BIOMATERIALS

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POWDERS SYNTHESIZED FROM CALCIUM ACETATE AND MIXED-ANIONIC SOLUTIONS, CONTAINING ORTHOPHOSPHATE AND CARBONATE IONS, FOR OBTAINING BIOCERAMIC

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X-ray amorphous powder was synthesized from a water solution of calcium acetate and a mixed-anionic (HPO_4^{2-}/CO_3^{2-}) water solution, including ammonium hydrophosphate and ammonium carbonate, at room temperature without pH regulation. The powders synthesized from the mixed-anionic (HPO_4^{2-}/CO_3^{2-}) solution can be recommended for fabricating composite materials with a polymer matrix or for obtaining ceramic containing tricalcium phosphate and calcite phases with firing temperature not exceeding 600°C.

Key words: synthesis, mixed anionic solution, amorphous powder, brushite, hydroxyapatite, calcium carbonate, composite, tricalcium phosphate.

Inorganic materials for bone implants are fabricated, as a rule, by means of powder technologies. For this reason synthetic powders containing compounds comprised of ions found in bone tissue are needed for the production of such materials. The primary component of the inorganic composition of bone tissue is carbonate hydroxyapatite (CHAP). This circumstance requires developing methods for obtaining powders that would include calcium phosphate, calcium carbonate (CC), and mixed calcium salts containing both ions (carbonate ion and phosphate ion).

Considering the existing trends toward using regenerative methods of treating defects of bone tissue the demand for biocompatible, bioactive, and bioresorbable materials is growing. For this reason attention must be devoted to developing composites containing phases possessing higher solubility than synthetic hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAP). In designing the phase composition of ceramic materials based on calcium orthophosphates and carbonate the proneness toward resorption (dissolution) will increase in the order

CHAP \ll composite CHAP/TCP³ \ll TCP \ll composite TCP/CC \ll CC.

Information about the synthesis and structure of carbonate substituted hydroxyapatite (CHAP) is presented in the literature [1]. During the formation of CHAP a portion of the hydroxyl groups in the structure of hydroxyapatite is replaced by the carbonate ion (A-type substitution), phosphate groups by the carbonate ion (B-type substitution), and possibly also mixed substitution of the AB-type. Materials based on CHAP possess higher solubility than materials based on HAP. Powder mixtures containing HAP and CC (calcite) were obtained by synthesis from solutions or mechanical activation from calcium hydroxide, ammonium phosphate, and ammonium hydrocarbonate [2].

The production of ceramic materials based on CHAP or powder mixtures containing CC is complicated by the low stability of their compounds upon heating. However, the problem can be surmounted by using sintering additives that form melts at quite low temperatures. For example, ceramic made from CHAP was obtained using as the sintering additive phosphate glass with the composition (content by weight, %) 54 Na₄CaP₆O₁₈ and 46 Na₂CaP₂O₇ [3]. Ceramics containing the phases HAP and CC were obtained using a sintering additive comprised of a mixture of calcium carbonate and sodium carbonate [4].

Owing to their uniform arrangement of phases high-quality ceramic composite materials can be obtained by using

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³ Tricalcium phosphate.

methods of preparing the initial powder that make it possible to attain the highest degree of homogenization of the components — precursors of the phases. Chemical homogenization presupposes synthesis of single-phase [5] or amorphous [6] powders — precursors for multiphase ceramic.

Amorphous calcium phosphate powder can be obtained by synthesis from

non-water solvents, by synthesis at lower temperatures, or by using mixed anion solutions. Convenient methods are synthesis not requiring additional pH regulation in the reaction zone, given that the pH in the reaction zone largely determines the result of synthesis of calcium phosphates [7]. Additional efforts to regulate pH are not required if the components present in the reaction zone form buffer systems, for example, such as CH₃COOH/CH₃COO [8, 9].

The aim of the present work was to obtain powder from water solutions of calcium acetate and mixed-anionic (HP HPO_4^{2-}/CO_3^{2-}) water solution containing ammonium hydrophosphate and ammonium carbonate and to study its properties. For comparison the following pairs of precursors were synthesized from water solutions: ammonium carbonate/calcium acetate and ammonium hydrophosphate/calcium acetate.

EXPERIMENTAL PART

Powders were synthesized from water solutions of calcium acetate, ammonium hydrophosphate, and ammonium carbonate at room temperature $(22 - 25^{\circ}C)$ without pH regulation. The average synthesis time was 30 - 45 min. The conditions of synthesis and the labeling of the powders are presented in Table 1. The amounts of the initial salts were calculated from following relations:

$$Ca(CH_{3}COO)_{2} + (NH_{4})_{2}CO_{3} = CaCO_{3} \downarrow + 2CH_{3}COONH_{4};$$
(1)

$$4Ca(CH_{3}COO)_{2} + 2(NH_{4})_{2}HPO_{4} + (NH_{4})_{2}CO_{3} + xH_{2}O = Ca_{3}(PO_{4})_{2} \cdot xH_{2}O\downarrow + CaCO_{3}\downarrow + 6CH_{3}COONH_{4} + 2CH_{3}COOH;$$
(2)

$$3Ca(CH_{3}COO)_{2} + 2(NH_{4})_{2}HPO_{4} + xH_{2}O = Ca_{3}(PO_{4})_{2} \cdot xH_{2}O \downarrow + 4CH_{3}COONH_{4} + 2CH_{3}COOH. (3)$$

During synthesis the initial components $(Ca(CH_3COO)_2 and (NH_4)_2CO_3 / (NH_4)_2HPO_4 formed, aside from the desired products, the following ancillary products of reaction (APR) during storage and heat-treatment — CH_3COONH₄ and CH₃COOH.$

To study the thermal evolution of the synthesized powder the samples in the form of compact powder blanks were fired at temperatures 600, 700, and 800°C at heating rate 5 K/min and soaked at a prescribed temperature for 2 h. Compact blanks with diameter 12 mm were obtained under specific pressing pressure 50 MPa.

TABLE 1. Conditions of Synthesis and Labeling of Powders

Synthesis no.	Expected product	Labeling	Concentration of water solutions of salts		
			$(\mathrm{NH}_4)_2\cdot\mathrm{CO}_3$	$(\mathrm{NH}_4)_2 \cdot \mathrm{HPO}_4$	$Ca(CH_3 \cdot COO)_2$
1	CaCO ₃	P-CC	1 M	_	1 M
2	Ca ₃ (PO ₄) ₂ /CaCO ₃	P-CC/TCP	0.5 M	0.3 M	
3	$Ca_3(PO_4)_2 \cdot xH_2O$	P-TCP	_	0.6 M	

X-ray phase analysis (XPA) of the synthesized powder and samples after heat-treatment was performed using a Rigaku D/Max-2500 diffractometer with a rotating anode (Japan). The ICDD PDF2 database was used to determine the phase composition of the samples after synthesis and firing [10]. The measurements were conducted in reflection using CuK_{α} radiation (angle interval $2\theta = 10 - 70^{\circ}$, step 0.02° , spectrum recording rate 5 deg/min).

Scanning electron microscopy (SEM) with a LEO SUPRA 50VP scanning electron microscope (Carl Zeiss, Germany; field-emission source) was used to study the microstructure of the samples of synthesized powders. The measurements were performed in a low-vacuum regime with accelerating voltage 20 kV (VPSE secondary electron detector) and voltages 3 - 20 kV (SE2 detector). The images were obtained in secondary electrons with magnifications to $\times 20,000$ and stored in digital form in a computer.

A NETZSCH STA 409 PC Luxx (NETZSCH, Germany) thermal analyzer was used for thermal analysis. The composition of the gas phase formed during decomposition of the samples was studied with a QMS 403C Aëolos (NETZSCH, Germany) quadrupole mass spectrometer, combined with a NETZSCH STA 409 PC Luxx. The mass spectra were recorded for mass numbers 44 (CO₂), 18 H₂O, and 15 (NH). The rate heating was 10 K/min, the temperature interval 40 – 1000°C, and the sample mass \geq 10 mg.

RESULTS AND DISCUSSION

Powder shown by XPA (Fig. 1) to contain calcium carbonate $CaCO_3$ (modifications of calcite and faterite) was obtained from ammonium carbonate and calcium acetated in the first synthesis (see Table 1). The synthesis can be reflected by the reaction (1). Powder containing $Ca_{10}(PO_4)_6(OH)_2$ (HAP) (reaction (4)) and brushite $CaHPO_4 \cdot 2H_2O$ (reaction (5)) was obtained in the third synthesis (see Table 1):

$$10Ca(CH_{3}COO)_{2} + 6(NH_{4})_{2}HPO_{4} + 2H_{2}O = Ca_{10}(PO_{4})_{6}(OH)_{2}\downarrow + 20CH_{3}COONH_{4};$$
(4)

$$Ca(CH_{3}COO)_{2} + (NH_{4})_{2}HPO_{4} + 2H_{2}O = CaHPO_{4} \cdot 2H_{2}O \downarrow + 2CH_{3}COONH_{4}.$$
 (5)

X-ray amorphous powder was obtained by synthesis from a mixed-anionic solution containing phosphate ions and



Fig. 1. XPA data for powders synthesized from a water solution of calcium acetate and water solutions of P-CC — ammonium carbonate, P-TCP — ammonium hydrogen phosphate; P-CC/TCP — mixed-anionic solution containing orthophosphate ion and carbonate ion. Phase notation: b) brushite CaHPO₄ · 2H₂O; g) Ca₁₀(PO₄)₆(OH)₂; v) faterite CaCO₃; c) calcite CaCO₃.

carbonate ions (see Fig. 1). These powders are characterized by high uniformity of the component distribution.

Photomicrographs of the powders are displayed in Fig. 2. The powder P-CC consists of spherical particles ranging in size from 2 to 10 µm, comprising aggregates of smaller filamentary particles, and particles in the form of $2-5 \,\mu\text{m}$ parallelepipeds jointed together end-to-end. It is known from the literature that the spherical particles are calcium carbonate in the faterite modification. For powder synthesized from calcium acetate and ammonium carbonate the data from microscopic studies agree with the XPA data. The powder synthesized from water solution of calcium acetate and mixed-anionic solution (P-CC/TCP) and from water solution of calcium acetate and ammonium hydrogen phosphate (P-TCP) consists of aggregated particles no larger than 100 nm. Particles with lamellar morphology characteristic for brushite, found by XPA, are not found in the photomicrograph of P-TCP powder. It is possible that such particles did not get into the survey field or are surrounded by particles of HAP and hydrated TCP, whose diffraction patterns are practically indistinguishable.

The data obtained from thermal analysis of the synthesized powders (Fig. 3) attest that total mass loss to be 47% for the powder P-CC, 37% for P-CC/TCP, and 27% for P-TCP.

The curve for the powder P-CC reflects decomposition processes at 400° C of the ancillary product of reaction (APR) and at 800° C – decomposition of calcium carbonate (reaction (6), Fig. 3).

The thermal analysis and mass spectrometry data for the powder P-TCP reflect the processes of decomposition of APR, degradation of $Ca_3(PO_4)_2 \cdot yH_2O$ (reaction (7)) and degradation of brushite $CaHPO_4 \cdot 2H_2O$ (200°C, reaction (8)), conversion of monetite into pyrophosphate $Ca_2P_2O_7$ (CPP)



Fig. 2. Photomicrographs of powder synthesized from a water solution of calcium acetate and water solutions of: *a*) ammonium carbonate (P-CC); *b*) mixed-anionic solution containing orthophosphate ion and carbonate ion (P-CC/TCP); *c*) ammonium hydrogen phosphate (P-TCP).

(400°C, reaction (9)), and the formation of β -tCC (β -Ca₃(PO₄)₂) upon interaction of HAP and CPP (reaction (10)):

$$CaCO_3 = CaO + CO_2; (6)$$

$$Ca_{3}(PO_{4})_{2} \cdot xH_{2}O = Ca_{3}(PO_{4})_{2} + xH_{2}O;$$
 (7)

$$CaHPO_4 \cdot 2H_2O = CaHPO_4 + 2H_2O; \qquad (8)$$

$$CaHPO_4 \cdot 2H_2O = Ca_2P_2O_7 + 3H_2O;$$
 (9)

$$Ca_{10}(PO_4)_6(OH)_2 + Ca_2P_2O_7 = 4Ca_3(PO_4)_2 + H_2O.$$
 (10)

The first step of the mass loss (to 200°C) is associated with the removal of adsorbed water and acetone, in which disaggregation of the powder was performed after synthesis



Fig. 3. Thermal analysis data for powders synthesized from water solutions of calcium acetate and ammonium hydrophosphate P-TCP, ammonium carbonate P-CC, and mixed-anionic solution containing orthophosphate ion and carbonate ion (P-CC/TCP).

and drying. Since the ancillary product in the synthesis in all samples is CH_3COONH_4 , the second mass-loss step could be associated with decomposition (combustion in a stream of air) of this salt. As a result the gases CO_2 and NH_3 can form, and at temperatures $700 - 800^{\circ}C$ active release of carbon dioxide gas occurs, which is associated with decomposition of CaCO₃ (for the powders P-CC and P-CC/TCP) or formation of CO₂ upon combustion of carbon formed as result of carbonization of APR (for the powders P-CC, P-CC/TCP and P-TCP, Fig. 3).

The release of H_2O , CO_2 , and NH_3 was discovered by mass spectrometry while recording the temperature dependences of the ion current for particles with mass 15 (NH), 18 (H_2O), and 44 (CO_2) with decomposition of the synthesized powders P-CC and P-TCP.

The temperature variation of mass for the powder P-CC/TCP, synthesized from mixed-anionic solution, suggests that the reactions indicated for the powders P-CC and P-TCP occur in this powder.

The XPA data for the powders after firing at temperatures 600, 700, and 800°C are displayed in Figs. 4 - 6.

According to the XPA data, after firing at 600 and 700°C the primary phase in the P-CC powder is calcite (see Fig. 4). In addition, portlandite $Ca(OH)_2$ was found in the powder after firing at temperatures 600, 700, and 800°C. Intensity reduction of the calcite peak from 100% to practically complete vanishing at 800°C is also observed. The intensity of the portlandite peak increases. After heat-treatment of the powder P-CC at 800°C its phase composition also contains CaO.

It can be suppose that the highly dispersed particles of $CaCO_3$ corresponding to the faterite spheres (see Fig. 2*a*) are less resistant to heating. For this reason they could have undergone decomposition with formation of CaO even at the temperature 600°C. Portlandite could have formed during in-



Fig. 4. XPA data for P-CC powder after firing at different temperatures; labeling of phases: c) CaCO₃ (PDF card No. 5-586); L) CaO (PDF card No. 37-1497); p) Ca(OH)₂ (PDF card No. 4-733).

teraction of CaO with water vapor, which is released upon decomposition of APR.

It can be supposed that a very small amount of calcium acetate did not enter into reaction and remained in the powder after synthesis and drying. The water formed upon decomposition of the ammonium acetate at high temperature could have created conditions for pyrohydrolysis of calcium acetate to occur by the reaction (11) with the formation of portlandite Ca(OH)₂:

$$Ca(CH_3COO)_2 + 2H_2O = Ca(OH)_2 + CH_3COOH.$$
(11)

In addition, if calcium acetate was still present in the ARP, it is not ruled out that its decomposition by the reaction (12) also occurs:

$$Ca(CH_{3}COO)_{2} + 4O_{2air} = CaCO_{3} + 3H_{2}O + 3CO_{2}$$
. (12)

Under further heating this CC will separate the fate of CC synthesized by the exchange reaction (1).

The presence of calcium oxide or calcium hydroxide (portlandite) in ceramic biomaterials is undesirable in connection with the fact that upon contact with water media the pH level in them reaches 12 (strongly alkaline reaction). In addition to everything else, subsequently in storage the formation of calcium oxide or portlandite during firing will result in decomposition of the compact sample owing to reactions occurring with large volumetric changes, if calcium oxide transforms into calcium hydroxide and the latter then transforms into calcium carbonate.

In firing the powder P-CC/TCP, synthesized from the mixed-anionic solution, at different temperatures the phases HAP and CaO are present in the powder (Fig. 5). The intensity of the CaO peak increases with temperature.

Upon heating the powder P-TCP (Fig. 6), which after synthesis contains brushite and HAP phases, γ -CPP forms, which is followed by β -CPP, which interacts with HAP and β -TSP forms. In addition, β -TCP also forms from hydrated TCP Ca₃(PO₄)₂ · *y*H₂O. After firing at temperature at least 800°C a biphase powder or ceramic material containing the phases β -TCP and β -CPP can be obtained from powder syn-



Fig. 5. XPA data for P-TCP/CC after firing at different temperatures: g) HAP (PDF card No. 9-432); L) CaO (PDF card No. 27-1497).

thesized from 1 M water solution of calcium acetate and 0.6 M water solution of ammonium hydrogen phosphate.

Comparing the XPA data for the powders P-TCP and P-CC/TCP makes it possible to draw the conclusion that the calcium carbonate present in amorphous P-CC/TCP powder interacts with the formed calcium phosphate with ratio Ca/P = 1 (CaHPO₄/Ca₂P₂O₇) and HAP forms, probably, via the reaction

$$6CaHPO_4 + 4CaCO_3 = Ca_{10}(PO_4)_6(OH)_2 + 4CO_2 + 2H_2O.$$
 (13)

The occurrence of the reaction (13) explains the noticeable step in the curve of the mass variation versus temperature near 400°C for P-CC/TCP powder (see Fig. 3). For this reason, after firing calcium oxide is also present in the P-CC/TCP powder. The formation of calcium oxide in the P-CC/TCP powder could be due to the occurrence of the reactions examined for the powder P-CC upon heating.

The XPA data for powders after annealing agree with the thermal analysis and mass spectroscopy data.

CONCLUSIONS

X-ray amorphous powders were synthesized from a water solution of calcium acetate and mixed-anionic (HPO_4^{2-}/CO_3^{2-}) water solution, including ammonium hydrogen phosphate and ammonium carbonate, at room temperature without pH regulation. Powder containing brushite CaHPO₄ · 2H₂O and hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ was synthesized from calcium acetate and ammonium hydrophosphate. Powder containing calcium carbonate CaCO₃ of two modifications — calcite and faterite — was synthesized from calcium acetate and ammonium carbonate.



Fig. 6. X-ray diffraction pattern of P-TCP data after firing at different temperatures: g) $Ca_5(PO_4)_6(OH)_2$ (PDF card No. 9-432) or $Ca_3(PO_4)_2 \cdot xH_2O$ (PDF card No. 18-303); γ) γ- $Ca_2P_2O_7$ (PDF card No. 17-499); β) β- $Ca_2P_2O_7$ (PDF card No. 9-346); w) β- $Ca_3(PO_4)_2$ (PDF card No. 9-169).

Powders synthesized from mixed-anionic solutions can be recommended for fabricating composite materials with a polymer matrix or for obtaining ceramic containing the phases tricalcium phosphate and calcite at firing temperature not exceeding 600°C.

The powder synthesized from calcium acetate and ammonium hydrophosphate can be used to obtain biphasic ceramic β -Ca₃(PO₄)₂/ β -Ca₂P₂O₇ and firing temperature in the interval 800 – 1100°C. The synthesized calcium carbonate powder can be recommended for obtaining biocompatible calcium phosphate ceramic as one of the components of the initial powder mixture.

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