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Study of the Structural-Phase State of Hydroxyapatite Coatings Obtained by Detonation Spraying at Different O_2/C_2H_2 Ratios

Daryn Baizhan [1,2], Zhuldyz Sagdoldina [1,2,*], Dastan Buitkenov [1], Yedilzhan Kambarov [1], Aiym Nabioldina [1], Venera Zhumabekova [3] and Gulsym Bektasova [1]

[1] Research Center «Surface Engineering and Tribology», Sarsen Amanzholov East Kazakhstan University, Ust-Kamenogorsk 070000, Kazakhstan; daryn.baizhan1@gmail.com (D.B.); buitkenovd@mail.ru (D.B.); yedilzhan@gmail.com (Y.K.); anabioldina@gmail.com (A.N.); gulsimbektasova07@gmail.com (G.B.)
[2] Research Center «Material Surface Modification», Shakarim University, Semey 071412, Kazakhstan
[3] Theoretical and Nuclear Physics Department, Al Faraby Kazakh National University, Almaty 050040, Kazakhstan; zhumabekova.venera@kaznu.kz
* Correspondence: zh.sagdoldina@gmail.com; Tel.: +7-747-663-61-13

Abstract: This work studies the influence of the composition of an acetylene–oxygen explosive O_2/C_2H_2 mixture on the structure and properties of hydroxyapatite coatings obtained by detonation spraying. The molar ratios of O_2/C_2H_2 were 2.61; 3.03 and 3.35; the explosive charge was between 73 and 77%. The results of X-ray phase analysis showed partial conversion of the hydroxyapatite (HA) phase to the tricalcium phosphate (α-TCP) phase and formation of the amorphous phase during detonation sputtering. The formation of a small amount of the α-TCP phase during detonation spraying of HA is obviously due to structural transformations occurring during the heating of the material by detonation products. In addition, very rapid cooling of molten particles leads to the formation of the amorphous phase. The study results of the microstructure of the cross sections of the formed coatings, conducted using scanning electron microscopy, indicate that an increase in the O_2/C_2H_2 ratio leads to increased porosity in the coatings. Additionally, an increase in the explosive charge by 77% results in the appearance of transverse cracks in the coating.

Keywords: detonation spraying; oxygen/fuel ratio; coating; hydroxyapatite; tricalcium phosphate; structural-phase state

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1. Introduction

The development and production of biomaterials for bone tissue replacement represent a prominent domain within the high-tech sectors of the economy. Nevertheless, the current type and quality of existing implant materials, along with their manufacturing technology, necessitate further refinement. Furthermore, the primary challenge does not lie in medical technologies associated with the implantation process, but rather in the engineering and materials science aspects related to creating implants with specific chemical and phase compositions, as well as distinct morphological structures.

Titanium and its alloys have been widely used in medicine for the production of various kinds of implants, including friction implants. Titanium alloys and metal–ceramic compositions based on these alloys are still the most effective materials for creating implants and other medical devices. From the point of view of biocompatibility, it is preferable to use pure titanium for implants working for a long time in a living organism, which unlike its alloys does not contain alloying additives harmful for a living organism, has high plasticity, but insufficient strength characteristics, in particular, in terms of cyclic durability [1].

Currently, there are a number of modern methods aimed at changing the structure of the implant surface. These methods include surface activation and application of special coatings in order to improve the adherence of new bone tissue to the implant and accelerate the osseointegration process. In this regard, a promising approach that has been proposed

is the application of calcium phosphate coatings on titanium implants to accelerate the bone healing process. These coatings not only fulfill the function of ensuring the normal function of implants in the body, but also promote their interaction with body tissues [2]. The most frequently used bioactive ceramics are calcium phosphate-based ceramics—hydroxyapatite (HA) or other calcium phosphates close to it in composition [3]. In the field of biomedical material science and bone tissue engineering, the formation of biocomposite coatings based on hydroxyapatite plays a special role in the creation of new implantation materials with bioactive properties.

Given the importance of biocompatible coatings, the selection of a suitable technology for depositing such coatings becomes a key aspect. There are several common methods for this purpose including thermal spraying, immersion method, dynamic mixing, micro-arc oxidation, sol–gel method, pulsed laser deposition and many others [4–8]. Micro-arc oxidation (MAO, micro-arc oxidation) has recently become quite widespread due to the relative simplicity of the coating process [9,10]. Among other deposition methods, gas–thermal methods are also widely used to create various biocompatible coatings. These methods include conventional air plasma spraying (APS), microplasma spraying, high velocity (HVOF, HVAF) spraying and cold spraying [11–13]. For most of these methods, the low or medium adhesion strength of the coatings and the low crystallinity of the resulting coatings are important limiting factors affecting their application. Therefore, the development of new methods or approaches to improve the properties of such coatings is required.

Among other methods, detonation sputtering is a highly efficient method that allows the application of hydroxyapatite on various surfaces, with high speed and accuracy [14]. This method provides uniform coating and good adhesion, which is important for quality implant performance. Gledhill and colleagues conducted a comparative study on the fatigue behavior of HA coatings in Ringer's solution produced by two different methods: air plasma spraying (APS) and detonation spraying (DS) [15]. The study revealed that after 1 million cycles in Ringer's solution, the coatings applied by the APS method completely peeled off from their substrates, while the coatings obtained by the DS method remained stable even after 10 million cycles. In addition, the results of another study indicated that the HA coatings obtained by the APS method were characterized by very low crystallinity and the presence of a significant number of additional phases in the coatings. According to the authors, this phase change may be the result of the extremely high temperature in the plasma atomizer when using the APS method [16]. It should be emphasized that many widely used techniques such as HVOF, HVAF, microplasma and air plasma spraying apply continuous flame or plasma atomization to coatings [17,18]. This process can lead to undesirable overheating or melting of particles and a significant increase in the substrate temperature, which limits their effective application. The DS method utilizes a pulsed regime of operation [19]. On the one hand, this provides an opportunity to reduce the above negative effects. On the other hand, the particle velocity in the DS method is much higher compared to the HVOF, HVAF, MPS and APS methods, which positively provides a coating of high density and adhesion strength with the substrate. At the same time, the temperature of the base material remains low, precluding its deformation or other physical change, which allows this sputtering method to be used for precision parts [20]. In addition, the Ca/P ratio of ≈1.67 can be achieved by optimizing the parameters of the DS process [21]. Achieving the required quality of DS coatings requires a very careful selection of the process regime and automation of the process equipment to exclude the human factor.

Due to important improvements in the design of detonation spraying machines and successful process modeling, Computer-Controlled Detonation Spraying CCDS2000 has become a promising thermal spraying method with high potential for various material systems [22]. It should be noted that a significant advantage of CCDS2000 is the ability to control the composition of the atomized atmosphere. In this method, the volumes of fuel and oxidizer are accurately measured, and since their ratio can be varied, this allows for

unique spraying conditions. Also, by adjusting these parameters, it is possible to change the chemical effect of detonation products on the particles of the sprayed powder. For example, under conditions of oxygen deficiency, incomplete combustion of acetylene occurs by the reaction $2C_2H_2 + O_2 = 4C + 2H_2O$. To reduce the conditions of sputtering with the formation of carbon as a result of incomplete combustion, it is possible to choose the ratio $O_2/C_2H_2 < 1$. However, a lower oxygen content seems to be inexpedient because of the low calorific value of the mixture, which leads to the insufficient heating of powder particles to form covers. The reaction of acetylene combustion in a mixture with the ratio $O_2/C_2H_2 = 1$ can be simplified in the form of $C_2H_2 + O_2 = 2CO + H_2$. When the oxygen content in the explosive mixture is increased to $O_2/C_2H_2 = 2.0$, more material is oxidized.

The aim of this work is to investigate the effect of changing the ratio of the acetylene–oxygen explosive mixture on the structural-phase state and mechanical and tribological properties of detonation hydroxyaptite coatings.

2. Materials and Methods

Spherical HA powder (Medicoat, Mägenwil, Switzerland) with a particle size of 45–63 μm was used as a raw material. Commercial pure titanium (Grade 2) with a size of $30 \times 30 \times 4$ mm^3 was used as substrates. The titanium substrates were sandblasted before coating. A computer-controlled CCDS2000 (LIH SB RAS, Novosibirsk, Russia) detonation spraying unit was used for coating [23]. The detonation gun barrel had a length of 450 mm and a diameter of 26 mm. Acetylene C_2H_2 was used as fuel and oxygen (O) was used as the oxidizer. Nitrogen gas was used to purge the system before each shot and to feed the initial powders through the powder feeder. The chemical composition of the detonation products depends on the O_2/C_2H_2 ratio, which ranged from 2.61 to 3.35 in the present study. The proportion of the gun barrel volume filled with gas mixture (explosive charge) varied between 73% and 77%. The volume/explosive charge is the fraction of the barrel volume filled with the acetylene–oxygen gas mixture (denoted in the paper as a percentage of the total gun barrel volume). The samples of coatings were produced with 50 shots of the detonation gun. The parameters of detonation spraying of the HA powder are given in Table 1.

Table 1. Parameters of detonation spraying of HA powder.

Coating Type	O_2/C_2H_2 Molar Ratio	Explosive Charge, % (Volume of Barrel Filling with Gas Mixture)	Spraying Distance, mm
C1	2.61	73	100
C2	3.03	74	100
C3	3.35	77	100

The surface and cross-sectional morphology of the coatings was characterized using TESCAN MIRA3 LMH scanning electron microscopy (TESCAN, Brno, Czech Republic). SEM observation of the initial powders shows that the powders have a spherical shape (Figure 1a). The studied samples were subjected to X-ray phase analysis using a Shimadzu XRD-6000 diffractometer (monochromatic Cuα-radiation, wavelength 1.54056 Å) with the following imaging parameters: accelerating voltage: 45 kV, beam current: 30 mA, scanning step: 0.02° in the angle range 20–70°; signal acquisition time: 0.5 s. The phase composition analysis was performed using PDF4+ databases as well as the POWDER CELL (version 2.4) full-profile analysis program [24]. It should be noted that the diffractograms of the initial powders (Figure 1b) show that all the diffraction peaks correspond to the standard HA powder pattern (ICDD 09-0432). The hardness and modulus of elasticity of the coatings were measured using a FISCHERSCOPE HM 2000 S (Fischer, Sindelfingen, Germany) with WIN-HCU software [25]. This computer-controlled measurement system is designed to evaluate microhardness and characterize materials in accordance with the international standard ISO 14577 [26]. For all hardness and modulus tests, the dwell time was set to 10 s at a load of 1 N. Average hardness values were obtained based on the results of

10 measurements. The distribution of pores in cross-sections was studied using the Altami image analyzer. Profilograms and surface roughness values were obtained using a model 130 profilometer (Proton Plant, Moscow, Russia). Measurement of surface roughness of coatings was carried out in 5 points with the length of the base line (trace) of 10 mm and the average value was considered. Tribological testing of samples was carried out on a tribo-meter TRB^3 (Anton-Paar, Buchs, Switzerland) using the standard technique "ball-on-disk" (ASTM G 133-95) in Ringer's solution, which is called artificial organism fluid. The chemical composition of Ringer's solution is 9.0 g/L NaCl, 0.42 g/L KCl, 0.48 g/L $CaCl_2$, and 0.2 g/L $NaHCO_3$. In tribological testing, a 6 mm diameter Si_3N_4 silicon carbide ceramic ball was selected as a counterbody. The tribological test regime was as follows: normal load: 6N; ball sliding velocity: 3 cm/s; friction path: 100 m.

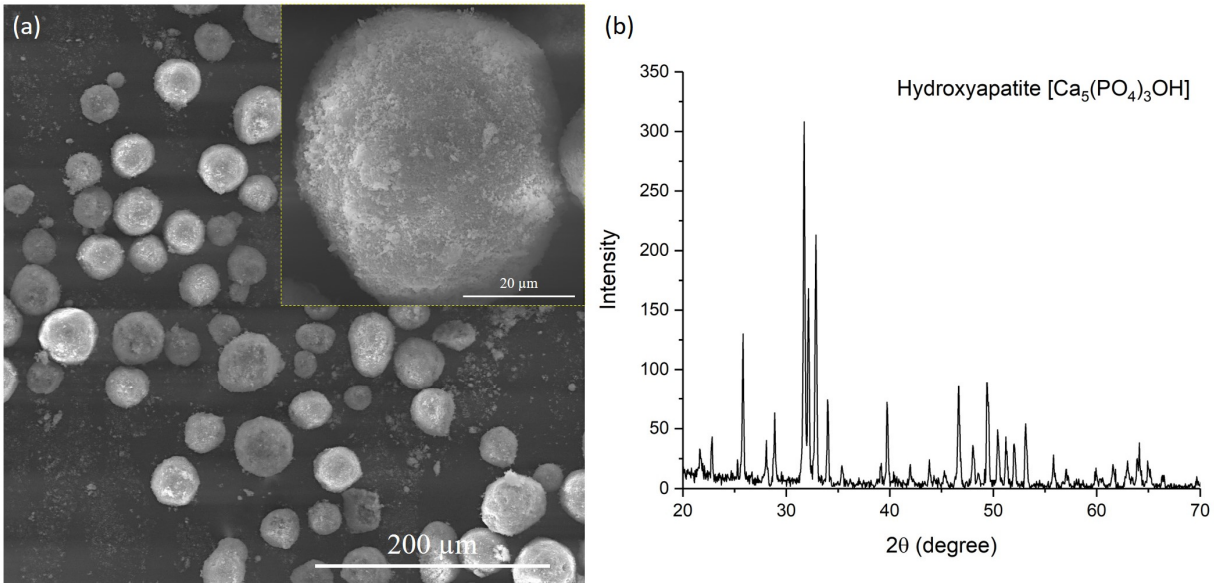

Figure 1. SEM images (**a**) and diffractogram (**b**) of HA powder.

3. Results and Discussion

The results of the study of phase compositions of hydroxyapatite coatings obtained by detonation spraying at different O_2/C_2H_2 ratios are presented in Figure 2. The diffractograms of the coatings show the main phase of hydroxyapatite HA [$Ca_5(PO_4)_3OH$] and the formation of tricalcium phosphate α-TCP [α-$Ca_3(PO_4)_2$] as a result of the partial decomposition of HA. It is reported in [27] that the decomposition of HA occurs when a critical point is reached where complete and irreversible dehydroxylation occurs, resulting in damage to the HA structure with decomposition into tricalcium phosphate (α-TCP at 1200 °C and β-TCP at higher temperatures) and tetracalcium phosphate (TTCP). This decomposition mechanism can be called the solid-state decomposition of HA [28], since the melting point of HA is conventionally considered to be T_m = 1570 °C, which is simultaneously the liquidus temperature of the mixture of α-TCP and TTCP [29]. According to the X-ray diffractogram data, an amorphous-diffusion background can be seen at diffraction angles of 25–35° (Figure 1). Similar results were obtained in [30]. During detonation spraying, an amorphous phase of calcium phosphate and calcium oxide can also form in the particles where the temperature exceeds T_m because of the high cooling rate (cooling rate 10^4–10^6 K/s). According to [31], the temperature of detonation products at O_2/C_2H_2 = 2.9 was found to be 3855 °C, and at O_2/C_2H_2 = 3.6, it was 3725 °C.

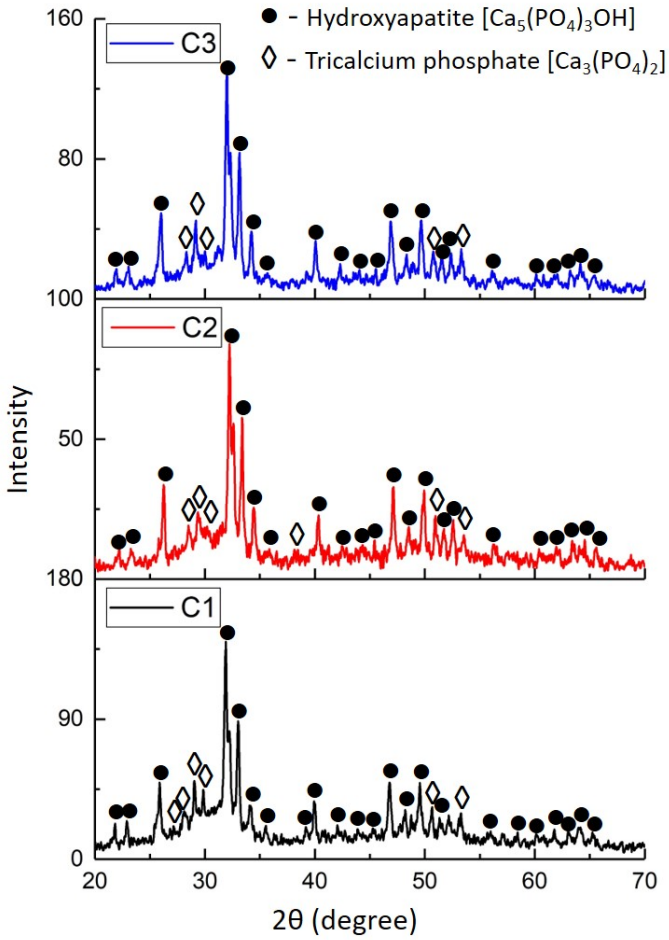

Figure 2. Diffractogram of sprayed HA coatings.

The diffractograms of HA coatings obtained at different O_2/C_2H_2 ratios were identical in phase composition. However, a slight change in the intensity of diffraction peaks depending on the O_2/C_2H_2 ratio was observed. A comparison of the intensity of the diffraction peaks of the coatings showed a weakening of the diffraction maxima in the C2 coatings compared to the C1 and C3 coatings. Weakening of intensity occurs due to two processes: absorption of X-ray photons by the substance and change in their direction during scattering. On this basis, according to the results of quantitative X-ray phase analysis, the weakening of the intensity of diffraction maxima of C1 coatings is probably associated with a relatively high content of the $Ca_5(PO_4)_3OH$ phase in the composition of coatings (Table 2). In addition, weakening of the intensity of diffraction maxima in C2 coatings can be connected with the porosity of the coatings according to the results of electron-microscopic research.

Table 2. Results of X-ray phase analysis.

Sample	Detected Phases	Phase Content, Mas. %	Lattice Parameters, Å	CSR Size, nm	$\Delta d/d \times 10^{-3}$
C1 (O_2/C_2H_2—2.61)	$Ca_5(PO_4)_3OH$	50	a = 9.3949 c = 6.8811	48	1
	$Ca_3(PO_4)_2$	19	a = 12.9870 b = 27.2012 c = 12.9328	18	0.7
	Amorphous phase	31	-	-	-

Table 2. *Cont.*

Sample	Detected Phases	Phase Content, Mas. %	Lattice Parameters, Å	CSR Size, nm	$\Delta d/d \times 10^{-3}$
C2 (O_2/C_2H_2—3.03)	$Ca_5(PO_4)_3OH$	53	a = 9.3949 c = 6.8897	59	1
	$Ca_3(PO_4)_2$	19	a = 12.9515 b = 27.3361 c = 12.9063	25	1
	Amorphous phase	28	-	-	-
C3 (O_2/C_2H_2—3.35)	$Ca_5(PO_4)_3OH$	51	a = 9.3896 c = 6.8866	60	0.8
	$Ca_3(PO_4)_2$	20	a = 12.9492 b = 27.3800 c = 12.8901	18	0.7
	Amorphous phase	29	-	-	-

It is reported in [30] that as the molar ratio of O_2/C_2H_2 increases, the amount of atomic oxygen increases in the detonation products, which may contribute to the oxidation of particles during the spraying process. At an O_2/C_2H_2 ratio of 1.1, the detonation products contain significant amounts of atomic and molecular hydrogen and carbon monoxide (CO) and are therefore reductive in nature. The results of [32] showed that when the O_2/C_2H_2 ratio increases from 1.1 to 2.0, the content of the amorphous phase decreases. Based on these data, the molar ratios of the components of the explosive mixture O_2/C_2H_2 were varied from 2.61 to 3.35 to obtain the crystalline phase of HA. It is reported in [33] that at a ratio of O_2/C_2H_2 = 3.6 and 70% explosive mixture charge, HA coatings without impurity phases were obtained. However, in the present work, by varying the O_2/C_2H_2 ratio from 2.61 to 3.35 and with an explosive charge of 73–77 %, the phase composition of the coatings consists of HA, α-TCP and amorphous phases. Thus, according to the XRD results, it can be concluded that there is a possible partial decomposition of the surface layer of HA particles in the detonation spraying process, which may be the result of short-term exposure to high temperatures in the detonation wave, leading to the formation of the α-TCP phase and very rapid cooling of molten particles leads to the formation of the amorphous phase.

Figure 3 shows the results of measuring the surface roughness of coatings obtained by detonation spraying at different O_2/C_2H_2 ratios. Studies on the roughness of the coatings obtained by detonation spraying showed that changing the O_2/C_2H_2 ratio from 2.61 to 3.35 affects the roughness parameter, which was 4.34 and 5.41 μm, respectively. It was found that increasing the O_2/C_2H_2 ratio from 2.61 to 3.35 can increase the surface roughness.

Figure 4 shows the morphology of the coatings obtained in different O_2/C_2H_2 ratios. From the surface morphology, it is clear that the coatings have a pronounced relief and porous structure that positively influences the bone ingrowth and implant fixation. Partial melting of the coating surface was observed in all the investigated regimes of detonation spraying. The number of melted spots was higher on the surface of the coatings obtained at the ratio O_2/C_2H_2 = 2.61. A decrease in the oxygen/fuel ratio can increase the detonation spraying temperature and leads to the melting of the HA particles [32].

An important parameter of bioactivity is the calcium to phosphorus ratio. It is known that bone bioapatite can display a deviation in the stoichiometric calcium to phosphorus ratio from the corresponding theoretical value, equal to 1.67. The results of the EDS spectra of HA coatings showed the presence of major constituent elements such as Ca, P and O in different atomic percentages. The calculated Ca/P ratios (extracted from the relative atomic percent values in the EDS results) of the HA coatings in different areas are shown in Table 3. The ratios, in turn, can be related to the calcium phosphate compounds present in the sputtered coatings as follows [33]: Ca/P = 1.5 corresponds to α- and β-TCP; Ca/P = 1.67 corresponds to HA; Ca/P = 2 corresponds to TTCP. The average chemical composition

shows a decrease in the ratio of calcium to phosphorus in the sprayed coating relative to the original powder from 1.67 to a value of ~1.5, which is due to the decomposition of HA.

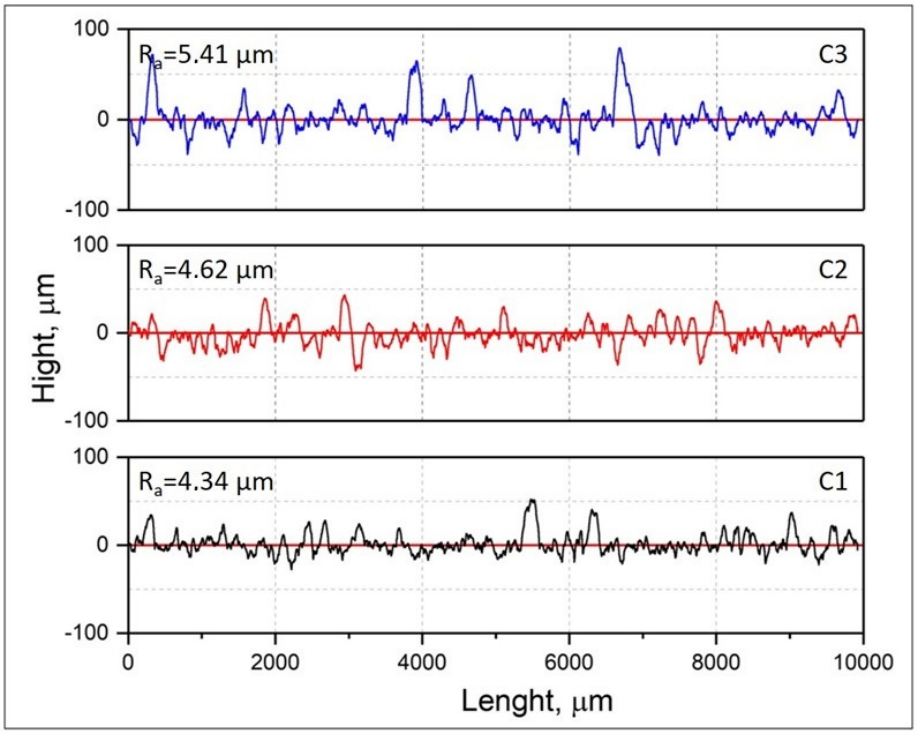

Figure 3. Surface roughness of the coating surface.

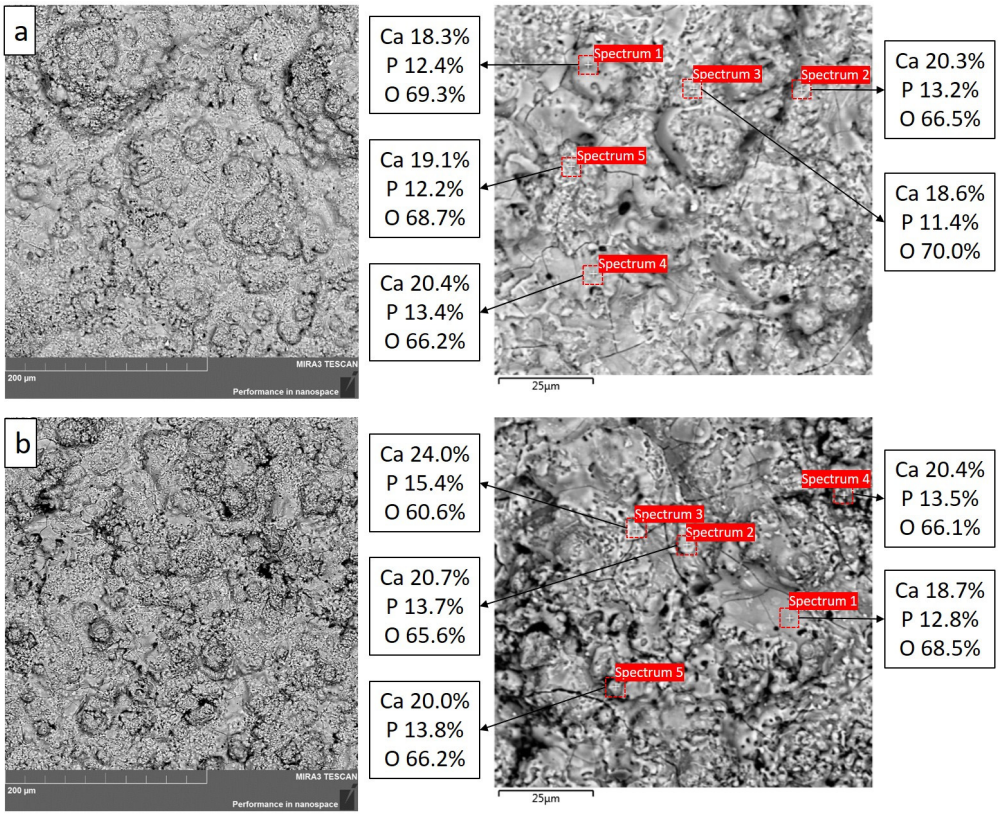

Figure 4. *Cont.*

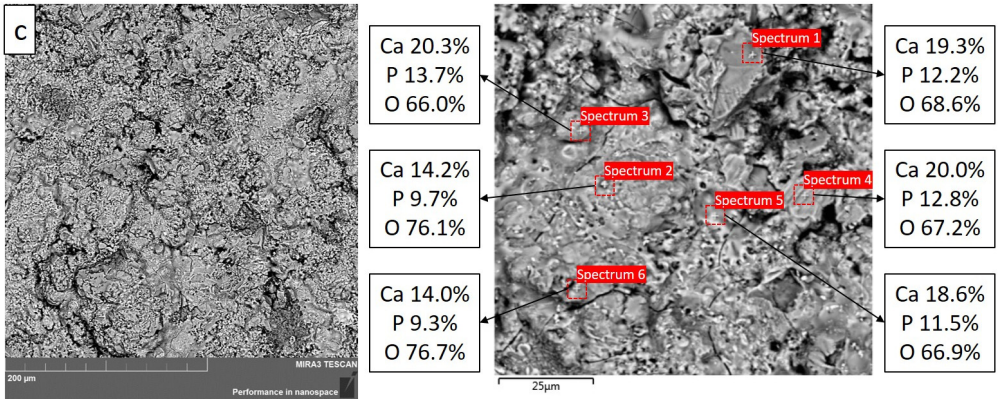

Figure 4. SEM micrographs of the surface of HA coatings with EDS analysis results: (**a**) C1 coating; (**b**) C2 coating; (**c**) C3 coating.

Table 3. The Ca/P ratio in HA coatings at different spectrums.

Sample	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5
C1 (O_2/C_2H_2—2.61)	1.47	1.53	1.63	1.52	1.56
C2 (O_2/C_2H_2—3.03)	1.46	1.51	1.55	1.51	1.44
C3 (O_2/C_2H_2—3.35)	1.58	1.46	1.48	1.56	1.61

Figure 5 shows the cross section of HA coatings with elemental mapping results. The pore volume fraction in relation to the total cross-sectional area (%) was calculated for each coating. C2 coatings are characterized by the highest pore volume fraction with an average value equal to 18.8% of the total coating volume, while C1 coatings are characterized by the lowest pore volume fraction with an average value equal to 5.1% of the total coating volume. And at O_2/C_2H_2 ratios equal to 3.35, the C3 coating has a pore volume fraction of 6.5% of the total coating volume. According to the results of [33,34], the porosity and the number of unmelted particles increase with an increasing O_2/C_2H_2 ratio during detonation spraying. In the present work, the same effect is observed. From the data of electron microscopic studies, it can be seen that with increasing O_2/C_2H_2, an increase in porosity (coating C2) and a decrease in the cohesive strength of the coatings with crack formation (coating C3) are observed. This may be due to the ceramic composition of the coatings. It should be noted that an increase in the O_2/C_2H_2 ratio will lead not only to a high degree of melting of powders, but also to an increase in the dynamic effect of detonation products on the sprayed particles. As a rule, in detonation spraying, the coating is formed from heated and melted powder particles. Due to the rapid cooling of the sprayed material, the formation of the first layer is accompanied by the appearance of pores. Subsequent layers deform the already deposited layers and increase their density, which ensures the complete elimination or significant reduction in porosity in the finished coatings. The presence of porosity in HA coatings with increasing explosive energy is explained by the low consolidation of ceramic powders during detonation spraying.

The results of cross-sectional mapping of the studied samples showed the main elements of the coatings Ca, P, O and the substrate Ti, without foreign impurities. It can be seen that oxygen is present at the coating–substrate interface (Figure 5a,b). During the sandblasting process, the titanium surface becomes rough. These “scalloped” interfaces between the coating and substrate represent areas subject to oxidation during detonation coating. Analysis of cross sections of the coatings shows a uniform distribution of elements

with the main phase of the HA coating. It can be assumed that the mechanical properties of the coatings will also be stable.

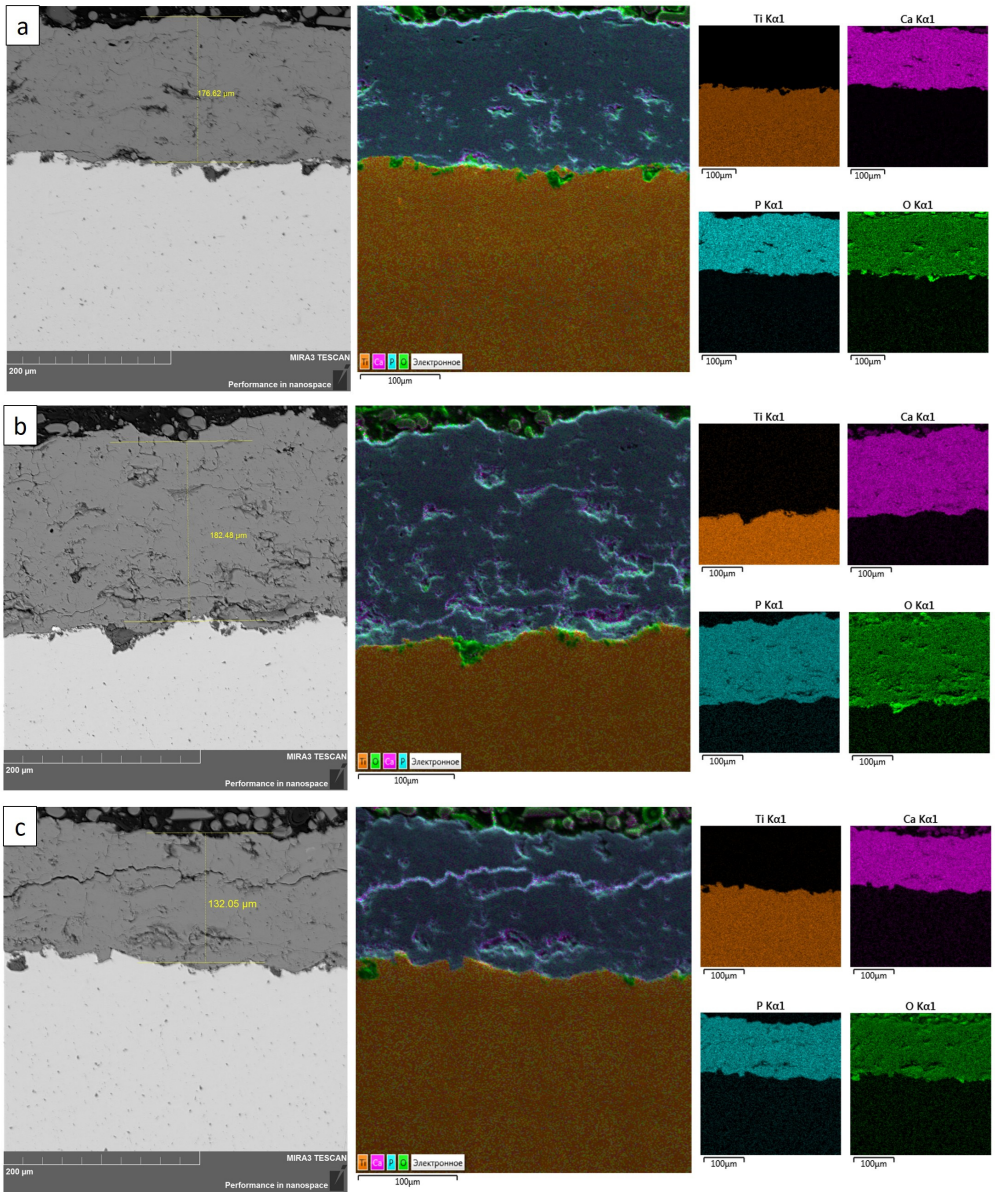

Figure 5. Cross section of HA coatings with the result of elemental mapping: (**a**) C1; (**b**) C2; (**c**) C3.

A cross section of each HA coating was used to determine the microhardness and elastic modulus (Figure 6). The average hardness of the HA coatings obtained under C1 and C2 regimes has a single value and is approximately 2.5 ± 0.1 GPa. One of the requirements for the surface of bone implants is the close values of the elastic modulus and hardness of the artificial material and bone. Bone tissue has the following characteristics: H = 2–4 GPa, E = 7–26 GPa [35]. The C3 coating shows a lower hardness of 1.5 ± 0.2 GPa and a lower elastic modulus because there are cracks in the coating structure (Figure 6). The distribution of the elastic modulus and hardness depends on the characteristics of the coating at each specific point, i.e., grain size, presence of pores and defects.

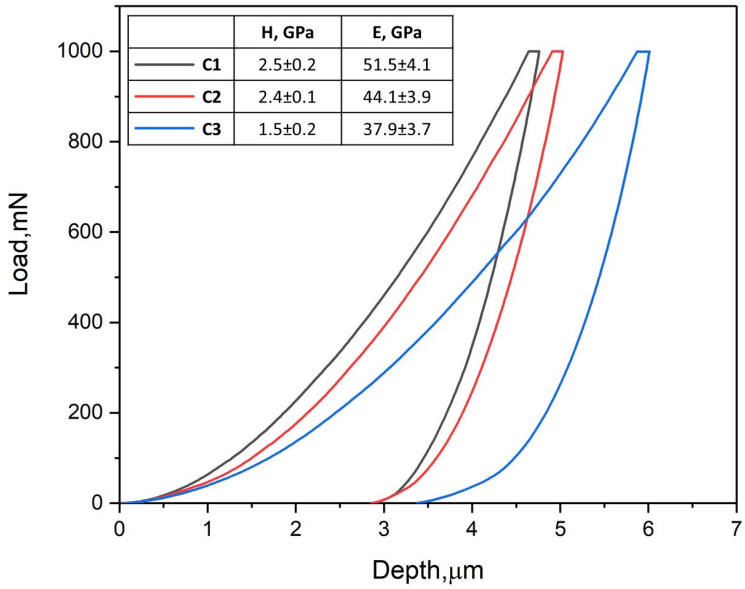

Figure 6. Loading and unloading curves for HA coating.

Figure 7 shows the result of the tribological tests of hydroxyaptite coatings and titanium (Grade 2) in Ringer's solution. The friction coefficient between titanium and the counterbody made of silicon carbide Si_3N_4 is 0.470 ± 0.029 on average. During friction, titanium alloys tend to adhere to the contacting material even at low loads. On this basis, the dependence of the friction coefficient on the friction path has a scatter of values. The friction coefficient of hydroxyaptite coatings showed identical values of 0.296–0.319 on average. The decrease in the friction coefficient shows an increase in the wear resistance of the sample surface after the application of hydroxyaptite coatings on titanium surfaces by detonation spraying.

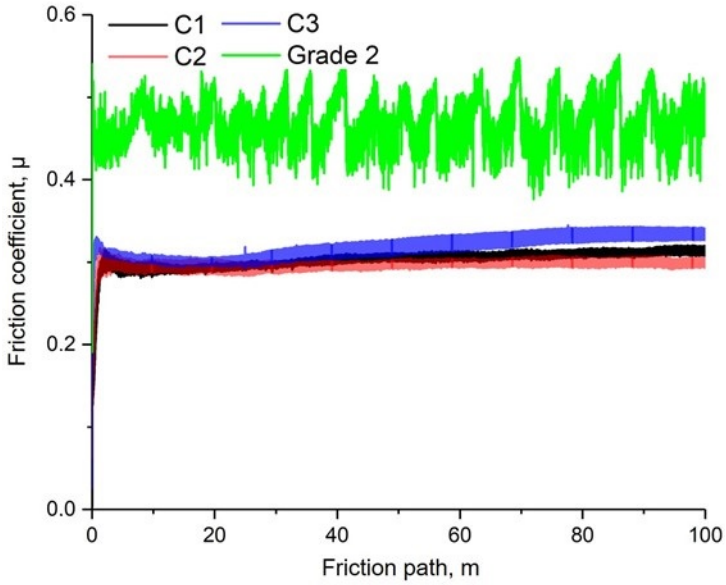

Figure 7. The dependence of friction coefficient of titanium (Grade 2) and hydroxyaptite coatings on the friction path length (Si_3N_4 counterbody, in Ringer's solution).

4. Conclusions

The influence of the composition of the acetylene–oxygen explosive O_2/C_2H_2 mixture during detonation spraying on the structure and properties of hydroxyapatite coatings has been investigated. The results of the study can be summarized as follows:

- When varying the molar ratio of O_2/C_2H_2 components from 2.61 to 3.35 and the explosive charge in the range of 73–77%, coatings containing hydroxyapatite (HA, predominant phase), tricalcium phosphate (α-TCP) and amorphous phases were formed. Variation in the above parameters of detonation spraying did not reveal any change in the phase composition of the coatings;
- During the detonation spraying of HA coatings, the formation of amorphous phases occurs due to the rapid cooling of particles heated to the melting point;
- The study of coating surface morphology showed that partial melting of the coating surface was observed in all the studied regimes of detonation spraying;
- An increase in the O_2/C_2H_2 ratio from 2.61 to 3.35 leads to an increase in the roughness of the coating structure and with an increase in the explosive charge of 77 %, transverse cracks appear in the coating;
- The results of the EDS analysis of coatings showed the presence of major constituent elements such as Ca, P and O in different atomic percentages. The calculated Ca/P ratio mainly corresponds to Ca/P = 1.5 (α-TCP) and Ca/P = 1.67 (HA), which is in agreement with the XRD results;
- The average hardness of the HA coatings obtained by C1 and C2 regimes has a single value and is about 2.5–2.4 GPa, and the elastic modulus is 51.5–44.1 GPa. Bone tissue has the following characteristics: H = 2–4 GPa, E = 7–26 GPa. In further development of the research topic, special attention will be paid to the possibility of obtaining single-phase HA coatings by detonation spraying with a close value of mechanical properties to bone tissue.
- The application of hydroxyaptite coatings on titanium surfaces reduces the friction coefficient in Ringer's solution about 1.5 times.

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