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Preparation of bio-ceramic composite coatings on Ti6Al4V titanium alloy by gas-detonation spraying

The paper presents study of a new approach to manufacturing carrier implants with a combination of bioactivity, biocompatibility, and mechanical properties, composite powders of hydroxyapatite and titanium with a mass content of 50:50 % when sprayed by gas detonation spraying. Experimental studies of the surface morphology and cross-section microstructure, phase composition and mechanical properties of HATi composite coatings are obtained. The experimental results showed that the cross-section microstructures of HATi composite coatings are typical plate structures comprising curved strips formed by well-deformed and oxidized Ti plates and limited deformed HA plates. Composite coatings' morphology and phase states were studied using scanning electron microscopy and X-ray diffractometry. It was found that the deprived coatings mainly consist of the phases HA, Ti and TiO. The elemental composition study results designated that the atomic ratio of calcium and phosphorus in the obtained coatings is Ca/P ~ 1.64, which is close to the value of the initial powder — Ca/P ~ 1.67. This indicates a limited change in the chemical composition during the coating formation.

Keywords: gas-detonation spraying, HATi composition coating, microstructure and phase composition, mechanical properties.

Introduction

In modern medicine, progress is closely linked with new drugs and treatment methods and the development of materials designed to interact with biological systems. Such materials, called biomaterials, are used mainly in restorative medicine, where they replace the tissues of a living organism as implants [1]. The modern direction in the development of implantable biomaterials is modifying their surfaces by obtaining coatings [2]. These coatings ensure the functioning implants in the environment of a living organism and promote integration with its tissues [3]. One of the most important materials widely used for this purpose is hydroxyapatite (HA) — $Ca_{10}(PO_4)_6(OH)_2$ [4]. Besides improving biocompatibility, hydroxyapatite shows high bioactivity and contributes to the intensification of osseointegration [4]. Hydroxyapatite owes such properties to its chemical and biological similarity to bones, contributing to new bone tissue [5]. Metals coated with hydroxyapatite are usually used to manufacture implants since they combine the biological properties of hydroxyapatite and the mechanical properties of metals [6]. However, the hydroxyapatite coating suffers from poor mechanical properties, such as low viscosity, fretting fatigue and resistance to abrasive wear due to the internal fragility of hydroxyapatite [7]. To coordinate the bioactivity, biocompatibility, and mechanical properties of the biomedical implant carrier, research is continuing on substrate materials [3–6], coating materials, and manufacturing technologies [1, 2]. For coating materials, amplification phases or ions are usually entered into hydroxyapatite to form composites based on hydroxyapatite [2–5]. Alloying of cati-

ons (Na^+, K^+, Mg^{2+}, Mn^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}) and anions (HCO^{3-}, HPO_4^{2-}, Cl^- and F^-) is considered as an effective approach to changing the bioactivity of hydroxyapatite [4]. On the contrary, the addition of a second reinforced phase has been confirmed as an appropriate way to improve and optimize the mechanical properties of the hydroxyapatite coating [1, 2, 4]. Metals, Ti [2, 5, 6], Al [7], Co [8] and Zn [9], ceramics, including TiO_2 [3, 10], SiO_2 [11], Y_2O_3 [12], ZrO_2 [13], Al_2O_3 [14], and other materials are commonly used as the second amplified phases. Many studies [2–14] have investigated changes in the microstructure, compositional, morphological, or surface properties of such coatings and their effect on bioactivity, mechanical strength, and adhesion strength. Titanium (Ti) is a traditional biometal, which is a widely used reinforced phase for HA. When Ti particles are added to HA, the mechanical properties of composite coatings significantly improve compared to the HA coating [2, 5, 6]. The homogeneous distribution of Ti particles can strengthen the brittle HA matrix due to the mechanism of dispersion hardening [15]. Besides, Ti particles added to HA improve the melting degree and spatter plastic deformation and reduce the size of the spatter crystals of HA [16], which is favourable for the formation of the coating with a dense microstructure and better adhesive strength. The addition of Ti particles to HA can also reduce the mismatch of thermal expansion coefficients between HA-Ti coatings and metal substrates, which leads to a decrease in thermal stress inside the coatings, which favourably affects the improvement of the coating/substrate surface adhesion [17].

Given the high importance of biocompatible coatings, the selection of appropriate coating technology is therefore an important consideration. The most common coating methods include thermal spraying, immersion, dynamic mixing, sol-gel, pulsed laser deposition, and others [17–23]. Among other spraying methods, gas thermal spraying methods are widely used to obtain various biocompatible coatings. These methods include conventional plasma spraying (PS), high-velocity oxygen fuel spraying (HVOF) and cold spraying [16, 17, 21–23]. For most methods, low or intermediate adhesive strength of the coating and low crystallinity of the resulting coatings are some of the important factors limiting their application. It is necessary to develop new methods or approaches to improve the properties of coatings.

Among the coating methods by thermal spraying, gas detonation spraying (GDS) technology has been used to obtain biocompatible coatings, such as HA coatings, for orthopedic applications [17, 21, 24, 25]. Gledhill et al. conducted a comparative study of HA-based coatings obtained using air plasma spraying (APS) and GDS technologies [26]. This study demonstrated that APS coatings have higher crystallinity and lower residual stress compared to GDS coatings, which can lead to a slow dissolution rate in vitro and in vivo. The authors suggested that APS coatings are preferable to further clinical use. At the same time, Gledhill et al. studied the fatigue behavior of HA coatings obtained using the APS and GDS methods in Ringer's solution. It was shown that the APS coatings completely peeled off from the substrates after 1 million cycles in Ringer's solution, while the GDS coatings turned out to be stable even after 10 million cycles [27]. In addition, the results of another study showed that HA-based coatings obtained by the APS method exhibit low crystallinity and the appearance of a significant content of additional phases in the coatings. Such phase transformation may be the result of an extremely high temperature in the plasma atomizer of the APS approach [28]. It is important to emphasize that in the HVOF and PS methods, continuous flame or plasma spraying is used for coating [21–23]. This can lead to undesirable overheating or melting of particles and a significant increase in substrate temperature, which is the main limitation of these methods. The GDS method uses a pulsed operating mode [29, 30]. This makes it possible to minimize the aforementioned negative consequences. On the other hand, the particle velocity in the GDS method is much higher compared to the HVOF and PS methods [21], which has a positive effect on important parameters of coatings, such as adhesion strength. The results of early studies devoted to the evaluation of HA coatings obtained on Ti-based substrates were not very encouraging, mainly due to the low crystallinity [26] and high porosity of the coatings. However, recent results of Popova et al. demonstrated that uniform coatings with a regular thickness can be obtained by the GDS method using HA powders with a particle size between 50–300 μm [31]. In addition, the Ca/P ratio equal to ≈1.67 can be achieved by optimizing the parameters of the GDS process [32]. To achieve the required quality of the GDS coatings, a very careful selection of the technological regime and the automation of technological equipment are required to exclude the human factor [33, 34]. Gryshkov et al. used the GDS method to design the endoprostheses for various applications, as well as to obtain HA coatings on pure magnesium with a low melting point of 650 °C, to develop biodegradable magnesium-based implants with bioactive coatings for temporary bone fixation. Thus, the results of [33–35, 36] show that the GDS process is effective for modifying the surface of implants.

The purpose of this work is to get composite coatings based on HATi applying gas detonation spraying.

Experimental

HATi composite coatings with a thickness of about 60 microns were applied to the Ti6Al4V substrate using the CCDS2000 gas detonation complex (CCDS-2000, developed by Siberian Protective Coating Technologies LLC, Novosibirsk, Russia), the working principle is described in [37]. The general view and detonation spraying process schematic diagram are shown in Figure 1. The gun barrel is filled with gases using a high-precision gas distribution system controlled by a computer. The process begins with filling the barrel with carrier gas. After that, a particular explosive mixture is fed so that a layered gas medium consisting of an explosive charge and a carrier gas is formed. With the help of a carrier gas flow, the powder is injected into the barrel (using a computer-controlled feeder) and forms a cloud. After a part of the powder is injected, the computer signals initiate detonation. This is implemented with the help of an electric spark. The duration of the explosive combustion charge is about 1 ms. A detonation wave is formed in the explosive mixture, passing into a shockwave in the carrier gas. Detonation products (heated to 3500–4500 K) and carrier gas (heated by a shock wave to 1000–1500 K) move at supersonic speed. The interaction time of gases with sprayed particles is 2–5 ms [38]. By characterizing the phase composition of the resulting coatings HA, applied at various spraying parameters, it is possible to determine suitable spraying conditions in the GDS. Our previous studies have shown [21] that by controlling the modes of detonation spraying (the filling percentage of the barrel with an explosive gas mixture, the spraying distance), the temperature and the coating rate can be varied, respectively, this significantly affected the melting and decomposition of HA. Preliminary studies of the microstructure, phase composition and chemical structure of GDS HA coatings applied under various spraying modes and optimal spraying conditions for applying HATi composite coatings without thermally decomposed HA phase were carried out were determined (Table 1).

Table 1

Spraying conditions

Parameters	Values
Fuel/oxidizer ratio	1,856
Barrel filling volume, %	30
Spraying distance, mm	100
Shot number	10

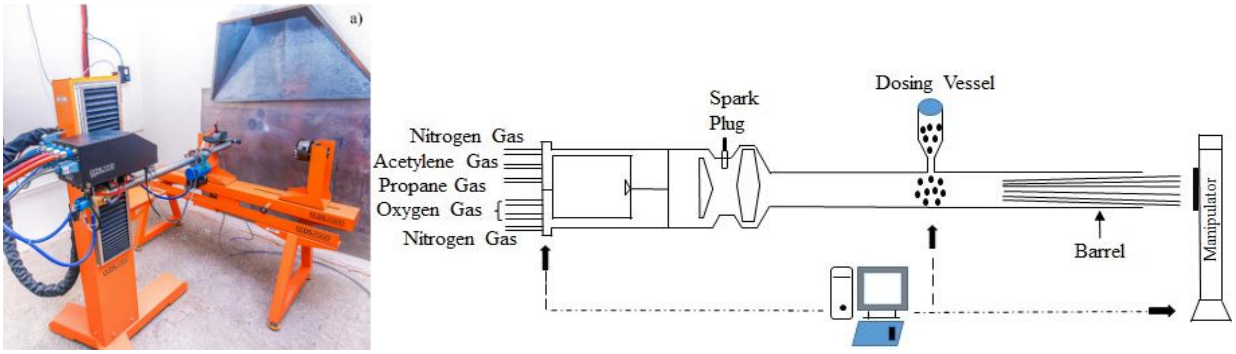

Figure 1. Schematic diagram of the CCDS2000 detonation complex

Ti6Al4V titanium alloy was used as the substrate material. The sample used to observe the microstructure was a rectangular size of 30 mm × 20mm × 3 mm. The composition of the Ti6Al4V titanium alloy is shown in Table 2. The samples were sanded (using SiC paper with a grain size of 100 to 2000). Before coating, the substrates were sandblasted with a grain size of 250–300 microns of aluminum oxide and treated with an ultrasonic bath.

Table 2

Chemical composition of Ti6Al4V alloy (weight percent).

Ti	Al	V	Fe	C	O	N	H
88,5–92,5	5,5–6,5	3,5–4,5	<0,25	<0,08	<0,13	<0,05	<0,012

Angular hydroxyapatite (HA) powder (99.95 %, produced by Sigma-Aldrich, Steinheim, Germany) with a diameter of 5–25 microns and spherical titanium powder (CL42TI) (made by Concept Laser, Germany) with a diameter of 15–45 microns were used as feedstock. HATi composite powders were obtained by mechanically mixing HA powder with Ti powder for 0.5 x using a PULVERISETTE 23 planetary ball mill. The mass ratio HA to Ti for composite powders HA-Ti was 50:50.

The sample's phase composition was studied by X-ray structural analysis on X'PertPro diffractometer using CuKα –radiation λ=2,2897 A0. The survey was carried out in the following mode: voltage across the tube U = 40 kV; tube current I = 30 мА. The decoding of diffractograms was carried out using the HighScore program. The coating's surface roughness was estimated by the parameter Ra using profilometers of model 130. The obtained coating's mechanical properties (Young's modulus, nano hardness) were studied using the NanoScan-4D Compact nanohardometer. Nano-indentation of coatings was carried out by the Oliver and Farr method using a Berkovich indenter at a load of 100 mN (ASTM E2546–07). The surface morphology and sample cross-section were studied by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a TESCAN MIRA scanning electron microscope at accelerated voltages.

Results and Discussion

According to the results of scanning electron microscopy, the surface morphology of the composite coating comprises a layered-porous structure with a pronounced relief, which is typical of detonation coatings. In the resulting coatings, pores are observed that form when the coating particles melt. According to the analysis results of the coatings elemental composition, other elements besides the basic powder composition were not identified. One of the main parameters in determining bioactivity is the Ca/P ratio. The elemental analysis allows comparing the elements' concentrations that make up the coating and calculating the Ca/P ratio. The study results of the elemental composition showed that the atomic ratio of calcium and phosphorus in the sprayed coating is Ca/P ~ 1.64, which is close to the value of the initial powder — Ca/P ~ 1.67 indicates a limited change in the chemical composition during the coating formation. Figure 2 shows the SEM image and the elemental analysis of the composite coating surface.

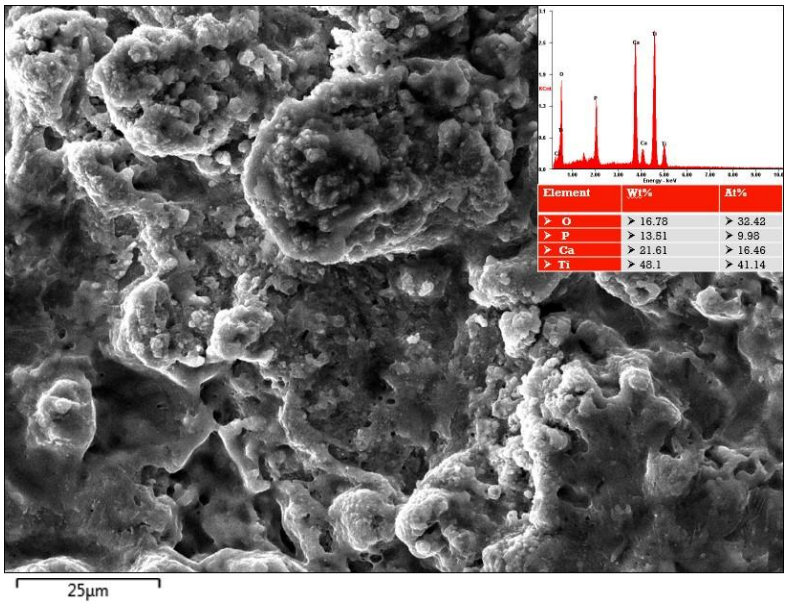

Figure 2. SEM image and EDS analysis of the HATi composite coating surface.

Plenty of scientists notes [32–37] that the coatings phase composition significantly affects the growth of bone tissue during the osseointegration of implants. The phase compositions of HATi composite powders are shown in Figure 3a. The peaks appearing at about 35°, 38°, and 40° in the Ti diffractogram (Fig. 3a) were identified as Ti crystal planes corresponding to (100), (002), and (101) [24]. Peaks appearing at approximately 26°, 32°, and 33° in the diffractogram (indicated by HA in Figure 3a) were identified as crystal planes of HA corresponding to (020), (211) and (030) [11, 38]. The characteristic sharp peaks of HA and Ti demonstrate good crystallinity of the phases of HA and Ti. In the HATi composite coatings, there was a phase of HA, Ti and TiO. However, there was no calcium oxide (CaO), tricalcium phosphate (α or β TCP) or tetra

calcium phosphate (TTCP), which are usually present in other thermal-coated HA coatings [3, 14, 23]. This confirms good phase transplantation during the formation of the HA coating by the GDS method. Compared with the corresponding composite powder, the intensity of the HA phase peaks in the coating of the HATi decreased somewhat, and some new phases formed by Ti oxidation appeared. However, the positions of the characteristic peaks of the HA phase were slightly changed. The decrease in Ti content is due to its strong oxidation during the coating formation, which was confirmed by significant titanium oxides.

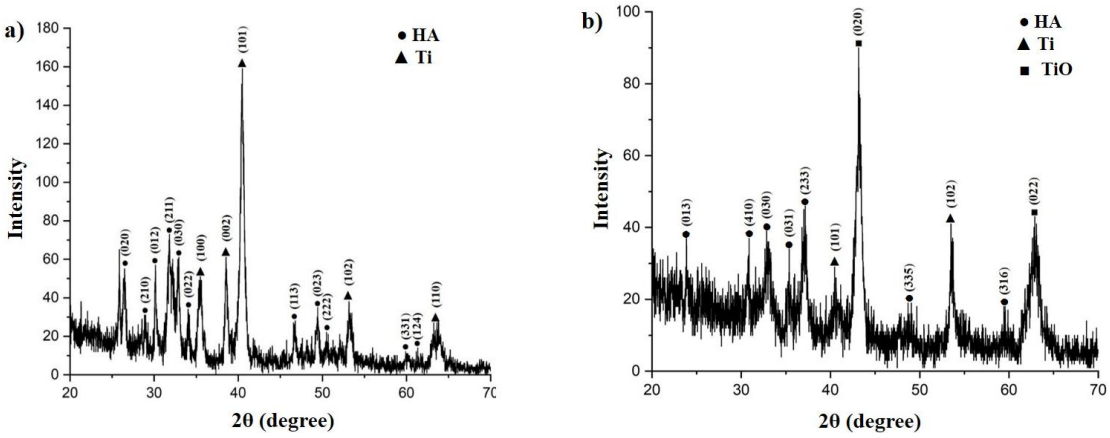

Figure 3. Diffractogram of composite powder and coating HATi.

The microstructure study of the composite coating cross-section showed a layered structure with a thickness of 60 microns (figure 4). According to the microstructure results of the coating cross-section, no visible cracks were found at the coating/substrate interface, which indicates good surface contact. A thorough microstructure study showed that most of the small grey stripes have a dense structure. The grey areas are a non-compact structure with some irregularly shaped micropores. These paid shallow grey stripes were formed due to compaction caused by the impact of falling HA particles that occurred in a dense area on the upper and lower surfaces of HA splashes. In addition, there was also a porous layer on the coating's upper surface. This may result from limited deformation of the HA spray due to little melting in the process GDS [21] and minor compaction of the coating surface layer caused by the impact of falling particles [27]. This porous structure on the top surface of coatings helps improve biological properties.

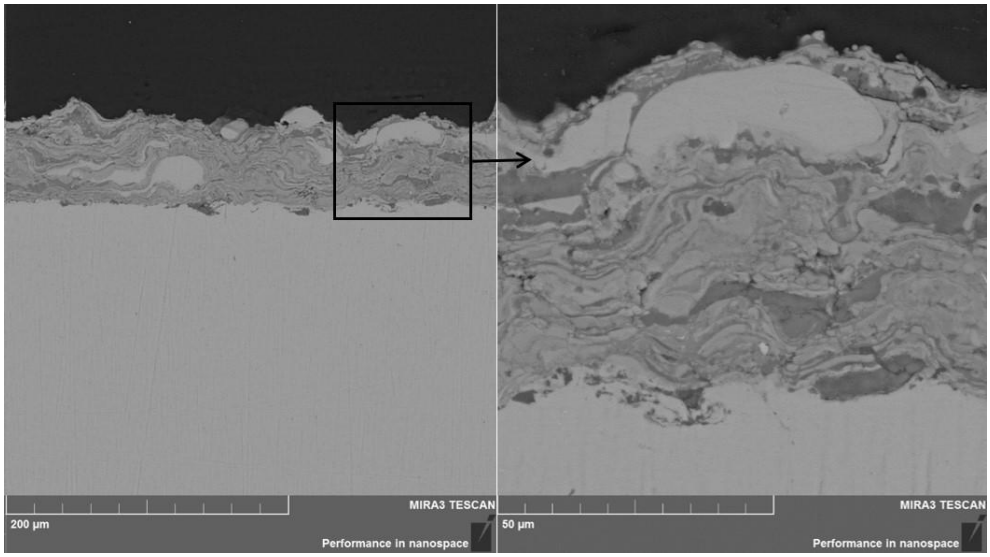

Figure 4. Microstructures of the HATi composite coating cross-section.

The EDS analysis showed that the white curved bands mainly consist of Ti and O, with a small content of Ca, P. The grey areas and shallow grey stripes are mainly Ca, P, O with some quantity Ti. In combination with the phase composition, it is recognized that the white curved stripes are mainly composed of TiO. Grey

areas and small grey stripes are mainly composed of HA. A thorough microstructure study showed that the white curved stripes shape differed from the initial Ti particles microstructure shape, demonstrating that during the HATi coating formation, significant plastic deformation and some oxidation of Ti spots occurred. There were few pores or cracks at the interface between the white curved stripes and the grey matrix, indicating suitable contact interfaces between the HA and TiO spots. Figure 5 shows the EDS analysis of the cross-section of the HATi composite coating.

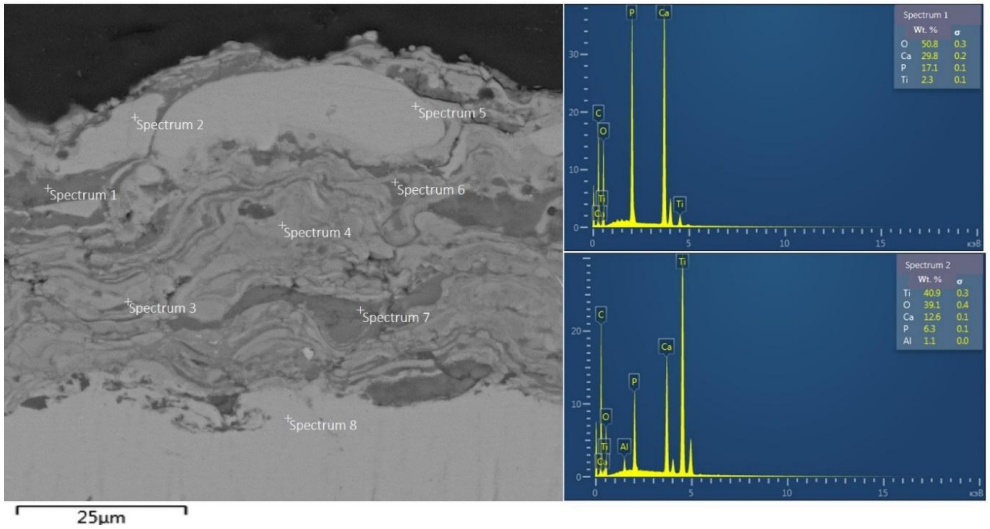

Figure 5. Cross-sectional microstructure and EDS analysis of the HATi composite coating.

Figure 6 illustrates the results of EDS analysis along the lines of the cross-section. The EDS analysis on the line showed that the HATi coverage comprises Ca, P, O, C and Ti. The SEM photos were taken in BSE mode, so areas with high brightness may indicate a high Ti content. Combined with the X-ray results, the bright white areas in the composite coating of the HATi are mainly composed of Ti, and the white regions are primarily formed of TiO. The above experimental results demonstrate that HATi coatings are dense microstructures with layered properties and compact interfaces with the Ti6Al4V substrate. During the HATi composite coating formation, strongly deformed and oxidized Ti spots led to the appearance of white curved stripes consisting of TiO and a certain amount of Ti. Limited deformation of HA spots formed a grey matrix and light grey stripes. During detonation spraying, Ti and TiO phases evolved from separate and white curved bands into interconnected and aggregated ones, forming improved frameworks in HATi composite coatings.

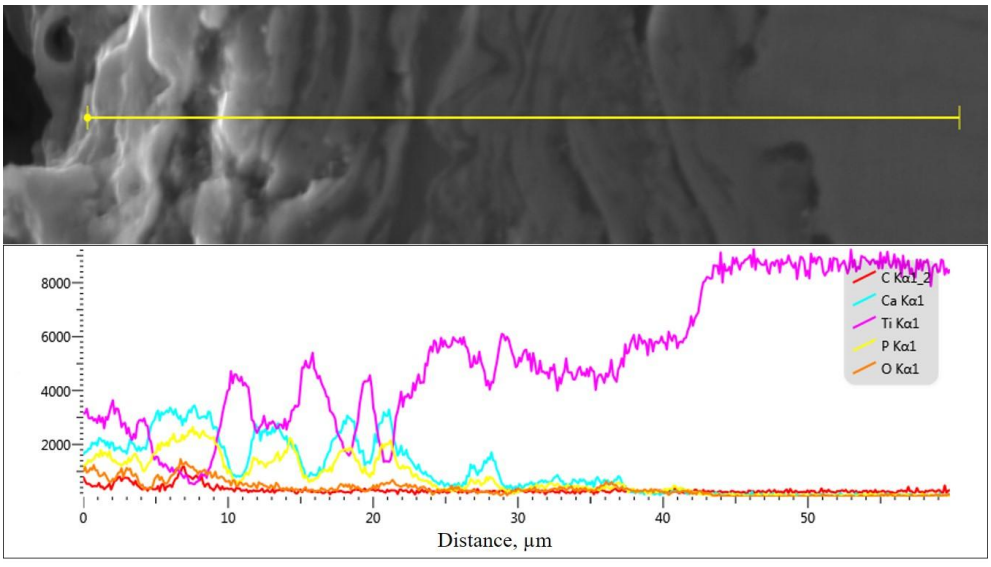

Figure 6. EDS analysis along the cross-sectional line of the HATi composite coating

Table 3 represents the measurement results of composite coatings' roughness. The coating surface has an inhomogeneous structure with pores, and typical layered wavelike arrangements of structural components are also observed. The surface roughness of composite coatings was measured using a model 130 profilometer on a 7 mm length segment on the sample surface. From the data obtained, it is established that the roughness of composite coatings by parameter has a value of Ra = 6.58.

Table 3

Measurement results of composite coatings roughness

	R_a (μm)	R_z (μm)	R_t (μm)	R_q (μm)	R_{pk} (μm)	R_k (μm)	R_v (μm)
HATi	6,58	44,3	46,6	8,42	19,9	20,3	27,6

To study the effect of Ti particles on the mechanical properties of coatings, the hardness and modulus of elasticity of composite coatings HATi were determined (Figure 7). The hardness and modulus of elasticity of composite coatings HATi were determined by nano-indentation using a triangular Berkovich pyramid. The nano-indentation curves analysis was carried out by the Oliver–Farr method. Figure 7 shows distribution graphs of hardness and modulus of elasticity over the coating depth. The average hardness and modulus of elasticity of HATi composite coatings were 7.11 = 0.16 GPa and 90.37 = 0.29 GPa, respectively. Thus, it can be argued that the formation of solid phases, TiO and Ti, can significantly improve the hardness and modulus of elasticity of coatings based on HATi. The microhardness of TiO and Ti is 9.3 GPa [17] and 4.4 GPa, respectively [38]. The interconnected textures of TiO and Ti in HATi composite coatings can increase the modulus of elasticity. The addition of Ti can increase deformable effects and enhance the impact effect of falling particles during impact, which helps to improve the phase ratio between the coating and the substrate. On the other hand, the formation of interconnected solid phases TiO by oxidation of Ti can enhance the interfacial connection of thin composite coatings HATi. The synergistic effect of these factors has significantly improved mechanical properties, including microhardness and modulus of elasticity.

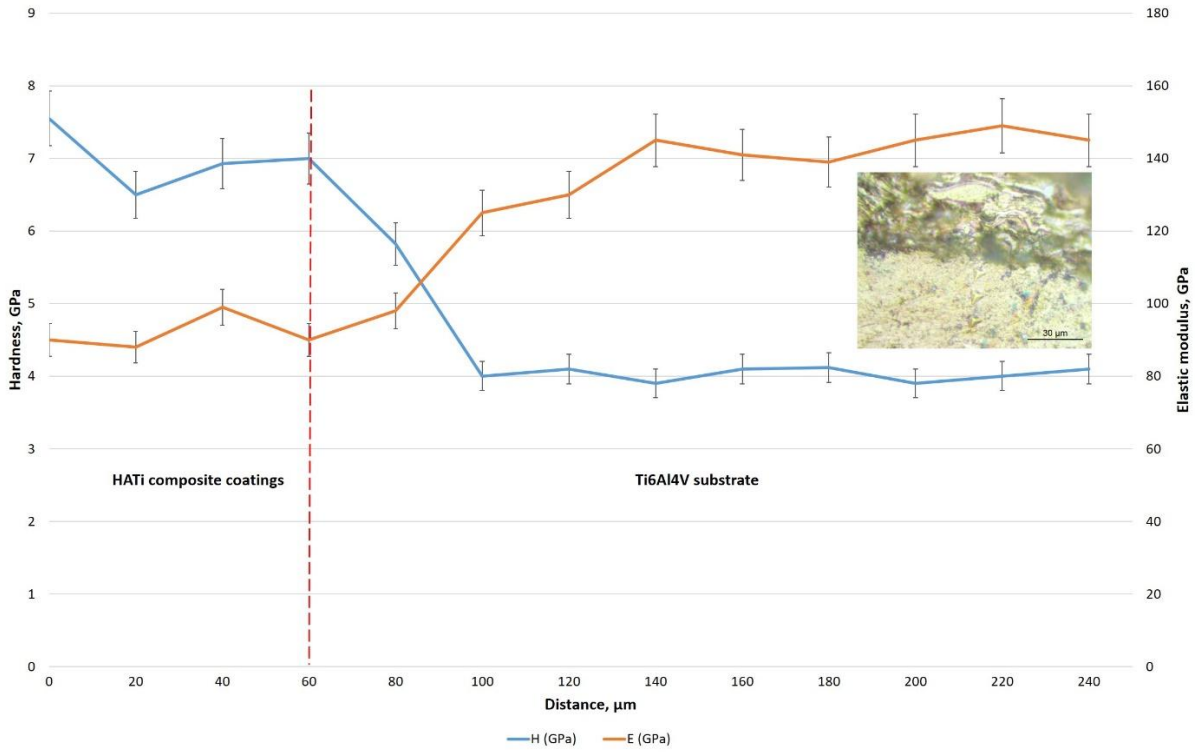

Figure 7. The hardness distribution graph and the modulus of elasticity over the depth of coatings..

Conclusions

The method of gas-detonation spraying makes it possible to successfully produce HATi composite coatings using mechanically mixed HATi powders without decomposition of the HA phase. HATi composite coatings with gas detonation spraying are a lamellar microstructure with a compact coating-substrate interface. The Ca/P ratio in composite coatings was comparable to the ratio of the initial powder. Composite coatings of HATi with gas detonation spraying showed significantly improved hardness, modulus of elasticity. The increased compactness explains these mechanical properties improvements and textures formed by well-deformed and oxidized Ti spots in HATi coatings obtained by gas-detonation spraying. According to the analysis of the results, the HATi based composite coatings obtained by gas detonation spraying demonstrate potential use as load-bearing implants in the biomaterial.

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Газ-детонациялық тозаңдату әдісімен Ti6Al4V титан қорытпасында биокерамикалық композиттік жабындарды алу

Жұмыста биобелсенділік, биосәйкестік және механикалық қасиеттері үйлескен көтергіш имплантанттарды және газды-детонациялық тозаңдату әдісімен тозаңдату кезінде массалық құрамы 50:50 % болатын гидроксиапатит пен титан композитті ұнтақтарын дайындаудың жаңа тәсілін зерттеу ұсынылған. Көлденең қиманың беткі морфологиясы мен микроқұрылымының, ГаТі композиттік жабындарының фазалық құрамы мен механикалық қасиеттерінің эксперименттік зерттеу нәтижелері алынды. Эксперименттердің нәтижелері көрсеткендей, Ті композиттік жабындарының көлденең қимасының микроқұрылымдары жақсы деформацияланған және тотыққан Ті тақталарынан және шектеулі деформацияланған ГА тақталарынан құралған қисық жолақтардан тұратын типтік тақтайша құрылымдарды қамтиды. Растрлық электронды микроскопия және рентгендік дифрактометрия әдістерімен композиттік жабындардың морфологиясы мен фазалық күйлері зерттелді, оған сәйкес алынған жабындар негізінен ГА, Ті және TiO фазаларынан тұрады. Элемент құрамын зерттеу нәтижелері алынған жабындардағы кальций мен фосфордың атомдық қатынасы са/P~1,64 екені анықталды, бұл бастапқы ұнтақ — Ca/P 1,67 мәніне жақын, бұл өз кезегінде жабынды қалыптастыру кезінде химиялық құрамның шектеулі өзгеруін көрсетеді.

Кілт сөздер: газ-детонациялық тозаңдату, ГАТі композиттік жабындар, микроқұрылымдар және фазалық құрамы, механикалық қасиеттері.

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Получение биокерамических композитных покрытий на титановом сплаве Ti6Al4V методом газо-детонационного напыления

В работе представлены исследования нового подхода изготовления несущих имплантатов с сочетанием биоактивности, биосовместимости и механических свойств, композитных порошков гидроксиапатита и титана с массовым содержанием 50:50 % при напылении методом газо-детонационного напыления. Получены результаты экспериментальных исследований морфологии поверхности и микроструктуры поперечного сечения, фазового состава и механических свойств композитных покрытий ГАТi. Результаты экспериментов показывают, что микроструктуры поперечного сечения композитных покрытий ГАТi представляют собой типичные пластинчатые структуры, состоящие из изогнутых полос, образованных хорошо деформированными и окисленными пластинами Ti и ограниченными деформированными пластинами ГА. Методами растровой электронной микроскопии и рентгеновской дифрактометрии были исследованы морфология и фазовые состояния композитных покрытий, согласно которым установлено, что полученные покрытия в основном состоят из фаз ГА, Ti и TiO. Результаты исследования элементного состава показали, что атомное соотношение кальция и фосфора в полученных покрытиях составляет Ca/P~1,64, что близко к значению исходного порошка — Ca/P 1,67, что, в свою очередь, указывает на ограниченное изменение химического состава во время формирования покрытия.

Ключевые слова: газо-детонационное напыление, ГАТi композитные покрытия, микроструктуры и фазовый состав, механические свойства.