ИЗВЕСТИЯ ВЫСШИХ УЧЕБНЫХ ЗАВЕДЕНИЙ
Т. 57, № 12/3 ФИЗИКА 2014

UDC 533.9, 538.7

K.S. KULYASHOVA, Yu.P. SHARKEEV***, A.A. MAMAEVA***, A.V. PANICHKIN***, R.K. AUBAKIROVA***, Yu.A. GLUSHKO*, A.B. SAINOVA*****

BIOACTIVE CALCIUM PHOPHATE COATINGS DEPOSITED BY RF-MAGNETRON METHOD: STRUCTURE AND PROPERTIES

Results of investigate of the surface morphology, structure, adhesive strengths and microhardness of calcium phosphate coatings were presented. The radiofrequency magnetron calcium phosphate coating has a homogenous structure, non-porous. The Ca/P ratio is depended on the applied radiofrequency discharge power, it decreases from 5.64 to 2.86 in interval of RF-discharge power of 100–250 W. It was experimentally established that the increase of power of RF-discharge up to 250 W provides a denser and thicker coating and promotes the formation of amorphous phase of the higher concentration. Molecular bonds typical for hydroxyapatite are formed for annealed coatings. The increase of RF-discharge power from 150 to 250 W leads to growth of the amplitude of PO_4^{3-} and OH^- molecular bonds. The coatings characterized high value of the adhesive strength to the titanium surface. Mechanical properties of the composite material on the basis of the titanium substrate and a calcium phosphate coating are higher than ones of individual components.

Keywords: *calcium phosphate coating, radiofrequency magnetron method, infrared spectroscopy, Ca/P ratio, microhardness, adhesive strengths.*

Introduction

Implants from titanium and titanium alloys are widely used in medical applications for correction of bone defects or bone's replacement [1, 2]. However the titanium implants are characterized the significant difference in the physicochemical and mechanical properties in comparison with bone tissue. Therefore the implants must be converted by different way of physical or chemical treatment. To reduce the negative influence of these factors it is necessary to create an intermediate layer between metallic implant and bone. For this purpose, calcium phosphate coatings (CaP) are deposited on the implant surface using the different methods. The most suitable calcium phosphate material for formation of coatings is hydroxyapatite – $Ca_{10}(PO_4)_6(OH)_2$. Hydroxyapatite is the main constituent of a mineral component of the bone tissue, it has a relatively low solubility and, consequently, low bioresorption, that leads to a gradual degradation of the coating while an implant is located in the body [3]. Deposition of the thin dielectric CaP coating on the implant surface is a complex problem. Today, some methods is offered for deposition of biocoatings [4–6]. The method of radiofrequency (RF) magnetron sputtering has a set of advantages [4] and it allows to form coatings with the controlled composition and high mechanical properties.

Materials and methods

Technically pure titanium (VT1-0) was used as substrate material. The samples had dimensions of 15×15×3 mm. A subsequent mechanical grinding of sample surfaces on an abrasive paper from coarse-grained state up to fine-grained one was carried out before deposition of the coating. Grinded samples were cleaned with distilled water in an ultrasonic bath.

Formation of the CaP coatings was carried out using a RF-magnetron installation "Yakhont-2M" with a power source frequency of 13.56 MHz [7]. The sputtering mode was as following. Working gas is argon, working gas pressure is 1 Pa, sputtering time is 3 hours, and the RF-discharge power is 100, 150, 200 and 250 W. The magnetron CaP target was formed from the hydroxyapatite powder by pressing and annealing in the air at 1273 K.

The morphology of sample surfaces before and after deposition of coating was studied using the scanning electron microscopy with JEOL JXA-8230 equipped with energy dispersive X-ray analysis (EDX-analysis). Infrared (IR) spectroscopy was carried out with spectrometer Nikolet Avatar 370 CsI in the range of wave length of 4000–400 cm^{-1}. Value of the adhesion strength of CaP coating to the titanium substrate was determined using the scratch-test method on the installation CSM Macro Scratch Tester Revetest. Three ranges of the indentation load were used. They were 0.3–10, 0.3–20 and 0.3–30 N. The microhardness of tested samples was measured on the microhardness tester PMT-3M using the Vickers method under indentation loads of 0.2, 0.4, 0.5, 0.7, 1, 1.2, 1.5 and 2 N. The microhardness of coatings

was calculated on the basis of the measurement results of the integral microhardness of the coated metal samples in accordance with the technique proposed in [8]. The technique was based on dependence of the microhardness on the indentation depth. A critical depth of indentation h_k was determined as an intersection point of the lines obtained from the graph representing the results of the experiment. This value was determined by load value when the coating was completely "punctured" by the indenter. Under higher loads contribution to the microhardness of the composite "metal substrate – CaP coating" is insignificant.

Experimental results

The EDX-mapping images of sample surfaces before the CaP coating deposition and element composition of coating are shown respectively in Fig. 1 and Table 1. The CaP coating is homogenous, nonporous, without any defects. The Ca/P ratio depended on the applied RF-discharge power. Increase of the RF magnetron discharge power leads to lighter element spraying, namely P. Thus the Ca/P ratio is decreasing from 5.64 to 2.86, but this value is large enough. It was experimentally established that increasing of power of RF-discharge up to 250 W provide a denser and thicker coating and promoted the formation of amorphous phase of the high concentration that it is greater than 20 % [9]. In this case the long-time strength of the coatings is determined by the ratio of the amorphous and crystalline phases.

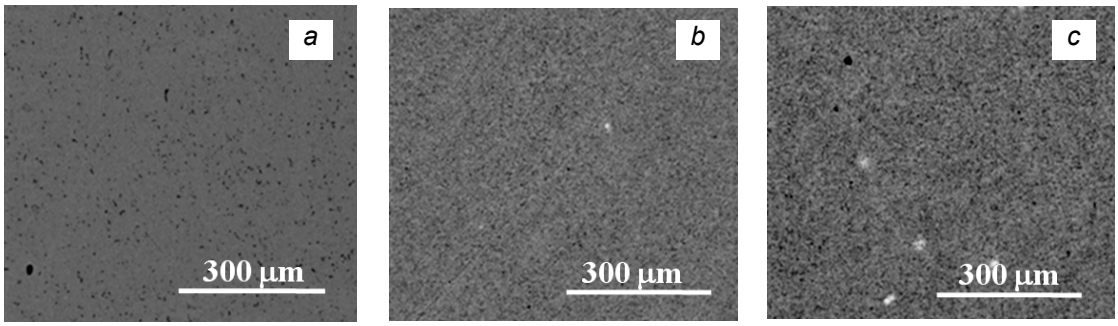

Fig. 1. EDX-mapping images of CaP coatings surfaces formed at RF- discharge power of 100 (*a*), 200 (*b*) and 250 W (*c*).

Table 1

The element composition, Ca/P-ratio and phase composition of coatings

RF-discharge power, W	Element content, at. %				Ca/P ratio	Crystal phase, % [9]	Amorphous phase, % [9]
	Ca	P	O	Ti			
100	1.41	0.25	53.45	42.40	5.64	-	-
200	3.10	0.83	61.02	34.19	3.73	78.1	21.9
250	4.37	1.53	64.06	27.30	2.86	74.9	25.1

Structure of coatings was studied after isothermal annealing at 700 °C. The coating structure depends on the RF-discharge power. Molecular bonds typical for hydroxyapatite are formed in the annealed coatings (Fig. 2). The PO_4^{3-} antisymmetric and symmetric fluctuations of P–O phosphoric bonds at 1130–1030 and 960–930 cm^{-1}, the absorption bands of OH^- groups at 3550–3200 cm^{-1}, 1650–1620 cm^{-1} and bands at 600–520 cm^{-1}, corresponding to triple-degenerated deformation oscillations of O–P–O bonds in the phosphate group are observed on IR spectra. The increase of RF-discharge power from 150 to 250 W leads to growth of the amplitude of PO_4^{3-} molecular bonds, that is confirmed with EDX data analyses.

Figure 3 shows typical indentations obtained during the scratch-test on the surface of titanium. According to measurement results of the adhesive strength of coatings it has been determined that under loading conditions of a spherical indenter in the load ranges of 0.3–10 N (Fig. 3, *a*) and 0.3–20 N (Fig. 3, *b*) the delamination of the CaP coating does not take place. However, in the case of indentation load in the range of 0.3–30 H the delamination of the CaP coating takes place under the load of 18.2 N (Fig. 3, *c*). Under this load the value of acoustic emission reaches 15 % and the friction coefficient takes a value of 0.23. In the load range of 20–23 N, a sharp increase in the friction coefficient value (up to 0.43) and the acoustic emission value (34 %) takes place. Further increase of the load leads to delamination of the calcium phosphate coating from the titanium substrate. Under the final indentation load of 30 N the value of the friction coefficient was 0.32 and the value of the acoustic emission was 32 %.

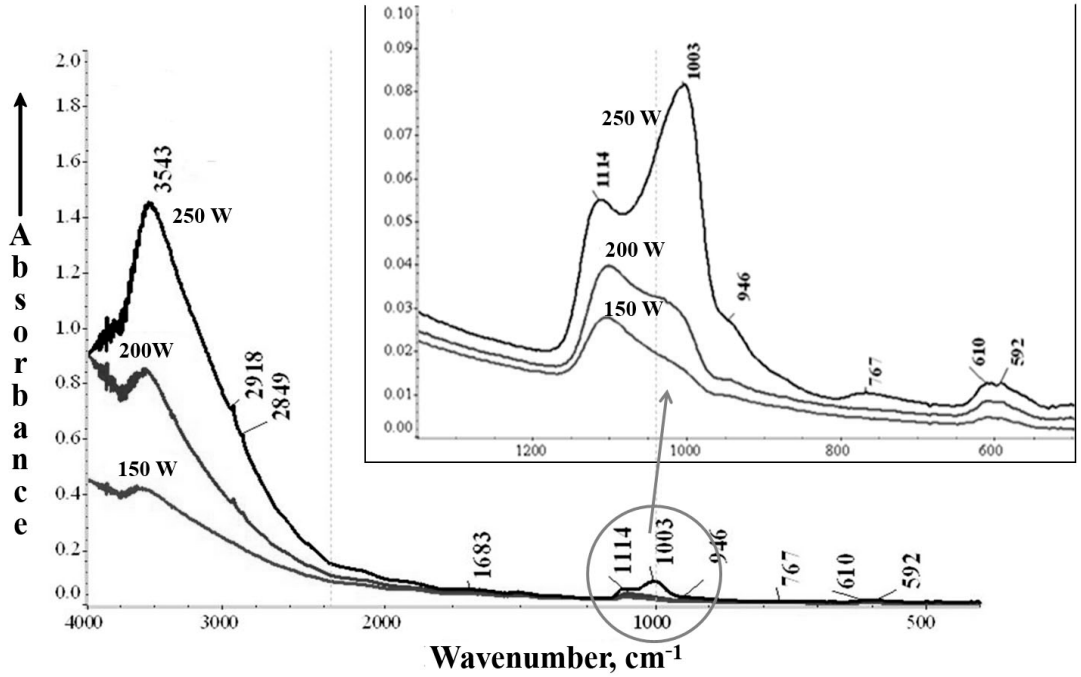

Fig. 2. IR spectra of the CaP coatings formed on titanium substrate at RF-discharge power of 150, 200, and 250 W.

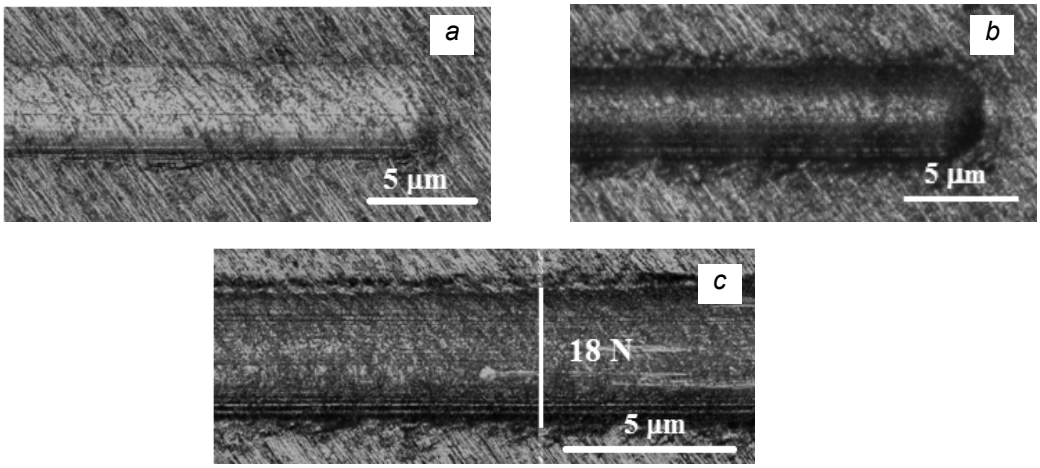

Fig. 3. Optical images of indentation on the CaP coating on titanium obtained during the scratch test under the final indentation load of 10 (*a*), 20 (*b*), and 30 N (*c*).

Based on the results of the microhardness measurements for Ti samples the dependence of the microhardness on the indentation load was plotted (Fig. 4, *a*). Figure 4, *b* shows the dependence of the microhardness on the indentation depth. The dependence of the microhardness on the load can be divided into two linear segments. The first segment has a large slope and the second one has a smaller slope. The change of angle slope occurs under the load 1.4 N. Under the specified load value the coating is completely "punctured" by the indenter and practically does not affect on the microhardness of the composite "metal substrate – CaP coating". It is evident that in the first straight-line part the microhardness decreases with a high rate. However, in the second part the loading effect on the microhardness is not observed.

Based on graphical dependences of the microhardness on the indentation depth (Fig. 4, *b*), the experimental values of critical indentation were obtained. The critical depth of indentation h_k was 2.98 μm.

The contribution of the coating microhardness and the substrate microhardness in the integrated microhardness of the composite "metal substrate – CaP coating" was evaluated according

$$H_f = H_s + \frac{h(H_\mu - H_s)}{C \cdot t}, \qquad (1)$$

where H_f is the coating microhardness; H_s is the substrate microhardness; H_μ is the microhardness of the composite "metal substrate – CaP coating". The contribution of the coating microhardness and the titanium microhardness were found to be 1780 and 2900 MPa. The microhardness of the composite "metal substrate – CaP coating" is equal to 3200 MPa.

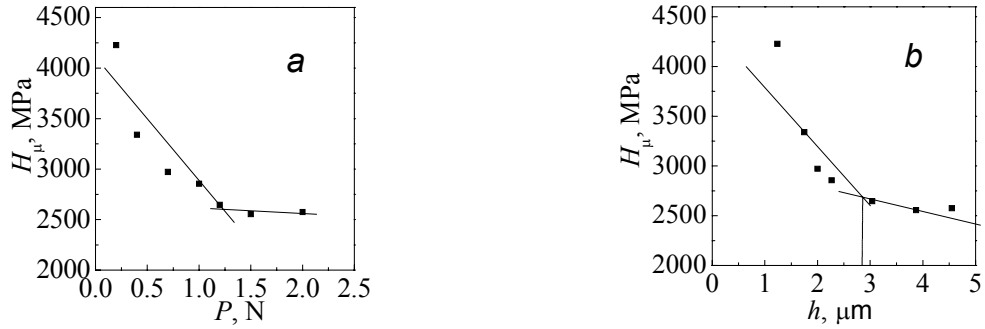

Fig. 4. The dependencies of the microhardness on the indentation load (*a*) and indentation depth (*b*).

Conclusions

The RF-magnetron calcium phosphate coating is homogenous, non-porous, without any defects. The Ca/P ratio is depended on the applied RF-discharge power, it decreases from 5.64 to 2.86 in interval of RF-discharge power of 100–250 W. It was experimentally established that the increase of power of RF-discharge up to 250 W provides a denser and thicker coating and promotes the formation of amorphous phase of the higher concentration. Molecular bonds typical for hydroxyapatite are formed in annealed coatings. The increase of RF-discharge power from 150 to 250 W leads to growth of the amplitude of PO_4^{3-} and OH^- molecular bonds. RF-magnetron CaP coatings characterized high value of the adhesive strength to the titanium surface. Mechanical properties of the composite material on the basis of the titanium substrate and a calcium phosphate coating are higher than ones of individual components.

REFERENCES

1. Valiev R.Z., Semenov I.P., Latysh V.V., et al. // Adv. Eng. Mater. – August 2008. – V. 10. – Iss. 8. – P. B15–B17.
2. Sharkeev Yu., Bratchikov A., Kolobov Yu., et al. // Physical Mesomechanics. – 2004. – V. 7. – P. 107–110.
3. Dorozhkin S. // Materials. – 2009. – V. 2. – P. 399–498.
4. Surmenev R.A. // Surf. Coat. Tech. – 2012. – V. 206. – P. 2035–2056.
5. Suminov I.V., Epelfeld A.V., Lyudin V.B. // Microarc Oxidation (theory, technology, equipment). – Moscow: ECOMET, 2005.
6. Hawking M. // Metallic and Ceramic Coatings: Production, Properties, and Application. – Moscow: Mir, 2000.
7. Sharkeev Yu.P., Glushko Yu.A., Kulyashova K.S., et al. // Izvestiya Vyschih Uchebnyh Zavedenii. Fizika. – 2014. – V. 3/3. – P. 275–279.
8. Manika I.P., Maniks Ya.E., Muktepavel F.O. // Determination of the microhardness of thin films and coatings. – Salaspils: Institute of Physics of the Academy of Sciences of the Latvian SSR, 1990.
9. Mamaeva A.A., Sharkeev Yu.P., Panichkin A.V., et al. // Kompleksnoe ispol'zovanie mineral'nogo syr'ya. – 2013. – V. 3.

*ISPMS of SB RAS, Tomsk, Russia
**National Research Tomsk Polytechnic University, Tomsk, Russia
***Center of Earth Sciences, Metallurgy and Ore Beneficiation, JSC, Almaty, Republic of Kazakhstan
****National Research Tomsk State University, Tomsk, Russia
E-mail: kseniya@ispms.tsc.ru

Article submitted October 1, 2014

Kulyashova Kseniya Sergeevna, Ph. D., researcher in the Laboratory of Physics of Nanostructured Biocomposites;
Sharkeev Yurii Petrovich, Dr., prof., head of the Laboratory of Physics of Nanostructured Biocomposites;
Mamaeva Axaule Alipovna, Ph. D., head of the Laboratory of Metals and Materials;
Panichkin Alexander Vladimirovich, Ph. D., vice-president of Center of Earth Sciences, Metallurgy and Ore Beneficiation, JSC;
Aubakirova Rashida Karimovna., Ph.D., leading researcher in the Laboratory of Metals and Materials;
Glushko Yurii Alekseevich, engineer in the Laboratory of Physics of Nanostructured Biocomposites;
Sainova Aizhan Bauyrzhanovna, Bachelor of Department Physico-Technical Faculty.