Surface Morphology and Properties of Calcium Phosphate Thin Films Formed by Plasma of rf-Magnetron Discharge[1]

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Abstract – Radio frequency magnetron sputtering process has been used for the deposition of calcium-phosphate (Ca-P) coatings from 0.1 to 2.7 μm thickness on the material of medical implants. The structure of deposited coating is uniform, dense, without any visible defects. Elements content in the film is: oxygen O – 41.1 ± 0.7 at.%, calcium Ca –45.4 ± 1.0 at.%, phosphorus P – 13.6 ± 0.5 at.%. The elements are distributed uniformly in the coating. The mechanical properties such as nanohardness (*H*), Young's modulus (*E*) were determined, besides the values of *H* and *E* of the coatings are higher than that ones for titanium substrate. The adhesion strength (along with cohesive resistance) has a high value, besides the behavior of coating's destruction differs from that one for thicker coatings.

1. Introduction

Hydroxyapatite (HAP)-$Ca_{10}(PO_4)_6(OH)_2$ is one of the representatives of the calcium-phosphate materials and it is widely used as the initial material for synthesis of the coatings for medical application, moreover HAP may be used as a powder having different particles size or granules. HAP is the main part of the bone matrix with the stochiometric ratio calcium – Ca to phosphorus – P equals 1.67. Due to this fact HAP is known as a material with high biocompatibility [1].

Nowadays there are many techniques to deposit the coatings for medical application. The most widely used techniques are: plasma spray technique [2, 3, 4, 5], sol-gel method [6], the ablation method [7, 8], the micro-arc deposition method [9]. The each of above-mentioned techniques have the own limitations, for example, low value of the adhesion strength of the coating to the substrate, the limitation for choice a material for coating's preparation (for instance, it is impossible to deposit the coating on the surface of 316L stainless steel using the micro-arc deposition method) etc.

At the end of the XX century an intensive application of the radio frequency magnetron (rf-magnetron) sputtering began [10 – 13]. The frequency of the working generator is 13.56 MGz. The radio-frequency system was chosen because a usage of this way is easier for HAP sputtering, which is an insulation material. The sputtering of the HAP is more effective on high (radio) frequency due to specific character of this technique. The carried out investigations shown that using rf-magnetron sputtering one can obtain a high values of the adhesion strength between a material – basis and the coating, and a composition of the coating is closer to stochiometric composition of initial target for sputtering. Carried out biomedical investigations promote more fast propagation of the marrow cells on coated surface with comparison of uncoated one.

The aim of the present work is deposition of calcium-phosphate thin ceramic coatings (Ca-P coatings) for medical application by the rf-magnetron sputtering technique and investigation of their texture, elemental composition, mechanical and physicochemical characteristics.

2. Materials and methods

For carrying out of the aims of this study the following experimental equipment and methods were used. The method of Rutherford backscattering (RBS) (at an angle of $\Theta = 175^O$) of the 1.7 MeV alpha particles has been applied (the spectrometer energy resolution is less then 11 keV) to investigate the elemental composition of the Ca-P coating; the surface morphology was investigated by Scanning Electron Microscopy (SEM PHILIPS 515); the surface texture was plotted using the optical profilometer 3D-MICRO MEASURE 3D station; mechanical characteristics were studied by the dynamic nanoindentation method (nanohardness – *H*, Young's modulus – *E*, contact stiffness – *S*); the scratch test (adhesion strength) was carried out on the device Micro scratch tester MST-S-AX-0000; IR spectroscopy technique have been used to differentiate the chemical bonds in different groups of coating elements. The optical absorption spectra are studied in transparent light by IR Fourier spectrometer Nicolet 5700, the spectral region 500 – 4000 cm $^{-1}$. The FTIR spectra are controlled by a computer program Origin 41, and described in accordance with the atlas standards.

As materials for deposition were chosen the following materials: technical pure titanium, 316L stainless steel, the titanium alloy Ti6Al4V. All these materials are the wide-used in orthopedy and stomatology.

Thin Ca-P coatings were deposited with the installation "Cathode 1M", where a source of rf sputtering was placed into a vacuum chamber. The working frequency of the source is 13.56 MGz. The target for

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spattering was made by ceramic technology from hydroxyapatite. The conditions of deposition are follows: working gas is Ar at the pressure 0.5 Pa, the distance between the magnetron and the substrates is 50 mm, the incident power is 2 kW, reflected power is 250 W. The procedure of surface preparation before sputtering was carried out according to such sequence: boiling into carbon tetrachloride, drying by gas nitrogen in vapors of the isopropyl alcohol, ion cleaning in the Ar atmosphere at the pressure 5 Pa.

3. Results and Discussions

In the Figure 1 shown the texture of the surface coating on the titanium substrate. It is shown that the coating is solid without pores and micro cracks.

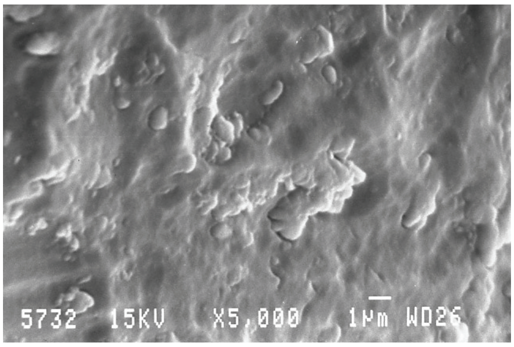
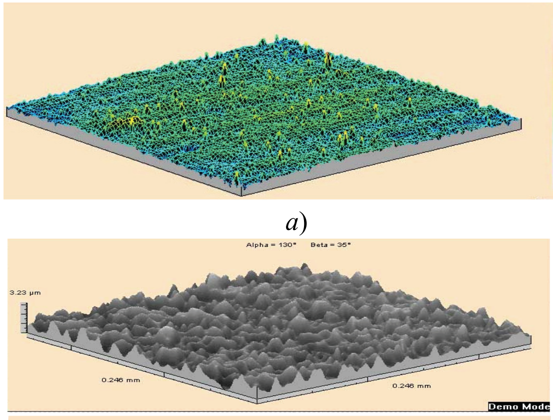


Fig. 1. The texture of the Ca-P coating on the titanium substrate. Magnification is 5000

The morphology of the surface obtained with 3D-MICRO MEASURE 3D station shown in the Figure 2*a* (the sputtering time is 50 min, the film thickness is 450 nm) and in the Figure 2*b* the morphology of the coating surface having thickness 2.7 μm (5 hour sputtering). The dimension of scans is 0.246×0.246 mm. It is necessary to notice that the roughness of the coatings is greatly different. In the Figure 2 *a* as we suppose the centers of crystallization are observed (like uniform distributed inhomogeneity), which only begin to appear. In the Figure 2*b* this phenomenon is observed clearer. The texture of the surface has the determined waveness that were reported by the authors in the study as well [11], when they were investigating the Ca-P coatings, deposited with using the rf-magnetron sputtering technique, but at the different conditions. Increasing of the roughness was reported in study [12] as well. Moreover many authors explain this phenomenon by the magnetron sputtering process that is the sputtering atoms from the target flying at the substrate in all directions, then collide with it and such a way the layer grows. The surface roughness will promote the early collisions with the surface rises and prevent the atoms penetration into the cavities. This phenomenon will increase during the growth of thick layers.



a)

b)

Fig. 2. Morphology of the coating's surfaces

a) The surface roughness ($R_a = 0.219$ μm), the film thickness is 450 nm

b) The surface roughness ($R_a = 0.574$ μm), the film thickness is 2700 nm

The Figure 3 demonstrates the distribution profile of elements in atomic percent within Ca-P coating (rf-sputtering technique) on the sample of 316L stainless steel. The thickness of the film equals 1.3 μm, the average content of the elements according to the depth: Ca-45.4 ± 1.0 at.%, P – 13.6 ± 0.5 at.%, O – 41.1 ± 0.7 at.%, besides the coasting includes the carbon till the thickness of approximately 0.1 μm, that may be explained by the atmosphere influence. As shown in the Figure 3, the elemental concentration within the coating is almost uniform, the maximal fluctuation of the atomic content from the average value is 1.1 at.%. It is interesting to notice that a diffusion layer at the interface between the Ca-P coating and the substrate exists. It has the thickness about 0.3 – 0.4 μm and this fact probably significantly increases the mechanical properties of the Ca-P coatings deposited using the rf-magnetron sputtering technique [9].

The average ratio Ca/P equals 1.7, that higher than that one in the bone tissue.

According to the opinion of the authors of the study [13], too high ratio Ca/P can be the result of the magnetron sputtering deposition technique influence, that is the atoms of calcium Ca, which have a little more mass, displace the atoms of less mass, in particular phosphorus – P.

In the work [10] the Ca/P ratio within the coatings deposited by the rf-magnetron sputtering equals 1.77 – 1.79. This circumstance according to the values obtained in the present study.

Besides the structure and composition of the coatings, there are other important characteristics, affecting on long-term stability of the implants. These are such strength characteristics as nanohardness – *H*, Young modulus – *E*, contact stiffness – *S*, the values of adhesion strength and cohesion resistance of the coating.

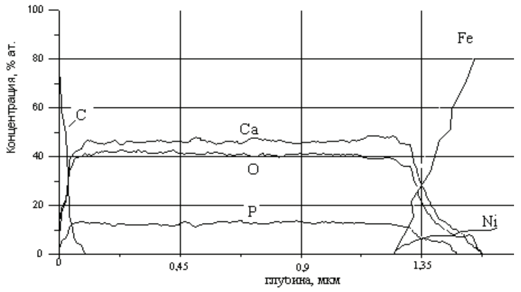


Fig. 3. The profiles of the elements distribution within the Ca-P coating on the 316L stainless steel substrate

Analysis of the coating absorption infrared spectra (there is a wide band in the range 1100 – 975 cm^{-1}) shows that there is a great amount of basic phosphates PO_4^{3-}. Weak absorption at 1300 cm^{-1} confirms presence of small quantities of pyrophosphate anions $H_2PO_4^{-}$. Such bands are typical for appetites. A weak band of absorption water O-H-O at 1698 cm^{-1} is typical for hydroxyl apatite. Weak bands at 3000–3500 cm^{-1} and 676.06 cm^{-1} demonstrate small quantities of hydroxyl groups. The mechanical properties of the Ca-P coatings were investigated by the method of dynamic nanoindentation and the adhesion strength by the method of scratch test.

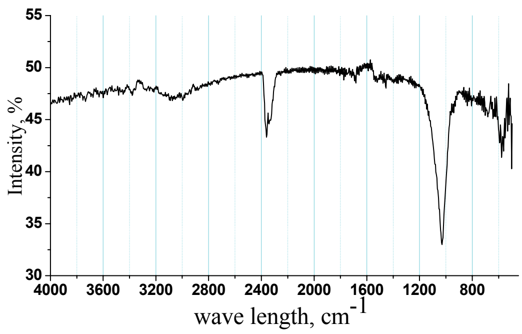


Fig. 2. The pattern of FTIR spectra of the Ca-P – coating

Nanohardness was determined by

$$H = P_{\max} \big/ A_c , \qquad (1)$$

where $P_{\max}$ is the maximal load and A_c is the area of the indent after unloading.

The contact stiffness of the film was determined at the part of unloading curve $S = \frac{dp}{dh}$. The Young's modulus (E) of the samples was determined by the same way as S at the part of unloading curve according to expression [14] $E = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}$.

The method of dynamic nanoindentation allows not only to determine directly nanohardness and Young's modulus, but also to estimate a porosity of the coating, to determine of the deformation behavior and, therefore the composition of the coating, the structure of the material, to measure the absorbed at the contact interaction an energy and other coatings properties [14].

Some load-displacement curves for Ca-P coatings and the uncoated titanium substrate were shown in the Figure 4.

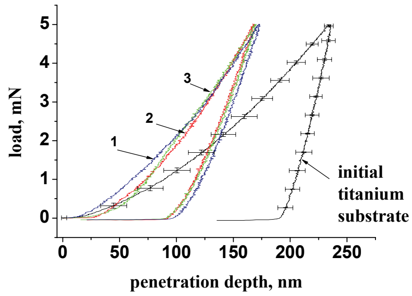


Fig. 4. Comparison between load-displacement curves for Ca-P coating and titanium substrate. The film thickness is 1.6 µm. Curves 1, 2, 3 obtained for Ca-P coating

Table 1. The values of nanohardness, Young module and contact stiffness of coatings, having different thickness.

The penetration depth/film thickness, (µm)	H, MPa	E, GPa	S, mN/nm
0.61 (0.09)	11000	100	0.0342
0.609 (0.27)	5000	100	0.121
0.45 (0.45)	65000	96	0.0983
0.21 (0.72)	11800	130	0.099
0.14 (1.08)	13000	140	0.096
0.08 (1.6)	9000	110	0.094
0.06 (2.7)	9000	120	0.1013
titanium	3900	110	0.144

Thus, the values of nanohardness – H, Young's modulus – E and contact stiffness – S of the Ca-P coatings are higher than that ones for titanium substrate. According to the obtained load-displacement curves the deformation behavior as the coating as the substrate is elasto-plastic, that is after unloading occurs a relaxation of an energy saved during the process of elasto-plastic deformation.

The adhesion properties of the coatings were determined using the device "Micro scratch tester" of the CSEM company. This technique has been already used for a long time and all it capabilities have been already studied very well [15]. The method consists of programming penetration of an indenter into a coating. In this case, the diamond indenter was used by us, having the tip radius equals 20 µm. The scratch technique is semi-quantitative technique that is it helps only to estimate adhesion strength values.

The parameters of scratching is the following: the lateral speed of the indenter is 7 mm/min, the rate of vertical penetration is 5 mN/min.

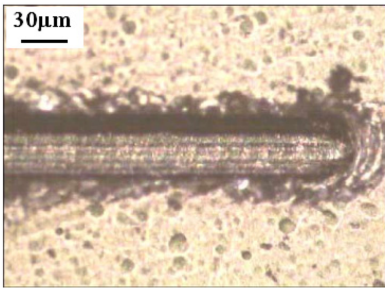


Fig. 5. The results of one experiment, where a coating hasn't been damaged during scratch-test (The loading rate 2 N/min). The film thickness is 1.6µm

We can see in the Figure 5 that the coating was not damaged, when the maximal load 2 mN has been reached. Therefore in particular we can state that deposited using rf-magnetron technique coatings possess not only high values of adhesion strength, but also they have a high value of cohesive resistance, which characterizes the bonding strength of the coating.

The behavior of the failure of the coatings having the thickness more than 1.6 µm differs from the failure behavior of the coatings having less thickness. During scratching of the coating with the thickness less than 1.6 µm, the cracks and chips along the edges of the scratch are not occurred and the damage of the coating occurs only after the moment, when the coating has been punched. The films having the thickness more than 1.6 µm are damaged after delaminating and cracks and chips occurring along the direction of the scratching. The results of the adhesion strength determination of the coatings having thickness 2.7 µm shown in the Figure 6.

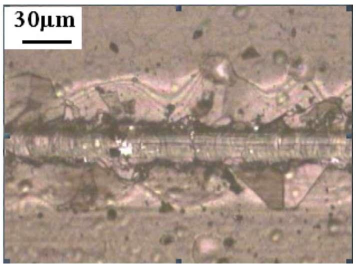


Fig. 6. The results of one experiment, where a coating has been damaged during scratch-test (photo was made at the loading rate 0.66 N/min). The film thickness is 2.7 µm

4. Conclusions

1. The Ca-P coating prepared by rf-magnetron deposition has morphology without pores and micro cracks. The average content of the elements with the depth of the coating is: Ca-45.4 ± 1.0 at.%, P – 13.6 ± 0.5 at.%, O – 41.1 ± 0.7 at.%. The elemental distribution in the coating is uniform.
2. The adhesive strength of thin Ca-P coatings deposited by rf-magnetron spattering was found to be in the order 100 MPa.
3. Roughness of Ca-P coating surface increases with increasing of it thickness.

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