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Investigations of corrosion on the surface of titanium substrate caused by combined alkaline and heat treatment

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Vukoman Jokanović [a,*], Miroljub Vilotijević [a], Bojan Jokanović [b], Monika Jenko [c], Ivan Anžel [d], Dragoslav Stamenković [e], Vojkan Lazic [e], Rebeka Rudolf [d,f]

[a] Vinča Institute of Nuclear Sciences, Mike Petrovića Alasa 12-14, Belgrade, Serbia
[b] SGL Carbon, Meitingen, Germany
[c] Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
[d] University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, Slovenia
[e] University of Belgrade, High School of Dental Medicine, Dr. Subotića 8, 11000 Belgrade, Serbia
[f] Zlatarna Celje d.d., Kersnikova 19, 3000 Celje, Slovenia

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ABSTRACT

In this research, the structure changes along the depth of gradient layers of titanium substrate, after etching with NaOH and subsequent thermal treatment at various temperatures between 300 and 800 °C, were investigated by XRD, FTIR and AES. Particularly, the changes of Ti substrate after etching with NaOH, subsequent ionic exchange of Na^+ with Ca^{2+} ions and thermal treatment at 700 °C were analysed. Due to this approach, it was possible to get insight into the chemical changes and changes of Ti oxidation states and consequent phase analysis, along the depth of the titanium oxide coatings.

In addition, Secondary Electron Imaging (SEI) showed very interesting nanotopology of all samples. Particularly interesting topology, consisting of very thin nano-designed walls between mutually interconnected pores, was observed for the sample in which Na^+ were replaced with Ca^{2+} ions. This structure might be suitable for deposition of hydroxyapatite by biomimetic or plasma methods and as an appropriate scaffold for cell adhesion and proliferation.

1. Introduction

Titanium and titanium alloys have been used widely as implant materials for total hip replacements, bone fixation and replacements of various bone defects, due to their good properties like low module of elasticity, good fatigue strength, formability, mechanical workability and corrosion resistance [1,2]. Despite all this, titanium and its alloys cannot fulfil all necessary clinical requirements, particularly those related with biological properties of the material [3,4]. Therefore, surface modification of titanium and its alloys is necessary, by formation of thin oxide layers, using various methods of chemical and electrochemical preparation [5–7].

Kim et al. first introduced alkali and heat treatments, which have been further widely studied in many papers [8]. The treatments of titanium and titanium alloys using NaOH should be adjusted to obtain a titanium oxide layer of optimal thickness which enables gradual transition from the mechanical and corrosion properties of titanium implant to the properties of top oxide layer. Chemical composition of the layer changes with the distance from the surface (with the maximal quantity of bound oxygen on the top layer and minimal on the contact with pure metal) causing the changes of physical, particularly mechanical properties. Besides the improvement of mechanical stability of gradient oxide layer, this approach enables the optimization of implant biological properties, and formation of a reliable and reproducible titanium oxide/hydroxide surface.

To the present, the knowledge about the quantitative composition of the oxide/hydroxide overlayer and the mechanism of the overlayer formation is not satisfactory. The distribution of various titanium oxidation state oxides was subjected to thermodynamic analysis of the oxygen, which had been used to oxidize the titanium to a range of oxidation states ((IV), (III) and (II), respectively) under chosen temperature and pressure conditions [9]. Generally, Ti oxidation is characterized by fast oxygen adsorption, followed by slower oxygen uptake until saturation is reached. Obviously, a systematic study of the oxidation and hydroxylation of the titanium surface has a particular importance as a first step in the full understanding of the process of oxide/hydroxide formation as overlayers on titanium surfaces [9,10].

It is expected that the formation of sodium titanates on titanium and titanium alloys' surfaces, by their etching with NaOH solution and a subsequent heat treatment, can be very helpful for

* Corresponding author. Tel.: +381 113408724; fax: +381 113408607.
E-mail address: vukoman@vin.bg.ac.rs (V. Jokanović).

further formation of apatite on their surfaces in a living body [11–13]. However, the apatite forming ability of NaOH and heat-treated Ti metal decreases when it is stored in a humid environment for long periods, since the sodium ions of the sodium titanate are released slowly by exchange with H_3O^+ ions from the moisture in the atmosphere. Uchida et al. [14] first reported that Ti metal which forms anatase and rutile on its surface by etching in NaOH solution, has been very useful for the formation of apatite on its surface in SBF. Wang et al. [15] reported that Ti metal which forms anatase on its surface after corresponding heat treatment is especially useful for the formation of apatite on its surface in an SBF.

The fine network structure formed by NaOH treatment has been composed of nano-sized sodium hydrogen titanate ($Na_xH_{2-x}Ti_yO_{2-y+1}$, where $0 < x < 2$ and $y = 2, 3$ or 4), which has been converted into sodium titanate ($Na_2Ti_yO_{2y+1}$, $y = 5, 6, \ldots$) and rutile by the subsequent heat treatment [10,16]. These structural changes due to NaOH and heat treatments are particularly effective for Ti and Ti-based alloys in inducing bioactivity [10,16]. In addition, Kasuga proposed that the NaOH treatment broke some surface Ti—O—Ti bonds, forming Ti—O—Na and Ti—OH bonds in their place, while the subsequent acid washing leads to dehydration of the Ti—OH bonds and formation of Ti—O—Ti bond and (Ti—O$\cdots$H—O—Ti). The formation of Ti—OH bonds has probably been caused by decreasing of the Ti bond distance on the Ti surface during the dehydration process, while a residual electrostatic repulsion from the Ti—O—Na bonds induced a specific morphological design of TiO_2 structures, as a consequence of different crystal structures and compositions of the obtained titanates $Na_xH_{2-x}Ti_3O_7$ [16,17].

Besides, as is well-known, the sodium hydrogen titanates formed on Ti metal and its alloys by the NaOH treatment have a layered structure in which sodium ions in the interlayers can be replaced not only by H_3O^+ ions but also by Ca^{2+} ions [18,19]. Kizuki et al. [20] showed that the higher apatite-forming capacity was obtained when the Na^+ ions were replaced by with Ca^{2+} ions in the surface sodium titanate layer, and then subjected to heat treatment. Such surface modification resulted in significantly improved stability of apatite formed on Ti in the simulated body fluid, since the Ca^{2+} ions released from the surface layer could increase the ionic activity product of the apatite in the surrounding fluid more effectively than Na^+ ions, and the diffusion of the Ca^{2+} ions in the surface layer would be lower than that of Na^+ ions [19,20]. Also, in histological investigations of Jinno et al. [18], it was shown that Ca^{2+}-implanted stems had greater new bone apposition than non-Ca^{2+}-implanted stems and they concluded that Ca^{2+} implantation may be beneficial for early fixation of titanium-alloy implants.

The investigation presented in this paper has the intention to give a new insight into the layered structure formed on the surface and sub-surface of titanium substrate during NaOH etching, and profound analysis of the diffusion processes and generated phases during these processes, taking into account that exchange of Na^+ with Ca^{2+} ions in real biological processes can give better results. Such a procedure can be particularly important for the preliminary process of preparation of a Ti metal surface for plasma jet technology, which was applied in our previous investigations, as a method for deposition of calcium hydroxyapatite coatings.

2. Experimental

DC titan was used in this investigation. Its main characteristics were given by its producer (Bien-Air Medical Technologies, Switzerland). It is relatively pure titanium, used in medical devices, with physical properties given as follows: Melting point 1668 °C, hardness 180 HV, tensile strength >350 MPa, elasticity modulus 110 GPa, yield strength >275 MPa and chemical composition: C_{max} 0.08 at.%, N_{max} 0.03 at.%, O_{max} 0.025 at.%, Fe_{max} 0.30 at.%, H_{max} 0.015 at.%, Si_{max} 0.3 at.%, Mo_{max} 0.02 at.%, V_{max} 0.01 at.%, Al_{max} 0.05 at.%, Ni_{max} 0.01 at.% and others individual max. 0.01 at.%, while the content of Ti was 99.2 at.%. The biocompatibility of this material has been described extensively in the literature and in producer data. The rods of these materials (diameter – 1 cm, height – 2 mm) were polished on one side using fine Al_2O_3 powders with granulation of 5–0.05 mm.

The specimens were then immersed in 5.0 ml of 5 M NaOH aqueous solution for 24 h. Afterwards they were removed from the solution, and washed gently with distilled water, followed by drying at 40 °C for 24 h in an air atmosphere. The treated metal was then heated up to 300, 500, 700 and 800 °C at a rate of 5 °C/min in an Ni—Cr electrical furnace in an air atmosphere during 5 h. One of the samples was treated under pressure of oxygen at 0.13 Pa in a tube chamber with continuous oxygen flow, at 700 °C. After thermal treatment all the samples were cooled to room temperature in the furnace.

XRD analysis was made on the surface of the treated samples, by using Philips PW 1050 powder diffractometer with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å) and scintillation detector within 2θ in the range 25–85°, in steps of 0.05°, with the scanning time of 3 s per step. The crystallite sizes of various Na-titanates, Ti_2O and TiO_2 phases, were calculated by Sherer's equation $d = K\lambda / B\cos\theta$, where d (in nm) is the average diameter of crystallites, K is the shape factor, B is the width of the characteristic diffraction peak for the given phase at half of its maximum height, λ is the wave length of the used X rays, and θ is the Brag diffraction angle. The plane corresponding to $2\theta = 22°$ was chosen for calculation of the crystallite size of $Na_4Ti_5O_{12}$, while the plane corresponding to $2\theta = 14.26°$ was used for calculation of the crystallite size of $Na_2Ti_9O_{19}$. For the rutile phase, plane (1 1 0) at $2\theta = 27.6°$ was used and for the $NaTiO_3$ phase – plane (2 3 2) at $2\theta = 40°$.

The obtained phases were also examined by a Fourier transform infrared spectrometer (Nicollet 380 FTIR, Thermo Electron Corporation) in the Attenuated Total Reflectance (ATR) mode. FTIR spectra were recorded in the spectral range 4000–400 cm^{-1}.

The Field Emission Auger Electron Spectroscopy (FE-AES) instrument used in this study was a Thermo Scientific Microlab 310-F spectrometer, equipped with a spherical-sector analyzer and a field emission electron gun with a thermally assisted Schottky field emission source that provides a stable electron beam in the accelerating voltage range of 0.5–25 keV. The electron analyzer is of a double focusing spherical sector type with an electrostatic input lens and can provide energy resolution between 0.02% and 2%. The spectrometer has five sequential channeltrons (electron detectors), each of which detects 2.5% of the pass energy. Spectra are mostly acquired with a constant retard ratio (CRR) of 4 which provides an energy resolution that is 0.5% of the pass energy. At a fixed pass energy channeltrons can be assigned separately to provide peak or background signals for simultaneous elemental mapping. The samples surfaces were cleaned with Ar^+ ions ($E = 2$ keV, $r = 12$ mAc m^{-2}, $Q = 47$) to remove contaminants. For the depth profiling, the samples were sputtered with a 3 keV Ar^+ sputtering rate of about 1.2 nm/min and the analysis was performed before the first sputtering and after each sputter cycle.

To analyze the morphology, size distribution and average size of $Na_4Ti_5O_{12}$, $Na_2Ti_9O_{19}$, $NaTiO_3$, Ti_2O and TiO_2 particles, Electron Microscope Quanta 200 3D was used, operating in high vacuum with resolution 3.5 nm at 30 kV. The microscope is equipped with classical Everthart–Thornley detector with Photomultiplier (SEI) for observing the morphology and other characteristics of the area covering the secondary electrons in high vacuum. The microscope is also equipped with ion gun (FIB – Focused Ion Beam) which generates focuses ion stream Ga ions, which was used to crop cross-section of the sample in the micro-area. The resolution of the ion gun is 10 nm at 30 kV.