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BIOMATERIALS

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COMPOSITE BIOCERAMIC BASED ON OCTACALCIUM PHOSPHATE DECOMPOSITION PRODUCTS

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A composite bioceramic with density at least 80% of the theoretical value was obtained from thermolyzed octacalcium phosphate (OCP). The treatment temperatures of OCP were 450, 600, and 700°C. The ceramic was obtained by firing thermolyzed powders at maximum temperature 1000, 1050, and 1100°C with soaking for 3, 6, and 9 h. Samples obtained from OCP treated at 450°C demonstrate the highest strength in bending (up to 125 MPa).

Key words: octacalcium phosphate, brushite, bioceramic, sintering.

Bone tissue is a composite material based on ultradisperse calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) and collagen protein with multilevel structural organization of the components. Because of the similarity of their chemical composition calcium phosphate materials are regarded as most promising for restoration and replacement of defects in bone tissue. For this reason an important direction of modern inorganic materials science is development of biomaterials based on calcium phosphates (CP).

Because of its chemical and phase similarity to the inorganic component of bone tissue synthetic HA was for a long time the most widely used material in medicine for restoration of bone damage [1 – 3]. However, ceramic materials based on HA have a low resorption (dissolution) rate in tissues of the organism, promote growth of new tissue (osteoinduction) only weakly, and possess low crack resistance and low fatigue strength under physiological conditions.

In recent years there has been great interest in a new concept of the reconstruction of bone tissues based on materials that are gradually resorbed in the organism and replaced by newly formed bone tissue; the implanted material are active sources of the elements required for building bone tissue and have a bearing function only initially [4].

Several approaches to obtaining resorbable materials now exist. Most works are aimed at improving the bioactive properties of hydroxyapatite materials by obtaining composite ceramic materials based on hydroxyapatite and more soluble calcium phosphates, for example, tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) [5, 6]. A different approach envisages chemical modification of apatite [7, 8]. Finally, a third approach rejects hydroxyapatite in favor of more soluble calcium phosphates [9].

Calcium pyrophosphate $Ca_2P_2O_7$ (CPP) and tricalcium phosphate are biodegradable materials in which the molar ratio $Ca/P < 1.67$. However, ceramic materials based on them have not been studied much.

The main difficulty in obtaining such biphase materials is synthesis of the highly disperse powders used to obtain bioceramics. The conventional method of preparing batch for obtaining ceramic composite materials requires careful mixing of the powders of the desired phases (physical homogenization). However, such mixtures are distinguished by low degrees of homogeneity, which can adversely affect the microstructure and, therefore, the mechanical and biological properties of the bioceramic obtained from them [10].

One chemical method of homogenization could become obtaining a precursor in which the atoms of the primary components are arranged in the required proximity to one another. For fabricating a bioceramic it is proposed that octacalcium phosphate be used: $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ (OCP) with molar ratio $Ca/P = 1.33$. The crystal structure of OCP consists of alternating layers similar in structure to HA or amorphous calcium phosphate $Ca_3(PO_4)_2 \cdot xH_2O$ (ACP) and

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brushite $CaHPO_4 \cdot 2H_2O$. For treatment temperature above 700°C OCP transforms into a mixture of TCP and CPP [11, 12].

EXPERIMENTAL PART

Tricalcium phosphate was used as a precursor to obtain powder mixtures and subsequently a ceramic; OCP was synthesized by hydrolysis of freshly prepared brushite [13] (brushite was obtained by precipitation from solution by the reaction (1)) in a 0.1 M buffer solution of acetate CH_3COOH/CH_3COONa at pH = 5.75, temperature 60°C, in 1 h. The pH was monitored with an Ékoniks-Ékspert-001 multichannel ion ohmmeter (Russia), equipped with a combination electrode for measuring pH.

The synthesis and hydrolysis of brushite with formation of OCP can be described by the following reactions:

$$(NH_4)_2HPO_4 + Ca(NO_3)_2 \rightarrow CaHPO_4 \cdot 2H_2O\downarrow + 2NH_4NO_3; \quad (1)$$

$$8CaHPO_4 \cdot 2H_2O + 2CH_3COONa \rightarrow Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O + 2NaH_2PO_4 + 2CH_3COOH + 11H_2O. \quad (2)$$

The octacalcium phosphate (OCP) precipitate obtained was separated from the mother solution, washed on a Buechner filter, and dried at 30°C for 20 h. The heat-treatment of the synthesized OCP powder was conducted at temperatures 450, 600, and 700°C [14]. The crucible with the powder was inserted in a furnace heated up to the processing temperature and held at this temperature for 2 h.

The heat-treated powders were disaggregated in a planetary mill (Fritsch) for 5 min in acetone and then passed through a 200 μm sieve.

The initial OCP and its products of heat treatment (thermolysis) at 450, 600, and 700°C (with production of OCP-450, OCP-600, and OCP-700, respectively) were investigated by x-ray phase analysis (XPA) performed with a Rigaku D/Max-2500 diffractometer with a rotating anode (Japan) in the reflection regime (Bragg – Brentano geometry) using CuK_{av} radiation (average wavelength $\lambda = 1.54183$ Å) in the angle range $2\theta = 2 - 60°$, 2θ step size 0.02°, spectral recording rate 5 °/min. Silicon powder was used as the internal standard. Phase analysis was conducted using the WinXPOW code and the ICDD PDF-2 database.

The microstructure of the powders of OCP and its products of heat- treatment (thermolysis) was investigated using a scanning electron microscope (SEM) with a LEO SUPRA 50VP autoemission source (Carl Zeiss, Germany) with accelerating voltage of the electron gun 15 kV. Images were obtained in secondary electrons.

A mixture of the powders β-TCP and β-CPP in the ratio 2 : 1 (TCP/CPP) was prepared as a comparison sample. To obtain calcium pyrophosphate (CPP) the brushite prepared using the reaction (1) was mixed in a crucible and fired in a muffle furnace at 600°C for 5 h:

$$CaHPO_4 \cdot 2H_2O \rightarrow 2CaHPO_4 \rightarrow \beta\text{-}Ca_2P_2O_7 + H_2O. \quad (3)$$

Tricalcium phosphate (TCP) was obtained by the solid-phase method according to the reaction (4) by firing at temperature 900°C in an aluminum-oxide crucible for 14 h in a muffle furnace:

$$CaCO_3 + Ca_2P_2O_7 \rightarrow \beta\text{-}Ca_3(PO_4)_2 + CO_2\uparrow. \quad (4)$$

The β-$Ca_3(PO_4)_2$ and β-$Ca_2P_2O_7$ powders obtained in the reactions (3) and (4) in the ratio 2 : 1 were mixed in a planetary mill with ball : powder : medium (acetone) ratios equal to 1 : 1 : 3. The dried TCP/CPP powder was passed through an about 200 μm sieve.

The powders obtained by heat treatment of OCP at 450, 600, and 700°C as well as the powder mixture TCP/CPP were used to prepare the ceramic. The samples were compacted in a Carver C manual press (USA) at pressures about 200 – 400 MPa in the form of 0.2 g pellets. In order to facilitate the pressing process and reduce the likelihood of overpressing cracks a plasticizing additive was added in the amount 10% by weight of powder to the powders intended for preparing the ceramic.

Paraffin (chemically pure grade), dissolved in carbon tetrachloride CCl_4 (analytically pure grade) was used as the plasticizer.

The compacts were fired at the maximum temperature 1000, 1050, and 1100°C with soaking for 3, 6, and 9 h. The heating rate was 2 K/min; the samples were soaked at 250°C for 2 h in order to remove the plasticizer. The fired samples allowed to cool together with the furnace.

After firing the mass and linear dimensions were measured (to within 10^{-4} g and 10 μm, respectively) in order to calculate the geometric and relative densities of the compacts and samples.

The phase composition and microstructure of the ceramic samples were studied by means of XPA and SEM. To evaluate the uniformity of the distribution of the phases TCP and CPP in the ceramic samples x-ray spectral microanalysis was conducted using an electron microscope of the FIB system NVision 40 (Carl Zeiss, Germany), equipped with an energy-dispersive microanalysis system INCA Energy+ (Oxford Instruments, Great Britain). The samples were first subjected to grinding and an additional layer of carbon was deposited on them (Univex300 vacuum coating system, Leybold, Germany). The lines of the Ca and P spectra were chosen for analysis. The composition was determined for large sections of the surface, 20 × 20 μm in size, and locally at individual points with signal generation region about 1 μm.

For testing the mechanical strength in bending samples were prepared in the form of small 2 × 0.4 × 0.5 cm bars. The bars were sintered at maximum temperature 1100°C with soaking for 3 h. At least five samples were tested in order to determine the reproducibility of the strength values. The measurements were conducted using an Instron 5581 machine by the three-point bending method with a stiff system of loading at strain rates ranging from 0.02 to 20 mm/min.

RESULTS AND DISCUSSION

According to the XPA data the powder obtained as a result of the reaction (2) comprises single-phase OCP with no admixtures of the initial brushite or HA. The OCP crystals are thin ribbons several tens of microns in length and 5 – 6 μm in width (Fig. 1*a*). An investigation of the thermolysis of OCP is described in [14]. The x-ray phase analysis showed that at 450°C the products of thermal decomposition of OCP are HA and CPP and at 600°C the product consists of HA, CPP, and TCP; the HA phase is not observed at 700°C.

The electron microscopy data show that the products of thermolysis partially retain the plate-like structure of the initial OCP (Fig. 1), but an evaluation of the regions of coherent scattering showed that the equivalent average size of the powder particles ranges from 30 to 50 nm depending on the decomposition temperature of the initial OCP, which corresponds to average distance between pores (escape tracks of water vapor) in Fig. 1*b* (inset in the upper right-hand corner).

It can be supposed that the small plates of the products of decomposition consist of smaller particles or, if water is removed rapidly enough from OCP, structures preserving initial shape but possessing significant numbers of defects are formed upon decomposition.

Studying the microstructure of the powder prepared at 450°C, it can be supposed that the obtained product retains the habitus of the initial OCP. However, now it consists not of alternating brushite and apatite layers; upon removal of water from the brushite layer the pyrophosphate ion $P_2O_7^{2-}$ starts to form partially in a plate itself.

Judging from everything, regions where the process of the transformation of HPO_4^{2-} from the brushite layer into the pyrophosphate ion did not occur are preserved. Therefore, now the OCP-450 structure can be represented in the form of alternating apatite-like layers and layers containing the pyrophosphate ion and dehydrated brushite. The layers are distributed in the powder precursor of maximum homogeneity, located in each small plate, which makes it possible to count on a high degree of homogeneity of the distribution of the component phases in the ceramic obtained.

The properties of the compact powder blanks were investigated by means of isothermal soakings in order to study the shrinkage processes. The ceramics were fired at temperatures 1000, 1050, and 1100°C with sintering times 3, 6, and 9 h.

Analyzing the iso- and polythermal compaction data, several conclusions can be drawn.

Ceramic samples obtained from a mechanical mixture TCP/CPP, demonstrate the lowest density upon sintering in practically all regimes. In this case we are dealing with the material containing CPP sintered by a solid-phase mechanism. Diffusion of large pyrophosphate ions is strongly inhibited, and for this reason sintering as such practically does not occur.

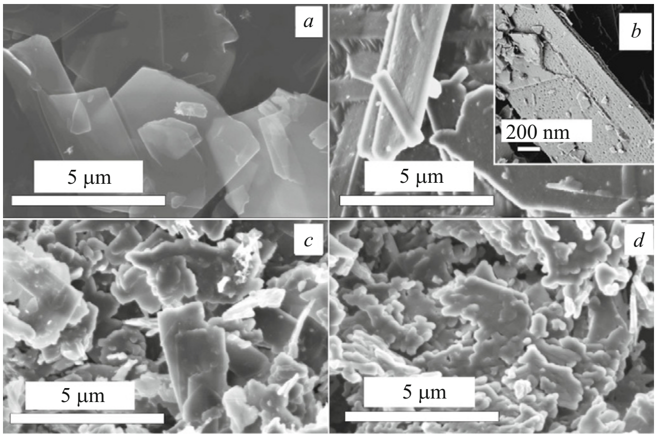

Fig. 1. Photomicrographs of OCP and its products of heat-treatment: single-phase OCP was synthesized in an acetate buffer solution at 60°C and pH = 5.75; *a*) OCP powder without heat-treatment; *b*) OCP powder heat-treated at 450°C (OCP-450); *c*) at 600°C (OCP-600); *d*) at 700°C (OCP-700).

Ceramic samples obtained upon annealing of powder blanks OCP-600 and OCP-700 also demonstrate low density, which could be associated with the initial low density of the compacts (Table 1) and possible presence in them of overpressing cracks.

The highest density obtains in a series of samples obtained from OCP-450 powder. When these powders are fired, a chemical reaction occurs that not only makes it possible to attain quite high density of the ceramic (up to 80%) but it can favorably affect the mechanical properties. As the firing temperature increases, the relative density of the ceramic increases; but, as the firing time increases, the density of some samples decreases. Most likely, a secondary recrystallization process is observed; here, anomalous grain growth starts and coalescence, enlargement, and redistribution of pores occur, while practically no compaction is observed.

TABLE 1. Properties of Ceramic Materials Obtained from Precursors with Different History after Annealing at 1100°C with 3-h Soaking

Powder	Pressing pressure, MPa	Relative density, %		Strength, MPa
		before firing	after firing	
OCP-450	400	72 ± 2	80 ± 3	125 ± 2
OCP-600	250	58 ± 2	79 ± 3	16 ± 3
OCP-700	200	57 ± 3	82 ± 2,5	20 ± 3
TCP/CPP*	250	62 ± 3	65 ± 2	24 ± 3

* Mechanical mixture of the powders β-TCP and β-CPP in the ratio 2 : 1.

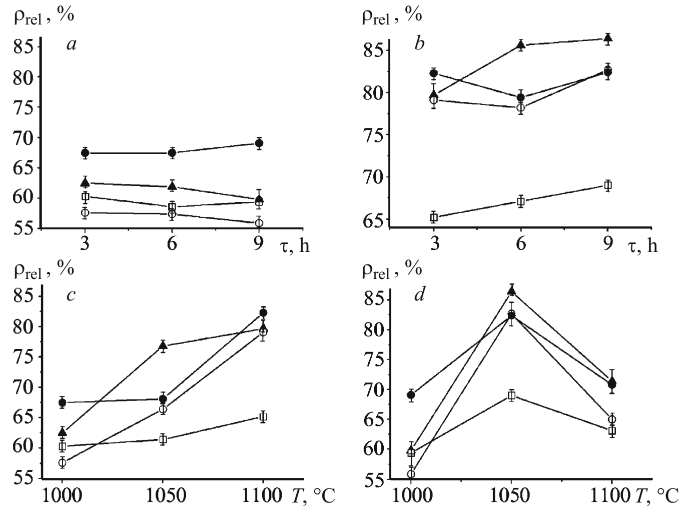

Fig. 2. Relative density of ceramic versus heat treatment conditions: *a*, *b*) firing temperature 1000 and 1100°C, respectively, with different isothermal soaking times; *c*, *d*) isothermal soaking for 3 and 9 h, respectively, at different firing temperature; □) TCP/CPP; ▲) OCP-450; ○) OCP-600; ●) OCP-700.

Electron microscopy data confirm the conclusions obtained in an analysis of the sintering curves (Fig. 2). The microstructure of ceramic obtained from the mixture TCP/CPP is demonstrated in Fig. 3. No differences are observed in the microstructure and density of the ceramic obtained either with increasing soaking time or with increasing firing temperature. In spite of the uniformity of the microstructure and quite small grain size the ceramic obtained from OCP-600 powder (Fig. 4*c* and *d*) has low density owing to the presence of large pores. The ceramic obtained from OCP-450 (Fig. 4*a* and *b*) does not have such defects.

Figure 5 shows thin sections of ceramic samples obtained from OCP powder treated at different temperatures and soaking times 3, 6, and 9 h. As the sintering time increases, pore coalescence occurs. This effect occurred in all series of ceramic samples and for all firing temperatures. To a lesser degree this effect occurs in ceramic samples obtained from OCP-450.

Quite large pores appear only after firing, where the soaking time was 9 h. The ceramic sintered from OCP-600 and OCP-700 powders shows the presence of large pores already after 3 h of soaking.

In summary, it can be stated that the densest ceramic can be obtained at firing temperature 1100°C, and the soaking time should not exceed 3 h in order to minimize secondary recrystallization and therefore prevent the formation of large pores.

X-ray phase analysis shows that all ceramic materials correspond to the composition β-TCP and β-CPP. X-ray spectral microanalysis was used to determine the distribution of the phases in the ceramic samples.

Figure 6 shows maps of photomicrographs of thin sections of ceramic obtained from OCP-450 and ceramic obtained from the mechanical mixture TCP/CPP, as well as maps of the elemental distribution in them. The zones where

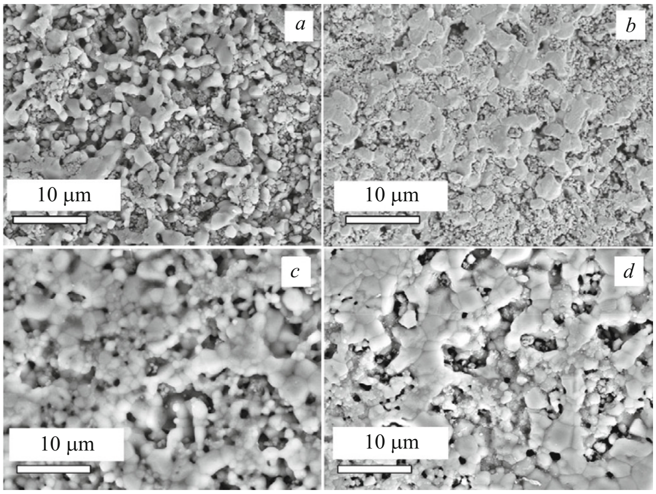

Fig. 3. Photomicrographs of thin sections of ceramic obtained from a mechanical mixture of powders TCP/CPP at firing temperature: *a*) 1000°C, 3 h; *b*) 1000°C, 9 h; *c*) 1100°C, 3 h; *d*) 1100°C, 9 h.

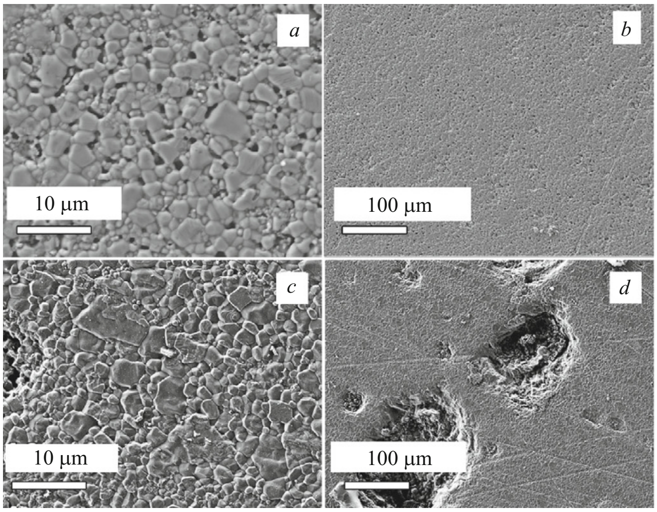

Fig. 4. Photomicrographs of thin sections of ceramic obtained from OCP powder: *a*, *b*) OCP-450; *c*, *d*) OCP-600; firing temperature 1100°C, soaking time 3 h.

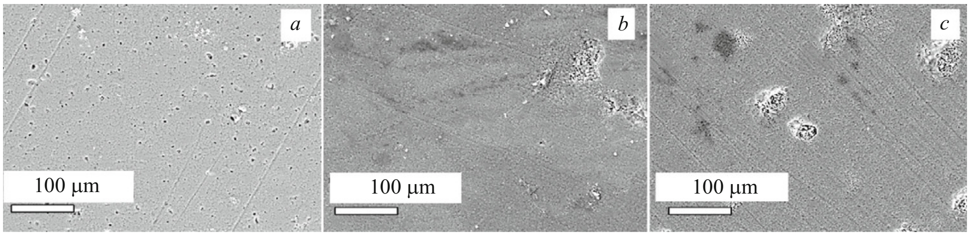

Fig. 5. Photomicrographs of thin sections of ceramic samples obtained from OCP-450 at firing temperature 1100°C: isothermal soaking time: *a*) 3 h; *b*) 6 h; *c*) 9 h.

there is more phosphorus correspond to calcium pyrophosphate $Ca_2P_2O_7$ (ratio Ca/P = 1), the darker regions are enriched with calcium — $Ca_3(PO_4)_2$ (Ca/P = 1.5). The data on the distribution of the elements show that in the ceramic obtained from OCP the CPP and TCP phases are distributed more uniformly than in the ceramic obtained from mixtures of TCP and CPP. Moreover, comparing the images obtained in secondary electrons with the phase distribution maps one can conclude that the smaller grains of the ceramic comprise a pyrophosphate phase, while the larger grains comprise a tricalcium phosphate phase, which corresponds to the difference in the rates of mass transfer of phosphate and pyrophosphate anions.

Measurement of the strength characteristics of the samples showed that samples obtained from OCP-450 exhibit the greatest strength (of the order of 125 MPa) (see Table 1). It can be supposed that such high strength is due to the initial dense setting of the powder particles in the compacts obtained as well as a chemical reaction occurring during sintering. Preliminary organization of OCP-450 powders can give rise to texturing of the compact material. In materials of this type strengthening mechanisms occurring in anisotropic native coatings (nacre-type) and resulting in effective reorientation and branching of cracks can operate [15].

The ceramic obtained from OCP-600 and OCP-700 shows much lower strength (16 – 20 MPa). Probably, pore coalescence cannot be avoided in the process of preparing ceramics from these powders. The ceramic obtained from the mechanical mixture TCP/CPP likewise shows low strength, which could be due to the absence of a chemical reaction in the sintering process.

CONCLUSIONS

Powders for preparing biphase ceramic were obtained by decomposition of OCP at temperatures 450, 600, and 700°C. The obtained powders were used to prepare samples of ceramic with density at least 80% (OCP-450) of the theoretical value and strength reaching 120 – 125 MPa (OCP-450). Sintering of the ceramic appears to proceed by a solid-phase mechanism (for OCP-700 powders) and with a chemical reaction occurring (for OCP-450 powders), which favorably affects the properties of the ceramic. Prolongation of soaking time during firing causes anomalous growth of grains and coalescence of pores. The samples obtained from powder precursors formed by decomposition of OCP have higher density compared with ceramic obtained from the mechanical mixture TCP/CPP. Samples obtained from OCP-450 demonstrate the greatest strength.

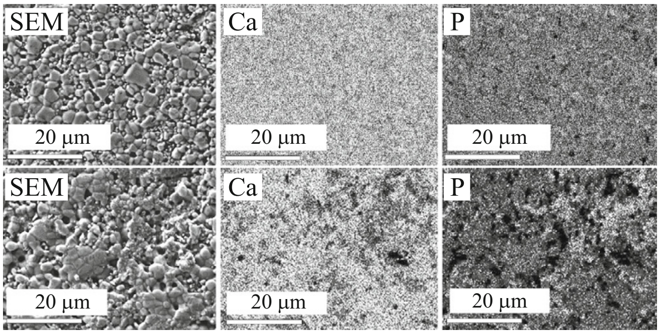

Fig. 6. Photomicrograph of a thin section of ceramic made from OCP-450 (top) and a thin section of ceramic made from TCP/CPP (bottom) and maps of the calcium and phosphorus distributions in them: in the maps of the phosphorus distribution the light-colored sections correspond to calcium pyrophosphate.

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