BIOACTIVITY OF CHEMICAL, ELECTROCHEMICAL AND THERMAL TREATMENT OF Ti6Al4V

H. Lukáčová[1], B. Plešingerová[1], M. Vojtko[2]
[1] Department of Ceramics, Faculty of Metallurgy, Technical University of Košice, Letná 9, SK – 042 00, Slovakia,
[2] Department of Materials science, Faculty of Metallurgy, Technical University of Košice, Park Komenského 5, SK – 042 00, Slovakia

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Corresponding author: H. Lukáčová, Telephone number: 00421055602 2773, Department of Ceramics, Faculty of Metallurgy, Technical University of Košice, Slovakia, E-mail: helena.lukacova@tuke.sk

Abstract
This work deals with surface modification of Ti6Al4V alloy. Compared are the morphology, structure, adhesion and bioactivity of Ti6Al4V after chemical treatment in alkali solution, anodic oxidation in mixed solution of $NH_4F + H_3PO_4$ and thermal treatment. In both cases of chemical and electrochemical treatment an amorphous layer of TiO_x is formed. Results showed that the alkali treatment leads to formation of a 1μm thick bioactive layer with net-structure, which offers a good basis for the growth of Ca-P compounds. The in vitro test confirmed a good bioactivity of this layer. The thermal treatment caused dehydration of this layer, what did not affect the good bioactivity as confirmed by the in vitro test. Anodic oxidation forms a nanotubular layer, which is not bioactive, but the thermal treatment activated this layer.

Keywords: surface treatment, adhesion, bioactivity, hydroxyapatite

1 Introduction

Titanium and its alloys are important materials in the production of implants for substitution of hard tissues for their good bioactivity, mechanical properties and corrosion resistance. To achieve good bioactivity the surface of titanium and its alloys is adjusted. Modifications of titanium surfaces, for example chemical treatment in alkali solution and anodic oxidation leads to formation of active TiO_x coatings. Different surface treatments have dissimilar effect on bioactivity of implants surface [1-6].

Chemical treatment in alkali solution generates an amorphous hydrated titanium oxide layer containing alkali ions (Na^+) on the surface of titanium [2-5,7,8]. Alkali treatment by 3 - 10 $mol.l^{-1}$ NaOH at 60 - 80 °C for 24 h forms an about 1 μm thick $TiO_2.nH_2O$ continuous layer with a porous net-structure.

Anodic oxidation (AO) is an electrochemical process that forms oxide layers on the metal surface. Compact or nanotubular solid oxide layer can be formed by anodic oxidation depending on the anodizing conditions as well as on the composition of electrolytes. If fluoride ions are present in the electrolytes a nanotubular layer of TiO_2 can be formed. The type of electrolyte and oxidation conditions (applied potential, the time of anodization) can affect the surface morphology, the chemical composition and the crystalline structure of the oxide films formed by anodic oxidation [6, 9-11].

Some surface treatments are combined with thermal treatment to obtain a high biocompatibility or to stabilize a surface layer. The thermal treatment brings some chemical, structural and morphological changes to the surface of Ti and its alloys. In order to form a more stable or more reactive layer, the hydrated titania gel layer is annealed at a temperature below 600 °C. The annealing dehydrates and compacts the layer and a partial crystallization of amorphous layer to anatase and/or rutile occurs [6,8,12,13]. It is stated in the works [10,14,15] that the anodic oxidation with the thermal treatment to 500-600 °C for 1-2 h have a positive effect to bioactivity. Amorphous TiO_2 nanotubes formed by AO were crystallized to anatase and rutile through a thermal treatment process.

The bioactivity is tested in vitro in solution of simulated body fluid (SBF) and the covering of the metal substrate by hydroxyapatite (HA) is evaluated [1,2,4]. The composition of SBF corresponds to the inorganic part of human blood plasma. Formation of apatite layer, similar to the bone apatite on the surface of the implants is a crucial condition of binding of the implant with a human bond. The surface that is able to support the process of HA precipitation, to firmly anchor hydorxyapatite (HA) on the surface, and so to accelerate and assure a direct bond of implant with bone is know as bioactive.

The aim of this paper was to compare the effect of surface treatments like alkali, electrochemical and thermal treatment to bioactivity.

2 Material and experimental methods

Experiments were carried out on Ti6Al4V alloy samples of a size of 10 x 10 x 0,8 mm^3. The samples were cleaned by fine-grinding and thereafter were washed by ultra-sound in acetone and in chloride acid solution (1:1) for 30 min. and in the end three-times washed in distilled water and dried in desiccator.

The surface of samples was treated by:

- Alkali solution of NaOH of a concentration of 10 $mol.l^{-1}$. The samples were exposed to alkali solution at a temperature of 60 °C for 24 h.
- Anodic oxidation (AO) in mixed solution of NH_4F and H_3PO_4 with $c(NH_4F)$=0,135 $mol.l^{-1}$ and $c(H_3PO_4)$ = 0,5 $mol.l^{-1}$. The samples were treated by AO at constant voltages of 10V for 30 min.. The samples of Ti6Al4V acted as the anode and the Pt – net served as the cathode [6].

One part of the alkali- and AO-treated samples was subsequently annealed at a temperature of 450 °C in duration of 3 hours. The speed of heating-up in LM 212.11 oven was 10° C/1min.

Before the in vitro test in SBF solution all samples were washed in distilled water and dried at room temperature. Then they were incubated in SBF solution for 7 days at a stable temperature of 37 ºC. The composition of SBF solution is given in **Table 1**. After exposure the samples were washed with distilled water and dried at room temperature.

Table 1 Composition of simulated body fluid (SBF) [2]

Solution	Ion concentration in solution [$mmol.l^{-1}$]								
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	$H_2PO_4^-$	SO_4^{2-}	HCO_3^-	pH
SBF	142	5	2.5	1	131	1	1	5	7.3*

*buffer TRIS/HCl

The changes of oxide layer on the treated surfaces were studied by electron microscope SEM-EDX (JEOL JSM-7000 F). The thickness of the oxide layer was measured by SEM on the fracture of the samples. The weight changes of the samples were weighted on Sartorius 4504

MP8-1 scales, with precision ± 0.005 mg. The adhesion of the layers to Ti6Al4V substrate after individual treatments was evaluated by X-cut tape test ASTM D 3359 [16].

3 Results and discussion

3.1 Comparison of affect of the surface treatment on the morphology of Ti4Al6V

The surfaces of the Ti6Al4V treated samples created by alkali solution (NaOH) and anodic oxidation (AO) show a different character.

The concentrated alkali solution creates a continuous net-structure of a thickness about 1 μm on the surface of the sample (**Fig.1**). The upper part of the surface layer, as shown in Fig 1.b, has a character of scaffold of a thickness of about 500 nm, the lower part is thicker. In the area of fracture the surface layer scales off.

By chemical treatment the weight of the samples increases a bit in average by over 0,1 mg.cm^{-2}. The thermal treatment reduced the weight of samples in average by 0,13 mg.cm^{-2} compared to the samples after alkali treatment. Probably the weight loss is a result of the dehydration of $TiO_2.nH_2O$ surface layer. The dehydration and densification of the surface layer causes cracking (**Fig.2**). The cracked surface layer in the area of fracture scales significantly off.

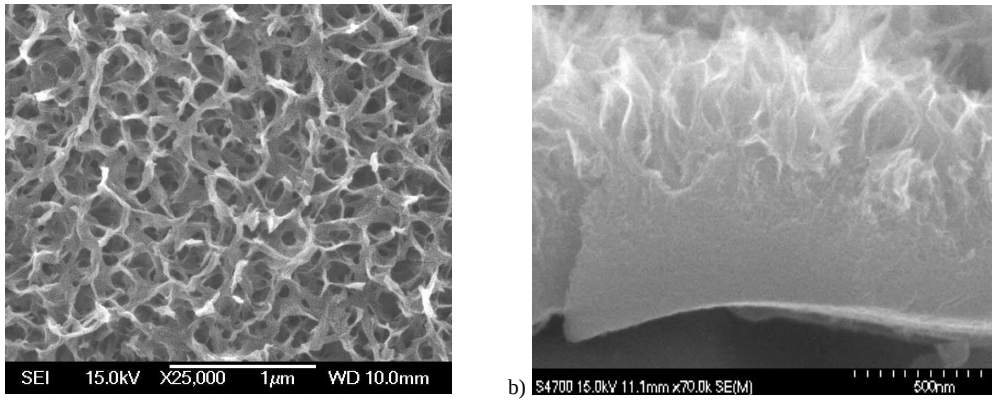

Fig.1 (SEM) Ti6Al4V after alkali treatment in 10 mol.l^{-1}NaOH a) surface, b) cross-section of the layer

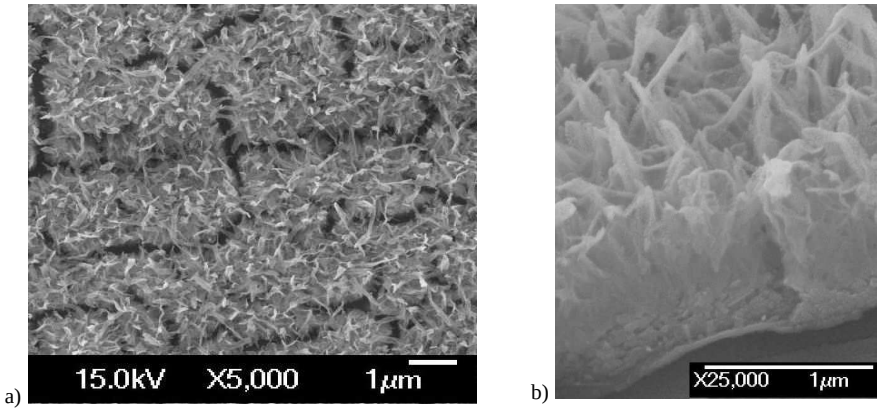

Fig.2 (SEM) Ti6Al4V after alkali- and thermal-treatment a) surface, b) cross-section of the layer

The surface of Ti6Al4V sample treated by anodic oxidation in mixed electrolyte (NH_4F a H_3PO_4) at condition of DC voltage of 10 V and time 30 min. is getting covered by nanotubular oxide layer. Although the Ti6Al4V surface oxidizes in AO there is a weight loss of sample. As show in [6,7] the nanotubes of TiO_x of in inner diameter of 30 - 50 nm and a length of 100-130 nm are vertically oriented and the nanotubes layer is continuous. By breaking the sample at the fracture point the tubes separate but do not break (**Fig.3a**). By annealing of the samples at a temperature of 450 °C the nanotubes get partially damaged. The oxide layer appears to be more dense (**Fig.3b**) and the tubes extend along the rest of the layer to the depth of about 70-100 nm. The weights of samples negligibly increase after annealing. By breaking the tubes do not separate like the samples that were not annealed.

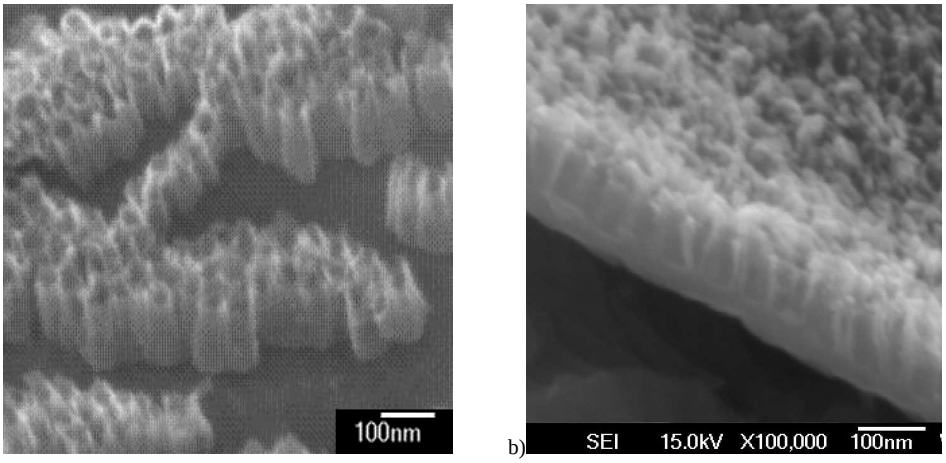

Fig.3 (SEM) Cross-section of Ti6Al4V sample treated a) by AO b) by AO and annealing

The representation of the elements Ti, Al, V, O and Na in surface layer before and after thermal treatment was comparable (**Table 2**). EDX analysis confirms content of Na^+ ions in the treated surface layer. The results of analysis do not show significant oxidation of the chemically modified surface of the sample annealed at a temperature of 450 °C. In the cases of AO treatment the surface layer of nanotubes is thinner than in case of alkali treated samples and, accordingly, the value of oxygen is lower. The analyzed fluoride ions in the surface layer come from the applied electrolyte. Phosphoric ions were not detectable in treated layer by AO. The results, obtained by EDX analysis of thermally treated and non-thermally treated samples are comparable.

Table 2 EDX analysis of Ti6Al4V samples after particular treatments

Ti6Al4V samples - treatment	**Composition of Ti6Al4V surface [weight %]**						
	Ti	**Al**	**V**	**F**	**O**	**Na**	**Ca**
Initial samples	90	6,4	3,6	-	-	-	-
Alkali treatment	30 - 35	1 - 2	0,5	-	59- 61	6 - 7	1
Alkali and thermal treatment	31,2	1,5	0,4	-	60,2	5,8	0,8
Anodic oxidation	68,7	4,7	2,6	8,88	15,1	-	-
Anodic oxidation and thermal treatment	71,8	5,3	3,7	5,9	13,3	-	-

The cohesion of oxidized layer to the substrate of the alkali treated samples was very good. The layer did not scale off by tape test and the surface remained covered by remnants of glue. The

surface layer of alkali- and thermally treated samples partially peeled off from the substrate by tape test.
In case of both thermally and non-thermally treated samples too the tubes remained almost continuously covered by remnants of glue after the tape test and the tubs remained without damage.

3.2 Comparison of the effect of the surface treatment on the bioactivity of Ti4Al6V

The bioactivity of chemically, electrochemically and thermally treated samples has been evaluated for 7 days by in vitro test in SBF solution. The samples treated by alkali solution showed good bioactivity; the same is valid for the alkali- and thermally treated samples. The surface in SBF solution got continuously covered with crystals of Ca-P compounds (**Fig.4**). Globulous character of microcrystal clusters is typical for hydroxyapatit. Molar ratio of Ca/P in apatite coating ranges of 1.5 – 1.8. The thicknesses of defective hydroxyapatite layers were about 2 μm and the crystals overgrew to the activated surface of Ti4Al6V alloy.
The sample treated by anodic oxidation with nanotubes layer haven`t been covered with Ca-P compounds during the 7-day test in SBF solution (**Fig. 5a**). HA-spherulites were formed only exceptionally on TiO_x tubes. In contrast to the AO treated samples which were non-bioactive the AO and subsequently thermally treated samples were bioactive. Thermal treatment caused degradation of tubes and re-crystallization of TiO_x [6]. The thermally-treated sample was covered by a continuous layer of the Ca-P crystals after the in vitro test. The typical HA coating of a thickness of about 5 μm is shown in **Fig. 5b** and **5c**. The observed cracks of thick hydroxyapatite layer under SEM were formed during the drying of the HA-layer. At fracture of sample the apatite layer scaled off on the apatite/ nanotubes interface.

4 Conclusion

Treatment of Ti6Al4V surface in concentrated 10 $mol.l^{-1}$ NaOH solution at the temperature of 60 °C for 24 h leads to the formations of an about 1 μm thick bioactive layer which incorporates Na^+ ions. The in vitro test confirmed good bioactivity; the surface is continuously covered by Ca-P compounds. The net-structure creates a good basis for the growth of Ca-P compounds.
The bioactivity of alkali- and thermal treatment samples is good, too. The alkali treated layer on the Ti6Al4V surface dehydrates, re-crystallizes and densifies at annealing. The surface layer of alkali-treated samples is less resistant to mechanical damage after thermal treatment.
No obvious hydroxyapatite is formed on the amorphous nanotubular layer prepared by anodic oxidation of Ti6Al4V at 10V for 30 min in mixed solution of NH_4F and H_2SO_4. Anodic oxidation formed a very thin layer of TiO_x on the surface (only 100 nm thick) which is non-bioreactive. Thermal treatment at a temperature of 450 °C for 3 h. activated the AO layer and the surface becomes bioactive. The nanotubular layer did not peel off from metal substrate which fact was confirmed by the tape test.
The difference between the surface activities of chemically and electrochemically treated Ti6Al4V is due to the different surface morphology and structure. It is assumed that amorphous layers of TiO_x-OH and TiO_x are the result of these treatments. It is likely that thermal treatment causes a re-crystallization of amorphous oxide to rutile or anatase. The structural similarity of rutile and hydroxyapatite accelerates the heterogeneous nucleation of HA from SBF solution on the modified surface.

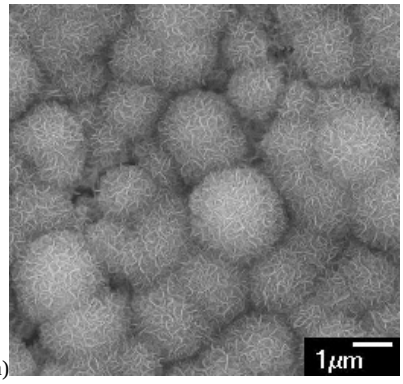

Fig.4 (SEM) Alkali treated Ti6Al4V after 7 days of in vitro test in SBF: a) sample treated in alkali solution, b) cross-section of alkali treated sample; c) cross-section of alkali treated and annealed sample

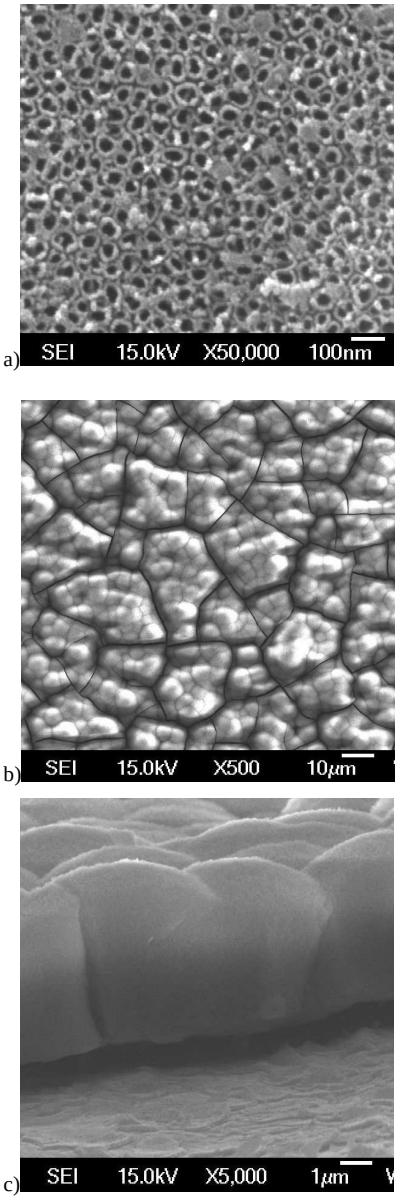

Fig.5 (SEM) AO treated Ti6Al4V after 7 days of in vitro test in SBF: a) surface without thermal treatment b) AO treated sample annealed at a temperature of 450 °C / 3 h., c) cross-section of AO treated sample annealed after in vitro test

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