corrosion resistance and biocompatibility, some concerns have been raised about to the release of aluminum and vanadium from the Ti–6Al–4V alloy. Both Al and V ions have been associated with long-term health problems, such as Alzheimer disease, neuropathy and ostemomalacia [18]. In addition, vanadium is toxic both in its elemental state and as the V_2O_5 oxide, which is present at the surface [19,20]. Further, titanium has poor shear strength, making it less desirable for bone screws, plates and similar applications. Titanium also tends to undergo severe wear when it is rubbed between itself and other metals [21]. Titanium-based alloys with a high coefficient of friction can lead to the formation of wear debris that produce an inflammatory reaction, causing pain and the loosening of implants due to osteolysis [22]. The growing requirements for long-term implants, as well as doubts regarding the bioinertness of titanium alloys containing vanadium have contributed to the growing number of investigations of vanadium-free titanium alloys. Among the studied alloys, the most promising metallic biomaterials include [17] titanium–aluminum–niobium

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(Ti–6Al–7Nb), titanium–niobium–zirconium (Ti–13Nb–13Zr), titanium–niobium–tantalum–zirconium (Ti–29Nb–13Ta–4.5Zr) and titanium–niobium (Ti–50Nb). Instead of the harmful aluminum and vanadium, other metals such as zirconium, niobium and tantalum are predominantly used because these alloys are much more resistant to corrosion in the presence of bodily fluids than other alloys [23–30]. Previous studies have shown that pure Ti, Nb, and Zr metals and alloys exhibit excellent corrosion resistance in chloride, which is related to the presence of a stable and protective oxide film on the surface (mainly TiO_2, Nb_2O_5 and ZrO_2) [28,31]. The addition of Nb and Zr increases the thermodynamic and kinetic stability of Ti in the alloy and thus reduces the dissolution rate of Ti [25]. Moreover, the oxide Nb_2O_5 has a more negative heat of formation than Al_2O_3 and V_2O_5, and Zr and Nb ions have lower solubility than Al and V ions in aqueous media [26,29].

Silicon (Si) is an essential element for the normal growth and development of bone and connective tissues [32,33]. The role of Si as an essential element for higher biological organisms was discovered through deficiency studies [34]. In recent years, increasing evidence supports the hypothesis that the presence of Si contributes to the enhanced bioactivity of some bioactive glasses and ceramics and significantly increases the up-regulation of osteoblast proliferation and gene expression [35]. Si-containing calcium phosphate ceramics were widely investigated and proven to be more bioactive and favorable for the attachment and spread of osteoblasts [33]. The incorporation of Si into conventional films by PEO is a promising approach for introducing certain elements into the film to enhance its bioactivity and thus favor skeleton formation.

Herein, the results of plasma electrolytic oxidation of pure zirconium for the preparation of vanadium-free titanium alloys are reported. The process was carried out in aqueous solutions of potassium silicate and potassium hydroxide. The morphology, chemical composition as well as the corrosion resistance of surface-modified zirconium were evaluated.

2. Materials and methods

Pure zirconium (BIMO Metals, Wrocław, Poland) samples in the shape of a plate with dimensions of 10 mm × 10 mm were used in this study. The samples were polished with #320 and #600 abrasive paper and cleaned for 5 min in an ultrasonic wash in 2-propanol and deionized water. The pretreatment of samples was conducted as follows: polishing with abrasive paper of 600 granulation, etching in a solution containing H_2SO_4 (4 mol dm^{-3}) and HF (1 mol dm^{-3}) for 1 min, rinsing in distilled water and cleaning ultrasonically for 5 min (sample Zr).

After the etching process, the samples were oxidized anodically in a bath containing potassium hydroxide (KOH – 5 g dm^{-3}) and potassium silicate (K_2SiO_3; different concentration). The anodization was carried out at a current density of 0.1 A dm^{-2} for 5 min. The sample labels and treatment conditions are provided in Table 1. After anodization, the samples were rinsed with distilled water and cleaned in an ultrasonic bath with 2-propanol and deionized water. A DC power supply (PWR800H, Kikusui, Japan) was used for the anodization reaction, in which the zirconium specimen served as the anode and a titanium plate served as the cathode.

The morphology and the cross sectional and chemical composition of the anodic layer formed on the surface were examined using a scanning electron microscope (SEM, Hitachi S-3400N, accelerating voltage = 25 kV) equipped with an energy-dispersive X-ray spectrometer (EDX, Thermo Noran).

The X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultrahigh vacuum (3×10^{-10} mbar) system equipped with a hemispherical analyzer (SES R4000, Gammadata Scienta). An un-monochromatic Mg Kα X-ray source of incident energy of 1253.6 eV was applied to generate core excitations. The energy resolution of the system, measured as a full width at half maximum for an Ag 3d5/2 excitation line, was 0.9 eV. The energy scale of the analyzer was calibrated according to ISO 15472:2001, and the energy scale of the acquired spectra was calibrated for a maximum C 1s core excitation at the electron binding energy (BE) of 285 eV. The analytical depth for the measured samples (approximated as SiO_2 layers) was 10.4 nm.

The roughness (Ra parameter) of the samples was measured using a Mitutoyo Surftest SJ-301 profilometer according to ISO 4287:1997. The Ra parameter is the arithmetic mean of the sum of roughness profile values:

$$\mathrm{Ra} = \frac{1}{l} \int_0^l \left| Z(x) \right| dx, \qquad (1)$$

where $|Z(x)|$ is the absolute ordinate value inside the elementary measuring length and l is the elementary length in the x direction (average line) used to determine the unevenness of the profile.

The corrosion resistance of the zirconium samples was investigated in the presence of Ringer's simulated body fluid, which is composed of 8.6 g dm^{-3} NaCl, 0.3 g dm^{-3} KCl, and 0.48 g dm^{-3} $CaCl_2{\cdot}6H_2O$ (Baxter, USA). The main components of the research apparatus included a standard two-chamber electrolysis cell with three electrodes: a working electrode, a platinum auxiliary electrode and a Haber–Luggin capillary with a reference electrode (saturated calomel electrode – SCE). The electrolysis cell was powered by a PARSTAT 4000 potentiostat operated by the Versa Studio software. The study included the following measurements: (a) recording the open-circuit potential (E_{OCP}) as a function of time, (b) determining the $\log i = f(E)$ curve in the potential range of E_{OCP} −20 mV to E_{OCP} +20 mV ($dE\,dt^{-1}$ = 1 mV s^{-1}), which provides information about: (i) the corrosion potential E_{CORR}, mV, (ii) the corrosion current density i_{CORR}, nA cm^{-2}, and (iii) the polarization resistance R_p, kΩ cm^2, and (c) recording the cyclic polarization curve (CV) in the potential range from E_{OCP} −0.1 V to 3 V ($dE\,dt^{-1}$ = 10 mV s^{-1}).

All solutions were prepared using analytical grade reagents manufactured by POCh Gliwice, Poland. Deionized water was obtained from the Millipore Milli-Q system.

3. Results and discussion

The surface of the polished and etched zirconium exhibits the expected morphology following such a treatment (Fig. 1). The

Table 1
The sample labels, treatment condition, Zr/Si surface atomic ratio, roughness, and thickness of the samples; KOH – 5 g dm^{-3}.

Sample	K_2SiO_3, mol dm^{-3}	U, V	Zr/Si surface atomic ratio	Ra, μm	Thickness, μm
Zr-ANO-0.5-100	0.5	100	51.63	0.24	0.32–0.38
Zr-ANO-0.5-200		200	29.30	0.26	0.56–0.76
Zr-ANO-0.5-400		400	0.085	3.70	10.2–18.0
Zr-ANO-0.1-400	0.1	400	12.42	1.46	5.16–5.56
Zr-ANO-1.0-400	1.0		0.005	4.09	41.3–70.6

Zr Ra = 0.23 μm.

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