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MORPHOLOGICAL AND CHEMICAL RELATIONSHIPS IN NANOTUBES FORMED BY ANODIZING OF Ti6Al4V ALLOY

ABSTRACT

The electrochemical formation of oxide nanotubes on the Ti6Al4V alloy has been so far difficult due to easy dissolution of vanadium rich β -phase of the two phase material. Due to the topographical heterogeneity of the anodic layer in nano and microscale at anodizing of the Ti6Al4V alloy we focused to establish the relationships between nanotube diameters on both phases of the alloy and fluorides concentration in electrolyte. We studied the effect of fluoride concentration (0.5-0.7 wt.%) in 99% ethylene glycol on morphological parameters of nanotube layer on the Ti6Al4V alloy anodized at 20V for 20 min. Nanotubes with diameter $\sim 40\text{-}50\text{ nm} \pm 5\text{nm}$ on the entire Ti6Al4V alloy surface in electrolyte containing 0.6% wt. NH_4F were obtained. Microscale roughness studies revealed that nanotubular layer on α -phase is thicker than on β -phase. The annealing of nanotube layers at 600°C for 2h in air, nitrogen and argon, typically performed to improve their electrical properties, influenced chemical composition and morphology of nanotubes on the Ti6Al4V alloy. The vanadium oxides (VO_2 , V_2O_3 , V_2O_5) were present in surface nanotube layer covering both phases of the alloy and the shape of nanotubes was preserved after annealing in nitrogen.

Key words: *Ti6Al4V, oxide nanotubes, vanadium oxides, titanium dioxide*

INTRODUCTION

Formation of layer by anodizing of the two phase Ti6Al4V alloy has been so far a difficult task because vanadium rich β -phase easily dissolves in fluorides. Only few works describe formation of nanotubes on Ti6Al4V [1-4], though nanoscale electrochemical modification of surface layer properties may be beneficial to obtain implant coatings able to induce bone growth and/or to immobilize drugs. The Ti6Al4V alloy has been for years the most popular titanium implant material due to its mechanical properties[5], irrespective of the release of vanadium and aluminum. Recent intensive studies on biological effect of vanadium have revealed its advantageous role as the anti-diabetic and anti-carcinogenic element [6]. Electrochemical treatments carried out on titanium in inorganic and organic electrolytes, with or without small amounts of fluoride ions, may change surface layer composition and produce compact, porous, gel-like, and/or nanotubular layers [7,8]. Due to simplicity of electrochemical methods such anodic layers are cheaper than obtained by nitriding [9] sol-gel coating [10], plasma oxidation [11] or biological modifications [12]. Particularly titania nanotubes are very useful for numerous applications due to the excellent adsorption,

hydrophilic and photonic properties [13,14], the inertness and good biocompatibility [15], as well as sensing abilities [13,16]. Nanotubes on the Ti6Al4V alloy with their unique chemical composition consisting titania and vanadium oxides should prove their beneficial effect in biomedical applications due to chemical and biological activity [13,17,18]. The expected heterogeneity of oxide coating may enhance osteoblasts ingrowth and increase biocompatibility of implant surface covered with porous nanotube layer of mixed oxides. Vanadium oxides belong to “smart materials” [19] with potential use in sensing and optoelectronic applications [20]. Vanadium oxides, which form Magnelli phases [21], are excellent electrical conductors [22]. as for example vanadium oxide, VO with its partially filled conduction band and delocalized electrons in the *d* orbitals [23]. The aim of this work was to produce oxide nanotubular layers with highly ordered structure on both phases of the Ti6Al4V alloy. In such nanotubular layers, the mixture of vanadium oxides may convert during thermal treatment into vanadium (IV) oxide [24-26]. Thus, the establishing of the chemical and electrochemical characteristics of nanotube layers on the Ti6Al4V alloy, thermally treated in three atmospheres: air, nitrogen and argon, was another task for this work.

MATERIALS AND METHODS

Samples of the Ti6Al4V alloy Gr5 (5×10×0.5 mm) were cut off from the alloy sheet (William Gregor Co., UK), sonicated in isopropanol, acetone and deionized (DI) water, and dried in nitrogen stream. Anodizing and electrochemical examination were carried out using AutoLab PGSTAT 302N potentiostat/galvanostat, equipped with voltage multiplier, and Nova 1.8 software. Anodizing was carried out in two stages: first the potentiodynamic stage from the Open Circuit Potential (OCP) up to 20 V, and the potentiostatic, when the sample was hold at 20 V for 1200 s. Ethylene glycol (99% water solution) with addition of 0.5, 0.6, 0.7 %wt. of NH₄F was used as electrolyte. All solutions were prepared from high purity reagents: ethylene glycol, NH₄F, Phosphate Buffered Saline (PBS) (Sigma Aldrich) and DI water. The thermal treatment of the anodized samples was carried out in nitrogen, argon and air atmosphere at 600 °C (30 °C/min) for 2 h. The OCP was recorded in 0.01 M PBS solution (pH 7.4) 1800s, immediately after immersion in three electrode system, with the Ti6Al4V alloy sample as a working electrode, platinum gauze as a counter electrode, and the Ag/AgCl reference electrode (+0.220 V, 25 °C). The SEM and EDS analysis were performed with FESEM JEOL 7600F and (Oxford INCA) analyzer at 8 kV voltage. Surface composition was studied using the X-ray Photoelectron Spectroscopy (XPS) in VSW (Vacuum Systems Workshop, Ltd.) equipped with a concentric hemispherical electron analyzer with radius of 150 mm and the two-plate 18-channel detector (Galileo). The electron analyzer was operated in fixed transmission mode (FAT) with constant energy of 22 eV. Samples were exposed to the MgK α (1253,6 eV) X-ray radiation working at power of 210 W (22.5 kV - voltage, 14 mA – emission current). The background pressure during the analyses was lower than 5×10⁻⁸ mbar. Calibration of the binding energy scale was done by assuming the position of the adventitious C 1s line of C-C and C-H bonding at 284.6 eV. XRD measurements were performed on the X-ray Diffractometer Empyrean DY 1061 (PANalytical) operating in the reflection mode with Cu-K α radiation, diffracted beam monochromator using step scan mode with the step of 0.03° (2 θ) and 20s per step in range 20-100°.

RESULTS AND DISCUSSION

Figure 1 shows SEM images of nanotubes on the Ti6Al4V samples anodized in 99% ethylene glycol with different amounts of fluoride ions. As it was expected, regular nanotubes with diameter ranging from 35-65 nm are obtained on both phases at all applied concentrations of NH_4F (Fig. 1d). The etching of nanotubes on β -phase causes also that they are located lower than on α -phase of the alloy.

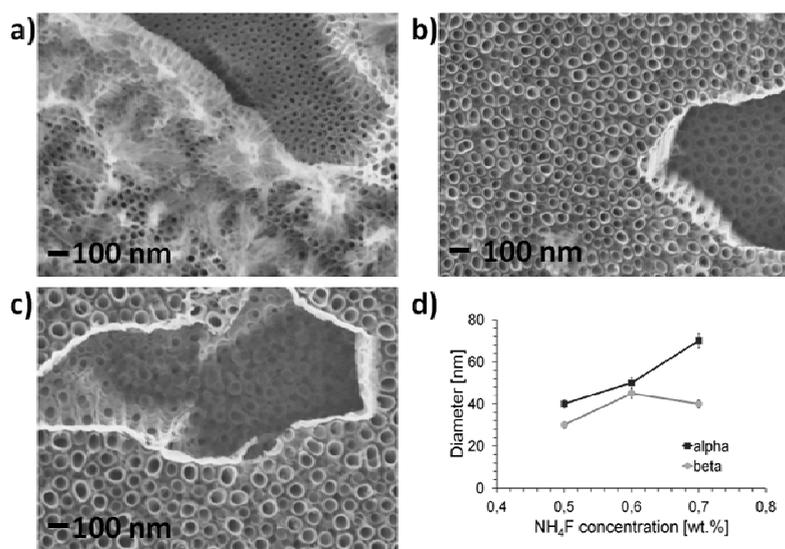


Fig. 1. SEM images for nanotubes formed on the Ti6Al4V alloy by anodizing at 20V for 20 min in 99.0% ethylene glycol with 0.5 (a), 0.6 (b), and 0.7%wt. NH_4F (c) and diameters of nanotubes above two phases of the Ti6Al4V alloy vs. fluorides concentration in ethylene glycol (d)

Current transients for two stages of anodizing (Fig. 2) show the effect of fluoride ions concentration on nanotubes formation process. Particularly in the second stage of anodizing of the Ti6Al4V alloy in both applied electrolytes with different amounts of fluorides the current transients are typical to recorded for other metals, including titanium [13]. The proportionality between anodizing parameters (the anodic current, the fluorides concentration) and nanotube diameters on α -phase formed in ethylene glycol, observed in Fig. 2b, is clearly revealed in Fig. 1d for the relation between fluoride ions concentration and nanotube diameters on both phases of the alloy. Thus, according to the conditions described in experimental details, nanotubes of highly ordered and uniform morphology of diameter $50 \text{ nm} \pm 5 \text{ nm}$ can be formed on both phases the Ti6Al4V alloy in ethylene glycol with 0.6% wt. of NH_4F . Such samples were selected for further studies- the thermal treatment in three atmospheres at 600°C ($30^\circ/\text{min.}$) for 2 h and for electrochemical, XPS and XRD examinations.

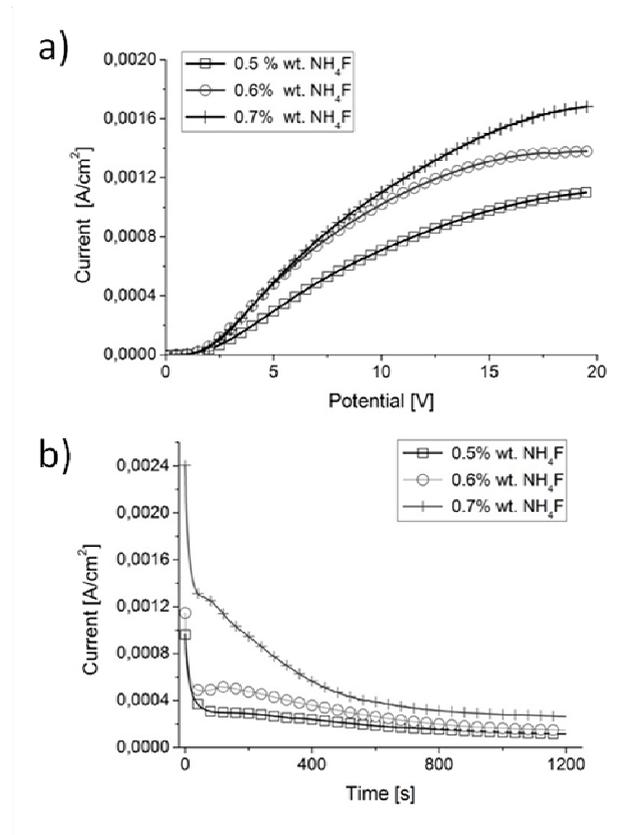


Fig. 2. Polarization curves of first (a) and second (b) stage of anodizing the Ti6Al4V alloy at 20V in 99.0% ethylene glycol with addition of NH_4F

The SEM images (Fig. 3) and results of the EDS analysis (Table 1) for thermally modified nanotube layers, illustrate apparent changes of their structure caused by the annealing process. Only after thermal treatment in nitrogen (Fig. 3a,b) the nanotubular character is well preserved and vanadium is present in oxide layer on both phases (Table 1), unfortunately a lack of oxygen in beta phase after thermal treatment is observed, and the stoichiometric ratio between elements is not calculable. After thermal treatment in argon (Fig. 3c,d) some oxide deposits are observed on β -phase, whereas oxides on α -phase became non-regularly porous. Similarly, nanotubes treated thermally in air show significantly decreased inner diameters due to thickening of tube walls (Fig. 3e,f).

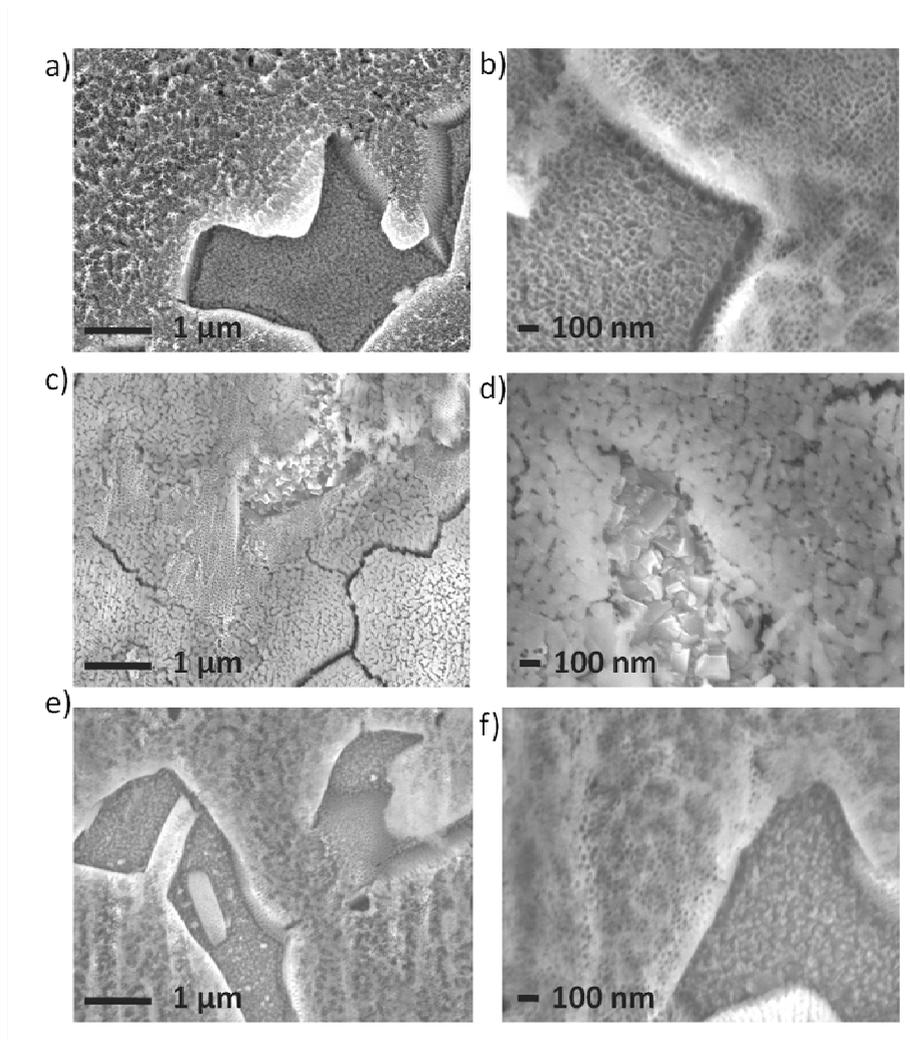


Fig. 3. SEM images for nanotubes on α -phase and β -phase of the Ti6Al4V alloy formed by anodizing at 20V for 20min in 99.0% ethylene glycol with 0.6%wt. NH_4F , after thermal treatment at 600°C (30°C/min) in nitrogen (a,b), argon (c,d), and air (e,f)

Table 1. Results of EDS analysis for nanotubes covering α -phase and β -phase of the Ti6Al4V alloy, formed by anodizing in 20V for 20 min. in 99% ethylene glycol with 0.6%wt. NH_4F after thermal treatment at 600°C in nitrogen, argon and air

| Atmosphere | Air | | Argon | | Nitrogen | | Non-annealed | |
|------------|----------|---------|----------|---------|----------|---------|--------------|---------|
| Phase | α | β | α | β | α | β | α | β |
| [% weight] | | | | | | | | |
| Ti | 57.84 | 59.05 | 62.47 | 51.89 | 43.24 | 59.23 | 63.9 | 52.70 |
| O | 39.26 | 14.15 | 34.84 | 10.03 | 29.78 | 14.72 | 33.96 | 17.13 |
| V | - | 25.98 | - | 36.97 | 25.01 | 25.13 | - | 28.98 |
| Al | 2.29 | 0.82 | 2.69 | 1.13 | 1.91 | 0.93 | 2.34 | 1.24 |

The measurements of the OPC, were carried out on the annealed samples. The OPC records (Fig. 4) for nanotube layers on the Ti6Al4V alloy in PBS solution (pH 7.4) show stable values for samples annealed in nitrogen (~ 10 mV vs. Ag/AgCl), contrary to values recorded for nanotubes thermally treated in argon (~ 120 mV) and air (~ 150 mV vs. Ag/AgCl). For the latter, as also for the non-annealed ones the curves show current oscillations, which may prove their metastable nature and ongoing processes in PBS solution. The positive value of the OPC for samples thermally treated in nitrogen are advantageous for an example their adsorption abilities towards negatively charged proteins.

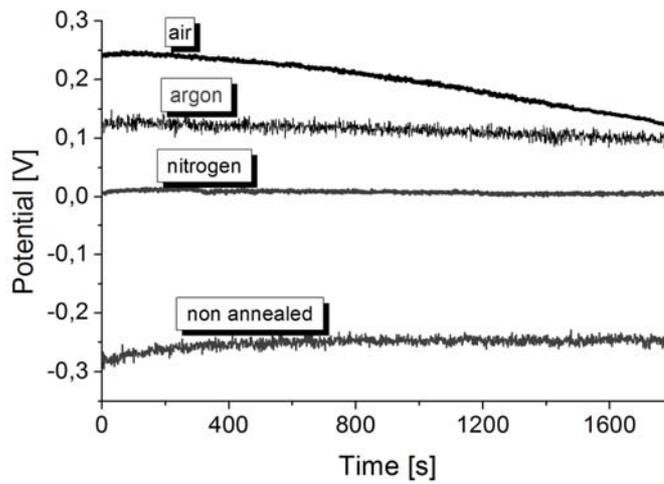


Fig. 4. Corrosion potential values measured during 1800s in the PBS solution for nanotubes on the Ti6Al4V alloy formed by anodizing at 20V for 20min in 99.0% ethylene glycol with 0.6%wt. NH_4F , before and after thermal treatment at 600°C in nitrogen, argon and air

The results of XPS (Fig. 5a) and XRD (Fig. 5b, Table 2) analyses carried out for the nitrogen treated samples revealed the presence of titania and three vanadium oxides in nanotube layer: TiO_2 , VO_2 , V_2O_3 , V_2O_5 in form of anatase and rutile.

Table 2. XRD results for nanotubes on Ti6Al4V after thermal modification in different atmospheres in 600°C for 2h

| Modification atmosphere | Crystalline structures |
|-------------------------|---|
| Non- annealed | TiO_2 (R) (A); VO_2 (R); V_2O_5 , Al_2O_3 |
| Nitrogen | TiO_2 (R); VO_2 (R); V_2O_5 , Al_2O_3 |
| Argon | TiO_2 (R) (A); VO_2 (R); V_2O_5 , Al_2O_3 |
| Air | TiO_2 (R); VO_2 (R); V_2O_5 , Al_2O_3 |

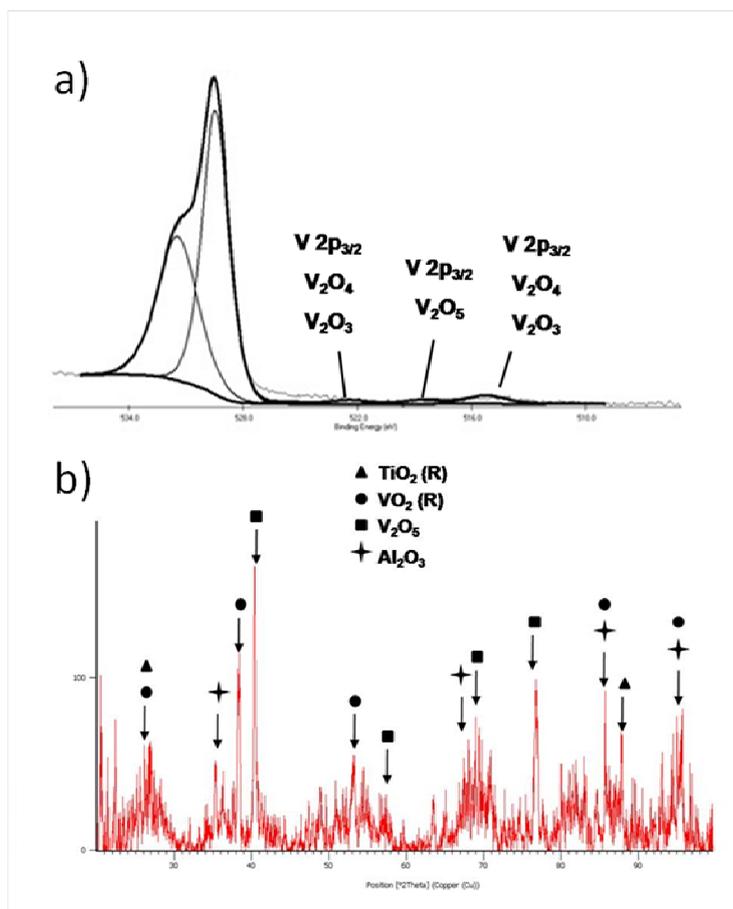


Fig. 5. Results of XPS (a) and XRD (b) analysis for nanotubes on the Ti6Al4V alloy obtained by anodization in 20V for 20 min. in 99% ethylene glycol with addition of 0.6 %wt. NH₄F after thermal treatment in 600°C in nitrogen

After thermal modification at high temperatures vanadium occurs in its most common oxidation states as VO, V₂O₃, VO₂ and V₂O₅ and can change the oxidation states in relation to anatase- rutile transformation. The identification of vanadium oxides in uniform nanotubes on both phases of the Ti6Al4V alloy is the first step to further studies on using these layers as the platforms of biosensors.

CONCLUSIONS

The layer of regular nanotubes with 50nm±5nm diameter and rich in vanadium oxides was formed on both phases (α and β) of the Ti6Al4V alloy by anodizing in 99.0% ethylene glycol with the addition of 0.6% wt. NH₄F. The developed method allowed to produce nanotubes of uniform morphology which after thermal treatment in nitrogen consisted three vanadium oxides VO₂, V₂O₃ and V₂O₅ on both phases and making them a promising novel platform for highly sensitive biosensors and the efficient electrode nanomaterial. Movement of the vanadium atoms inside oxide layer on both phases of Ti6Al4V alloy during thermal modification in nitrogen is still an open task.

ACKNOWLEDGMENTS

This work was financially supported in the project ERA-NET-/MNT/TNTBIOSENS/1/2011 by the NCBR (Polish National Centre for Research and Development).

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