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Powder Mixtures Based on Calcium Hydroxyapatite and Sodium Salts

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Abstract—Powder mixtures based on calcium hydroxyapatite (HAP) and sodium salts in the amount corresponding to 25 mol % of Na_2O in the $Na_2O–CaO–P_2O_5$ system were studied by isothermal exposures in the range of 600—1200°C. According to XRD data, the phase composition of the samples of HAP/Na_2CO_3 after calcination included HAP, β-$CaNaPO_4$, and CaO. The phase composition of the ceramic samples from the HAP/Na_2HPO_4 powder mixture after calcination contained the phases of β-$CaNaPO_4$ and $Na_4P_2O_7$. The phase composition of the ceramic samples from the powder mixture of HAP/NaH_2PO_4 after calcination contained $Ca_2P_2O_7$, $Ca_{10}Na(PO_4)_7$, β-$CaNaPO_4$, $CaNa_2P_2O_7$, and $Na_4P_2O_7$. The presence of sodium salts in the amount corresponding to 25 mol % of Na_2O in the $Na_2O–CaO–P_2O_5$ system provided the occurrence of liquid-phase sintering in compact preforms from the studied powder mixtures. However, the presence of the water-soluble salt $Na_4P_2O_7$ in ceramic samples of HAP/Na_2HPO_4 and HAP/NaH_2PO_4 after calcination imposes a restriction on the use of such materials in contact with an aqueous medium. And the presence of CaO in the HAP/Na_2CO_3 samples excludes the use of such materials as bone implants.

Keywords: bioceramics, hydroxyapatite, sodium carbonate, sodium hydrogen phosphate, sodium dihydrogen phosphate, tricalcium phosphate, rhenanite, double sodium calcium pyrophosphate, sodium pyrophosphate, Na-substituted tricalcium phosphate

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INTRODUCTION

Ceramic materials based on calcium phosphates are necessary to create bone implants [1]. Powder systems (powder mixtures, suspensions) are used for the production of ceramic materials [2]. The composition of powder mixtures is limited by the chemical composition of the inorganic component of bone tissue, which, in addition to carbonate hydroxyapatite, includes Na, K, Mg, Si, Cl, F, and other ions [3, 4]. Therefore, the following phase diagrams are most often used to design the phase composition of ceramic materials for bone implants and the choice of technological strategy: $CaO–P_2O_5$, $CaO–P_2O_5–CO_3$, $Na_2O–CaO–P_2O_5$, $K_2O–CaO–P_2O_5$, $MgO–CaO–P_2O_5$, $CaO–SiO_2–P_2O_5$, $Na_2O–CaO–SiO_2–P_2O_5$ [5].

Regenerative methods of treatment, involving active interaction of the implant and patient's bone tissue, use porous matrixes from bioresorbable materials [6]. The list of resorbable phases includes $Ca_3(PO_4)_2$, $Ca_2P_2O_7$, $Ca(PO_3)_2$, $Ca_{10}Na(PO_4)_7$, $Ca_{10}K(PO_4)_7$, $CaNaPO_4$, $CaKPO_4$, amorphous phases in the above systems, and other crystalline phases [7].

Technological strategies for production of ceramic materials aimed at saving energy during annealing and the use of available thermal equipment, use liquid-phase sintering and chemical methods of obtaining active powders. The search for sintering additives forming biocompatible bioresorbable phases during annealing is an urgent task.

The proportion of sodium in bone tissue is fairly large. Therefore, sodium salts or sodium-calcium-phosphate glasses are used as sintering additives in the preparation of ceramic materials based on calcium phosphates. Alkali metal phosphates were used as sintering additives in the preparation of ceramics based on hydroxyapatite (HAP) in the amount of 5 wt % [8], and glasses were used in the $Na_2O–CaO–P_2O_5$ system in the amount of 2.5 wt % [9].

The additives of sodium salts or crushed glasses in the $Na_2O–CaO–P_2O_5$ system to the powder systems based on calcium phosphates in the production of ceramics make it possible to lower the annealing temperature, convert sintering to a liquid-phase regime, and create conditions for the formation of biocompatible bioresorbable phases, such as Na-substituted tricalcium phosphate or rhenanite.

The purpose of this work was to study the properties of powder mixtures including HAP and various

Table 1. Marking and composition of the powder mixtures

No.	Marking	Components of powder mixtures			
		$Ca_{10}(PO_4)_6(OH)_2$	Na_2CO_3	$Na_2HPO_4 \cdot 12H_2O$	$NaH_2PO_4 \cdot 2H_2O$
1	HAP	+	–	–	–
2	HAP/Na_2CO_3	+	+	–	–
3	HAP/Na_2HPO_4	+	–	+	–
4	HAP/NaH_2PO_4	+	–	–	+

sodium salts (Na_2CO_3, Na_2HPO_4, NaH_2PO_4). When heated, these salts are transformed into Na_2O, $Na_4P_2O_7$, $NaPO_3$, respectively. The salts were taken in the quantities that ensure the Na_2O content in the Na_2O–CaO–P_2O_5 system corresponding to 25 mol %. Study of powder mixtures based on HAP containing a significant amount of sodium salts will provide information on the processes occurring in the preparation of ceramic materials in the Na_2O–CaO–P_2O_5 system.

EXPERIMENTAL

Powder mixtures were prepared from hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (Riedel-deHaen, Sigma-Aldrich Laborchemikalien, 04238, lot 70080, Germany) and sodium salts Na_2CO_3 (GOST 83-79, chemically pure qualification grade, LabTech, Russia), $Na_2HPO_4 \cdot 12H_2O$ (GOST 4172-76, chemically pure qualification., LabTech, Russia), and $NaH_2PO_4 \cdot 2H_2O$ (GOST 4328-77, chemically pure qualification, LabTech, Russia). When preparing the initial mixtures Na_2CO_3 was used as a precursor of Na_2O; $Na_2HPO_4 \cdot 12H_2O$ was used as a precursor of $Na_4P_2O_7$; $NaH_2PO_4 \cdot 2H_2O$ was used as a precursor of $NaPO_3$ (Table 1).

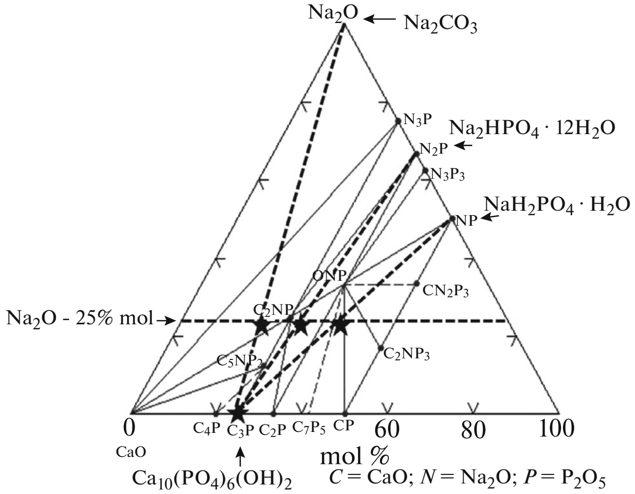


Fig. 1. The studied compositions of model powder mixtures including HAP and sodium salts (Na_2CO_3, $Na_2HPO_4 \cdot 12H_2O$, $NaH_2PO_4 \cdot 2H_2O$) with the content of Na_2O of 25 mol % are marked (★) on the phase diagram from the ACerS NIST Phase Equilibria Diagrams Database, 2004 (Fig. 06587 (700–1050°C)).

The studied compositions are indicated on the phase diagram (Fig. 1) by crossing of the line of 25 mol % of Na_2O and lines of HAP–Na_2O, HAP–N_2P ($Na_4P_2O_7$), and HAP–NP ($NaPO_3$). The marking of powder mixtures and samples after annealing is presented in Table 1.

The powders of the starting components (HAP, Na_2CO_3, $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$) were ground in acetone in a ball mill for 15 min at the rate of 7000 rpm. The ratio of acetone : powder : balls was 1 : 1 : 5, respectively. Powders after grinding in a ball mill were dried at temperature of 20°C for 2 h and then passed through a sieve with a mesh size of 200 μm.

To prepare mixtures under investigation, powders of HAP and sodium salts dried after disaggregation and grinding were mixed in a predetermined ratio, passing a given pair of the components four times through a sieve. Crushed sodium salts (Na_2CO_3, $Na_2HPO_4 \cdot 12H_2O$, $NaH_2PO_4 \cdot 2H_2O$) and HAP were taken in the amount corresponding to 25 mol % of Na_2O for the phase diagram of Na_2O–CaO–P_2O_5.

The phase composition, density, and shrinkage after burning at the given temperature in the range of 600–1200°C was tested on compact powder samples. As a temporary technological binder (TTB), paraffin was used, which was introduced into the powder mixture as a solution in CCl_4. The powder containing TTB was wiped through a sieve with mesh size of 1 mm. On a hand press, from the granulated powder containing TTB, samples were prepared in the form of disks with a diameter of 12 and a height of 1.5–2 mm at the specific molding pressure of 50 MPa. The samples were annealed with the heating rate of 5°C/min and exposure at the final temperature for 2 h.

The X-ray phase analysis (XRD) of the samples after heat treatment was carried out on Rigaku D/Max-2500 diffractometer with a rotating anode (Japan). For the qualitative phase identification, the ICDD PDF2 database was used [10]. The investigation was conducted in the mode of reflection using CuK_α radiation (the interval of angles was $2\theta = 2°–70°$

with a step of 0.02°; the rate of recording of the spectra was 5°/min).

The microstructure of the samples after heat treatment was studied by scanning electron microscopy (SEM) on a LEO SUPRA 50VP scanning electron microscope (Carl Zeiss, Germany; field emission source); the survey was carried out in a low vacuum mode at the accelerating voltage of 20 kV (VPSE secondary electron detector) and at voltages of 3–20 kV (SE2 detector).

RESULTS AND DISCUSSION

The data of XRD of compact preforms from the studied powder mixtures after annealing at 900°C are shown in Fig. 2.

According to the XRD data, phase composition of the samples of HAP after annealing in the interval of 600—1200°C did not change and corresponded to the PDF no. 9-432 card.

The content of CaO in $Ca_3(PO_4)_2$ (on the diagram, it is denoted by C_3P) is 75 mol %. The CaO content of 77 mol % corresponds to synthetic hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. Consequently, the point corresponding to HAP lies on the $CaO–P_2O_5$ line on the phase diagram and is in the triangle formed by $CaO–Ca_3(PO_4)_2–Ca_5Na_2(PO_4)_4$.

Since diffusion mobility of Na cations is fairly high at the temperatures used during annealing, then the interaction of HAP and sodium salts can be represented as largely one-sided diffusion of Na ions from the corresponding sodium salt into particles or crystallites of HAP. Interaction in the considered powder mixtures (HAP/Na_2CO_3, HAP/Na_2HPO_4, and HAP/NaH_2PO_4) can be described as movement of a figurative point on the phase diagram from the composition corresponding to HAP along the lines to Na_2O, $Na_4P_2O_7$(**N_2P**) or to $NaPO_3$ (**NP**).

For the HAP/Na_2CO_3 powder mixture, the figurative point moves, successively intersecting the triangles of $CaO–Ca_3(PO_4)_2–Ca_5Na_2(PO_4)_4$ and $CaO–Ca_5Na_2(PO_4)_4–CaNaPO_4$, stopping at the intersection point of the line **$HAP–Na_2O$** with the line of **25% Na_2O** in the $CaO–CaNaPO_4–Na_3PO_4$ triangle.

According to the XRD data, the phase composition of HAP/Na_2CO_3 after calcination at 600°C was represented by hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (PDF no. 9-432 card). The phase composition of HAP/Na_2CO_3 after calcination in the range of 700—1200°C was represented by hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (PDF card no. 9-432), rhenanite β-$CaNaPO_4$ (PDF card no. 29-1193), and calcium oxide CaO (PDF card no. 37-1497). The intensity of the peaks of rhenanite and calcium oxide increased with increasing temperature.

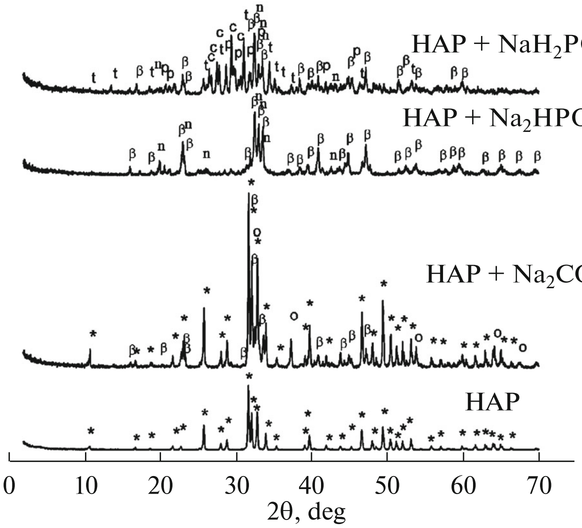


Fig. 2. XRD data after annealing at 900°C for the samples of ceramic made from HAP and powder mixtures of HAP/Na_2CO_3, HAP/Na_2HPO_4, and HAP/NaH_2PO_4 at Na_2O = 25 mol %. (*) HAP (PDF card no. 9-432); (β) β-$CaNaPO_4$ (PDF card no. 29-1193); (o) CaO (PDF card no. 37-1497); (n) $Na_4P_2O_7$ (PDF card no. 10-187); (c) β-$Ca_2P_2O_7$ (PDF card no. 9-346); (t) $Ca_{10}Na(PO_4)_7$ (PDF card no. 45-339); (p) $CaNa_2P_2O_7$ (PDF card no. 48-557).

The process occurring upon heating in the powder mixture of HAP/Na_2CO_3 can be represented by the reaction

$$\begin{aligned} &Ca_{10}(PO_4)_6(OH)_2 + 3Na_2CO_3 \\ &= 6CaNaPO_4 + 4CaO + H_2O + 3CO_2. \end{aligned} \quad (1)$$

Upon heating, used as a component of the powder mixture of HAP/Na_2HPO_4, hydrated disubstituted sodium orthophosphate $Na_2HPO_4 \cdot 12H_2O$ is converted sequentially to Na_2HPO_4 and then to $Na_4P_2O_7$. For a powder mixture of HAP/Na_2HPO_4, the figurative point moves from the triangle of $CaO–Ca_3(PO_4)–Ca_5Na_2(PO_4)_4$ through $Ca_3(PO_4)_2–Ca_2P_2O_7–CaNaPO_4$, with stopping at the intersection point of the **$HAP–Na_4P_2O_7$** line with the line of **25% Na_2O** in the triangle of $CaNaPO_4–Ca_2P_2O_7–Na_4P_2O_7$.

The phase composition of the ceramic samples from the powder mixture of HAP/Na_2HPO_4 after annealing in the interval of 600—900°C included rhenanite β-$CaNaPO_4$ (PDF card no. 29-1193) and $Na_4P_2O_7$ (PDF card no. 10-187), and after calcination at 1000°C, the phase composition of the sample according to XRD data included rhenanite β-$CaNaPO_4$ (PDF card no. 29-1193) and the X-ray amorphous phase.

Presumably, there are the reactions

$$\begin{aligned} &Ca_{10}(PO_4)_6(OH)_2 + Na_4P_2O_7 \\ &= 2Ca_5Na_2(PO_4)_4 + H_2O. \end{aligned} \quad (2)$$

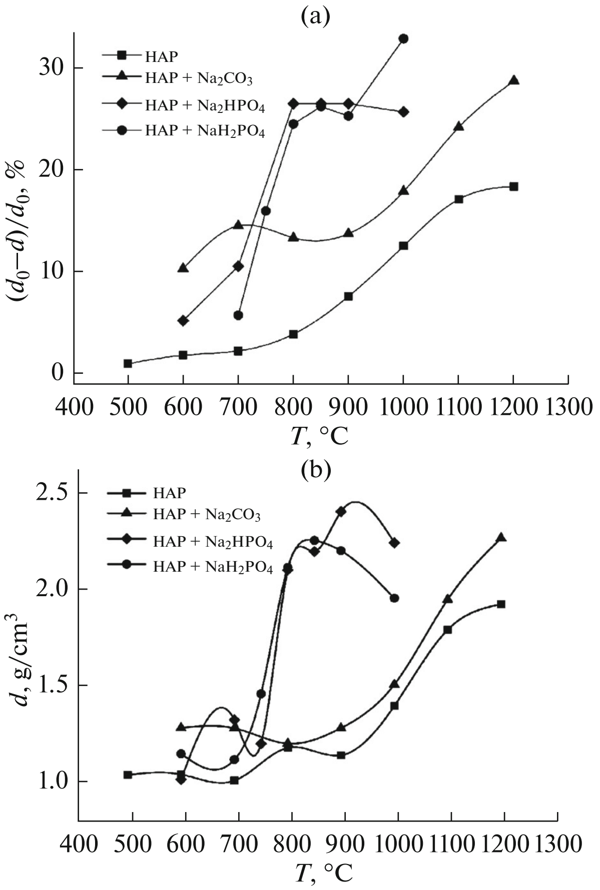


Fig. 3. Dependences of linear shrinkage (a) and density (b) of the samples made from powder mixtures of HAP and sodium salts (Na_2O = 25 mol %) on temperature.

$$\begin{aligned} &2Ca_5Na_2(PO_4)_4 + Na_4P_2O_7 \\ &= 8CaNaPO_4 + Ca_2P_2O_7. \end{aligned} \tag{3}$$

Upon heating, hydrated monosodium orthophosphate $NaH_2PO_4 \cdot 2H_2O$ used as a component of the powder mixture of HAP/NaH_2PO_4 is converted to NaH_2PO_4 and then to $NaPO_3$. For the powder mixture of HAP/NaH_2PO_4, the figurative point moves from the triangle $CaO–Ca_3(PO_4)_2–Ca_5Na_2(PO_4)_4$ through the triangles of $Ca_3(PO_4)_2–Ca_2P_2O_7–CaNaPO_4$ and $CaNaPO_4–Ca_2P_2O_7–Na_4P_2O_7$ with a stop at the intersection point of the **HAP–$NaPO_3$** line with the **25% Na_2O** line in the triangle of $Ca_2P_2O_7–Ca(PO_3)_2–CaNa_2P_2O_7$.

The phase composition of the ceramic samples from the HAP/NaH_2PO_4 powder mixture after annealing in the region of 600—1000°C contained Na-substituted TCP $Ca_{10}Na(PO_4)_7$ (PDF card no. 45-339), rhenanite β-$CaNaPO_4$ (PDF card no. 29-1193), sodium pyrophosphate $Na_4P_2O_7$ (PDF card no. 10-187), double pyrophosphate Na/Ca $CaNa_2P_2O_7$ (PDF card no. 48-557), and CPP β-$Ca_2P_2O_7$ (PDF card no. 9-346). The interaction that takes place in the powder preform during heating can be represented by the reactions

$$\begin{aligned} &Ca_{10}(PO_4)_6(OH)_2 + NaPO_3 \\ &\rightarrow CaNaPO_4 + Ca_2P_2O_7 + CaNa_2P_2O_7 + H_2O. \end{aligned} \tag{4}$$

The interaction between the components of the mixtures of HAP/Na_2CO_3, HAP/Na_2HPO_4, and HAP/NaH_2PO_4 causes the formation of the phase composition of ceramic upon heating.

Ceramic with the phase composition that includes water soluble $Na_4P_2O_7$ salt (used in solution synthesis) cannot be recommended as a material intended for use in contact with aqueous media. Precursors of $Na_4P_2O_7$ or $NaPO_3$ phases such as $Na_2HPO_4 \cdot 12H_2O$, $Na_4P_2O_7 \cdot 10H_2O$, and $NaH_2PO_4 \cdot 2H_2O$ to prepare biocompatible and bioresorbable materials can be used in the preparation of initial powder mixtures. However, they must be taken in such quantities that would preclude the formation of rapidly soluble compounds, such as sodium pyrophosphate $Na_4P_2O_7$. At the same time, it is important to create ceramic multiphase composites, including phases of Na-substituted TCP $Ca_{10}Na(PO_4)_7$ or $Ca_5Na_2(PO_4)_4$, CPP $Ca_2P_2O_7$, double pyrophosphate Na/Ca $CaNa_2P_2O_7$, and rhenanite $CaNaPO_4$ prone to gradual dissolution. Such phases have been shown to be formed as a result of heterogeneous reactions that occur upon heating powder mixtures including HAP and hydrated sodium acid phosphates.

The dependences of shrinkage and density of samples after annealing on temperature are shown in Fig. 3. Shrinkage and density of the samples of HAP increase with increasing annealing temperature and reach the maximum values after annealing at 1200°C—18.0% and 1.9 g/cm^3, respectively.

The shrinkage and density of the samples of HAP/Na_2CO_3 also increase with increasing annealing temperature and reach the maximum values after annealing at 1200°C—28.6% and 2.26 g/cm^3. The large values for shrinkage with respect to diameter and density are apparently related to the formation of the melt in the $Na_2O–CaO–P_2O_5$ system upon annealing. Photomicrographs of the HAP and HAP/Na_2CO_3 ceramics (Fig. 4) confirm this assumption, because the grain size in the HAP/Na_2CO_3 ceramic (1–4 μm) is larger than the grain size in the HAP ceramic (up to 1 μm). Both materials with respect to of HAP (3.16 g/cm^3) have low relative density: 61% for HAP and 72% for HAP/Na_2CO_3. At the same time, the microstructure of HAP/Na_2CO_3 cannot be considered homogeneous.

After annealing at 1100°C, samples from powder mixtures of HAP/Na_2HPO_4 and HAP/NaH_2PO_4 melted. Curves reflecting the change in geometric sizes of samples from HAP/Na_2HPO_4 and HAP/NaH_2PO_4 powder mixtures have a nonmonotonic character. Up to 850°C for HAP/NaH_2PO_4 and up to 900°C for

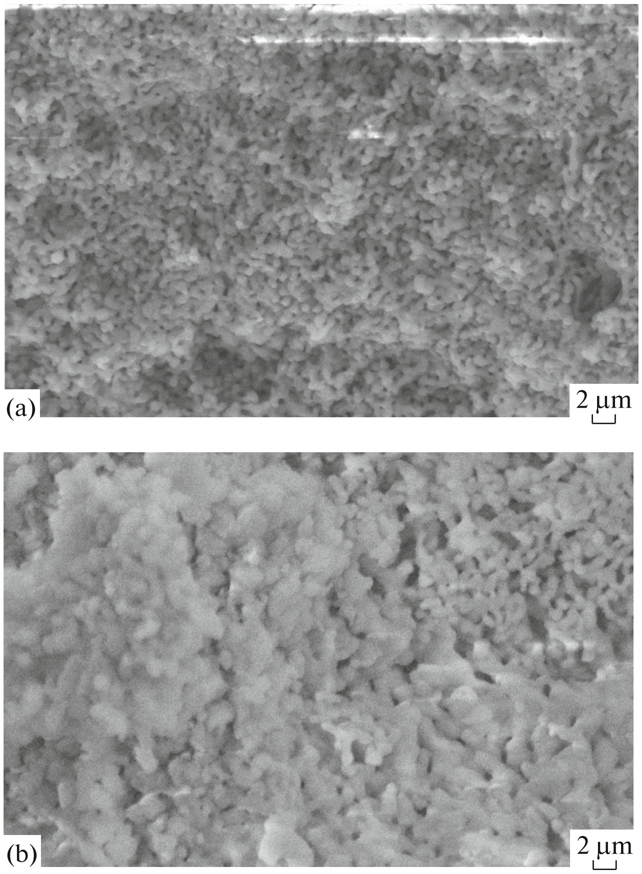


Fig. 4. Photomicrographs of ceramic chips obtained from the powder of HAP (a) and from the powder mixture of HAP/Na_2CO_3 (b) after annealing at 1100°C.

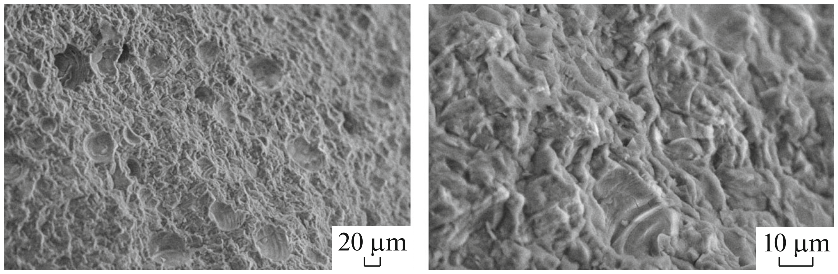
HAP/Na_2HPO_4, shrinkage of the samples with respect to diameter increases, reaching 32.7 and 25.7%, respectively. The density in this case achieved 2.25 g/cm^3 for the samples of HAP/NaH_2PO_4 and 2.40 g/cm^3 for the samples of HAP/Na_2HPO_4. Above 800°C, shrinkage with respect diameter for HAP/Na_2HPO_4 hardly changes (26.4–25.7%), and the density, reaching the maximum at 900°C, with further heating decreases. The density of HAP/NaH_2PO_4 drops after annealing at temperatures above 800°C. The presence of melt in the Na_2O–CaO–P_2O_5 system may explain the compaction, after which the expansion of samples follows, dictated, to all appearances, by boiling of the low-temperature melt.

Photomicrographs of ceramic samples from powder mixtures of HAP/Na_2HPO_4 and HAP/NaH_2PO_4 after annealing at 900°C are shown in Fig. 5. The observed porosity is consistent with the data on the dependence of density on annealing temperature. The grain size can be estimated as 5–15 μm for HAP/Na_2HPO_4 ceramic and as 2–5 μm for HAP/NaH_2PO_4 ceramic.

CONCLUSIONS

Powder mixtures based on HAP and sodium salts (sodium carbonate, sodium hydrogen phosphate, and sodium dihydrogen phosphate), taken in the amount corresponding to 25 mol % of Na_2O in the system of Na_2O–CaO–P_2O_5, were studied in the paper. The phase composition of the samples based on HAP powder after annealing in the interval of 600—1200°C did

(a) HAP/Na_2HPO_4 –900°C



(b) HAP/NaH_2PO_4 –900°C

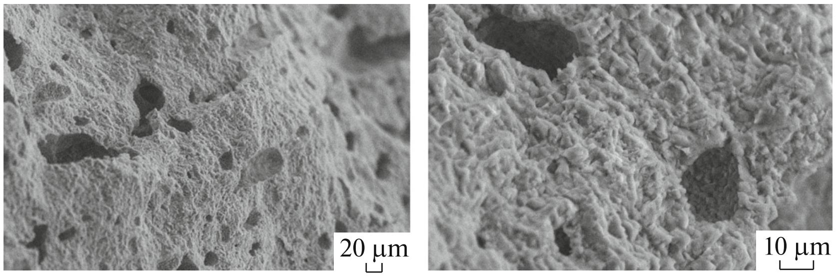


Fig. 5. Photomicrographs of ceramic chips obtained from the powder mixtures of HAP/Na_2HPO_4 (a) and HAP/NaH_2PO_4 (b) after annealing at 900°C.

not change. The phase composition of the HAP/Na_2CO_3 samples after annealing included HAP, β-$CaNaPO_4$, and CaO. The phase composition of the samples of ceramic from the HAP/Na_2HPO_4 powder mixture after calcination contained the phases of β-$CaNaPO_4$ and $Na_4P_2O_7$. The phase composition of the ceramic samples from the HAP/NaH_2PO_4 powder mixture after calcination contained $Ca_2P_2O_7$, $Ca_{10}Na(PO_4)_7$, β-$CaNaPO_4$, $CaNa_2P_2O_7$, and $Na_4P_2O_7$. The presence of sodium salts in the amount corresponding to 25 mol % of Na_2O in the system of Na_2O–CaO–P_2O_5 provided the flow of liquid-phase sintering in compact billets from the studied powder mixtures. However, the presence of water-soluble $Na_4P_2O_7$ salt in ceramic samples of HAP/Na_2HPO_4 and HAP/NaH_2PO_4 after annealing imposes a restriction on the use of such materials in contact with an aqueous medium, and the presence of CaO in the samples of HAP/Na_2CO_3 excludes the use of such materials as bone implants.

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