

## Strengthening of Bone Cements Based on Tribasic Calcium Phosphate by Calcium Carbonate Granules

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**Abstract**—The influence of the size and number of calcium carbonate granules introduced to the cement matrix of an alpha-tribasic calcium phosphate–orthophosphoric acid solution on the compression strength of the composite material was studied. A potential increase in strength by a factor of six by the introduction of an optimal amount of granules into the matrix was determined.

**Keywords:** calcium phosphates, calcium carbonate, bone cements, dispersion strengthening

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### INTRODUCTION

Bone cements based on calcium phosphates were developed and applied in clinical practice for replacement of the damaged bone tissue [1–4]. Low strength is the drawback of such cements. One of the promising trends is reinforcement of the cements by ceramic granules [4, 5]. Introduction of granules may solve not only the problem of strengthening but also the problem of the bioresorption kinetics depending on porosity, solubility, and other characteristics of the granules. Applicability of calcium carbonate (CC) granules for the above purposes is of interest. It is known that formation of bone tissue based on CC is similar to the hydroxyapatite process [6]. The presence of large pores in granules contributes to osteosynthesis.

Cement pastes may be obtained by mixing of powders of calcium phosphates and CC with the formation of the carbonate-containing apatite phases in the products of setting and hardening. The prospect of application of cements based on tricalcium phosphates (TCP) of alpha modification with the introduced calcium carbonate phases is shown. Carbonate-containing hydroxyapatite has increased osteoconduction potential [8]. Processes that may occur in TCP-based cements with large CC granules as the reinforcing phase were not studied earlier. Investigation of the influence of the size and amount of CC granules on the strength of the calcium phosphate cement was the target of this work.

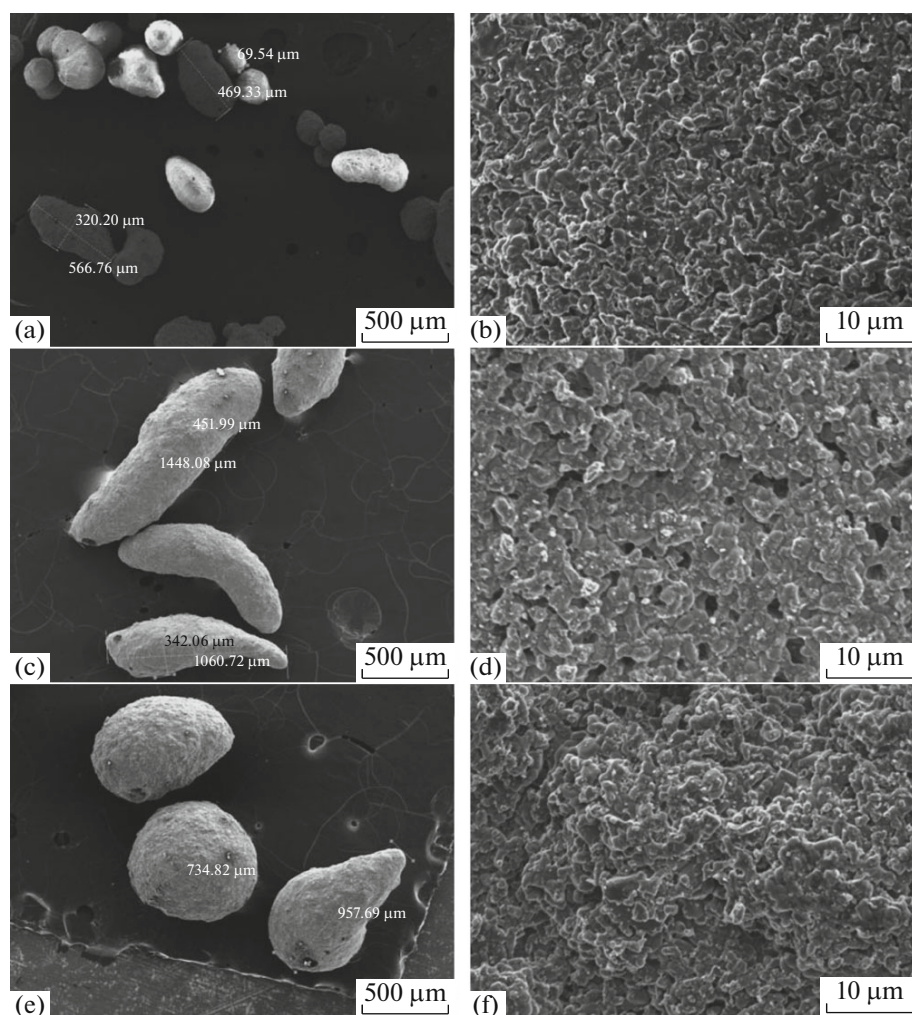
### EXPERIMENTAL

The CC granules were obtained by the suspension technology based on the effect of immiscible fluids [9, 10]. Sintering additives containing lithium oxide in the

amount of 0.1–0.2 wt % were introduced to the CC powder to reduce the sintering temperature of the granules. The powder was mixed with a gelatin solution to obtain a stiff slurry and was gradually introduced into vegetable oil with constant stirring. Rounded particles (granules) were formed from the slurry in the process of stirring; the size of granules depended on the mixer rotation rate. The granules were separated from the oil, washed, and dried. Then they were sintered in air at temperatures from 540 to 560°C. Separation of granules by fractions was carried out by capronic sieve screening with the mesh size of 300, 470, and 1100 μm. As a result, three series of granules of not less than 300, 300–470, and 470–1100 μm were obtained.

Granules in the amount of 20, 40, 60, or 80 wt % were introduced into the TCP powder. The cement was dissolved by an acid magnesium phosphate solution with pH 2–3.

The obtained mass was mixed by a putty knife on a glass slide. After mixing, within 2–4 min, the thick creamy mass was put into Teflon molds for formation of cylindrical samples 8 mm in diameter and 10 mm in height. After hardening for 3 days, the samples were tested for strength with the help of an Instron 5581 device at the traverse speed of 0.5 mm/min. The load measurement error was 0.1%. Three samples were tested for each composition. The spread of the measured strength values did not exceed 20%. The density of the samples was determined by weighing. X-ray phase analysis (XPA) was carried out with a Shimadzu XRD-6000 X-ray diffraction meter with phase identification on the basis of the standard JSPDS card catalog. Images of the fractured surface were obtained with a Tescan Vega scanning electron microscope (SEM).



**Fig. 1.** Microphotograph of the CC granules: (a, b) small granules, less than 300  $\mu\text{m}$ ; (c, d) average granules, 300–470  $\mu\text{m}$ ; (e, f) large granules, 470–110  $\mu\text{m}$ .

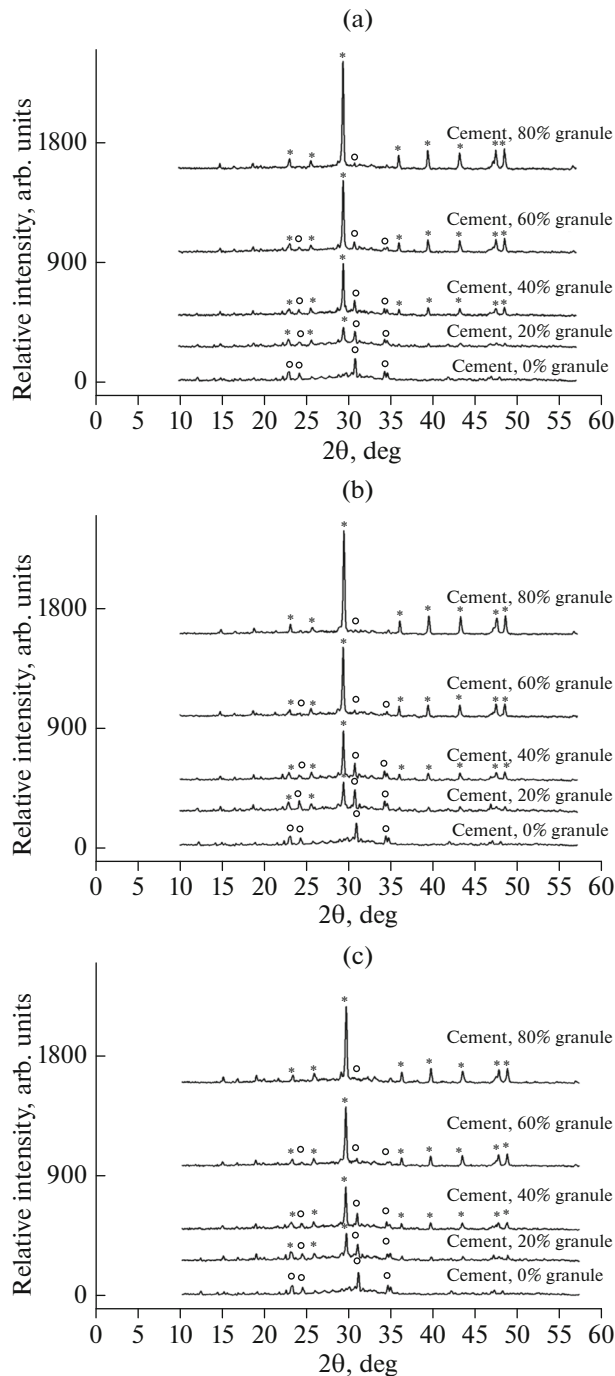
## RESULTS AND DISCUSSION

Sintered granules by the phase composition corresponded to dense calcium (100%); other polymorphic CC modifications, as well as calcium oxide, were not revealed. The latter was due to the low sintering temperature, lower as compared to the temperature of initiation of CC degradation. The size of calcite crystals in granules did not exceed 1–3  $\mu\text{m}$ . SEM images of granules and their surface are given in the Fig. 1. Granules up to 300  $\mu\text{m}$  have a different shape: from spherical, mainly for granules with size of 150–200  $\mu\text{m}$ , to ellipsoid, with the length of 600  $\mu\text{m}$  along the larger ellipsoid axis. Pores in granules are 10–20  $\mu\text{m}$ ; branching systems of pores are not present. Larger granules have mainly an ellipsoid or drop shape and contain pores with size up to 100  $\mu\text{m}$  as well as micropores with size up to 5  $\mu\text{m}$ .

Hardened cement material reinforced with granules contained two crystal phase components: TCP and CC; also, they contained the X-ray amorphous

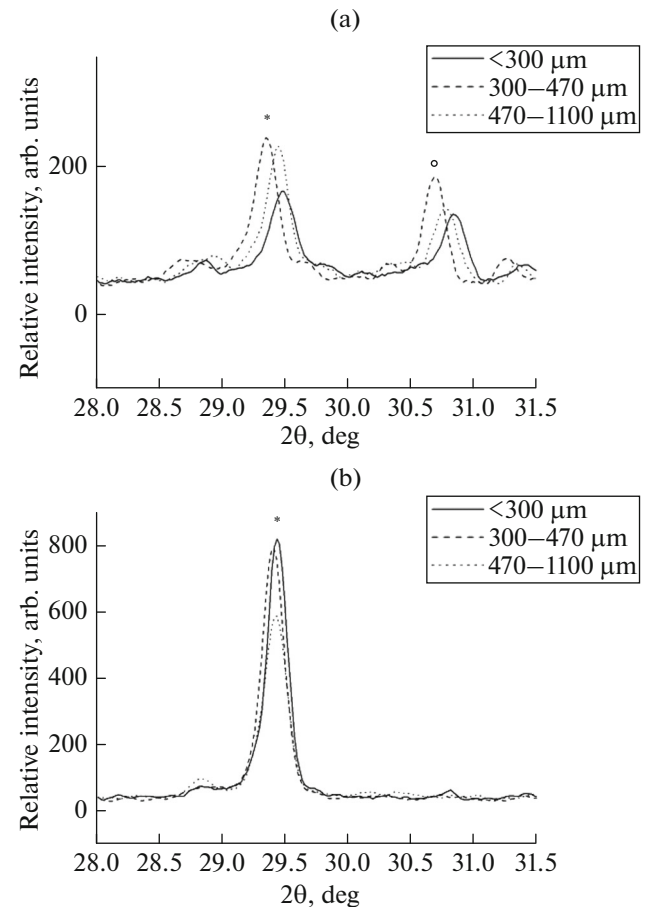
phase. The X-ray diffraction patterns of the cement samples are shown in Fig. 2. The intensities of the main peaks of the crystal phases change in accordance with the quantitative content of granules. The intensity of the CC peak (Fig. 3) decreases with the increase in the size of granules, which may be explained by the level of interaction between CC, TCP, and gauging liquid in the process of the cement setting. Dicalcium phosphate may be formed during CC interaction with the orthophosphoric acid of the gauging liquid. But XPA did not find this phase in the ultimate product. It is possible that the crystal hydrates of the magnesium-containing components harden the cement matrix.

The compression strength rises sharply after introduction of granules into the cement matrix (table). This is explained by the mechanisms of dispersive strengthening connected with envelopment of granules by a crack, which are harder as compared to the cement matrix and have higher adhesion at the interface, and with formation of residual stress fields, as in



**Fig. 2.** X-ray diffraction pattern of cements containing granules of the following size: (a) less than 300  $\mu\text{m}$ ; (b) 300–470  $\mu\text{m}$ ; (c) 470–1100  $\mu\text{m}$ ; (\*—CC peaks; o—TCP peaks).

concrete. The highest strength is achieved in materials containing 20–60 wt % of granules with size of 300–470  $\mu\text{m}$ . The strength values of such materials exceed the strength of the cement matrix by approximately a factor of six. Strength reduction at higher content of granules is due to a shortage of the cement solution,



**Fig. 3.** Influence of the granules size on the phase ratio containing cement: (a) 20 wt %; (b) 80 wt % CC granules (\*—CC peaks; o—TCP peaks).

which leads to porosity at the boundaries of granules. The density of such cements was 1.7  $\text{g}/\text{cm}^3$ , which was considerably less than the density of the material (2  $\text{g}/\text{cm}^3$ ) with 20–40% granules. SEM studies showed that the most advanced microstructure of the regions of boundaries between granules and cement matrix is characteristic of the materials reinforced by granules of average size. This may be the reason for the difference in strength for cements reinforced with granules of difference size.

## CONCLUSIONS

Thus, introduction of ceramic CC granules into TCP based cements with the gauging liquid—acid magnesium phosphate—results in considerable strengthening of the cement stone. The dependence of the strength on the composition of granules is nonmonotonic. Reinforcement with granules 300–470  $\mu\text{m}$  in size in the amount of 20–40 wt % results in an increase in the strength of the material by a factor of six as compared to the strength of the cement matrix. Materials may be the base for the development of cements

Influence of the size and quality of granules on the cement compression strength (MPa)

Content of granules, wt %	Strength, MPa		
	Size of granules <300 μm	Size of granules 300–470 μm	Size of granules 470–1100 μm
0	6	6	6
20	25	32	19
40	18	39	18
60	15	34	17
80	17	26	6

intended for medical applications for plastics of damaged bone tissue.

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