DEPOSITION OF CALCIUM PHOSPHATE COATING ON TITANIUM DEPENDS ON ELECTROLYTE COMPOSITION

ROMAN PROSKURNIAK, OLEH TKACHUK

Karpenko Physico-Mechanical Institute of NAS of Ukraine

The influence of the concentration (0.5M…2M) of potassium hydroxide on the formation of calcium phosphate coatings on commercially pure titanium was investigated. They were deposited by the method of plasma electrolytic oxidation at the applied voltage of 160 V for 1 min. The phase composition, morphology and corrosion behaviour of the coatings in a physiological environment were studied. It was shown that the coatings formed at 1M and 2M KOH, when the predominant phases are hydroxyapatite or calcium titanate, have the optimal surface characteristics.

Keywords: titanium, plasma electrolytic oxidation, hydroxyapatite coating, alkaline electrolyte, potassium hydroxide

Introduction. Nowadays, the development of dental medicine is aimed at creating new bioactive materials [1]. In an ideal case, the material should be compatible with the body tissue, and form the bonds with biological system of the body with the formation of bone tissue. Titanium implants with the modified surface, in particular a protective bioactive coating, have the greatest interest [2]. These coatings must meet strict requirements for phase and elemental compositions, as well as for mechanical properties. Recently, besides of the development of the coating composition, its macro- and microstructure, more and more attention is paid to the surface morphology. The bone tissue is a composite material with a multi-level structure. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ of biological or artificial origin is mainly used as a coating for titanium implants [3]. The formation of hydroxyapatite coatings on titanium and its alloys is carried out by such methods as hydrothermal [4], sol-gel [5], plasma spraying [6], but recently the method of plasma electrolytic oxidation (PEO) became widespread [7]. This method makes it possible to form porous, rough, strongly adherent coatings on titanium implants. Thus, the effectiveness of usage of an alkaline medium (NaOH or KOH) for the formation of hydroxyapatite on titanium was shown [4]. However, there is no information in the literature regarding the study of the influence of the electrolyte concentration on the incorporation of calcium and phosphorus ions into the surface layer of titanium during the PEO process. Therefore, the purpose of this work is to determine the optimal KOH in the electrolyte for hydroxyapatite formation on the surface of cp-Ti.

Experimental procedure. The samples of cp-Ti with dimensions of 10×15×1 mm were used for investigations. The composition of the electrolyte

for PEO was as follows: powder of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ – 100 g/l, the concentration of potassium hydroxide – 0.5; 1; 1.5; 2 M. The PEO process was carried out at the applied voltage of 160 V for 1 min using pulse regime.

The phase composition of the surface layers was determined by X-ray phase analysis using DRON-3.0. The porosity and average pore size were determined by the ImageJ software. The surface roughness was evaluated by a profilometer type 170621, determining the Ra parameter.

The microstructure and chemical composition of surface layers of titanium after PEO were studied using an EVO-40XVP scanning electron microscope with an INCA Energy 350 EDX system.

Results and discussion. According to X-ray phase analysis, the reflections of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (00-055-0592), dicalcium phosphate anhydrite $CaHPO_4$ (3-423) and calcium titanate $CaTiO_3$ (22-153) were fixed on the surface of cp-Ti after PEO at a content of 0.5M KOH in the alkaline electrolyte (Fig. 1a). In addition, the peaks of the α-Ti phase of relatively high intensity were detected, which indicates the formation of a thin film.

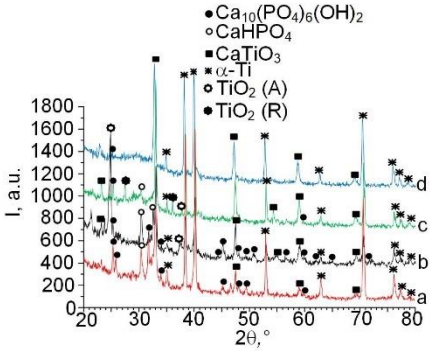

Fig. 1. XRD patterns of cp-Ti after PEO at different concentrations of KOH: 0.5M (a); 1M (b); 1.5M (c); 2M (d).

By increasing concentration of KOH to 1M in the electrolyte, an increase of a number of $Ca_{10}(PO_4)_6(OH)_2$ reflections, as well as the intensity of $CaHPO_4$ and $CaTiO_3$ reflections was observed (Fig. 1b). In addition, the anatase reflections appear in the diffraction spectrum.

A further increase of the concentration of KOH to 1.5M and 2 M leads to a decrease of a number and intensity of reflections of $Ca_{10}(PO_4)_6(OH)_2$ phase and an increase of $CaTiO_3$ phase (Fig. 1c, d). The transformation of anatase into rutile is also observed (Fig. 1c). Higher concentrations of KOH in the electrolyte contribute to an increase of the content of Ti^{4+} and OH^- ions that provides the

formation of larger number of Ti-OH groups, which accelerates the reaction rate of the formation of the $CaTiO_3$ phase.

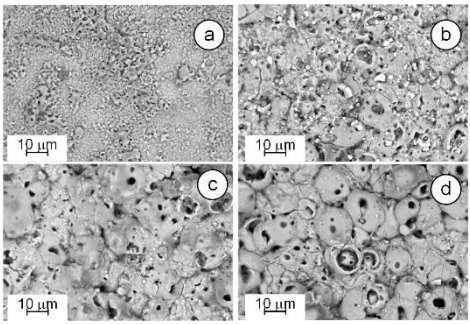

Fig. 2. Surface of cp-Ti with PEO coatings formed at different concentrations of KOH: 0.5M (a); 1M (b); 1.5M (c); 2M (d).

Fig. 2 shows the surface morphology of PEO coatings formed on cp-Ti. It depends on the KOH concentration in the electrolyte. At 0.5M KOH (Fig. 2a), a porous coating of uneven thickness (3-5 μm) with a high roughness (R_a = 2.82 μm) is formed on the surface. It is known that a highly rough surface (R_a > 2 μm) leads to a poorer osseointegration and would induce higher risk of bacterial colonization [8]. The average pore size is 2.02 μm, the porosity of the coating is 4.03%. According to EDX analysis, the content of Ca is 14.86 at. % and P – 8.67 at. %, the Ca/P ratio is 1.71.

By increasing content of KOH to 1M, an uniform porous coating with a thickness of 65 μm with a spheroidal structure is formed on the titanium surface, which is characteristic of hydroxyapatite (Fig. 2b). The parameter of surface roughness Ra decreases by ~ 2 times and is equal to 1.52 μm, and such moderately rough surface can improve the formation of new bone [8]. As the concentration of KOH increases, the electrical conductivity of the electrolyte increases, which leads to an increase of a number of spark discharges, which causes a 4-fold increase of the coating porosity (16.16%); the average pore size is 2.39 μm. According to EDX analysis, there is an increase of the content of Ca (17.71 at. %) and P (10.88 at. %) on the surface. The Ca/P ratio is 1.69 which is close to the ratio proper for biological hydroxyapatite (1.67). It should be noted that such microstructure can accelerate the formation of the interfacial bond between the dental implant and bone tissue.

With an increase of the concentration of KOH in the electrolyte to 1.5M and 2M, the moderately rough (R_a=1.62...1.68 μm) porous coatings are formed on the titanium surface (Fig. 3c, d). According to the EDX analysis, a decrease of the content of calcium (7.02...8.45 at. %) and phosphorus (2.24...3.28 at. %) is fixed on the surface. However, an increase of oxygen and titanium content is

observed, and this trend increases with increasing KOH concentration. This is well correlates with the results of X-ray phase analysis, where we recorded an increase of the content of the $CaTiO_3$ phase in the surface layer (Fig. 1). The Ca/P ratio is 2.57 and 3.13 for 1.5M and 2M, respectively. The tendency to increase of the porosity of the coating remains (up to 18.14% and 25.37%), the average pore size is 3.46...3.99 μm.

Conclusions. The porous hydroxyapatite coatings were deposited on cp-Ti by the method of PEO in an alkaline electrolyte with different concentration of KOH (0.5; 1; 1.5; 2M) at the applied voltage of 160 V for 1 min. It was established that moderately rough (Ra=1.52...1.68 μm) surfaces are formed on titanium at concentrations of KOH ≥ 1M, which should improve their osseointegration. As the electrolyte concentration increases, the phase composition of the coating changes from hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ to calcium titanate $CaTiO_3$. It was shown that for 1M KOH, the Ca/P ratio is 1.69, i.e., the composition of hydroxyapatite is close to biological one.

1. *Santos-Coquillat A., Mohedano M., Martinez-Campos E., Arrabal R., Pardo A. and Matykina E.* Bioactive multi-elemental PEO-coatings on titanium for dental implant applications // Mater. Sci. Eng. C. – 2019. – 97. – P. 738–752.
2. *Pohrelyuk I.M., Tkachuk O.V., Proskurnyak R.V., Boiko N.M., Kluchivska O.Yu., Stoika R.S. and Ozga P.* Cytocompatibility Evaluation of Ti-6Al-4V Alloy After Gas Oxynitriding // J. Mater. Eng. Perform. – 2020. – 29. – P. 7785–7792.
3. *Ghadami F., Amani Hamedani M., Rouhi G., Saber-Samandari S., Dehghan M.M., Farzad-Mohajeri S. and Mashhadi-Abbas F.* The correlation between osseointegration and bonding strength at the bone-implant interface: In-vivo & ex-vivo investigations on hydroxyapatite and hydroxyapatite/titanium coatings // J. Biomech. – 2022. – 144. – P. 111310.
4. *Okido M., Kuroda K., Ishikawa M., Ichino R. and Takai O.* Hydroxyapatite coating on titanium by means of thermal substrate method in aqueous solutions // Solid State Ion. – 2002. – 151. – P. 47–52.
5. *Domínguez-Trujillo C., Peón E., Chicardi E., Pérez H., Rodríguez-Ortiz J.A., Pavón J.J., García-Couce J., Galván J.C., García-Moreno F. and Torres Y.* Sol-gel deposition of hydroxyapatite coatings on porous titanium for biomedical applications // Surf. Coat. Tech. – 2018. – 333. – P. 158–162.
6. *Qi J., Yang Y., Zhou M., Chen Z. and Chen K.* Effect of transition layer on the performance of hydroxyapatite/titanium nitride coating developed on Ti-6Al-4V alloy by magnetron sputtering // Ceram. Int. – 2019. – 45. – P. 4863–4869.
7. *Lederer S., Sankaran S., Smith T. and Furbeth W.* Formation of bioactive hydroxyapatite-containing titania coatings on CP-Ti 4+ alloy generated by plasma electrolytic oxidation // Surf. Coat. Tech. – 2019. – 363. – P. 66–74.
8. *Pierre C., Bertrand G., Rey C., Benhamou O. and Combes C.* Calcium phosphate coatings elaborated by the soaking process on titanium dental implants: Surface preparation, processing and physical–chemical characterization // Dent. Mater. – 2019. – 35. – P. e25–e35.