

# SCIENCE FOR CERAMIC PRODUCTION

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## CERAMICS BASED ON CALCIUM HYDROXYAPATITE SYNTHESIZED IN THE PRESENCE OF PVA

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The properties of powder synthesized from calcium nitrate and ammonium hydrophosphate phosphate hydrophosphate hydrophosphohydroin the presence of polyvinyl alcohol are investigated. It is established that the presence of 0.25 – 0.50% PVC strongly influences the rheological and thermal properties of the powder. A tendency toward anomalous growth of grains appears in the microstructure of ceramic based on hydroxyapatite synthesized with PVA.

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Materials based on calcium hydroxyapatite (HAP) are finding wide application in medicine for creating bone implants and carriers of medicines, for filling chromatographic columns, as adsorbents, and so forth. Various chemical methods are used to obtain high-quality powders of calcium phosphates, including HAP. The most popular methods are chemical coprecipitation from water solutions containing the ions  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{OH}^-$ , which, interacting with  $\text{pH} > 7$ , form primary crystallites of insoluble HAP. The process of obtaining powder for ceramics includes chemical interaction between the initial components, separating and drying the precipitate, and disaggregating the dried product.

A great deal of attention is now being devoted to obtaining nanopowders, i.e., powders with particle sizes not exceeding 100 nm. However, the use of such powders for obtaining ceramic remains problematic. Nanopowders have a high specific surface area and therefore excess surface energy — the driving force of the sintering process. Obtaining ceramic with uniform structure from nanopowders is a quite difficult problem. Nanoparticles aggregate, and the average particle size (aggregates) in the powder is 1 – 3  $\mu\text{m}$ . It is such aggregates that play the determining role in the formation of the microstructure of ceramic [1]. The use of chemical synthesis to obtain HAP powder with individual particle sizes less than 100 nm results in the formation of 1 – 15  $\mu\text{m}$  grains, depending on the sintering regime and the method used to prepare the powder [2].

An obvious way out of the technological situation which has developed is to use a number of techniques that make it possible to decrease the aggregation of the powder material at different stages. One such technique is to use surfactants, which modify the surface of particles [3], and to eliminate milling of the powder material, assuming formation from highly concentrated suspensions. A number of other techniques can also be used.

The use of various surfactants is well known for obtaining oxide nanoparticles or particles with intricate shapes [4 – 9]. However, in most cases, the influence of the surfactants or other soluble high-molecular compounds (HMC) used in synthesis on the behavior of powder material during formation of a ceramic is not studied.

The use of gelatin [10, 11] or polyvinyl alcohol (PVA) [12] in the synthesis of oxide powders is well known. However, in these cases HMC are used in substantial quantities to perform synthesis in a viscous medium, where the mobility of the components is decreased.

Polyvinyl alcohol is a widely used substance in the technology of technical ceramics based on pure oxides (containing no other components) that give plasticity to the forming paste and ensure consolidation of material at the formation stage. Polyvinyl alcohol meets all requirements for an ideal temporary technological binder: chemically inert, nontoxic, including at the decomposition stage, completely removed during calcination before the sintering starts for most oxide materials.

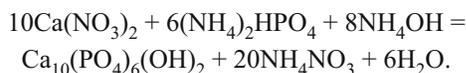
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Polyvinyl alcohol  $(-CH_2-CH(OH)-)_n$  contains OH groups which can interact with the surface of HAP, which, as in many oxide materials, is hydrated. The interaction with OH groups belonging to PVA can also occur on the surface of HAP as a result of interaction with  $Ca^{2+}$  ions [13, 14]. Thus, it can be supposed that the role of PVA in the synthesis of HAP will be to block the growth of crystallites as a result of the adsorption of PVA on their surface.

The objective of the present work was to study the effect of PVA used in the synthesis of HAP from solutions on the properties of the powder obtained and to study the formation of the microstructure of a ceramic.

The interaction of calcium nitrate and ammonium hydrophosphate was used to synthesize HAP:



We added 300 ml of 0.6 M water solution of ammonium hydrophosphate  $(NH_4)_2HPO_4$  in drops to 300 ml of 1 M water solution of calcium nitrate  $Ca(NO_3)_2$ , making sure that the ratio Ca : P = 1.67 holds. Polyvinyl alcohol was added to the calcium nitrate solution in the amounts 0, 0.25, and 0.5%<sup>2</sup> with respect to the mass of the HAP synthesized. The reaction was performed at 60°C with intensive mixing. The pH of the reaction was held at 9.0 using a 25% solution of  $NH_3$ . After the solutions were decanted, the suspension obtained was held in the mother liquor for 30 min. The precipitate was filtered on a paper filter using a water-steam vacuum pump.

The filtered precipitate was dried in a thin layer at 20°C for 48 h. The product obtained was disaggregated in acetone in a ball mill. The acetone : powder : balls ratio was 1 : 1 : 3. After disaggregation the powder was dried at 20°C for 2 h and passed through a sieve with 200  $\mu m$  cells. These samples were formed into 1.3 – 1.5 g  $3 \times 6 \times 40$  mm bars under compaction pressure 50 – 100 MPa. The relative density of the samples was calculated assuming the theoretical density of HAP to be 3.16 g/cm<sup>3</sup>.

The method of isothermal holding was used to investigate the evolution of the structure. These samples were heated up to different temperatures in the interval 250 – 1200°C at the rate 5°C/min and held at the final temperature for 4 h.

According to XPA data (DRON-3M diffractometer, Burevestnik Scientific – Industrial Association;  $CuK_\alpha$  radiation), the powder consisted of HAP and ammonium nitrate. The average particle size (primary crystallites) calculated from the XPA data using the Debye – Scherrer relation ( $hkl = 002$ ,  $d = 3.44 \text{ \AA}$ ) was 15 – 40 nm. The particle size distribution was obtained by the method of dynamic scattering of light in the range 3 nm — 18  $\mu m$  (FRITCSH Analisette, Germany). The powders obtained are characterized by an average aggregate size of the order of 3  $\mu m$ . The

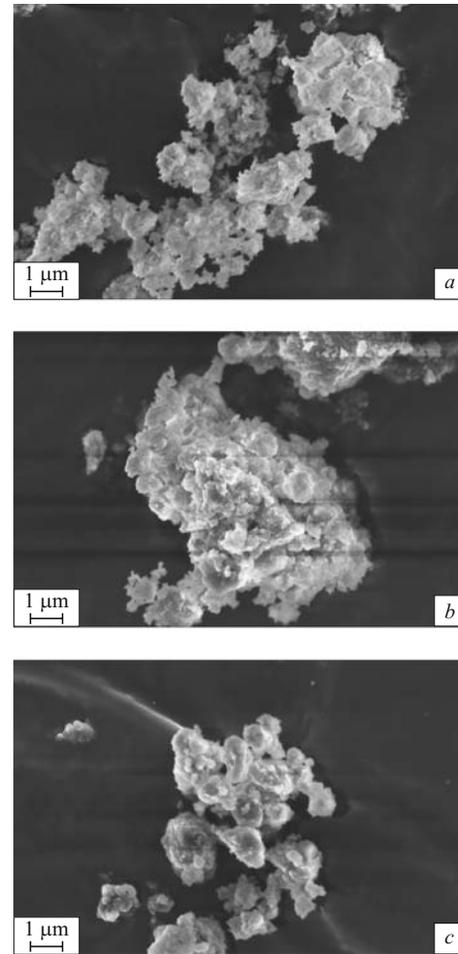


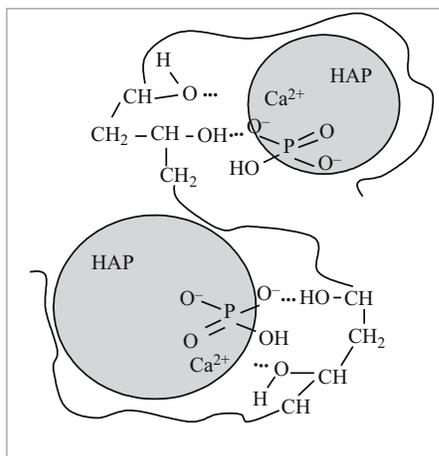
Fig. 1. The photomicrographs of HAP powders synthesized in the presence of PVA: a, b, and c) 0, 0.25, and 0.50% PVA, respectively.

data from granulometric analysis show an essentially identical particle size distribution for powders synthesized without PVA and in the presence of 0.25 and 0.50% PVA. The average size of the aggregates was 2.8 – 3.0  $\mu m$ , and the maximum size of the aggregates did not exceed 10  $\mu m$ . However, the bulk density of the powders, the density of the compacts, and the photomicrographs of the powders (Fig. 1) showed differences in the rheological properties of the powders and in the morphology of the particles. The properties of the powders and compacts as function of the PVA content during synthesis of HAP from solutions of calcium nitrate and ammonium hydrophosphate are presented in Table 1.

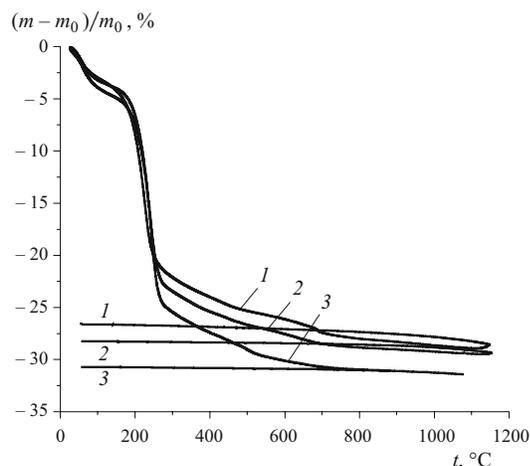
TABLE 1.

PVA content, %	Mass losses at 400°C, %	Apparent density of powders, g/cm <sup>3</sup>	Density of compacts, % (pressing pressure 50 MPa)
0	23.99	0.42	42
0.25	25.39	0.56	47
0.50	27.40	0.67	48

<sup>2</sup> Here and below — the mass content.

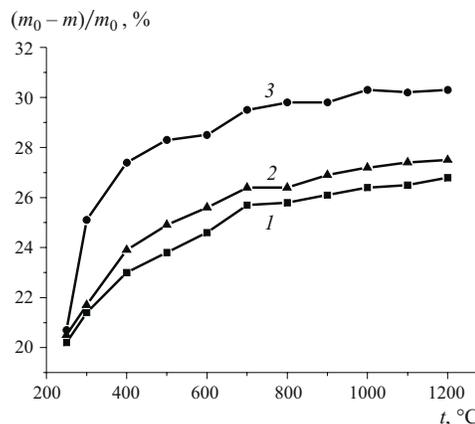


**Fig. 2.** Diagram illustrating the interaction of particles of HAP and PVA during synthesis.



**Fig. 3.** Thermogravimetric curves of HAP powders obtained in the presence of PVA: 1, 2, and 3) 0, 0.25, and 0.50% PVA, respectively.

As the PVA content increases, the bulk density and the density of the compacts increased and varied from 0.42 to 0.67 g/cm<sup>3</sup> and from 42 to 48%. The powders containing PVA consist of larger aggregates. Each aggregate, in turn, consists of smaller particles with a rounded shape. The effect of PVA on the size of individual crystallites can be explained by the capability of PVA to be adsorbed on the HAP surface and to manifest the properties of a surfactant. At the same time PVA promotes the formation of quite large aggregates, manifesting well-known properties of the binder which glues the material together. The presence of quite large aggregates together with small particles can provide a more dense packing of powder particles with a higher bulk density of the powder and density of the compacts. The proposed effect of PVA during synthesis is shown schematically in Fig. 2. PVA added during synthesis, settles on the surface, interacts with



**Fig. 4.** Mass losses versus temperature, determined by the isothermal holding method, for HAP samples obtained in the presence of PVA. The notation is the same as in Fig. 3.

the HAP particles as a result of the OH groups, and glues the particles together into quite large agglomerates.

It should be kept in mind that ammonium nitrate, water, and acetone are also present in the aggregates formed. The content of these products in the powder is substantial, as is indicated by the mass losses at 400°C, which are 24.0–27.4% (see Table 1 and Fig. 3).

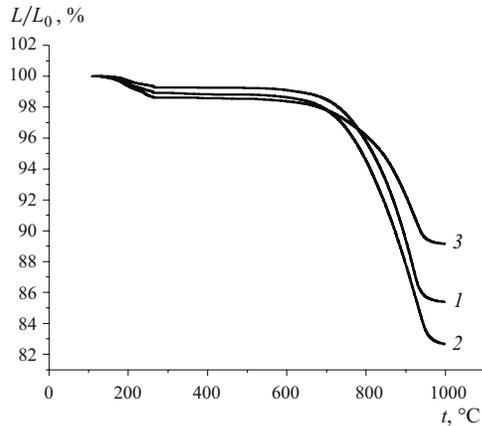
Thermogravimetric analysis (see Fig. 3, Perkin Elmer Pyris thermoanalyzer (USA)) revealed substantial mass losses (up to 30–32%) with heating up to 1150°C. These losses increase with PVA content. The mass losses occur in several stages.

Adsorbed water and acetone in which disaggregation of the powders was performed are removed at the first stage (about 5–6%, up to 200°C).

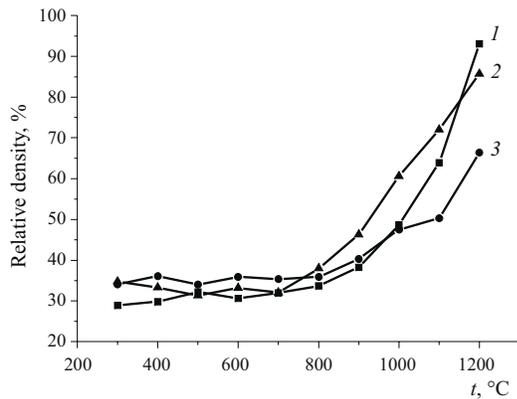
The second stage (up to 25% and 700°C) could be due to decomposition of ammonium nitrate. Since the synthesis was conducted in air, CO<sub>2</sub> is inevitably trapped and enters the structure of HAP as CO<sub>3</sub><sup>2-</sup>. Consequently, the further decrease of the mass could be due to release of CO<sub>2</sub>. The removal of carbonate groups can be accompanied by partial dehydration of HAP with formation of oxyhydroxyapatite at higher temperatures.

An increase of mass losses with increasing PVA content was also observed during an investigation of samples by the isothermal holding method (Fig. 4).

Figure 5 displays the dilatometric curves of the experimental samples (LIR-1400 dilatometer, Russia; heating rate 5 K/min up to 1000°C). The maximum rate of shrinkage is found in temperature interval 900–950°C. All curves characteristically have two steps. Melting and decomposition of sodium nitrate occur at temperatures 150–250°C. The change in the linear dimensions at temperatures 700–950°C is associated with the removal of pores and consolidation of the blanks, which corresponds to the initial stage of sintering. The greatest shrinkage is characteristic for the sample containing 0.25% PVA and the smallest shrinkage is characteris-



**Fig. 5.** Dilatometric curves of samples (compaction pressure 50 MPa) from powders synthesized in the presence of PVA. The notation is the same as in Fig. 3.

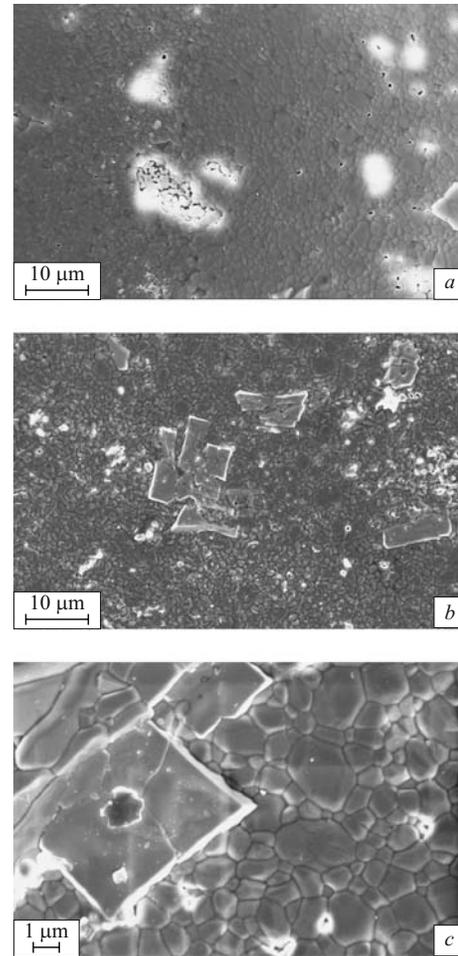


**Fig. 6.** Relative density of the samples versus temperature. The notation is the same as in Fig. 3.

tic for the sample with 0.50% PVA added. The sample without PVA exhibits intermediate shrinkage.

Figure 6 displays the temperature dependence of the relative density as determined by the isothermal holding method. Ceramics based on HAP powders with 0.50% PVA show the lowest shrinkage according to data from dilatometry and the isothermal holding method. The maximum shrinkage according to the data from dilatometry was observed for a ceramic based on HAP powder with 0.25% PVA (see Fig. 5). However, according to data obtained by the isothermal holding method, the shrinkage of HAP which does not contain PVA is higher. Starting at temperature 1000°C, the shrinkage tends to decrease for HAP with 0.25% PVA. All samples reached the maximum density at 1200°C. The density was 92% for ceramic made from HAP without PVA and 85 and 65% for HAP with 0.25 and 0.50% PVA, respectively. At 1200°C the density of the sample decreases with increasing PVA content in the synthesis process.

The investigations showed that the presence of PVA during synthesis results in the formation of an intermediate



**Fig. 7.** Photomicrograph of ceramic after calcination at 1200°C (compaction pressure of 100 MPa): *a*, *b*, and *c*) 0, 0.25, and 0.50% PVA, respectively.

microstructure consisting of large and small particles, which creates conditions for dense packing of the particles. Such a microstructure of the material at an intermediate stage evidently is responsible for the fact that sintering starts first in the densest sections and then the material sinters as if it consists of coarse particles. The adjustment occurring in the crystal lattices of the grains as the reason for the anomalous growth of grains is observed where the conditions for this are right [15].

After the powders are calcined at 1200°C the XPA data confirmed the presence of a single HAP phase in the powders. This shows that HAP obtained by this method in the presence of PVA is stable at high temperature.

Investigation of the microstructure of ceramic obtained in 1200°C (Fig. 7) indicates the formation of large grains approximately 10 μm in size in samples synthesized in the presence of PVA. The process of anomalous growth of grains could be associated with the formation of aggregates in the HAP powder. The aggregates formed, being the densest structural units of the powder and the compacts, start to sinter ear-

lier during high-temperature treatment with local densification. Local densification forms a large grain, which starts to grow at the expense of the surrounding fine-grain mass. As a result, a large grain (10  $\mu\text{m}$  or larger) surrounded by small grains (up to 1  $\mu\text{m}$ ) appears. As a rule, the anomalous growth of grains is a negative phenomenon when obtaining ceramic with a uniform microstructure. But the structures, described above, in ceramic (usually called duplex structures) can be used in some cases to improve the mechanical characteristics of the material, specifically, its crack resistance.

In summary, the use of PVA in the synthesis of HAP affects the properties of the powder material and makes it possible to control the structure of the ceramic obtained.

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