UDC 533.9;538.9 Complex Use of Mineral Resources. No 3. 2017

A. K. KENZHEGULOV[1,2], A. A. MAMAYEVA[1], A. B. PANICHKIN[1]*

[1]Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan
[2]Kazakh National Research Technical University named after K.I. Satpayev, Almaty, Kazakhstan,
**kazakh_1403@mail.ru*

ADHESION PROPERTIES OF CALCIUM PHOSPHATE COATINGS ON TITANIUM

Abstract: Biocompatible calcium phosphate coatings were obtained by high-frequency magnetron sputtering method on the titanium substrate of VT1-0 brand at a high-frequency plasma power of 200 W and a different sputtering time. The results of Auger spectroscopy study of the elemental concentrations of profiles along the depth of the obtained calcium phosphate films are presented. X-ray phase analysis results allowed to determine the detailed structure and phase composition of calcium phosphate coatings formed as a result of plasma-chemical reactions on a titanium substrate are presented. It was found that the diffraction peaks corresponding to hydroxyapatite shift toward larger angles and the magnitude of the interplanar spacing decreases, which is due to the process of formation of tri-calcium phosphate and titanium oxide. The data of sclerometric studies (scratch test) on the adhesion strength of the formed coatings to the substrate are given at different film thicknesses equal to 0.09 μm, 0.72 μm and 1.6 μm. According to the sclerometry data, films with a smaller thickness (0.09 μm) undergo degradation at much lower values of the load than samples with a higher thickness (0.72 and 1.6 μm). This is explained by the fact that films with a larger thickness have stronger adhesion and cohesive resistance. Thus, with an increase of the thickness of the calcium phosphate coating up to 1.6 μm, there is a significant improvement in adhesion characteristics.

Key words: calcium phosphate coating, high-frequency magnetron sputtering, indenter, acoustic emission, friction coefficient, titanium substrate

Introduction. Calcium phosphate (CP) compounds containing hydroxyapatite (HA) today are the most popular and implemented in medical applications, such as the manufacture of cement for regenerative surgery [1] or forming biocompatible coatings [2-4]. A number of methods have been developed to create coatings for HA on metal implants. Those already have commercial applications: plasma deposition [3], microarc oxidation [5] and methods based on crystallization coatings of different solutions [6], the method of detonation-gas spraying [7], electrochemical deposition, sol-gel dip coating [8], etc. Each technique has its own scope and certain limitations [9].

First of all, the coating must have a high adhesion to the substrate to ensure its high practicality. On medical implants with weakly-adhesive coatings, delamination can occur, which in turn significantly limits the effectiveness of the implant [10].

In accordance with current researches, the use of the magnetron sputtering method provides a high adhesion strength between the substrate and the coating. Under optimal experimental conditions, the coatings are close in stoichiometric composition to the composition of the initial target. High-frequency magnetron sputtering method (HFMS) is the most flexible, as it allows to vary the elemental composition of the coating by varying either the composition of the initial target for sputtering or deposition parameters (discharge power, the working gas, and others.) [11].

One of the most important features of biocompatible coatings is their resisting power. A scratch test method [12] is used to assess the adhesion strength of coatings and their physico-mechanical properties. The scratch test method is a simple, semi-quantitative method which can be applicable in measuring the adhesion strength of various coating-substrate systems. It consists of application of a normal load on the sample surface through the indenter, which moves along the surface of the sample at a constant speed [13]. The sclerometry method allows to reveal a threshold load on the coating at which the film breaks down and detaches from the substrate. Figure 1 shows the adhesion strength values of the HA coatings on Ti-6Al-4V using various production techniques.

Coatings obtained by magnetron sputtering have the highest adhesion to the substrate as compared to other methods. This is due to the possibility of combining the cleaning of the substrate surface by ion bombardment followed by sputtering [15, 16].

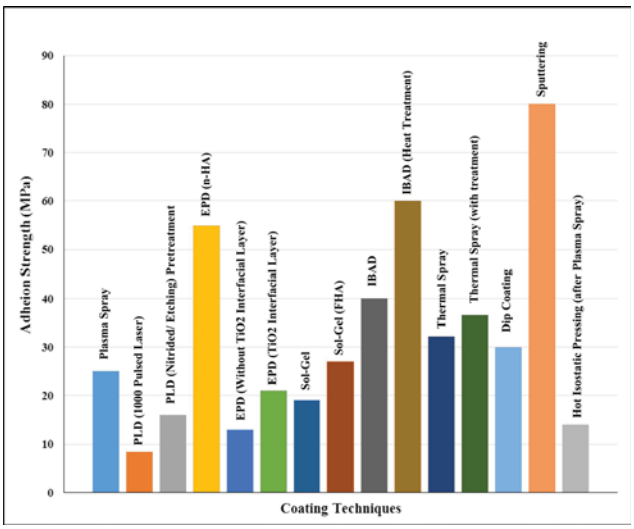


Figure 1 - Comparison of adhesion properties of coating obtained by different application methods [14]

The preliminary preparation of the substrate surface prior to deposition is important for high adhesion, since its purity determines the level of chemical bonding at the coating-substrate interface. In addition, the surface relief (roughness) greatly affects the strength of the adhesion of the bone tissue to the implant. This, in turn, creates the necessary conditions for germination of the cells of biostructures into cavities of various shapes with the formation of a strong connection between the implant and the tissue [17, 18]. In [19], coatings obtained by microarc oxidation were investigated, their structure, and morphology were studied. A high value of the roughness parameter, Ra, was noted. Also, in [20], the authors investigated the effect of heat treatment of biocomposites on their structure, morphology and, in particular, adhesion properties. To determine the scratch resistance and the mechanism of destruction of the CP films, a scratch test was carried out with an increasing load of 0.9 to 5 N. It was found that the coatings obtained had high wear resistance and adhesion characteristics, as well as low elasticity moduli and friction coefficient. CP coatings with high adhesion and cohesive properties, wear resistance are promising thin-film materials in medicine.

Thus, in order to reveal the adhesive properties of our samples, calcium phosphate coatings of different thicknesses on a titanium substrate were obtained by the authors. For rapid germination (ostiointegration), it is necessary to have a structure with a developed surface, which has high adhesion and cohesive properties, wear resistance. Proceeding from this, the aim of the work was to study the adhesion properties of calcium phosphate coatings on a titanium substrate of grade T1-0, formed with the help of plasma of high-frequency magnetron discharge.

Experimental part. *Research methods and materials*. For the application of CP coatings, an upgraded installation were used, defined as a vacuum universal post with a magnetron source VUP-5M. The operating frequency of the high-frequency (HF) generator is equal to 5.28MHz. The following sputtering coating modes were used: the working pressure in the chamber after the argon inlet was 0.1 Pa, the distance between the target and the substrate was 40 mm, the sputtering time, depending on the required thickness, was 10, 80, 190 min.

Prior to the deposition process, the pressure in the reaction vacuum chamber was reduced to a value of $9 \cdot 10^{-3}$ Pa. The substrate was heated to 900 °C. Further, an ultra high purity argon was fed into the chamber until the working pressure of 0.1 Pa was reached and stabilized in the chamber. The residual pressure was monitored automatically using the RGG-3 gas flow regulator system with an accuracy of ± 0.1 Pa. After reaching the required pressure, the power supplies of the heater and the power supply of the high-frequency generator were switched on, and in the working volume of the vacuum chamber a high-frequency plasma was ignited between the target and the substrate in the argon gas atmosphere. Then a magnetron was connected at a radiation power of the generator of 200 W, and due to plasma-chemical reactions on the titanium substrate a coating was deposited.

Titanium plates of VT1-0 brand with chemical composition in%: Fe-0.25, Si-0.1, Ti-99.7, O-0.2 were used as substrates. A disk with 120 mm in diameter target from a pressed powdered HA functioned as a target. The dispersion of the HA particles was equal to <63 μm.

The profiles study of the basic elements concentration in the depth of the obtained CP films was carried out by the Auger spectroscopy method using a Skhuna-2 device (NPO Electron, Russia). Adhesive properties of CP coatings were measured using a Revetest scratch tester (CSM Instruments, Switzerland). The studies were carried out in the Laboratory of Nanostructural Biocomposite Physics at the Tomsk Polytechnic University.

The phase composition study of the samples was carried out using the diffractometer D8 Advance (Bruker, USA) at the National Scientific Laboratory for Collective Use in the Priority Direction of "Technologies of the Hydrocarbon

and Mining and Metallurgical Sectors and Related Service Industries" of the Institute of Metallurgy and Ore Beneficiation. Radiographs were obtained using copper radiation (λ = 1.5406 Å) in a digital form. The processing of X-rays to determine the angular position and intensity of the reflexes was carried out by the program Origin Pro 8.1. During the phase analysis the PCPDFWIN program with the PDF-2 diffractometric data base were used.

Results and discussion. The main structural elements of the hydroxyapatite sputtered target such as calcium, phosphorus, oxygen, and also titanium (substrate) can be found on Auger spectra of CP coatings with a thickness of 0.72 μm. As can be seen in the Figure 2, the elements are equally distributed over the depth of the film and completely cover the substrate. In the contact area between the film and sample surface, the profile overlapping of the coating and substrate elements can be observed, which shows the formation of chemical connection of the film with the substrate and provides good adhesion.

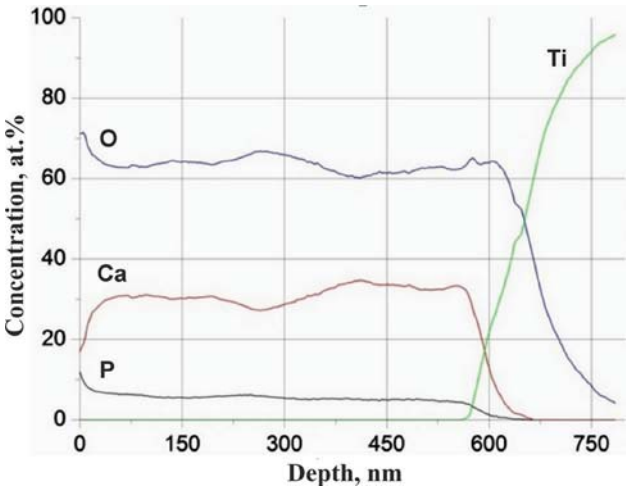


Figure 2 – The main elements concentration profiles along the thickness of CP coatings formed by the HFMS method within 80 min (thickness - 0.72 μm).

On the diffractogram (Figure 3) there are reflections from the (002), (211), (310), (213) planes corresponding to hydroxyapatite (JCPDS # 09-0432), Ti (200), (101) (JCPDS # 44 -1294), calcium oxide (220) (JCPDS # 77-2376) and titanium oxide (213) (JCPDS # 21-1272). The X-ray diffraction pattern of the target HA and the obtained coating shows the presence of the peaks $Ca_{10}(PO_4)_6(OH)_2$, Ti, CaO, TiO_2 и β-$Ca_3(PO_4)_2$. The diffraction lines corresponding to the HA are shifted toward larger angles, and accordingly the value of the interplanar distances decreases, which is apparently due to the formation of tricalcium phosphate and titanium oxide.

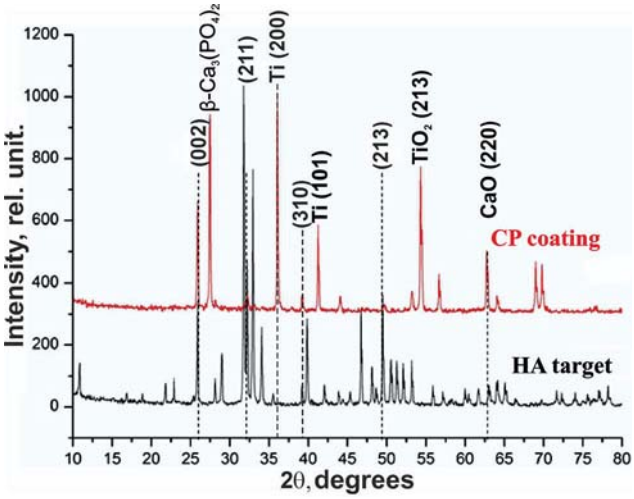


Figure 3 - X-ray patterns of HA target and synthesized CP coatings (thickness- 1.6 μm).

Adhesion of the resulting CP coating was measured by sclerometry method. The parameters of the scratch test were as follows: the maximum load was 2 N, the rate of change of the normal loading on the sample was 2 N/min, the speed of the indenter was 7 mm/min, the scratch length was 7 mm, and the tip curvature was 20 μm.

Adhesive properties were measured on coatings with thicknesses of 0.09 μm, 0.72 μm and 1.6 μm. Figures 4-7 show the measurements of acoustic emission (AE) and the coefficient of resistance (CR) obtained during the coating scratch test. By changing the curves of the dependence of the CR and AE on the load on the indenter, the critical values that characterize the plastic indentation of the indenter into the substrate with peeling of the coating are fixed. These results were monitored using the built-in optical microscope Revetest.

Figure 4 shows the dependence of the change in the CR and the signal AE, which arise when indenter is pressed into the coating. The parameters of the sample are as follows: the sputtering time of the HA is 10 minutes, the thickness of the formed coating is 0.09 μm. The destruction of the CP coating begins when the intensity of the indenter is 0.27 N, as shown in Figure 4a. In this case, there is a sharp increase in both AE and CR, which confirms the beginning of the process of destruction of the coating. The microphotographs of the coating surface show traces of scratches when the intensity of the indenter loading is 0.08 N and 0.27 N (Figures 4b and 4c, respectively).

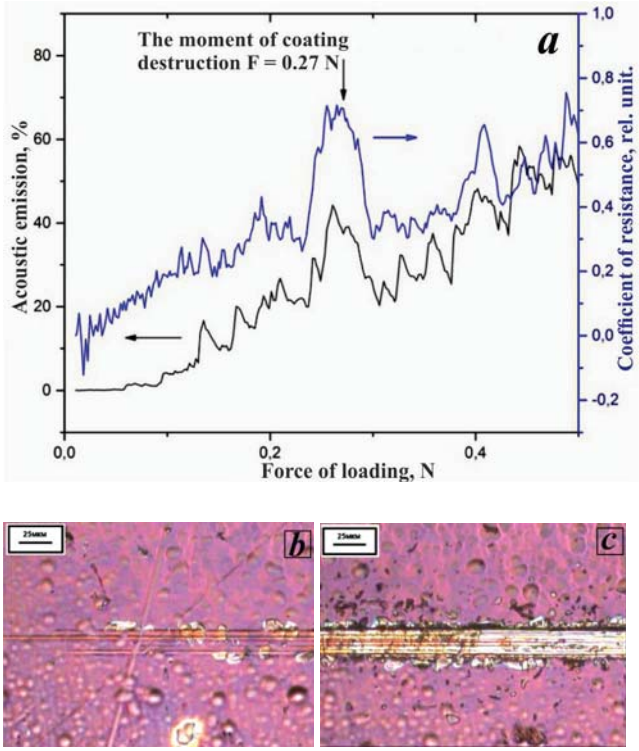


Figure 4 - Change in CR and AE signal with increasing applied load for CP coatings (4a) and coating microphotography under load F = 0.08 N (4b) and F = 0.27 N (4c)

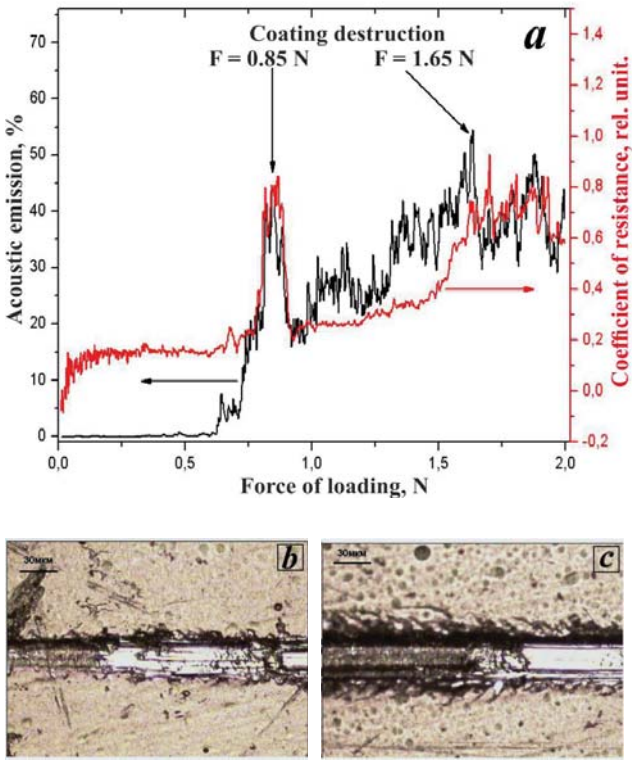
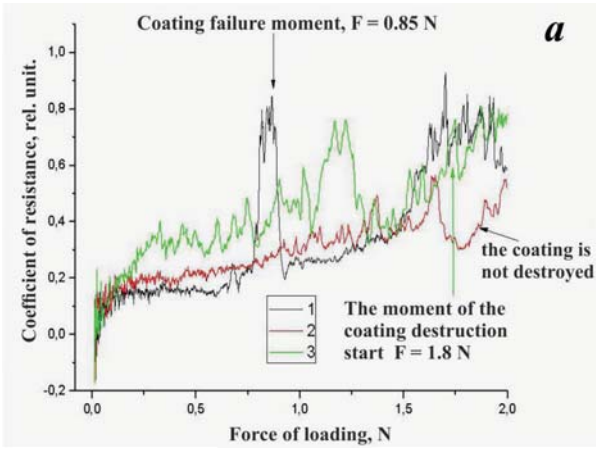


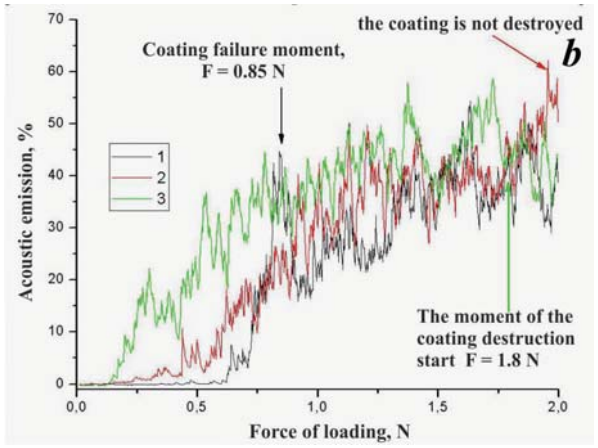
Figure 5 - Change in CR, AE signal (5a) with increasing applied load for CP coatings and surface microphotography under load F = 0.85 N (5b) and F = 1.65 N (5c).

Figure 5 shows the dependencies of the CR and AE on one of the three scratch tests performed for a sample with a coating thickness of 0.72 μm (the sputtering time is 80 minutes). The presence of the first minor changes in the amplitude of the AE is due to the parameters of the surface roughness. As the loading force increases, the coating degrades, but with further displacement of the indenter, there are no visible signs of destruction of the coating, both in the scratching zone and along its edges (Figure 5). This indicates a high cohesive and adhesion strength of CP coatings formed by the method of HFMS. The destruction of the CP coverage area at a load of 0.85 N is shown in a micrograph (Figure 5b). However, figure 5c confirms that individual areas of coating of CP on titanium have high adhesion.

To analyze the adhesion properties of the surface of the CP, scratch tests were performed at different sites. It should be noted that one of the three scratches made on a CP coating with a thickness of 0.72 μm did not lead to the destruction of the coating at a load of 2 N. On the microphotography of the scratch, the deformation front is noticeable in the form of waves of forward needles. At a maximum load of 2 N, at the end of the scratch, "bulk" is observed, which indicates a high plasticity of the coating (Figure 6c) [12]. There are no swelling of the surface near the scratch, which indicates a high value of adhesion. From the data presented on the graph of AE and CR dependences (Figures 6a and 6b) on the loading force, it is determined that the load at 1.8 N corresponds to the beginning of the surface destruction. In addition, the scratch test showed that further loading did not lead to the destruction of the coating, which is clearly seen in the micrograph (Figure 6c). This high adhesion strength is achieved through the formation of chemical bonds between the coating elements and the substrate at the interface.

In the case of a coating with a thickness of 1.6 μm, the nature of the coating damage was significantly different from the thin coatings of the CP (0.72 and 0.09 μm). Scratch test of this sample showed the formation of splits and chips along the scratching at a load of already 0.54 N (Figure 7b). The increase in the load leads to a change in the CR and the amplitude of the AE (Figure 7a). With a loading force of 0.81 N, the indenter pushes the coating, which is observed on a micrograph (Figure 7c). The beginning of the destruction of the film was fixed at a load value of 0.81 N (Figure 7a). Analysis of literature data showed that the adhesion strength of coatings with a thickness of up to 1.6 μm is greater than 40 MPa [21].





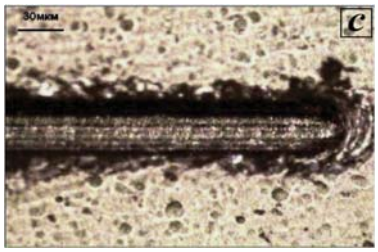
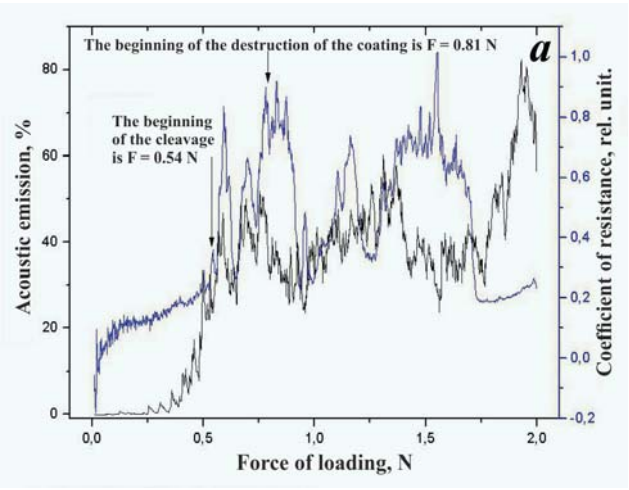


Figure 6 - Change in CR, AE signal (6a, 6b) with increasing applied load on the CP coating and surface microphotography under load F = 2 N (6c)

The reason for the high adhesion strength is most likely a thin oxide layer of TiO_2, which promotes the formation of a strong covalent bond between the substrate and the coating [22], and also correlates well with X-ray phase analysis data (Figure 3). In addition, this is confirmed by the fact that even with the force of the load on the CP coating in 2 N, there was no destruction.

Thus, sclerometry data suggest that films with a smaller thickness (0.09 μm) undergo disruption at significantly lower load values than samples with a higher thickness (0.72 and 1.6 μm). This is explained by the fact that films with a thickness of 0.72 and 1.6 μm have higher strength adhesion and cohesive resistance.



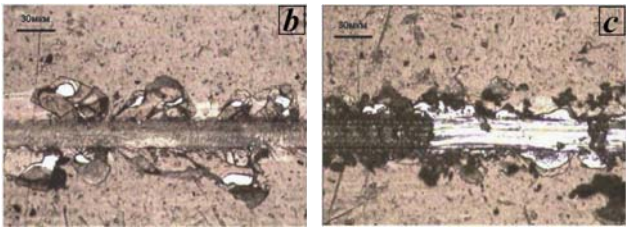


Figure 7 - Dependences of AE and CR (7a) CP coatings with a thickness of 1.6 μm and surface micrographs at a load of F = 0.54 N (7b) and F = 0.81 N (7c)

Conclusions. Through the use of high-frequency magnetron sputtering, thin calcium phosphate coatings with high substrate adhesion were formed. Analysis of the experimental results obtained in the study of the structure and adhesion properties of CP coatings of different thicknesses: 0.09 μm, 0.72 μm and 1.6 μm showed that with an increase in the thickness of calcium phosphate coatings up to 1.6 μm, adhesion properties improve. Films with a thickness of 0.72 and 1.6 μm had rather strong adhesion and cohesive resistance. Thus, as a result of the research, optimal experimental regimes and parameters were determined for obtaining qualitative CP coatings.

REFERENCES

1 Schnettler R., Stahl J.P., Alt V., Pavlidis T., Dingeldein E., Wenisch S. Calcium phosphate-based bone substitutes. *European Journal of Trauma*. **2004.** *30(4).* 219–229. (in Eng.)

2 Pichugin V.F., Surmenev R.A., Shesterikov E.V., Ryabtseva M.A., Eshenko E.V., Tverdokhlebov S.I. The preparation of calcium phosphate coatings on titanium and nickel-titanium by rf-magnetron sputtered deposition: composition, structure and micromechanical properties. *Surf. Coat. Technol.* **2008.** *202(39).* 13–20. (in Eng.)

3 Sun L., Berndt C.C., Gross K.A. et al. Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: a review. *Biomed. Mater.Res.* **2001.** *58(5).* 570–592. (in Eng.)

4 Callahan, T.J., Gantenberg, J.B., and Sands, B.E. Calcium phosphate coating draft guidance for preparation of food and drug

administration submissions for orthopedic and dental endosseous implants. *Characterization and performance of calcium phosphate coatings for implants: ASTM STP 1196, Emanuel Horowitz and Jack E. Parr, ASTM*, Philadelphia, **1994,** 185-197. (in Eng.)

5 Inagaki M., Yokogawa Y., Kameyama T. Apatite/titanium composite coatings on titanium or titanium alloy by RF plasma-spraying process. *Thin Solid Films.* **2001.** *386(2)*. 222–226. (in Eng.)

6 Zamoume O., Thibault S., Regnie G., Mecherri M.O., Fiallo M., Sharrock P. Macroporous calcium phosphate ceramic implants for sustained drug delivery. *Mater Sci Eng.* **2011.** *289*. 1352–1356. (in Eng.)

7 Yakovlev V.I. *Ehksperimentalno-dyagnosticheskij kompleks dlya issledovanya poroshkovykh SVS-materialov pri detonatsionno-gazovom napylenii* (Experimental-diagnostic complex for the investigation of powdered SHS-materials in detonation-gas spraying): *avtoref. dis… kand. tekhn. nauk* (Abstract of thesis for Cand. of Tech. Sci) / Altai State Technical University. Barnaul, **2003.** 19 (in Russ.)

8 Asri R.I.M., Harun W.S.W., Hassan M.A., Ghani S.A.C., Buyong Z., A review of hydroxyapatite-based coating techniques: sol-gel and electrochemical depositions on biocompatible metals. *Journal of the Mechanical Behavior of Biomedical Materials*. **2015**. *9*. 267-325. (in Eng.)

9 Yang Y., Kim K.H, and Ong J. L., A review on calcium phosphate coatings produced using a sputtering process – an alternative to plasma spraying. *Biomaterials.* **2005.** *26*. 327–337. (in Eng.)

10 Lacefeld W.R., Hydroxyapatite coatings. *An Introduction to Bioceramics.* Singapore: World Scientific Publishing Co. Pte. Ltd., **1993.** 223–238. (in Eng.)

11 Tverdohlebov S.I., Shesterikov E.V., Malchihina A.I. *Osobennosti formirovaniya kaltsij-phosphatnykh pokrytij metodom VCH mgnetronnogo napyleniya na implantatakh* (Features of formation of calcium-phosphate coatings by the method of high-frequency magnetron sputtering on implants). *Izvestiya Tomskogo politekhnicheskogo universiteta =Proceedings of Tomsk Polytechnic University.* **2012.** *320(2).* 73-79.(in Russ.)

12 Surmenev M.A., Surmenev R.A., Pichugin V.F., Koval N.N., Teresov A.D., Ivanova A.A., Grubova I.Yu., Ignatov V.P., Primak O., Epple M. *Issledovanie adgezionnyh svojstv kremnijsoderzhashego kaltsij-phosphatnogo pokrytiya, osazhdennogo metodom VCH magnetronnogo raspyleniya na nagretuyu podlozhku* (Investigation of the adhesive properties of a silicon-containing calcium-phosphate coating deposited by HF magnetron sputtering on a heated substrate). *Poverhnost. Rentgenovskie, sinkhrotronnye I nejtronnyeissledovaniya = Surface. X-ray, Synchrotron and Neutron Studies.* **2013**. *10*. 32–40. (in Russ.)

13 Valli J., Makela U., Matthews A., Murawa V. TiN coating adhesion studies using the scratch test method. *Vac. Sci.Technol. A: Vac. Surf. Films.* **1985.** *3*. 2411-2414. (in Eng.)

14 Mohseni E., Zalnezhad E., Bushroa A.R. Comparative investigation on the adhesion of hydroxyapatite coating on Ti-6Al-4V implant: a review paper. *International Journal of Adhesion & Adhesives.* **2014.** *48*. 238–257. (in Eng.)

15 Lin J.C., Liu M., Ju C. Structure and properties of hydroxyapatite–bioactive glass composites plasma sprayed on Ti6Al4V. *Journal of Materials Science: Materials in Medicine*. **1994.** *5*. 279–283. (in Eng.)

16 Lacefield W. Hydroxyapatite coatings. *Annals of the New York Academy of Sciences.* **1988.** *523.* 72–80. (in Eng.)

17 Li D., Ferguson S.J., Beutler T., Cochran D.L., Sittig C., Hirt H.P., Buser D. Biomechanical comparison of the sandblasted and acid-etched and the machined and acid-etched titanium surface for dental implants. *Biomed. Mater.Res.* **2002.** *60*. 325. (in Eng.)

18 Rodionov I.V. Sozdanie biosovmestimyh pokrytij na meditsinskih titanovyh implantatah anodirovaniem v sernokislyh eletrolitah (Creation of biocompatible coatings on medical titanium implants by anodizing in sulphate electrolytes). *Perspektivnyye materialy = Perspective materials.* **2008.** *6*. 45-54. (in Russ.)

19 Mamayeva A.A., Kenzhegulov A.K., Panichkin A.V., Kalipekova M.A. *Poluchenie kaltsij-phosphatnyh pokrytij na titanovoi podlozhke v usloviyakh mikrodugovoj obrabotki* (Preparation of calcium phosphate coatings on a titanium substrate under conditions of microarc oxidation). *Kompleksnoe ispol'zovanie mineral'nogo syr'ya = Complex Use of Mineral Resources.* **2017**. *2*. 33-40. (in Eng.)

20 Mamayeva A.A., Panichkin A.V., Kenzhegulov A.K. Merkibaev E.C. *Issledovanie vliyanie na sostav, strukturu, morphologiyu biokompozita* (Investigation of the effect of heat treatment on the composition, structure, morphology of the biocomposite). *Resursosberegeyushie tehnologij v obogoshenij rud i metallurgij tsetnyh metallov: mater. mezhduna. konf.* (Resource-saving technologies in the enrichment of ores and metallurgy of non-ferrous metals: proceedings of Internation. Conf.) Almaty, Kazakhstan. **2015.** 261-265. (in Russ.)

21 Chen M., Liu D., You C., Yang X., Cui Z. Interfacial characteristic of graded hydroxyapatite and titanium thin film by magnetron sputtering. *Surface & Coatings Technology.* **2007.** *201*. 5688–5691. (in Eng.)

22 A. von Keudell. Surface processes during thin-film growth. *Plasma Sources Sci. Technol.* **2000**. *9.* 445. (in Eng.)

ЛИТЕРАТУРА

1 Schnettler R., Stahl J.P., Alt V., Pavlidis T., Dingeldein E., Wenisch S. Calcium phosphate-based bone substitutes. // European Journal of Trauma. 2004. – N 30(4). – P. 219–229.

2 Pichugin V.F., Surmenev R.A., Shesterikov E.V., Ryabtseva M.A., Eshenko E.V., Tverdokhlebov S.I. The preparation of calcium phosphate coatings on titanium and nickel-titanium by rf-magnetron sputtered deposition: composition, structure and micromechanical properties. // Surf.Coat.Technol. 2008. – N 202(39). – P. 13–20.

3 Sun L., Berndt C.C., Gross K.A. et al. Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: a review. // Biomed. Mater.Res. – 2001. – N 58(5). – P. 570–592.

4 Callahan T.J., Gantenberg J.B., and Sands B.E. Calcium phosphate coating draft guidance for preparation of food and drug administration submissions for orthopedic and dental endosseous implants // Characterization and performance of calcium phosphate coatings for implants: ASTM STP 1196, Emanuel Horowitz and Jack E. Parr, ASTM, – Philadelphia, 1994, – P. 185-197.

5 Inagaki M., Yokogawa Y., Kameyama T. Apatite/titanium composite coatings on titanium or titanium alloy by RF plasma-spraying process. // Thin Solid Films. – 2001. – N 386(2). – P. 222–226.

6 Zamoume O., Thibault S., Regnie G., Mecherri M.O., Fiallo M., Sharrock P. Macroporous calcium phosphate ceramic implants for sustained drug delivery. // Mater Sci Eng. – 2011. – N 289. – P. 1352–1356.

7 Яковлев В.И. Экспериментально-диагностический комплекс для исследования порошковых СВС-материалов при детонационно-газовом напылению: автореферат дис… канд. техн. наук / Алтайский Государственный Технический Университет – Барнаул, 2003. – 19 с.

8 Asri R.I.M., Harun W.S.W., Hassan M.A., Ghani S.A.C., Buyong Z., A review of hydroxyapatite-based coating techniques: sol-gel and electrochemical depositions on biocompatible metals. // Journal of the Mechanical Behavior of Biomedical Materials. – 2015. – N 9. – P. 267-325.

9 Yang Y., Kim K.H, Ong J. L., A review on calcium phosphate coatings produced using a sputtering process – an alternative to plasma spraying. // Biomaterials. – 2005. – N 26. – P. 327–337.

10 Lacefeld W.R., Hydroxyapatite coatings // An Introduction to Bioceramics. – Singapore: World Scientific Publishing Co. Pte. Ltd., 1993. – P. 223–238.

11 Твердохлебов С.И., Шестериков Е.В., Мальчихина А.И. Особенности формирования кальций-фосфатных покрытий методом ВЧ магнетронного напыления на имплантатах. // Известия Томского политехнического университета. – 2012. – № 320(2). – С. 73-79.

12 Сурменева М. А., Сурменев Р. А., Пичугин В. Ф., Коваль Н. Н., Тересов А. Д., Иванова А. А., Грубова И. Ю., Игнатов В. П., Примак О., Эппле М. Исследование адгезионных свойств кремнийсодержащего кальций-фосфатного покрытия, осажденного методом ВЧ магнетронного распыления на нагретую подложку. // Поверхность. Рентгеновские, синхротронные и нейтронные исследования. – 2013. – № 10. – С. 32–40.

13 Valli J., Makela U., Matthews A., Murawa V. TiN coating adhesion studies using the scratch test method. // Vac. Sci.Technol. A: Vac. Surf. Films. – 1985. – N 3. – P. 2411-2414.

14 Mohseni E., Zalnezhad E., Bushroa A.R. Comparative investigation on the adhesion of hydroxyapatite coating on Ti-6Al-4V implant: a review paper. // International journal of adhesion & adhesives. – 2014. – N 48. – P. 238–257.

15 Lin J.C., Liu M., Ju C. Structure and properties of hydroxyapatite–bioactive glass composites plasma sprayed on Ti6Al4V. // Journal of materials science: materials in medicine. – 1994. – N 5. – P. 279-283.

16 Lacefield W. Hydroxyapatite coatings. // Annals of the New York Academy of Sciences. – 1988. – V 523. – P. 72–80.

17 Li D., Ferguson S.J., Beutler T.,Cochran DL, Sittig C., Hirt H.P., Buser D. Biomechanical comparison of the sandblasted and acid-etched and the machined and acid-etched titanium surface for dental implants. // Biomed. Mater.Res. – 2002. – N 60. – P. 325-333.

18 Родионов И.В. Создание биосовместимых покрытий на медицинских титановых имплантатах анодированием в сернокислых электролитах. // Перспективные материалы. – 2008. – № 6. – С. 45-54.

19 Мамаева А.А., Кенжегулов А.К., Паничкин А.В., Калипекова М.А. Получение кальций–фосфатных покрытий на титановой подложке в условиях микродуговой обработки. // Комплексное использование минерального сырья. – 2017. – № 2. – С. 33-40.

20 Мамаева А.А., Паничкин А.В., Кенжегулов А.К., Меркибаев Е.С. Исследование влияния термообработки на состав, структуру, морфологию биокомпозита // Ресурсосберегающие технологии в обогащение руд и металлургии цветных металлов: матер. междунар. конф. – Алматы, Казахстан, 2015. – С. 261-265.

21 Chen M., Liu D., You C., Yang X., Cui Z. Interfacial characteristic of graded hydroxyapatite and titanium thin film by magnetron sputtering. // Surface & Coatings Technology. – 2007. – N 201. – P. 5688-91

22 A. von Keudell. Surface processes during thin-film growth. // Plasma Sources Sci. Technol. – 2000. – N 9. – P. 445.

ТҮЙІНДЕМЕ

Жоғары жиілікті магнетрондық тозаңдандыру әдісімен 200 Вт плазма қуатымен және әртүрлі тозаңдандыру уақыты аралығында ВТ1–0 маркалы титан бетіне биоүйлесімді кальций-фосфаттық жабындылар алынды. Оже спектроскопиясы әдісімен кальций-фосфаттық жабындылардың тереңдігінен алынған элементтер конценрациясының профиль нәтижелері көрсетілген. Магнетрондық плазмада алынған кальций-фосфаттық жабындылардың фазалық құрамы мен құрылымы рентгенфазалық анализі арқылы сипатталған. ГА тиесілі дифракциондық шыңдардың үлкен шыңдар аймағына ығысатыны байқалды, оның себебі трикальцийфосфат пен титан оксидінің құрылуынан екені анықталды. Қалыңдығы 0.09 мкм, 0.72 мкм и 1.6 мкм болатын жабындыларға склерометриялық зерттеулер жүргізілген. Кальций-фосфаттық жабындылардың қалыңдығы 1.6 мкм шамасына дейін үлкейген сайын адгезиялық қасиеттерінің жақсаратыны анықталды.

Түйінді сөздер: кальций-фосфаттық жабынды, жоғары жиілікті магнетрондық тозаңдандыру, индентор, акустикалық эмиссия, үйкелу коэффициенті

РЕЗЮМЕ

Биосовместимые кальций-фосфатные покрытия получены методом высокочастотного магнетронного распыления на подложке из титана марки ВТ1–0 при мощности высокочастотной плазмы 200 Вт и различном времени напыления. Представлены результаты исследований профилей концентраций элементов по глубине полученных кальций-фосфатных пленок методом Оже спектроскопии. Приведены результаты исследований методом рентгенофазового анализа, который позволил детально определить структуру и фазовый состав кальций-фосфатных покрытий, образующихся вследствие плазмохимических реакций на титановой подложке. Было установлено, что дифракционные пики, соответствующие гидроксиапатиту, смещаются в сторону больших углов, а величина межплоскостных расстояний уменьшается, что связано с процессом образования трикальцийфосфата и оксида титана. Приведены данные склерометрических исследований (scratch test) на прочность сцепления сформированных покрытий с подложкой при разных значениях толщины пленок, равных 0.09 мкм, 0.72 мкм и 1.6 мкм. Согласно данным склерометрии, пленки с меньшей толщиной (0.09 мкм) претерпевают разрушение при значительно более низких значениях нагрузки, чем образцы с более высоким показателем толщины (0.72 и 1.6 мкм). Это объясняется тем, что пленки с большей толщиной обладают более прочной адгезией и когезионным сопротивлением. Таким образом, с увеличением толщины кальций-фосфатного покрытия до значений 1.6 мкм происходит значительное улучшение адгезионных характеристик.

Ключевые слова: кальций-фосфатное покрытие, высокочастотное магнетронное распыление, индентор, акустическая эмиссия, коэффициент трения, титановая подложка

Received 11.08.2017