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Original Research Article

Characterization of microporous oxide layer synthesized on Ti–6Al–7Nb alloy by micro-arc oxidation

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ABSTRACT

In this work a microporous oxide layer was formed on two phase (α+β) Ti–6Al–7Nb titanium alloy by the micro-arc oxidation process in an electrolyte containing $(CH_3COO)_2CaH_2O$ and Na_3PO_4. The thickness of the surface layer was in the range of 2.7 μm–3.6 μm.

Microstructure of the surface layer and the substrate alloy was characterized with use of scanning- and transmission electron microscopy as well as by X-ray diffractometry. The microstructure of the surface layer consisted of TiO_2 rutile and anatase nanocrystals as well as of amorphous regions containing mainly Ti, Ca and O atoms and a minority of P, Al and Nb ones. The surface layer was highly porous. The open pores, with diameter up to 6 μm, were homogenously distributed in the specimen surface. Electron tomography was used to investigate the pores morphology and spatial distribution. It was found that open pores exhibited a complex geometry. The closed pores had nearly spherical shape.

Adhesion of the surface layer to the titanium alloy substrate was investigated by means of the scratch-test. The value of critical load L_{C2}=14 N indicates a good layer adhesion to the underlying substrate.

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1. Introduction

Titanium based alloys are widely used in medicine [1,2]. Among the most important applications are the load bearing components of hip and knee joint prostheses. Two phase (α+β) Ti–6Al–4V and Ti–6Al–7Nb alloys are used predominatingly. These materials exhibit a high relative strength and a good corrosion resistance [2]. The Ti–6Al–7Nb alloy has a better biocompatibility than Ti–6Al–4V, due to replacement of a noxious vanadium alloy addition by a more biocompatible niobium one [2,3].

The surface of an implant material plays a crucial role in the interaction with the biological environment. In some medical applications, e.g. stem or acetabulum of joint prostheses, a

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strong bonding between the implant and the surrounding human tissue is required. In order to achieve this aim a particular surface treatment is required. The proper surface modification techniques do not change the excellent bulk properties of titanium alloys, such as good fatigue strength, formability, machinability and a relatively low Young's modulus. It also improves specific surface properties in conformity to different clinical requirements. The titanium alloy surface can be modified by means of a microporous surface layer containing bioactive agent [4]. Formation of a porous surface of the orthopedic implants by deposition of a porous layer might enhance the bone-implant integration process. It is well known that the osteoblastic cells adhere better to rougher surfaces, whereas the fibroblasts favor smooth ones. Although optimum pore size required for the best implant fixation remains undefined, in the most cases the pore sizes in the range of 100–400 μm are necessary in order to optimize mineralized bone ingrowth [5]. However, Itala et al. [6] demonstrated the formation of an osteonal bone structure in pore sizes as small as 50 μm. Similarly, Bobyn et al. [7] showed effective bone ingrowth into microporous coatings of the pore size as low as 50 μm. The surface porosity of coated implants is usually determined to compromise between a good adhesion of the porous coating to the substrate and an adequate pore size for tissue ingrowth.

Among the surface engineering methods used to produce the rough and microporous surface layer or coating the micro-arc oxidation (MAO) technique is frequently used in order to enhance the bonding strength of the titanium alloy implant to the host bone [8–11]. Therefore, in this study, in order to improve bonding between the titanium alloy and the surrounding osteoblastic tissue a microporous surface layer was synthesized on Ti–6Al–7Nb alloy by MAO. MAO, also called anodic spark oxidation or plasma electrolytic oxidation (PEO), is a complex plasma-enhanced physico-chemical process which involves micro-arc discharges, diffusion and plasma chemical reactions [8]. The difference between MAO and the conventional anodic oxidation is that MAO employs higher potentials to discharges and the resulting plasma modifies the structure of oxide layer [9]. MAO can be used to grow crystalline oxide layer of the thickness ranging from 10 μm to several hundred micrometers. It is a very promising process for medical applications, because it enables deposition of microporous surface layers containing Ca and P elements [10]. Zhao et al. [11] showed that the MAO coatings are conducive for osteoblast's adhesion. Preliminary ''in vivo'' tests of the MAO-treated specimens on rabbits showed a considerable improvement in their osseointegration capability as compared to that of the pure titanium implants [12]. In summary, MAO is a potential method for synthesis of porous multicomponent surface layers on titanium alloys, which promote osteoblast cells' adhesion. This technique can be applied for orthopedic and dental implant materials.

The main objective of the present study was to characterize of a microstructure and phase composition of the microporous surface layer and its adhesion to the Ti–6Al–7Nb alloy substrate. A particular attention was focused on characterization of the size and spatial distribution of pores in the surface layer using electron microscopy and 3-dimensional visualization of pores with use of electron tomography.

2. Experimental

The investigation was performed on a surface treated, two phase (α+β) Ti–6Al–7Nb titanium alloy. Nominal chemical composition of the alloy is as follows (in wt%): Ti–6Al–7Nb–0.25Fe–0.5Ta–0.2O–0.05N–0.009H–0.08C. The titanium alloy substrate was surface treated by MAO in an electrolyte containing $(CH_3COO)_2CaH_2O$ and Na_3PO_4. The equipment used for performing the MAO treatment consisted of a 30 kW bipolar power supply, a stainless steel container and an external cooling unit to stabilize the electrolyte temperature below 30 °C. The MAO process was conducted for 10 min. under a constant voltage mode using positive and negative voltages of 400 V and 80 V, respectively. Details concerning the surface treatment are described by Cimenoglu et al. in Ref. [13].

Microstructure of the titanium alloy and the surface layer was characterized by analytical scanning- and transmission electron microscopy (SEM, TEM) as well as by means of X-ray diffractometry (XRD). The SEM investigation was performed with use of a NEON® 40EsB of Zeiss. The TEM investigation was carried out with use of a JEOL JEM-2010 ARP microscope using the cross-section lamellas prepared by Focused Ion Beam (FIB). Chemical composition was investigated with use of energy dispersive X-ray spectroscopy (TEM–EDX and STEM–EDX). The XRD patterns were recorded by Bragg–Brentano method using Siemens D500 diffractometer and Cu Kα radiation on plan-view specimens. Phase identification was performed by means of selected area electron diffraction (SAED) and XRD. The SAED patterns were interpreted with the help of Java Electron Microscopy software (JEMS) [14]. Meso-scale electron tomography (FIB-SEM) was based on a serial sectioning procedure employing a dual beam workstation Zeiss NEON 40EsB CrossBeam with field emission electron gun [15]. The SEM images were taken using in-lens SE+EsB detectors at a low voltage of 2 kV. Repeated removal of layers as thin as a 15 nm allowed to explore a total volume of 13.3 μm×7.9 μm×1.2 μm with the voxel size 15 nm×15 nm×15 nm (the size of the raw data stack was 119 MB). The 3D visualization of reconstructed space for FIB-SEM tomography was performed using AvizoFire 6.3 software.

Adhesion of the surface layer to the substrate was measured using microscratch technique and conical Rockwell C diamond stylus with a 200 μm tip radius. Scratch tests were performed under increasing load from 0 to 30 N. The scratch length was 5 mm. The values of the critical loads, L_{C1} and L_{C2} for inducing cohesive and adhesive cracks (respectively), were determined from light microscopy (LM) observations as well as from acoustic emission and friction force signals.

3. Results and discussion

Microstructure of the substrate Ti–6Al–7Nb alloy consisted of α grains (hexagonal close-packed; hcp) and β grains (body-centred cubic; bcc) (Fig. 1). The average diameter of α and β grains was in the range of 3–15 μm and 1–3 μm, respectively. Linescan profiles and element distribution maps, recorded using the STEM–EDX method, showed an enrichment the α phase in Al atoms and of the β phase in Fe, Nb and Ta ones.

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