Formation of Bioactive Coatings with Micro-plasma Technique for Medical Use[1]

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Abstract – The physical, chemical and technological aspects of the bioactive coating formation with micro-plasma technique have been investigated. The scientific and technological technique has been developed. The influence of electro-physical parameters of micro-plasma calcium-phosphate coating on the properties such as thickness, spherolytes and pores sizes and adhesive behavior has been studied. It was shown that when the pulse period increases the line growth of coating parameters as thickness, spherolytes and pores sizes occurs and adhesive behavior keeps high. At the same time when the pulse period reduces and cathode current adds that adhesive behavior degrades. The optimal structure of electrolyte and optimal regime of coatings were established. It was found, calcium-phosphate coating providing high porosity up to 30% and adhesion strength no less than 25 MPa can be formed by micro-plasma technique in aqueous solutions of phosphoric acid, hydroxylapatite and calcium carbonate powders. Novel calcium-phosphate coatings are highly biocompatible, non-toxic and they can be used for medical use.

1. Introduction

The stressing problem of modern medicine is a replacement of the injured organs by artificial implants. Such materials as the titanium and its alloys find wide application in all areas of medicine: traumatology, orthopedy, stomatology etc. However now it is not enough to have an implant possessing only excellent mechanical properties. The postoperative complications concerned with implant rejection have led to the application of bioactive coatings on implants. The calcium phosphates have a significant place among bioactive coatings as they are hypoallergenious, have no carcinogenic and mutagen action, are well integrated with a bone tissue as a result they have high biocompatibility [1].

At present, there is a set of methods to form calcium-phosphate (Ca–P) coatings on titanium surfaces, such as sol-gel technology, plasma spraying technology, deposition from chemical or physical vapor, high-temperature pressing, etc. The micro-plasma method of Ca–P coatings formation in aqueous electrolytes is the most simple and technological one [2]. The biological behavior of coatings depends on their physical and chemical parameters (thickness, structure, porosity, phase and elemental composition, adhesion strength, wear resistance and so on), but in turn, they depend on electro-physical parameters of micro-plasma process and composition of electrolytes. In this connection to form bioactive calcium phosphate coatings, it is necessary to verify of coating properties.

The physical, chemical and technological aspects of the bioactive coating formation with micro-plasma technique have been presented in the paper.

2. Experimental details

In order to form calcium-phosphate coatings on the titanium surface the technological complex was developed [3]. The technological complex contains the pulse power source, computer to control of deposition process, galvanic bath with water cooling and electrodes. The pulse power source allows to vary the electro-physical parameters in wide range: voltage of positive and negative polarities is 50–700 V, voltage increment is 10 V, peak current is up to 800 A, pulse frequency is 10–150 Hz, frequency increment is 10 Hz, pulse period in 0.5 level is 50–500 μs, pulse period increment is 10 μs. The pulse power source supplies voltage and current regulation and allows setting voltage and current density rates, positive and negative pulse period by line law using software. The technological complex operates in anode, cathode, anode – cathode regimes and allows to simultaneously form Ca–P coating on total area of titanium implants up to 200 cm^2.

The Ca–P coatings were deposited from aqueous solutions of phosphoric acid (H_3PO_4, 10–30% wt %) with hydroxylapatite (HA, 6% wt %) and calcium carbonate powders ($CaCO_3$, 9–12% wt %) in anode and anode – cathode regimes. The Ca–P coating was formed under pulse mode in following parameters: pulse period was 50–500 μs; pulse frequency was 25–100 Hz; final voltage was 100–300 V, time was 5–30 min.

The phase composition was determined by X-ray diffraction method (XRD, Dron-7) using International Centre for Diffraction Data (JCPDS ICDD). The sur-

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face morphology was examined by Scanning Electron Microscope (SEM, Phillips SEM 515). To measure the sizes of structural element (spherolytes and pores) a “secant method” was applied.

The total porosity is a ratio of total segment length getting for pores, to total length of secant lines, is expressed by the following formula:

$$P = \frac{\sum l}{\sum L_1} 100\%,$$

where L_1 is the secant total length; l is the length of the secants corresponding to the pores.

Adhesion strength was estimated by two methods: express method and glued method. To measure adhesion by express method the diamond indenter was pressed in coating using hardness tester TC-2. The coating was fractured as a result indentation and deformation zone was formed. The conditional coefficient of adhesion was calculated with the relation

$$Y = 1 - (\Sigma S_1 / \Sigma S_2),$$

where ΣS_1 is the area amount of fractured coating under indentation; ΣS_2 is the area amount of deformed zone under indentation.

To measure adhesion of Ca–P coatings to titanium two cylinders were glued to both sides of titanium plate with Ca–P coating by Loctite Hysol 9514 and then they were fixed in sample grips to be tested under tension. The force required to tear the cylinder off the Ca–P coating was measured. The magnitude of adhesion was calculated with the relation

$$P = \frac{F}{S},$$

where F is the force required to tear the coating from titanium; S is the area of coating surface.

3. Experimental results

The investigations of influence of electro-physical parameters of micro-plasma process (pulse period, pulse frequency, voltage, time, anode and anode-cathode mode) on properties of Ca–P coatings as thickness, spherolytes and pores sizes and adhesive behavior are presented below.

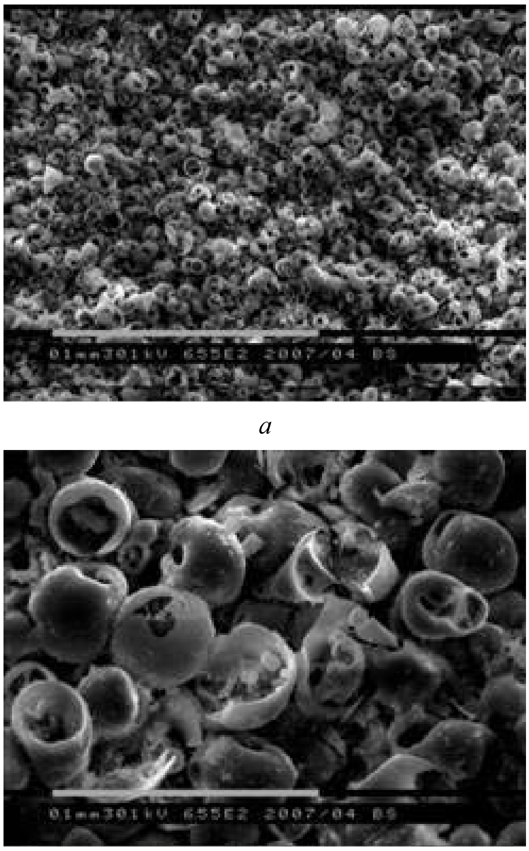
The SEM studies were shown that the porous structure of Ca–P coating is formed under micro-plasma process. The main components of structure are spherolytes which are pore.

Local micro-plasma discharges appear at the electric current flow through the boundary of electrode-electrolyte on titanium surface under influence of which pores are formed.

The pore sizes depend on the size of micro-plasma discharges in electrolyte which, in turns, are connected with modes of micro-arc process: formation time and electrolyte structure. Total porosity of the Ca–P coating is 20–35%. It should be noted, the porosity is the main characteristic which determines efficiency of a bone ingrowth into the implant.

It was established that large micro-plasma discharges producing large pore on coating surface have place at large value of pulse period.

It concerned with that pulse period stimulates current intensity on coating surface due to deposition rate growths. As consequence the coating thickness is increased. So, linear growth of coating parameters happens, the spherolytes and pores sizes are raised from 10 to 35 μm and from 5 to 20 μm correspondingly at increasing of pulse period from 50 to 500 μs (Fig. 1).



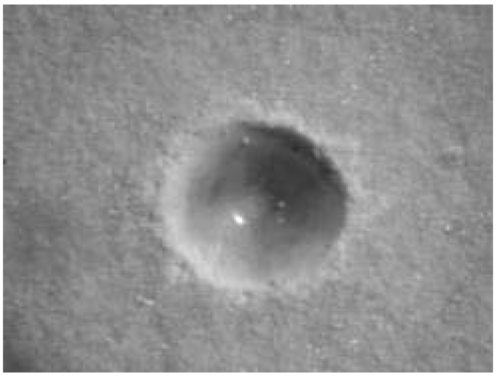
a

b

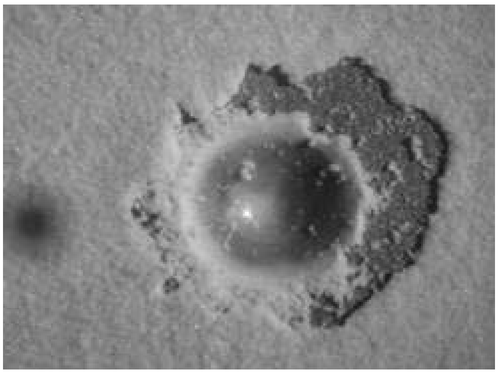
Fig. 1. SEM micrographs of micro-plasma Ca–P coatings: voltage is 275 V, pulse frequency is 50 Hz, pulse period is 100 (*a*) and 500 μs (*b*)

Adhesion testing by express method has shown that the varying of pulse period and frequency in anode mode does not lead to reduction adhesion strength of Ca–P coating to titanium (Fig. 2, *a*). However, the reducing of pulse period and frequency in anode – cathode mode causes the considerable reduction of adhesion strength (Fig. 2, *b*).

Thus, it was found, calcium-phosphate coating providing high porosity and adhesion strength can be formed by micro-plasma technique in following parameters: pulse period is 100 μs; pulse frequency is 50 Hz; voltage is 300 V, time is 10–20 min.



a



b

Fig. 2. Optical images of indentations in micro-plasma Ca–P coatings (express method to adhesion); *a* – anode mode: pulse frequency is 50 Hz, pulse period is 100 μs, and anode–cathode mode (*b*): pulse frequency is 10 Hz, pulse period is 250 and 100 μs, respectively

The results of study of influence of electrolyte composition on phase composition, porosity and adhesion strength are presented below.

The investigation of phase composition of Ca–P coatings has demonstrated that it does not depend from the varying concentration of phosphoric acid from 10 to 30%. The interpretation of X-ray diffraction pattern points to Ca–P coatings consist of – TiP_2O_7, TiO_2 (anatase), TiO, $CaTi_4(PO_4)_6$, β-$Ca_2P_2O_7$ (Fig. 3).

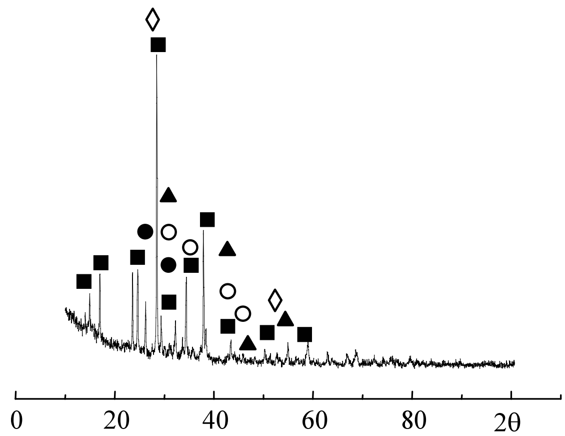


Fig. 3. X-ray difractogram of micro-plasma Ca–P coating deposited in electrolyte on base H_3PO_4, HA and $CaCO_3$: ■ – $CaTi_4(PO_4)_6$; ● – TiP_2O_7; ○ – β-$Ca_2P_2O_7$; ◊ – $TiO_{2(anatase)}$; ▲ – TiO

The addition to electrolyte the calcium carbonate powders provides the generation of β-tricalcium phosphate (β-TCP) (Fig. 4). According to [2], β-TCP has high biocompatibility as its structure is similar to structure of earlier mineralizing bone.

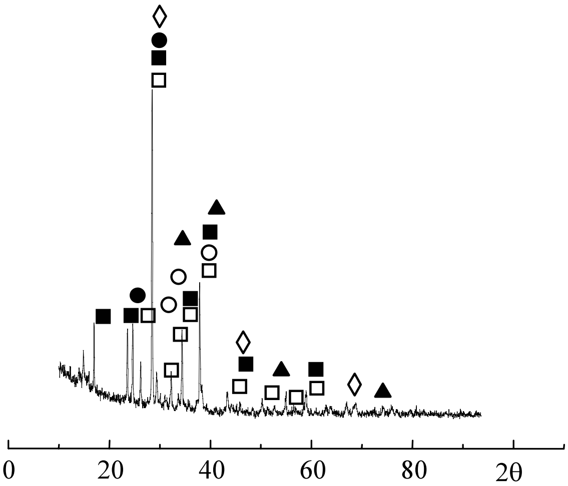


Fig. 4. X-ray difractogram of micro-plasma Ca–P coating deposited in electrolyte on base H_3PO_4, HA and $CaCO_3$: □ – $Ca_3(PO_4)_2$; ■ – $CaTi_4(PO_4)_6$; ● – TiP_2O_7; ○ – β-$Ca_2P_2O_7$; ◊ – $TiO_{2(anatase)}$; ▲ – TiO

MOREOVER, β-TCP structure, as well as the structure of a bone tissue is apatite like. Many researchers [2] consider that β-TCP accelerates resorption and provides "material" for bone growth.

However, the varying concentration of phosphoric acid and addition to electrolyte the calcium carbonate powders causes to change the porosity and adhesion strength.

SEM micrographs of Ca–P coatings deposited micro-plasma method in aqueous solutions of phosphoric acid, hydroxylapatite and calcium carbonate powders are presented in Figs. 5, 6.

It can be seen that coating formed in 10% phosphoric acid and hydroxylapatite (Fig. 5, *a*) and calcium carbonate powders (Fig. 6, *a*) have similar morphology. The main elements of structure are pores and craters. Total porosity of the Ca–P coating is 32–34%, adhesion strength testing by glue method is 8–14 MPa.

At increasing acid concentration to 30% the morphology changing have place and spherolytes with open pores are formed (Figs. 5 and 6, *b* and *c*). At the same time of total porosity of the Ca–P coating is decreased to 26–30%, but adhesion strength is improved up to 30 MPa.

Biological testing *in vivo* and *in vitro* showed that the novel coating increase integrated behavior with marrow cells and providing growth of bone tissue on surface coatings. Calcium-phosphate coating are high biocompatible, nontoxic and it can be used for osteosynthesis [4].

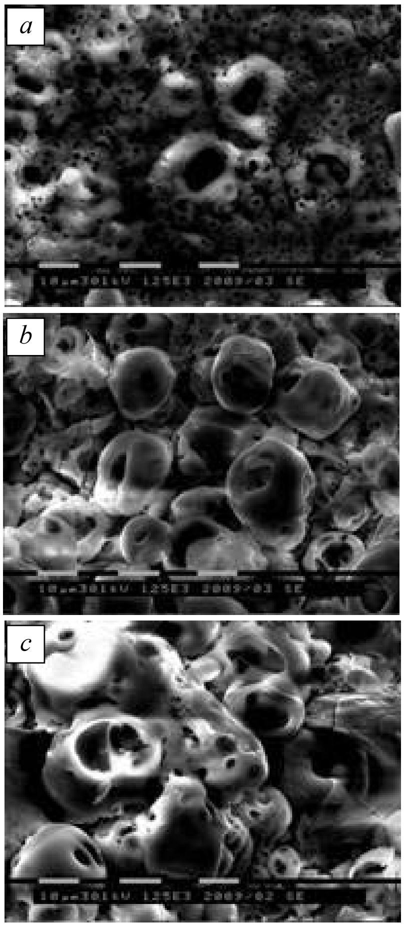


Fig. 5. SEM micrographs of Ca–P coatings deposited in electrolytes: *a* – 10% H_3PO_4 + HA; *b* – 20% H_3PO_4 + HA; *c* – 30% H_3PO_4 + HA

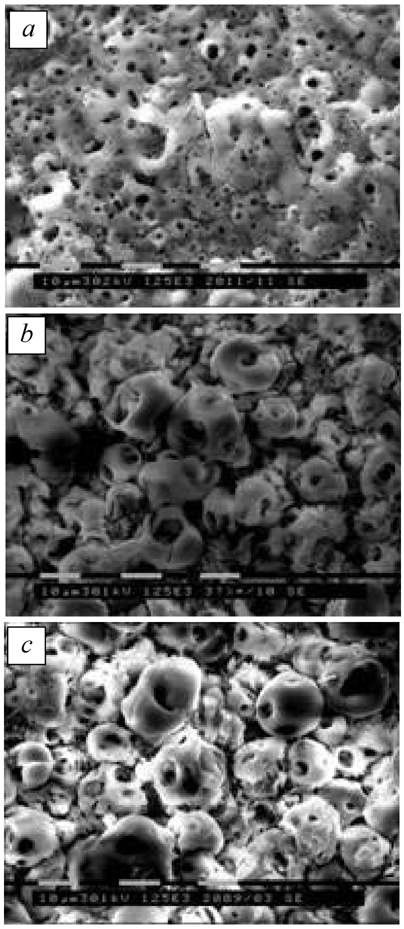


Fig. 6. SEM micrographs of Ca–P coatings deposited in electrolytes: *a* – 10% H_3PO_4 + HA +$CaCO_3$; *b* – 20% H_3PO_4 + HA + $CaCO_3$; *c* – 30% H_3PO_4 + HA + $CaCO_3$

4. Conclusions

The set of the above-described results allows stating the following conclusions:

1. It has been experimentally shown that linear growth of coating parameters happens and high level of adhesion strength have place at increasing of pulse period in anode mode. The reducing of pulse period and frequency and addition of cathode current causes the considerable reduction of adhesion strength.

2. It has been established that increasing phosphoric acid concentration from 10 to 30% causes to change the morphology from porous structure with craters to pronounced relief structure which have spherolytes with open pores. At the same time total porosity is decreased from 34 to 26%, it improves adhesion strength from 8 to 30 MPa.

3. It has been demonstrated that that the addition of the calcium carbonate powder in electrolyte provides to synthesis of the β-tricalcium phosphate, which is high biocompatibility as its structure is similar to structure of earlier mineralizing bone.

4. The optimal composition of electrolyte and optimal regime of micro-plasma process were established. It was found, calcium-phosphate coating providing high porosity up to 30% and adhesion strength no less than 25 MPa can be formed by micro-plasma technique in aqueous solutions of phosphoric acid (20% wt %) with hydroxylapatite (6% wt %) and calcium carbonate powders (9% wt %) in the following parameters: pulse period is 100 μs; pulse frequency is 50 Hz; voltage is 300 V, time is 10–20 min.

5. Novel calcium-phosphate coatings are highly biocompatible, nontoxic and they can be used for medical use.

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