

Tailoring of anodic surface layer properties on titanium and its implant alloys for biomedical purposes

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Received 03.09.2010; published in revised form 01.11.2010

Manufacturing and processing

ABSTRACT

Purpose: Presentation of different anodizing methods used for formation of thin, thick, gel like covered and nanostructural titania and alloy component oxides. Evaluation of their properties for various biomedical applications in implantology and biosensing.

Design/methodology/approach: Samples of titanium and its alloys were anodized in phosphoric acid solutions at different concentrations (0.5 ~ 4 M) with or without additions according to appropriate polarization regimes. Anodized samples were characterized by SED+EDS, electrochemical and impedance (EIS) tests and biocompatibility examination. Titanium and its alloys (Ti6Al4V and Ti6Al7Nb) samples were also used to form the nanostructural layer (nanotubes) by anodizing. The latter was used as a platform for glucose biosensing.

Findings: Anodizing of titanium materials in phosphoric acid solutions allowed to obtain surface layers of various morphology and topography. They differ in porosity, thickness and chemical composition and according to their specific properties can be used in various biomedical applications. The development of gel-like layer and formation of nanotube layer was observed while anodizing in higher concentration of electrolyte or anodizing in the presence of fluorides. Both surface layers are much more bioactive than anodic barrier oxide layers on titanium. The primary tests to use nanostructured layer as platform for the third generation biosensors were promising.

Practical implications: Use of medical implants covered with porous and nanostructural anodic layers tailored to particular biomedical purposes enables new practical applications in implantology and biosensing.

Originality/value: Phosphate gel-like layer over surface oxide layer on titanium materials and nanostructural surface layer rich in both: phosphates and fluorides, are highly bioactive, which is the desirable property of implant materials.

Keywords: Anodic layers; Titanium materials; Phosphoric acid solutions; Bioactivity; Nanostructural layer

Reference to this paper should be given in the following way:

E. Krasicka-Cydzik, Tailoring of anodic surface layer properties on titanium and its implant alloys for biomedical purposes, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 424-431.

1. Introduction

Anodic films on titanium have been of great interest due to their industrial applications [1]. Anodizing can also result in the

adsorption and incorporation of biologically important species into the oxide layer. Such surface layers are of a great importance for medical implants [2,3], which should not only be corrosion resistant in a biological environment, but also compatible with tissue response [2-4]. Formation of such layers

in phosphate solutions is of great importance due to the possibility of their incorporation into the layer and influence the bioactivity. Previous works [6,7] have shown that, phosphate ions can be incorporated into the anodic layer on titanium and Ti-6Al-4V, and in turn stimulate the formation of the bio-compatible hydroxyapatite [5,8]. Unalloyed titanium is resistant [2,3,9] to naturally aerated pure solutions of phosphoric acid up to 30 % wt. concentration (~3.6 M), but undergoes corrosion attack at higher concentrations and temperatures. Within the considered region of phosphoric acid concentrations and potential values, mainly non-dissociated acid molecules and one protonated form H_2PO_4^- of phosphate ions exist [10] and they exhibit a strong affinity or complexing power towards most metal cations.

In this paper the effect of phosphoric acid concentration (0.5-4 M) and different polarization techniques on the anodizing of titanium and its implant alloys is considered, aiming at presentation of their diversified properties and various biomedical applications. Both electrochemical (galvanostatic, potentiodynamic and impedance) and morphological examinations showed formation of either porous and thin oxide layer [11-23] or gel-like phosphates rich layer of $\text{H}_3\text{PO}_4 \cdot 0.5\text{H}_2\text{O}$ [11, 24-29], covering thicker oxide layer on titanium. Formation of self-organized titania nanotubes with high level organization of pores on large surfaces [30-35 42-47] became very useful technology applied to many purposes, i.e. to modification of the surgical implant surfaces and to environmental and biomedical sensing. Our efforts were focused on controlling the size and arrangement of pores [36-41], aiming at bone ingrowth and on use of titania nanotubes platform for biosensing. Oxide nanotubes covering, just like titanium covered by a limited number of nucleotide nanotubes forming a perfect basis for osteoblasts, combine very well with osseous tissue. Advantage of oxide nanotubes consists also in their capability to combine with e.g. enzymes, proteins or biological cells, which is used in biosensing. The first authors works in this field are promising [42, 43].

The passive film behavior on titanium and its alloys plays a crucial role for its suitability as the element of surgical implant system [44-46] and influences significantly their performance after implantation. The anodic oxides reduce dissolution currents making metal more resistant to corrosion, but they are also susceptible to fracture due to scratches, and fretting resulting from mechanical shaping, treatments and loading. If not mechanically disturbed, titanium alloys exhibit an excellent combination of high biocompatibility and mechanical properties. Plastic deformation during the pre-operative surgery shaping process induces changes in the structure of surface layer and their electrochemical behavior in biological environment, which may change the biocompatibility of these materials. Therefore, to investigate the influence of plastic deformation on the behavior of anodized implant rods made of the Ti6Al4V ELI alloy was another purpose of studies [47-55]. To study the electrochemical behaviour of the surface layers in the tensile and compressive stress zones activated during shaping in the pre-operative procedures, was of particular interest for surgical practice.

2. Oxides layers on titanium and its alloys formed in H_3PO_4 solution

2.1. Porous oxide layers

Anodic layers on pure Ti and its alloys Ti6Al4V ELI and Ti6Al7Nb (ASTM F136-84) in the annealed condition were formed by anodizing carried out at ambient pressure and room temperature in non-deaerated electrolyte solutions of 0.5-4 M H_3PO_4 at galvanostatic anodizing current density values varied in the range of 0.1 - 0.5 Am^{-2} . Mechanical and chemical retreatment was applied [12-20] and then the technology of anodizing [22] was implemented to titanium and its alloys: Ti6Al4V ELI and Ti6Al7Nb (Timet Ltd, UK). As the result the porous oxide layers were obtained of various morphology, thickness and composition (Fig. 1) [11, 24-26].

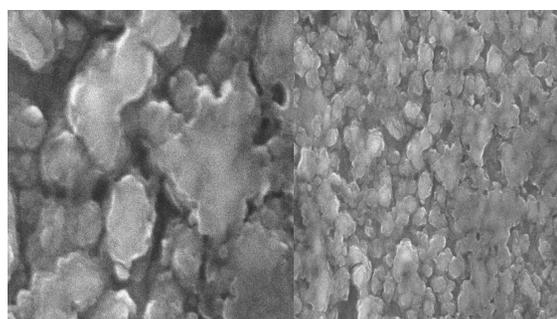


Fig. 1. Porous titania layers on Ti formed in 0.5 M H_3PO_4 [22]

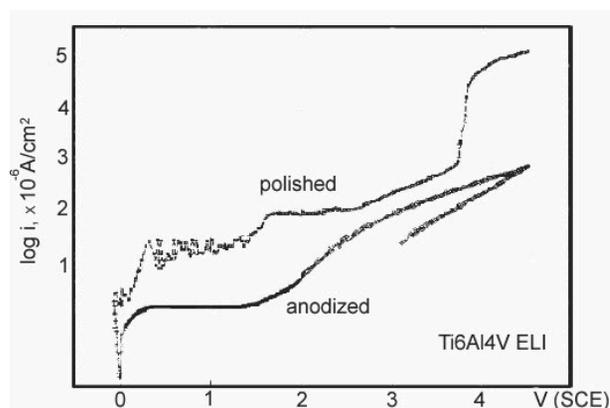


Fig. 2. Effect of Ti6Al4V ELI anodizing according to [22]

The obtained layers are goldish and porous (Figs. 1,3), show very stable values of currents in passive region up to 1 V (SCE) (Fig. 2) and bi-layer surface was revealed by impedance tests. The first time constant in Bode diagrams (Fig. 3 [11,17,23] in range of high and intermediate frequencies confirmed high R_f resistance of the barrier layer covering the anodized metal, thus its high corrosion resistance. The second time constant corresponds to

porous layer above the barrier one. Its lack in case of the Ti6Al4V ELI indicates the different characteristics of the coating on this implant material.

Due to the presence of phosphates in the anodic layer formed on titanium materials in the phosphoric acid solutions the obtained surface layers were highly bioactive in comparison to ordinary oxides. Just after 9 days in the SBF (simulated body fluid) solution they were nearly completely covered with hydroxyapatite deposits (Fig. 4) [27].

2.2. Gel-like phosphate rich layers on anodic oxides

The unusual surface chemistry of titanium as a function of electrolyte concentration was revealed while working with more concentrated H_3PO_4 solution [11, 19]. Under galvanostatic conditions at low current densities ($0.1-0.6 \text{ A m}^{-2}$) the slope of dE/dt always showed the minimum at the concentration about 2 M concentration, which resulted in a coating of an oxide film by an additional gel-like layer [28, 29], similar to the one observed in other media on aluminum.

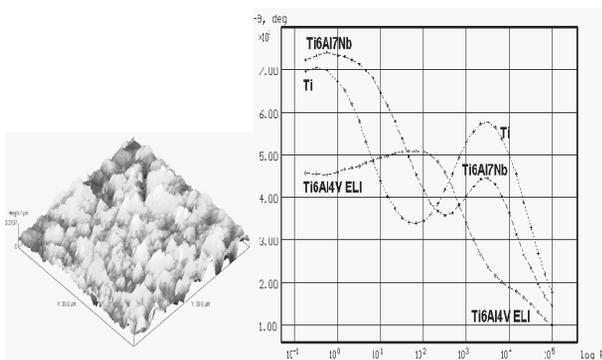


Fig. 3. AFM picture of porous oxide layer on Ti and results of EIS analysis for Ti and two alloys [11, 23]

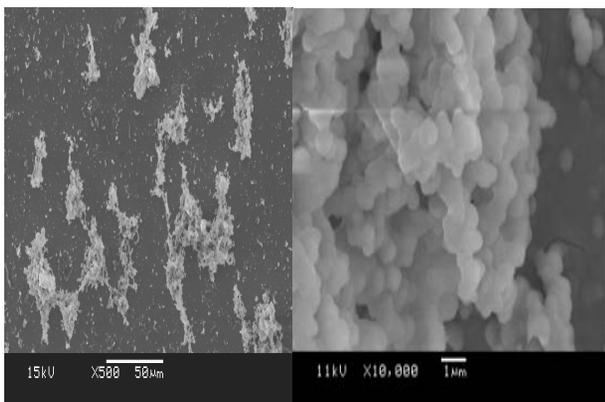


Fig. 4. Deposition of Hap particles on anodic layer after 9 days in SBF solution [21, 25, 27]

The picture of these layers is presented in Fig. 5, showing the whole surface covered by a gel-like of $H_3PO_4 \times 0.5H_2O$. It was found that the active-passive transition was a process in which an inhibiting effect of phosphate ions on a dissolution of oxide layer was observed. The slope of the linear section, dE/dt , which may be used as a parameter for comparing the rate of oxide formation at initial stages, when at potential lower than about 3 V (SCE) [4] oxygen evolution is excluded, demonstrates (Fig. 6) the lowest value in 2 M H_3PO_4 . Anodic curves for 0.5 M and 3 M H_3PO_4 solutions (Fig. 6), illustrate quasi-passive behaviour in active-passive transitions, while curves for 1 and 2 M H_3PO_4 , having the higher corrosion potential E_{cor} , do not show linear dependence in this potential region.

Also the differences in anodic Tafel slopes are observed which are accompanied by a shift of the E_{cor} value in the positive direction by $\sim 0.15V$ with the increase of H_3PO_4 concentration to 2 M (Fig. 6). The EIS spectra of titanium recorded in 0.9 % NaCl solution 1 h after anodizing at 0.5 A m^{-2} in 0.5M and 2M H_3PO_4 solutions (Fig. 7) represented in Nyquist and Bode phase angle plots, exhibit two time constants.

Such a behavior is typical of a metallic material covered by a porous film which is exposed to an electrolytic environment. Adsorbed phosphate ions which during the anodising developed into gel-like layer above the anodic film on the electrode surface played not an important role in inhibiting oxide dissolution, but also developed high bioactivity in physiological solution [30].

2.3. Nanostructural oxide layers

Significant progress [31-36] has been made recently in the application of anodizing as a method of forming nano-structural layers of oxides on metal surfaces. Formation of high level of the organization of pores on large surfaces as well as controlling the size and arrangement of pores were also the subject of our works [37-42]. Oxide nanotubes, just like titanium covered by a limited number of nucleotide nanotubes forming a perfect basis for osteoblasts, combine very well with osseous tissue. Formation of oxide layers conducted in the phosphoric acid solutions with additions of fluoride ions [37] at 25°C , is usually carried out in two stages: the first stage potentiodynamic to the desired potential and the second stage, potentiostatic with fixed potential on electrodes for over 2 hours. Figure 8 shows SEM images of the morphology of nanotubes on titanium and its two alloys. On the surface of anodized titanium 100nm diameter pores were formed and the entire surface was uniformly covered by nanotubes. Oxide nanotubes on the surface of the Ti6Al7Nb alloy are smaller (60 nm in diameter) and differ depending on location (Fig. 8e). Nanotubes formed on the α phase grains of the alloy are regularly shaped and cover the entire surface of the α phase. In case of Ti6Al4V alloy nanotubes formed over the β phase grains partially dissolved, whereas nanotubes over α phase are smaller ($45 \text{ nm} \pm 10 \text{ nm}$). The XPS analysis (Fig. 9) revealed that the highest amount of fluorides in surface layer is obtained when using $1M \text{ H}_3\text{PO}_4 + 0.3\% \text{ wt. HF}$, but in this case the lowest amount of phosphates adsorbed above nanotubes is observed. The use of higher concentrations of phosphoric acid ($2-3M \text{ H}_3\text{PO}_4$ with $0.4\% \text{ wt. HF}$) assures the formation of nanotubes containing the high concentration of both bioactivity enhancing elements, fluorides and adsorbed phosphates.

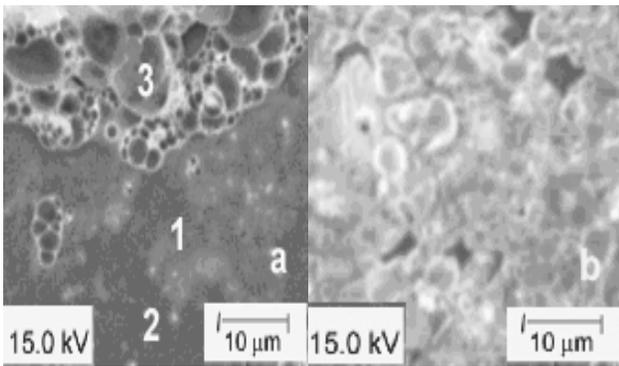


Fig. 5. SEM micrographs of titanium surface anodized at 0.5 A/m^2 in a) 0.5 M , b) $2 \text{ M H}_3\text{PO}_4$ [29]

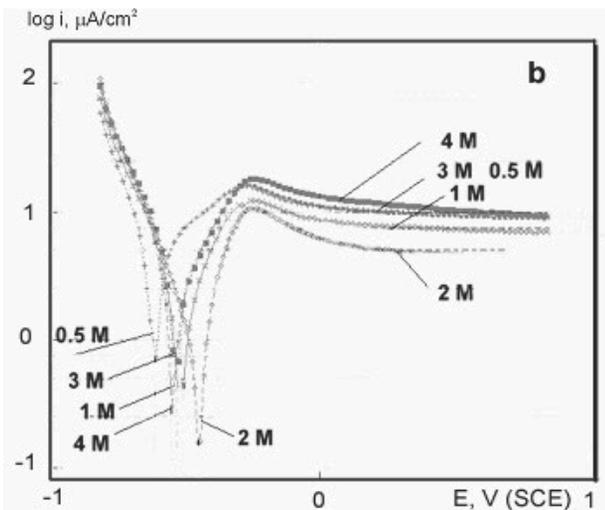
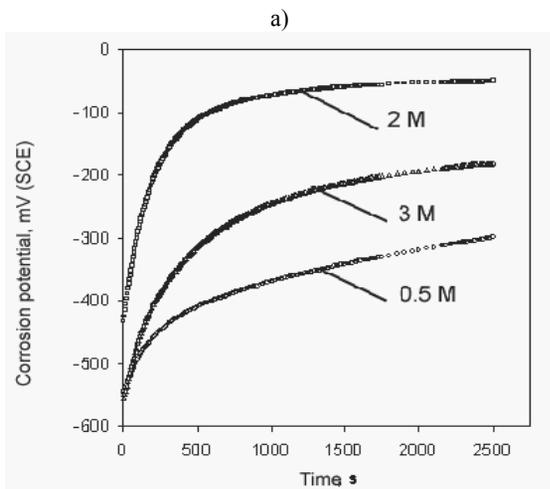


Fig. 6. Galvanostatic and potentiodynamic studies of Ti anodized at 0.5 A/m^2 in $0.5\text{-}2 \text{ M H}_3\text{PO}_4$ and active-passive transition region for titanium in $0.5\text{-}4 \text{ M H}_3\text{PO}_4$ [11, 29]

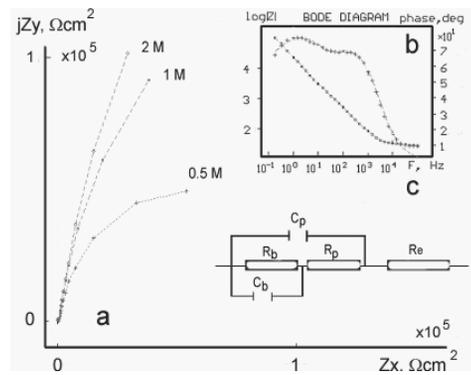


Fig. 7. Impedance spectra for titanium anodized in $2 \text{ M H}_3\text{PO}_4$ exposed to $0.9\% \text{ NaCl}$ solution a) Nyquist spectra, b) Bode diagrams and results their fitting to c) equivalent circuit [29]

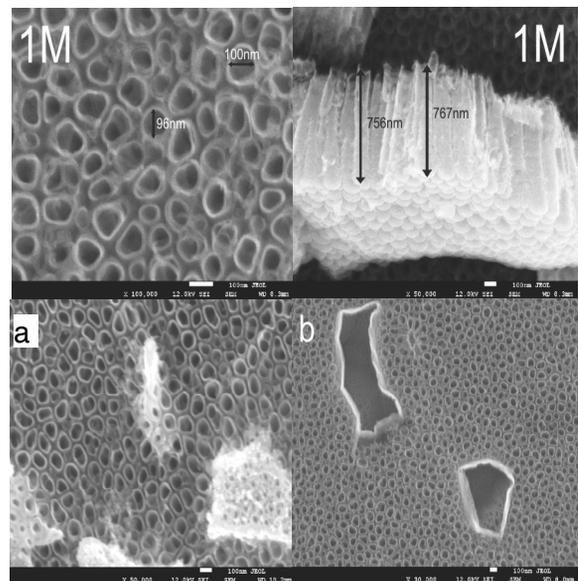


Fig. 8. SEM images of titania nanotubes formed anodically in $1\text{-}3 \text{ M}$ solutions of H_3PO_4 with $0.4\% \text{ wt. HF}$ (JEOL 7600F) on titanium and a) $\text{Ti}_6\text{Al}_7\text{Nb}$ alloy and b) $\text{Ti}_6\text{Al}_4\text{V}$ alloy [39-42]

3. Ti/titania nanotubes for biosensing

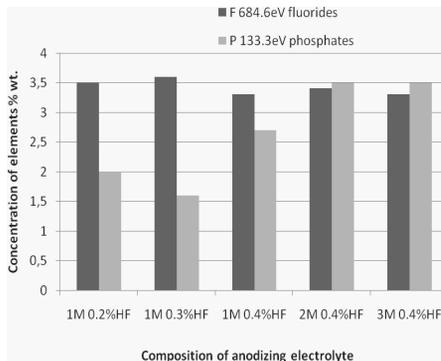
Additional advantage of oxide nanotubes consists in their capability to adsorb enzymes, proteins or biological cells. Testing the possibility of modifying the surface of these metals covered with layers of nanotubes has been another challenge [43,44]. the electrochemical behavior of modified titanium dioxide surface on titanium applied for H_2O_2 biosensing.

The Ti/TiO_2 electrode for biosensing was prepared by electropolymerization of conducting polymer (PANI) on the surface of electrode covered with titania [43] and by using titania nanotubes on Ti as a platform of the 3rd generation biosensors [44]. In both cases the HRP (horseradish peroxide) was

immobilized on the sensing surface and using either cyclic voltammetry or amperometric modes the feasibility and electrochemical parameters for H_2O_2 monitoring on Ti/TiO₂ surface were checked.

Two peaks seen on cyclic voltammograms (Fig. 10) for the Ti/TiO₂ (nanotube) electrode with immobilized HRP, indicate the sensitivity of the prepared platform to H_2O_2 , but only in the presence of thionine as the mediator [44].

a)



b)

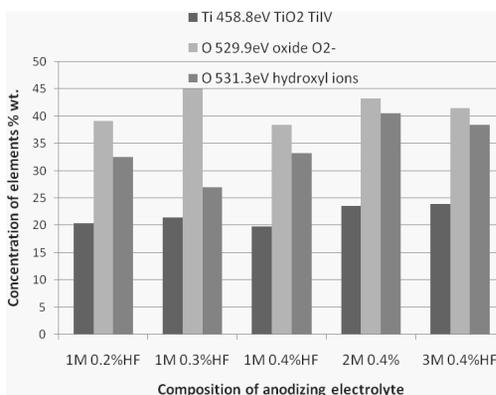


Fig. 9. a), b) Results of XPS analysis of nanotubes formed on titanium in 1-3 M H_3PO_4 solution containing different amount of fluorides, from 0.2% wt to 0.4% wt. HF [41]

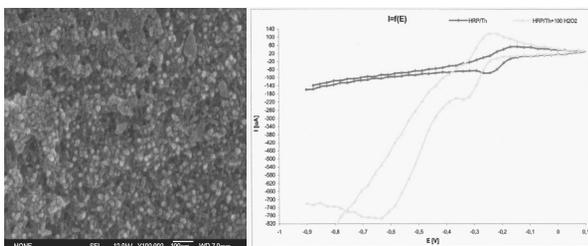


Fig. 10. SEM image Ti/TiO₂ covered with HRP and cyclic voltammograms of Ti/TiO₂/HRP in the presence of H_2O_2 in 0.1 M PBS (pH 6.8), scan rate 100 mV/s [43,44]

4. Effect of bending on the behavior of surface oxide in vitro

Most literature data deal with the evaluation of protective properties of flawless anodic layer with no-external loads applied. With bending stress on the specimen, the fracture of the passive film is possible, even if the specimen itself is not fractured. Plastic deformation of surface layer influences: topography of surface, surface energy, stress and strain distribution [45-47]. Such changes can effect in turn the in-growth of bone tissue and stimulate the osteointegration. In order to evaluate electrochemical behaviour *in vitro* of the anodic surface layer on implant Ti6Al4V ELI alloy after immersing in simulated body fluid, deformation by bending was applied [48, 49.]. For oxide layer deformation studies the test specimens were anodized with galvanostatic mode in phosphoric acid [22, PL Patent 185176, 2003]. Plastic deformation of specimens was performed by bending according to the typical pre-operative procedure of shaping the spinal rods (Fig. 11) at angles 10°, 20° and 30°, although the procedure was slightly different from the examples in the classical mechanics due to translocation of load (Fig. 10). The corrosion potential values (E_{corr}) and the electrochemical impedance spectroscopy (EIS) analysis, both performed after 1 hour and 1, 3, 6, 9, 12 days of immersion in simulated body fluid (SBF), were used to evaluate changes of the electrochemical properties of the anodic layer.

The lower values of the corrosion potential E_{corr} were observed for higher bending angles and a decrease of the E_{corr} values during immersion in SBF solution. The EIS impedance spectra were recorded at the E_{corr} with 5 mV (rms) wave of 10⁵ Hz-0.18 Hz frequency. On Bode curves for non-deformed specimens two time constants are observed, which correspond to bi-layer metal/oxide film model (thin porous layer over the barrier oxide layer). Bode curves (Fig. 12) reveal changes of impedance spectra after mechanical deformation at bending angle 20° after 1, 6, 10 and 16 hours in SBF solution. The observed changes are the evidence of gradual transformation of the one layer surface film into the bi-layered structure due to immersion in the electrolyte.

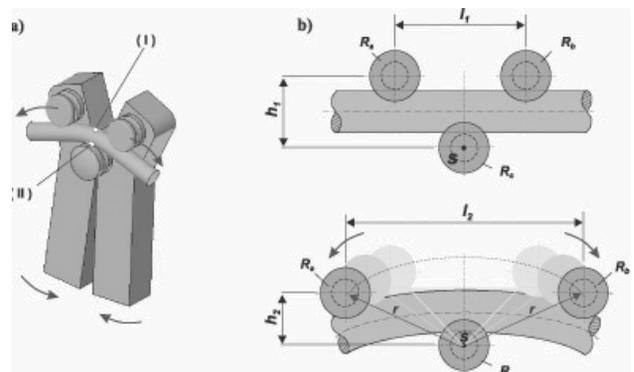


Fig. 11. Pre-operative bending of spinal rods, a) scheme of tool material arrangement, b) zones of surface stresses due to bending: (I)-max tensile and (II)-max compressive stress on tested specimens

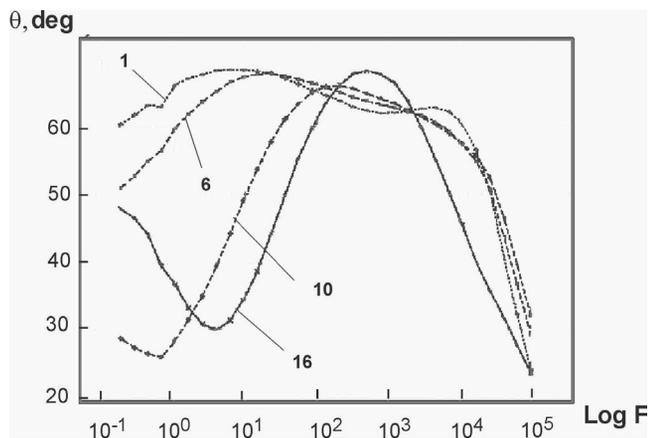


Fig. 12. Impedance spectra for the tensile zones of the Ti6Al4V alloy sample; bending angle 20° after 1, 6, 10 and 16 hours in SBF solution [48, 49]

The exchange of ions at electrolyte/biomaterial interface in two opposite processes: in oxide layer dissolution and in the deposition of electrolyte components generates the equilibrium of the whole system in SBF. The extent of mechanical deformation in metal/anodic layer system determined the domination of one of the above processes. According to the dominating process the direction of changes of electrochemical parameters (especially E_{corr}) was set up. The obtained results demonstrated that the equilibrium, which the oxide layers strove to achieve was characteristic for investigated sample/solution system, independently of the level of sample deformation and the characteristics of surface layer (Fig. 6).

The final corrosion potential values corresponded to conditions encountered in tissue environment (values of membrane potentials of tissues in living organisms are 0.2-0.45 V (SCE) [50]).

Bending is connected with changes of mechanical properties of the surface layer of the anodic alloy Ti6Al4V ELI, and after placing in a tissue environment has an influence on its electrochemical and biological behaviour *in vitro* (Fig. 13). The more negative surface polarization of deformed samples, in comparison to the non-deformed samples [51, 51], has the stimulating effect on bioactivity. It is clearly evidenced by the higher number of Ca-O-P deposits on the mechanically active surface. However, the effect of the mechanically induced bioactivity, decreased with time, as was expected due to approaching the equilibrium by the samples. Deposits of Ca-O-P blocked the pores of microcracks and stimulated osteointegration at the implant/bone interface through fine-crystalline hydroxyapatite.

All obtained results may confirm that due to the new coating the deleterious effect of the deformation of the implant titanium on its corrosion resistance is hindered by blocking the pores by precipitated Ca-P-O salts. The resulting deposited layer forms an additional barrier to metal dissolution in the system. When immersed in SBF solution for at least 3 days the samples showed the recovery of the layer structure and numerous Ca-P-O deposits on the surface (Fig. 14) [55]. The number of the deposits showed the stimulating effect of the surface polarization (more negative) and topography on the deposition of SBF components and formation of hydroxyapatite on the mechanically activated surface of the alloy. It is worth to mention that Ca-P-O coating is not an effective anticorrosion layer.

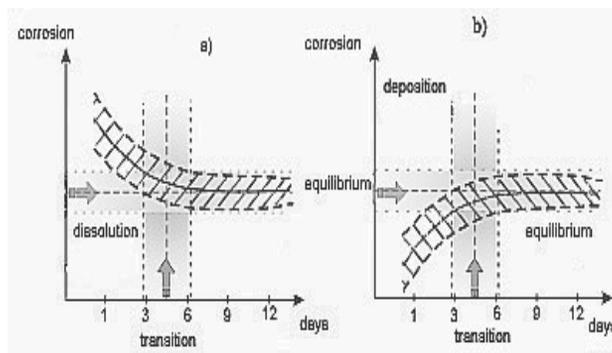


Fig. 13. The behaviour *in vitro* of deformed anodic layers: a) for specimens bent at 0° and 10° , b) for specimens bent at 20° and 30° (\uparrow increase, \downarrow decrease, \leftrightarrow constant, \rightarrow change) [53]

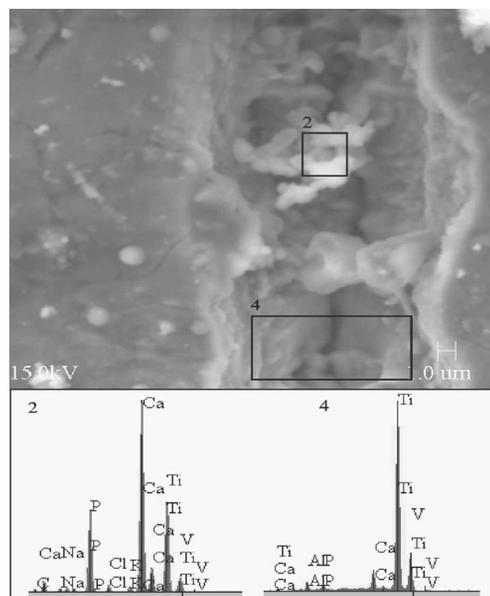


Fig. 14. SEM microphotograph and EDS results of EDS analysis for Ca-O-P deposits in the tensile stress zone of rebent specimen (bending angle 20°) after 30 days in SBF solution ($\times 5500$) [52]

It hinders to some extent the electrochemical processes occurring at the implant metal interface, thus contributing to a decrease in the metal ion release from the implant system.

All surface deformation processes and finishing treatments (polishing and anodizing with electrochemical polishing) change the surface energy of the alloy. After immersing in SBF the exchange of ions at electrolyte/biomaterial interface in two opposite processes: the oxide layer dissolution and the deposition of electrolyte components, form the equilibrium of the system (Fig. 14) [55]. Depending on the prevailing process during the first days of immersing, the decrease of the appropriate corrosion parameters are observed in case of the less deformed specimens, for which the anodic layers were not broken. As the result of breaking of anodic layer at higher bending angles, microcracks

and naked metal appear, giving raise to the deposition of the electrolyte components. Thus, deformation of anodic layer on implant titanium alloy induces the increase of bioactivity *in vitro* and enhances the coating of deformed area by SBF components, which form porous hydroxyapatite and stimulate faster growth bone tissue [53-55].

5. Conclusions

Galvanostatic and potentiodynamic anodizing of titanium and its implant alloys allows to tailor the properties of surface layers according to requirements of implantology. Due to the applied technology the oxide layers may differ in morphology, structure, thickness and chemical composition. According to the needs they can be amorphous, crystalline or nanostructural. If anodized in the phosphoric acid solutions they are enriched with phosphates, forming in more concentrated solution the gel-like layer of phosphates over the oxide. If anodized in phosphoric acid with addition of fluoride ions, then apart from phosphates they contain also fluorine. Both elements are crucial for enhanced bioactivity of anodic layers on titanium materials. Primary results with enzyme HRP (horseradish peroxidase) confirmed that anodic titanium nanotubes can be also used as a platform for biosensing.

Acknowledgements

The author acknowledges funding from the Polish Ministry of Science and Higher Education in the projects 0484/T02/2006/30 and N507 082 31/2009.

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