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# BIOMATERIALS

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# BIPHASE CaO–P₂O₅ CERAMIC BASED ON POWDER SYNTHESIZED FROM CALCIUM ACETATE AND AMMONIUM HYDROPHOSPHATE

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Biphase ceramic containing hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and β-tricalcium phosphate $\beta$-$Ca_3(PO_4)_2$ has been obtained from a uniform nanocrystalline calcium phosphate powder with the structure of apatite, synthesized from water solutions of calcium apatite and ammonium hydrophosphate with molar ratio Ca/P = 1.5 at room temperature without pH regulation. After firing at 1100°C the material contained 75% $\beta$-$Ca_3(PO_4)_2$ and the grain size did not exceed 600 nm. It is suggested that the carbon formed in the interval 200 – 500°C, as a result of the carbonization of the organic components of synthesis adsorbed by particles of powder, be used as a physical barrier impeding intense mass transfer up to 800°C, which makes it possible to obtain an ultradisperse ceramic with grains smaller than 1 μm.

***Key words:*** hydroxyapatite, tricalcium phosphate, biphase ceramic, sintering of nanopowders.

Until now, ceramic materials based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAP), tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) or composites containing both phases were of greatest interest to materials scientists and medical doctors [1]. To obtain a ceramic with a fine microstructure it is necessary to use powders synthesized by a chemical method. Calcium phosphate based ceramic is no exception. By using a definite precursor pair in the form of water solutions of calcium salt and a salt containing the orthophosphate ion different calcium orthophosphates can be obtained by precipitation simply by varying the conditions of synthesis (temperature and pH) [2]. The following calcium orthophosphates are of interest for biomedical applications and can be synthesized by precipitation or hydrolysis: brushite ($CaHPO_4 \cdot H_2O$), monetite ($CaHPO_4$), octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). Ordinarily, maintaining the pH at a prescribed level during synthesis guarantees that a powder with a prescribed phase composition will be obtained. In this case, if the pH regulation occurs within the system itself, then the precursor pair will determine the result of synthesis. For example, when $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ interact without regulation a pH in the range 4 – 5 is established in the system; this guarantees that brushite will be formed [3]. Hydroxyapatite is guaranteed to form with the interaction of a suspension of $Ca(OH)_2$ and $H_3PO_3$ (or any soluble orthophosphate) owing to the level pH = 12, which supplies the system with partially dissolved calcium hydroxide (RU Patent No. 2077475). However, TCP ($Ca_3(PO_4)_2$) cannot be obtained by precipitation from solution. Calcium phosphate with the TCP structure can be obtained from solution or by hydrolysis only by adding into the reaction zone a significant amount of magnesium ions, which are incorporated into the structure of calcium phosphate, replacing part of the calcium ions (to 12% of the total cations) even with pH in the interval 5 – 6 [4 – 6]. TCP can be obtained as a result of a solid-phase reaction, for example, with the interaction of calcium pyrophosphate $Ca_2P_2O_7$ (CPP) and HAP (RU Patent No. 2391316) or monetite $CaHPO_4$ and calcium carbonate $CaCO_3$ [7, 8]. Ca-deficient HAP synthesized at pH = 7 from calcium nitrate $Ca(NO_3)_2$ and ammonium hydrophosphate $(NH_4)_2HPO_4$ were used as a powder precursor in order to obtain the TCP phase [9]. Acetate and phosphate ions are often components of a buffer mixture with a prescribed pH. In synthesis from calcium acetate and soluble ammonium, potassium or sodium phosphates it has been observed that calcium phosphate forms with Ca/P > 1, even if the initial salts were taken in equal ratio [3, 10, 11]. The result obtained in these works was due to the formation of ace-

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tate buffer, which was formed with acetic acid and a soluble phosphate present at the same time.

The published data and our own experience suggest that when calcium acetate interacts with ammonium hydrophosphate the conditions required for the formation of a buffer system are created, making it possible to support pH = 7 in order to obtain Ca-deficient HAP, which on heating will be able to transform into TCP.

Due to their capability of decomposing with volatile compounds being formed on heating some byproducts of calcium phosphate synthesis can be classified as substances which are removed on heat-treatment (drying, firing) [12]. The choice of calcium acetate and ammonium hydrophosphate as initial reagents is due to the fact that the byproducts will include ammonium acetate and acetic acid, which substances are capable of easily leaving the synthesized powder during drying, storage or heat-treatment. The high volatility of the reaction byproducts suggests that their effect on the sintering of calcium phosphate powder will be negligible.

**The objective of the present work** was to obtain from calcium phosphate powder, synthesized from calcium acetate and ammonium hydrophosphate, a ceramic containing predominately a TCP phase. According to available databases, water solutions of the initial salts possess pH close to 8 [13]. The interaction of salts going into the formation of HAP lowers the pH because of phosphoric acid formation. Depending on the ratio $[CH_3COOH]/[H_2PO_4^-]$, the simultaneous presence of acetic acid and phosphate salt in the system will lead to the formation of an acetic or a phosphate buffer system. On this basis the expectation was that after the interaction of the solutions of the chosen salts and without any additional pH regulation Ca-deficient HAP will be synthesized at Ca/P = 1.5, and will transform into β-TCP during heat-treatment. Phase transformation occurring inside individual grains will impede their growth during sintering.

## EXPERIMENTAL PART

Calcium orthophosphate powder was synthesized from calcium acetate and ammonium hydrophosphate via the reactions

$$6(NH_4)_2HPO_4 + 9Ca(CH_3COO)_2 + H_2O \rightarrow Ca_9(HPO_4)(PO_4)_5(OH) + 12NH_4CH_3COO + 6CH_3COOH. \qquad (1)$$

Four hundred milliliters of a 1.33 M water solution of $(NH_4)_2HPO_4$ were added all at once to 400 ml $Ca(CH_3COO)_2$ with concentration 2 M. After the suspension was mixed for 15 min a vacuum pump was used to separate the precipitate from the mother solution, using Buchner funnel. The residue in a thin layer was dried for one week, after which the product obtained was subjected to disaggregation in acetone for 5 min with ratio acetone : powder : milling bodies = 1 : 1 : 5. After disaggregation and evaporation of the acetone the powder was passed through a 200 μm sieve.

Paraffin was used as a temporary process binder, added in the amount 10 wt.% in the form of a solution in $CCl_4$ to calcium phosphate powder. Samples in the form of 12 mm in diameter and 3 – 4 mm high disks were molded under specific pressing pressure 50 MPa.

Samples in the form of disks were fired in the range 500 – 1200°C with heating rate 5 K/min and soaking at the final temperature for 2 h.

X-ray diffraction studies were performed with a Rigaki D/Max-2500 diffractometer with a rotating anode (Japan). The measurements were performed in reflection with $CuK_\alpha$ radiation ($2\theta = 2 – 60°$ with step 0.02°, spectrum acquisition rate 5 K/min). Thermal analysis (TA) was performed with a NETZSCH 1200 thermal analyzer (Germany). The heating rate was 10 K/min and the temperature interval 30 – 1150°C. The mass of the sample was ≥ 10 mg. The linear shrinkage of the sample was measured in a polythermal regime with heating rate 5 K/min in the temperature interval 30 – 1400°C in a DIL 402 horizontal dilatometer from NETZSCH-Gerätebau-GmbH (Germany); the initial load on the sample was 15 cN. The microstructure of the sample was studied with a LEO SUPRA 50VP (Carl Zeiss, Germany) scanning electron microscope. The measurements were performed in a low-vacuum regime with accelerating voltage 20 kV.

## RESULTS AND DISCUSSION

The XPA data show that the phase composition of the precipitate is represented by low-crystalline synthetic HAP $Ca_5(PO_4)_3OH$ (card 9-432) or $Ca_9(HPO_4)(PO_4)_5(OH)$ (card 46-905). Since a reaction competing with octacalcium phosphate $Ca_8(HPO_4)_2(PO_4) \cdot 6H_2O$ (OCP) precipitation can occur under the synthesis conditions realized in the present work, special attention was devoted to analysis in the range $2\theta = 2 – 10°$, where the strong characteristic OCP (100) reflection $d = 19.7$ Å is usually found. Nonetheless, according to the XPA data, no OCP was found in the synthesized powder. This fact is explained by the high pH in the range 8 – 9 at the initial stage of precipitation, making possible the formation of embryos of HAP crystals and subsequent growth of precisely the HAP phase. In this case the OCP phase is a metastable, so that it is impossible for the HAP crystal embryos to transform subsequently into OCP. The appreciable broadening of the main peaks and the impossibility of confirming the low-intensity peaks attest to the smallness of the synthesized HAP particles and the high defectiveness of the crystal lattice of an individual crystallite, an indication that the powder obtained is potentially active in sintering.

According to data from thermal analysis (Fig. 1), the total mass loss of the synthesized powder reaches 23.3% at temperature 790°C, after which no mass change occurs to 1000°C. A 4% mass loss was recorded at 100°C. The maximum rate of mass loss for the first stage in the interval

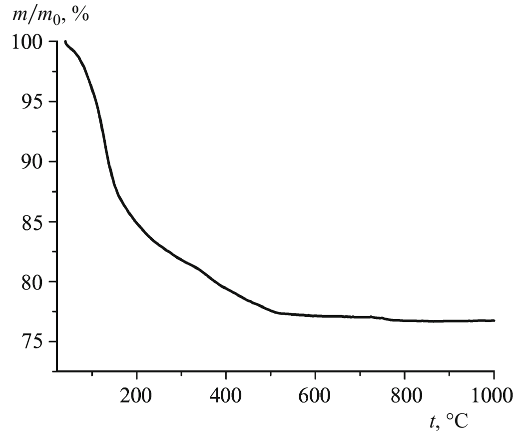

**Fig. 1.** The mass of powder synthesized from calcium acetate and ammonium hydrophosphate versus temperature.

50 – 300°C was observed at 130°C. The mass loss in this interval is due to the removal of physically bound water. The shift of the temperature of maximum rate of mass loss to high values is due to the rate of heating of the sample, which was quite high and equal to 10 K/min. The completion of the second stage (300 – 450°C) corresponded to a mass loss of 20%. The mass loss at 500°C was 22.7%. The mass loss in the interval 300 – 500°C could be due to the decomposition and removal of organic substances, which is present in the powder as a reaction byproduct comprising a mixture of ammonium acetate and acetic acid. The mass loss in the interval 500 – 790°C was 0.6%.

The mass loss during isothermal soakings in the interval 500 – 1200°C at all temperatures was 20 – 25%. It was noted that the samples were dark brown after firing at 500°C and light grey after firing at 800°C. After firing at 600 and 700°C the color of the samples fell between dark brown and light grey. This fact confirms the presence of acetate compounds in the powder after drying or adsorbed acetone on the surface of the particles of calcium orthophosphate powder after grinding. Apparently, conditions for carbonization of these compounds to carbon are created during heat-treatment up to 500°C, the carbon being removed completely, judging from the color of the samples, only above 800°C. A comparison of the color change of the samples with the data from thermal analysis suggests that the amount of carbon in the sample above 500°C did not exceed 0.6%.

The XPA data (Fig. 2) obtained for the samples after firing show that the phase composition of ceramic fired at 500 and 600°C was identical to that of the initial powder. The phase composition after firing at different temperatures in the range 700 – 1100°C was presented as β-TCP and HAP. A quantitative determination of the mass content of the phases (Fig. 3) based on the XPA data suggests that the content of the β-TCP phase in the ceramic sample increases with temperature and after firing at 1100°C reaches 70%, which corresponds to 88 mole % and Ca/P = 1.548.

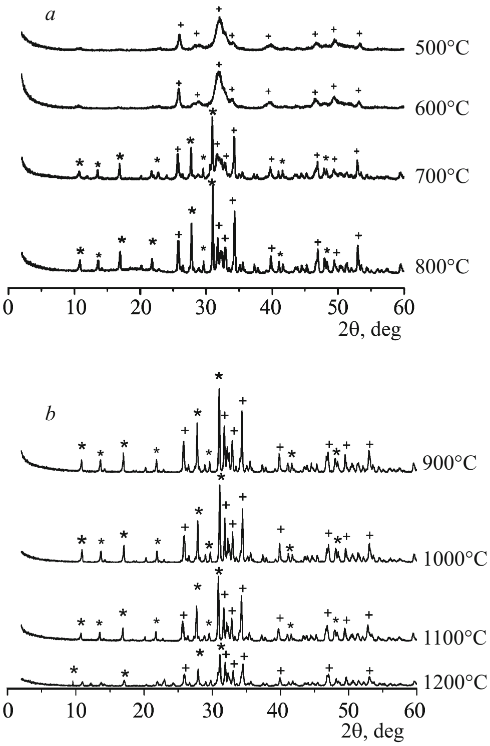

**Fig. 2.** XPA for samples fired for 2 h at temperatures 500 – 800°C (*a*) and 900 – 1200°C (*b*). Phases: +) HAP and ∗) β-TCP.

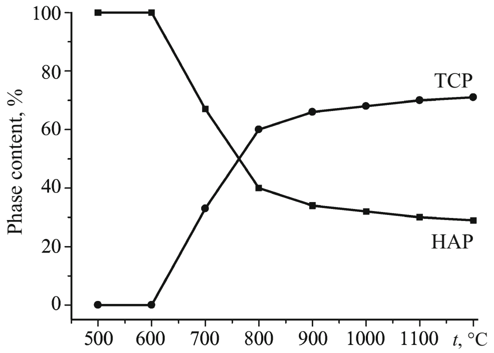

**Fig. 3.** Mass content of the phases versus the firing temperature in samples based on powder synthesized from calcium phosphate and ammonium hydrophosphate.

Dilatometric studies (Fig. 4) showed 1% densification in the range 150 – 250°C. The densification reached 2% in the range 250 – 800°C and 10% in the range 800 – 900°C. On heating to 1200°C the densification reached 26%. Then, a small expansion (1 – 2%) occurred on subsequent heating to 1300°C, which was associated with the phase transition β-TCP → α-TCP. The dilatometric curve on cooling reflects the natural decrease of the dimensions of the sample. The phase transition α-TCP → β-TCP does not occur on cooling because of the difficulty of restructuring the crystal structure [14]. Previous dilatometric data for powder blanks made

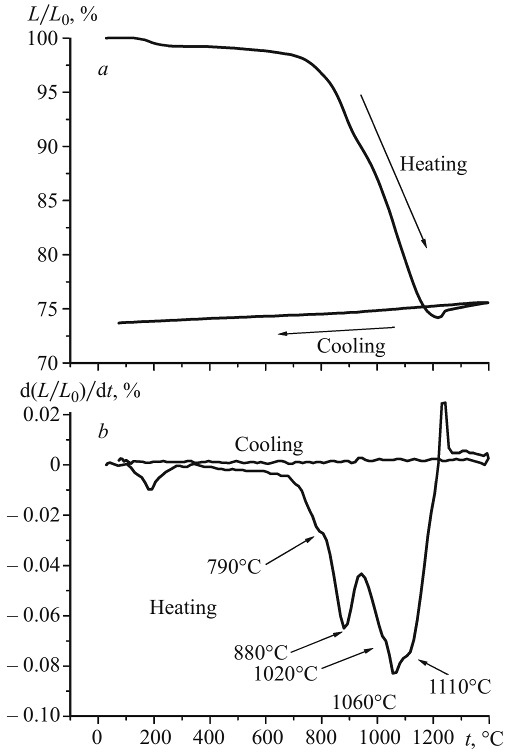

**Fig. 4.** Dilatometric data for a sample based on powder synthesized from calcium acetate and ammonium hydrophosphate: integral (*a*) and differential (*b*) curves.

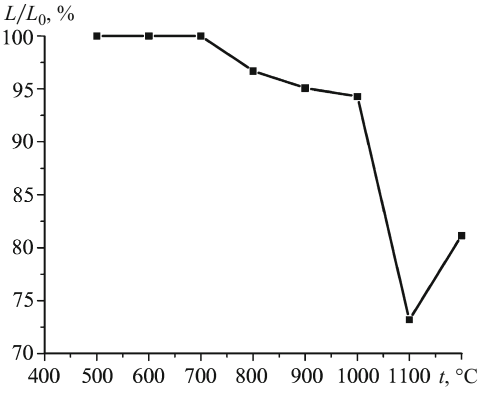

**Fig. 5.** Temperature dependence of the diameter of samples based on powder synthesized from calcium acetate and ammonium hydrophosphate after firing for 2 h.

from Ca-deficient HAP, which on heat-treatment converted into β-TCP, showed shrinkage onset in the range 500 – 700°C [15]. Dilatometric studies of a powder blank made from powder synthesized on the basis of the present work show that appreciable compaction starts only as 800°C. The start of compaction in nano-size active powder systems at high temperatures promotes the formation of a microstructure with small grains. An increase of the temperature of compaction onset to 800°C was achieved in the powder system based on Ca-deficient HAP by introducing the additive $CaCl_2$ [10], whose melt has been reported to possess surface activity with respect to calcium phosphates [16].

In summary, in order to increase the compaction onset temperature in a powder system based on nanosize powders of calcium phosphate a physical barrier preventing mass transfer between particles and grain growth at relatively low temperatures must be present. The presence of carbon in a powder blank based on Ca-deficient HAP synthesized in the present work is probably just such a barrier. After the carbon is completely removed (above 800°C) no physical barriers for compaction onset in very active nanosize power remain. Differentiating the dilatometric curve makes it possible to separate several most notable stages in the compaction of a sample based on powder synthesized from calcium acetate and ammonium hydrophosphate. The first stage with the maximum shrinkage rate at 200°C is related with the melting of the temporary process binder — paraffin, securing the primary regrouping of particles. In the interval 300 – 700°C one can talk about negligible and gradual increase of the compaction rate. The curve of the compaction rate in the interval 700 – 1200°C could have been obtained by superposing on one another five different processes with maxima at the temperatures 790, 880, 1020, 1060 and 1110°C. The highest shrinkage rate corresponds to 1060°C. Compaction at high temperatures is due to mass transfer of the inorganic component as well as restructuring of the crystal lattice of the adjoining grains.

The linear dimensions (diameter of samples) as a function of the firing temperature are displayed in Fig. 5. No change in the geometric dimensions of the samples was observed up to temperature 700°C. At 1000°C the shrinkage did not exceed 5%. After firing at 1100°C the shrinkage reached –26.8%. The decrease of the shrinkage at 1200°C to 18.9% is due to the phase transition α-TCP → β-TCP. The data on the change in the linear dimensions of samples obtained with ordinary firing (see Fig. 5) agree with the data obtained in the polythermal regime (see Fig. 4). The data presented in Fig. 5 confirm that at 800°C the compaction becomes appreciable.

The post-pressing density of the samples was 37 – 42% of the theoretical density of TCP (3.07 $g/cm^3$). The density of the samples in the temperature interval 500 – 1000°C changes very little and lies in the interval 1.0 – 1.3 $g/cm^3$ (Fig. 6).

The decrease of the relative density of the samples to 30 – 42% is due to a mass decrease of the samples on firing by 20 – 25% in the temperature range 500 – 1200°C, as shown in Fig. 1. The density of the samples (2.5 $g/cm^3$) reached its maximum value after firing at 1100°C for 2 h.

Photomicrographs of the synthesized powder and photomicrographs of a sample fired at different temperatures are presented in Fig. 7. A quite dense aggregate consisting of round particles of the order to 20 nm in size can be seen in Fig. 7*a*. The microstructure of the sample after firing at 500°C (Fig. 7*b*) is uniform, and the size of the particle is

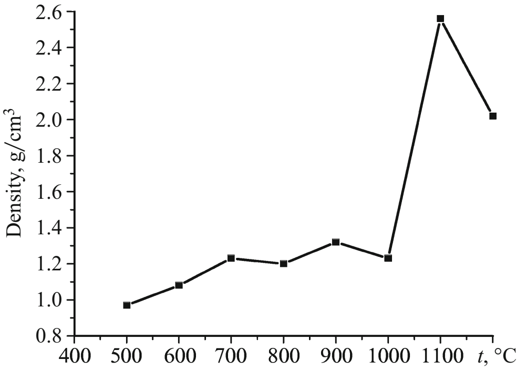

**Fig. 6.** Density of the samples based on powder synthesized from calcium acetate and ammonium hydrophosphate versus the firing temperature.

30 – 40 nm. From thermal analysis data (see Figs. 1 and 4) and data obtained by isothermal soakings (see Fig. 5) the temperature 800°C is viewed as the onset temperature of large changes in a powder blank. The microstructure of samples after firing at 800°C for 2 h (Fig. 7*c*) indicates some particle growth but does not confirm the formation of intergrain contacts. An openwork microstructure consisting of particles with well-formed intergrain contacts is evident that at 900°C (Fig. 7*d*). The relative density of the samples at this temperature does not exceed 50% (see Fig. 6). After firing at 1100°C for 2 h the microstructure of the ceramic is represented well by facetted grains with dense contacts (Fig. 7*e*). As temperature increases from 800 to 1100°C the grains grow from 50 – 300 to 400 – 600 nm. Judging from the photomicrograph of the sample fired at 1200°C, it is difficult to talk about uniformity of the microstructure. The image shows several individual grains of the order 1 μm in size as well as cracks, which, apparently, are a consequence of the phase transition β-TCP → α-TCP.

## CONCLUSIONS

Water solutions of calcium acetate and ammonium hydrophosphate with a definite sequence of pouring decantations make it possible to obtain an active single-phase nanosize calcium phosphate powder. The prescribed molar

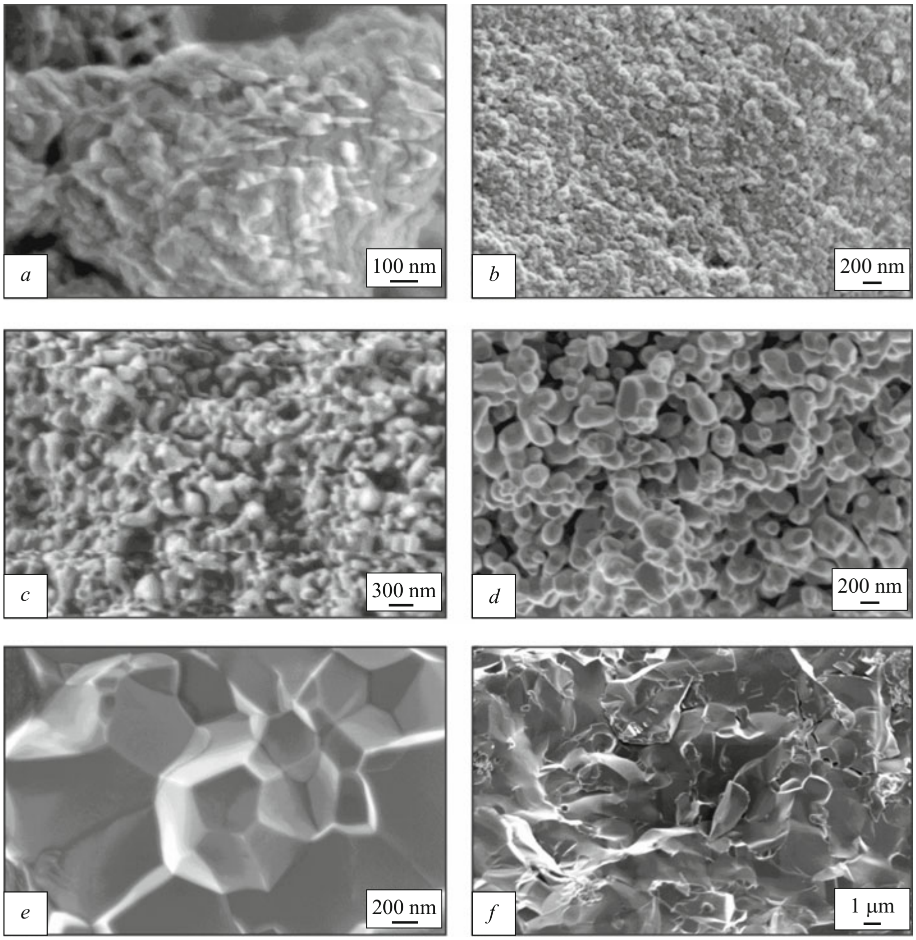

**Fig. 7.** Photomicrograph of powder synthesized from calcium acetate and ammonium hydrophosphate (*a*) and ceramic samples based on this powder after firing for 2 h at temperatures 500°C (*b*), 800°C (*c*), 900°C (*d*), 1100°C (*e*) and 1200°C (*f*).

ratio Ca/P in the initial solutions does not guarantee that a similar molar ratio Ca/P will be reproduced in the synthesized powder and then after firing in the ceramic. The phase composition of the ceramic based on single-phase powder synthesized from water solutions of calcium acetate and ammonium hydrophosphate was represented by HAP and β-TCP. A determination of the quantitative ratio of the phases from XPA data shows that for initially prescribed molar ratio $Ca/P = 1.5$ calcium phosphate with $Ca/P = 1.548$ was synthesized. A change in phase composition occurs in a wide temperature interval 700 – 1200°C, the amount of the β-TCP increasing with temperature. The presence of organic (acetate) compounds in the powder and then in the sample after formation is the reason for the formation of a small quantity of carbon. Carbon remains in samples after firing at temperatures 500 – 800°C and acts like a physical barrier preventing particle growth in the powder blank and promoting together with phase transformations the formation of ceramic with grain size no larger than 600 nm.

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