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Influence of the anodic oxidation on the physicochemical properties of the Ti6Al4V ELI alloy

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Abstract: Results of corrosion resistance tests of Ti6Al4V ELI alloy after electropolishing and anodic oxidation in new baths were presented in the paper. As a results of the electropolishing and anodic oxidation significant growth of corrosion resistance was obtained. The alloy was also crevice corrosion–proof. Chemiluminescence investigation proved low chemical activity of the passive layer and AFM test showed that the layer is uniform. The main component of the passive layer of the specimens that has the highest corrosion resistance was titanium dioxide TiO_2. In the layer lower concentration of aluminum and vanadium was observed which is beneficial for the implants. The aluminum and vanadium occurred in oxide form.

Keywords: Implants; Passive layers; Titanium alloy; AFM, Chemiluminescence method, XPS, Corrosion resistance investigation

1. INTRODUCTION

Titanium and its alloys are commonly used in medicine. Due to a low density, good mechanical properties and very good corrosion resistance are the materials used to produce a heart valve, a subassembly of pacemakers, orthopedic implants etc. The most popular titanium alloy which has been used since ’80 is Ti6Al4V. After many years of using this alloy the high cytotoxity of V and tissue response of capsule type owing to Al was demonstrated [1].

A titanium and its alloys are corrosion resistive biomaterials which are characterized by a wide passive range [1÷3]. The breakdown potentials are higher then membrane potentials of tissue in a living body (0,2-0,45V)[4]. It should be assumed that the loss of passivity in the electrochemical fluids and tissue system is rather impossible. However, a passive layer can be mechanically or chemically damaged. Metallic surface is then uncovered and corrosion processes are initiated. A fabrication of coating that protects the biomaterial from the corrosion in the working life seems to be purposeful. To achieve that aim changes of the chemical and phase composition of biomaterials and surface layer are necessary. Currently the scientific research is focused on surface layer modification techniques in order to increase the corrosion resistance of implants. It should be said that implants undergo a plastic deformation. For this reason prepared layers should be characterized by the plastic deformation ability. The aim of the work was to work out the conditions of producing passive layers on Ti6Al4V ELI alloy surface and the evaluation of influence on the corrosion resistance and flexibility properties. To increase the chemical properties (biotolerance, corrosion resistance) and protect against adverse tissue reactions a modification of chemical composition are carried out. The modification consists in removing Al and V and in their place are located elements which belong to loose connective vascularised (vital) groups as a Zr, Nb, Pd, and Ta. On the basis of this trials a new group of titanium alloys was promoted. They have excellent chemical and very good mechanical properties [5÷8]. In this group it can be enumerated the following alloys: Ti13Zr13Nb, Ti35Nb5TaZr, TiZr4Nb2Ta0,2Pd. Moreover, Young module's value of the alloys is very close to the bone module which is favourable. Because of the high cost of the alloy elements as well metallurgical process the usage of these alloys is limited. An alternative solution could be surface modification of the Ti6Al4V alloy by the use of surface engineering methods [9÷12]. The most popular technique actually used for modifying the surface are as following: polishing, anodic oxidation, carbon layer (DLC- Diamond Like Coating), SiC, TiC, multilayer coatings (Ti- carbon, Si-carbon), hydroxyapatite and nitriding. The surface engineering techniques cause change of physiochemical properties of the surface that lead to improvement the corrosion resistance and tribological properties and eventually the biotolerance rise. This surface treatment is economically benefice comparing to chemical composition changes of the alloy.

2. METHODOLOGY AND SCOPE OF INVESTIGATION

The aim of the work was to evaluate usefulness of the electropolishing and anodic oxidation in new worked out bath for titanium alloys used in medicine. Ti6Al4V ELI was used in the research. Specimens in the disc form (diameter 20 mm) were prepared as following: grinding on the paper 600, electropolishing and anodic oxidation. The electropolishing was carried out in a new bath composed of: sulfuric acid, hydrofluoric acid, ethylene, glycol, acetanilide. Anodic oxidation was made in CrO_3 solution which wasn't used for implantation alloys. Device Surtronic 3x, Taylor-Hobson was applied to roughness measurement. Topography of the surface was evaluated by the use of AFM method. The corrosion resistance of the specimens was evaluated on the basis of potentiodynamic curves [15, 16]. The tests were carried out in the Tyrode's solution at temperature 36,6±1 °C. Potentiostat PG 201 was used to the electrochemical tests. Calomel electrode as a reference electrode, and platinum electrode as an auxiliary electrode was applied. Before the electrochemical tests specimens were cleaned in a ultrasound cleaner and then they stayed over an hour in the physiological solution.

In other to evaluate the electrochemical activity of passive layer on the Ti6Al4V ELI surface chemiluminescence method was used. Distribution of the light intensity on the specimen surface showed the level of their activity. Luminol/H_2O system was used as an electrolyte. Exposure time was equal to 15 s and the potential was from the range of 0÷2 V versus chlorosilver electrode. Luminescence light was recovered by the use of camera SBIG type ST 7.

The investigation was carried out for grinded, electropolished and electropolished plus anodic oxidized specimens.

In the X-ray Photoelectron Spectroscopy the electron and chemical structures of the oxide layers were evaluated.

3. INVESTIGATION RESULTS

The roughness measurements of the specimens revealed value of R_a parameter as following:

- for grinded specimens R_a= 0.82 μm
- for electropolished specimens R_a= 0.11 μm
- for electropolished specimens plus anodic oxidized R_a= 0.11 μm.

Investigation of topography with the use of the AFM method did not reveal any damages of the passive layer. Roughness of the layer did not exceed R_a=27 nm – fig.1.

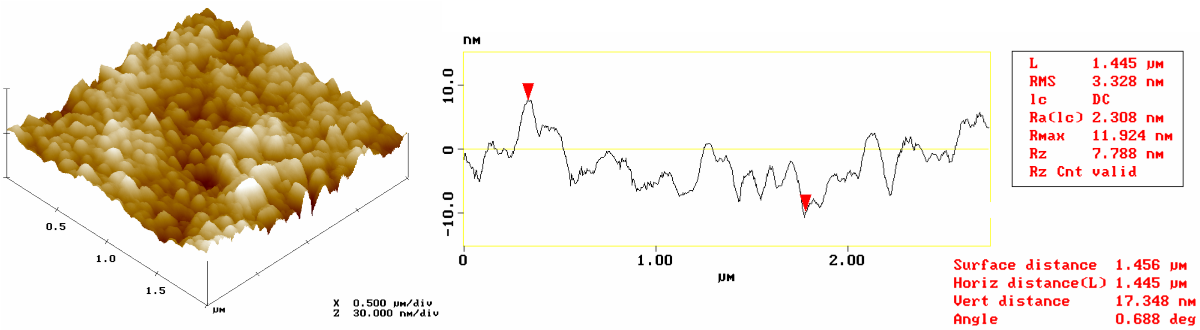

Figure 1. Topography of the passive film on Ti6Al4V ELI alloy

Table 1.
Results of corrosion resistance investigations of Ti6Al4V ELI alloy

Surface preparation	**Corrosion potential E_{cor}, mV**	**Transpassivity potential, E_B, mV**	**Polarization resistance, R_p, kΩcm^2**	**Corrosion current, I_{cor}, nA**	**Corrosion rate , μm/year**
Grinding	-343 ÷ -253	+1730 ÷ +1910	+285 ÷ +398	+40,5 ÷ +78,5	+823,6 ÷ +1596
Electropolishing	-266 ÷-120	+2010 ÷2205	+304 ÷ +798	+10,84 ÷ +24,8	+221 ÷ +504
Electropolishing + anodic oxidation	-15 ÷ -2	> +4000	+1310÷ +1460	+4,80 ÷ +5,61	+95 ÷ +132

The potentiodynamic curves showed diverse corrosion resistance of Ti6Al4V ELI alloy depending on the way of surface preparation. For the grinded specimens parameters describing corrosion resistance were in the range: corrosion potential E_{cor}= -343 ÷ -253 mV, tranpassivity potential E_B= +1730 ÷ +1910 mV.

The electropolishing process increased metioned above parameters to the value of the range E_{cor}= -266 ÷ -120 mV and E_B= +2010 ÷ +2205 mV. The specimens which were electropolished and then passivated had corrosion potential in the range E_{cor}= -15 ÷ -2 mV. The passivated specimens were polarized up to potential 4000 mV and curves didn't revealed meaningful rise of anodic current density fig. 2. Additionally polarization resistance R_p,, corrosion current i_{cor}, and corrosion rate were evaluated – table 1.

In the next stage crevice corrosion resistance was investigated. Potentiostatic tests at the value of +800 mV was carried out [16]. On the potentiostatic curve substantial drop of the anodic current was observed. This kind of behaviour indicates the Ti6Al4V ELI alloy is resistant for crevice corrosion – fig. 3.

The chemiluminescence investigation revealed diverse chemical activity of the surface prepared in different way. The first luminescence effects were observed at potential: +800 mV for grinded surface, +1100 mV for electropolished surface- fig. 4a, b, and +2000 mV for electropolished and oxidized specimens – fig. 4 c, d.

The survey spectrums obtain from the XPS tests of polished and oxidized specimens revealed the following elements: Al, C, Ca, F, Cr, Fe, N, Na, O, P, S, Si, Ti and V - fig. 5. The chemical compounds and their concentration was identified by the use of the XPS high resolution spectrums – table 2.

Titanium was predominantly in oxide form TiO_2 – fig. 6, 7. The lower concentration of the vanadium and aluminium (both in oxide form Al_2O_3, V_2O_5) in the passive layer comparing to the bulk material was observed. Minute amount of chromium and fluorine was observed on the surface. Chromium occurred as a trioxide and fluorine as a fluoride.

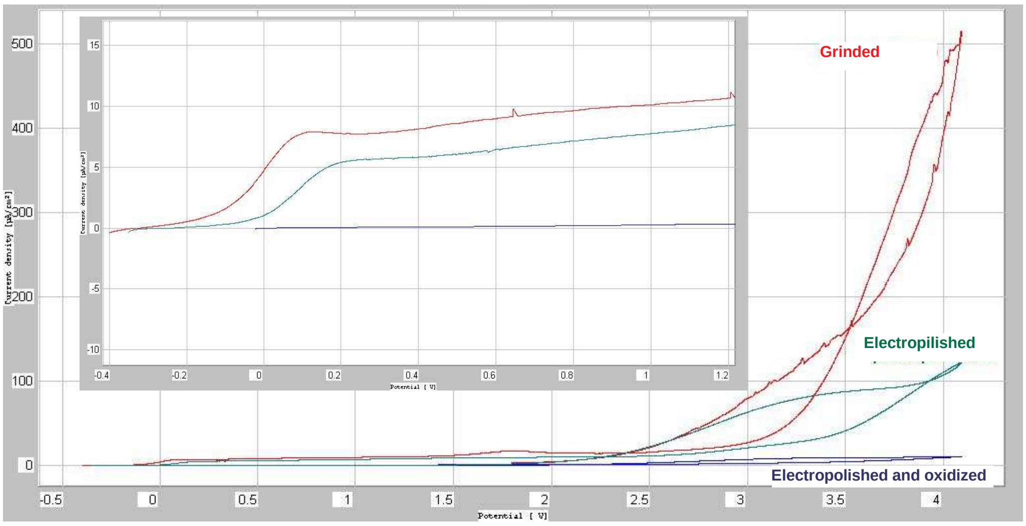

Figure 2. Potentiokinetic curves of Ti6Al4V ELI with different surface preparation

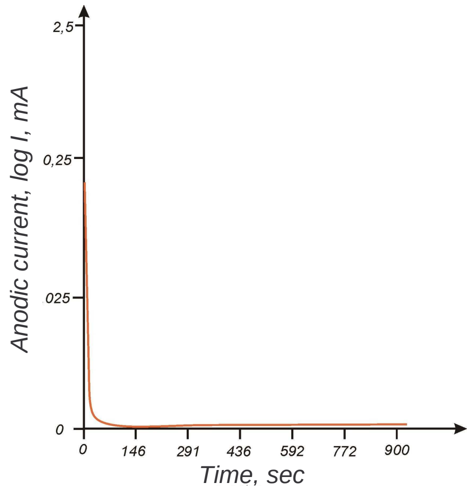

Figure 3. Potentiostatic curve (+800 mV) for Ti6Al4V ELI with grinded surface

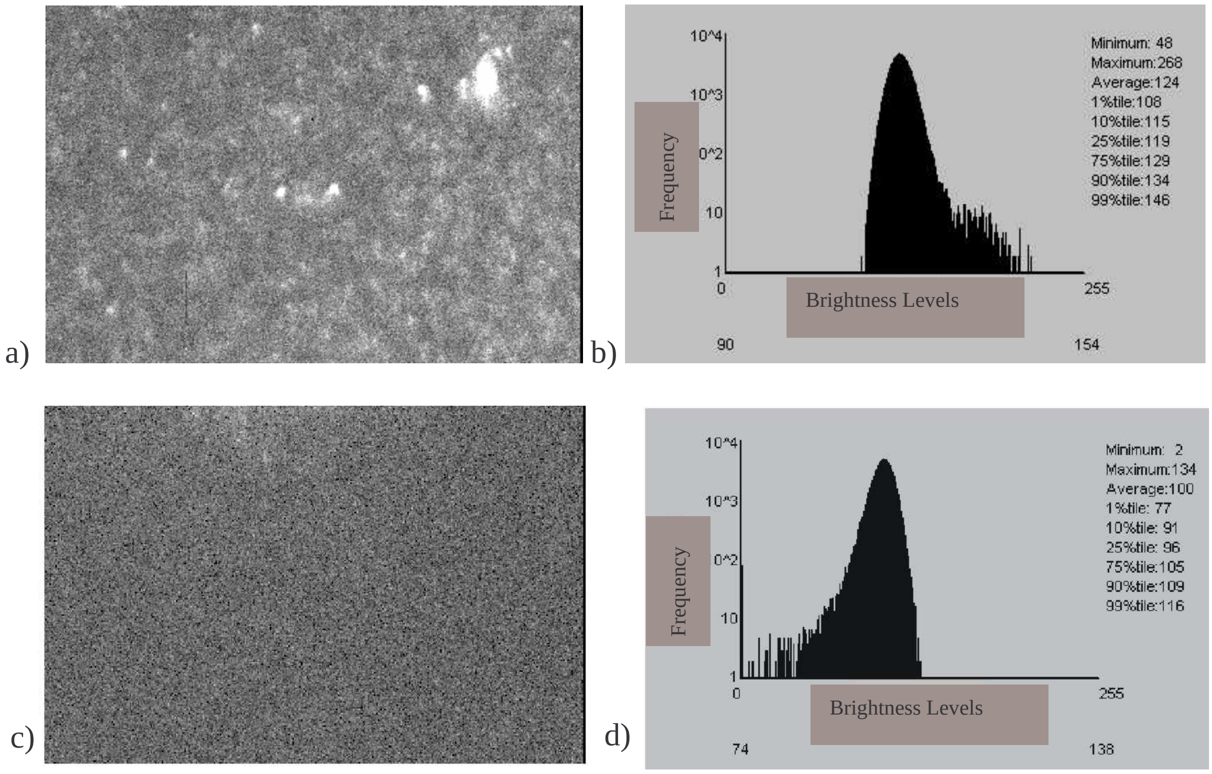

Figure 4. Chemiluminescence results of Ti6Al4V ELI alloy for electropolished specimens (a, b) and electropolished + passivated specimens (c, d): view of the surface after chemiluminescence activation (a, c), chemical activity histogram of the surface (b, d)

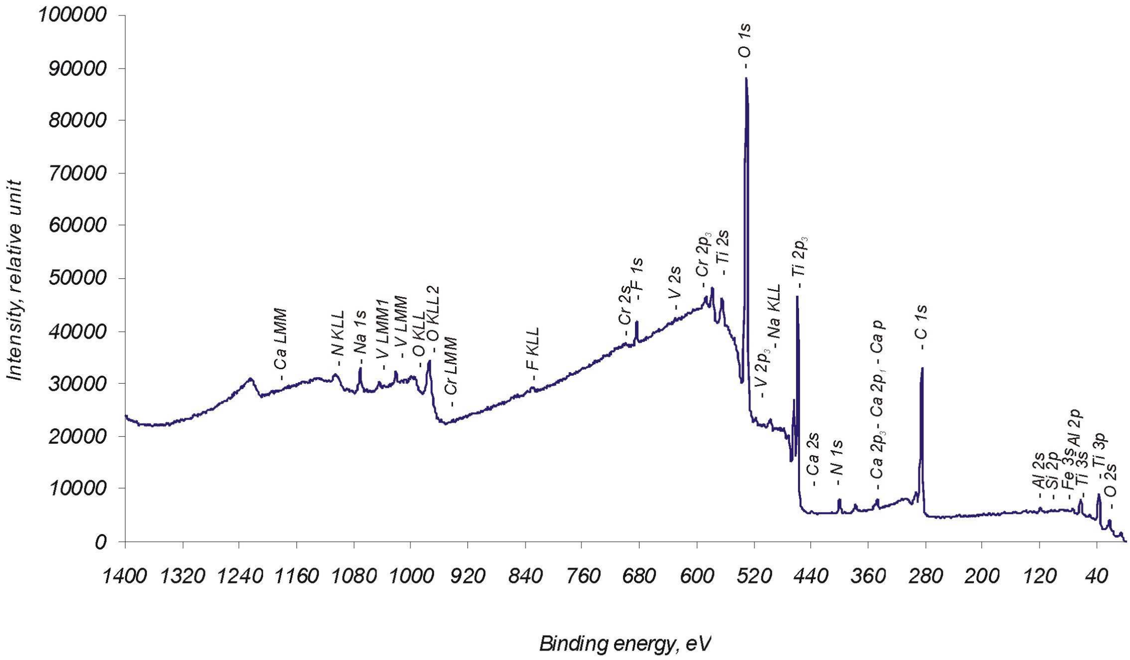

Figure 5. The survey spectrum of the polished and oxidized Ti6Al4V ELI specimen

Table 2.
Chemical composition of oxide layers produced on the titanium alloy on the base of the XPS examinations

Elements	O	Ti	Al	V	F	N	C	Cr	S	Na	Ca	K
Atomic concentration, %	41,29	9,29	2.08	0,33	1,68	2,03	37,17	2,15	0,48	1,30	0,56	1,01
Chemical compound	TiO_2+ *contamination*	TiO_2	Al_2O_3	V_2O_5	Ca_2F	-	*contamination*	Cr^{3+}	*sulfates*	-	Ca_2F	-

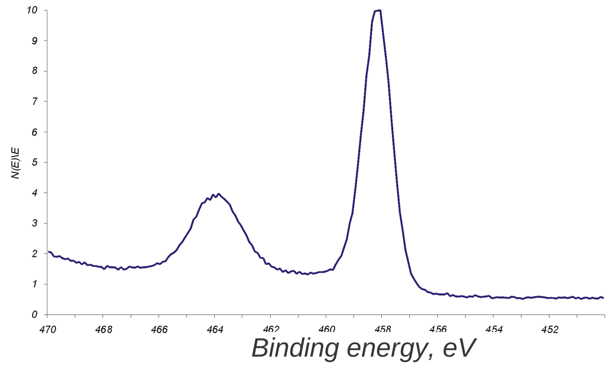

Figure 6. Typical XPS high-resolution spectrum of the Ti2p region for anodized specimen

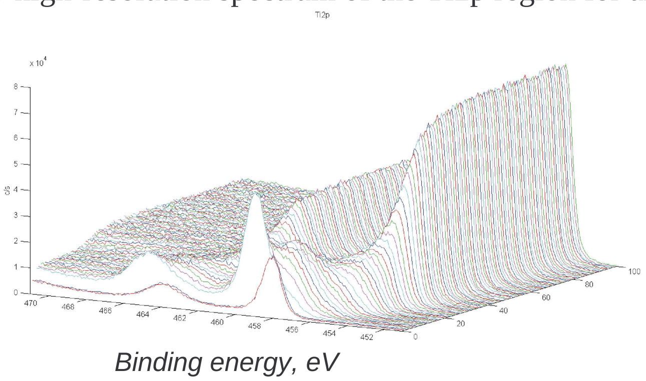

Figure 7. Depth profile of XPS high resolution spectrums of the Ti2p region for anodized specimen

4. CONCLUSIONS

The results of surface analysis of Ti6Al4 ELI alloy proved that the electrochemical preparation of the surface by the use of worked out procedure ensure roughness R_a under 0.16 μm. This value of roughness is assented for short-time implants. Moreover oxide layer constituted on the alloy was uniform that was revealed by the AFM methods.

Electrochemical investigations of corrosion resistance showed that the electropolishing increased corrosion and transpassivity potential with reference to grinded specimens. This results indicate rise of the corrosion resistance. Additional growth of the parameters was obtained for oxidized specimens. The value of the calculated parameter as polarization resistance R_p, corrosion current i_{cor} and corrosion rate confirmed that the electrochemical treatment improved corrosion resistance of the alloy. R_p increased significantly while corrosion current and corrosion rate declined. The crevice corrosion test lead at the +800 mV potential exhibits that Ti6Al4 ELI alloy is resistant for this kind of corrosion. The benefit conformation of the electrochemical treatment was proved also in the chemiluminescence investigation. From this investigation follows that passive layer cause a decrease in the chemical activation in relation to grinded and electropolished surface. A high value of the potential which cause the first luminescence effect for the oxidized specimen proved very good protective properties of the passive layer. Results show that there is correlation between individual test and they show higher corrosion resistance of the oxidized specimens.

The main component of the passive layer of the specimens that has the highest corrosion resistance was titanium dioxide TiO_2.

In the layer prepared in the conditions worked out in the study lower concentration of aluminum and vanadium was observed which is beneficial for the implants. The aluminum and vanadium occurred in oxide form.

To sum up it can be said that described surface preparation procedure increase corrosion resistance and decrease chemical activity of the surface. In order to verify technological usefulness of this way of surface modification for preparing the implant the following investigations are planed: detailed analysis of passive layer, analysis of polishing and passivation process, electrical behavior and biological activity.

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