

Heat Treatment-Induced Phase Transformations of Materials in a System of Calcium Phosphates and Magnesium Phosphates with $(Ca + Mg)/P = 2$

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Abstract—We have studied the effect of heat treatment in a wide temperature range (from 300 to 1500°C) on the phase composition, heat effects and weight loss of powder materials in a system of calcium phosphates and magnesium phosphates with $(Ca + Mg)/P = 2$. The results demonstrate that crystalline magnesium-substituted whitlockite phases begin to form at temperatures above 600°C. Raising the heat treatment temperature reduces the degree of magnesium substitution for calcium in the structure of the magnesium-substituted whitlockite. Tetracalcium phosphate, a high-temperature phase, is formed through apatite phase recrystallization.

Keywords: magnesium-substituted whitlockite, apatite phase, degree of substitution

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INTRODUCTION

The use of biomaterials containing magnesium ions is aimed at the treatment of diseases caused by an improper calcium–magnesium balance in the human body, which leads to osteoporosis and aplastic osteopathy [1]. In connection with this, there is a need for bone substitution and regeneration materials based on magnesium-containing calcium orthophosphates, capable of replenishing magnesium levels [2]. Magnesium is present in natural bone tissue and plays an important part in bone mineralization processes, stimulating osteoblast proliferation [3, 4]. In addition, it controls the formation of a calcium acid phospholipid–phosphate complex, which influences hydroxyapatite (HA) formation [5]. Magnesium-substituted HAs known today have the form of powders and ceramic materials with a degree of magnesium substitution for calcium up to 8.9 wt %, which offer a higher bioresorption rate in comparison with unsubstituted HA [6, 7]. The transition of magnesium-substituted calcium phosphates from a calcium/phosphorus atomic ratio $Ca/P = 1.67$ to $Ca/P = 2$ is of interest. The material of this composition, tetracalcium phosphate (TTCP), offers the highest solubility at a nearly neutral pH (6.5–7.5) among the calcium phosphates that are used in medical applications [8]. However, TTCP is a high-temperature compound and can only be prepared using heat treatment of intermediate synthesis products [9].

The ratio $(Ca + Mg)/P = 2$ is of interest primarily for the preparation of cement materials to be mixed with acid liquids [10]. The technology of biocements employs magnesium–calcium materials with enhanced strength due to the use of magnesium phosphate-based cement liquids [2]. Moreover, the addition of magnesium, which is less alkaline than calcium, will help to reduce the pH of ceramic materials with $(Ca + Mg)/P = 2$, which will allow such ceramics to be thought of as promising for implantation [11].

Advances in the technology of such materials are highly dependent on knowledge of the phase formation processes involved and the thermal stability of the materials in a wide temperature range. HA dehydration and decomposition processes during heat treatment at temperatures of up to 1500°C are known to depend significantly on the Ca/P ratio in the starting mixture [12]. There are data on phase transformations at $(Ca + Mg)/P = 1.5$ due to the incongruent melting of $Ca_3Mg_3(PO_4)_4$ in the $Ca_3(PO_4)_2$ – $Mg_3(PO_4)_2$ system [13]. Data on phase transformations of materials with $(Ca + Mg)/P = 2$ and a degree of magnesium substitution for calcium up to 40 wt % during heating in a wide temperature range are not available in the literature.

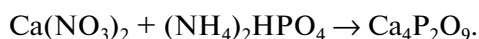
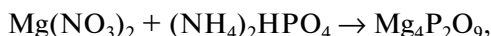
In this paper, we report a physicochemical study of phase formation in a system of calcium phosphates and magnesium phosphates with $(Ca + Mg)/P = 2$ during heat treatment at temperatures of up to 1500°C.

Characteristics of the powders

Degree of magnesium substitution for calcium, wt %	0	5	10	20	40
Specific surface area, m ² /g	20.9 ± 0.5	38.6 ± 1.1	27.8 ± 0.7	36.4 ± 1.0	38.9 ± 0.7
Average agglomerate size, μm	0.4–0.5	0.2–0.3	0.3–0.4	0.2–0.3	0.2–0.3
Average particle size, nm	50–60	30–40	40–60	30–40	30–40

EXPERIMENTAL

Powder materials in a system of calcium phosphates and magnesium phosphates with a (Ca + Mg)/P weight ratio of 2 were synthesized via coprecipitation from aqueous solutions. Starting-mixture compositions were calculated theoretically to give a mixture of TTCP and tetramagnesium phosphate:



In agreement with the calculated reaction schemes, we obtained mixtures with the following degrees of magnesium substitution for calcium: 0, 5, 10, 20, and 40 wt %. The starting chemicals used were Mg(NO₃)₂ · 6H₂O (analytical grade), (NH₄)₂HPO₄ (analytical grade), and Ca(NO₃)₂ · 4H₂O (analytical grade). Mg(NO₃)₂ and Ca(NO₃)₂ solutions were added dropwise to an (NH₄)₂HPO₄ solution with constant stirring at a rate of 300 rpm. The pH of the reaction mixture was maintained at a level of 9–10 by adding aqueous ammonia.

After synthesis, the powders were dehydrated by evaporation, dried in a drying oven at a temperature of 50°C, and preheat-treated at 300°C to remove ammonium nitrate, an impurity phase. The powders were then heat-treated at *t* = 600 and 900°C for 1 h in a muffle furnace in air. The powders were also heat-treated at 1200 and 1500°C for 2 h in a furnace with lanthanum chromite heating elements. Next, the materials were ground in an agate mortar to a powder particle size under 100 μm.

The powder materials were characterized by X-ray diffraction analysis (Shimadzu XRD-6000 diffractometer, Japan) with CuK_α radiation. Their phase composition was determined using JCPDS Powder Diffraction File data, the PCPDFWIN database, and an automatic experimental data acquisition and processing system. Differential scanning calorimetry (DSC) and thermogravimetry (TG) data were obtained in a Netzsch STA 409 Luxx simultaneous thermal analysis system in the temperature range from 25 to 1350°C during continuous heating, without holding at any fixed point temperatures. The heating rate was 10°C/min. The temperature was measured by a Pt/Pt–10% Rh thermocouple, and the maximum sample weight was 18 g. An empty crucible was used as a reference, and the samples were heated in an inert atmosphere. The composition of the gases released during thermal decomposition was determined by

mass spectrometry from the molecular masses of the released gases, using a Netzsch QMS 403 C Aëolos quadrupole mass spectrometer with a capillary inlet system. The specific surface area (*S*) of the powders was determined by low-temperature nitrogen adsorption BET measurements (Micromeritics TriStar analyzer). The particle morphology and size were assessed by scanning electron microscopy (SEM) (TeScan VEGA II microscope, secondary electron imaging, accelerating voltage of 15 kV).

RESULTS AND DISCUSSION

The measured specific surface areas and SEM results are presented in the table. The addition of magnesium was found to reduce the average particle size from 50–60 to 30–40 nm with increasing magnesium content and to reduce the agglomerate size from 0.4–0.5 to 0.2–0.3 μm. The particle morphology changed only slightly: from rounded to anaxial (Fig. 1). The changes in particle size correlated with the observed increase in specific surface area from 20.9 ± 0.5 m²/g for the magnesium-free materials to 38.9 ± 0.7 m²/g for the powders with a 40% degree of magnesium substitution for calcium ions.

According to X-ray diffraction data, the materials heat-treated at 300°C after synthesis had a low degree of crystallinity and broad lines in the region characteristic of amorphous calcium phosphate (Fig. 2a). The X-ray diffraction patterns of the magnesium-free materials contained weak lines characteristic of Ca(OH)₂. The degree of crystallinity of the materials was found to decrease with increasing magnesium content (Fig. 2), indicating structural instability. The powders with degrees of magnesium substitution for calcium of 20 and 40 wt % were X-ray amorphous.

After heat treatment of the powders at 600°C, the degree of crystallinity of the materials increased (Fig. 2b). The magnesium-free materials contained up to 40 wt % apatite phase and calcium oxide. CaO formation is the result of the Ca/P = 2 ratio used in our syntheses. After heat treatment at 600°C, the material with a 5% degree of magnesium substitution for calcium had the lowest degree of crystallinity compared to the powders with the other compositions and the position of the observed lines was characteristic of amorphous calcium phosphate. At degrees of substitution of 10, 20, and 40 wt % magnesium, the X-ray diffraction patterns of the powders showed peaks of an

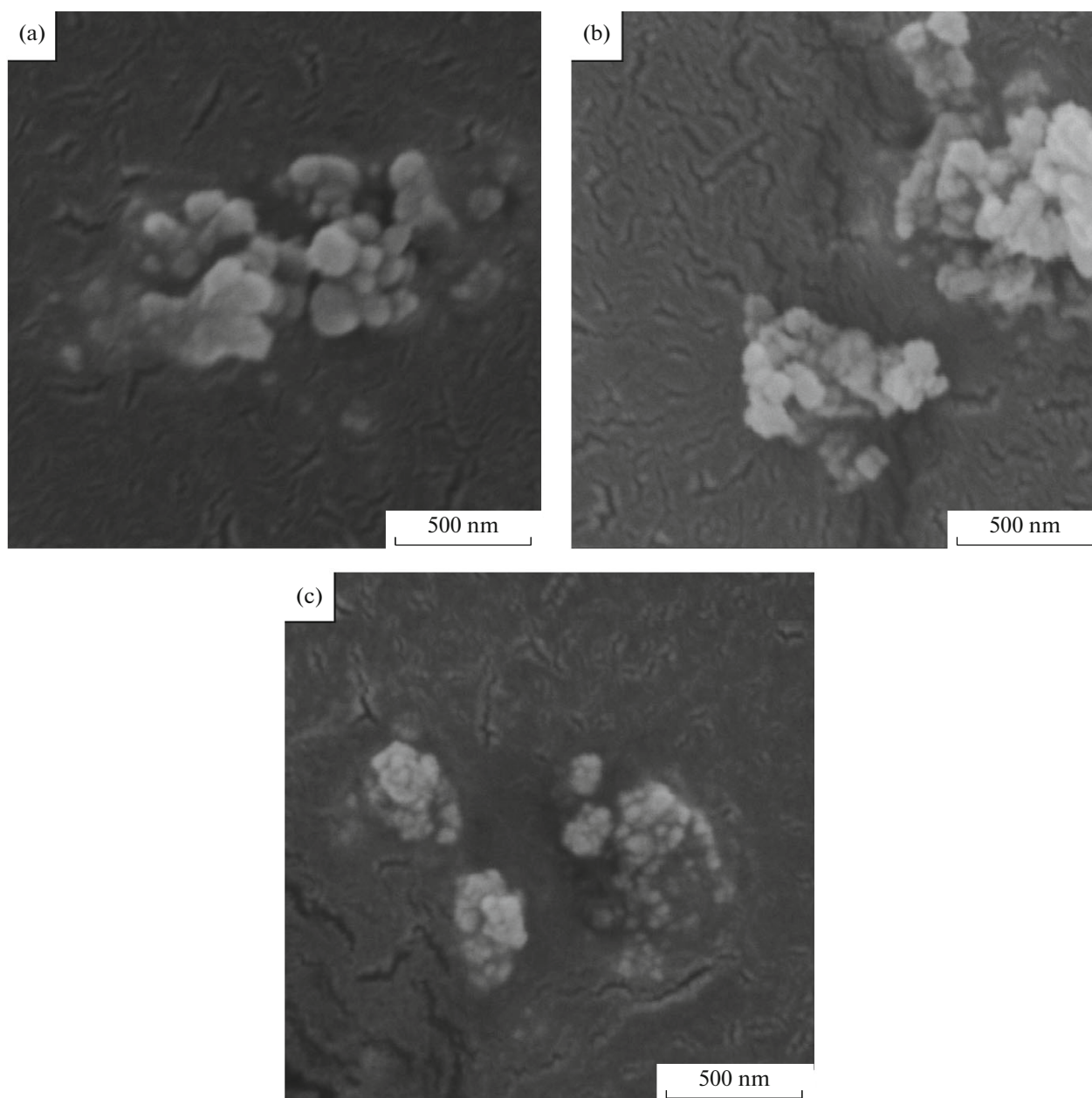


Fig. 1. SEM images of the powders: (a) 0, (b) 5, and (c) 40 wt % Mg.

apatite phase. Their intensity was observed to decrease with increasing magnesium ion concentration in the materials. The X-ray diffraction patterns of the powders with degrees of substitution of 20 and 40 wt % also contained peaks characteristic of magnesium oxide: about 5 and 10 wt %, respectively.

Raising the calcination temperature of the magnesium-free powders to 900°C led to an increase in the degree of crystallinity of the major phases, apatite and calcium oxide (Fig. 2c), which continued even at 1200°C (Fig. 2d). In the magnesium-containing materials, we observed the onset of $(\text{Ca},\text{Mg})_3(\text{PO}_4)_2$ magnesium-substituted whitlockite formation. The materials with a 5 wt % degree of substitution were single-

phase and contained a whitlockite phase with a low degree of crystallinity. In the materials containing 10 and 20 wt % substituted magnesium, a whitlockite phase was formed through apatite phase recrystallization, which led to magnesium precipitation from their structure. This process was accompanied by an increase in the intensity of the reflection from magnesium oxide. In the materials with a 40 wt % degree of substitution, two whitlockite phases were formed at 900°C: $(\text{Ca},\text{Mg})_3(\text{PO}_4)_2$ and the calcium-enriched phase $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$.

Heat treatment of the magnesium-containing materials at 1200°C led to further increase in the degree of crystallinity of all the materials (Fig. 2d).

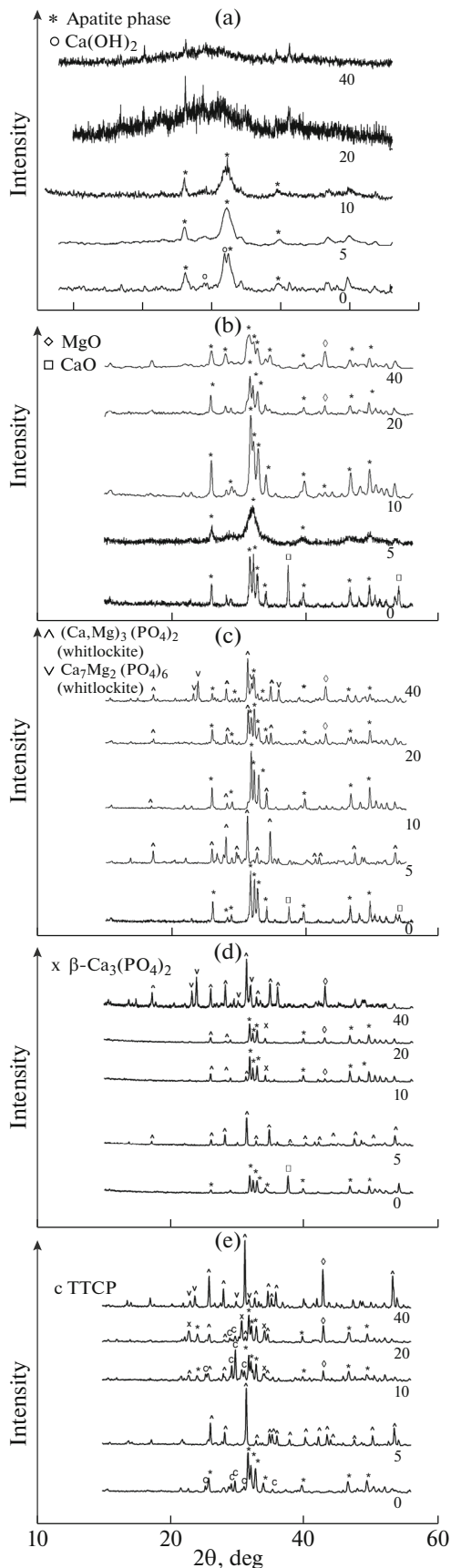


Fig. 2. X-ray diffraction patterns of the powders heat-treated at (a) 300, (b) 600, (c) 900, (d) 1200, and (e) 1500°C.

The powders with a 5 wt % degree of substitution were observed to have a small tendency toward the formation of a magnesium-substituted whitlockite, with calcium prevalence, $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$, as evidenced by the observed shift of the major peaks to smaller diffraction angles as the temperature was further raised to 1500°C. In this process, no magnesium oxide was formed, and the excess of cations led to structural instability, which showed up as a low degree of crystallinity of the material. The materials containing 10 and 20 wt % substituted magnesium were characterized by further apatite phase recrystallization into magnesium-substituted whitlockite phases: $(\text{Ca},\text{Mg})_3(\text{PO}_4)_2$ and $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$.

Raising the calcination temperature to 1500°C led to the formation of pure TTCP in the magnesium-free materials (Fig. 2e). In the materials with a 5 wt % degree of magnesium substitution, no TTCP was formed, and the only phase present was whitlockite. In the powder materials with a 10 wt % degree of magnesium substitution for calcium ions, the TTCP content reached 50 wt %. At a 20 wt % degree of substitution, the materials contained 10 wt % TTCP. The powders with a 40 wt % degree of substitution contained no TTCP. All of the materials also showed a tendency toward magnesium removal from the whitlockite lattice, resulting in the formation of $\text{Ca}_7\text{Mg}_2(\text{PO}_4)_6$. In addition, at a 20 wt % degree of magnesium substitution, we observed the formation of a small amount of $\text{Ca}_3(\text{PO}_4)_2$ and an increase in MgO content. Thus, TTCP was formed through the recrystallization of the apatite phase, which was present in the materials with a degree of magnesium substitution for calcium of 0, 10, and 20 wt %. If there was no apatite phase (in the materials containing 5 and 40 wt % substituted magnesium), no TTCP was formed, and further crystallization of the whitlockite phase took place. Thus, our results demonstrate that raising the calcination temperature of the powders leads to magnesium removal from the structure of the whitlockite phase and the formation of magnesium oxide as an individual phase.

The DSC curves of the materials show endothermic peaks at $t = 110\text{--}140$ and $540\text{--}580^\circ\text{C}$ (Fig. 3). According to mass spectrometry data, the former peak is due to the removal of adsorbed water and other reaction products (ammonium nitrate). The latter peak corresponds to the crystallization of the major phases. In the temperature range $680\text{--}700^\circ\text{C}$, the DSC curve of the material with a 5 wt % degree of substitution shows an exothermic peak arising from amorphous calcium phosphate recrystallization into a whitlockite phase. Above 600°C , all of the materials experience an exothermic reaction associated with the increase in the degree of crystallinity of the major phases. Starting at 1200°C , the DSC curves of the materials containing 5 and 40 wt % substituted magnesium show an endotherm, which is due to the melting onset of the major phase: magnesium-substituted whitlockite.

The DSC results are confirmed by TG data (Fig. 4). According to the TG data, the largest weight

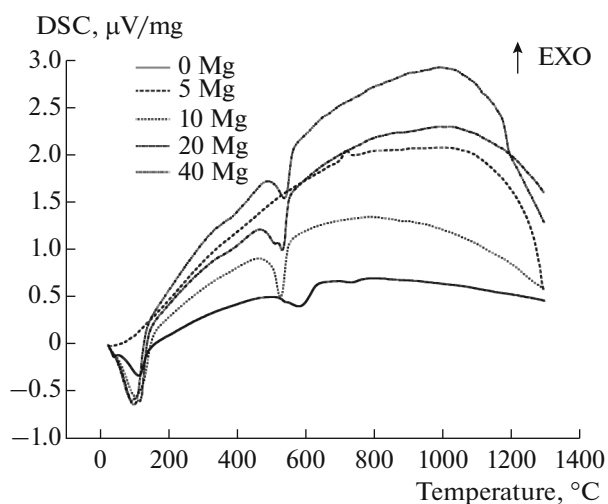


Fig. 3. DSC curves.

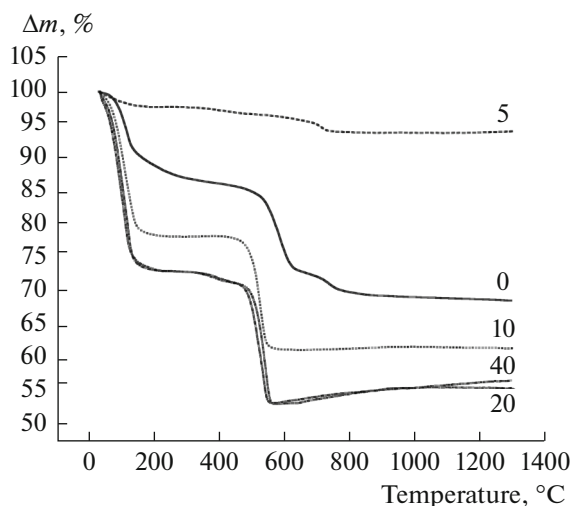


Fig. 4. TG results for the powders (the numbers at the curves specify the weight percentage of Mg).

loss in the course of thermal decomposition occurs in the range 500–600°C over the entire composition range studied. The weight loss is about 25 wt % for the powders with degrees of magnesium substitution for calcium ions of 0, 10, 20, and 40 wt %. At a 5 wt % degree of substitution, the weight loss is about 5 wt %.

CONCLUSIONS

Crystalline magnesium-substituted whitlockite phases begin to form at temperatures above 600°C. Raising the heat treatment temperature reduces the degree of magnesium substitution for calcium ions in the structure of the magnesium-substituted whitlockite. The high-temperature phase TTCP is formed through apatite phase recrystallization. Heating leads to magnesium removal from the structure of the calcium phosphates and the formation of magnesium

oxide. According to differential thermal analysis data, the major phases crystallize in the temperature range from 540 to 700°C. The materials in which the magnesium-substituted whitlockite phase prevails begin to melt at 1200°C.

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