



Influence of electropolishing and anodic oxidation on morphology, chemical composition and corrosion resistance of niobium



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ABSTRACT

The work presents results of the studies performed on electropolishing of pure niobium in a bath that contained: sulphuric acid, hydrofluoric acid, ethylene glycol and acetanilide. After the electropolishing, the specimens were subjected to anodic passivation in a 1 mol dm⁻³ phosphoric acid solution at various voltages. The surface morphology, thickness, roughness and chemical composition of the resulting oxide layers were analysed. Thusly prepared niobium samples were additionally investigated in terms of their corrosion resistance in Ringer's solution. The electropolished niobium surface was determined to be smooth and lustrous. The anodisation led to the growth of barrier-like oxide layers, which were enriched in phosphorus species.

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1. Introduction

Niobium is a valve metal and popular alloying element used for carbon and alloy steel production [1]. It is classified as an element that improves mechanical properties of alloys [2]. Furthermore, Nb acquires superconducting properties at relatively high temperatures (below $T_c \sim 9.25$ K) which makes it a material of choice for superconducting radio-frequency (SRF) cavities for linear particle accelerators [1,3–5]. High biocompatibility of this element [6,7] has led to its application in biomedical engineering, e.g. load-bearing elements of orthopaedic implants. Niobium, either in its pure form or as a dopant for titanium alloys, is considered to be hypoallergenic [8]. Titanium alloys are one of the most prominent representatives of the metallic biomaterials, because of their superior biocompatibility, osteoinductivity and mechanical properties [9]. A popular material which belongs to this group is Ti–6Al–4V ELI (Extra-Low Interstitial) alloy [10]. However, because of concerns regarding the presence of cytotoxic vanadium (and possibly neurotoxic aluminium) these alloying elements are

sought to be replaced with more biocompatible elements (e.g. Nb). So far, the following range of niobium-containing titanium alloys for biomedical applications was proposed: Ti–13Nb–13Zr, Ti–35Nb–5Ta–7Zr, Ti–35Nb–5Ta–7Zr–0.4O, and Ti–6Al–7Nb [2,11–13]. However, some researchers conducted studies concerned with pure niobium as a potential biomaterial [14–18]. Fathi and Mortazavi have shown that coating of stainless steel (SS) with niobium significantly increases corrosion resistance of SS in 0.9% NaCl solution and Ringer's solution [14]. Similar Nb coatings were more thoroughly investigated by Olivares-Navarrete et al. with the use of in vitro studies which yielded promising results [15]. The niobium coatings which were subsequently anodised were prepared on Ti alloy dental implant screws by Mackey et al. [16]. In addition, the results of in vivo tests performed on rabbits by Johansson and Albrektsson suggest that pure niobium developed better contact with the surrounding bone than commercially pure titanium, as it was discerned from the torque removal and histomorphometric analyses [17].

Niobium exhibits an exceptional corrosion resistance in the majority of mineral acids and in natural environment. This behaviour is owed to the presence of relatively thin native oxide layer, which adheres tightly to the substrate and protects the metal from chemical attack [1,19].

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Metal–tissue interactions depend strongly on the microstructure (and nanostructure) of the oxide layer [20]. Therefore, an appropriate surface modification treatment is required to tune the physicochemical properties of a metal surface. Anodic passivation is a technique that provides with the means to accomplish this goal. However, prior to anodising metallic implants are frequently subjected to electropolishing, which yields uniformly smooth and lustrous surfaces [8]. Thusly modified materials are more likely to be successfully implanted in the human organism [19].

Electropolishing is a surface finishing technique which is used to eliminate the unevenness of the material's surface and to achieve possibly the highest surface smoothening effect. The resulting surface is tension- and occlusion-free. Furthermore, the corrosion resistance of the material is enhanced, because of a reduction in the effective surface area exposed to a corrosive environment [21]. Niobium, when contacted with aqueous electrolyte solutions, reacts with water molecules which ultimately leads to the formation of pentavalent niobium oxide according to the following reaction scheme [22]:



The thickness of the oxide layer ranges between 5 and 10 nm. The presence of this non-conductive coating hinders the process of electropolishing. To alleviate this problem the composition of the electrolyte bath has to be chosen carefully to induce controlled dissolution of the oxide layer. A popular component of such baths is hydrofluoric acid [9]. The oxide layer present on the surface of niobium can undergo the following reactions in the presence of HF [22]. A few nm thick oxide layer forms onto niobium after electropolishing which is predominantly composed of niobium suboxides: NbO, Nb₂O and NbO₂ [8,10]. The oxide coating can be grown thicker by thermal or electrochemical oxidation techniques [23,24]. Anodic oxidation can yield oxide coatings with thickness up to micrometric range, when appropriate conditions are maintained. The colour of the treated surface can change due to the light interference effects, depending on the oxide layer thickness [1,25–27]. Such a behaviour is observed only when the treatment is performed below the breakdown potential of the oxide layer. When this threshold is breached, oxide dissolution or plasma discharge can occur, which has an impact on the resulting surface morphology [28]. The properties of the anodic oxide films can be controlled by the choice of electrolyte composition, process voltage, temperature, current density and time of treatment [29,30]. When anodic oxidation of niobium is performed in a solution that contains sulphuric acid and hydrofluoric acid the resulting oxide layer is nanoporous [31]. The oxide dissolution is enabled by the presence of hydrofluoric acid [32,33], while sulphuric acid (or phosphoric acid) hinders the activity of hydrofluoric acid towards the workpiece because they participate in competitive reactions [29].

In the present study results of electropolishing of niobium in an electrolyte bath of the composition proposed by the authors are reported. Anodic passivation in a 1 mol dm⁻³ phosphoric acid solution was performed after the electropolishing. The effect of the anodising voltage on the surface morphology, thickness, roughness and chemical composition of the oxide layer was determined. Furthermore, the corrosion resistance of the resulting oxide coatings was assessed in Ringer's solution.

2. Materials and methods

Pure niobium metal sheets (BIMO Metals, Wrocław, Poland) were cut into 10 × 10 × 1 mm samples. Surface pretreatment of the metal specimens comprised of mechanical grinding with SiC abrasive paper (up to 1000#). Then, the samples were subjected to electropolishing (EP) in a bath of the following composition: sulphuric acid – 10 mol dm⁻³, hydrofluoric acid – 5.8 mol dm⁻³, ethylene glycol – 3.5 mol dm⁻³ and acetanilide – 0.75 mol dm⁻³. The treatment was conducted at 60 A dm⁻² for 5 min.

The electropolished samples were anodised in a 1 mol dm⁻³ phosphoric acid solution. The process was run at a constant current of 60 A dm⁻² up to limiting voltages of 20, 60, 100, 120 and 140 V. A Kikusui 800H DC power supply was used to conduct the process. Data concerning the sample labels and corresponding treatment conditions are presented in Table 1.

Afterwards, the specimens were rinsed with distilled water and cleaned ultrasonically in a mixture of deionised water and 2-propanol. A standard thermostated electrolyser supplied with a stream of cooling water was used for the anodisation. The cylindrical cathode was made from titanium, while the niobium sample served as the anode. The electrolyte solution was mixed by means of a magnetic stirrer.

The surface morphology of the modified niobium samples was investigated using a scanning electron microscope (SEM, Hitachi S-3400N, accelerating voltage = 25 kV). Planar views of the specimens were taken. The chemical composition of the surface images of the ground (Nb-Gr) and electropolished (Nb-EP) niobium samples was analysed by the use of an electron-dispersive X-ray spectrometer (EDX, Thermo Noran) which was coupled with the SEM.

Further studies on the surface topography of the niobium samples were carried out using an atomic force microscope (NanoScope E, Digital Instruments). The surface roughness (*R_a* parameter) and difference between the real and geometric surface areas of the investigated section of the samples (ΔA) were calculated on the basis of registered surface profiles.

The contact angle measurements of the niobium specimens were made by a drop shape analysis system (DSA 10Mk2, Krüss). The shape of the drop was recorded using a video camera and then it was used by an image analysis system (DSA software) to calculate the contact angle. 10 droplets (0.2 μL) of ultra-high purity water (produced by UHQ-PS system, Elga) at room temperature were analysed for each of the niobium samples. The results are presented as average \pm standard deviation.

Spectroscopic ellipsometric measurements were performed using an EP3 ellipsometer (Nanofilm). The wavelength range was 360–1001 nm and the angle of incidence was 80°. To calculate the thickness of the oxide the EM-Bruggemann model was used [34].

A high spatial and energy-resolution PHI XPS Versaprobe 5000 spectrometer (ULVAC-Physical Electronics, USA) was employed for the X-ray photoelectron spectroscopy experiments. The spectrometer was equipped with a spherical quartz monochromator and energy analyser working in the binding energy (BE) range of 0–1500 eV. The X-ray optical scheme was additionally supplied with an electrostatic focusing and magnetic screening. An Al K α X-ray source with the energy resolution of $\Delta E \sim 0.5$ eV and a spot size of 200 μm was used throughout the measurements. Ultra-high vacuum of 10⁻⁷ Pa was maintained in the vacuum chamber that contained all the studied samples for 24 h prior to the experiments. The ULVAC-PHI MultiPak 9.2 software was used for the spectra post-processing and the residual background was removed by the use of the Tougaard method. The XPS spectra were calibrated relative to the energy of the C 1s core-level at BE equal to 284.5 eV.

Table 1

Sample labels, process conditions, Nb/P surface atomic ratios, differences between image and geometric surface areas, oxide layer thicknesses, roughnesses and water contact angles of the niobium sample surfaces.

Sample	Electropolishing	U, V	ΔA , %	Thickness, nm	<i>R_a</i> , nm	Contact angle, deg
Nb-Gr	×	–	82.1	–	227	70 \pm 2
Nb-EP	✓	–	1.1	–	16	75 \pm 2
Nb-EP-ANO-20	✓	20	5.4	76–76	9	78 \pm 5
Nb-EP-ANO-60	✓	60	3.2	82–95	6	90 \pm 4
Nb-EP-ANO-100	✓	100	1.8	269–281	3	75 \pm 2
Nb-EP-ANO-120	✓	120	0.2	412–413	7	72 \pm 4
Nb-EP-ANO-140	✓	140	2.5	446–446	4	80 \pm 2

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