MANUFACTURING OF HIGHLY POROUS MAGNESIUM-SUBSTITUTED HYDROXYAPATITE BIOCERAMICS VIA GEL-CASTING

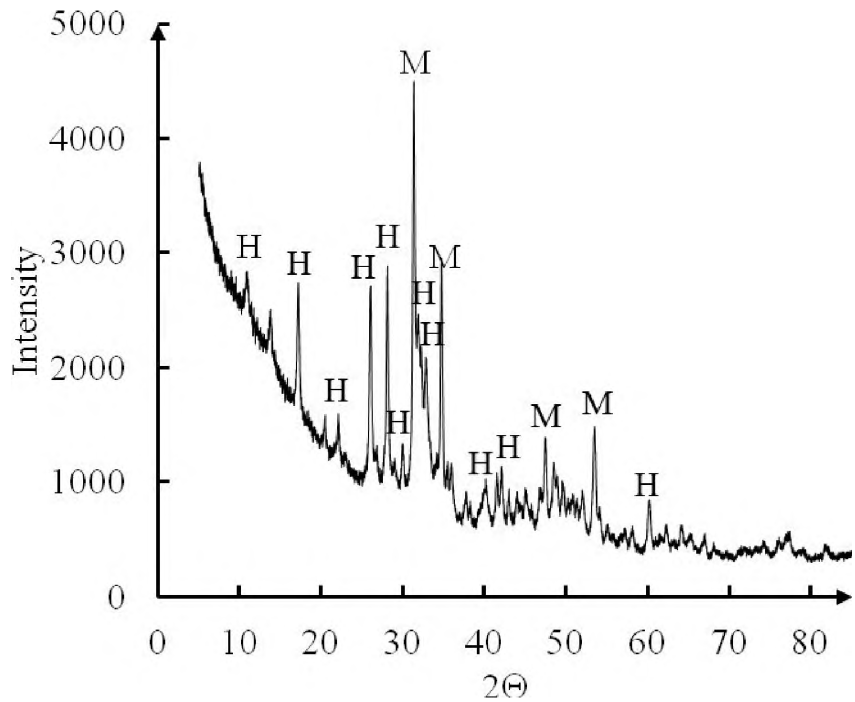
Shymanskaya H.N., PhD; Podsosonnaya A.D.
Belarusian State Technological University, Chemical Technology and Engineering Faculty, Minsk, Republic of Belarus

The aim of this work is to development of compositions and technological parameters for the production of magnesium-substituted hydroxyapatite bioceramics by gel-casting, to establish the relationship between physicochemical properties of the synthesized materials, their structure and composition of initial mixture. In this study, agar-agar was used as gelling agent.

The synthesis of magnesium-substituted hydroxyapatite was conducted using calcium nitrate tetrahydrate $Ca(NO_3)_2{\cdot}4H_2O$ (chemically pure grade, GOST 4142); magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ (analytical grade, GOST 11088); ammonium hydrogen phosphate $(NH_4)_2HPO_4$ (grade A, GOST 8515); ammonium hydroxide NH_4OH (25 % NH_3 in H_2O, ultrapure grade, GOST 24147) and distilled water according to the following equation:

$$(10{-}x)Ca(NO_3)_2 + xMg(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{(10-x)}Mg_x(PO_4)_6(OH)_2 + \\ + 20NH_4NO_3 + 6H_2O\ (0.55 \le x \le 0.65).$$

The solution obtained by dissolving Ca $(NO_3)_2{\cdot}4H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ in a beaker was added dropwise into a solution of $(NH_4)_2HPO_4$ with constant stirring. By adding NH_4OH, the pH of the solution was kept constant at 7–7.5 throughout the synthesis process. The synthesis was carried out at 60 °C. The precipitate and the mother liquor were cooled down to room temperature and left for 7 days. The resulting precipitate was separated by filtration, washed with distilled water and dried at 80 °C. Particle size of obtained powder was between 5–10 μm (Analysette 22, Germany), X-ray phase analysis (diffractometer DRON-2, Russia) indicated hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and $2Ca_3(PO_4)_2{\cdot}CaMg_2(PO_4)_2$ (Figure 1).

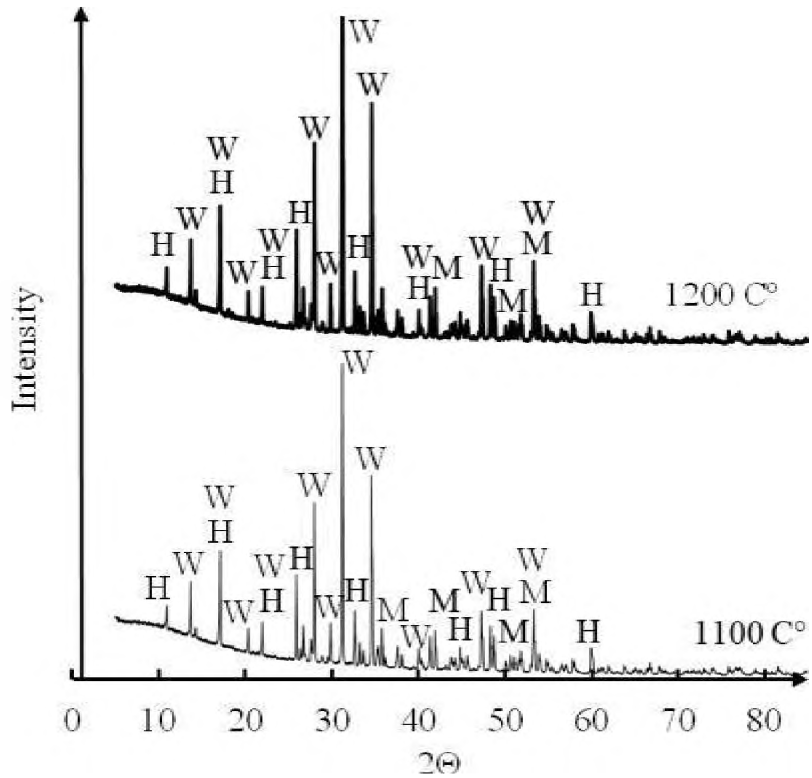


H – hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (ICCD file 9-432);
M – $2Ca_3(PO_4)_2{\cdot}CaMg_2(PO_4)_2$ (ICCD file 20–348)
Figure 1 – X-ray diffraction pattern of the synthesized powder

Prepared agar-agar solutions were mixed with hydroxyapatite at 60 °C. Ratio of magnesium-substituted hydroxyapatite/agar-agar was 17.1:1. The fluidity of the suspensions ranged between 15 and 16 s. The samples were prepared by gel-casting in plastic molds. After freezing, they were removed from the molds, dried at 80 °C, and fired at 1100, 1150 and 1200 °C.

The physical and chemical properties of the bioceramics sintering at 1100–1200 °C were the following: water absorption – 24.8–114.7 %, apparent porosity – 38.5–76.7 %, bulk density – 677–1643 kg/m^3, compressive strength – 0.2–3.0 MPa.

XRD study revealed that crystalline phases were represented by hydroxyapatite, $2Ca_3(PO_4)_2{\cdot}CaMg_2(PO_4)_2$ and tricalcium phosphate β-$Ca_3(PO_4)_2$ (Figure 2). The pore size was approximately 2–150 μm (Figure 3).



H – hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (ICCD file 9-432);
M – $2Ca_3(PO_4)_2{\cdot}CaMg_2(PO_4)_2$ (ICCD file 20–348);
W – tricalcium phosphate β-$Ca_3(PO_4)_2$ (ICCD file 9–169)
Figure 2 – X-ray diffraction patterns of magnesium-substituted hydroxyapatite bioceramics

× 1000 × 2000

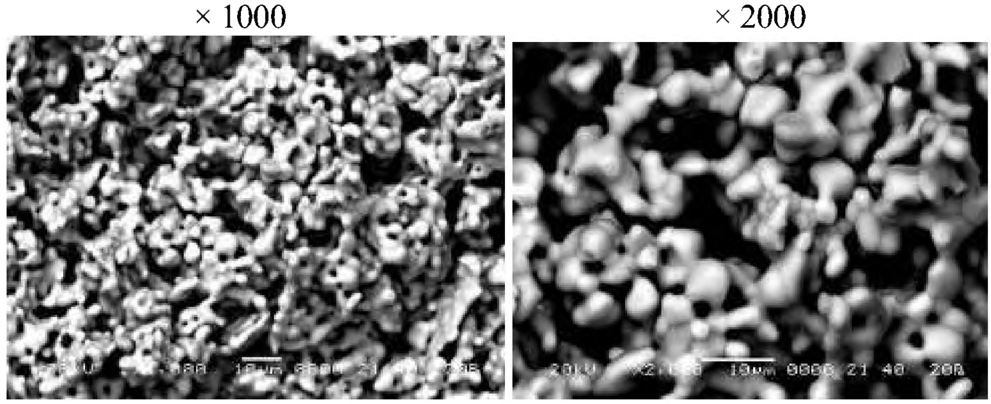


Figure 3 – SEM micrographs of magnesium-substituted hydroxyapatite bioceramics

Thus, the obtained porous material seem to be a promising bone substitution material.