Properties of the hydroxyapatite coatings obtained by gas-detonation deposition onto titanium substrates

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In this study GDD technology optimization is carried out. It was indicated, that gas-detonation deposition technique allows obtaining hydroxyapatite coatings with thickness of 280 μm during 20 s. The adhesion of those coatings to substrate is significantly exceeds relative values for ISO standard (ISO — not less than 15 MPa, plasma spraying — 20–40 MPa, GDD coating — 71.7±4 MPa). The crystal and phase structure of initial powder and deposited coating were investigated by the layerwise X-ray diffraction. Particularly, from the X-ray spectra analysis it was determined the absence of irrelevant HA phases in both initial powder and obtained coating. Moreover, the Ti substrate's lines are appeared with minimal coating thickness less than 30 μm.

Исследованы покрытия биоактивной керамики гидроксиапатита на титановых подложках, полученных методом газо-детонационного осаждения. Показано, что метод газо-детонационного осаждения позволяет получать покрытия гидроксиапатита толщиной до 250 мкм за 20 с. Адгезия и значение ISO таких покрытий к подложке в 4–6 раз превышает адгезию при плазменном осаждении. Методом послойного рентгеноструктурного анализа исследованы кристаллическая структура и фазовый состав исходного порошка и осажденного покрытия. Показано отсутствие посторонних фаз гидроксиапатита как в исходном порошке, так и в осажденном покрытии. Минимальная толщина покрытия, при которой проявляются линии подложки, не превышает 30 мкм.

1. Introduction

Among the known bioactive ceramic coatings used in medicine for surgical implants production the hydroxyapatite (HA — $Ca_{10}(PO_4)_6(OH)_2$) based coatings are most widely used and studied. This is due to the fact that exactly HA coatings not only form the inorganic bone tissue and tooth enamel [1, 2] and possess biological compatibility with the human body, but also form direct chemical bonds with bone tissue and able to be gradually replaced by living one. This requires the coating in its phase, chemical composition, crystal structure to be fully complied with the relevant characteristics of the initial powder. Mostly, these coatings must have minimum of defects, maximum

adhesion of the coating to the substrate, minimum porosity, absence of amorphous phase, etc. Titanium is usually used as a basis for medical implants.

For the HA based coatings deposition the methods for plasma spraying (APS — air plasma spraying, VPS — vacuum plasma spraying) are most widely used. However, it is found to have some significant disadvantages, such as an extremely high temperature in plasma being resulted in partial melting of HA powder particles. When the molten particles steam comes up to the colder metal substrate, the abrupt cooling leads to both significant disordering of the HA crystal structure and the formation of amorphous HA phase at the coating-substrate interface. On the one hand, this effect improves the mechanical properties of the coating, in particular, its adhesion [3, 4]. On the other hand, the amorphous phase has the ability to very rapid dissolution that was observed in-vivo and in-vitro [5]. This fact is important when using these materials as coatings for surgical implants. In addition, due to significant difference in thermal expansion coefficients of the HA and the substrate material during cooling of the deposited HA based coatings to room temperature at the boundary of the HA — substrate the thermal stresses and microcracks occur resulting in adhesion decreasing and increasing the coating dissolution rate in organism. To reduce the thermal stress the coating thickness is limited (less than 50 μ). However, such a thick coating dissolves much faster than their required live-times (20 years). Such effects are typical for all high temperature deposition methods, such as plasma spraying, magnetron sputtering, pulsed laser deposition and others. Furthermore, most deposition methods have a number of other shortcomings, such as low adhesion, high porosity, imperfection of the crystal structure, chemical and phase structure disordering of the coatings, as well as the deficient coating thickness — due to low productivity of these methods.

In gas-detonation deposition (GDD) method the high coating adhesion to substrate is provided by high kinetic energy of HA particles incident on the substrate. Powder particles are injected into detonation wave formed by gas confined explosion with definite composition. This accelerates the powder particles and transports to substrate. Furthermore, in time of initial HA powder deposition the particles are spread in a regen-erating environment preventing the influence effects of ambient air on a hot powder.

Gas-detonation method allows obtaining high quality coatings. This is due to considerably lower substrate temperature during deposition than in plasma spraying. GDD is a highly productive and high-technology process providing to obtain coatings of a wide thickness range. Adhesion of obtained bioactive ceramic coatings can be 4−6 times higher than the required standard ISO for those HA coatings.

On the other hand, the hydration degree, phase composition and crystal structure of the coating and the initial HA powder may differ due to high-energy HA particle flux interaction with a cold metal substrate and subsequent cooling of the deposited layer. These issues have been already studied for plasma and laser deposited coatings [6, 7]. In this paper HA based coatings deposited by GDD technology onto titanium substrates were investigated with the view of optimization of the technological GDD process.

2. Experimental

The deposition of hydroxyapatite layers was carried out onto titanium substrates with different thicknesses — from 0.2 up to 1 mm. The original gas-detonation setup was used for the deposition. The stoichiometric HA powder was used for gas detonation deposition. HA powder was synthesized by precipitation from a solution of calcium nitrate and ammonium hydrogen phosphate, in accordance with the following reaction:

$$CaNO_3 + 6(NH_4)_2H(PO_4) + 8(NH_4)OH = \quad (1)$$
$$= Ca_{10}(PO_4)_6(OH)_2 + 20(NH_4)NO_3 + 3H_2O.$$
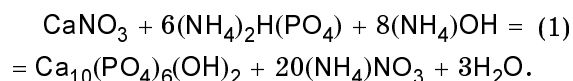
Precipitation was carried out at room temperature and pH = 12 with vigorous stirring of the solution. The precipitate was left for 24 h. in the parent solution. The solution was periodically stirred, boiled for 1 h., cooled, defended, filtered, added to distilled water and again advocated. After a five-fold repetition of this procedure, the precipitate was washed with hot distilled water. The resulting powder was dried at the 120°C and annealed in air at 1000°C for 1 hour. When annealing the sintering and grain shrinkage (about 10 % of linear dimensions) were observed. After this precipitate was transformed into a uniform conglomerate, which has a porosity of 30 % and strength of 5−7 MPa. In accordance with the X-ray analysis, the synthesized

material was a pure crystalline HA with specific surface area of about 1 m^2/g (measured by Brunauer-Emmett-Teller method) corresponding to the initial powder particles size of 2 μm. The X-ray reflections from other phases were absent. As it has been earlier assigned [8], for gas-detonation deposition technology the size of HA powder particles should be about 60–80 μm. Such powder was obtained by crushing in a porcelain mortar and sieving to a powder by appropriate sieves with an optimum size for gas detonation deposition (60–80 μm). The resulting powder was found to be in the irregular fragments form with the same porosity as the sintered conglomerate.

The resulting powder was used for deposition on the titanium substrate with dimensions of 20×10 mm^2. Deposition was carried out with a mixture of gases that are capable of detonation (propane/butane-oxygen) in purging between the cycles by compressed air.

The "fabricated section" method was used to study the adhesive properties of obtained coatings. This technique eliminates the disadvantages of the cementing process for determining the coating adhesion to substrate [12]. In order to determine the phase composition, the HA coating with thickness of 470 μm was deposited. To study the coating phase composition and its thickness change the cross-sectional X-ray diffraction studies with a gradual polishing of the obtained layer with a step of 70 μm were performed. The X-ray diffraction patterns were measured on a standard DRON-2 X-ray spectrometer using CuKα-radiation. The chemical content and dispersion parameters of the initial powder and obtained coating were studied using scanning electron microscope (SEM) ZEISS 50 XVP (Germany).

The principle of gas-detonation technology is based on the acceleration of particles of required powder which is introduced into the barrel through the spout, to a high velocity, and further deposition on the substrate. Acceleration is carried out in a detonation wave, which is formed as a result of the explosion gas mixture (in this case oxygen + propane-butane). The GDD technology is cyclic one with frequency range from 3 to 9 Hz. In our case, the short frequency was fixed and equal to 6 Hz.

After explosion and powder deposition the purification of the gas-detonation barrel is carried out by compressed air or neutral gas. The numerical values of the operations
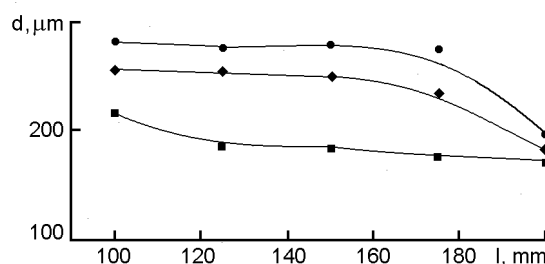

Fig. 1. Thickness dependences of the HA based GDD coating on the distance between GDD gun section to example. *1*– on GDD gun axis; *2* – 10 mm from the axis; *3* – 20 mm from the axis.

duration are specified by configuring the remote control [9-11].

Development of deposition technology was carried out in the direction of change, selection and optimization of the following process parameters: 1) the explosive mixture composition (oxygen and propane-butane); 2) the frequency of GDD cycles; 3) the distance from the gas-detonation gun outlet to the substrate; 4) the amount of a powder which is introduced into the detonation wave in the GDD process.

3. Results and discussion

3.1. Optimization of the deposition technology

The dependences of coating thickness (d) on the distance of gas-detonation (GD) gun section (l) to specimen — are presented in Fig. 1. The remaining GDD process parameters were corresponded to so-called "basic" mode. As can be seen from Fig. 1, the coating thickness, measured at the center of deposition spot (on the axis of GD gun), in time of changing l to 200 mm, begins to decrease. This behavior is due to the fact that for small l values, the flux dispersion of accelerated particles is small and begins to affect the thickness of the coating only for sufficiently large l values. A similar form has a dependence $d(l)$, obtained from the coating thickness investigation at a distance of 10 mm from the axis of GD gun (Fig. 1). Coating thickness in distance of 20 mm from the GD gun axis is almost independent of l.

From these results it follows that the coating thickness of ~280 μm can be obtained in a wide range of l. In addition, the relatively small spread of d values (<30 %) of the coating in the center of GD spot and on the edge indicates the possibility of
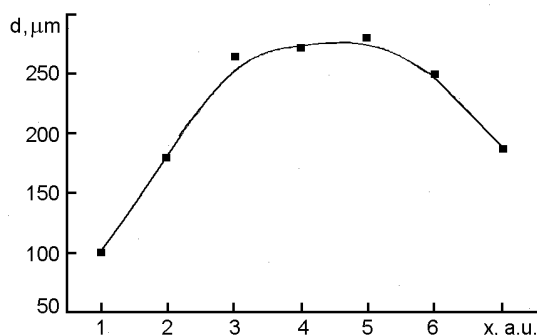
Fig. 2. Thickness dependence of the HA based GDD coating on explosive mix proportion. The regime number corresponds to x value.

Fig. 3. Thickness dependence of the HA based GDD coating on transport gas flux. The regime number corresponds to f value.

forming coatings without scanning GD gun (or sample) on a fairly large area. Both this fact and the possibility of obtaining HA based coatings of considerable thickness, indicates a high productivity of the GDD method.

As seen from Fig. 2, the dependence of d on the composition of the explosive mixture (ratio x = propane-butane / oxygen) is non-monotonic. For small values of x (depleted mixture — regimes *1*, *2*) the coating thickness is small (<200 μm). With increasing x the thickness of the coating increases and in regimes *3–5* is approximately the same. The further mixture enrichment (regimes *6*, *7*) leads to a decrease of d. When using lean mixture the required temperature and velocity of a detonation wave is can not reached leading to a low speed of the powder particles. The latter, in turn, drastically reduces the efficiency of coating formation. On the other hand, a similar effect was observed when using highly-enriched mixture that leads to incomplete combustion of the working gas.

Thus, there is an optimum range of x values, which corresponds to the *3–5* regimes on Fig. 2.

The intensity of the transport gas flow (f) determines the amount of powder which is introduced into the detonation wave. On this basis, it becomes clear, why for small values of f the forming coating thickness is small (regimes *1* and *2* on Fig. 3). In these cases, the amount of powder is not enough for effective coating formation. With f value increasing (regime *3*) the efficiency of coating formation becomes maximum. Further the dependence of $d(f)$ saturates, i.e., increasing the amount of powder, inserted in the detonation wave, does not resulted in increase of d. In this case, it is only the portion of the powder that is effectively
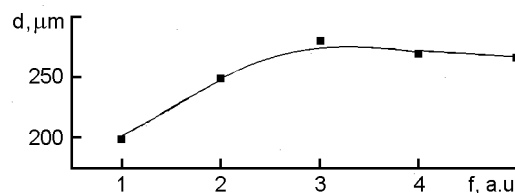
used. Therefore, in terms of efficient use of powder the optimum regime (by the flow of transport gas) is regime *3*.

Shown in Fig. 4 dependences of the deposited coatings thickness on the deposition time indicate the possibility of obtaining layers with a thickness higher than 200 μm. Furthermore, as can be seen from Fig. 4 the dependence $d(t)$ is practically linear. The appropriate technological route was proposed on the basis of determined optimum GDD process parameters for the formation of HA based coatings.

The obtained results of GDD process optimization make possible to conclude the next:

— estigation of the coating thickness dependence on the main technological parameters of the GDD setup allows us to optimize coating technology;

— position process parameters changing, such as distance from the edge of the gun to the target, the temperature of the explosive mixture composition, and the deposition time can vary coating thickness significantly.

3.2. Properties of HA based coatings obtained by GDD

For successful application of developed coatings in medicine it is necessary to ensure the following conditions:

— ensuring a high adhesion of the coating to the substrate, necessary hardness and durability of the coating;

— providing the correspondence of coating structure with structure of initial powder;

— relevance of the coating composition to the initial powder composition (the absence of pollution and contaminations);

— the high rate of the coatings formation in order to ensure the effectiveness and method efficiency for the deposition.
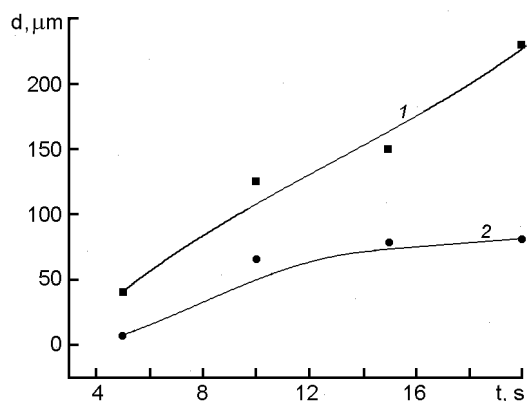
Fig. 4. Thickness dependences of the HA based GDD coating on deposition time for different explosive mixtures: (oxygen / propane — butane ratio): *1* — 6:5, *2* — 7:1.
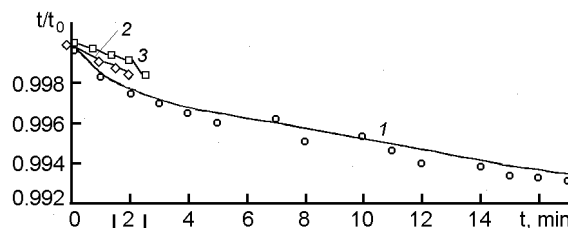

Fig. 5. Cyclic durability of HA based GDD coatings and SYNTHETBONE bioceramic: 1 — SYNTHETBONE biocomposite, *2* — hydroxyapatite, *3* — bioactive glass.

3.2.1. Mechanical properties of the HA based coatings.

In order to compare the properties of obtained coatings by "fabricated section" technique the mechanical properties of HA coatings deposited by GDD with thickness of 100 ± 10 μm were investigated. In accordance with the "fabricated section" technique [12], the coating elastic modulus is calculated as:

$$E_c = \frac{E_s H}{h}\left(\frac{\varepsilon_z}{\varepsilon_z^c} - 1\right), \qquad (2)$$

where E_c, E_s — elastic modulus of coating and substrate, respectively; ε_z, ε_z^c — relative longitudinal strain of coating and substrate, respectively; $2H$, h — thickness of coating and substrate, respectively.

The elastic modulus values for coating and substrate, obtained in this way, are used to determine the adhesion and the cohesion strength of the coatings [13]. The same sample with coating, partially deposited on the substrate is used. The test results of samples with HA coating are given in Table 1. From the table one can conclude

the adhesive strength of GDD coatings is being significantly higher than these listed in the ISO standard (ISO-13779-2) for plasma sprayed coatings (15 MPa). The elasticity modulus of detonation HA coatings is 15–25 GPa. It is less than that of sintered hydroxyapatite (50–90 GPa) [14] and being explained apparently by GDD process influence.

At the same time the results of samples strength testing are well-coordinated with the bending test results of sintered hydroxyapatite (σ_{fl} = 39 MPa) [15].

Fig. 5 shows the results of cyclic stability tests of the HA based coatings, bioceramics and SYNTHETBONE biocomposite. The technological process of the samples investigations on the coatings cyclic stability is simple. The sample is fixed in a special clamping device, and starts to shake it with a very high rate as long as the separation of coating from the substrate is being started. From Fig. 5 one can see that HA based coatings are bear not less than $1.5 \cdot 10^6$ cycles.

3.2.2. X-ray studies of gas-detonation coatings

The crucial questions in GDD coating designing are phase changes in the obtained coating, its amorphization and interaction with substrate. It is known that similar

Table 1. Mechanical properties of the HA based coatings

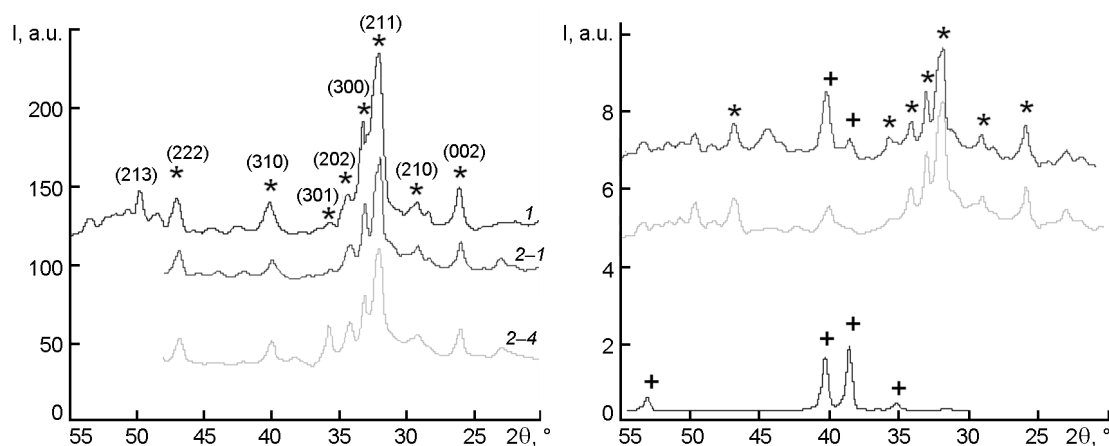| No. of example	Spalling deformation, %	Peeling deformation, %	Elastic modulus of coating, GPa	Elastic modulus of substrate, GPa	Adhesion strength, MPa	Cohesion strength, MPa
90	0.18	0.21	25.6	112	75.9	39.9
91	0.24	0.28	15.4	101	65.0	33.5
94	0.21	0.24	24.5	102	82.1	44.3
95	0.51	0.18	25.4	107	64.1	32.8

Fig. 6. X-ray diffraction spectra of initial hydroxyapatite powder (*1*), Ti substrate (*4*), and HA based GDD coatings measured after deposition (*2–1*) and after layer-by-layer removal of the coating (*2–4*, *2–5*, *2–7*): * — HA, + — Ti.
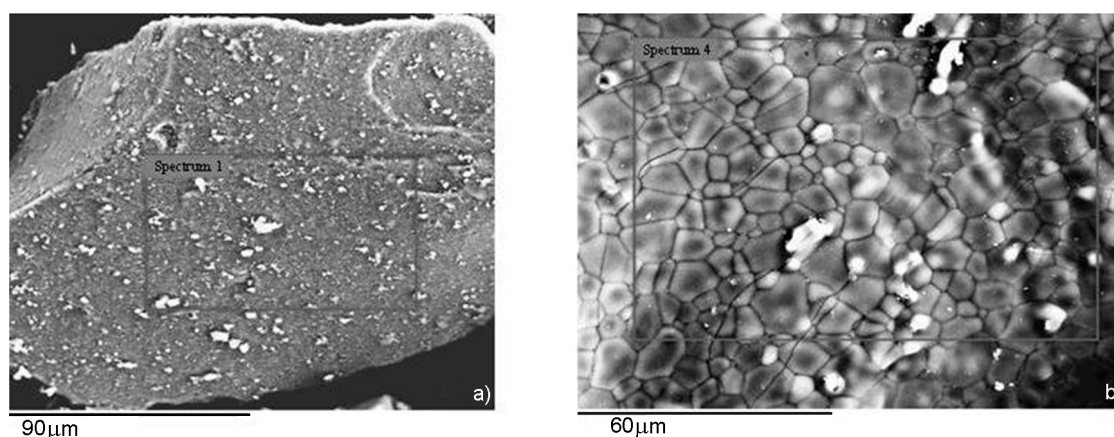

Fig. 7. Electron microscopic images of HA powder particle (a), HA based GDD coating (b).

studies of plasma sprayed deposited HA layer found the substantial amorphization of the HA layer, the vitreous phase appearance and interaction with titanium [16]. For these issues study the layerwise X-ray diffraction with a gradual thickness reduction by mechanical grinding of the layer was carried out. Fig. 6 shows the X-ray spectra for the initial HA powder (curve *1*), untreated HA layer surface, subsequent internal layers with a gradual decrease in thickness (curves *2–4*, *2–5*, *2–7*), and pure titanium substrate (curve *4*). From the obtained spectra one can conclude that coating structure is corresponded with initial powder one. The Miller indices (*hkl*) for hydroxyapatite being crystallized in a hexagonal lattice with space group $P6_{3/m}$ are inscribed over the diffraction lines of the initial X-ray spectrum.

As can be seen that along the full thickness of the deposited layer the coating ma-

terial found to be a well-crystallized HA without foreign phases and identical to the initial powder. The minimum thickness of hydroxyapatite displaying the substrate X-ray spectrum lines is found as few as 30 μm (Fig. 6, curves *2–5*, *2–7*). From the absence of X-ray bands, which are correspond to irrelevant HA phases, we can conclude the possible amount of other phases in the deposited coating is to be less than the analysis sensitivity.

3.2.3. The chemical composition of initial powders and gas detonation HA based coatings

Fig. 7 shows electron microscopic images of the initial powder particle and HA based coating obtained by GDD. The results of their chemical composition studies, performed by electron microprobe analysis, are shown in Table 2. Interestingly, the ratio of
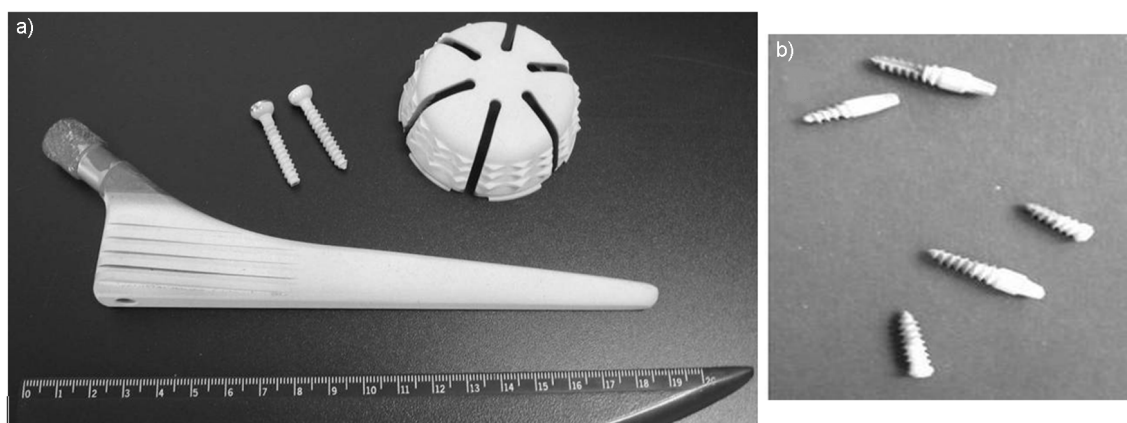
Fig. 8. Hip joint (a) and teeth (b) medical implants with HA based GDD coatings.

Table 2. Chemical composition of the initial powder (Fig. 8a) and deposited coating (Fig. 8b)

Element	Wt., %	At., %	Element	Wt., %	At., %
O	54.88	73.61	O	49.99	69.84
Al	0.00	0.00	Al	0.06	0.05
Si	0.23	0.18	Si	0.23	0.19
P	14.35	9.87	P	15.68	11.14
Ca	30.53	16.29	Ca	33.77	18.67
Sr	0.01	0.05	Sr	0.27	0.12
Total 100.00			Total 100.00		
Ca/P = 1.65			Ca/P = 1.675		

calcium and phosphorus in the deposited coating is even closer to the well-known from the literature optimal value of $Ca/P = 1.67$, than the corresponding value in the initial powder. It should be noted that this method does not allow hydrogen content determining in the material. Therefore, for further study and correct determining the chemical composition of raw materials and coatings based on them should be optional to use the method of secondary ion mass spectroscopy.

Fig. 8 shows the images of titanium implants with developed gas-detonation coatings.

4. Conclusions

As a result of optimization on technology of gas detonation depositing the HA coating onto titanium substrates it was determined the process technological parameters to effectively use the source powder and obtain high quality coatings with the required properties.

Results of the mechanical properties study of HA coatings have showed significant advantage of the gas-detonation deposition method compared with conventional HA coating deposition methods. Coatings with adhesion to substrate being in 4–6 times higher than the corresponding value established by international ISO-13779-2 standard for a HA coatings (ISO — no less than 15 MPa) have been obtained. GDD coating adhesion is up to 60–80 MPa.

Layerwise X-ray analysis of HA coatings has revealed perfect correspondence between the obtained coating structure and initial powder one. Irrelevant phases in the coating (such as tricalcium phosphate, amorphous calcium phosphate, etc.) which are presented at coatings obtained by conventional deposition methods have not been observed. Moreover, the minimum coating thickness, through which the X-ray spectrum lines of the substrate are observed, is about 30 μm. Even for this layer the possible amount of irrelevant phases in the deposited coating is less than the sensitivity analysis being lower a few percent.

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Властивості гідроксиапатитових покриттів, отриманих методом газодетонаційного осадження на титанових підкладках

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Досліджено покриття біоактивної кераміки гідроксиапатиту на титанових підкладках, що отримані методом газо-детонаційного осадження. Показано, що такий метод дозволяє отримувати покриття гідроксиапатиту товщиною до 250 мкм за 20 с. Адгезія таких покриттів до підкладки в 4—6 разів перевищує відповідне значення ISO при плазмовому осадженні. Методом пошарового рентгеноструктурного аналізу досліджено кристалічну структуру і фазовий склад вихідного порошку та осадженого покриття. Аналіз рентгенівських спектрів показав відсутність сторонніх фаз гідроксиапатиту як у вихідному порошку, так й в осадженому покритті. Мінімальна товщина покриття, при якій проявляються лінії підкладки, не перевищує 30 мкм.