

Ceramics Based on Calcium Phosphate Powder Synthesized from Calcium Saccharate and Ammonium Hydrophosphate

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Abstract—A microporous ceramic with a pore size ranging from 1 to 6 μm and a relative density up to 56% was obtained from the calcium phosphate powder synthesized from aqueous solutions of monocalcium saccharate ($\text{CaC}_{12}\text{H}_{22}\text{O}_{11}$) and ammonium hydrophosphate. The composition of the synthesized nanosized powder is found to include hydroxyapatite and sucrose. The phase composition of the ceramic after calcination in the range from 900 to 1200°C is represented by β -tricalcium phosphate and hydroxyapatite. The resulting ceramic material can be recommended for the manufacture of bone implants.

Keywords: calcium saccharate, hydroxyapatite, tricalcium phosphate, nanosized powder, bioceramic

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INTRODUCTION

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP) is the main inorganic component of bone tissue. That is why the materials for bone implants are made mainly either on the basis of or with the use of calcium phosphates [1]. Materials based on HAP and tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (TCP) find the widest application in medical practice today [2]. The advantage of artificial ceramic and other inorganic materials consists in the absence of immune response in the case of their use for the treatment of bone defects. Synthetic fine powders with specified chemical and phase composition active with respect to sintering are required for the production of ceramic materials for bone implants, as well as for the manufacture of other ceramic materials with special functions [3].

In order to synthesize calcium phosphate powders, one uses chemical precipitation from solutions of soluble calcium salts and phosphates. The result of the synthesis is sensitive to the pH level in the reaction zone. At pH higher than 6, the most likely reaction product of soluble calcium salts and sodium, potassium, and ammonium orthophosphates or phosphoric acid is hydroxyapatite, whereas at pH less than 4 the most likely product of the synthesis is brushite [4].

It should be noted that there exist such pairs of starting salts that can form a buffer system in the reaction zone with a particular pH level upon interaction. Thus, the choice of a pair of precursors represents a way to organize a convenient synthesis that does not require a laborious pH control. Such pairs are exem-

plified by $\text{Ca}(\text{OH})_2\text{--H}_3\text{PO}_4$ for the synthesis of hydroxyapatite [5], by $\text{Ca}(\text{NO}_3)_2\text{--}(\text{NH}_4)_2\text{HPO}_4$ for the synthesis of brushite [6], and by $\text{Ca}(\text{CH}_3\text{COO})_2\text{--}(\text{NH}_4)_2\text{HPO}_4$ for the synthesis of hydrated tricalcium phosphate [7].

The pair of salts used determines the composition of the mother liquor, as well as the composition of a reaction by-product (RBP) of the synthesis that could affect the course of sintering and the formation of the microstructure and phase composition of the ceramics if it remains in the powder intended for producing the ceramic [8]. Calcium nitrate and ammonium hydrophosphate are frequently used for synthesizing calcium phosphate powders for the production of ceramic materials, since in the synthesis ammonium nitrate is formed, which can be readily removed in the course of heat treatment [9]. Ammonium acetate that is formed via the interaction between calcium acetate and ammonium phosphate also belongs to RBP, which can be removed in the course heat treatment. The feature of ammonium acetate contained in calcium phosphate powder and in the powder workpieces after molding consists in a tendency to carbonization during the heat treatment [7]. The carbon formed in this case remains in the powder workpieces up to 800°C.

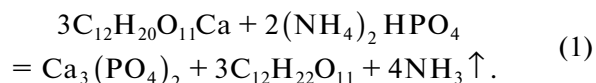
Carbon in the composition of a powder workpiece upon obtaining the ceramic can affect the course of various processes. Being a physical barrier that can prevent the sintering of nanosized powder at relatively low temperatures, the carbon causes a submicron

ceramic structure formation at traditionally used sintering temperature values [7]. The carbonized byproduct is also known to be used as a pore-forming agent in the preparation of porous ceramic materials [10]. In this regard, the development of methods for obtaining calcium phosphate powders, the RBP of which contains organic components that undergo carbonization and can be removed via heat treatment, is of urgency.

Earlier, the synthesis of hydroxyapatite from different calcium saccharates $\text{Ca}_n\text{C}_{12}\text{H}_{22-2n}\text{O}_{11}$ (where $n = 0.5, 1, \text{ and } 2$) and ammonium phosphate was reported [11]. Transparent solutions of calcium saccharate prepared from calcium oxide and an aqueous solution of sucrose were obtained for the cases of $n = 0.5$ and $n = 1$. An aqueous solution of calcium saccharate prepared from calcium oxide and a solution of sucrose has a pH level of at least 11. Using such a solution would facilitate the synthesis of calcium phosphate with a Ca/P ratio greater than 1.5. The convenience of such a synthesis consists in the absence of any necessary additional pH adjustment in the course of the preparation of calcium phosphate with a Ca/P ratio greater than 1.5. Sucrose as an ARP of organic nature can undergo carbonization, and then it can be completely removed from a powder workpiece in the course of calcination with no formation of additional phases. The present work was aimed at studying the process of obtaining a ceramic from powder synthesized from calcium saccharate $\text{CaC}_{12}\text{H}_{21}\text{O}_{11}$ and ammonium hydrophosphate $(\text{NH}_4)_2\text{HPO}_4$.

EXPERIMENTAL

The calculation of the amount of initial components for the synthesis of calcium phosphate was performed according to the equation



In order to obtain calcium phosphate, to 300 mL of a 0.5 M aqueous solution of $\text{C}_{24}\text{H}_{42}\text{O}_{22}\text{Ca}$ was added 200 mL of a 0.5 M aqueous solution of $(\text{NH}_4)_2\text{HPO}_4$ dropwise for 15 min. For carrying out the synthesis, we used diammonium hydrophosphate $(\text{NH}_4)_2\text{HPO}_4$ (GOST (State Standard of the Russian Federation) 3772-74, Labteh, Russia). A 0.5 M solution of calcium saccharate was prepared from calcium oxide and sucrose (GOST 5833-75) from Labteh (Russia). For obtaining calcium oxide, we used calcium carbonate (GOST 4530-76, Labteh, Russia), which was calcined at 1000°C for 3 h (heating rate of 5°C/min). The decomposition of calcium carbonate occurs according to the reaction



In order to obtain a 0.5 M solution of calcium saccharate, calcium oxide was added to an aqueous solution of sucrose heated to 60°C. The synthesis of calcium saccharate from CaO, and sucrose can be expressed by the following equation:



Synthesized calcium phosphate was separated from the mother liquor using a Buchner funnel. The resulting precipitate was then dried in a thin layer at a room temperature for a week. The dried product was disaggregated using a planetary-type ball mill for 10 min at the ratio “grinding media (ZrO_2) : powder : acetone” = 5 : 1 : 1. After the evaporation of acetone, the powder was passed through a nylon sieve with a mesh size of 200 μm .

Powder workpieces in the form of tablets 12 mm in diameter and about 2 mm thick having a weight of about 0.25 g were molded by means of pressing at 50 MPa. The mean density of the samples after molding on average was 1.1 g/cm³. In order to study the thermal evolution of synthesized calcium phosphate and the compaction of powder workpieces, the samples were calcined after formation in the temperature range from 900 to 1200°C with a step of 100°C, holding them at the final temperature for 2 h and with a heating rate of 5°C/min.

The X-ray diffraction (XRD) phase analysis of synthesized products (calcium saccharate and calcium phosphate powder), as well as of the samples after heat treatment, was carried out using a Rigaku D/Max-2500 diffractometer (Japan) with a rotating anode using CuK_α radiation. For the qualitative determination of phases we used ICDD PDF2 database [12]. The registration was performed in a reflection mode using CuK_α radiation (the angular range from 2° to 70° with an increment of 0.02°, recording speed of spectra of 5°/min). The thermal analysis (TA) was performed a STA 409 PC Luxx thermal analyzer (NETZSCH, Germany). The investigation of the composition of the gas phase formed via the decomposition of the samples was performed using a QMS 403C Aeolos quadrupole mass spectrometer combined with a STA 409 PC Luxx thermal analyzer (NETZSCH, Germany). The mass spectra were registered for mass numbers 18 (corresponding to H_2O), 44 (CO_2), 30 (NO), and 28 (N_2). The heating rate was 10°C/min, and the studies were carried out in a temperature range from 40 to 1000°C. The weight of the samples was not less than 10 mg. The electron microscopic study was performed using a SUPRA 50 VP scanning electron microscope (Carl Zeiss, Germany); the imaging was performed in a low vacuum mode at an accelerating voltage of 21 kV (VPSE secondary electron detector) and in the voltage range from 3 to 21 kV (SE2 detector).

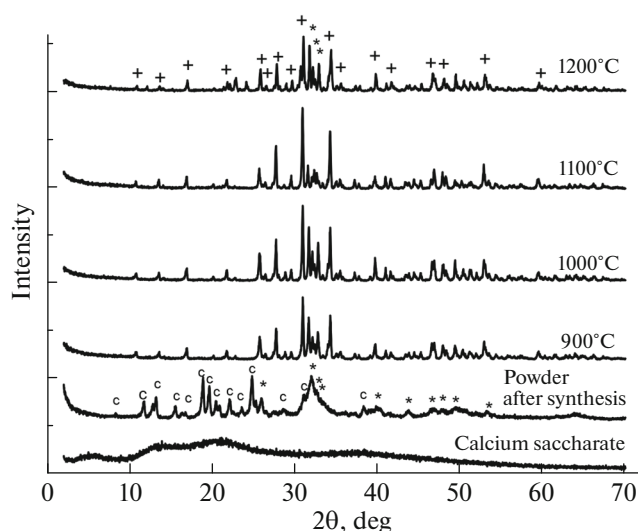


Fig. 1. XRD patterns of calcium saccharate, calcium phosphate powder after synthesis, and ceramic samples after calcination at different temperatures in the range from 900 to 1200°C. Designations: (*) HAP (# 9-432 PDF2); (s) saccharose (# 24-1977 PDF2); (+) β -TCP (#9-169 PDF2).

RESULTS AND DISCUSSION

According to XRD phase analysis, the obtained calcium saccharate after drying represents an amorphous product; it does not exhibit any reflections of the initial reactants such as calcium oxide and sucrose. After the reaction between calcium saccharate and ammonium phosphate, the powder represented a mixture of hydroxyapatite and sucrose (Fig. 1). A SEM image of the powder after synthesis and disaggregation is shown in Fig. 2a. The particle size of the synthesized calcium phosphate powder was much smaller than 100 μm . After a test calcination of the powder at 1000°C for 2 h, the particle size reached 100–300 nm. According to the thermal analysis (Fig. 3), the total weight loss at 1000°C was 64%. Below 200°C, the sample weight decreased by 3% owing to the loss of adsorbed water. In the temperature range from 200 to 225°C, the mass loss was 22%. The data of mass-spectrometric studies allow one to consider that the weight loss is connected with the decomposition of an associated reaction product, sucrose, which, being a carbohydrate, decomposes with a release of carbon dioxide (mass number 44) and water (mass number 18).

In the same range, we detected particles with the mass numbers of 28 and 30 corresponding to N_2 and NO , which indicates that some amount of ammonia is contained in the associated reaction product. In the range from 225 to 475°C, the change in mass was 40%, being mainly connected with a release of CO_2 and H_2O . In this temperature range, on the line reflecting the liberation of CO_2 , two peaks (at 350°C and at 460°C) are observed, whereas on the line reflecting the release of water, only a small peak at 350°C is observed. This fact allows one to suggest that, in the case of heating above a temperature of 400°C, the sample contains a carbonized residue of RBP that

undergoes further decomposition. Figure 4 shows a photograph of samples based on calcium phosphate powder synthesized from saccharate and ammonium

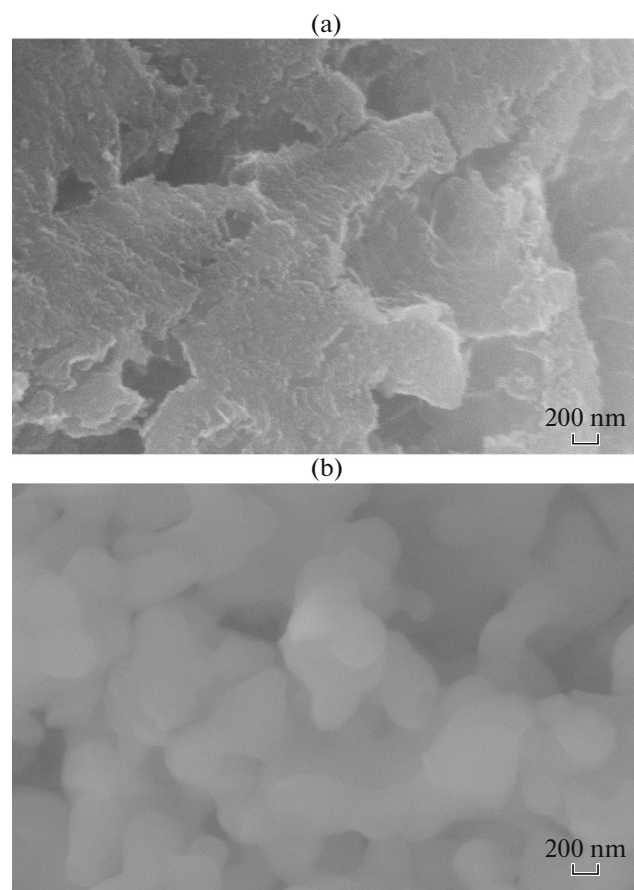


Fig. 2. SEM images of calcium phosphate powder after synthesis (a) and after calcination at 1000°C (b).

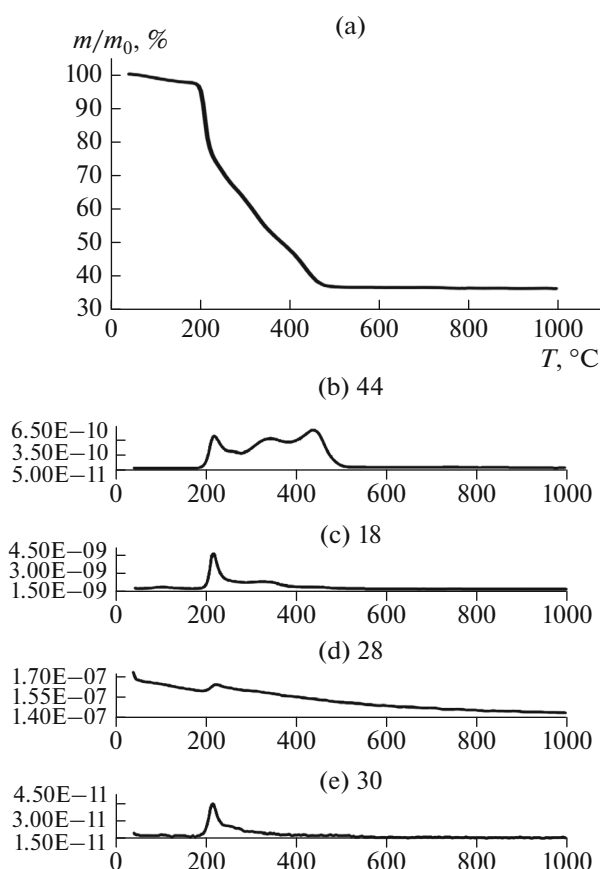


Fig. 3. Thermal analysis data for the synthesized powder: sample mass depending on temperature (a); ion current values (A) depending on temperature for particles with the mass numbers 44 (b), 18 (c), 28 (d), and 30 (e). The correspondence of mass numbers: 44—CO₂; 18—H₂O; 30—NO; 28—N₂.

hydrophosphate after heat treatment at 500°C for 15 and 30 min, as well as for 1 and 2 h. The tablets had a characteristic black-brown color. The weight loss in the range from 475 to 1000°C was 1%.

According to the XRD phase analysis (see Fig. 1), the phase composition of the samples after calcination in the range from 900 to 1200°C is represented by β -

TCP and HAP. The weight content of β -TCP is assessed to be 70%. Some of the properties of ceramic samples produced from the synthesized powders after calcination at a temperature ranging from 900 to 1200°C are shown in the table. The weight loss of the samples after isothermal exposing is fairly high, ranging from 68 to 73%, which is in a good agreement with data on weight loss obtained by using a polythermal heating mode. A high content of the component of the powder workpiece removed upon calcination resulted in destruction of the sample calcined at 900°C and in a cracking of the sample calcined at 1000°C. The samples after calcination at 1100 and 1200°C held their form and exhibited sufficient strength, which allowed us to carry out measurements. After calcination, all the samples exhibited a significant linear shrinkage ranging from 26% after calcination at 1000°C to 40% after calcination at 1200°C. High shrinkage values indicated a high activity of the powder with respect to sintering. The density of the samples in this case was low and ranged from 27% after calcination at 1000°C to 56% after calcination at 1200°C.

Figure 5 presents the SEM images of ceramic samples produced from the calcium phosphate powder after sintering for 2 h at 1000°C (a), 1100°C (b), and 1200°C (c). The SEM images demonstrate that the size of the ceramic grains increases from 100–300 μ m at 1000°C to 2–4 μ m at 1200°C. The sample after calcination at 1000°C does not look sintered in the SEM images. Only the increase in particle size as compared to the particle size of the powder after synthesis indicates a high temperature impact. In the micrographs of the samples after the calcination at 1100 and 1200°C, one can see the porosity uniformly distributed over the volume of the sample, as well as sites with grains sintered together. Obtaining such a microstructure was promoted by a low density of the powder workpiece after molding (relative density of 30%), a high RBP content (64%), and a high activity of calcium phosphate nanosized powder obtained via precipitation with respect to sintering. In the SEM images, one can see pores from 2 to 4 μ m in size after calcination at 1100°C and pores size from 1 to 6 μ m in size after calcination at 1200°C. The surface of the

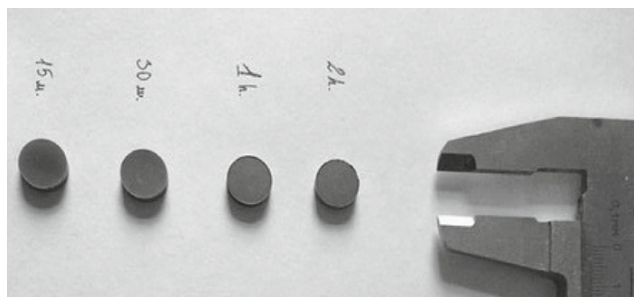


Fig. 4. Appearance of samples produced from the powder synthesized from calcium saccharate and ammonium hydrophosphate after heat treatment at 500°C for 15 and 30 min, and well as for 1 and 2 h.

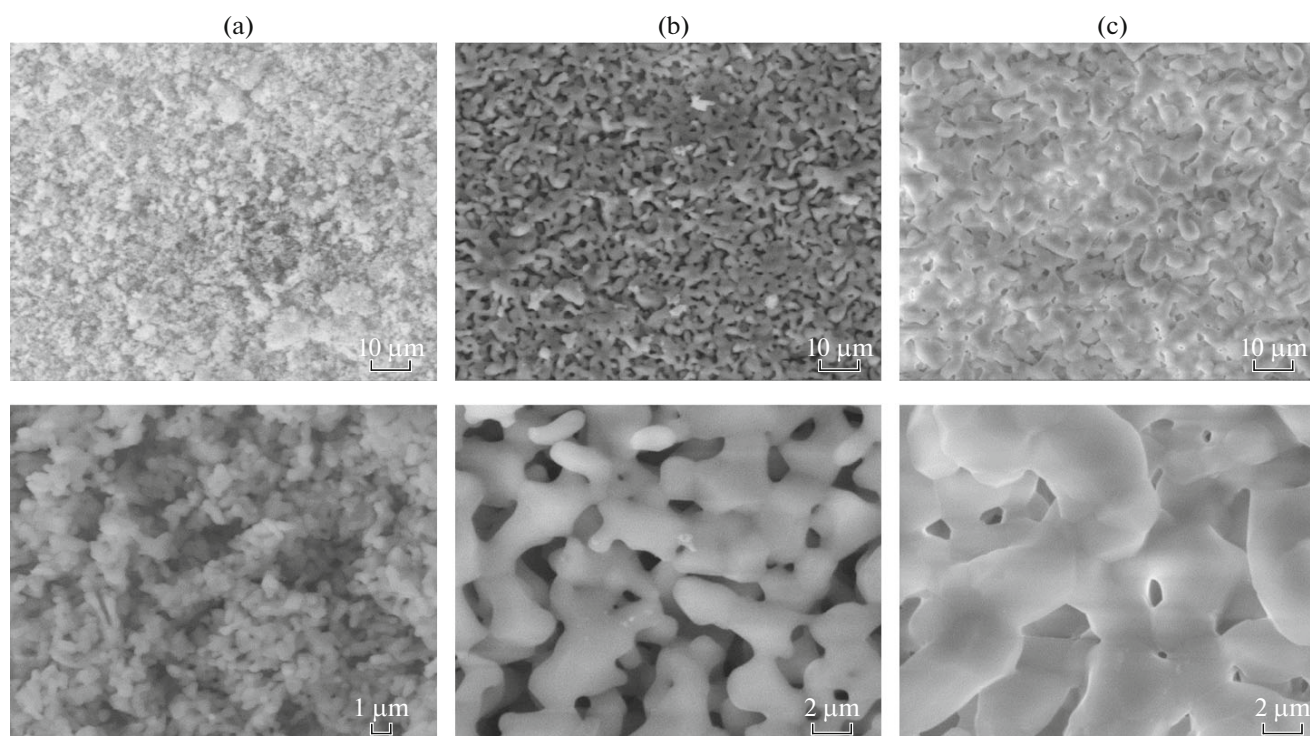


Fig. 5. SEM images of ceramic samples after calcination for 2 h: (a) 1000°C; (b) 1100°C; (c) 1200°C.

microporous material should be considered suitable for the spreading and propagation of bone cells, since such a value of porosity makes the surface of the material rough.

CONCLUSIONS

Nanosized calcium phosphate powder synthesized from 0.5 M solutions of calcium saccharate and ammonium hydrophosphate contained a significant amount (64%) of sucrose as the reaction by-product. A microporous ceramic with a pore size from 1 to 6 μm and a relative density of 56% was obtained on the basis of calcium phosphate powder synthesized from aqueous solutions of monocalcium saccharate ($\text{CaC}_{12}\text{H}_{20}\text{O}_{11}$)

and ammonium hydrophosphate. A significant linear shrinkage of powder workpieces after calcination (up to 40% after calcination at 1200°C) indicates a high activity of the synthesized powder with respect to sintering. The phase composition of the ceramic represented by β -TCP and HAP allows one to consider the synthesized powder to be acceptable for the manufacture of bone implants. Ceramic composites containing these phases are widely used as materials for bone implants.

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Some properties of the ceramic samples produced from the synthesized powder after calcination in the temperature range from 900 to 1200°C.

T of calcination, °C	Linear shrinkage D_l/D_0 , %	Relative density* ρ_l/ρ_{TCP} , %	Weight loss $(m_0 - m_l)/m_0$, %	Sample after calcination
900	—	—	70 ± 2	Crumbled in hands, cracked
1000	26 ± 3	27 ± 5	73 ± 2	Held its shape, cracked
1100	34 ± 3	42 ± 5	68 ± 2	Held its shape
1200	40 ± 3	56 ± 5	69 ± 2	Held its shape

* Density β -TCP—3.07 g/cm³.

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