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ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 125−133
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Structure and properties of micro-arc calcium phosphate coatings on pure titanium and Ti−40Nb alloy

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Received 19 January 2016; accepted 26 August 2016

Abstract: The microstructure, physical and mechanical, and chemical properties of micro-arc calcium phosphate (CaP) coatings deposited under different process voltages in the range of 150−400 V on the commercially pure titanium (Ti) and Ti−40%Nb (Ti−40Nb) (mass fraction) alloy were investigated by the SEM, TEM, XRD and EDX methods. The coating thickness, roughness, and sizes of structural elements were measured and showed similar linear character depending on the process voltage for the coatings on both substrates. SEM results showed the porous morphology with spherical shape structural elements and rough surface relief of the coatings. XRD and TEM studies exhibited the amorphous structure of the CaP coating. With increasing the process voltage to 300−400 V, the crystalline phases, such as $CaHPO_4$ and β-$Ca_2P_2O_7$, were formed onto the coatings. The annealing leads to the formation of complex poly-phase structure with crystalline phases: $CaTi_4(PO_4)_6$, β-$Ca_2P_2O_7$, TiP_2O_7, $TiNb(PO_4)_3$, TiO_2, NbO_2, and Nb_2O_5. The applied voltage and process duration in the ranges of 200−250 V and 5−10 min, respectively, revealed the coating formed on Ti and Ti−40Nb with optimal properties: thickness of 40−70 μm, porosity of 20%−25%, roughness (R_a) of 2.5−5.0 μm, adhesion strength of 15−30 MPa, and Ca/P mole ratio of 0.5−0.7.

Key words: calcium phosphate coating; micro-arc oxidation; Ti−40%Nb alloy; commercially pure titanium; microstructure

1 Introduction

At present metal implants are widely used in medicine to bone tissue replace and to correct its damages and defects. Titanium-, cobalt-, and stainless steel-based alloys are most often used as metal implants in traumatology and orthopaedics [1]. Lately, the third-generation low-modular titanium alloys containing niobium, tantalum, zirconium, and molybdenum become more and more widely used since they are characterized by good ductility and high mechanical strength. The main requirements to metal biomaterials are low elastic modulus compared with that of the human bone (less than 30 GPa) and non-toxicity of alloying components. Regarding the increased biomechanical compatibility, alloys of titanium−niobium system are attractive because they can also possess pseudoelasticity effect approaching their properties to those of the bone tissue [2]. YAO et al [3] reported that the phase stability and elastic modulus of the Ti−Nb β-alloy increased monotonically when the niobium content increased from 5% to 40% (mass fraction). Thus, the Ti−40%Nb (Ti−40Nb) (mass fraction) alloy is the most suitable material for the medical implants providing good biomechanical interaction with the bone tissue.

To increase the biological, chemical, and mechanical properties, different modification methods of the implant surface, such as machining, ion implantation, plasma coating deposition, and electrochemical anodizing are used [4]. The micro-arc oxidation (MAO) method, also known as plasma electrolytic oxidation (PEO) or spark anodizing, is a promising method of surface treatment, since it allows one to obtain

Foundation item: Project (III.23.2.5) supported by the Fundamental Research Program of the Siberian Branch of Russian Academy of Sciences; Project (15-03-07659) supported by the Russian Foundation for Basic Research; Project (CR16-22) supported by the China and Russia on the Implementation of Inter-governmental Scientific and Technological Cooperation Projects of the Notice (NSC foreign word [2012] No. 269)

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DOI: 10.1016/S1003-6326(17)60014-1

biologically active coatings with porous structure. The main advantage of this method is the possibility to control Ca and P ions deposition on the substrate surface due to changing of the electrolyte solution and concentration. Moreover, the MAO method is well suited for the modification and functionalization of the complex shape metal substrates, providing an efficient chemical barrier that prevents escaping of metallic substrate ions and increases the corrosion resistance of titanium alloys [5−7].

It is assumed that after implant introduction into the human organism, transition from the primary mechanical stability caused by the material and design of the implant (primary stability) to the biological stability caused by the surface relief and chemical and hydrophilic properties occurs in the bone tissue–implant joint, which provides the formation of a new bone tissue in the process of osseointegration (secondary stability). Thus, the mechanical strength, structure, morphology, surface implant relief, and chemical properties are important factors in the process of osseointegration which influence the force of contact in the bone tissue–implant interface and can also reduce terms of healing after implant introduction into the human organism [8−10].

The present work is aimed at comparative investigation of the microstructure and physical and mechanical, and chemical properties of the calcium phosphate (CaP) coatings deposited on pure titanium and Ti−40Nb alloy by the MAO method.

2 Experimental

Sample plates (10 mm × 10 mm × 1 mm) were fabricated from commercially pure titanium (Ti, grade 2) and Ti−40Nb alloy. The Ti−40Nb alloy was produced in General Research Institute for Non-ferrous Metals, Beijing, China [11]. The samples were successively ground using SiC abrasive paper with 180, 600, and 1200 grits to remove the natural surface oxide. Then, samples were ultrasonically cleaned sequentially in distilled water and ethanol for 10 min and dried in the air. FEGOSTAEVA et al [12] reported that to carry out micro-arc oxidation for deposition of CaP coatings on specimens, the Micro-arc-3.0 technique was used. The calcium phosphate coatings were deposited from an aqueous solution prepared from 20% phosphoric acid (H_3PO_4) (mass fraction), 6% biological hydroxyapatite (HA, $Ca_{10}(PO_4)_6OH_2$) (mass fraction), and 9% carbonate calcium ($CaCO_3$) (mass fraction) in the anode regime [13]. Micro-arc oxidation process was performed with initial current densities in the range of 0.2−1.0 A/cm^2 using a regulated pulse power supply unit. In the previous works [12−14], we found the optimal micro-arc oxidation parameters for deposition of the CaP coatings on the titanium as follows: pulse frequency of 50 Hz, pulse duration of 100 μs, process duration in the range of 5−10 min, and electrical voltage in the range of 150−400 V. In this work, we used the same MAO parameters for the coating synthesis on the Ti−40Nb alloy substrate. It is known that ordinarily, the MAO method allows to form amorphous coatings with good bioresorption [4−7,9,10,14]. To obtain the crystalline structure of the CaP coatings, some specimens after MAO treatment were subjected to the crystallization annealing at 800 °C for 1 h and the subsequent cooling in the air.

The surface morphology and the structure of the CaP coatings were investigated by scanning electron microscopy (SEM, JEOL JSM−7001F and LEO EVO 50, Zeiss) and transmission electron microscopy (TEM, JEOL JEM−2010). In addition, the elemental compositions and distributions of the coatings were also analyzed using energy-dispersive X-ray spectroscopy (EDX, Pegasus XM2 and INCA, Oxford Instruments) in combination with the SEM systems. The EDX microanalysis was performed in CaP coating micro-areas of top and cross-sectional SEM images. The porosity of the CaP coatings was measured using SEM images. To measure the size of the coating structural elements, the secant method was applied according to the ASTM E1382−9 and DD ENV 1071−5. The porosity (P) was calculated from the formula: $P=\sum l/\sum L\times 100\%$, where L is the length of a secant randomly put on the SEM images and l is the length of the secant part which falls on pores. The number of secants was 50 for each specimen.

For TEM analysis, two types of CaP coating replica were prepared: the first one, indirect method of analysis due to replica removed from CaP layer; the second one, preparation of the cross-section CaP films including cutting slices, polishing slices, and ion milling. Firstly, slices with 2 mm in width and 10 mm in length were cut from the appropriate samples using a diamond wire saw on a slicer (Buehler Isomet low speed saw). Then, stacks were formed by bonding together two slices of the substrate with CaP coating and the substrate was cleaned so that the CaP coating was in the middle. For gluing, Gatan two-component epoxy glue was used. At 100 °C, the hardening time was about 5 min. After annealing, the stack was cut into slices with 1 mm in width on the slicer. Secondly, polishing the slices from each side down to a thickness of about 500 μm was carried out by hand on wet grinding paper. Then, appropriate slices were glued on the metal ring with an outer diameter of 3 mm and an inner diameter of 1.5 mm. After this, appropriate films were polished down to a thickness of about 100 μm. Thirdly, a Gatan 691 precision ion polishing system (PIPS) was used for the ion milling.