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DISPERSE SYSTEMS IN CALCIUM HYDROXYAPATITE CERAMICS TECHNOLOGY

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Hydroxyapatite ceramics technology is examined. Disperse systems and their evolution in each process state are determined. Data from gravimetric and dilatometric analysis and scanning microscopy are reported. The aggregate distribution by size in the initial powder and the grain distribution by size in the sintered ceramic are compared. The inheritance of the properties of the initial powders by the structure characteristic of ceramic materials is demonstrated.

The evolution of modern materials science is related to the creation of new materials with unique properties. Production of such materials implies improvement of existing technologies or creation of new schemes. Considering different materials as disperse systems (DS) with defined properties allows applying the general principles of the existence of DS in technologies for different ceramic materials. An examination of preparation of the initial materials [1], molding [2, 3], and high-temperature treatment [4, 5] in materials technology with consideration of the existence of disperse system and surface phenomena makes it possible to perfect existing technologies [6] and develop new materials [7], including nanoceramics [8, 9].

The basic stages in fabrication of ceramics are preparation of the initial components and molding and firing [10] or, in other words, preparation of the initial material in the form of powder or slip and consolidation [11]. Without any doubt, according to many determinations in ceramics, this concerns transforming the material from a granulated state to a monolithic state. Technology for ceramics, like many other high-melting nonmetallic and silicate materials, is a set of processes of creation, evolution, and in some cases destruction of DS consisting of disperse phase and dispersion medium. The most important distinctive features of DS are the continuity of the dispersion medium, state of comminution of the disperse phase, and presence of phase boundaries, which is due to their heterogeneity [12, 13].

The classification of disperse systems by the aggregate state of the substance of the disperse phase and dispersion medium is the most popular. According to this classification, most existing ceramic materials can be assigned to solid-in-solid (S/S), gas-in-solid (G/S), or solid, gas-in-solid (S, G/S) disperse systems. The real materials are unconditionally

more complex DS and can contain more than one disperse phase, as well as more than one dispersion medium. With respect to all formal features, many ceramic materials that are DS (S/S, G/S, or S, G/S) can be assigned to composite materials (CM) formed by bulk combination of chemically heterogeneous components with different physical and mechanical properties with a distinct interface between them. CM are characterized by properties that none of their components individually have [14, 15]. In other words, such composite materials as DS can be polymatrix or polyfilled.

According to the traditional approach to composite materials, one of the components, continuous in volume, is the matrix — the basic phase and basic substance containing continuous additional components separated in the volume. In the evolution of materials science, a deliberate step was taken to even out the number of phases and to obtain materials with interpenetrating continuous phases in which the quantitative difference between the basic and nonbasic phases disappeared [16]. This approach is very important for bone bioimplants based on calcium phosphates [17, 18]. Bone itself can be considered as a complex CM with interpenetrating continuous phases. It is not possible to say which structural element of bone is basic and which is not. Moreover, bone implants must have a porous structure for intergrowth and attachment of bone, and the porous material can be considered as the simplest example of CM in which one of the phases is air [19].

We examined ceramics technology with respect to the evolution of DS on the example of a calcium hydroxyapatite (HAP) ceramic. Use of this material for preparation of bone implants is predetermined by the fact that its composition is identical to the composition of the inorganic constituent of mammalian bone tissue.

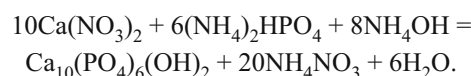
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The stages of fine industrial ceramics technology and the characteristics of each stage with consideration of the existence of DS are reported below.

Process stage, product	Description of disperse system and processes
(NH ₄) ₂ HPO ₄ and Ca(NO ₃) ₂ · 4H ₂ O salt powders	DS (S/G)
Preparation of homogeneous aqueous solutions	DS (S/L)
Solution	Disappearance of DS
Synthesis of highly disperse HAP, Ca ₁₀ (PO ₄) ₆ (OH) ₂ powder from homogeneous solutions	Formation of DS (S/L) using the condensation method. Occurrence of aggregation
Separation of HAP sediment from mother liquor (solution of NH ₄ NO ₃)	Change in characteristics of DS — increase in content of solid phase, then formation of DS (S, G/L). Occurrence of aggregation
Drying of sediment	Transformation of preceding DS (S, G/L) into S (S, L/G), and then into DS (S/G). Decrease in surface energy due to aggregation, which is unavoidable, undesirable, and uncontrollable
Disaggregation of dried powder in acetone	Formation of DS (S/L). Changes in the quality of the DS (surface and particle size of disperse phase — destruction of aggregates of particles)
Drying after disaggregation of HAP powder – NH ₄ NO ₃	Transformation of DS (S/L) into DS (S, L/G), then into DS (S/G). Decrease in surface energy due to aggregation from different initial conditions than in the occurrence of aggregation in the preceding stages
Formation of a sample or article in molding; NH ₄ NO ₃ plays the role of a temporary process binder	Formation of bound-disperse DS (S/G)
Firing:	
compacting due to melting of NH ₄ NO ₃	DS (S/G) into DS (L, S/G), then into DS (G, S/L) and in the limiting case into DS (S/L)
elimination of NH ₄ NO ₃ in heating	Transformation of previous DS into DS (S/G)
Sintering:	Evolution (change) of DS:
initial stage	DS (S/G)
development of sintering due to diffusion in solid-phase sintering of HAP	DS (S/G, then G/S)
concluding stage*	Formation of rigidly bound DS (S _{grains} /S _{grain boundaries}), a conglomerate of fine polycrystalline particles
Cooling	Fixation of the desired state of DS (S/S) — phase structure and grain size

* Further heating at high temperature can degrade the polycrystalline structure of the ceramic due to recrystallization and in the limiting case causes formation of a single crystal, i.e., destruction of the given DS.

The reaction of calcium nitrate and ammonium hydrophosphate at pH = 9 was used for synthesis of HAP [20]:



Precipitation of sediment in the given case is not only a sign of the occurrence of the chemical reaction, but also the formation of DS (S/L) by the condensation method, used to obtain the initial powders for materials with a fine microstructure. The nonequilibrium conditions of formation of sediment favors obtaining powder with a small particle size, large specific surface area, and high defectiveness of the individual crystal most active in sintering. From the time of formation of HAP particles 30 – 60 nm in size, calculated with XPA data on peak broadening with the Debye – Scherrer equation ($hkl = 0.02$, $d = 3.44 \text{ \AA}$), DS (S/L), in which the liquid is represented by a solution of NH₄NO₃, an attempt is made to reduce the excess surface energy by aggregation. To preserve the high sintering activity of the powder, the duration of aging of the sediment in the mother liquor, which increases the crystallinity of HAP and growth of primary crystals according to a dissolution – crystallization mechanism, was reduced to 30 – 40 min. The sediment content (solid phase) in the mother liquor was 2.6%.

Subsequent separation of the sediment from the mother liquor changes the properties of the DS (S/L), accompanied by an increase in the fractionated phase to 30 – 40%. In some cases, this highly concentrated suspension can be used for molding to overcome aggregation, unavoidable in drying and compression molding. Drying of the sediment involves transformation of DS (S/L → S, G/L → S/G), and transition of DS from the free-disperse to the bound-disperse state. After drying, the powder layer consists of relatively large and strong fragments formed as a result of shrinkage and cracking of the layer of the highly concentrated suspension. In the powder examined, after drying, the solid phase was represented by HAP and ammonium nitrate adsorbed on the surface of the HAP particles (Fig. 1).

Subsequent disaggregation, preferably in a liquid with a low boiling point, allows breaking up primary aggregates and obtaining a homogeneous powder. In disaggregation of HAP – NH₄NO₃ powder in acetone, this is a DS (S/L). After drying of the HAP – NH₄NO₃ powder, it is a DS (S/G). The disaggregated powder has fluidity and homogeneity, which is inherited by the ceramic material from stage to stage. The bulk density of this powder was 0.36 g/cm³. The distribution of the HAP particles by size in the disaggregated powder obtained by laser diffraction (FRITCSH Analisette, Germany) is shown in Fig. 2. The size of the aggregates is much larger than the size of the individual particles. A photomicrograph of HAP powder after disaggregation is shown in Fig. 3a (the photomicrographs of the ceramic were made on a Zeiss LEO SUPRA-50VP scanning electron microscope, Germany).

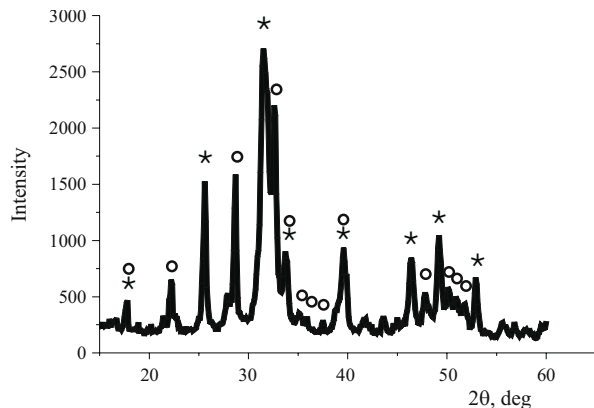


Fig. 1. XPA of HAP after synthesis: ☆) HAP; ○) NH_4NO_3 .

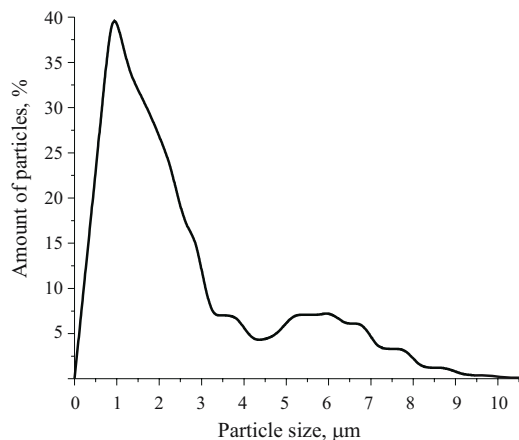


Fig. 2. Particle distribution by size.

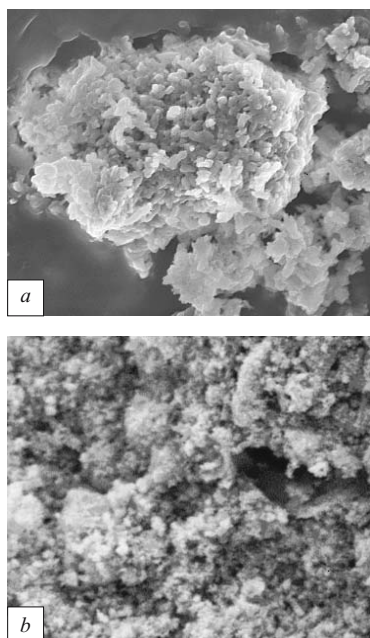


Fig. 3. Photomicrographs of HAP powder (*a*) and molded pieces (*b*, molding pressure of 100 MPa).

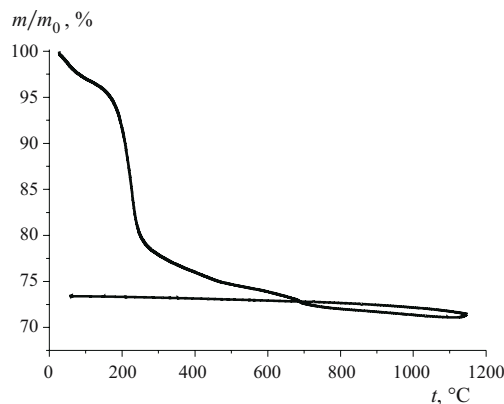


Fig. 4. Change in the mass of the powder after synthesis and disaggregation as a function of temperature at a heating/cooling rate of 10 K/min (Perkin Elmer Pyris thermal analyzer, USA).

During preparation of the material from stage to stage, the system is usually transformed from free-disperse to bound-disperse. This situation is characteristic of all materials obtained by powder technologies (ceramics, glass, and cements). Photomicrography of molded pieces made from the synthesized HAP powder containing ammonium nitrate are shown in Fig. 3*b*. The molded semiproduct is a bound-disperse DS (S/G), only with a lower content of gas phase than in the powder. In the given case, the density of the molded piece, which was approximately 35–40% (relative to the theoretical density of HAP of 3.16 g/cm^3), could be a characteristic of DS. In preparing ceramics from HAP, an additional temporary process binder (TPB) was not used in the present study. The ammonium nitrate, which caused compacting of the molded pieces, acted as TPB.

Further compacting and strengthening of the HAP ceramic took place during firing. Melting of the ammonium nitrate in the molded piece in the 150–250°C temperature range forms DS (S, G → L, S/G → G, S/L, and in the limiting case, in DS — S/L). Compacting of the semiproduct and regrouping of HAP particles take place due to wetting–spreading processes and the effect of capillary forces. At temperatures above 200°C, the ammonium nitrate begins to decompose and is removed from the semiproduct (Fig. 4). The subsequent change in the properties of DS (S/G) as a result of compacting is reflected in the dilatometric curve (Fig. 5). Heating to 500°C causes transformation of DS (S/L or S, G/L → S/G). Point contacts are formed, which corresponds to the first stage of sintering — baking.

An important change in the linear dimensions of HAP is observed at temperatures above 600°C and is due to elimination of pores and compacting of the semiproduct (see Fig. 5). The shrinkage rate maximum is located in the 850–950°C temperature range. Heating in the 500–900°C range causes transformation of the DS (SG → G/S). A system is formed with continuous and interpenetrating solid and gas phases, which corresponds to the second stage of sintering. A photo-

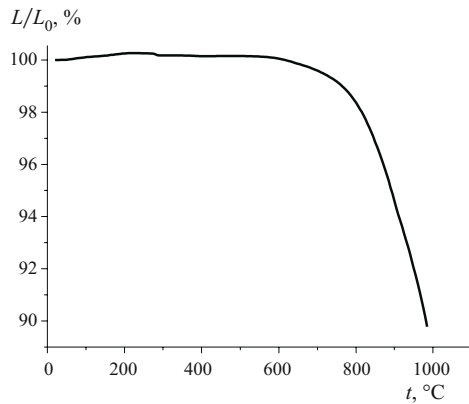


Fig. 5. Change in the linear dimensions of HAP molded piece in heating at the rate of 10 K/min (DIL 402 PC dilatometer, NETSCH, Germany).

micrograph of the HAP ceramic after firing at a temperature of 1100°C with isothermal holding for 6 h is shown in Fig. 6a. After such heat treatment, the ceramic is a DS (G/S), i.e., undersintered material characterized by intercrystalline porosity.

After firing at 1200°C with isothermal holding for 6 h, the material contained no pores, had a homogeneous microstructure (Fig. 6b) with a most probable grain size of 1 μm , and was DS ($S_{\text{grains}}/S_{\text{grain boundaries}}$). One of the examples of description of DS is the description of the microstructure of a material.

The grain size distribution of the HAP ceramic obtained was calculated with data from scanning electron microscopy in the semiautomatic mode using AnalySIS[®] software with four to seven microphotographs from macroscopically different sections of the sample, and the minimum number of grains was 900). The most probably grain size of 1 μm corresponds to the most probable size of the aggregates in the initial powder. These data illustrate the principle of structure inheritance, well-known in materials science.

Distinguishing the DS in each stage of ceramics technology is a convenient methodological approach in modern materials science which allows optimizing production of materials with the desired microstructure and properties by applying the principles of colloid chemistry and surface phenomena. Surface-active, high- or low-molecular-weight substances can be used in the stage of synthesis and disaggregation of inorganic powder; in reacting with the surface of the newly formed crystal, they block its further growth and aggregation with other crystals [21]. As a function of the concentration of the high-molecular-weight compound (PVA, for example) in the synthesis zone, it can bind together the primary crystals, ensuring controllable aggregation of the powder [22].

Incorporation of additives that form eutectic melts in ceramics is considered a reliable method of controlling sintering. This method can also be examined with respect to the change in the surface tension of the basic crystalline phase

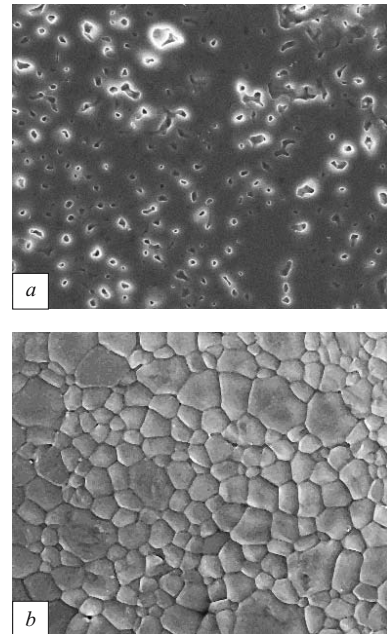


Fig. 6. Photomicrographs of HAP ceramic after firing at temperatures of 1100°C (a) and 1200°C (b) with holding for 6 h.

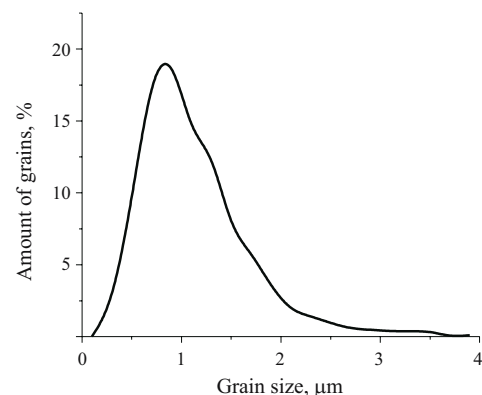


Fig. 7. Grain distribution by size in HAP ceramic.

due to wetting and spreading of a melt with surface-active properties [23]. The change in the surface properties of the disperse phase in using surfactants during synthesis and sintering can be a reliable tool for controlling the microstructure of ceramic materials.

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