



Features of medical implant passivation using anodic oxide films

V.V. Starikov,^{1,*} S.L. Starikova,² A.G. Mamalis³ and S.N. Lavrynenko¹

¹ National Technical University "Kh.P.I.", Kharkov, Ukraine

² Kharkov Medical Academy of Postgraduate Education, Kharkov, Ukraine

³ Project Centre for Nanotechnology and Advanced Engineering, NCSR "Demokritos", Athens, Greece

The passivation ability of metals from groups IV and V of the Periodic Table is considered. Anodic treatment is able to neutralize the increase of metal hardening when comminuting grains to nanometre sizes. The deposition of metal oxide film coatings on a cobalt–chromium alloy surface results in substantial passivation of its surface and prevents cobalt and chromium accumulation in bone tissues. The decrease of surface activity of titanium implants can be achieved both by cleaning the surface during vacuum annealing before oxidation and by the increase of the anodic oxide film thickness, which limits mass and charge transfer through the implant surface. Recommended titanium implant treatment regimens are vacuum annealing at 650 °C and anodic oxidation to attain an oxide thickness less or equal to 300 nm.

Keywords: anodic oxide, coating, electrode potential, implant, passivation, titanium

1. INTRODUCTION

The optimal choosing of material for the production of medical implants today is quite a challenging problem [1, 2]. Most metals have insufficient chemical inertness. At the same time, more extensive use of inert ceramics is limited by their high brittleness, low strength and processing difficulty.

Metals for implant fabrication are selected if they form a protective oxide film on their surface, resulting in diminished reactivity [3–6]. The protective oxide film must meet the following requirements: uniformity; good adhesion to the metal; thermal expansion coefficient close to that of the metal; chemical passivity; high hardness and wear resistance [7–9]. The oxides formed on the surface of metals from groups IV and V of the Periodic Table satisfy most of these requirements [10, 11].

In order to intensify the natural oxide's protective properties, anodic oxidation of the metal can be used. It provides an increase of oxide thickness under high external electric fields in gas or liquid [12]. Such oxides have a disordered structure, can withstand considerable deformation (up to 50%) and strongly adhere to the metal substrate [13]. Most anodic oxides are not dissolved in the manner of biodegradable calcium phosphate coatings when in contact with bone tissue; it has been found that a greater oxide film thickness increases adsorption of initial tissue response proteins and improves implant–bone contact at the metallic implant surface. Nevertheless, some questions, related to additional forced oxidation of the implant metal surface at passivation, remain open.

Titanium is the most widely used metal for the production of medical implants [14, 15]. Its chemical inertness is determined by the surface film of TiO₂, which

covers the entire free metal surface when it reacts with oxygen. The continuity of surface oxide and, consequently, its chemical resistance are determined by the presence of impurities in the base metal and the purity of its surface before oxidation. With a good TiO₂ layer, reactions between body fluids and titanium are minimal.

In some cases implants are made by casting, so the use of compact titanium to make them is difficult or impractical. Implants made from other metals, such as cobalt–chromium alloy of the following composition (in atomic percent): 62% Co, 30% Cr, 5% Mo, 0.4% C [16], has titanium applied as a thin-film coating. It is also interesting to use titanium for coating after comminuting the metal grains down to nanometre dimensions. The titanium in the thin-film and nanodispersed states has a different electrochemical activity from the metal in the compact, bulk state.

Despite the considerable amount of research, a number of questions connected with materials use remain open. The present aim was a comparative study of IV and V group metals' stability with respect to galvanic corrosion, along with evaluation of the efficiency of the anodic oxidation method and to find the optimal (with respect to inhibiting the electrochemical corrosion processes) condition of metal surface passivation.

2. EXPERIMENTAL

The method employed plates, simulating medical implants made of titanium in the normal and nanosized states (prepared by equal channel angular pressing), zirconium, hafnium, niobium, tantalum, as well as uncoated Co–Cr alloy and with a titanium coating deposited by vacuum sputtering.

Some of the titanium implants had an additional heat treatment in vacuum ($P = 10^{-3}$ Pa) at $T = 200, 500, 800$

* Corresponding author. E-mail: vadym_starikov@mail.ru

and 1150 °C. The purpose of this annealing was additional cleaning of the surface and partial relaxation of mechanical stresses in the near-surface layer of the metal.

Metal implants were studied in the initial state (having a natural oxide coating ~0.5–1 nm thick) and after anodic oxidation when an amorphous oxide is formed with a thickness of 300 nm; it was carried out in an 0.01% aqueous solution of phosphoric acid, with a tantalum plate used as the counterelectrode [11].

Electrochemical activity of the metals was determined by the values of their electrode potentials and the degree of galvanic corrosion using the corrosion current value determined by the procedure described in ref. 11. The measurements were carried out in an electrochemical cell filled with a 0.9% aqueous solution of NaCl.

The conductivity of the Ti–TiO₂ bilayer systems was investigated by a power source external to the electrochemical cell. A positive potential was applied to the titanium, the tantalum plate was the cathode and the current density was measured at a voltage $U = 5$ V.

3. RESULTS AND DISCUSSION

The electrode potentials of the metals in their initial states are plotted according to their atomic weights in Fig. 1. It shows that there is some advantage in the ability of metals with the body-centred crystal lattice structure—niobium and tantalum—to become passivated naturally. Moreover, tantalum's potential, even without additional processing, is close to those of the noble metals. It should be noted that metal activity decreases with increasing atomic weight. This can be explained by the greater initial reactivity of heavy metals, including a higher rate of reaction with oxygen, and therefore higher speeds of natural passivation. Oxides grown on such metal surface have high density and large specific electric resistance, hence almost completely block subsequent galvanic corrosion.

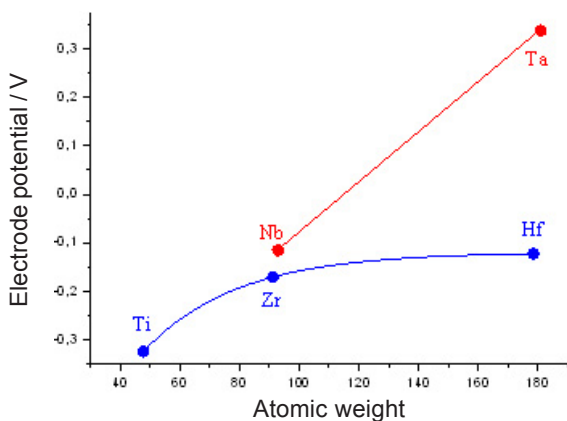


Figure 1. Dependence of electrode potentials of the metals tested in their initial states on their atomic weights.

After anodic oxidation of the metal surface, the oxide thickness was increased approximately 130-fold. Fig. 2 shows that after such treatment the electrode potentials of the metals shifted towards positive values. In this case the dependence of potential on atomic weight is preserved: the heavier metals are passivated better. Despite the fact that the magnitude of this shift for metals with the hexagonal close-packed lattice (Ti, Zr, Hf) is 1.5–2 times higher than that for metals with the body-centred lattice (Nb, Ta), the relative position of the electrode potentials of metals with different crystal lattices after anodic oxidation does not change, except for niobium and zirconium.

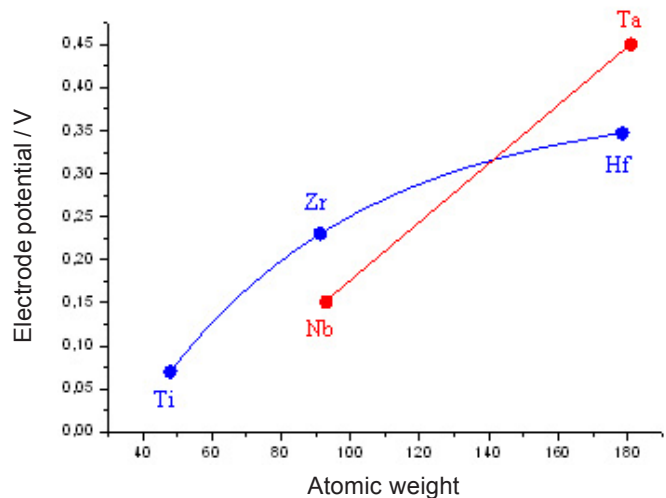


Figure 2. Dependence of electrode potentials of the metals tested after anodic oxidation on their atomic weights.

The experimental dependence shows that for the manufacture of implants it is advisable to use the heavier metals of both crystal lattice types. The only thing that can restrict this choice is when it is necessary to manufacture an implant of considerable size. In this case, the total mass of the implant can be significant (the atomic weights of hafnium and tantalum are twice those of zirconium and niobium) and could cause discomfort to the patient. A solution may be the application of thin coatings on implants and to subsequently oxidize them. Thus, the passivity of the implant will be maximized and the change in mass almost imperceptible.

Metals with the cubic lattice generally showed greater passivity than metals with the hexagonal lattice; if we take into account their higher modulus of elasticity, plasticity and absence of polymorphic transformations upon heating, it can be concluded that their use is more favorable.

All of the selected metals in this study are exemplars of the so-called “valve” metals, due to the unipolar conduction of their oxides (the oxide conductivity at positive polarization of the base metal is much lower than for negative polarization); they have similar properties.

Therefore, the rest of this research was carried out with titanium specimens because of their much wider application in medicine than the other metals [15].

In order to increase the ultimate strength and yield strength of the implant material it is interesting that its preliminary processing is connected with intensive plastic deformation; for example, by equal channel angular pressing. In this process the blank is pressed sequentially through several channels of the same cross-section, intersecting at a certain angle; during deformation, there is significant crushing of the metal grains down to nanometre sizes. In our experiment the final size of titanium grains after deformation was approximately 30 nm, while in the compact condition without further processing the titanium grain size was 100 μm .

Electrochemical test results of nanodisperse titanium in comparison with the compact form before and after surface oxidation are shown in Fig. 3. The electrode potential of titanium after deformation decreased by 40% to the value $E = -0.45$ V, indicating an increase of its electrochemical activity. This can be explained by the increase of internal stresses in the titanium and a significant increase of grain boundary length. When nanodisperse titanium forms a galvanic pair with other metals it will more clearly exhibit anodic properties and actively break down in the electrochemical corrosion process. The natural oxide film is unable to completely prevent such changes. After forced anodic oxidation of the titanium implant with the nanodisperse structure, the titanium electrode potential increases to $E = 0.07$ V, like that of titanium without deformation.

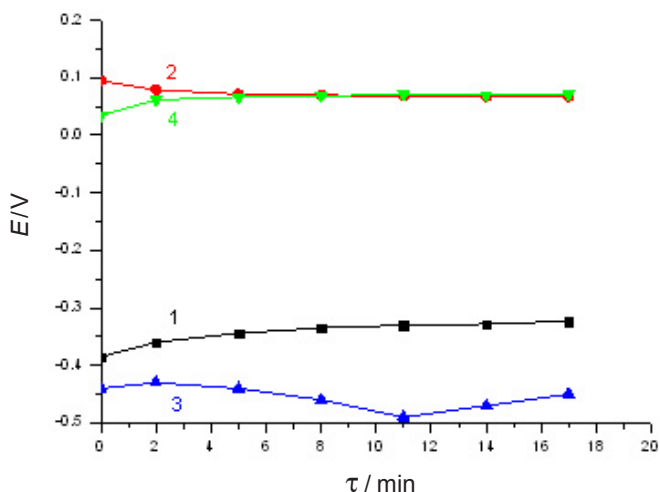


Figure 3. Electrode potentials of compact (1, 2) and nanodispersed (3, 4) titanium in the initial state (1, 3) and after anodic oxidation (2, 4).

Therefore, anodic surface treatment of the titanium implant not only reduces its electrochemical activity but also is able to eliminate the possible growth of implant activity associated with its premachined state (due to flexural deformation, polishing etc.).

In some cases, the production of a titanium implant is difficult; for example, when preparing subperiosteal constructions that must exactly fit to the bone. Then the implant is manufactured by casting. However, it is known that titanium casting requires a vacuum for all operations involving metal heating. Improper execution of this technology can lead to significant embrittlement of the titanium due to absorption of active gaseous impurities, which make it impossible to use the titanium in this form for implant manufacturing. Applying a titanium thin film to a Co–Cr implantable construction surface is an effective solution to this problem.

Changing the electrochemical activity of the Co–Cr alloy in the initial state and after deposition of a titanium film is shown in Fig. 4. The initial electrode potential of the Co–Cr alloy was $E = -0.27$ V. After deposition of the titanium coating by magnetron sputtering the electrode potential increased to $E = 0.033$ V, becoming close to the electrode potential of oxidized titanium (Fig. 3, curve 2). It was inferred that partial oxidation of titanium occurred in the residual atmosphere during its spraying, which favorably affected the final result of the passivation.

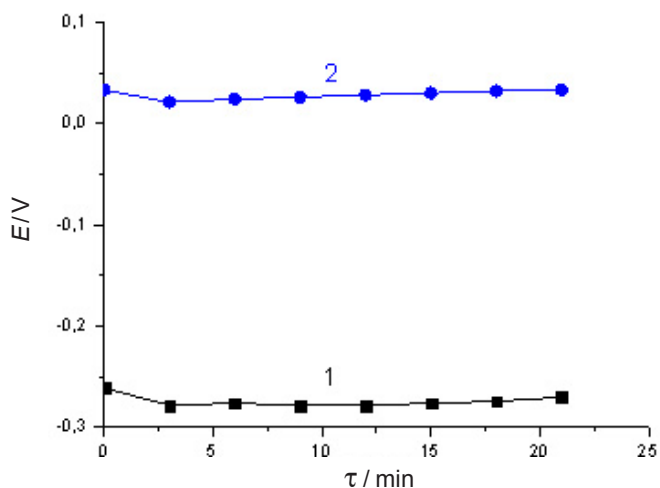


Figure 4. Cobalt–chromium alloy electrode potentials before (1) and after (2) deposition of titanium.

An attempt has been made to further augment the coated Co–Cr alloy electrode potential by anodic oxidation. However, further diminution of sample activity did not occur. This could be due to heterogeneity of the coating thickness; the total activity of the system is limited by its weak points within the thinnest zones of the metal oxide layer and, thus, subsequent increase of oxide film thickness turned out to be nugatory.

A comparative study of the electrochemical activity of titanium implants depending on the purity of the metal surface and anodic oxide film thickness was made.

Fig. 5 shows the dependencies of electrode potential and corrosion current as a function of titanium implant vacuum annealing temperature. Implant potential shifts to the positive region as temperature increases, indicating an increase of passivity as a result of both surface cleaning and the relaxation of stresses in the material during annealing. Refining the titanium surface creates favorable conditions for the formation of a defect-free oxide film. The electrode potential after substantial initial growth saturates and further increase of the vacuum annealing temperature ($T > 800\text{ }^{\circ}\text{C}$) does not lead to a significant increase in this parameter. Considering it as a recrystallization process at $T \geq 700\text{ }^{\circ}\text{C}$, which affects the mechanical properties, it is actually futile to carry out a vacuum heat treatment at $T > 650\text{ }^{\circ}\text{C}$.

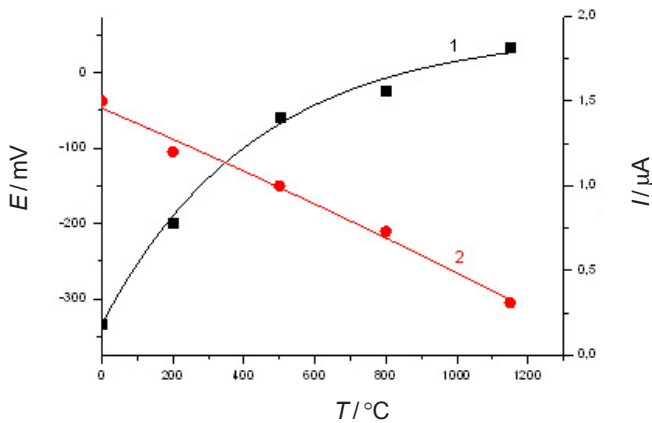


Figure 5. Dependence of electrode potential (1) and corrosion current (2) of titanium on vacuum annealing temperature.

The corrosion current (Fig. 5, curve 2) and, hence, rate of corrosion process decrease with increase of annealing temperature is inferred to indicate improvement of natural oxide quality via removing impurities from the implant surface, resulting in uniform oxidation and, hence, inhibition of the corrosion processes. With the increase of annealing temperature, the corrosion current does not exceed saturation, in contrast to the electrode potential dependence.

The increase of annealing temperature also lessens the conductivity of the anodic oxide films that can be formed on the titanium surface (Fig. 6): this effect is significant for thin anode films (to about 1000 \AA). Further increase of oxide thickness during the oxidation of deeper layers of the titanium substrate led to smaller changes in oxide conductivity. Such behaviour, as in the case of the natural oxide, is also explained by surface purification and diminished mechanical stresses in the metal during annealing.

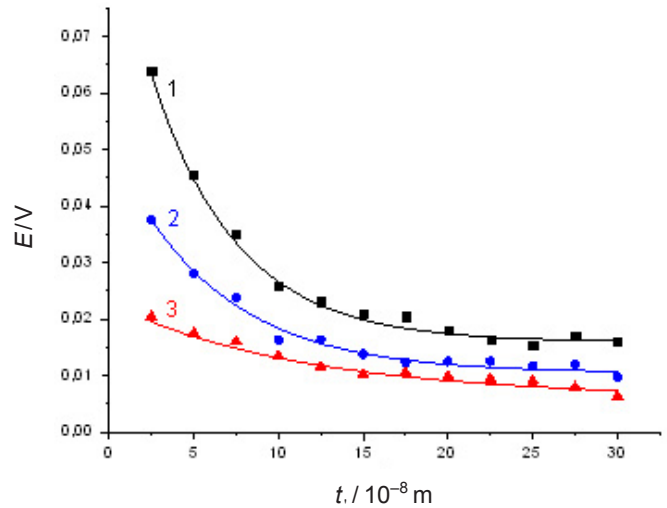


Figure 6. Dependence of current density on oxide thickness of the Ti-TiO₂ system with the titanium substrate in its initial state (1) and after vacuum annealing at $T = 430\text{ }^{\circ}\text{C}$ (2) and $T = 680\text{ }^{\circ}\text{C}$ (3) prior to oxidation.

The dependencies of electrode potential and corrosion current on titanium anodic oxide thickness are shown in Fig. 7.

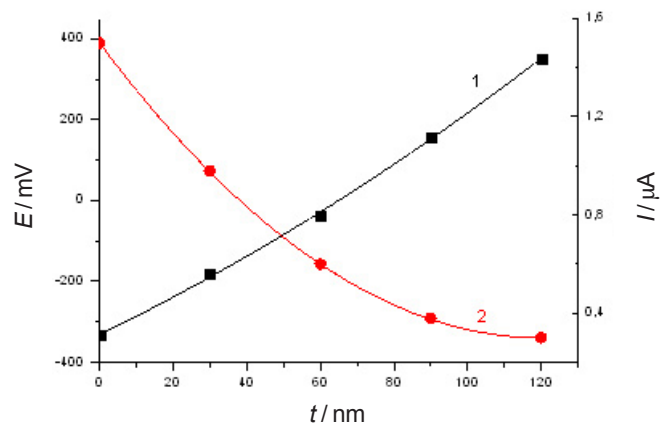


Figure 7. Dependence of electrode potential (1) and corrosion current (2) of titanium on the thickness of anodic surface oxide.

As mentioned earlier, during anodic oxidation the titanium electrode potential is shifted to positive values but saturation of dependence was not reached over the entire range of oxide thicknesses. The passivation associated with anodic oxidation is more effective than cleaning the surface during vacuum annealing. This is due to the fact that a significant increase of oxide thickness leads to inhibition of metabolic processes at the interface between implant and electrolyte because the oxide is an effective diffusion barrier. However, a restriction on surface oxide thickness exists. It is due to the fact that when the thickness of amorphous oxide reaches $t \sim 400\text{ nm}$, it begins spontaneously to crystallize, leading to destruction of the anodic oxide film and activating corrosion processes of the titanium implant. Therefore, after anodic oxidation of the implant surface,

the oxide thickness should not exceed 300 nm in order to maintain the integrity of the oxide layer.

The value of the corrosion current depends on the conductivity of the anodic oxide film and, with increase of its thickness, decreases gradually, reaching saturation, which is consistent with the discussion of Fig. 6.

It should be noted that in all cases the anodic oxide film gives a dual protection against corrosion. On the one hand the oxide exhibits properties of a diffusion barrier for release of metal ions from implant to electrolyte. On the other hand, the oxide, having a sufficiently high electrical resistance, prevents deionization of solution cations. Both processes result in significant corrosion inhibition, which can be enhanced by preliminary vacuum heat treatment of the metal before oxidation and increase of anodic oxide thickness. For maximum passivation of the implant surface, it seems appropriate to use both types of treatment at the same time.

After growing anodic oxide films on the surface of titanium implants it was found that they have electret properties and bear a negative electrical charge on the surface activates a process of implant osseointegration in bone [17, 18]. Measurement of electret charges was conducted by electrostatic induction. Measurements and calculations yielded a value of $\sigma \sim 7.3 \times 10^{-4} \text{ C/m}^2$ for the titanium oxide surface charge density. Use of implants with an electret coating excludes local inflammatory complications, shortens the period of reimplantation and stimulates the formation of new tissue in the body [12].

4. SUMMARY

The growth of passivation ability for metals of groups IV and V of the Periodic Table by increasing their atomic weight was established. Cultivation of anodic oxide films on the metal surface causes their corrosion resistance to approximate to that of noble metals.

Deposition of metal oxide film coatings on a Co–Cr alloy surface results in substantial passivation of its surface and excludes cobalt and chromium accumulation in the bone tissue.

A decrease of titanium implant activity can be achieved by both cleaning the surface during vacuum annealing before oxidation and increasing the anodic oxide film thickness, which limits mass and charge transfer through the implant surface. Recommended titanium implant treatment regimens are as follows: vacuum annealing at temperature $T = 650 \text{ }^\circ\text{C}$ and anodic oxidation to oxide thickness $t \leq 300 \text{ nm}$. Use of nanostructured titanium for the manufacture of medical implants increases their reactivity, but this effect can be offset in the process of anodic oxidation.

REFERENCES

1. Zhao, X., Courtney, J.M. and Qian, H. (eds). *Bioactive Materials in Medicine: Design and Applications*. Abington: Woodhead Publishing (2011).
2. Steinemann, S.G. Titanium—the material of choice? *Periodontology* 2000 **17** (1998) 7–21.
3. Olmedo, D., Guglielmotti, M.B. and Cabrini, R.L. An experimental study of the dissemination of titanium and zirconium in the body. *J. Mater. Sci.: Mater. Med.* **13** (2002) 793–796.
4. Schider, S. and Bildstein, H. Tantalum and niobium as potential prosthetic materials. In: *Advances in Biomaterials* (eds G.D. Winter, D.F. Gibbons and H. Plenk, Jr.), pp. 13–20. New York: Wiley (1980).
5. Larsson, C.C., Thomsen, P., Lausmaa, J., Ridahl, M., Kasemo, B. and Ericson, L.E. Bone response to surface modified titanium implants: studies on electropolished implants with different oxide thicknesses and morphology. *Biomaterials* **15** (1994) 106–274.
6. Liu, X., Huang, A., Ding, C. and Chua, P.K. Bioactivity and cytocompatibility of zirconia (ZrO_2) films fabricated by cathodic arc deposition. *Biomaterials* **27** (2006) 3904–3911.
7. Singh, A.V., Patil, R., Thombre, D.K. and Gade, W.N. Micro-nanopatterning as tool to study the role of physico-chemical properties on cell-surface interactions. *J. Biomed. Mater. Res.* **101** (2013) 3019–3032.
8. Lowe, T.C. and Reiss, R.A. Understanding the biological responses of nanostructured metals and surfaces. *IOP Conf. Series* **63** (2014) 012172.
9. Dub, S.N. and Starikov, V.V. Elasticity module and hardness of niobium and tantalum anode oxide films. *Functional Mater.* **14** (2007) 347–350.
10. Galante, J.O., Lemons, J., Spector, M., Wilson, P.D. and Wright, T.M. The biological effect of implant materials. *J. Orthopaedic Res.* (1991) 760–775.
11. Starikov, V.V., Starikova, S.L., Mamalis, A.G., Lavrynenko, S.N. and Ramsden, J.J. The application of niobium and tantalum oxides for implant surface passivation. *J. Biol. Phys. Chem.* **7** (2007) 141–145.
12. Kutsevlyak, V.I., Starikov, V.V., Starikova, S.L., Mamalis, A.G., Lavrynenko, S.N. and Ramsden, J.J. Influence of implant surface modification on integration with bone tissue. *J. Biol. Phys. Chem.* **8** (2008) 147–150.
13. Maissel, L.I. and Glang, R. *Handbook of Thin Film Technology*. New York: McGraw Hill (1970).
14. Ungersboeck, A., Geret, V., Pohler, O. et al. Tissue reaction to bone plates made of pure titanium: a prospective, quantitative clinical study. *J. Mater. Sci.* **6** (1995) 223–229.
15. Ramsden, J.J. *Biomedical Surfaces*, Table 3 (p.14). Norwood, Mass.: Artech House (2008).
16. Niinomi, M., Narushima, T. and Nakai, M. (eds). *Advances in Metallic Biomaterials*. Berlin: Springer (2015).
17. Montero, I., Albella, J.M., Ortega, C. and Siejka, J. Space charge and electret behaviour in anodic Ta_2O_5 films. *Thin Solid Films* **167** (1988) 95–100.
18. Starikov, V.V., Starikova, S.L., Mamalis, A.G. and Lavrynenko, S.N. Stimulation of calcium phosphate crystal formation by implant surfaces with electret properties. *J. Biol. Phys. Chem.* **15** (2015) 200–203.