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Surface modification of Ti 13Nb 13Zr by plasma electrolytic oxidation

S. Lederer*, P. Lutz, W. Fürbeth

DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt a. M., Germany

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ABSTRACT

Titania coatings were produced on Ti 13Zr 13Nb by a unipolar pulsed DC plasma electrolytic oxidation (PEO) process in an electrolyte containing 1 M H_2SO_4 + 0.1 M H_3PO_4. The samples were galvanostatically anodized under a constant charge-carrier density of 63 C cm^{-2} and current-densities reaching from 14 mA cm^{-2} up to 700 mA cm^{-2}. Both a constant current mode and a unipolar pulsed mode with a duty-cycle of 50% and frequencies of 1 Hz to 50 Hz were performed. The surface layers were characterized by scanning electron microscopy (SEM/EDX), X-ray diffraction (XRD) and nanoindentation. Titanium oxide coatings with a thickness of several micrometers and a porous structure could be generated. The coatings morphology was evaluated. It can be shown that the porosity can be reduced with increasing frequency. The coatings consist of anatase and rutile, the phase composition of the coatings can be adjusted by the PEO current density. The corrosion resistance of the layers was tested in a simulated body fluid (SBF) with the addition of 0.1 M H_2O_2 by open circuit potential measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). EIS data fitting indicates a composed layer structure of an outer porous layer and an inner barrier layer. Higher current densities during the PEO process formed thicker coatings, which consequently resulted in lower corrosion currents. The addition of zirconia nanoparticles into the electrolyte increased the surface hardness to an average value of 12.8 GPa, compared to that of an untreated sample (4.1 GPa) and PEO samples without particle addition (8.5 GPa).

1. Introduction

Titanium and its alloys have been used for about 30 years in the field of osteosynthesis and implant technology. Titanium materials combine high strength with comparatively low stiffness, which minimizes the risk of implant failure (stress shielding effect). Because of the natural passive layer consisting of titanium oxide, they are also biocompatible and show excellent corrosion resistance. However, the thin oxide layer (of a few nanometers) can be damaged and harmful metal ions (e.g. Al, V) can be released into the body and thus into the blood circulation. Moreover wear resistance as well as the conditions for osteosynthesis are not well adjusted o the applications as implants. In order to improve the surface performance, several surface modification methods have been employed, e.g. sol-gel coating [1,2] chemical vapor deposition [3], hydrothermal treatment [4,5] or anodic oxidation [6–8]. The plasma-electrolytic oxidation (PEO) or micro-arc oxidation (MAO) is an electrochemical method that has been developed from anodizing, enabling to generate thick, ceramic coatings on the surface of light metals [9–11]. The coatings show an improved corrosion resistance [12,13] and enhanced mechanical properties [14,15] compared to conventionally anodized samples. DC [16], AC [17] and pulsed electrical modes [18] are used under high anodic potentials (several 100 V), creating discharges at the treated surface. The high electrical field strengths involve the electrophoretic transport of anionic components of the electrolyte, e.g. O^{2-}, OH^{-} or $PO_4{}^{3-}$ along the discharge channels inside the material and the incorporation of these ions into the material. In rapid solidification, a crystalline ceramic coating is formed. Due to the discharges and gas formation, the coatings show also a significant porosity [9,10]. By varying the electrical and chemical process parameters, surface morphology, porosity, layer composition and layer thickness can be adjusted [19,20]. For CP-Ti a transition of the PEO coatings from a grooved structure to a porous morphology is observed [19]. Recent work is given on the addition of particles to the electrolyte in order to further enhance the coating's properties [21]. Using Ca- and P-containing electrolytes bioactive hydroxyapatite coatings can be generated, improving the osseointegration of implants [22–24]. Addition of Ag and Cu-particles enhances the antibacterial properties [25,26]. Introducing zirconia nanoparticles improves the wear resistance and corrosion resistance of the generated layers [27].

In the present work coating formation is investigated for galvanostatic and unipolar pulsed PEO, the influence of PEO current density and total charge density. It can be shown that for the alloy Ti 13Nb 13Zr

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* Corresponding author.
E-mail address: lederer@dechema.de (S. Lederer).

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the coating's morphology is subjected to a transition from a grooved surface structure to a porous structure dependent on the applied charge density. The formed crystalline phases consist mainly of anatase and rutile, where the anatase/rutile ratio can be varied in a wide range depending on the current density. Introduction of zirconia nanoparticles to the electrolyte leads to an enhancement of the coating's mechanical properties.

2. Experimental

2.1. Preparation of the samples

The substrate material used for the PEO treatment was the alloy Ti 13Nb 13Zr. Cylindrical samples with a height of 10 mm were cut from a rod of 15 mm diameter. The samples were ground using 180#, 280#, 320# and 500# grit SiC paper, rinsed with distilled water and ultrasonically treated for 10 min in ethanol.

2.2. Plasma electrolytic oxidation

A Sorensen SGI 800/6 power unit with a maximum output power of 5 kW was used for the plasma electrolysis of the samples. The samples were anodized in galvanostatic mode with an upper voltage limit of 400 V at different current densities of 14 mA cm^{-2}, 70 mA cm^{-2}, 140 mA cm^{-2}, 420 mA cm^{-2}, and 700 mA cm^{-2}. Time dependent cell voltage and current data were recorded by Labview software. In order to keep the surface charge density of 63 C cm^{-2} constant the minimum processing time was 1.5 min, while the maximum time of treatment was 75 min. The temperature of the electrolyte was adjusted to a constant value of 20 °C using a recirculation thermostat LAUDA ECO RE 420. For the PEO process a two-electrode electrochemical cell system was used with the titanium specimens as the anode (surface area A = 7.1 cm^2). The cathode was a cylindrical platinized titanium mesh with a diameter of 10 cm. As electrolytes for the PEO treatment, acidic solutions consisting of 0.1 M H_2SO_4 + 0.01 M H_3PO_4, and respectively, 1.0 M H_2SO_4 + 0.1 M H_3PO_4 were used. In order to improve the wear resistance of the layers, monoclinic zirconia nanoparticles (primary particle diameter 5–25 nm) were added to the electrolyte. The composition of the used electrolytes is summarized in Table 1. Zirconia nanoparticles with 4 g/L were dispersed ultrasonically for 10 min. Particle size and zeta potential was measured using a Malvern Instruments Zetasizer Nano ZS in order to determine the dispersion stability. In general zeta potentials close to zero tend to result in unstable dispersions due to agglomeration of the particles, whereas high potentials have a stabilizing effect ($\zeta > |30|$ mV). Zirconia containing dispersions were used for PEO treatments of Ti 13Nb 13Zr samples at current densities of 14, 140, 420 and 700 mA cm^{-2} and frequencies of 1, 10 and 50 Hz. After the treatment, the samples were rinsed with distilled water and dried in air.

2.3. Characterization

The generated oxide layers were characterized with respect to their corrosion properties, the layer morphology, the phase composition and their mechanical properties.

Table 1
Composition of used electrolytes.

Electrolyte	Composition	pH	Conductivity [µS cm^{-1}]
[A]	1 M H_2SO_4 0.1 M H_3PO_4	0.1	380
[B]	0.1 M H_2SO_4 0.01 M H_3PO_4	1.0	47
[C]	1 M H_2SO_4 0.1 M H_3PO_4 4 g/L ZrO_2	0.1	380

Coatings were analyzed by scanning electron microscopy (SEM) with a Philips XL 40 instrument. Thicknesses of the coatings were determined by preparing metallographic cross-sections and subsequent analysis by SEM.

Phase composition was investigated by XRD measurements using a diffractometer (D8 ADVANCE, Bruker) with Cu-K$_\alpha$ radiation (λ = 1.54 Å), a voltage of 40 kV and a current of 30 mA. A step width of 0.02° and a scanning speed of 0.24° min^{-1} scanning the angular range from $10° < 2\theta < 100°$ was chosen. Since the PEO layers are thin (d ~ µm), they were analyzed under grazing incidence of 7°, reducing the contribution of the substrate.

Integral corrosion investigations were carried out for PEO treated samples and for the substrate material Ti 13Nb 13Zr. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used. OCP measurements and potentiodynamic polarization curves were performed using a Voltalab PST050 potentiostat. The investigations were carried out in a simulated body fluid (SBF) with the addition of hydrogen peroxide at 37 °C. The addition of H_2O_2 simulates a natural inflammation reaction which is caused by the introduction of a foreign body into the human body. To examine the barrier properties of the layers electrochemical impedance spectra were recorded. The experiments were performed using a potentiostat ZAHNER Zennium. For the measurements, sinusoidal alternating voltages with amplitudes of ± 10 mV in the frequency range from 10 mHz to 100 MHz were applied. As for the OCP and polarization measurements, an electrolyte consisting of SBF + 0.1 M H_2O_2 was used.

The mechanical properties of the PEO layers were investigated by nanoindentation measurements. A nanoindentation instrument Anton Paar with a Berkovich indenter was used. 36 indentations were applied on the surface in a 6 × 6 matrix, respectively. The maximum applied force was 25 mN. The model according to Oliver & Pharr was used to evaluate the data [28] and to determine the hardness and the elastic modulus of the layers.

3. Results and discussion

3.1. Coating growth and morphology

In Fig. 1 the time dependent voltage responses during PEO at 14, 140, 420 and 700 mAcm^{-2} are shown. Depending on the slopes of the voltage increase, four stages of layer growth can be determined, as

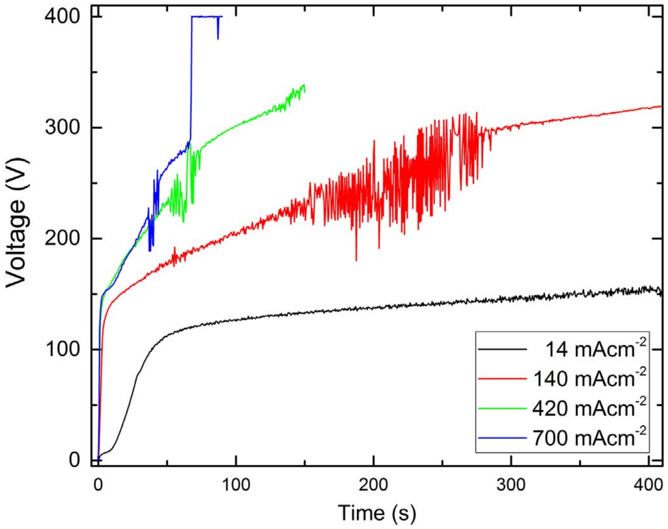

Fig. 1. Voltage responses during PEO of Ti 13Nb 13Zr at current densities of 14 mA cm^{-2}, 140 mA cm^{-2}, 420 mA cm^{-2} and 700 mA cm^{-2} obtained in 1 M H_2SO_4 + 0.01 M H_3PO_4.