Mechanochemical Synthesis of Hydroxyapatite with Substitutions for Depositing the Coatings on Medical Implants by Means of High-Frequency Magnetron Sputtering

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Abstract

Data on the mechanochemical synthesis of single-phase hydroxyapatite (HA) with the substitution of phosphate ions by silicate ions, having the composition $Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28}$, for use as the material for target for magnetron sputtering are presented. The elemental composition of the coating deposited on titanium substrates of the type of Ti6Al4V used as medical implants is similar to the elemental composition of the target material. According to the data of IR spectroscopy, SiO_4^{4-} ions are built into the lattice of the coating which has the HA structure according to the XPA data. The Si–HA coating is likely to have the amorphous-crystalline structure.

Key words: hydroxyapatite with substitutions, mechanochemical synthesis, coatings of implants, magnetron sputtering

INTRODUCTION

During the recent decades, extensive search for biocompatible materials for the purpose of using them in traumatology, orthopaedy and stomatology has been carried out all over the world [1]. These studies are aimed at obtaining the materials that would be able to conserve the functional properties during the prescribed performance time having no negative effects on organism. Investigations develop towards obtaining the materials based on elementary substances and compounds with different degrees of biological activity: biologically inert, biologically active, and bioresorbed [2]. The lists of new biocompatible materials are continuously replenished, however, isomorphous sorts of apatite remain the most promising biocompatible material, both in the form of stoichiometric pure hydroxyapatite (HA) and with various substitutions [3]. Unrelenting attention to HA is explained by the identity of its structure with the mineral component of the human bone tissue which is represented by HA $Ca_{10}(PO_4)_6(OH)_2$ with partial substitution of phosphate by carbonate ion and the inclusion of different elements into the lattice as microimpurities [4].

At present, the majority of works are aimed at the improvement of the bioactive properties of HA. One of the approaches to solve this problem is chemical modification of HA. Due to the specificity of the use of materials in medicine, the choice of possible dopants is very limited. The anions of silicon oxide (SiO_4^{4-}) can be proposed as a possible modifying agent for synthetic HA because these ions are a natural component of the inter-tissue liquid.

Synthesis of apatite samples of the required composition is not a simple problem. The conventional methods of its synthesis include the

following: obtaining from solutions [4, 5], ceramic method involving annealing of the reaction mixture at a temperature of 900−1000 °C [6], hydrothermal method [7]. The problem of HA synthesis from solution and according to the hydrothermal method is connected not only with the complicacy of obtaining a single-phase product but also with the low yield of the product [6, 7]. The thermal method is also considered to be labour-intensive because the synthesis is carried out in several stages in order to obtain a single-phase product: repeated grinding and annealing are involved.

Unlike for the conventional methods, the mechanochemical synthesis is very promising. The initial compounds for the mechanochemical method are hydroxides or hydrated salts [8]. Mechanochemical synthesis usually proceeds in these systems in the solid phase but the crystal water of initial substances and water formed as a result of acid-base reactions participates in the interaction between components. Due to this, the final product is obtained easier with smaller mechanical load. This approach is known as a soft mechanochemical synthesis [9, 10].

A number of publications that appeared in the recent years describe different versions of the mechanochemical method of HA synthesis [11−14]. However, the authors of those works did not succeed to obtain apatite as a crystal product by means of synthesis in the solid state directly in the mill. In some works, the synthesis is carried out in the liquid phase [11] or the initial materials are $Ca(OH)_2$ and P_2O_5 [12], which is also close to the liquid-phase synthesis due to the rapid hydration of phosphorus oxide. During the liquid-phase synthesis, the mechanical action is reduced to mixing the components, so these methods can hardly be related to mechanochemical methods. The authors of [13] carried out hydrothermal treatment of the mixture after mechanical activation, while the authors of [14] performed annealing of the reaction mixture at 1373 K after mechanical activation for many hours.

Hydroxyapatite and β-tricalcium phosphate $Ca_3(PO_4)_2$ can be used as the material to obtain bioceramics, but only in the absence of high mechanical load. The most promising direction is the use of HA as a coating to increase bioactive properties of implants made of materials with multiply confirmed medical merits.

The major methods used to form coatings include: 1) plasma spraying [15]; 2) laser ablation [16]; methods based on crystallization of coatings from various solutions [17]; 4) high-frequency (HF) magnetron sputtering [18, 19]. In a number of methods, the initial substance is changed during the deposition of the coating, and the coating is a new, often multiphase system. For example, the coating deposited using the micro-arc method on titanium implants is composed of the double salt of titanium and calcium phosphate ($CaTi_4(PO_4)_6$, TiP_2O_7, $CaTiO_4$) and titanium oxide [20]. It is important that the method under use should allow one to conserve the chemical composition of the initial material (HA) during the deposition of the coating on the implant. The method of HF magnetron sputtering meets this requirement; moreover, it allows one to vary both the elemental composition of the coating by changing the composition of the initial target for sputtering and the parameters of sputtering (discharge power, working gas *etc.*) [21]. Another indisputable advantage of this method is high adhesive strength of the coatings.

Silicon ions play an active part in the arrangement of conjunctive bone tissue, so biologically active materials containing silicon win broadening applications in clinical practice [22, 23]. A number of works dealt with the synthesis of apatite with the inclusion of silicate group into the structure with substitution parameters varied within the range $0 < x < 1$ for apatite composition $Ca_5(PO_4)_{3−x}(SiO_4)_xO_{(1−x)/2}$ [24, 25].

It was substantially interesting for our work to study the limit of phosphate substitution for $SiO_4^{4−}$ group in the mechanochemical synthesis of HA, and then to study the synthesized material as a coating for implant deposited by means of HF magnetron sputtering. The amount of the substituent in apatite is determined by lattice parameters and the relations between the ion radii of the components of the product to be synthesized. For the heteroionic substitution of trivalent phosphate group for the quadrivalent silicate anion, vacancies appear in the structure of HA $Ca_{10}(PO_4)_6(OH)_2$ in the position of hydroxyl group at axis 6_3 [4]. The limit of the vacant positions of OH groups restricting the amount of the substituting anion

has not been determined yet. However, a definite amount of them is necessary in the structure because otherwise apatite structure falls apart and β-tricalcium phosphate $Ca_3(PO_4)_2$ or other phases are formed [4]. According to the data reported in [26], the phosphate coating containing silicon 4.9 % was obtained by magnetron sputtering from two separate targets: pure silicon and synthesized non-substituted HA. Using the mechanochemical method we synthesized the HA sample in which silicon was substituting the phosphorus ion also in the amount of 4.9 mass % but directly in the apatite lattice; the composition of apatite corresponded to the formula $Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28}$. In this case, a small part of OH^- groups (in comparison with the stoichiometry of $Ca_{10}(PO_4)_6(OH)_2$) still remains in the structure.

The goal of the present work was to study the possibility to use mechanochemically synthesized HA with maximal possible substitution of phosphate ion by SiO_4^{4-} as the material for sputtering into the plasma of magnetron discharge for the deposition of coatings on medical implants by means of HF magnetron sputtering [21].
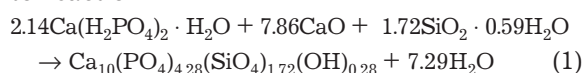
EXPERIMENTAL

Mechanochemical synthesis (MCS) of HA was carried out in a planetary mill APF in two steel cylinders 750 mL in volume. Steel balls with the mass of 1 kg (the mass ratio of balls to the mixture was 10 : 1.1) were loaded into each water-cooled cylinder. The frequency of cylinder rotation in the activator was 900 min^{-1}. The power of the mill allowed us to obtain the ready product in the nanocrystalline state without subsequent thermal treatment.

Before the synthesis of the samples, we carried out preliminary auto-fettling of the inner part of cylinders and the balls with a mixture of the identical composition in order to avoid iron wear. For this purpose, the reaction mixture was activated in the mill for 30 s. The walls of cylinders and the balls were coated with the mixture. The residual mixture not covering the working surfaces of the mill was removed. Then the reaction mixture for subsequent synthesis was charged into the mill. Analysis of the syn-

thesized apatite with a Varian AA-280FS spectrometer showed that iron content was 0.04 % with the relative error of 1 %.

To synthesize HA with partial substitution of phosphate for SiO_4^{4-}, we used $Ca(H_2PO_4)_2H_2O$, CaO, $SiO_2 \cdot 0.59H_2O$ of "ch." and "ch.d.a." reagent grade. The phase composition of the initial substances was monitored through the data of X-ray phase analysis; water content of silicon and calcium oxides was determined from the data of differential thermal analysis (DTA) on a Netzsch STA 409 instrument. According to the DTA data, calcium oxide in the initial state contained more than 20 % water, with its major part removed within temperature range 400–500 °C with the maximum at 483.7 °C, and CO_2 (1.75 %) that was removed within temperature range 600–700 °C. As a consequence, for the synthesis of each portion of HA, we annealed calcium oxide and then used it. Amorphous hydrated silicon oxide ($S_{sp} = 420$ m^2/g) contained water sorbed on its surface. It was removed at temperatures up to 900 °C, starting from the endo-peak at 57 °C and exo-peak at 109 °C. On the basis of DTA data, we calculated the amount of water and determined the composition of silicon oxide; it corresponded to the formula $SiO_2 \cdot 0.59H_2O$.

Mechanochemical synthesis of silicon-substituted HA (Si–HA) was performed according to reaction

$$2.14Ca(H_2PO_4)_2 \cdot H_2O + 7.86CaO + 1.72SiO_2 \cdot 0.59H_2O$$
$$\rightarrow Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28} + 7.29H_2O \qquad (1)$$

The mass composition of the mixture in agreement with the components ratio of this equation was 53.94 g $Ca(H_2PO_4)_2 \cdot H_2O$, 44.08 g CaO, 12.16 g $SiO_2 \cdot 0.59H_2O$ (total amount: 110.18 g).

In order to choose optimal synthesis time, we studied the activation of reaction mixture for 3, 6, 9 and 12 min. The phase composition of the mixture activated for different time intervals was determined by means of XPA. It was established that even after activation for 3 min the reflections of apatite appear (Fig. 1). Only one weak reflection of initial calcium phosphate remained in the diffraction patterns of this sample, but weak reflections of calcium hydroxide were detected. Calcium hydroxide is formed from calcium oxide during the activation of the mixture. A clear diffraction pattern
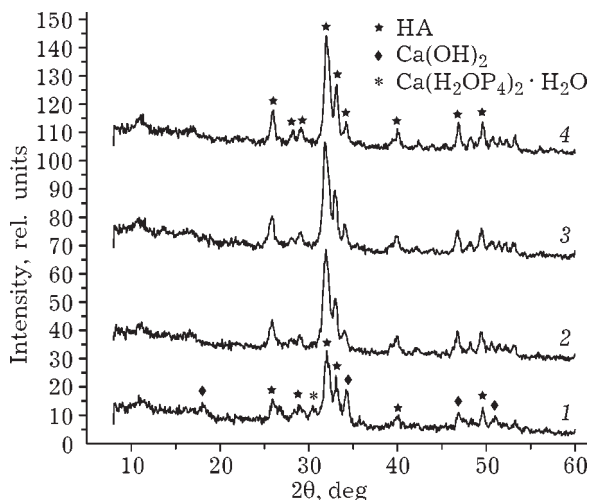
Fig. 1. X-ray diffraction patterns of the reaction mixture for the synthesis of hydroxyapatite after mechanical activation for, min: 3 (*1*), 6 (*2*), 9 (*3*), 12 (*4*).

with the reflections of apatite and the absence of other phases was obtained after the activation of the mixture for 12 min. On the basis of the data obtained, we performed mechanical activation of the reaction mixture during the synthesis of HA with partial substitution of phosphate by silicate ion for 12 min.

The target for the HF magnetron sputtering, 220 mm in diameter and 10 mm thick, was prepared according to the ceramic technology under the pressure of 70 MPa, followed by annealing of the resulting press mold at a temperature of 1100 °C for 1 h in the air. The single crystals of especially pure KBr and silicon plates, as well as titanium alloy Vt6 (Ti6Al4V) were used as substrates for sputtering.

The industrial set-up 08PKhO-100T-005 with magnetron source (5.28 MHz) was used to deposit the coatings. The following parameters were established for deposition: working pressure, 0.1 Pa (limiting rarefaction in the vacuum chamber: 10^{-4} Pa), distance between the target and the substrates: 40 mm, sputtering time: 6 h, working gas: argon, power of the HF generator: 290 W.

Investigations of the morphology and elemental composition of the materials of the target and coatings obtained by sputtering the target composed of Si−HA that was formed according to reaction (1) were carried out using a Quanta 200 FEG ESEM (FEI, USA) with the built-in attachment for energy-disperse X-ray

analysis (EDX). The phase composition of the formed Si−HA coating and the material of the target was determined using XPA (Shimadzu XDR-7000 diffractometer). To reveal chemical bonds of the phosphate and substituent groups, we used infrared spectroscopy (IRS) with Termo Nicolet 3700 within wavenumber range 400-4000 cm^{-1}. To change the structure of the coatings, we heated them in the air to 500 °C.

RESULTS AND DISCUSSION

According to the XPA data, mechanochemically synthesized apatite with the composition $Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28}$ is a single-phase product (see Fig. 1). To make the target, we synthesized 2 kg of this kind of HA. The target, obtained according to the procedure described above from mechanochemically synthesized Si−HA, is rather strong ceramics, which allows us to carry out uniform sputtering on the substrates.

Typical morphology of the coatings obtained through HF sputtering on the substrate made of titanium alloy Vt6 (Ti6Al4V) is shown in Fig. 2. It was established that the coatings formed by means of HF magnetron sputtering are continuous, dense, without visible surface defects.

Figure 3 shows the EDX spectra of the material of Si−HA target ($x = 1.72$). Both the target material and the coating contain carbon, oxygen, calcium, phosphorus and silicon; oth-
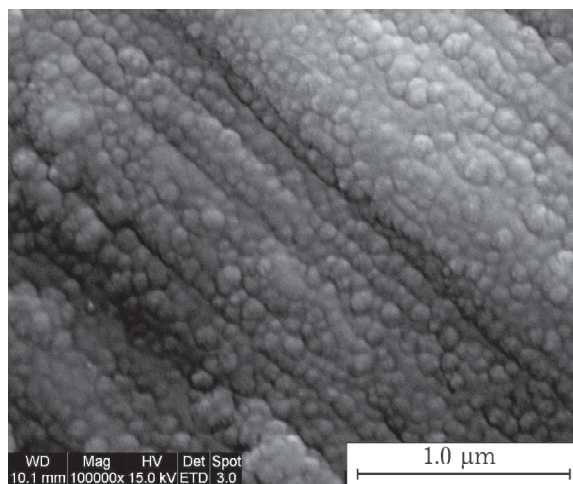

Fig. 2. Electron microscopy image of the surface of Si−HA coating ($x = 1.72$) deposited by the HF magnetron sputtering of Si−HA target.
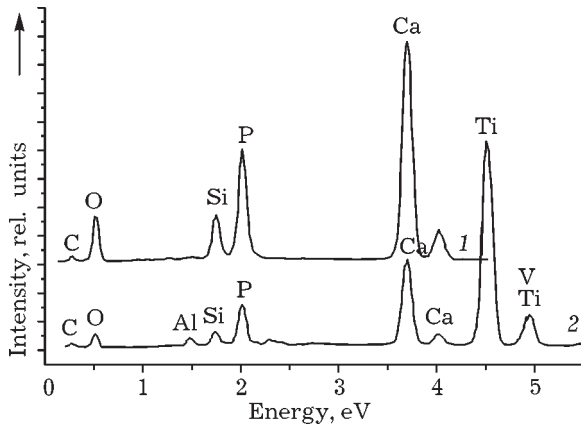
Fig. 3. EDX spectra of the Si−HA ($x = 1.72$) target material (*1*) and the HF magnetron coating (Vt6 substrate) (*2*).

er elements belong to the substrate. According to the data of EDX analysis, the ratio of calcium to phosphorus for the coating (Ca/P = 1.42) is smaller in comparison with that for the material of the target (Ca/P = 1.89). The use of HF magnetron sputtering of multicomponent targets may affect the elemental concentration due to the interactions between particles in the plasma. It was stressed in [27] that it is easier for PO_4^{3-} ion than to Ca^{2+} ion to reach the substrate surface, which causes a decrease in Ca/P ratio. In addition, as a result of bombardment of the coating with the particles, rearrangement of the structure may occur through the formation of defects and sputtering of the formed surface, which also may lead to changes in the chemical composition of the coating with respect to the composition of the material of the target.
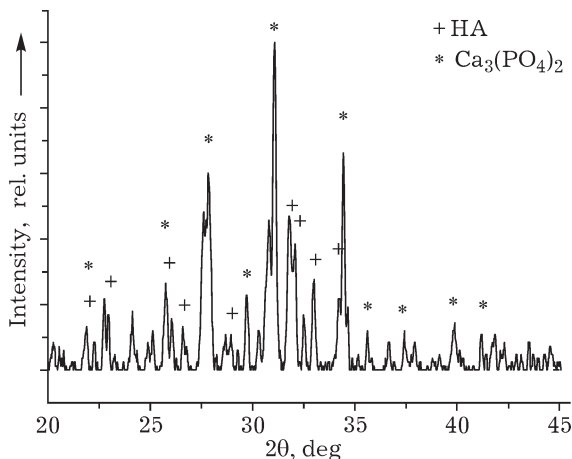

Fig. 4. X-ray diffraction patterns of the material of ceramic target Si−HA with the substitution $x = 1.72$.
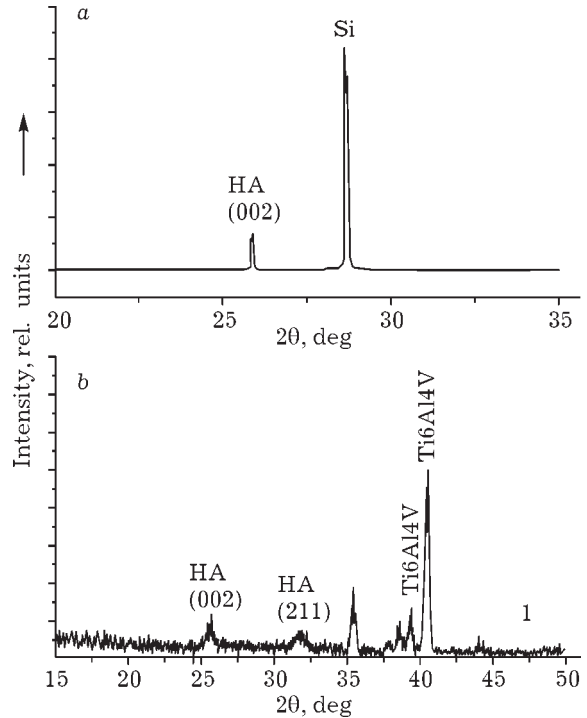

Fig. 5. X-ray diffraction patterns of the Si−HA coating ($x = 1.72$) on the silicon substrate (*a*) and on Ti6Al4V (*b*).

The X-ray diffraction patterns of the material of ceramic target and the Si−HA coating with substitution ($x = 1.72$), formed on the substrates composed of silicon and titanium alloy Vt6 by means of HF-magnetron sputtering, are shown in Figs. 4, 5.

According to the XPA data, the material of the target (see Fig. 4) consists of two phases: α-tricalcium phosphate α-$Ca_3(PO_4)_2$ with the prevailing crystallographic orientation (170) at 30.7° [28] (09-348 JCPDS) and HA with the maximal reflection at 31.7° (211) (09-432 JCPDS). The initial Si−HA powder obtained by means of MCS has the single-phase composition with HA structure (see Fig. 1). So, unlike for the initial powder, the material of the target is a mixture of two phases: crystalline HA and α-tricalcium phosphate. No reflections corresponding to CaO were detected.

The X-ray diffraction patterns of the coatings were recorded in the sliding beam mode. The diffraction patterns of the coating (see Fig. 5, *a*) on the silicon substrate before and after heating contain only the reflections corresponding to HA 25.9° (002) and silicon 28.7° (100), according to the JCPDS database [28]. Sputtering leads to the change of the preferential orientation of crystal faces of the formed prod-
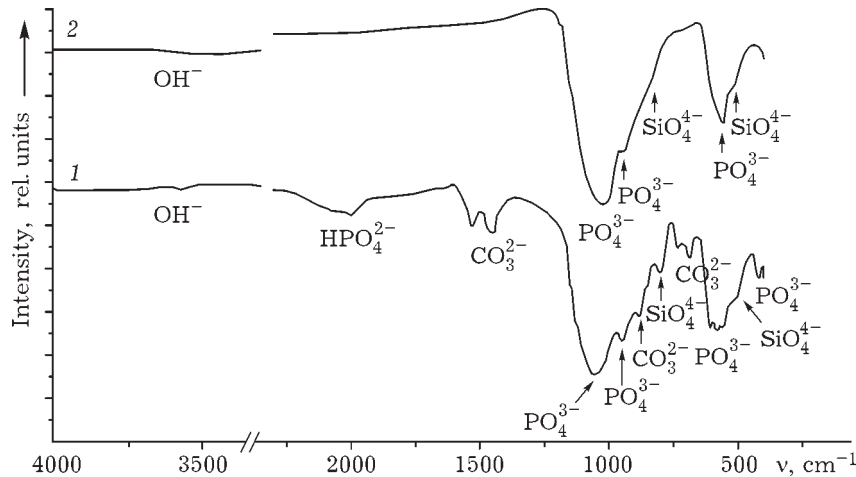
Fig. 6. IR absorption spectra of the material of target (1) and Si–HA ($x = 1.72$) coating deposited by means of the HF magnetron sputtering (2).

uct from (211) to (002). The absence of reflections corresponding to $Ca_3(PO_4)_2$ which is present in the material of the target allows us to assume that either this phase is present in the coating in the amorphous state or the intensity of these reflections with respect to the reflection of the substrate is insufficient. Annealing of the Si–HA coating at a temperature up to 500 °C in the air causes only a decrease in the intensity of reflection (002) at 25.9°.

The X-ray diffraction patterns of Si–HA ($x = 1.72$) coatings on the substrate Ti6Al4V contains the reflections of the substrate material (44-1294 JCPDS) and HA (see Fig. 5, b). No other phases such as CaO and α-$Ca_3(PO_4)_2$ were revealed. Thus, the Si–HA coatings are likely to have mixed amorphous-crystalline structure.

The IR spectra of the Si–HA target material (Fig. 6, curve 1) contain absorption bands corresponding to HA [4]: 1) at 1058 and 950 cm^{-1} (asymmetrical v_3 and symmetrical v_1 stretching vibrations of PO_4^{3-} bonds of the phosphate tetrahedron in apatite structure, respectively); a doublet of absorption bands at the frequencies of 600–550 cm^{-1} which is due to the asymmetrical bending v_2 vibrations of P–O bonds; 2) absorption band at 3570 cm^{-1} is due to the stretching vibrations of OH$^-$ groups. In addition, there are also IR absorption bands characteristic of Si–O and C–O bond vibrations. The absorption band of the vibrations of the bonds in silicate group in the structure of apatite at the frequency of 510 cm^{-1} is due to the bend-

ing vibrations of Si–O bonds; the stretching vibrations of these bonds may overlap the intense absorption band of the phosphate group within the frequency range 900–1200 cm^{-1}. The absorption band at 880 cm^{-1} relates to the bending vibration of C–O bonds of the carbonate group in apatite structure, while a broad absorption band within the spectra region 1400–1550 cm^{-1} relates to the stretching vibrations of these bonds.

The IR spectra of the coatings (see Fig. 6, curve 2) also contain the absorption bands corresponding to Si–HA: 1) at 1025 and 950 cm^{-1} (asymmetrical v_3 and symmetrical v_1 stretching vibrations of PO_4^{3-} bonds of the phosphate tetrahedron), at 560 cm^{-1} (asymmetrical bending v_2 vibrations of P–O bonds), 2) at 3570 cm^{-1} (stretching vibrations of OH$^-$ groups) in HA structure. The absence of bending vibrations of P–O bonds in the region of doublet at 597 cm^{-1} means that the apatite structure has not been formed yet. A broad absorption band in the region 1400–1500 cm^{-1} which is characteristic of the stretching vibrations of C–O groups is also absent.

CONCLUSION

Hydroxyapatite with the substitution of 1.72 mol PO_4^{3-} by SiO_4^{4-} anion having the composition $Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28}$, or 4.9 mass % calculated for silicon was synthesized using the mechanochemical method, for use as

a material of the target for the HF magnetron sputtering. According to XPA and IR spectroscopic data, the resulting product is single-phase, with rather clear reflections and absorption bands characteristic of apatite structure.

While manufacturing the target according to the ceramic technology from Si−HA powder having the composition $Ca_{10}(PO_4)_{4.28}(SiO_4)_{1.72}(OH)_{0.28}$ at 1100 °C the phase composition changes during agglomeration of the mould and differs from the composition of initial powder: in addition to HA, the material of the target contains also α-tricalcium phosphate. The IR spectroscopic data demonstrate that the SiO_4^{4-} groups are built into the lattice of the material of the target.

The elemental composition of the coatings deposited by means of the HF magnetron sputtering of the ceramic target prepared by agglomeration of Si−HA powder according to the ceramic technology is similar to the composition of the target. The data of IR spectroscopy provide evidence that SiO_4^{4-} ions are built into the lattice of the coating which has the HA structure as suggested by XPA data. The structure of Si−HA coatings formed by means of the HF magnetron sputtering at the desired process parameters is likely to be amorphous-crystalline.

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