

Brief communication

Electrochemical formation of self-organized anodic nanotube coating on Ti–28Zr–8Nb biomedical alloy surface

X.J. Feng, J.M. Macak, S.P. Albu, P. Schmuki *

Department of Materials Science, WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany

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Abstract

In recent years, Ti–Zr–Nb alloys have become increasingly attractive as biomedical implant materials. In the present communication, we report the formation of self-organized nanotube oxide layers on a Ti–28Zr–8Nb biomedical alloy surface in 1 M (NH₄)₂SO₄ containing 0.25 M NH₄F. The morphology of the nanotube layers (the diameter and the length) is affected by the electrochemical conditions used (applied potential and time). Under specific conditions oxide layers consisting of highly ordered nanotubes with a wide range of diameters and lengths can be formed, varying, respectively, from approx. 50 to 300 nm and from approx. 500 nm to 22 μm. The present results are highly promising for this biomedical alloy, as the large surface area and the tunable nanoscale geometry of the surface oxide provide novel pathways for the interaction of the materials with biorelevant species, such as cells and proteins.

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1. Introduction

Titanium and its alloys are widely used as implants in orthopedics, dentistry and cardiology due to their outstanding properties, such as high strength, high level of hemocompatibility and enhanced biocompatibility [1,2]. However, conventional alloys, such as Ti–6Al–4V and Ti–6Al–7Nb, which are frequently used for biomedical applications, suffer from some degrees of biochemical incompatibility due to their relatively high Young modulus when compared with that of the bone and in certain cases due to the release of toxic ions (e.g., V and Al) from the alloy, leading to undesirable effects [3,4]. In the recent past, new alloys that do not contain these elements have received a great deal of attention. Tissue reaction studies have identified Nb and Zr as non-toxic elements as they do not cause any adverse reactions in the human body [5]. Moreover, Nb is found to reduce the modulus of elasticity when

alloyed with Ti; the addition of Zr results in a high level of blood compatibility when used as implants and leads to better corrosion resistance due to the formation of a stable oxide surface layer [5,6]. Thus, the attractive properties of Nb and Zr mentioned above are the forces driving the introduction of Ti–Zr–Nb alloys into the field of biomaterials.

The high degree of biocompatibility of Ti alloys is usually ascribed to their ability to form stable and dense oxide layers consisting mainly of TiO₂. The native oxide layers on Ti are usually 2–5 nm thick and are spontaneously rebuilt in most environments whenever they are mechanically damaged. It is believed that thicker and more stable TiO₂ based oxide surfaces are generally favorable for surface bioactivity [7,8]. Spark anodization is one of the conventional routes to increase the biocompatibility of titanium and its alloys. This process typically leads to the formation of a disordered oxide structure (irregular pores with lateral features from 1 to 10 μm) several hundreds of nanometers thick [9,10]. In contrast to this approach, the electrochemical formation of novel highly ordered oxide nanotube layers has been reported for Ti anodization in fluoride-

* Corresponding author. Tel.: +49 9131 852 7575; fax: +49 9131 852 7582.

E-mail address: schmuki@ww.uni-erlangen.de (P. Schmuki).

containing acid electrolytes at moderate voltages [11]. Such TiO₂ structures consist of arrays of nanotubes with diameters in the 100 nm range and thickness up to about 500 nm. Recently, by controlling the composition of aqueous electrolytes and using organic electrolytes, high aspect ratio self-organized oxide nanotube structures have been reported [12–17]. Moreover, by extending this electrochemical method to metal alloys, ordered oxide nanotube layers on Ti–Nb [18], Ti–Zr [19] and Ti–Nb–Ta–Zr alloys [20] have also been obtained. In view of biomedical applications, these oxide nanotube layers can improve apatite formation ability and cell activity compared with conventional flat TiO₂ layers [21,22].

In this present work, we investigate the feasibility and fabrication of self-organized nanotubes on Ti–28Zr–8Nb biomedical alloys relevant to biomedical applications by anodization in NH₄F/(NH₄)₂SO₄ electrolytes. The formation parameters that lead to nanotubes with controlled diameters and thickness on the biomedical alloys surface are discussed.

2. Experimental

All experiments were carried out on alloy plates of Ti–28Zr–8Nb obtained from ATI Wah Chang Co., USA. The alloy has a β -phase structure, with a minor amount of α -phase. Prior to electrochemical experiments, the sheets (with a thickness of 5 mm) were ground up to 2400-grit emery paper and polished with diamond paste (6 μ m). The polished samples were then sonicated successively in acetone, isopropanol and methanol, rinsed with deionized water and dried in a nitrogen stream. The electrolyte was 1 M (NH₄)₂SO₄ (99%, anhydrous; Sigma Aldrich Co.) solution with an addition of 0.25 M NH₄F (98%, anhydrous; Sigma Aldrich Co.) at ambient temperature.

A three-electrode system was used for electrochemical experiments. The working electrode was the alloy plate exposed to an electrolyte with an area of 1 cm² using an O-ring. A platinum mesh was used as the counter electrode. The reference electrode was a Haber–Luggin capillary with an Ag/AgCl (1 M KCl) electrode. Electrochemical treatments and measurements were performed by using a

high-voltage potentiostat (IMP 88 PC, Jaissle). Anodization was conducted by sweeping the potential from 0 V (vs. Ag/AgCl) to a target potential (between 10 and 40 V) at a rate of 50 mV s⁻¹, and then keeping the terminal potential for a fixed time. After the anodization, the sample surface was rinsed with deionized water followed by drying in a nitrogen stream. Some samples were annealed at 600 °C for 3 h in air with a heating and cooling rate of 30 °C min⁻¹ by using a Jetfirst Rapid Thermoanalyzer (RTA, Jipelec, France).

The structure and morphology of the nanotube films were characterized using a field emission scanning electron microscope (Hitachi FE-SEM S4800). The cross-sectional thickness measurements and bottom views were carried out directly on mechanically cracked samples. The crystal structure of the samples was identified using an X-ray diffractometer (Phillips X'pert-MPD PW3040). The chemical composition of the annealed samples was carried out by X-ray photoelectron spectroscopy (PHI 5600 XPS) using Al K α monochromatic radiation (1486.6 eV; 300 W) as the exciting source.

3. Results and discussion

In the present work, anodization consisted of two parts – a potential sweep from the 0 V to a desired potential and the following potential holding for different times. The solid line in Fig. 1 shows a typical current vs. potential curve (Fig. 1a) and the current–time behavior during potentiostatic anodization at 30 V (vs. Ag/AgCl) (Fig. 1b) for the Ti–28Zr–8Nb alloy in 1 M (NH₄)₂SO₄ + 0.25 M NH₄F electrolyte. During the potential sweep stage (Fig. 1a), the current density first rapidly increases up to about 9 mA cm⁻² and then drops to a steady value of about 6.1 mA cm⁻². This behavior has been found for pore formation on several valve metals, including Ti [15,16], Zr [23] and Nb [24,25]. In the initial stage, with a current increase, an oxide layer is formed which then becomes perforated and converted to a porous worm-like initial layer (the latter is combined with an increase in the active surface area). With time, the pore growth becomes increasingly ordered, and finally a self-organized nanotube

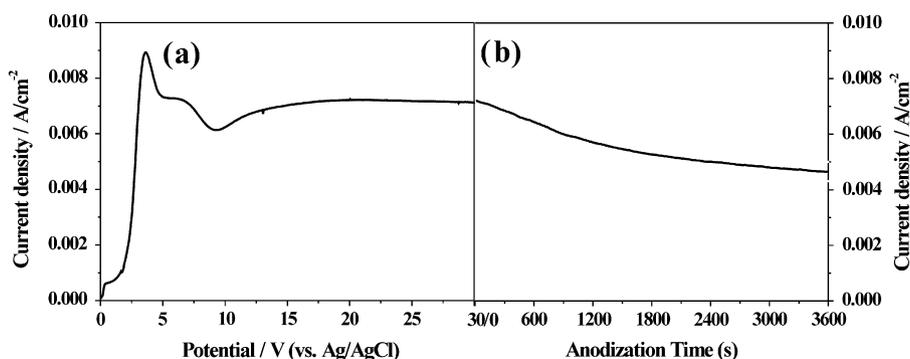


Fig. 1. Current density curves for the anodization of Ti–28Zr–8Nb alloy in 1 M (NH₄)₂SO₄ + 0.25 M NH₄F electrolyte during (a) the potential sweep from 0 to 30 V at a rate of 50 mV s⁻¹ and (b) the potentiostatic anodization at 30 V for 1 h after the potential sweep process.

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