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OBTAINING OF HYDROXYAPATITE COATINGS ON A TITANIUM SUBSTRATE BY DETONATION-GAS SPRAYING

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The article considers research results of the formation process of a hydroxyapatite coating on a titanium substrate during detonation spraying. Powders for sputtering and obtained coatings of hydroxyapatite were studied by Raman spectroscopy and X-ray structural analysis. It was determined that the appearance of α-tricalcium phosphatephase is characteristic of a pure hydroxyapatite coating obtained by detonation spraying. Still, the hydroxyapatite phase is retained in the coating composition. Results obtained by Raman spectroscopy indicate that hydroxyapatite is the main phase in coatings. The morphology of the sprayed coatings was characterized using scanning electron microscopy, and the coatings elemental composition analysis was obtained using an energy-dispersive spectrometer detector. Energy-dispersive spectrometer analysis showed that the elemental composition of the obtained coatings is similar to the elemental composition of the initial powder, which is very important for preserving the coatings services life.

Keywords: hydroxyapatite, detonation spraying, structure, phase composition, microhardness.

Introduction

The requirements for the functional, strength and aesthetic parameters of orthopaedic structures have increased significantly with the development of new concepts in the technology, production and application of implants for the bioengineering of bone tissue [1]. First of all, this refers to creating biocoatings, which are most close to the structure of human bone tissue [2]. Natural bone is a composite consisting of a mineral fraction containing tiny crystals of apatite and non-stoichiometric calcium phosphate and an organic fraction, which together give the material mechanical strength.In recent years, to stimulate the structure of natural bone, the synthesis of hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$has attracted considerable attention [3-5]. Hydroxyapatite (HA) – $Ca_{10}(PO_4)_6(OH)_2$, which is the main mineral component of bone tissue, is traditionally used as a material for obtaining biocoatings on metal implants for dentistry and orthopaedics.

Despite the many different coating methods, it is difficult to obtain crystalline HA coatings with characteristic hydroxyl and phosphate groups. The mechanical tests show that the destruction of the bone-(coating)-implant joints are associated with the amorphous phase, which is the cause of the coatings mechanical and adhesive instability. These disadvantages are inherent in sol-gel technologies [6]. It should be noted that a set of techniques is used to achieve the required mechanical and adhesive strength. For example, it is possible to control the coatings composition and structure by varying the parameters of the magnetron sputtering process, which makes it promising for the coatings deposition on implants. The use of the self-propagating high-temperature synthesis method expands the capabilities of the magnetron sputtering method, providing high density, structure homogeneity and achieving the required mechanical properties. The detonation-gas spraying method has good prospects using the medicine, primarily due to the initial material's identity of the phase composition and the formed coating.

The authors of [7] found that the coatings obtained by detonation-gas spraying on the “Katun-M” installation consist of particles and conglomerates of particles that form a pronounced surface relief. The adhesion strength of detonation coatings based on calcium hydroxyapatite varies from 10 to 30 MPa. The coatings physical-mechanical characteristics are showed that the detonation spraying method can be used to obtain high-quality biocoatings on titanium implants. However, there are few works aimed at obtaining hydroxyapatite coatings by detonation gas spraying. In addition, in connection with the emergence of new detonation spraying devices, it is interesting to study hydroxyapatite coatings obtained by detonation-gas spraying. In this regard, this work aims to study the structural-phase state of hydroxyapatite coatings

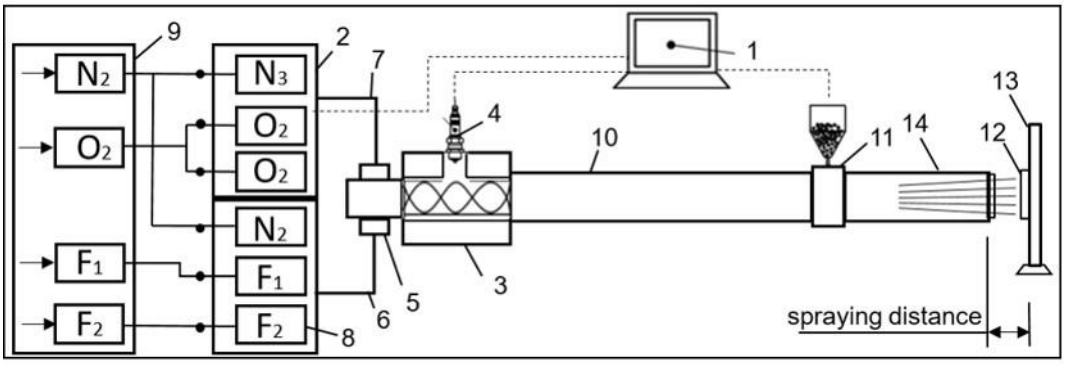
obtained by detonation-gas spraying on an automated installation of a new generation CCDS2000 (Computer-Controlled Detonation Spraying) [8].

1. Materials and methods

The detonation complex CCDS2000 was used to obtain coatings, which has a system of electromagnetic gas valves that regulate the supply of fuel and oxygen and control the purging system (Fig. 1) [8-10]. An acetylene-oxygen mixture was used as combustible gas. It is the most demanded fuel for the detonation spraying of powder materials. The deposition was carried out at the ratio of the O_2/C_2H_2 = 1.856 acetylene-oxygen mixture. The barrel filling volume with an acetylene-oxygen mixture was 50%. Nitrogen was used as a carrier gas. The distance between the sample treated surface and the detonation barrel was 70 mm. Straight barrel diameter - 20 mm.

As a substrate, we used technically clean VT1-0 titanium (99.5%), which is widely used in medicine. Before spraying, VT1-0 plates with dimensions of 30×30×3 mm were sanded and polished, after which they were subjected to sandblasting.Sandblasting was carried out on the detonation unit itself using corundum powders with grain sizes of 0.5-1.3 mm in the following mode: the barrel filling volume with an acetylene-oxygen mixture - 30%, the ratio of acetylene-oxygen mixtures O_2/C_2H_2 = 1.856.

a)



b)

Fig.1. Computerized detonation complex CCDS2000: general view (a) and schematic diagram of the installation (b): 1 - control computer, 2 - gas distributor, 3 - mixing-ignition chamber, 4 - spark plug, 5 - barrel valve, 6 - fuel line, 7 - oxygen line, 8 - gas valves, 9 - gas supply unit, 10 - breech, 11 - powder dispenser, 12 - workpiece; 13 - manipulator, 14 - muzzle of the barrel

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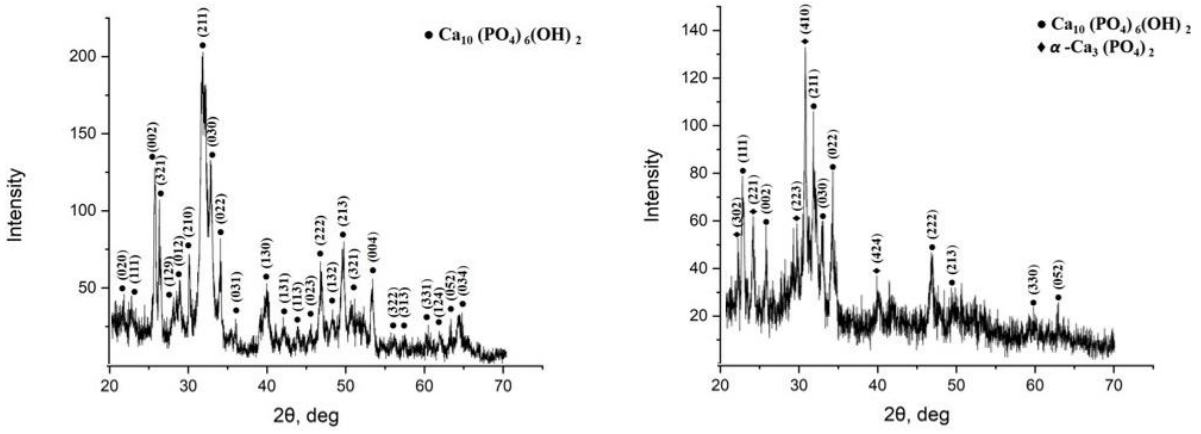
The research of surface morphology was carried out by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a JSM-6390LV scanning electron microscope. The structure of the obtained samples was studied using Raman spectroscopy on a spectrometer of AFM-Raman Solver Spectrum, NT-MDT. A blue laser with a wavelength of 473 nm and a maximum laser power of 35 mW with an objective lens of 100× and a spot size of $2 \cdot 10^{-6}$ m was used to excite vibrational modes. The obtained spectra were processed by the Savitzky-Golay method [11] by using a 2nd order polynomial. The error in register the spectra was 4 cm^{-1}. The samples phase composition was studied by X-ray structural analysis on X'PertPro diffractometer using CuK_α -radiation. The survey was carried out in the following mode: voltage across the tube U = 40 kV; tube current I = 30 mA; exposure time 1 s; shooting step 0.02º. The coating roughness surface was measured by the Ra parameter using a model 130 profilometer on a section with a length of 7 mm on the sample surface.The samples microhardness was measured by the Vickers method on a "Metolab-502" microhardness meter according to GOST 2999-75.

2. Research results

As noted in several works [12, 13], the phase composition of coatings has a significant effect on the growth of bone tissue during the osseointegration of implants.The implants compatibility is improved due to the approximation of the resulting coating phase-structural state and its properties to the bone tissue parameters.The phase state of the bone-implant biocoatings also determines the nature of their physicochemical and mechanical properties [14]. Therefore, in this work, the phase composition of the obtained calcium-phosphate coatings was studied by X-ray diffraction analysis. The X-ray powder diffraction pattern of the HA sample is shown in Figure 2a. The XRD pattern shows the characteristic peaks of hydroxyapatite, according to the International Center for Diffraction Data database, ICDD-PDF 9-0432.The hydroxyapatite structure was published nearly simultaneously by Náray-Szabó and Mehmel in 1930. it possesses a hexagonal structure with a $P6_3/m$ space group and cell dimensions a=b=9.42Å, and c=6.88Å, where $P6_3/m$ refers to a space group with a six-fold symmetry axis with a threefold helix and a mirror plane [15]. Figure 2b shows diffraction patterns of a calcium-phosphate coating obtained by detonation spraying. In the case of detonation spraying of pure HA, the appearance of phases of α-Tricalcium phosphate (ICDD-PDF 9-0348) is characteristic, but the HA(ICDD-PDF 9-0432) phase is retained in the coating composition. It is known [16]α-TCP crystallizes in the monoclinic crystal system and belongs to the space group $P2_1/a$. α-TCP phase is not very strong, and its mechanical strength is low compared to the cortical bone, limiting its use in areas subject to low mechanical stress. However, α-TCP is completely replaced by biological tissues when interacting with the body's environment, which ensures high bioactivity [17].



a) b)

Fig.2. Diffraction pattern of hydroxyapatite powder (a) and coating (b) obtained bythe detonation spraying method

Figure 3 presents the Raman spectrum of a hydroxyapatite coating obtained by detonation spraying. In the obtained Raman spectrum of the hydroxyapatite coating, the most intense band is the band with a frequency shift of 961 cm^{-1}, which indicates that HA is the main phase in the coatings. This band belongs to

the P-O symmetric extension mode (ν_1) of the PO_4 group is the most characteristic band of carbonized apatites. The sharpness of this band confirms the good crystallinity of the HA coating, which is also confirmed by other authors [18]. Similarly, the bands associated with the antisymmetric stretching mode (ν_3) of the PO_4 groups show a shift from 1045 cm^{-1} to the shoulder at 1033 cm^{-1}. In addition, it should be emphasized that this change in the carbonate content in the coatings is closely related to changes in the growth morphology and crystallite size, which are known to occur with a temperature change - higher atomic disorder corresponding to smaller crystal sizes (nanometer scale).

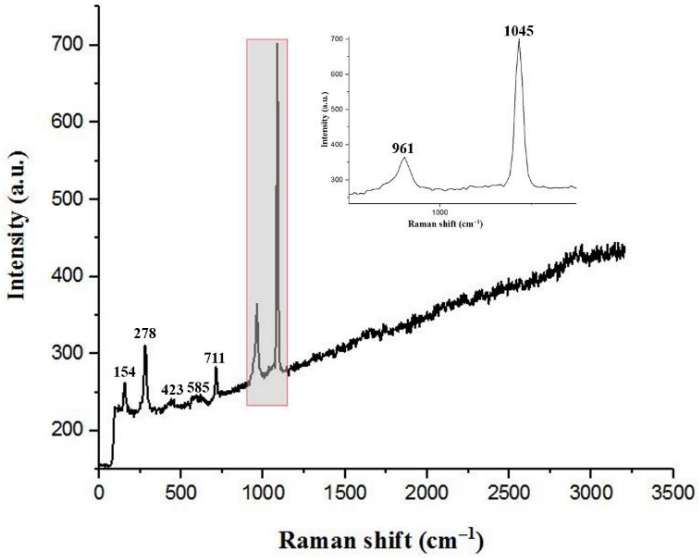


Fig.3. Raman spectrum of a hydroxyapatite coating obtained by the detonation spraying method

Table 1. Results of hydroxyapatite coating with different frequencies of the corresponding lines

Raman frequency shift, cm^{-1}	Fragment, wobble
154	(Ti-O) – (Anataz)
278	(Ti-O) – (Anataz)
423	$(PO_4)^{3-}(\nu_2)$ (P-O vibrational)
585	$(PO_4)^{3-}(\nu_4)$ (P-O deformation)
711	$(PO_4)^{3-}(\nu_4)$ (P-O deformation)
950–965	$(PO_4)^{3-}(\nu_3)$ (P-Oasymmetric valence)
1030–1045	$(PO_4)^{3-}(\nu_3)$ (P-Oasymmetric valence)

The morphology of the hydroxyapatite coating showed the formation of a layered porous structure, which, in turn, facilitates the effective growth of bone tissue into the implant's pores.Pores are observed in the obtained coatings, which are formed when the coating particles melt. As previously observed, detonation coatings have a porous structure and a pronounced relief.According to the analysis results of the coatings elemental composition, other elements besides the basic composition of the substrate and powder weren't identified. It can be argued based on elemental analysis results that detonation spraying did not cause a change in the chemical composition of the coating, which is critical for the biocompatibility and preservation of the coating service life. There is a uniform coating structure consisting of a molten powder sprayed with single particles.

Figure 4 presents the energy-dispersive X-ray spectra of the coating. The elemental composition analysis did not reveal other elements, except for the basic composition of the substrate and powder. According to the obtained results of the coating elemental analysis, it can be argued that detonation spraying does not cause changes in the chemical composition of the coating, and this factor is of decisive importance for biocompatibility and preservation of the coating service life. The Ca/P ratio in the coatings is one of the main parameters that determine bioactivity. The elemental analysis allows comparing the concentrations of the elements that make up the coatings and calculate the Ca/P ratio. The research results of the chemical composition showed that the ratio of calcium and phosphorus in the sprayed coating is Ca/P - 2.2, which is

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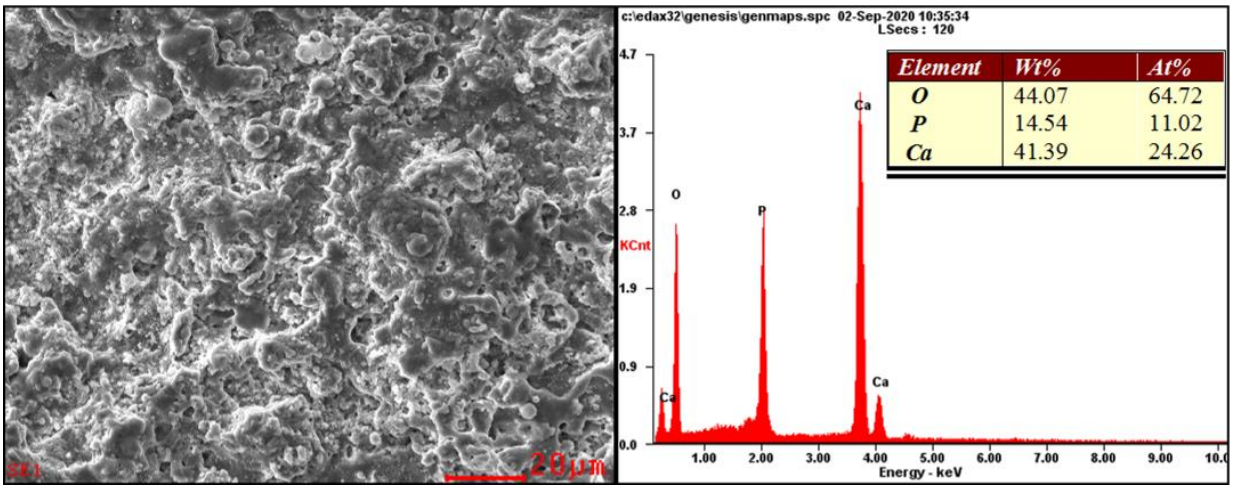
significantly higher than for the initial powder - Ca/P - 1.67. This fact may indicate the presence of impurity phases in the coating.

In figure 4 presents an SEM image and elemental analysis of detonation coating based on HA.Cross-sectional micrographs of detonation coating on the bases of HA showed a high coating density at the substrate interface. The result showed (Fig.5) the formation of a layered-porous structure of coatings with a thickness of 100-120 μm, and there are no pores and cracks at the interface.



a) b)

Fig.4. SEM (a) imageand (b) elemental analysis of hydroxyapatite coating

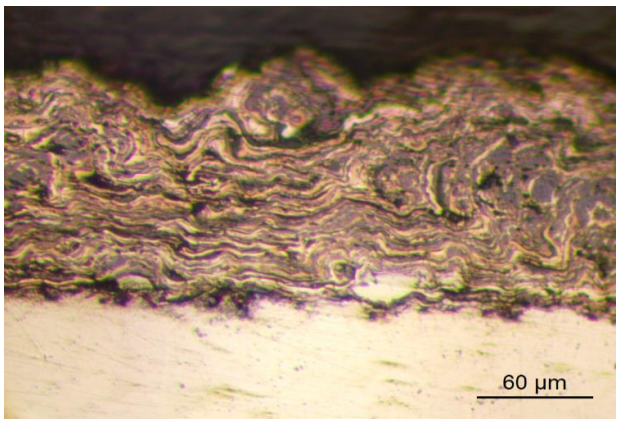
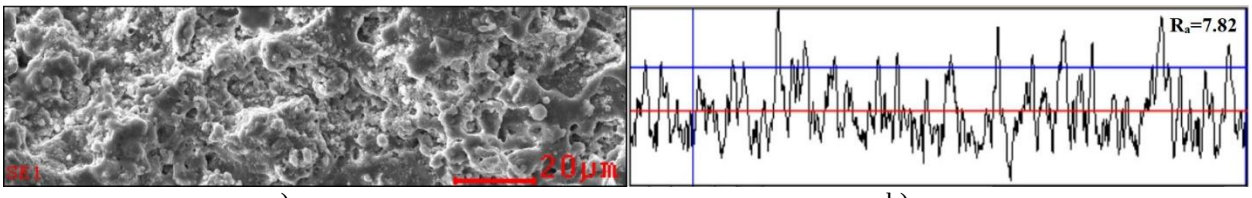


Fig. 5. Micrograph of a cross-section of a hydroxyapatite coating obtained by the detonation spraying method

Figure 6 shows micrographs of the surface and the roughness measuring results of the hydroxyapatite coating obtained by the detonation spraying method. The coating surface has a heterogeneous structure with pores, a typical layered, wavy arrangement of structural components. The coating roughness surface was measured by the Ra parameter using a 130 profilometer model on a section with a length of 7 mm on the sample surface. The coating roughness is 7.82 from the obtained data.The hydroxyapatite coating obtained by the detonation spraying method has a developed surface, which will serve as their improved fusion with bone tissue.



a) b)

Fig.6. Micrograph and roughness of hydroxyapatite coating obtained by the detonation spraying method

The cross-section microhardness of the hydroxyapatite coating obtained by the detonation spraying method was carried out at an angle of 45° along with the coatings. The average microhardness of HA coatings obtained by the detonation spraying method is 380 $HV_{0.1}$. Figure 7 shows a hardness distribution graph over the depth of coating.

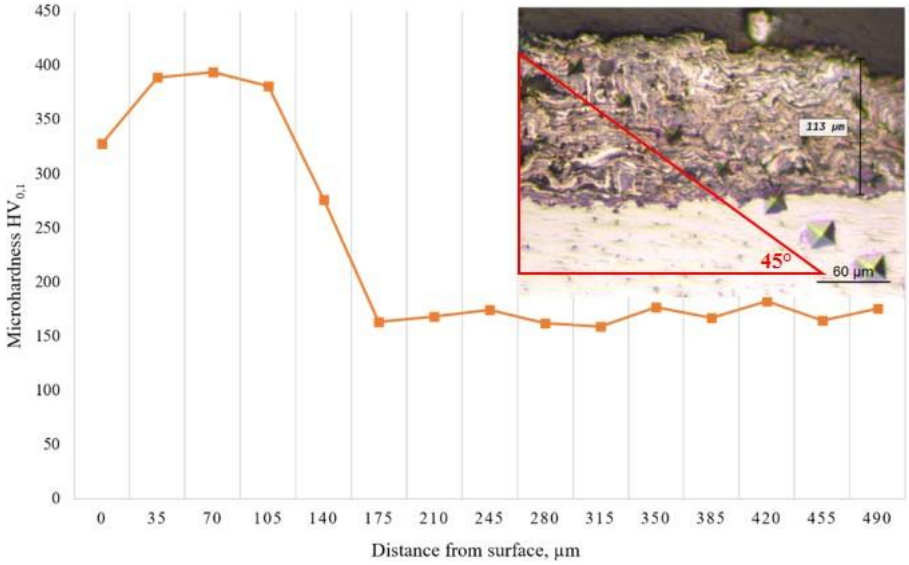


Fig.7. Hardness distributiongraph over the depth of coatings

Conclusion

The structural-phase states and microhardness of the calcium-phosphate coating obtained by detonation spraying were studied. The study of hydroxyapatite coating morphology showed that the coating has a pronounced relief and a layered porous structure. The results of X-ray diffraction analysis showed that the obtained coating consists of HA and α-TCP phases (α-$Ca_3(PO_4)_2$ - tricalcium phosphates). The Raman spectroscopy study method results showed that HA is the main phase in the coating and the coating has high crystallinity. Despite the presence of α-TCP phases, the coating has a high hardness, and the average microhardness of the obtained calcium-phosphate coating was 380 $HV_{0,1}$. Thus, the high hardness, porous structure and the formation of α-TCP phases can provide high service characteristics of the detonation calcium-phosphate coating used in medical implants.

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