



Electrochemical behavior of plasma electrolytically oxidized niobium in simulated physiological environment

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ABSTRACT

Niobium is a β -stabilizing element in the new generation of low modulus Ti alloys. Like titanium, it is characterized by good chemical stability in physiological conditions, however, it suffers from lack of bioactivity as well. In the last few decades plasma electrolytic oxidation (PEO) was used to form bioactive interfaces on Ti and its alloys, which promoted bone growth. However, little attention was devoted to the PEO treatment of pure niobium. This paper describes the process of formation of the oxide coatings on Nb from $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solutions with addition of either $\text{Ca}(\text{HCOO})_2$ or $\text{Mg}(\text{CH}_3\text{COO})_2$ salts via galvanostatic DC PEO up to 200, 300, 400 or 500 V. The coatings were all good quality (essentially crack-free), had a tri-layer structure and their thickness ranged from 2.45 to 120 μm , depending on the limiting anodization voltage. The corrosion resistance of the modified surfaces was tested using electrochemical impedance spectroscopy (EIS) and DC polarization techniques, such as linear polarization resistance (LPR) and potentiodynamic polarization (PDP) in Ringer's solution at 37 °C. A new equivalent electrical circuit (EEC) was proposed to model the PEO coatings on niobium and possibly other metals, such as titanium in dilute chloride environments. The coatings formed at lower voltages (200 V) in the more concentrated PEO solutions were more resistant, while the higher voltage (300–400 V) during the processing in the less concentrated solution had a positive effect on the corrosion resistance of the modified niobium surfaces.

1. Introduction

Biomaterials that are intended for bone reconstruction implants, such as in total hip or total knee replacement procedures are in vast majority made of metals and their alloys. There are many requirements imposed upon these materials because their long-term stability in the host organism is innate to the successful treatment of such illnesses as arthritis or osteoporosis. Therefore, it is imperative that the properties of a metallic implant do not degrade over time due to corrosion. Tissue environment of the human body is an aqueous medium containing relatively high concentrations of dissolved oxygen and ions, including aggressive chlorides. Furthermore, the inflammatory state is an integral part of the “foreign body reaction” following surgery which leads to local acidification and production of enzymes, reactive oxygen metabolites etc. aimed to degrade the implant [1]. Given the corrosion of metals manifests itself according to the electrochemical mechanism, the existence of potential differences between various parts of the organism accentuates the problem even further.

The most notable group of metallic biomaterials, which were designed to overcome these problems is titanium and its alloys. Superior

mechanical strength and chemical stability of this element combined with its low density made it a material of choice in many medical appliances. Among Ti-based materials, the Ti-6Al-4V alloy is frequently used because of its greater corrosion resistance and lower elastic modulus as compared with commercially pure titanium (Cp Ti), while remaining relatively inexpensive [2]. However, the prolonged exposure to the physiological conditions may result in an extensive metal ion release into the host organism [3,4]. Vanadium and vanadium pentoxide are carcinogenic and there are concerns regarding neurotoxicity of aluminium [5], so the researchers were prompted to search for substitutes in the new generation of Ti alloys [6].

Niobium, like titanium, is considered to be a member of so-called “vital metals”, owing to its chemical stability in the physiological conditions [7]. Their exceptional inertness is thanks to the presence of a thin, tightly-adherent passive oxide layer on top of the bare metal, which regenerates in the presence of oxygen (e.g. from the air or aqueous environment). At the same time, Nb similarly to V stabilizes the β phase in Ti alloys, which is responsible for lower Young's modulus of the resulting material, effectively reducing the stress-shielding effect of an implant. Ti-6Al-7Nb and Ti-13Nb-13Zr are some of the most

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extensively studied Ti-Nb biomedical alloys [2,6].

Modern bioimplants for bone reconstruction are not only required to remain harmless to the recipient but also induce osteointegration. Thus, an additional requirement imposed on these materials is bioactivity [8], i.e. an ability of the implant to bond directly with the surrounding bone through naturally precipitated hydroxyapatite (HA). Bioactive surfaces can be attained by forming a ceramic coating containing Ca, P and/or Si on the metallic substrate [9]. One of the methods for attaining such a goal is electrochemical oxidation [10–13].

The treatment involves the formation of an oxide layer on the passivating metals' surface, as a result of the passage of current through the metal-electrolyte interface. As the oxide layer of the anodically polarized metal thickens the process voltage rises. At the point when the voltage drop across the oxide layer exceeds the dielectric breakdown voltage of the metal oxide, the process enters a new regime called plasma electrolytic oxidation (PEO), micro-arc oxidation (MAO) or micro-plasma oxidation (MPO). Following the breakdown, the surface of the metal becomes covered with a large number of short-lived sparks (or microdischarges) that promote the further growth of the oxide [14]. As the voltage of the process increases, the treatment transitions into several sparking regimes of differing intensities, after which relatively thick coatings with considerable porosity can be formed [15,16]. Moreover, high plasma temperature (several thousand Kelvin [17]) fuses the resulting oxide coating with the surrounding electrolyte, effectively enriching the surface with additional elements. These features are beneficial for creating bioactive interfaces from the electrolytes containing bioelements (e.g. Ca, P, Mg) responsible for stimulating the bone growth [18–21].

Many attempts were made to form bioactive PEO coatings on Ti and many biomedical Ti alloys (including Ti-Nb alloys [11–13,15,16]). Still, not much has been done regarding the PEO treatment of pure niobium for biomedical applications. Aside from two reports by the present authors [22,23], there are a few papers published by two groups working with this element to produce bioactive surfaces. Pereira et al. utilized the approach whereby niobium plates were PEO-ed in calcium acetate or phosphoric acid + calcium acetate solutions under potentiostatic conditions, producing surfaces highly enriched with electrolyte components [19,24]. On the other hand, Rokosz et al. [25] used a phosphoric acid solution with the addition of copper nitrate to form bioactive and bacteriostatic PEO coatings on niobium also following the DC constant-voltage route. In the present study, the authors will demonstrate the influence of some process parameters (i.e. the limiting voltage of the treatment and electrolyte composition) of the DC PEO of pure niobium on the corrosion resistance of the resulting modified surfaces (enriched with Ca, P and Mg) in Ringer's solution. The samples subjected to this procedure were labeled as "Etched Nb".

2. Experimental

2.1. Niobium specimen preparation

The samples of commercially pure niobium (BIMO Metals, Wrocław, Poland) were obtained by cutting a 3-mm metal sheet into 2 cm × 2 cm squares with a small rectangular protrusion working as a current lead. The working surface area of the samples was pretreated by mechanical grinding using SiC emery papers (240, 600 and 800 grades) followed by degreasing in a 2-propanol/water mixture (1:1 vol.) for 5 min under ultrasonication and chemical etching in a 1 M HF and 4 M H₂SO₄ solution for 2 min under stirring. The samples were dried in the stream of warm air after the subsequent pretreatment steps.

2.2. Plasma electrolytic oxidation

The etched Nb samples were anodically oxidized using a high-voltage power supply (PWR800H, Kikusui, Japan), in three different solutions:

- 1) Ca – 0.5 M Ca(H₂PO₂)₂,
- 2) Ca + Ca – 0.5 M Ca(H₂PO₂)₂ + 1.15 M Ca(HCOO)₂,
- 3) Ca + Mg – 0.1 M Ca(H₂PO₂)₂ + 0.23 M Mg(CH₃COO)₂.

The process was run under DC regime with a two-step procedure. In the first step, the samples were anodically polarized galvanostatically (150 mA cm⁻²) up to a limiting voltage of 200, 300, 400 or 500 V. After attaining the selected value of voltage, the process was switched into voltage control, and the current was allowed to drop keeping the limiting voltage constant. The total processing time was limited to 5 min, except that for the Ca 500 V samples, for which it had to be elongated to 10 min to allow the voltage to rise to the designated value. Transition into constant-voltage step was realized to passivate the treated surface further, without exposing it to more energetic microdischarges occurring at higher voltages. The treatment was carried out in a glass electrolyzer under cooling (solution temperature was set to 15 °C), with a magnetic stirrer. The cathode was made of titanium. After the processing was complete the samples were thoroughly cleaned with deionized water and put in a stream of warm air until dry. All reagents used throughout the investigations were analytical grade.

2.3. Surface characterization

2.3.1. SEM/EDS surface analysis

The changes in the surface morphology before and after the PEO treatment were determined using a scanning electron microscope (SEM, Hitachi, S-3400-N; acc. voltage = 25 kV). The surface elemental analysis was performed with an energy-dispersive X-ray spectrometer (EDS, Thermo Noran), which was coupled with the SEM.

2.3.2. Surface roughness determination

A profilometer (SurfTest SJ-301, Mitutoyo, Japan) was used to measure surface profiles of the Nb specimens along 3 parallel paths (4 mm long). The Ra roughness factor was calculated according to the formula [26]:

$$Ra = 1/l \int_0^l |H(x)| dx \quad (1)$$

|H(x)| is the absolute value of the ordinate inside the elementary length (l) in the x-direction (baseline – average).

2.3.3. SEM cross-sectional analysis

The thickness of the PEO coatings on Nb was assessed by observing the obtained samples (mounted in an acrylic resin, cut to reveal the cross-section and polished) under an SEM (accelerating voltage = 10 kV; Phenom ProX, Phenom-World BV, Netherlands).

2.4. Electrochemical corrosion measurements

The electrochemical analysis of the niobium specimens before and after the PEO treatment under different conditions was performed using a PARSTAT 4000 potentiostat-galvanostat (Ametek, Princeton Applied Research, USA). The experiments were performed in a naturally aerated Ringer's solution (8.6 g dm⁻³ NaCl, 0.3 g dm⁻³ KCl and 0.33 g dm⁻³ CaCl₂·2H₂O (Fresenius Kabi, Poland)) at 37 °C. A 250 cm³ corrosion cell fitted with the saturated calomel electrode (SCE) and platinum mesh counter electrode was used throughout the experiments. The niobium samples served as working electrodes (the surface area exposed to the solution was limited by a rubber seal to 0.785 cm²). The experiments were performed using VersaStudio software and the following experimental procedure was adopted during the research:

- 1) the samples were allowed to stabilize for 5 h prior to the measurements, while their stationary (open-circuit) potential, E_{OC}, was measured (the drift rate at the end of this period was typically under 3 mV h⁻¹);

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