

BIOMATERIALS

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CERAMICS BASED ON HYDROXYAPATITE SYNTHESIZED FROM CALCIUM CHLORIDE AND POTASSIUM HYDROPHOSPHATE

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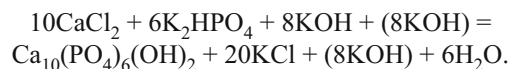
The properties of powdered hydroxyapatite (HAP) synthesized from calcium chloride and potassium hydrophosphate are investigated. The powder material consists of HAP and an secondary product of the reaction, which is predominately KCl. After sintering at a temperature above 800°C, the ceramic contains HAP as the main phase as well as CaO and chloroapatite. The maximum density (2.2 g/cm³) and the smallest grain size (200–500 nm) are observed in material after sintering at 700°C.

The development of a technology of materials for bone implants based on calcium phosphates is predicated on the study of the relation between the conditions under which the powders are synthesized and the processes occurring during the formation of the microstructure of the ceramic. Calcium hydroxyapatite (HAP) is an analogue of the mineral component of mammalian bone tissue. To obtain a ceramic based on HAP, it is necessary to use powder which is activated to sinter. Such powders can be synthesized by co-precipitation from water solutions of calcium salts and soluble phosphates, for example, from Ca(NO₃)₂ and (NH₄)₂HPO₄, CaCl₂, and Na₂HPO₄ or Ca(CH₃COO)₂ and K₂HPO₄ [1–3]. When water solutions of the indicated salts interact the result is the formation of the insoluble target calcium phosphate and a secondary product of the reaction.

In most works studying the sintering of HAP, powders are synthesized from Ca(NO₃)₂ and (NH₄)₂HPO₄, since in this case the secondary product is ammonium nitrate, which is removed on heating to the onset of sintering [1, 4]. Biocompatible ancillary products such as potassium or sodium chloride or acetate can have a large effect on the formation of the microstructure of ceramic based on calcium phosphates. The amount of the adsorbed ancillary product from the synthesis of powders by co-precipitation from water solutions reaches 35 wt.% [1, 2]. The melting temperature of the potassium or sodium chlorides as well as acetates or carbonates formed from them does not exceed 900°C. Consequently, these salts can play the role of additives which promote sintering by the liquid phase method.

A number of salts were studied as sintering additives [5]. The effect of the salts as sintering additives was investigated using a 5% addition after calcination at 1000 and 1100°C. It was found that the presence of potassium chloride does not give rise to decomposition of HAP, accompanied by the formation of Ca₃(PO₄)₂ or CaO. The processes occurring during the production of the ceramic based on the HAP powder synthesized from CaCl₂ and K₂HPO₄ and containing the secondary product of the reaction have not been studied before. Consequently, the objective of the present work was to investigate such processes.

The HAP powder was synthesized in accordance with the formal reaction



One liter of a 1 M water solution of calcium chloride was added by drops to 1 liter of a 0.6 M water solution of potassium hydrophosphate containing KOH. The reaction was conducted at 60°C with constant mixing. Synthesis was conducted at pH = 8–9. The pH level was maintained by adding a two-fold KOH excess relative to the amount calculated from the equation of the reaction. The precipitate obtained was allowed to sit in the mother liquor for 30 min. Then, the precipitate was separated from the mother liquor and dried in a thin layer over a period of 48 h. The dried product was disaggregated in a planetary mill in 5 min. The milling bodies : powder : acetone ratios were 5 : 1 : 1. Samples with dimensions 10 × 5 × 3 mm were pressed in a steel mold under specific pressure 100 MPa. The samples were calcined in the

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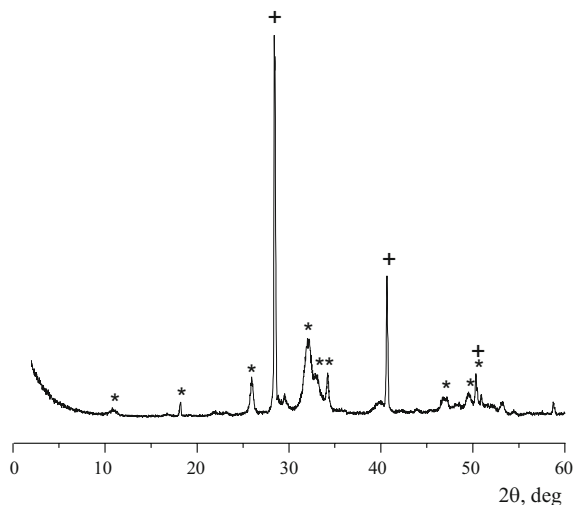


Fig. 1. XPA of HAP powder after synthesis (Rigaku D/Max-2500 diffractometer, $\text{CuK}\alpha$): *) HAP; +) KCl.

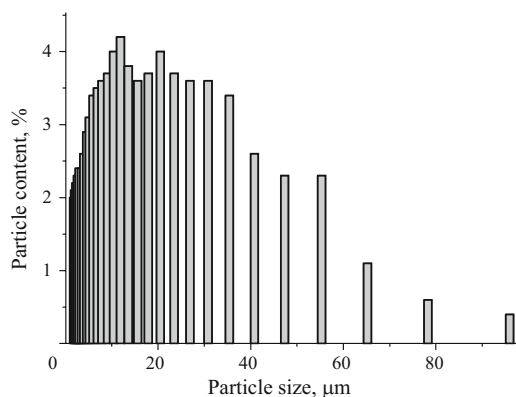


Fig. 2. Particle size distribution after synthesis and disaggregation (determined by dynamic light scattering in the Fritch Analysette-22 apparatus).

temperature interval 500–1200°C with heating rate 5 K/min and a holding at the final temperature 6 h.

Comparing the mass of the powder after synthesis with the mass calculated according to the reaction gave the amount of adsorbed secondary product to be approximately 36%. The mother solution contained KCl, in accordance to the reaction, and KOH, in accordance with the conditions of synthesis. The alkali solution interacts with carbon dioxide in air, forming potassium carbonate. Thus, the expected qualitative composition of the secondary product is KCl, KOH, and K_2CO_3 . X-ray phase analysis shows that after synthesis the powder contained HAP and potassium chloride (Fig. 1). The absence of peaks corresponding to KOH and K_2CO_3 could be due to the fact that the method is too insensitive to determine these substances in the quantities present in the powder.

The bulk density of the powder was about 0.4 g/cm³. According to the particle size distribution data (Fig. 2) the

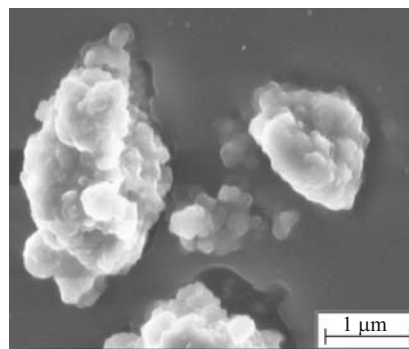


Fig. 3. Photomicrograph of HAP powder after synthesis and disaggregation (LEO SUPRA 50VP, Carl Zeiss, Germany, scanning electron microscope).

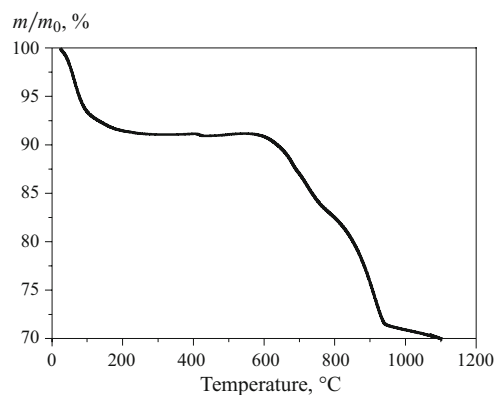


Fig. 4. Mass of HAP powder containing an ancillary product of the reaction versus temperature. The heating rate is 5 K/min (“Perkin Elmer Pyris” thermoanalyzer, Perkin Elmer USA).

maximum size of the particle aggregates did not exceed 100 μm. The most likely size of the aggregates is 10–30 μm.

Electron-microscope photographs (Fig. 3) of the powder after synthesis show that the size of the aggregates is 2–4 μm, and the primary particles comprising the aggregates are 100–200 nm in size.

According to thermal analysis (Fig. 4), the total mass losses on heating to 1150°C are about 30%. Loss of adsorbed water and acetone occurs up to 200°C. No mass change was observed in the temperature interval 200–600°C. The mass losses in the temperature interval 600–950°C could be due to the formation of new phases, for example, chlorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ (Cl-HAP). According to published data, the melting temperature of KCl is 772°C. After this temperature a transition is observed to occur from $\text{KCl}(\text{liq})$ into $\text{KCl}(\text{g})$. A kink is observed in the mass loss curve at this temperature. After 950°C the mass losses are of linear nature, which can be seen with evaporation of chlorides or decomposition of HAP or carbonate-hydroxyapatite (CHAP).

According to the XPA data, after calcination for 6 h up to 800°C, only HAP and KCl were observed in the material;

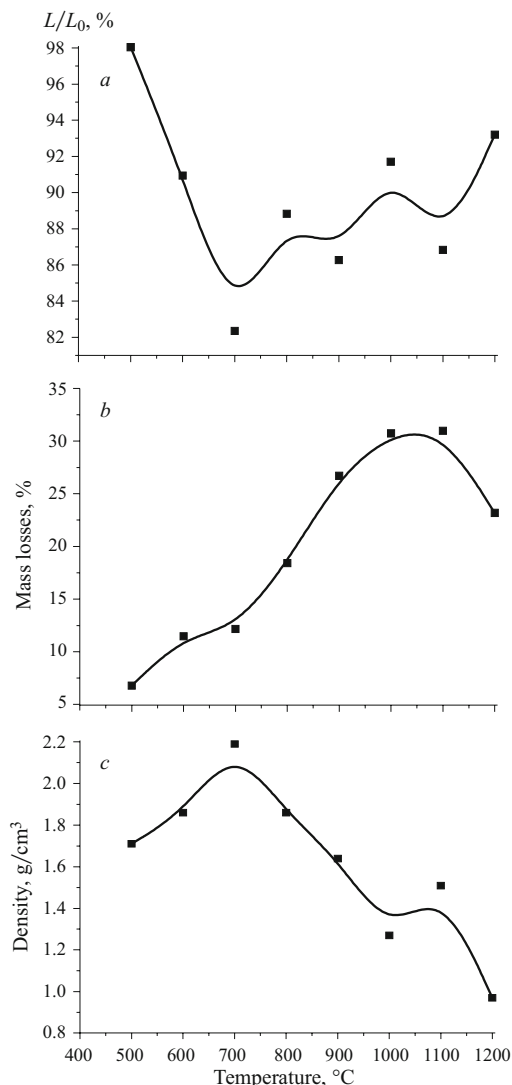
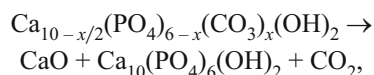
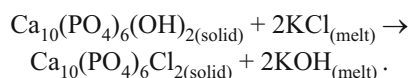


Fig. 5. Variation of the linear dimensions (a), mass (b), and density (c) of a HAP sample containing a secondary product of the reaction, after calcination for 6 h at different temperatures.

above 800°C — HAP, CaO, and chlorapatite. The presence of CaO, which can form, for example, in accordance with the reaction

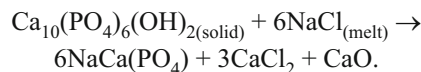


confirms the presence of carbonates or carbonate-HAP in the initial powder. In [6] it is indicated that chlorapatite (Cl-HAP) can form from HAP and KCl melt according to the reaction



It should be noted that according to the RF patent No. 2007109482 and the data of [7], the interaction of HAP

and NaCl results in the formation of double sodium calcium phosphate — β -renanite NaCaPO_4 :



Double potassium calcium phosphate does not form in the case of KCl, possibly because of the larger ionic radius of K^+ .

The density of the compact was 1.6 g/cm³, which corresponds to 40% of the density of HAP (3.16 g/cm³).

According to dilatometric studies, the shrinkage of the sample after cooling was about 12%. A small amount of shrinkage due to the removal of the adsorbed water and acetone and not exceeding 1% was observed up to 200°C. No changes of length were observed up to 400°C. The shrinkage at 550°C was 1.5%. A substantial decrease of the linear dimensions of the sample was recorded in the temperature interval 550 – 700°C; the shrinkage at 700°C was 6%. The dimensions of the sample start to decrease. A small expansion of the sample was observed in the interval 700 – 750°C; this could be due to the removal of volatile products. A further change of the length of the sample occurred above 750°C; this could be due to the formation of melt and the action of capillary forces.

The spreading of NaCl melt on a HAP surface was studied as a way to simulate the interaction of HAP with alkali halide melts. A drop of melt formed on a wire loop was transferred onto the surface of a HAP pellet at the melting temperature of the alkali halide. The spreading process was recorded with a digital video camera at 25 frames per second. The melt spread completely in < 0.1 sec, which attests to the high adhesion of the alkali halide – HAP — at the boundary of the melt. The complete spreading observed in the system promotes effective permeation of the pressed HAP samples with formation of the alkali halide melt.

In the investigation of the length change of the samples by the isothermal holding method (Fig. 5a) the maximum shrinkage (24%) was observed at 700°C. The temperature dependence of the sample length is nonmonotonic with a general tendency to increase, possibly because of competing processes of melt formation and thermal decomposition or evaporation of the components of the powder mixture. As temperature increases, the mass of the samples decreases, the maximum change (32%) being reached at 1000 – 1100°C (Fig. 5b). The density of the samples at 700°C increases to 2.2 g/cm³ or 72% of the relative density of the HAP (3.16 g/cm³). A further increase of the calcination temperature results in a decrease of the density (Fig. 5c). The minimum density determined at 1200°C was 0.95 g/cm³, or 30% of the relative of HAP.

The microstructure of the samples of a ceramic calcined at different temperatures is shown in Fig. 6. After calcination at 700°C the grains, which have a rounded shape, are 200 – 500 nm in size. For smaller increases, larger crystals

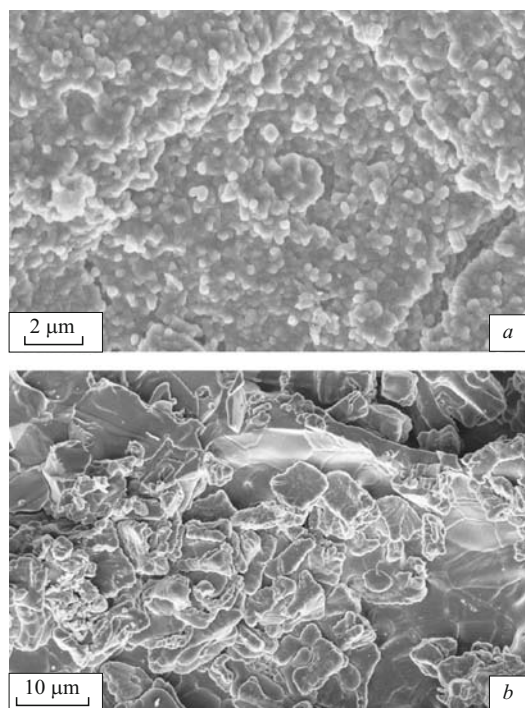


Fig. 6. Microstructure of ceramic after calcination at temperature 700°C (a) and 1200°C (b).

(probably KCl) can be observed; these crystals formed as a result of crystallization from melt on cooling. After calcination at 1200°C the microstructure is nonuniform. Pores (100 – 150 μm in size) as well as sintered sections with grain size up to 10 μm are present in the material. The size of the grains in the ceramic based on powder containing an easily removed secondary product was 1 – 3 μm after calcination at 1200°C [1]. The large grain size in the ceramic based on powder containing KCl is the result of recrystallization through the liquid phase.

In summary, various chemical and physical – chemical processes occur in the powder material consisting of HAP and secondary product of the reaction predominately containing KCl: thermal decomposition of the components, formation of new phases, melting, evaporation, recrystallization, and sintering. The CaO forming after calcination at

temperature above 800°C is an undesirable phase of the material for bone implants. Cl-HAP is a biocompatible phase and its amount is negligible. A mixture of HAP and the secondary product of the reaction, containing predominately KCl, cannot be regarded as an initial mix for obtaining a ceramic composite material. However, it should be noted that the formation of HAP-based ceramic with a uniform microstructure and grain size less than 1 μm is possible because of the low formation temperature and surface activity of the melt, whose main component is KCl.

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