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Anodic Layer Formation on Titanium and Its Alloys for Biomedical Applications

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1. Introduction

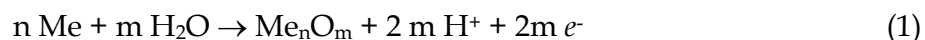
Properties of the oxide layers on titanium and its implant alloys can be tailored to desired applications by anodizing parameters. Electrochemical oxidation in various electrolytes and different polarization regimes may shape the morphology, structure and chemical composition of oxide layers to enhance the use of titanium materials in electronics, photovoltaic and medicine. Phosphate electrolytes play specific role in the anodizing process. Besides forming compact barrier layer they enable also to form porous and nanostructural oxide layers enriched with phosphates, which enhance their bioactivity.

The formation of anodic layers: thick or thin, compact or porous, gel-like and nanostructural on titanium and its alloys Ti6Al4V and Ti6Al7Nb in phosphoric acid solutions of different concentrations is described in this charter. Basing on morphological and chemical composition analysis (SEM, XPS) as well as on the electrochemical examination the influence of electrolyte composition on enrichment of surface oxide layers with phosphates and fluorides, enhancing their bioactivity, is presented. Studies to use Ti/titania systems as the platforms of the electrochemical biosensors to detect H_2O_2 and glucose proved the opportunity to use the nanotubular titania material as a platform for the 2nd generation biosensors.

2. Oxide layers on titanium and its implant alloys formed in H_3PO_4 solutions

Anodic films formed on titanium and its alloys are of great interest due to the industrial applications of metal covered with oxide layers of various and unique properties [1-7]. These layers have been investigated extensively by many authors [8-11]. Thick oxide layers on titanium, obtained by anodizing, provide improved resistance to local corrosion [12]. Anodizing can result in the adsorption and incorporation of inorganic and organic, biologically important species, e.g. phosphate ions, into the oxide layer. Such surface layers, desirable for medical implants, are not only corrosion resistant in a biological environment, but also compatible with tissue response [13-15]. Anodizing titanium and its alloys has been investigated in a wide range of parameters [16-20], which include also the participation of the electrolyte components, e.g. anions, in the formation of anodic films [21, 22].

At anodizing oxide layers are formed according to the following reaction [17, 23]:



Studies in this field [24, 25] 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 [26].

Anodizing in phosphate solutions exhibit some advantages over other acid and base electrolytes. First of all less corrosive attack of phosphoric acid on titanium and its alloys, when compared with other acidic media, is related to the strong adsorption of phosphate anions on the surface [27,28]. Although unalloyed titanium is resistant [11] to naturally aerated pure solutions of phosphoric acid up to 30 % wt. concentration (~3.6 M) in phosphoric acid of lower concentrations (0.5-4 M), mainly non-dissociated acid molecules and H_2PO_4^- of phosphate ions exist [29,30] and they exhibit a strong affinity or complexing power towards most metal cations.

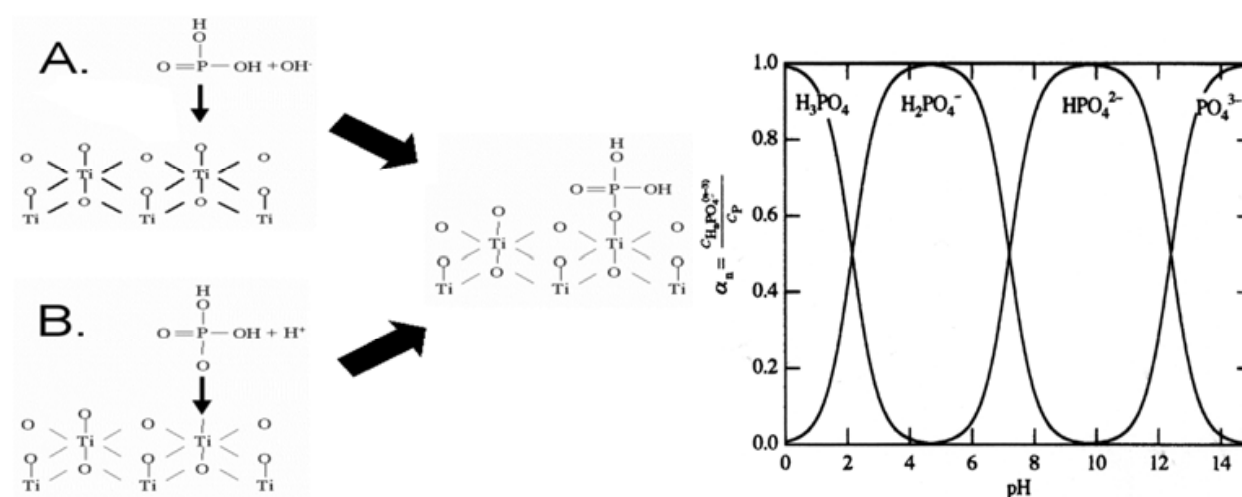


Fig. 1. Adsorption of phosphates onto TiO_2 [28] and effect of pH on phosphoric acid composition [30]

Thus, anodizing in phosphate solutions leads to the incorporation of phosphate ions into the oxide layers on titanium and Ti-6Al-4V [5-8] influencing their bioactivity and stimulating deposition of the biocompatible hydroxyapatite. The latter may be used to shape properties of titanium implant materials for medical purposes.

2.1 Thin porous anodic layers

Anodic layers on pure Ti and its alloys Ti6Al4V ELI and Ti6Al7Nb (ASTM F136-84), alloys in the annealed condition) can be formed by anodizing carried out at ambient pressure and room temperature in non-deaerated electrolyte solutions of 0.5 M H_3PO_4 . Both techniques, the galvanostatic at anodizing current density values varied in the range of 0.1-0.5 Am^{-2} and the potentiostatic at up to 60V [22] are used. The oxide layers, 30-120nm thick, enriched with phosphorus are formed in these conditions. With mechanical and chemical pre-treatment applied to titanium and its alloys: Ti6Al4V ELI and Ti6Al7Nb (Timet Ltd, UK) [12-20], the layers obtained at 60V in phosphoric acid are golden and porous [11, 24-26] (Fig. 2) and they show very stable values of currents in passive region up to 1 V (SCE) (Fig.3) [11]. At other

polarization parameters however layers of different thickness and colorization are formed [11]. Due to the presence of phosphates in the anodic layers they are highly bioactive in comparison to oxides formed in other electrolytes. Just after 9 days in the SBF solution (Simulated Body Fluid) they are covered with hydroxyapatite deposits (Fig. 2) [27].

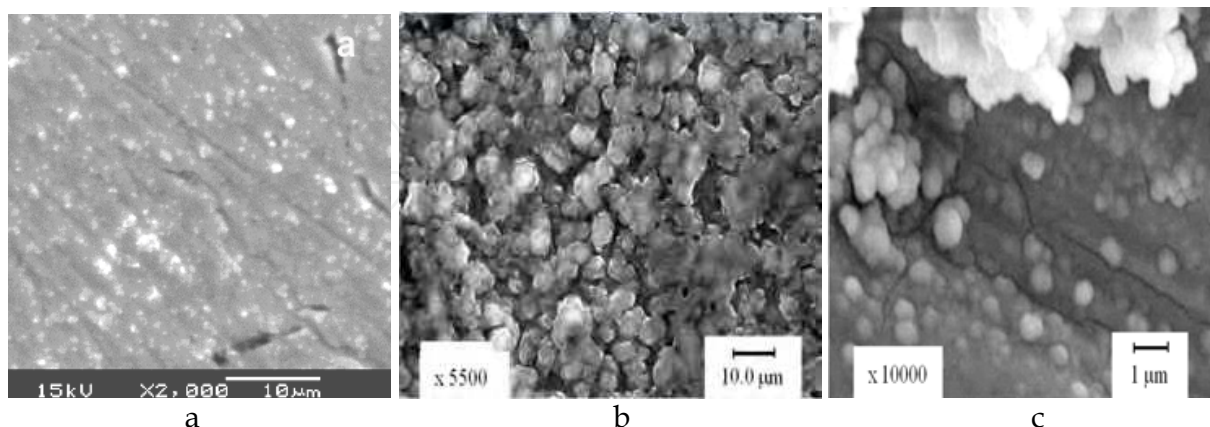


Fig. 2. Porous titania layers on Ti formed at 0.5 A/m^2 in $0.5 \text{ M H}_3\text{PO}_4$ [22] (a,b) and HAp particles on anodic layer after 9 days in SBF solution [21, 25, 27] (c), JEOL JLM 5600 EDS

The bilayer structure of compact oxide covered with HAp particles can be demonstrated also in the impedance tests (Fig. 3). The first time constant in Bode diagrams in range of the high and intermediate frequencies confirmed the high R_t resistance of the barrier layer covering the anodized metal, thus giving the evidence of 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.

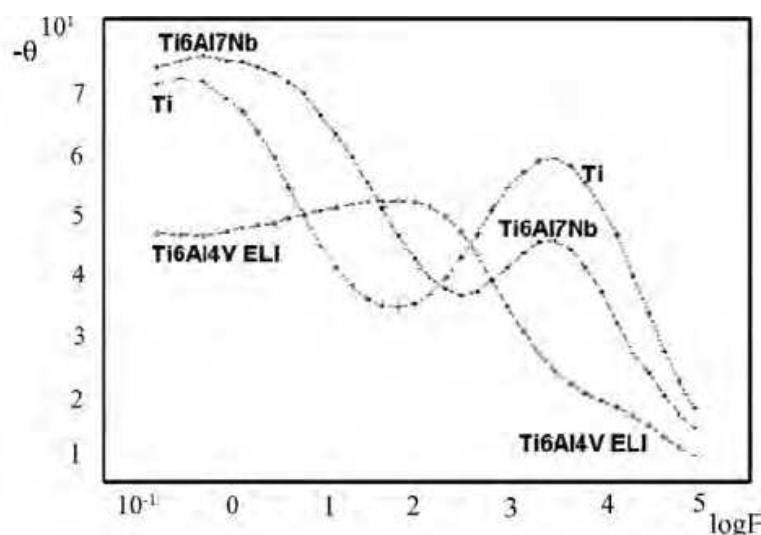


Fig. 3. EIS spectra recorded after 9 days in SBF solution [21, 25, 27] for anodic layers on Ti, Ti6Al4V and Ti6Al7Nb formed at 0.5 A/m^2 in $0.5 \text{ M H}_3\text{PO}_4$ [22]

To investigate the effect of phosphoric acid concentration ($0.5 - 4 \text{ M}$) on the anodising of titanium and its alloys the galvanostatic and potentiodynamic techniques have been applied [11,19]. Particularly, the galvanostatic method with low current densities, up to 0.6 A m^{-2} ,

applied in order to minimize side effects (ie. oxygen evolution), and more importantly to determine processes responsible for the growth of the oxide layer on the anodised metal at the early stages of its formation, allowed to observe the abnormal behaviour of titanium at anodizing. In Fig. 4 the results presenting the minimum rates of potential growth at initial stages of galvanostatic anodising in 2 M H_3PO_4 solutions are shown.

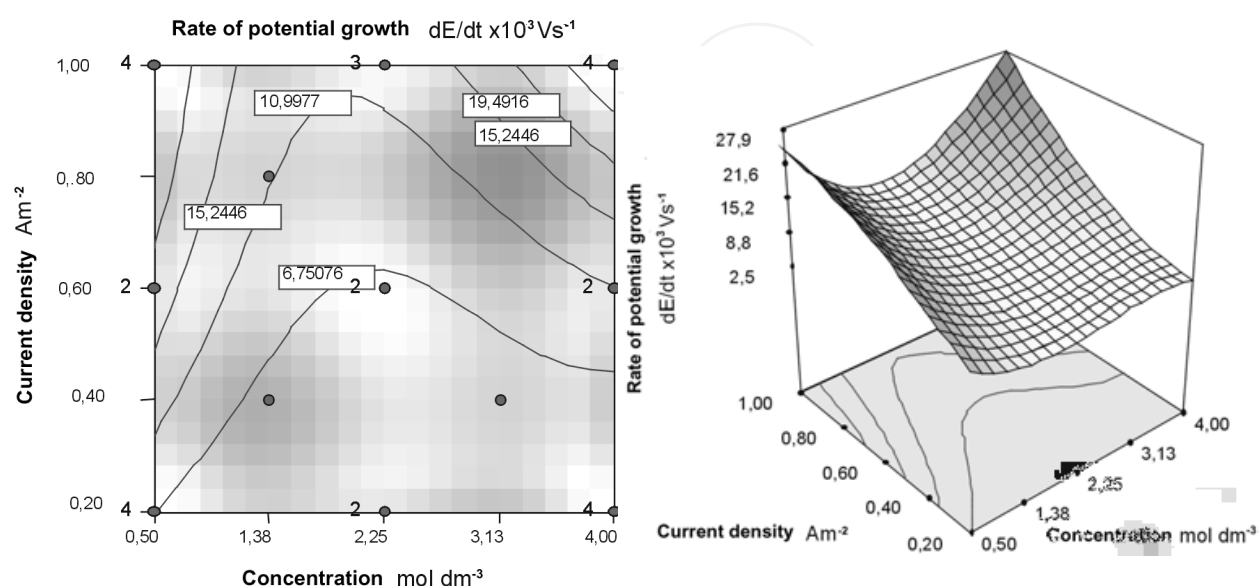


Fig. 4. Surface response for the investigation of the effect of H_3PO_4 concentration and polarization current on the rate of potential growth dE/dt at galvanostatic anodizing of titanium [11]

Also the anodic polarization curves for titanium in electrolytes of different concentration show various shapes and different slopes in active-passive region (Fig.5). Potentiodynamic control at a comparable rate in 2 M H_3PO_4 applied to titanium and two of its implant alloys, Ti6Al4V ELI and Ti6Al7Nb, revealed a shift in corrosion potential toward the anodic direction with the lowest current densities in the passive region. This was possibly due to the effect of adsorption of phosphate ions onto the surface layer.

2.2 Gel like layers on anodic titania

Active-passive transition of titanium in phosphoric acid solutions of 0.5-4 M [11,19] reveals that the growth of anodic layer is affected proportionally by the applied anodic potential, but shows the unusual influence of electrolyte concentration. Under galvanostatic conditions at low current densities (0.1-0.6 Am^{-2}) the slope of dE/dt shows the minimum at the concentration $\sim 2 \text{ M } \text{H}_3\text{PO}_4$ (Fig. 4), which is resulted due to a coating of an oxide film by an additional gel-like layer during anodizing, [28, 29], similar to the one observed in other media on aluminum.

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 during anodizing [29]. Typical examples of voltage *vs* time transients (dE/dt) during the growth of the galvanostatic anodic oxide film on titanium for the current density of 0.5 A/m^2 (Fig. 5a) show that the continuous linear growth of potential to the steady state, demonstrates the lowest value in 2

M H_3PO_4 . Polarization curves (Fig.5b), show that after an initial range of cathodic depassivation, samples reach the corrosion potential E_{cor} . Then an active-passive transition is observed with passivating currents the order of a few microamperes, which are typically observed during the passivation of titanium and its alloys. Anodic curves for 0.5 M and 3 M H_3PO_4 solutions (Fig.5b), 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. The differences in anodic Tafel slopes are accompanied by a shift of the E_{cor} value in the positive direction by $\sim 0.15\text{V}$ with the increase of H_3PO_4 concentration to 2 M (Fig. 5b).

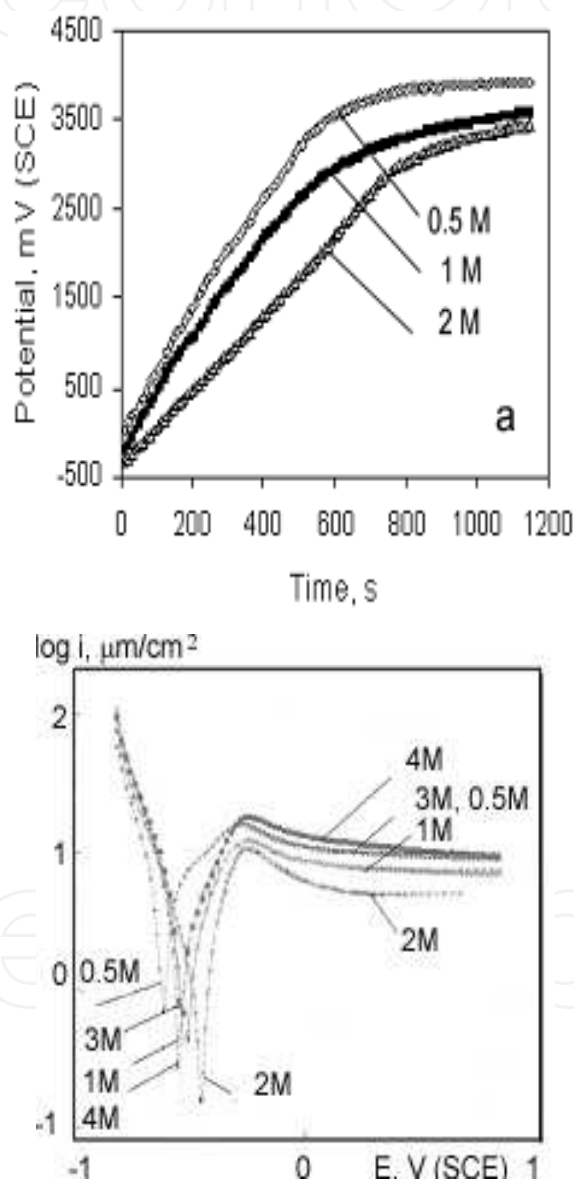


Fig. 5. Corrosion potential values E_{cor} of Ti anodised at $0.5 \text{ A}/\text{m}^2$ in 0.5-2 M H_3PO_4 in SBF solution [11,29] (a) and active-passive transition regions of polarization curves for titanium (scan $3 \text{ mV}/\text{s}$) in 0.5-4 M H_3PO_4 (b)

SEM/EDS examination confirm the evidence of two-layered surface film. Such layers presented in Fig. 6, show the whole surface covered by a gel-like layer of $\text{H}_3\text{PO}_4 \times 0.5\text{H}_2\text{O}$.

The SEM/EDS examinations reveal that thin films of anodic titania oxide are covered by gel-like layer with crystalline phosphates nuclei inside. Phosphates deposits are few in layers formed in 0.5 M H_3PO_4 , but numerous and uniformly dispersed in a surface oxide of sample anodised in 2 M H_3PO_4 . However, the oxide and phosphates are covered with the additional layer consisting of 76.3 ± 3.6 wt.% of phosphorus and 23.7 ± 1.5 wt.% of oxygen (Fig.6a and 6b).

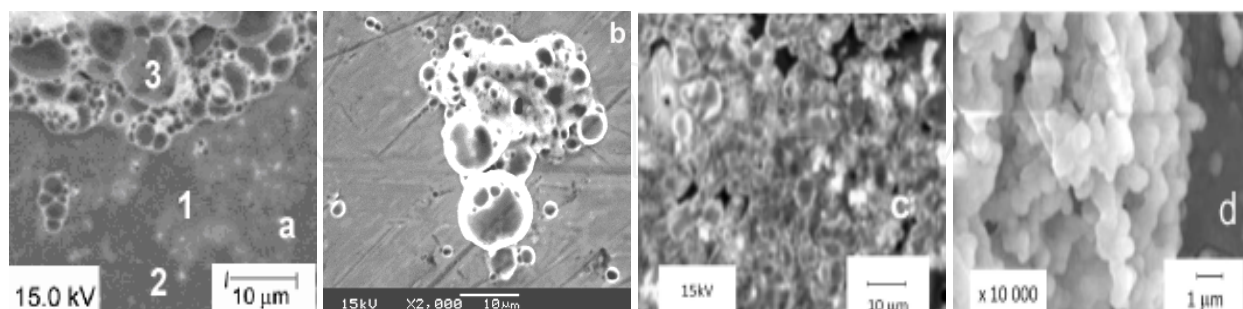


Fig. 6. SEM micrographs of titanium surface anodized at 0.5 A/m² in a,b) 0.5 M, c) 2 M H_3PO_4 [29], and d) HAP particles on anodic layer after 9 days in SBF solution [21, 27]

The EIS spectra of titanium after anodizing at 0.5 A/m² in 0.5-2 M H_3PO_4 (Fig. 7), exhibit a behavior typical of a metallic material covered by a porous film which is exposed to an electrolytic environment [6]. Two time constants are seen in the spectra: the first in the high-frequency part arises from the ohmic electrolyte resistance and the impedance resulting from the penetration of the electrolyte through a porous film, and the second in low-frequency part accounts for the processes at the substrate/electrolyte interface.

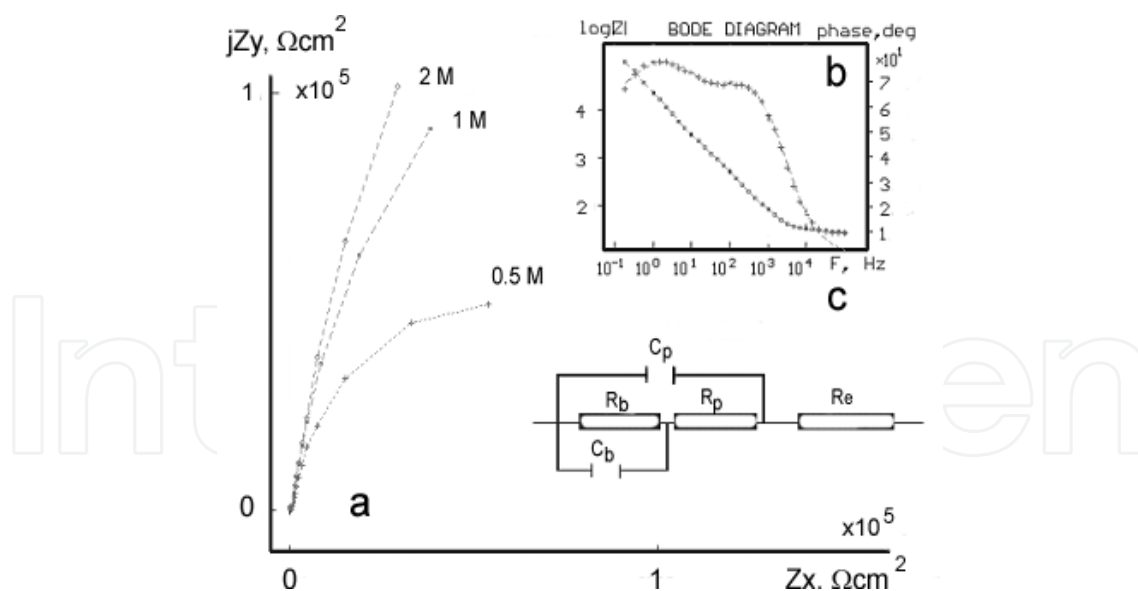
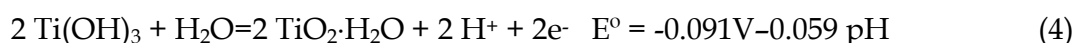
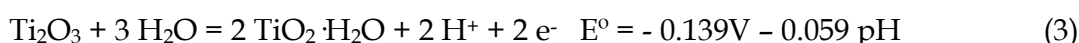
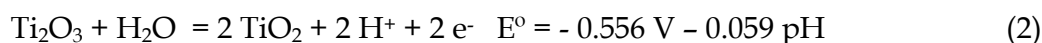
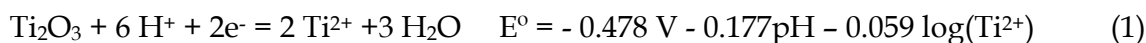


Fig. 7. Impedance spectra for titanium anodised in 2 M H_3PO_4 exposed to 0.9% NaCl solution a) Nyquist spectra, b) Bode diagrams and results of their fitting to c) equivalent circuit

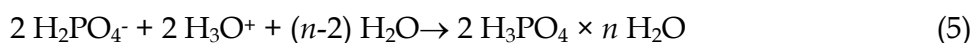
The EIS data can be fitted to the equivalent circuit in Fig. 7c, which consists of a solution resistance R_s , the capacitance C_p of the barrier layer, the charge transfer resistance associated with the penetration of the electrolyte through the pores R_p ; and the polarization resistance of the barrier R_b as well as the electrical double-layer capacitance at the substrate/electrolyte

interface C_b . In the case of surface layer formed in 2 M H_3PO_4 the specimen is covered by a passive oxide film of higher impedance (Fig.7a). The significant increase of the resistance R_b and R_p values for the 2 M H_3PO_4 anodized samples, over those determined for the 0.5 M H_3PO_4 anodized titanium, confirm that the EIS results are complementary to those obtained by E_{cor} measurements and potentiodynamic polarization studies [11,31].

Titanium as metal very sensitive to the pre-treatment [33], due to the polishing, rinsing with water and drying, is usually covered by an air-formed oxide film and on immersion into acid solution shows potentials of the active-transition region [32-34]. However, in solutions of low pH may become active. In sulphate solution the anodic oxide film on titanium dissolves giving Ti^{3+} ions [11]. Typical activation behaviour and slow decrease in the open-circuit potential (-0.3 V SCE), is observed on immersing titanium into 1M HCl [35,36]. Titanium behaves differently in H_3PO_4 solutions. Although the values of E_{cor} ranging from -0.1 V to -0.6 V (SCE) indicate in Pourbaix diagram [29] that the oxide film should dissolve to Ti^{3+} , on immersion to H_3PO_4 solutions titanium shows the continuous shift of potential towards the anodic direction [32]. Such a tendency indicates that the rate of the anodic reactions is continually decreasing, as a result of the presence of an adsorbed, additional layer on the metal surface [37]. Thermodynamic data [11,33] for the potential $E \geq -0.8$ V (SCE), indicate that the following reactions on titanium are likely:



In acidic solutions within the cathodic region, the only oxide dissolution is reaction (1). This reaction determines the potential-current changes in active-passive region of titanium in 0.5 M and 3-4 M H_3PO_4 , whereas due to the shift of the corrosion potential E_{cor} towards the anodic direction for titanium immersed in 1-2 M H_3PO_4 electrolyte, its direct oxidation proceeds according to reactions 3 and 4. These results indicate that, the layer of phosphates (Fig. 6) blocks the oxide dissolution. Insight into the adsorption of phosphates to TiO_2 surface revealed the hypothesis according to which they form covalent bonding to oxygen [38], or metal ions react with phosphate anions forming a gel of metal hydrophosphates [39]. Both proposed processes would lead to local increase of pH at the oxide surface and in consequence to the increase of concentration of dihydro-phosphate ions (E-pH diagram) [29]. Then, on phosphates covered titanium oxide electrode, the following gel like layer formation could proceed



This attribution agrees with Morligde's *et. al.* results on aluminum [40]. Both reactions: the phosphates adsorption and gel-like layer formation are non-faradaic, but are competitive towards the oxide dissolution (reaction 1) with regard to proton consumption. The advantageous effect of these two reactions on the anodizing, may be attributed to an inadequate supply of H^+ ions to keeping up with the demand for the reaction (1) of oxide dissolution. The increasing coverage of the anodized titanium surface by phosphates ions

with the electrolyte concentration provides the evidence of a direct influence of electrolyte anions in suppressing the formation of dissolved titanium ions. According to potential/pH diagram for P-Ti-H₂O system [41], H₃PO₄×0.5H₂O, the product of reaction 5, is stable thermodynamically in solutions of pH ranging to 3.

Thus, due to the applied anodizing conditions formation of either thin and porous oxide layer [11-23] or gel-like phosphates rich layer of H₃PO₄×0.5H₂O [11, 24-29, 42], covering thicker oxide layer on titanium can be obtained.

2.3 Bioactive layer

Apart from mechanical properties and biocompatibility, which make titanium and its alloys the materials of choice for various applications (artificial hip and knee joints, dental prosthetics, vascular stents, heart valves) also enhancement of bone formation is desired feature of a metallic implant developed through adequate surface treatments to obtain proper osseointegration.

Fast deposition of hydroxyapatite (HAp) coatings on titanium and its alloys Ti6Al4V and Ti6Al7Nb substrates anodized in H₃PO₄ was observed [21,23,25]. Anodizing in 0.5 M H₃PO₄, which produces phosphates enriched porous sub-surface layer on of titanium and its alloys Ti6Al4V and Ti6Al7N [22] or anodizing in 2 M H₃PO₄ which generates phosphates rich gel-like layer [31,42] may be used to enhance hydroxyapatite (HAp) deposition (Fig.8). For the latter anodic layers soaking the anodised substrates in simulated body fluid (SBF) resulted in the deposition of a uniform coating in 24 hours (Fig. 9). SEM and EDS investigations revealed that after 9 days thick coating consists of HAp globular of diameter varied from 100 to 300 nm aggregates. The Ca-O-P deposits merge in large clusters and they are seen in large numbers on both alloys, particularly on Ti6Al4V anodized in 2 M H₃PO₄.

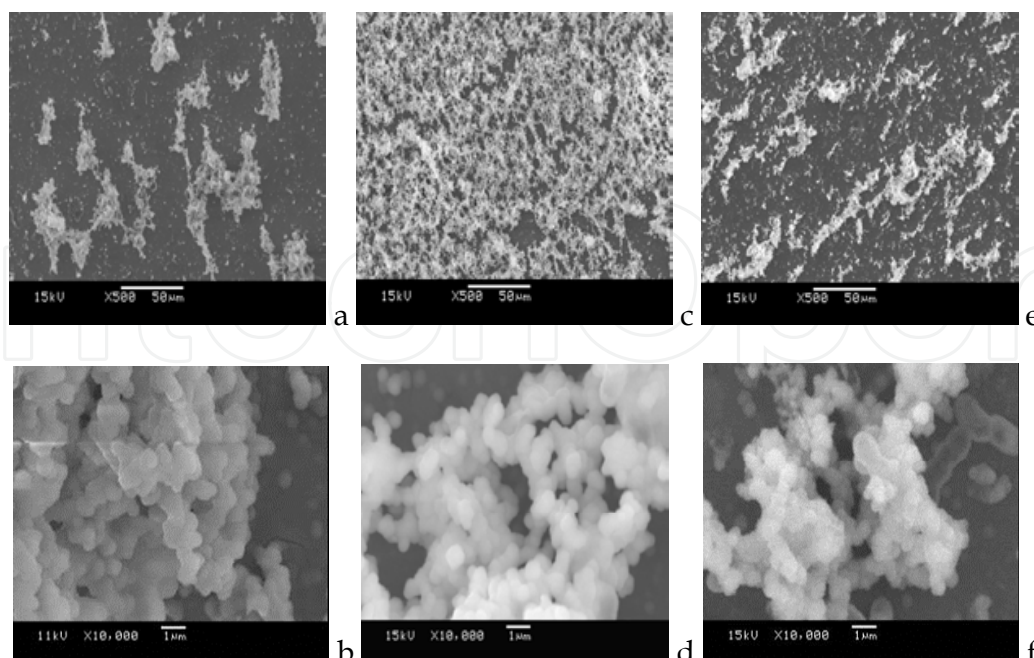


Fig. 8. SEM micrographs of titanium (a,b) and its alloys: Ti6Al4V (c,d) Ti6Al7Nb (e,f) surface anodized at 0.5 A/m² in 0.5 M H₃PO₄ after 24 h (abc) and 9 days (b,d,f) in SBF solution [21, 23]

SEM observations (Fig.8) and EDS microanalysis indicate the presence of deposits dispersed on the surface of anodised titanium and its implant alloys. However, deposits are non-uniformly dispersed on a surface. Titanium and its two alloys anodised in 0.5M H_3PO_4 are covered with very thin oxide layer, which includes numerous and more scattered Ca-O-P deposits of diameter varied from 200 to 800 nm, suggesting the heterogeneous nucleation of Ca-O-P on TiO_2 covered surface. Although just after 24 hours deposits are seen on the surface of the 3 materials (more deposits on the Ti6Al4V alloy) the continuous films cover the whole surfaces after 9 days in SBF solution. At higher magnification it is seen that the film on titanium is formed of more flatter layer of deposits and broken layer of titanium oxides with titanium phosphates, whereas film on both alloys comprise small globules of Ca-O-P. The ratio of Ca/P ranging from 1.26 to 1.42 corresponds to non-stoichiometric hydroxyapatite.

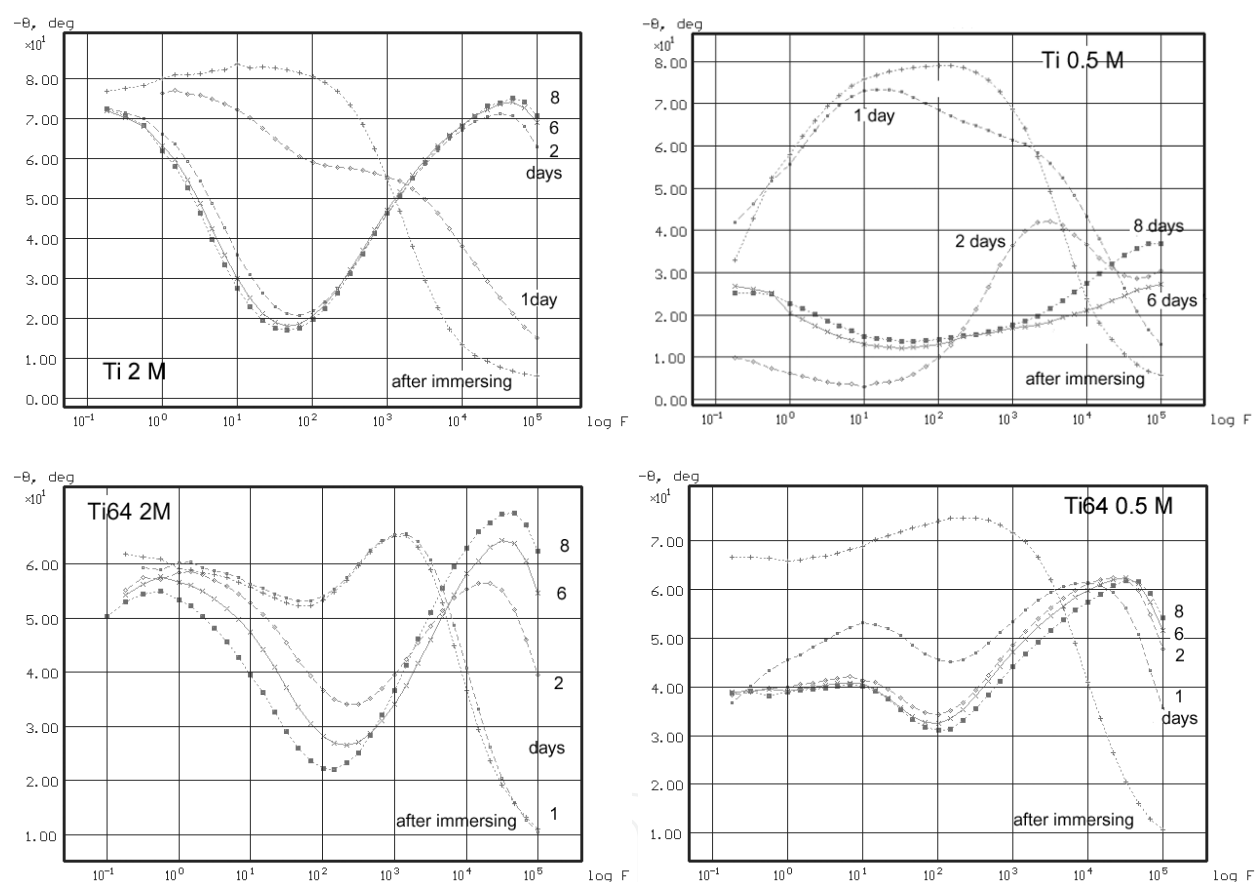


Fig. 9. EIS) spectra recorded during immersion of titanium and Ti6Al6V samples anodized in 0.5 M and 2 M H_3PO_4 in SBF solution [21,23]

Impedance (EIS) spectra (Fig. 9) recorded during immersion of the anodized titanium and the Ti6Al4V alloy in simulated body fluid (SBF) for titanium and Ti6Al4V alloy show changes in capacitance and structure of surface layers as well as differences between coatings on titanium and its alloy and confirm the SEM observations (Fig. 8). Titanium exhibits two-layered structure: the inner oxide layer is covered by an outer layer of more or less uniformly distributed various size Ca-P-O deposits. On contrary the Ti6Al4V alloy is coated by a more uniform and dense layer of deposits (Fig. 8 c,d) and much lower concentration of titanium oxide on a surface [25].

3. Nanostructural oxide layer formed in phosphate solutions

In the last 20 years anodizing has been also used as a method to form nanooxides on metal surfaces. Formation of self-organized titania nanotubes with high level organization of pores on large surfaces [43-48] became very useful technology applied to many purposes, i.e. to modification of surgical implant surfaces and to biomedical sensing. Titania nanotubes, just like barrier type titania, combine very well with osseous tissue and can be a perfect basis for osteoblasts in surgical implants. Studies focused on controlling the size and arrangement of pores [49-54], aiming at bone ingrowth and on use of titania nanotubes platform for biosensing, due to their capability to combine with e.g. enzymes, proteins or biological cells, brought promising results [55,56].

Formation of nanotubes at different polarization parameters in various electrolytes [57-60] as well as various scan rates during the very first seconds of anodizing, may help tailoring the oxides for effective implantation and improve their properties for biomedical and sensor applications. For the latter applications titania nanotubes require better ordering i.e. controlled diameter achieved during improved oxide growth kinetics. For the last 5 years in several papers [61-64] it has been revealed that the value of polarisation determines the diameter of nanotubes. Every additional 5V of potential increases the nanotubes diameter of about 20nm, whereas the time of anodizing determines the length of the nanotube layer. Moreover, the low pH and organic aqueous solutions assure more regular shapes of nanotubes.

3.1 Nanotubes on titanium in phosphate solutions

Electrochemical oxidization of titanium can be carried out in electrolytes with or without HF additives [65-67]. Attempts to assess the optimal scan rate/fluoride concentration ratio for formation of structurally uniform nanotubes [60] revealed that 1M H_3PO_4 +0.3% wt. HF is the most proper electrolyte for anodizing at 0.5Vs^{-1} . To study the effect of phosphates concentration, layers of titania nanotubes were produced in electrolytes of different phosphoric acid concentration. Their properties as the future coatings on titanium for medical uses were characterized by SEM/EDS observations and capacitance tests in simulated body fluids. Formation of oxide layers on titanium in phosphoric acid solutions with additions of fluoride ions [50] 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 (Fig. 10).

Fig. 10 shows the behavior of titanium polarized from the OCP (Open Circuit Potential) to 20V with a sweep rate of 0.5Vs^{-1} in phosphoric acid solutions of different concentration (1M, 2M and 3M H_3PO_4) containing 0.4 wt.% HF. Flat polarization curve confirm passive behavior of titanium anodized in 2 and 3M H_3PO_4 +0.4 wt.% HF, contrary to current transients recorded in 1M H_3PO_4 +0.4 wt.% HF. The increase of current with potential in that region usually can be explained by the presence of some pores [9]. Polarization curves for more concentrated phosphate solutions show the presence of the anodic peaks, which can be ascribed to the oxygen evolution [6] followed by a broad passive region. By fixing the concentration of HF (fixing the dissolution rate) the decrease of current with potential indicates that oxide formation dominates over oxide dissolution at relatively higher field strengths or/and passive layer of phosphates is formed over nanotube titania in 2 and 3M H_3PO_4 +0.4 wt.% HF solutions.

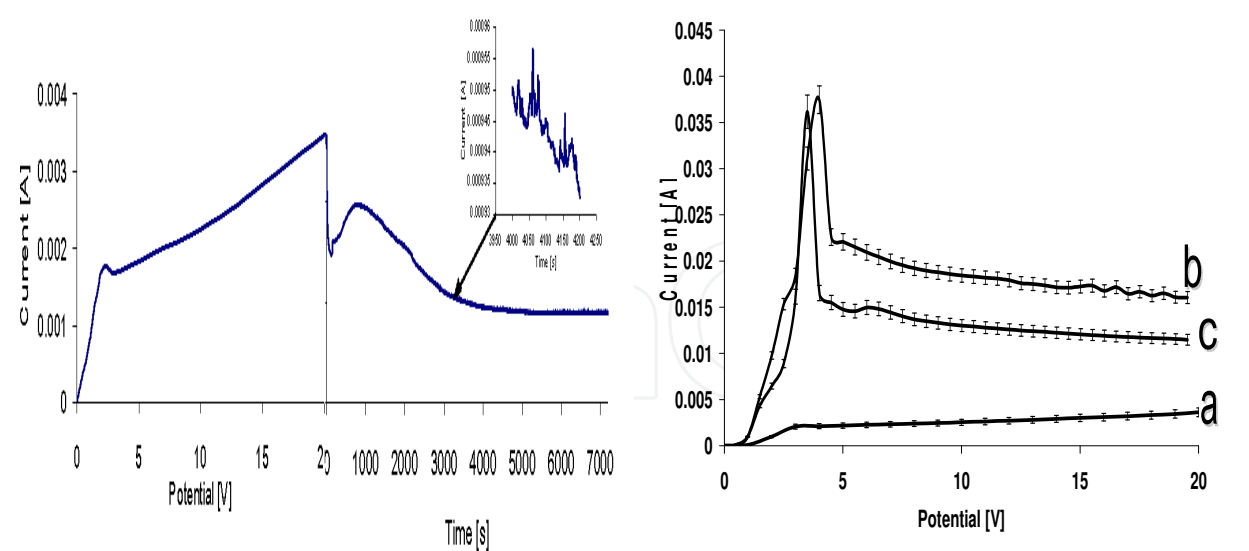


Fig. 10. Transients for potentiodynamic experiments recorded for titanium anodized to 20V (with scan rate 500mV/s) at various concentration of supporting electrolyte H₃PO₄, a) 1M, b) 2M, c) 3M with addition of 0.4% wt. HF [53]

Anodic titania nanotubes formed on titanium in 1-3 M H₃PO₄ with 0.4% wt. HF (Fig. 11) show the morphology of nanotubes on titanium which differ in diameter and the layer thickness due to electrolyte concentration.

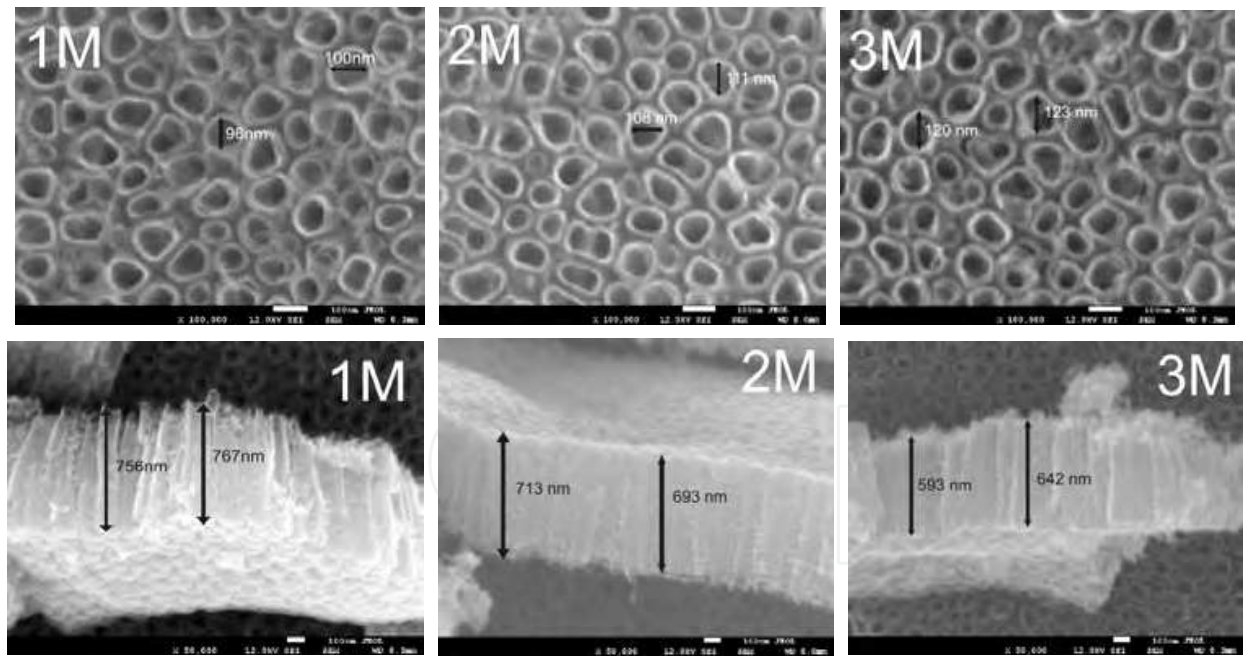


Fig. 11. SEM images of titania nanotubes formed anodically prepared at 20V for 2 h in aqueous solutions of H₃PO₄ ranging from 1 M to 3 M with 0.4% wt. HF (field emission JEOL 7600F) [53,54]

SEM observations (Fig. 11) confirmed formation of a highly organized nano-sized pores, ranging from 90 to 120 nm in all applied electrolytes. As apparent, the average nanotube diameter is slightly affected by the supporting electrolyte concentration. Also, the increase

of the latter from 1M to 3M under fixed HF concentration results in significant decrease of nanotube layer thickness, from 760±35 nm to 590±35 nm, respectively.

H ₃ PO ₄ Concentration	Diameter (+/- 10nm)	Thickness (+/- 35nm)
1M	100nm	750nm
2M	110nm	700nm
3M	120nm	590nm

Table 1. Diameters of nanotubes and the thickness of their layer on titanium formed in 1-3 M H₃PO₄ with 0.4% wt. HF

The XPS analysis (Fig. 12) revealed that the highest amount of fluorides in oxide surface layer was obtained in 1M H₃PO₄+0.3% wt. HF, but in this case the lowest amount of phosphates adsorbed above nanotubes was observed. Using higher concentrations of phosphoric acid 2-3 M H₃PO₄ Judging on the results of XPS analysis, the competition between fluorides and phosphates is observed during anodizing and the higher concentration of the latter is responsible for higher bioactivity of nanotubes formed in 2M H₃PO₄+0.4% wt. HF [53].

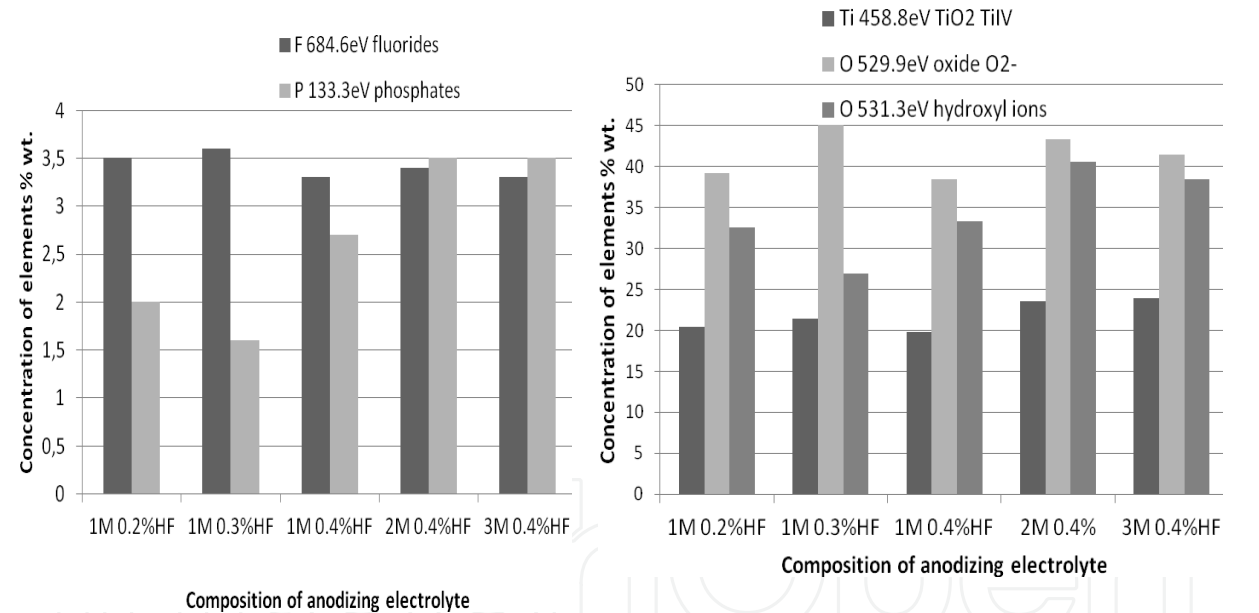


Fig. 12. Results of XPS analysis of nanotubes formed on titanium in 1-3 M H₃PO₄ solution containing different amount of fluorides, from 0.2% wt to 0.4% wt. HF VSW (Vacuum Systems Workshop, Ltd.) K α Al (1486.6 eV) X-ray radiation working at power of 210 W (15 kV - voltage, 14 mA – emission current) [53].

The XPS spectra (Ti 2p, O 1s, P 2p and F 1s) revealed that nanotube layers consist of Ti, O, F and P species. The Ti 2p spectra for all samples showed only one doublet line. The position of the Ti 2p_{3/2} peak on the binding energy scale at 458.8 eV corresponded to titanium dioxide and Ti IV phosphates [16]. One type of phosphorus was revealed by the P 2p_{3/2} peak position at 133.3 eV associated to phosphate type species, indicating that species from the electrolyte are indeed adsorbed over the oxide film during anodizing. Oxygen was

found to exist in two forms. The binding energies of the O 1s spectra corresponded to hydroxyl groups OH⁻ (531.3eV) and oxygen in oxides O²⁻ (529.9 eV). The presence of fluorine in the surface layer was confirmed by the F 1s spectra of binding energy 684.6 eV associated probably with Ti. As it is shown in Fig. 12 the concentrations of titanium corresponding to titanium dioxide and Ti IV phosphates are nearly the same in all tested samples, whereas the concentrations of the other elements vary with the composition of the anodizing electrolyte. Samples anodized in 1M H₃PO₄+0.3% wt. HF shows the highest amount of O²⁻ (asTiO₂) and fluorides, but the lowest amount of phosphates and hydroxyl ions. It means that previously recommended [6] conditions of uniform nanotubes formation on titanium implant materials favor titanium oxidation and enhance transport of fluorides in formed titania. The similarly high concentrations of relevant elements (Ti and O), together with the highest amount of phosphates of all controlled, are observed in samples anodized in 2-3M H₃PO₄+0.4% wt. HF. It indicates that the use of more concentrated phosphate electrolyte leads to the increase of phosphates adsorbed over the surface layer of nanotubes in competition with much smaller and more mobile fluorides.

3.1.1 Competition between phosphates and flurides

This is well known that at anodizing a competition between oxide formation and its dissolution exists, and that HF is the key factor, which causes the production of porous oxide layer. However, there is also a competition between phosphates and fluorides in the process of oxide nanotubes formation. These 2 anions differ in size, charge and rates of diffusion in oxides (Tabl. 2)

	Diffusion coefficient [mol/m ² s]	Van der Waals radius (pm)
Fluoride ion	2.82 10 ⁻⁴	147
Phosphate ion	0.88 10 ⁻⁹	484

Table 2. Values of diffusion coefficients and Van der Waals radius for fluoride and phosphate ions

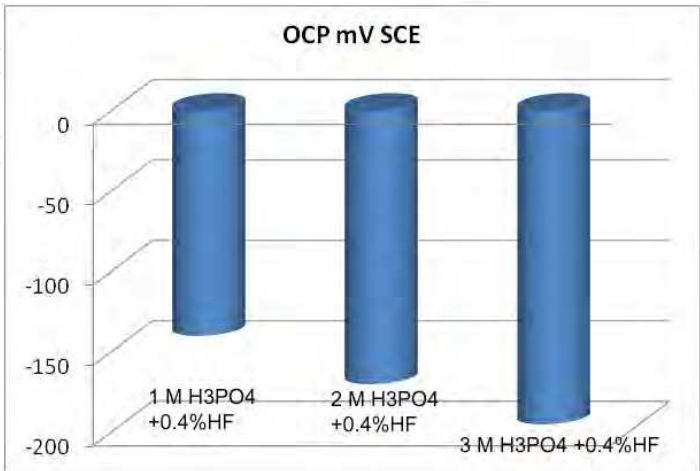


Fig. 13. Values of the OCP for nanotubes formed in 1M, 2M and 3M H₃PO₄ [unpublished results]

The effect of the phosphoric acid concentration in fluoride containing electrolytes on the properties of oxide nanotubes formed at anodizing was characterized by SEM/EDS observations and capacitance characteristics when immersed in simulated body fluids (SBF) in order to predict their behavior as the future coatings on titanium for biomaterial applications [53].

The values of the OCP (Fig. 13) for nanotubes formed in 1M, 2M and 3M H₃PO₄, each containing 0.4% wt. HF, measured at 25°C in SBF solution 1 h after anodizing are -0.140 V, -0.170V and -0.195V (SCE), respectively, indicate the observed earlier [68] decrease of the OCP of oxide produced in more concentrated phosphoric acid solution.

The impedance spectra for titanium anodized in 1-3M H₃PO₄+0.4% wt. HF were obtained at the OCP for frequency ranging from 10⁵ to 0.18 Hz with ac amplitude 10 mV. The spectra recorded 1 hour after immersion in SBF solution show that variations in chemical composition of the surface layer over obtained nanotubes are confirmed by variations in capacitance characteristics.

The results of EIS tests (Fig.14) indicate nearly the same properties (similar impedance and -θ angle values) for ohmic resistance of the electrolyte and its penetration through nanotube films. However in the low frequency range, the impedance values are sensitive to the

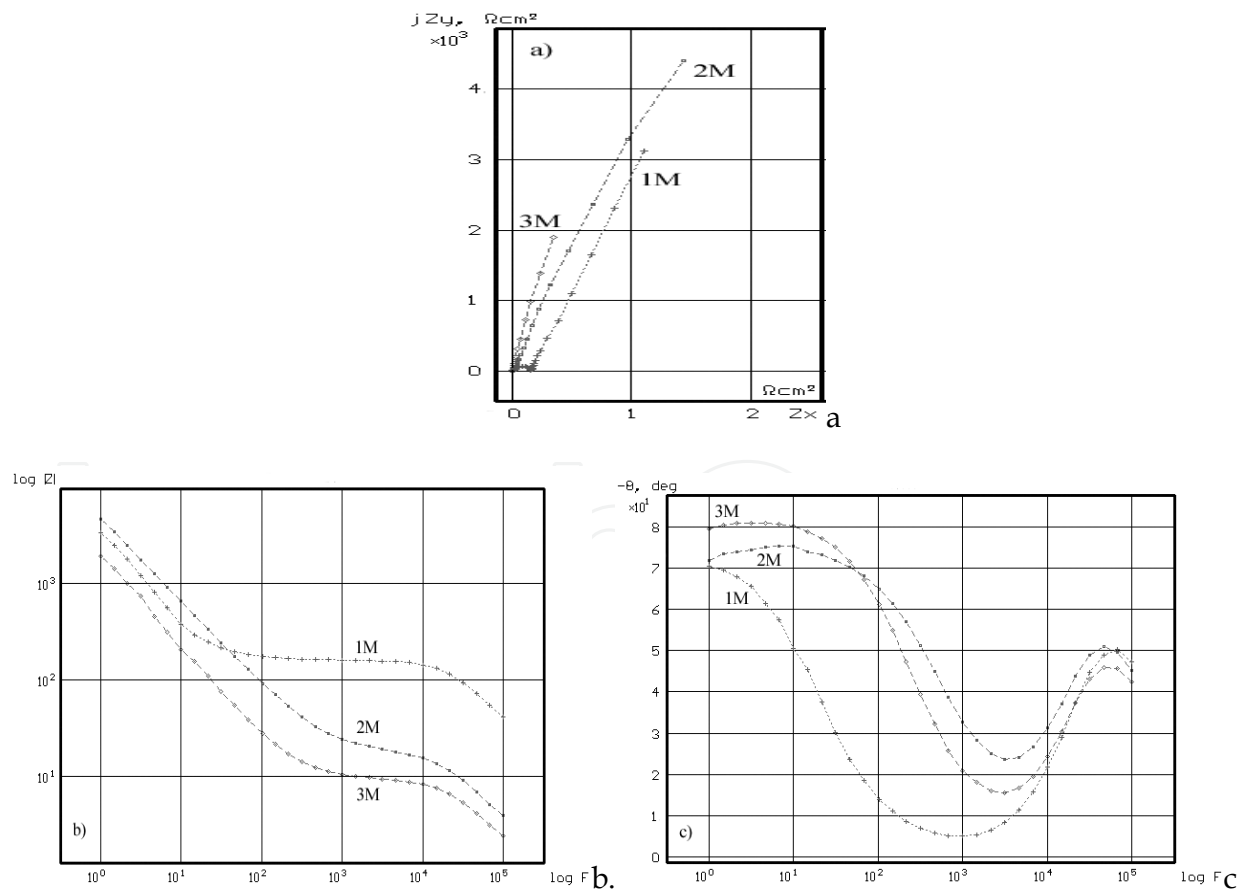


Fig. 14. EIS spectra (a- Nyquist, b,c- Bode spectra) for titania nanotubes formed on titanium in 1-3 M H₃PO₄ solutions with addition of 0.4% wt. HF recorded at the OCP in SBF solution at 25°C [53]

phosphate concentration in anodizing electrolyte, accounting for the processes at the nanotube layer/electrolyte interface which can be associated with deposited products. As the changes between spectra occurred during the first hour of exposure to SBF solution, one can assume that the deposition processes on nanotube layers formed in 2-3M H_3PO_4 +0.4% wt. HF are quick.

The formation of porous metal oxides, ie. titania and alumina, is explained by a field-enhanced model [11,61,63,69] that depends on the ability of ions to diffuse through the metal oxide. Thus, due to the large size the incorporation of the phosphate ions is difficult, but the increased fluoride concentration in solution leads to its ability to migrate and intercalate into the oxide films during the anodizing [70]. The XPS results show (Fig. 12), that the increased fluoride concentration is accompanied by the decreased phosphates and hydroxyl ions in adsorbed layer over nanotubes [53]. It correlates very well with the results of titanium anodizing in electrolyte not containing fluorides, where the gel-like protective layer of phosphates was formed over the oxide [42].

3.2 Nanotubes on implant alloys in phosphate solutions

Titanium and its implant alloys, mainly ternary alloys of Ti-6Al-7Nb or, are widely used in biomedical implants and dental fields due to their unique mechanical, chemical properties, excellent corrosion resistance and biocompatibility [71-73].

Further improvement of the unique properties of nanotube anodic layers for medical applications, particularly for enhancement of bone in-growth [74] and biosensing [75] require not only the development of the formation method on two phase titanium alloys, but also providing the proper morphology and structure. Reported efforts to form anodic nanotube layers on Ti alloys such as Ti-6Al-7Nb, TiAl [76], or Ti45Nb [77] showed the formation of highly inhomogeneous surfaces due to selective dissolution of the less stable phase and/or different reaction rates of the different phases of the alloys.

Studies on development of nanotubes growth on the Ti6Al4V [60] and Ti-6Al-7Nb alloys [54] were focused on varying the HF concentrations in the phosphoric acid media, in order to establish the pore size distribution and estimate the critical scan rate/concentration ratio for the initiation of nanopitting in compact oxide layer, which would be decisive for the formation of uniform nanotubes on both two-phase alloys.

Among several parameters influencing the quality of nanotubes formed anodically, such as potential, time of anodizing, fluoride ions concentration and scan rate of polarization, particularly the last two seem to be determiners for nanotubes structure and morphology. As an example to show the effect of fluoride ions concentration on the morphology of nanotubes on the implant alloy, the anodizing of the two phase (α + β) Ti6Al7Nb alloy samples in 1 M H_3PO_4 containing 0.2%; 0.3% and 0.4 % wt. HF to 20V using scan rate 500mV/s and then holding them at that potential for further 2h in the same electrolyte, was performed. Nanotubes of diameter ranging from 50nm to 80nm, with thicker walls over β -phase grains than over α -phase grains, were obtained. During the formation process, which includes two stages: the first potentiodynamic and the second potentiostatic (20V), different electrochemical behaviour was observed in electrolytes of various fluoride concentration.

The implant alloy Ti6Al7Nb (Fig 15) of black α phase (hcp) and white β phase (bcc) irregular shape platelets forming variously oriented colonies, with the surface fraction of α and β phases 78% and 22%, respectively, was enriched with aluminum in oxides over α phase and enriched with niobium over β phase anodic nanotubes.

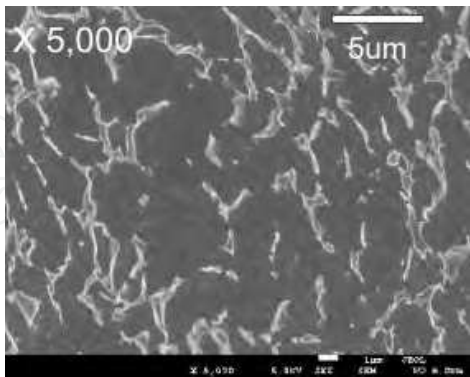


Fig. 15. Microstructure of the Ti-6Al-7Nb alloy [54]

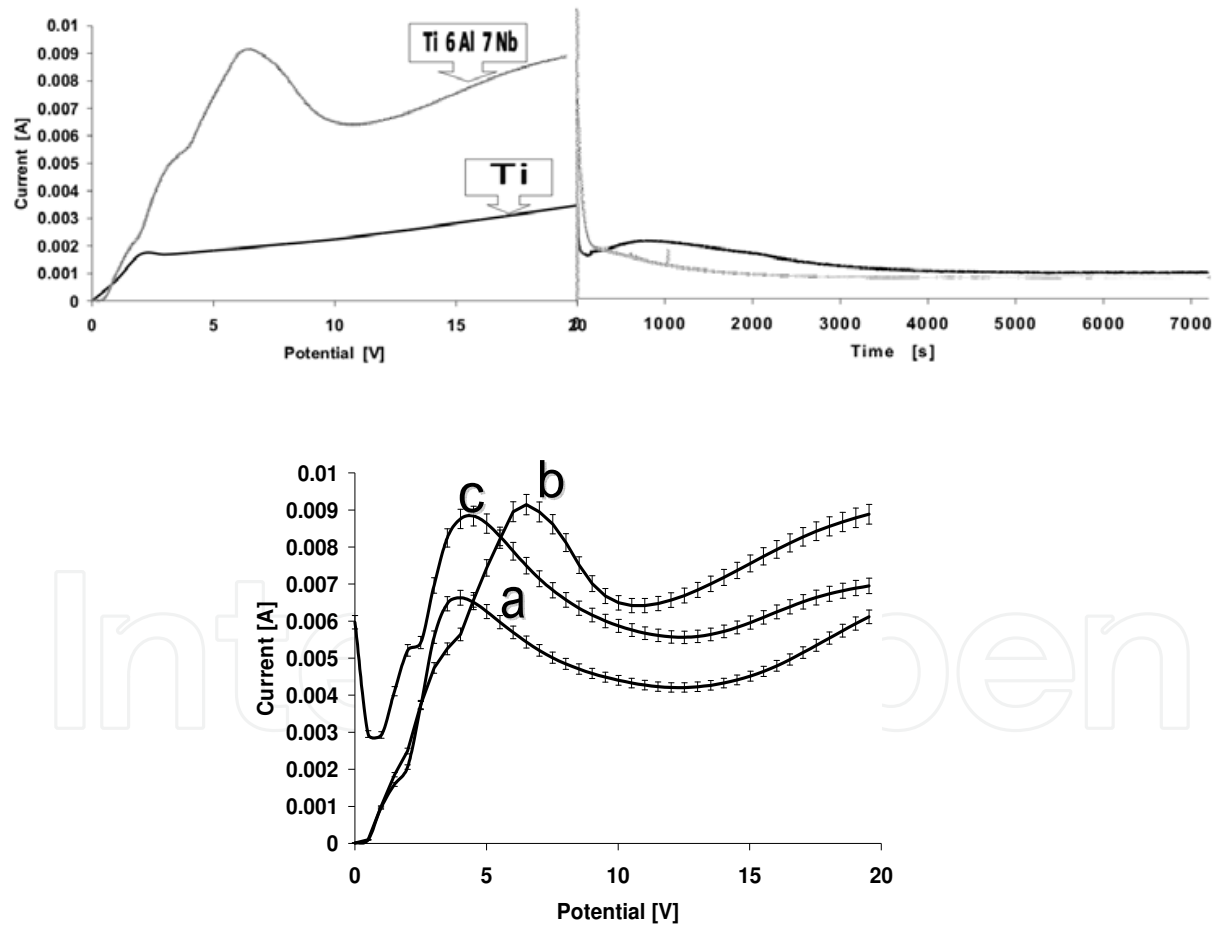


Fig. 16. Current transient for potentiodynamic and potentiostatic stages recorded at anodizing the Ti-6Al-7Nb alloy and titanium (for comparison) at 20V for 2h in 1M H_3PO_4 containing 0.3% HF (scan rate in the potentiodynamic stage 500mV/s) and current transients recorded during potentiodynamic stage of anodizing of the Ti6Al7Nb alloy in 1 M H_3PO_4 with different fluoride concentration, a) 0.2%HF b) 0.3%HF c) 0.4%HF [54]

The typical current transients Fig. 16 recorded during the anodizing of the Ti-6Al-7Nb alloy in 1M H_3PO_4 containing 0.3 wt.% HF are similar to current transients observed during nanotube oxide layers formation on other alloys in other electrolytes [78]. As in previously described process the whole treatment consists of the potentiodynamic polarization from the OCP to 20V with a scan rate of 0.5Vs^{-1} , followed by the potentiostatic polarization at 20V for further 2 h. However, contrary to constant current density increase observed at anodizing of pure Ti [49,50,79], during the potentiodynamic sweep to 20V at the alloy Ti-6Al-7Nb anodizing the current transients show 2 peaks: the first at about 2-3 V due to oxygen evolution and the second at about 4-6V linked probably to Al oxidation. In the potentiostatic stage of anodizing the current density for the alloy decreases until the end of the treatment, while in case of Ti a broad peak is seen at about 900 s of the anodizing (Fig. 16). According to [78,79] the broad peak, typically recorded in the potentiostatic stage of the process, indicates the dissolution of oxide before reaching final balance between both processes: oxide formation and oxide dissolution during nanotubes formation. Such the balance determines a steady-state oxide layer formation stage during anodizing of metals [11].

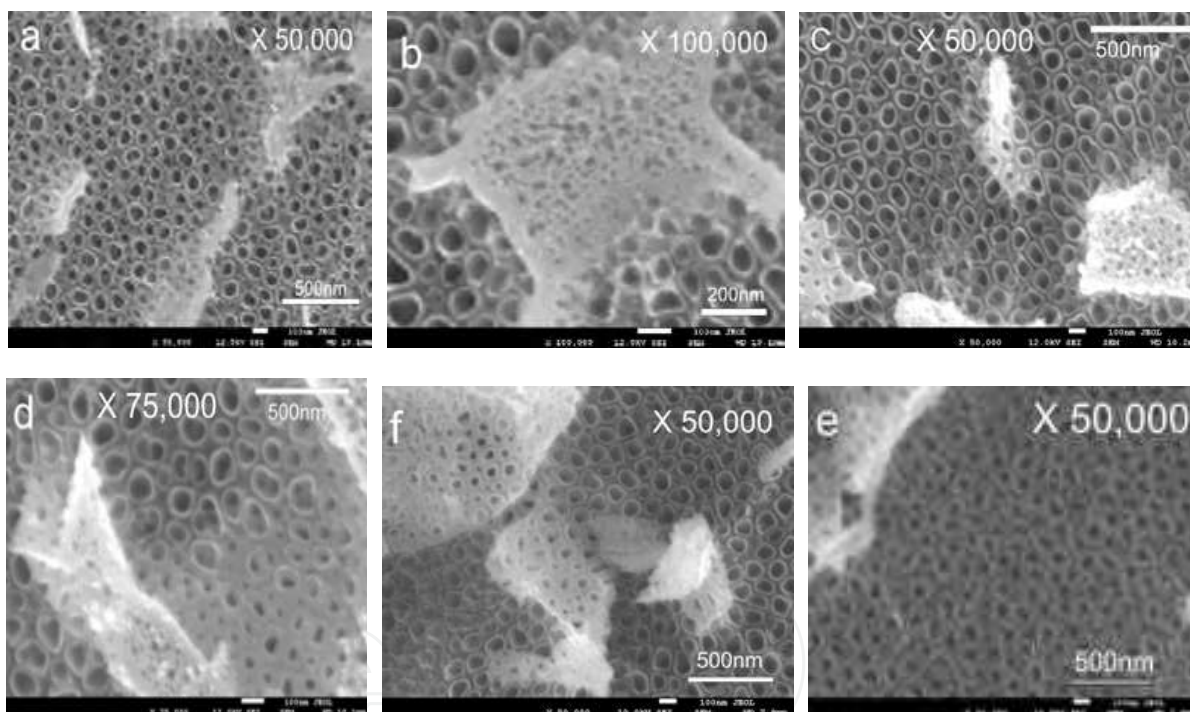


Fig. 17. SEM images of nanotubes produced on the Ti6Al7Nb (a, c, e α -phase; b, d, f- β -phase) by anodization at 20V for 2h in 1M H_3PO_4 containing (a),(b) 0.2%HF, (c),(d) 0.3% HF, (e),(f) 0.4% wt. HF

Small pits on β phase grains and regular nanotubes on α -phase are observed in 0.2 wt.% HF (Fig. 17a,b). Irregular tubes on β -phase and regular tubes on α -phase grains are seen after anodising in 0.3 wt. % HF (Fig. 17c,d). Both phases are covered with regular nanotubes in case of samples anodised in 0.4 wt. % HF (Fig. 17e,f), but on β - phase nanotube walls are thicker than on α - phase. Fig. 16 illustrates the dissolved oxide over α -phase on Ti6Al4V alloy and bigger size of nanotubes over β - phase in more concentrated phosphoric acid solution.

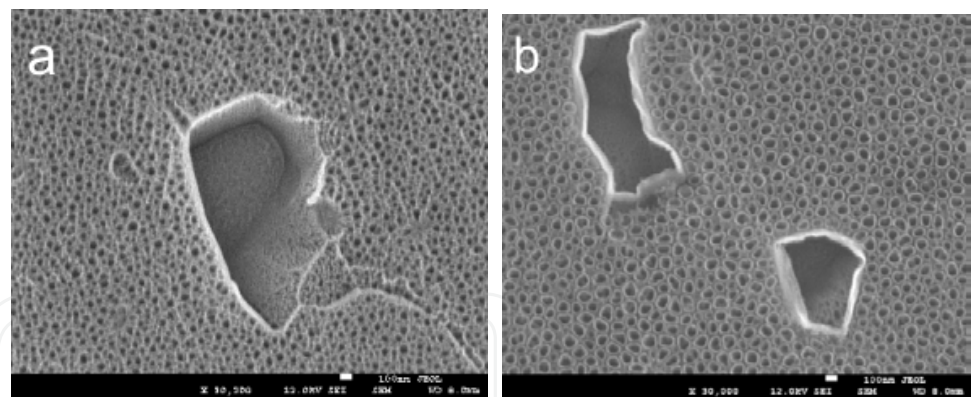


Fig. 18. SEM images of nanotubes produced on the Ti6Al4V by anodization at 20V for 2h in 1M H₃PO₄ containing (a) 0.2%HF, (b) 0.4% wt. HF

According to EDS analysis nanotubes formed on the Ti-6Al-7Nb alloy showed that those films are predominately TiO₂ with small amounts of Ti₂O₃, Al or Nb oxides (Table 3). Aluminium and niobium are present in their most stable oxidation states, Al₂O₃ and Nb₂O₃. The amount of alloying elements in the nanotube oxide layer was influenced by the underlying metal microstructure, where Nb was present in the β- phase and Al in the α- phase [80].

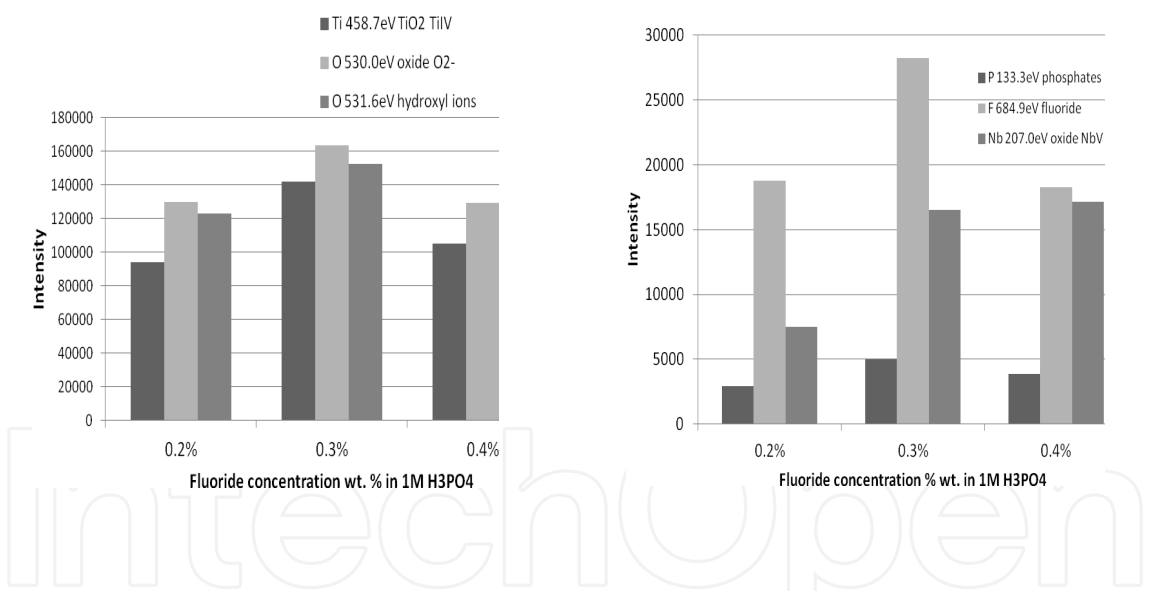


Fig. 19. Results of XPS examination of surface layer of nanotubes formed on the Ti6Al7Nb alloy in 1 M H₃PO₄ with different fluoride concentration

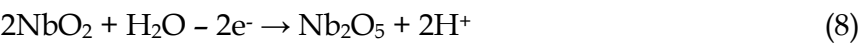
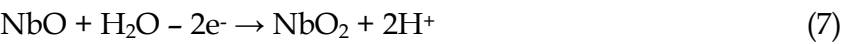
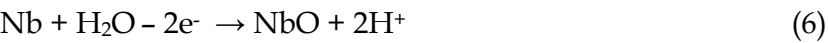
In the combined SEM and XPS examinations [54] (Fig. 17 and 19) the highest intensities for all controlled elements and groups: titanium oxide and titanium phosphates (458.7eV), oxides (530eV), hydroxyl ions (531.6eV), phosphates (133.3eV) and fluorides (648.6eV), clearly confirm that the most advantageous scan rate and electrolyte composition for the formation of uniform nanotube layer on the Ti6Al7Nb alloy, are 0.5Vs⁻¹ during potentiodynamic stage of anodizing in 1M H₃PO₄ containing 0.3% wt. HF. Interesting is that also the intensity of niobium (207.3eV) in the most stable of the niobium oxides Nb₂O₅ [81],

increases with fluoride concentration, but seems to reach the limit in these conditions for 0.3% wt. HF (Fig. 19). The highest current density (Fig. 14) is linked to the biggest nanotube diameters, as it was observed in case of pure titanium anodised in the same conditions [50].

Fluoride concentration	0.2%HF [weight %]		0.3%HF [weight %]		0.4%HF [weight %]		Compact oxide [weight %]
Phases	α	β	α	β	α	β	
Titanium	63.90	51.66	61.39	35.70	59.52	38.59	69.22
Oxygen	32.09	36.66	34.44	45.43	36.40	44.99	19.72
Aluminium	4.00	2.91	4.17	2.69	4.08	1.99	4.45
Niobium	---	8.77	---	16.18	---	14.43	6.53

Table 3. Results of EDS analysis of nanotube layers obtained by anodizing at 20V for 2h in 1M H₃PO₄ containing 0.2; 0.3; 0.4% wt. HF [53]

Due to chemical similarity of titanium and niobium [11, 82] electrochemical behaviour of the Ti-6Al-7Nb electrode should be qualitatively similar to that of the titanium and niobium electrodes in the potential range from -1 to 4V (SCE). Electrochemical oxidation of niobium electrode leads to formation of sub-oxides NbO and NbO₂ at the OCP, which partly transform into Nb₂O₅ oxide at 20V, according to the equations 6-7 [83,84]:



The dissolution process of niobium oxide (β-phase) (5) increases with increasing fluoride concentration [85], so the fluoride concentration is a crucial factor for nanotubes growth on Ti-6Al-7Nb. Structural and metallurgical aspects of the formation of self-organized anodic oxide nanotube layers on alloys are crucial for medical application to the advanced techniques of biological media immobilization which require morphologically uniform surface.

4. Titania layers formed in phosphate solutions for biosensing

The additional advantageous property of phosphate rich compact and nanotubular anodic oxide layers on titanium is its ability to attach enzymes, proteins or biological cells. To test such the possibility in order to apply anodic surfaces for H₂O₂ biosensing two electrodes were prepared: 1) the first electrode prepared by the electropolymerization of conducting polymer (PANI) on the surface of Ti/TiO₂ (compact) electrode [55], 2) the second electrode was prepared by using titania nanotubes on titanium as a platform of the 3rd generation biosensor [56]. In both cases the HRP (horseradish peroxide) enzyme was immobilized on the sensing surface. By using either cyclic voltammetry or amperometric modes the feasibility and electrochemical parameters for H₂O₂ monitoring on Ti/TiO₂ surface were checked in the simulated body fluid (SBF). Both electrodes were sensitive to H₂O₂, however the second electrode only in the presence of thionine as the mediator [56]. Two peaks seen on cyclic voltammograms (Fig. 18) for the Ti/TiO₂ (nanotube) electrode with immobilized HRP, indicate the sensitivity of the prepared platform to the presence of H₂O₂ in the analyte.

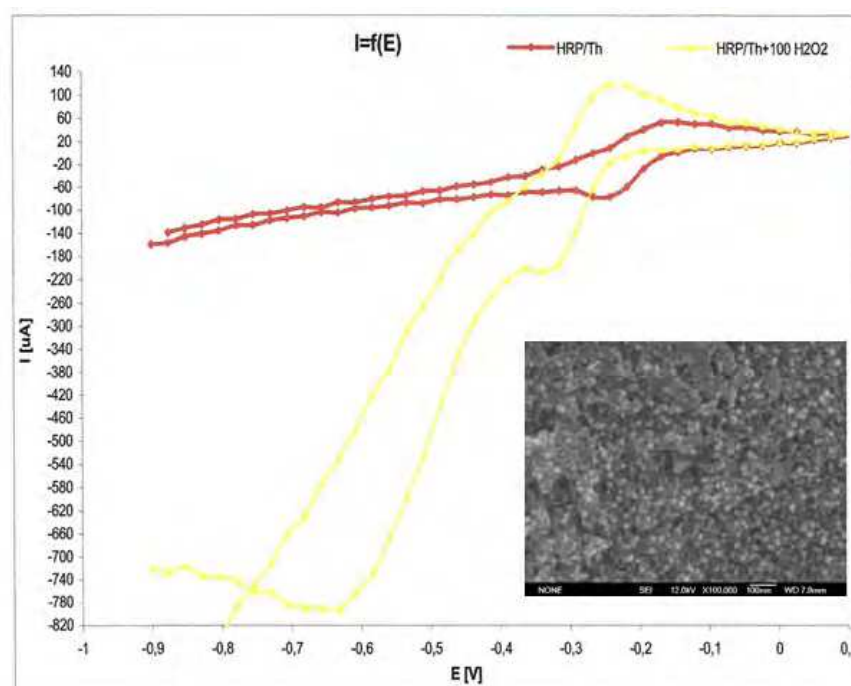


Fig. 20. SEM of Ti/TiO₂ (nanotube) covered with HRP and cyclic voltammograms for Ti/TiO₂/HRP in 0.1 M PBS (pH 6.8) in the presence of H₂O₂, scan rate 100 mV/s [56]

5. Conclusions

Titanium surfaces can be modified by electrochemical treatment in the phosphoric acid solutions for better corrosion resistance, improved physicochemical and electrochemical properties and bioactivity. The formation of oxide layers enriched with phosphorus of 30-120nm thick can be formed in 0.5 M H₃PO₄ at both galvanostatic anodizing current density values varied in the range of 0.1-0.5 Am⁻² and potentiostatically at up to 60V giving yellowish layers porous on the surface. Due to the presence of phosphates they are highly bioactive in comparison to oxides formed in other electrolytes and are covered with hydroxyapatite deposits after 9 days in the SBF solution.

Anodizing in more concentrated 2M solutions of the phosphoric acid generates a gel-like film with thickness of about 100nm on titanium. The film, containing a large number of phosphates nuclei, exhibits its effectiveness to activate titanium surface for biomimetic coating of calcium phosphate. The electrochemically treated titanium was able to form uniform Ca-P coatings on titanium after 48 hour immersions in the SBF solution. The treatment is a simple method to generate bioactive metal surfaces, besides other methods such as alkaline treatment applied to titanium implant materials.

Electrochemical treatment in the phosphoric acid solutions with the addition of 0.2-0.4% wt. HF allows to form on titanium and its implant alloys nano-sized pores (nanotubes) in more concentrated phosphoric acid solutions (1-3M). Their morphology, electrochemical properties and chemical composition are in close relation with the anodic polarization parameters and with the concentration of both ions: phosphates and fluorides. The highest amount of fluorides in surface layer is obtained when using 1M H₃PO₄+0.3% 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 H_3PO_4 with 0.4% wt. HF assures the formation of nanotubes containing the high concentration of both bioactivity enhancing elements, fluorides and adsorbed phosphates. The obtained titania nanotubes show the significantly higher bioactivity in vitro during the first hour of immersion in SBF in comparison to barrier titanium oxide.

Depending on fluoride ion concentrations in anodizing electrolyte morphologically different nanotubular layers have been obtained on both phases of two titanium alloys: the Ti6Al4V and the Ti6Al7Nb alloys. Self organized nanotubes grow on both phases (α and $\alpha+\beta$) in 1M H_3PO_4 containing 0.4% wt. HF, though smaller pore size and thicker wall tubes are obtained on the β phase. The electrochemical behavior of both phases of the alloys differs due to fluoride concentrations which is the key parameter in controlling their morphology. Uniform nanotubes are obtained in 2M H_3PO_4 containing 0.3% wt. HF at scan rate of polarization 0.5Vs^{-1} during potentiodynamic stage of anodizing. Such conditions assure the highest fluoride and phosphate concentrations in surface layer of nanotubes on titanium and nanotubes containing niobium oxide on the Ti6Al7Nb alloy. Both features promise a proper coating for improved osteoblast cell adhesion on artificial implants and for biosensing.

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7. References

- [1] Trasatti S., Lodi G.: *Electrodes of Conductive Metallic Oxides*. ed. S. Trasatti, Chapt. B, Elsevier Amsterdam (1981) 521.
- [2] Luckey H., Kubli F., *Titanium Alloys in Surgical Implants*. ASTM 796 (1981).
- [3] Marciniak J.: *Biomateriały* (in Polish) Technical University of Upper Silesia Press (2002), ISBN 83-7335-031-4.
- [4] Chrzanowski W., Szewczenko J., Tyrlik-Held J., Marciniak J., Zak J.: Influence of the anodic oxidation on the physicochemical properties of the Ti6Al4V ELI alloy. *J Mater Proces Techn* 162-163 (2005) 163-168.
- [5] Hanawa T., Mamoru O.: Calcium phosphate naturally formed on titanium in electrolyte solution. *Biomaterials* 12 (1991) 767.
- [6] de Assis S. L., Wolyneć S., Costa I.: Corrosion characterization of titanium alloys by electrochemical techniques. *Electrochimica Acta* 51 (2006) 1815-1819.
- [7] Krasicka-Cydzik E., Kowalski K., Głazowska I.: Bioactive surface layers formed electrochemically on titanium materials in phosphoric acid solution. 3rd Central Eur Conf. Krakow (2006) eds. K. Szaciłowski.
- [8] Sul Y.T.: The significance of the surface properties of oxidized titanium to the bone response: special emphasis on potential biochemical bonding of oxidized titanium implant. *Biomaterials* 24 (2003) 3893-3907.

- [9] Bylica J., Sieniawski J.: Titanium and its alloy. PWN, Warszawa (1985).
- [10] Corbridge D.E.C.: Phosphorus. the 5th Edit. Elsevier, Amsterdam – Lausanne - New York-Oxford –Shannon -Tokyo (1995).
- [11] Krasicka-Cydzik E.: Formation of thin anodic layers on titanium and its implant alloys. University of Zielona Gora Press, Zielona Góra (2003) ISBN: 83-89321-80-7.
- [12] Krasicka-Cydzik E.: Electrochemical and Corrosion properties of Ti6Al4V in phosphoric acid solutions. *Biomater. Eng.* (1999) 7-8, 26-32.
- [13] Krasicka-Cydzik E.: Electrochemical aspects of tailoring anodic layer properties on titanium alloys. *Corrosion Protection XLII* (1999) 48-52.
- [14] Krasicka-Cydzik E.: Influence of phosphoric acid on the rate of titanium alloys anodizing. *Arch. BMiAut.*, Poznań 20 (2000) 155.
- [15] Krasicka-Cydzik E.: Impedance properties of anodic films formed in H₃PO₄ on selected titanium alloys. *Mat. Eng.* 7, 2 (2000) 5-11.
- [16] Krasicka-Cydzik E.: Effect of polarization parameters on the selected properties of surface layer on Ti6Al4V alloy anodized in phosphoric acid solutions. *Arch. TM i Aut.* 21, 1 (2001) 171-178.
- [17] Krasicka-Cydzik E.: Impedance examination of titanium and its selected implant alloys. *Biomater. Eng.* 14 (2001) 27-31.
- [18] Krasicka-Cydzik E.: Formation and properties of anodic film on titanium in phosphoric acid solutions. *Mater. Eng. Vol. IX* (2002) 2, 9.
- [19] Krasicka-Cydzik E.: Passivity of implant titanium alloys in phosphoric acid solution of high concentration. *Corrosion Protection* (2002) 282.
- [20] Krasicka-Cydzik E.: Surface modification of phosphoric acid anodized implant titanium alloys. 7th World Biom. 2004, ISBN: 1-877040-19-3
- [21] Krasicka-Cydzik E., Głazowska I., Michalski M.: Bioactivity of implant titanium alloys after anodizing in H₃PO₄. *Biomater. Eng.* (2004) 38-42.
- [22] Krasicka-Cydzik E.: Method of anodic coating formation on titanium and its alloys. Polish Patent RP 185176, University of Technology Zielona Gora, LfC Ltd. 2003.
- [23] Głazowska I., Krasicka-Cydzik E.: Impedance characteristics of anodized titanium in vitro. *Biomater. Eng.* (2005) 8, 47-53, 127 – 130.
- [24] Krasicka-Cydzik E., Głazowska I., Michalski M.: Microscopic examination of anodic layers on implant titanium alloys after immersion in SBF solution. *Biomater. Eng.* (2005), 47-53, 130 – 133
- [25] Krasicka-Cydzik E., Kowalski K., Głazowska I.: Electrochemical formation of bioactive surface layer on titanium. *J Achiev Mater Manufact Engineering* 18 (2006) 1-2, 147 – 150.
- [26] Krasicka-Cydzik E., Głazowska I.: Influence of alloying elements on behavior of anodic layer in phosphoric acid solution. *Biomater. Eng.* (2007) 67 – 68, 29 – 31.
- [27] Krasicka-Cydzik E., Głazowska I., Michalski M.: Hydroxyapatite coatings on titanium and its alloys anodised in H₃PO₄. *EUROMAT 2005, European Congress on Advanced Materials and Processes. Prague, Czech Rep, 2005.*
- [28] Unal I., Phosphate Adsorption On Titanium Oxide Studied By Some Electron Spectroscopy, Diploma , Universite de Geneva, Sept. 1999
- [29] Pourbaix M., Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Engineers, Houston, 1974

- [30] Kurosaki M., Seo M., Corrosion behavior of iron thin film in deaerated phosphate solutions by an electrochemical quartz crystal microbalance, *Corrosion Science* 45 (2003) 2597.
- [31] Krasicka-Cydzik E.: Gel-like layer development during formation of thin anodic films on titanium in phosphoric acid solutions, *Corrosion Science* Vol. 46 (2004) 2487–2502.
- [32] Krasicka-Cydzik E.: Studies on transition of titanium from active into passive state in phosphoric acid solutions, in: *Passivation of metals and semiconductors, and properties of thin oxide layers.* ed. P. Marcus, V. Maurice .- Amsterdam: Elsevier (2006) 193–198.
- [33] Kelly E.J., in: J. O’Bockris, B.E. Conway, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, Plenum Press, New York, London, 1982, pp. 332–336
- [34] Torresi, R.M. Camara O.R., De Pauli C.P., Influence of the hydrogen evolution reaction on the anodic titanium oxide film properties, *Electrochim. Acta* 32 (9) (1987) 1357.
- [35] Kelly E.J., Anodic Dissolution and Passivation of Titanium in Acidic Media, *J. Electrochem. Soc.* 126 (12) (1979) 2064
- [36] Makrides A.C, Kinetics of Redox Reactions on Passive Electrodes, *J. Electrochem. Soc.* 111 (4) (1964) 392
- [37] Felhosi I., Telegdi J., Palinkas G., Kalman E., Kinetics of self-assembled layer formation on iron, *Electrochem. Acta* 47 (2003) 2335–2340.
- [38] Healy K.E., Ducheyne P., Hydration and preferential molecular adsorption on titanium in vitro, *Biomaterials*. 13 (1992) 553.
- [39] Wagh A.S., Yeong S.Y, Chemically bonded phosphate ceramics: I, a dissolution model of formation, *J. Am. Ceram. Soc.* 86 (11) (2003) 1838–1855.
- [40] Morlidge J.R. P. Skeldon, G.E. Thompson, H. Habazaki, K. Shimizu, G.C. Wood, Gel formation and the efficiency of anodic film growth on aluminium *Electrochim. Acta*, 44 (1999) 2423.
- [41] Roine A., HSC Ver. 2. 03, Outkumpu Research Oy, Pori, Finland, 1994
- [42] Krasicka-Cydzik E.: Method of phosphate layer formation on titanium and its alloys, Polish Patent, PL 203453, Univ. Zielona Gora, 2009.
- [43] Grimes C. A., Mor G. K.: *TiO₂ Nanotube Arrays*. Springer 2009, ISBN 978-1-4419-0067-8.
- [44] Bavykin D.V., Walsh F. C.: *Titanate and Titania Nanotubes*, RSC (2010).
- [45] Ghicov A., Tsuchiya H., Macak J. M., Schmuki P.: Titanium oxide nanotubes prepared in phosphate electrolytes. *Electrochem. Comm.* 7 (2005) 505–509.
- [46] Tsuchiya H., Macak J. M., Taveira L., Balaur E., Ghicov A., Sirotna K., Schmuki P.: Self-organized TiO₂ nanotubes prepared in ammonium fluoride containing acetic acid electrolytes. *Electrochem. Comm.* 7 (2005) 576–580.
- [47] Tsuchiya H., Macak J. M., Taveira L., Schmuki P.: Fabrication and characterization of smooth high aspect ratio zirconia nanotubes. *Chem. Phys. Letters* 410 (2005) 188–191.
- [48] Zhao J., Wang X., Chen R., Li L., Synthesis of thin films of barium titanate and barium strontium titanate nanotubes on titanium substrates. *Materials Letters* 59 (2005) 2329 – 2332.

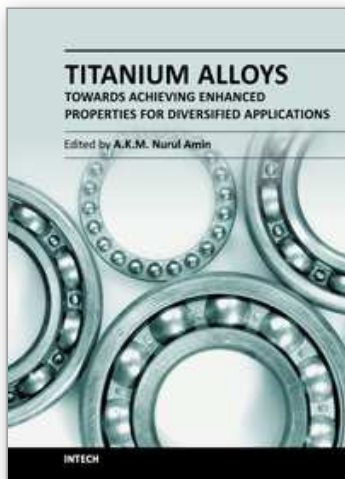
- [49] Krasicka-Cydzik E., Głazowska I., Kaczmarek A., Białas-Heltowski K.: Influence of fluoride ions concentration on growth of anodic self-aligned layer of TiO₂ nanotubes. *Biomater. Eng. R.* 11,77-80 (2008) 46.
- [50] Lukacova H., Plesingerova B., Vojtko M., Ban G., Electrochemical Treatment of Ti6Al4V, *Acta Metallurgica Slovaca*, 16, (2010) 3, 186-193.
- [51] Krasicka-Cydzik E., Kowalski K., Kaczmarek A.: Anodic and nanostructural layers on titanium and its alloys for medical applications. *Mater. Eng.* 5 (2009) 132.
- [52] Krasicka-Cydzik E., Głazowska I., Kaczmarek A., Klekiel T., Kowalski K.: Nanostructural oxide layer formed by anodizing on titanium and its implant alloy with niobium. *Biomater. Eng.* 85 (2009) 325.
- [53] Krasicka-Cydzik E., Kowalski K., Kaczmarek A., Głazowska I., Białas Heltowski K.: Competition between phosphates and fluorides at anodic formation of titania nanotubes on titanium. *Surface and Interface Analysis* 42, 6-7 (2010) 471 – 474.
- [54] Kaczmarek A., Klekiel T., Krasicka-Cydzik E.: Fluoride concentration effect on the anodic growth of self aligned oxide nanotube array on Ti6Al7Nb alloy. *Surface and Interface Analysis*, 42, 6-7 (2010) 510.
- [55] Machnik M., Głazowska I., Krasicka-Cydzik E.: Investigation for Ti/TiO₂ electrode used as a platform for H₂O₂ biosensing. *Mater. Eng.* 5 (2009) 363-365.
- [56] Łoin J., Kaczmarek A., Krasicka-Cydzik E.: Attempt to elaborate platform of the IIIrd generation biosensor for H₂O₂ on the surface of Ti covered with titania nanotubes. *Biomedical Eng.* Vol. 16, no 2 (2010) 54 – 56.
- [57] Beranek R., Hildebrand H., Schmuki P., Self-Organized Porous Titanium Oxide Prepared in H₂SO₄/HF Electrolytes, *Electrochem. and Solid-St. Lett.* 2003: 6, B12
- [58] Zhao J., Wang X., Chen R., Li L., Fabrication of titanium oxide nanotube arrays by anodic oxidation, *Solid State Commun.* 2005, 134, 705-710.
- [59] Macak J.M., Sirotna K., Schmuki P., *Self-organized porous titanium oxide* prepared in Na₂SO₄/NaF electrolytes, *Electrochim. Acta* 50, 2005, 629.
- [60] Krasicka-Cydzik E., Głazowska I., Kaczmarek A., Białas-Heltowski K., Influence of scan rate on formation of anodic TiO₂ nanotubes, *Engineering of Biomaterials*, 2008, 11, 77-80.
- [61] Gong D., Grimes C. A., Varghese, O. K Chen Z., Hu W., Dickey E. C., Titanium oxide nanotube arrays prepared by anodic oxidation *Journal Mater. Res.* 2001, 16, 3331-3334
- [62] Ghicov A., Tsuchiya H., Macak J. M., Schmuki P., Titanium oxide nanotubes prepared in phosphate electrolytes, *Electrochim. Comm.* 2005, 7, 505-509
- [63] Yasuda K., Schmuki P., Control of morphology and composition of self-organized zirconium titanate nanotubes formed in (NH₄)₂SO₄/NH₄F electrolytes, *Electrochim. Acta*, 2007 52, 4053-4061
- [64] Qiu J., Yu W., Gao X., X. Li, Sol-gel assisted ZnO nanorod array template to synthesize TiO₂ nanotube arrays, *Nanotechnology*, 2007, 18, 295604
- [65] Zwilling V., V, Aucouturier M, Darque-Ceretti E. Anodic oxidation of titanium and TA6V alloy in chromic media. An electrochemical approach, *Electrochim. Acta* 1999; 45921
- [66] Yang B., Uchida M. Kim H.M., Zhang X., Kokubo T.: Preparation of bioactive titanium metal via anodic oxidation treatment, *Biomaterials* 2004; 25, 1003

- [67] Sul Y.-T., Johansson C. B, Jeong Y, Albrektsson T. The electrochemical oxide growth behaviour on titanium in acid and alkaline electrolytes, ed. Eng. Phys. 2001; 23, 329]
- [68] Kodama A., Bauer S., Komatsu A., Asoh H., Ono S., Schmuki P., Bioactivation of titanium surfaces using coatings of TiO₂ nanotubes rapidly pre-loaded with synthetic hydroxyapatite, *Acta Biomaterialia* 2009; 5, 2322–2330.
- [69] Heusler K.E., The influence of electrolyte composition on the formation and dissolution of passivating films, *Corrosion Science*, 1989, 29, 131
- [70] De-Sheng K, The influence of fluoride on the physicochemical properties of anodic oxide films formed on titanium surfaces, *Langmuir* 2008, 24, 5324–5331
- [71] Gonzalez J.E.G., Mirza-Rosca J.C, *Study of corrosion behaviour of titanium and some of its alloys for biomedical and dental implant applications*, J. Electroanal. Chem. 1999; 471, 109.
- [72] Williams J. D.F, in Williams (Ed.) *Biocompatibility of clinical implant materials*, CRC Press, Boca Roton, FL, 1981, 45.
- [73] Fonseca C., Barbosa M.A, Corrosion behaviour of titanium in biofluids containing H₂O₂ studied by electrochemical impedance spectroscopy, *Corrosion Science* (2001); 43, 547–559
- [74] Velten D., Eisenbarth E., Schanne N., Breme J, Biocompatible Nb₂O₅ thin films prepared by means of the sol–gel process, *Journal of Materials Science: Materials in Medicine* 2004, 15, 457–461
- [75] Xiao P., Garcia B.B., Guo Q, Liu D., Cao G., TiO₂ nanotube array fabricated by anodization in different electrolytes for biosensing, *Electrochemistry Communications* 9, (2007), 2441–2447
- [76] Tsuchiya H.; Berger, S., Macak, J. M.; Ghicov, A., Schmuki, P., Self-organized porous and tubular oxide layers on TiAl alloys, *Electrochemistry Communications* (2007); 9, 2397–2402.
- [77] Zorn G., Lesman A., Gotman I. Oxide formation on low modulus Ti45Nb alloy by anodic versus thermal oxidation, *Surface & Coatings Technology* 2006; 210, 612–618
- [78] Macak J. M., Tsuchiya H., Taveira L., Ghicov A, Patrik Schmuki P., Self-organized nanotubular oxide layers on Ti-6Al-7Nb and Ti-6Al-4V formed by anodization in NH₄F solutions, *Journal of Biomedical Materials Research Part A*, 2008, 75A, 4, 928–933.
- [79] Macak J.M., Hildebrand H., Marten-Jahns U., Schmuki P, Mechanistic aspects and growth of large diameter self-organized TiO₂ nanotubes, *J. Electroanal. Chem.* (2008); 40 621, 254–266
- [80] Metikoš-Huković M. A Kwokal, J Piljac, The influence of niobium and vanadium on passivity of titanium-based implants in physiological solution, *Biomaterials* 2003; 24, 3765–3775
- [81] Halbritter J., On the Oxidation and on the Superconductivity of Niobium, *Applied Physics*, 1987, A 43, 1–28
- [82] I. Sieber I., Hildebrand H., Friedrich A., Schmuki P., Formation of self-organized niobium porous oxide on niobium, *Electrochem. Comm.* 2005; 7, 97–100
- [83] Freitas M.B, Bulhoes L., Breakdown and Crystallization Processes in Niobium Oxide-Films in Oxalic-Acid Solution, *J. Appl. Electrochem*, 1997; 27, 612–615

- [84] Heusler K.E., Schultze M., Electron-transfer reactions at semiconducting anodic niobium oxide films, *Electrochimica Acta*, 1975, 20, 237-244
- [85] El-Mahdy G.A, Formation and dissolution behaviour of niobium oxide in phosphoric acid solutions, *Thin Solid Films*, 1997; 307, 141-147.

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