

SHORT COMMUNICATIONS

Properties of Magnesium-Substituted Hydroxyapatite and the Plasma Coatings Based on It

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Abstract—Magnesium-substituted hydroxyapatite is synthesized and deposited by plasma spraying, and the coating and the products of hydroxyapatite decomposition are analyzed. The phase composition of magnesium-substituted hydroxyapatite deposited by plasma spraying undergoes changes. The coating consisting of molten magnesium-substituted hydroxyapatite powder particles with pores between them has a homogeneous structure over the surface and throughout the internal structure and adhesion characteristics that exceed those of hydroxyapatite coatings.

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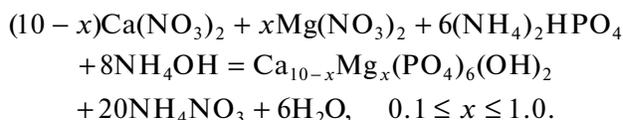
From a general standpoint, the family of calcium phosphate biocompatible materials can include numerous compounds and derivatives to be used in dentistry and orthopedics. However, calcium hydroxyapatite (CH) is the most important compound among them [1, 2]. As an active component of bone tissue, one can use CH partly isomorphically substituted by Group II metal ions M^{2+} with general formula $Ca_{10-x}M_x^{2+}(PO_4)_6OH_2$, where M^{2+} is Mg^{2+} and/or Zn^{2+} and $0.01 \leq x \leq 1.0$. Mg^{2+} -containing CHs are being extensively studied, since this cation substitution is characteristic of the bioapatite of tooth and bone tissue [2].

Biocompatible coatings are mainly produced by plasma spraying, RF magnetron sputtering, microarc oxidation, and so on. Plasma spraying is characterized by a high output, the possibility of formation of porous coatings with a developed morphology, the possibility of controlling the spraying parameters, and the deposition of high-quality coatings [1, 3]. Although the formation of magnesium-substituted hydroxyapatite has received much study [4–6], the information on the properties of plasma-sprayed magnesium-substituted coatings is very scarce.

The purpose of this work is to form Mg^{2+} CH, to perform its plasma spraying, to identify the products of its decomposition, and to study its physicochemical properties.

Mg^{2+} CH was synthesized by precipitation from aqueous solutions of calcium nitrate, magnesium nitrate, diammonium phosphate, and ammonium hydroxide [7].

Synthesis was carried out by precipitation from aqueous solutions according to the reaction



The initial substances were calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ (State Standard GOST 1922-84), diammonium phosphate $(NH_4)_2HPO_4$ (doubly substituted ammonium phosphate, diamphos) with a moisture mass fraction of 4 wt % (GOST 8515-75), 25% aqueous solution of NH_4OH (GOST 9-92), and magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$ (GOST 11088-75).

Synthesis was performed at room temperature $T = 20^\circ C$ and an air humidity of 58%, and solution pH was 9–12.

An aqueous solution of calcium nitrate was placed in a chemical beaker with a mixer, and a solution of diammonium phosphate was added drop by drop in 1 h. NH_4OH diluted by water to 1 : 10 was added to maintain solution pH.

The precipitate formed upon synthesis was matured in the chemical beaker for 24 h, filtered through a paper filter, dried at a temperature of 90–95°C, calcined at 200°C for 120 h to remove NH_4NO_3 residue, and calcined at 600°C for 6 h to acquire a crystal structure. The synthesized powder was cooled at room temperature for 2 h, milled in a ceramic mortar with a pestle for 15 min, and screened with sieves.

The morphology and phase composition of Mg CH deposited onto VT1-0 titanium samples were studied. The samples were cylinders 6.5 mm in diameter and 1.5 mm in height, and the adhesion of depos-

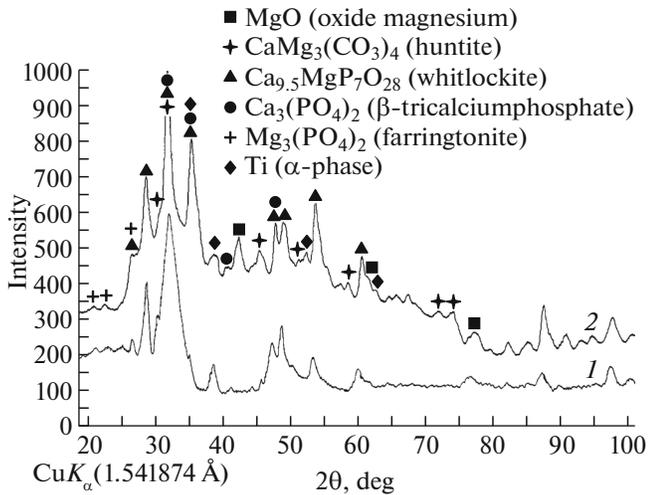


Fig. 1. X-ray diffraction patterns of powders (1) before and (2) after plasma spraying on a titanium base.

ited Mg CH was investigated on plane samples $10 \times 30 \times 2$ mm in size.

Once coated, the plates were cleaned in the ultrasonic bath of PSB-GALS at a frequency of 18 kHz in an aqueous surfactant solution at a temperature of 35–40°C for 3 min and were then subjected to air abrasive processing in an ASOZ 1.2 MEGA (OOO VEGA-PRO, Yekaterinburg) apparatus by a Belket 25 fused corundum powder (specifications 9391-094-45814830-2003) with a grain size of 250–300 μm for 5 min.

A composition coating was formed by sequential plasma spraying of a titanium sublayer for 10–12 s and an Mg CH powder layer for 6–8 s. Plasma spraying was performed with a semiautomatic UPN-28 (NPO REMPLAZMA, Moscow) setup under the following technological conditions: the arc current was 300 A, the titanium powder grain size was 100–150 μm , the Mg CH powder grain size was up to 90 μm , the plasma-forming gas (argon) flow rate was 20 L/min, the spraying distance of a titanium powder was up to 150 mm, and the spraying distance of an Mg CH powder was up to 50 mm.

X-ray diffraction (XRD) analysis of the initial Mg CH powder and the samples coated with a layer formed by plasma spraying of the powder was carried out with an Xcalibur/Gemini A diffractometer using a copper anode X-ray tube ($\text{CuK}\alpha$ radiation). To analyze X-ray diffraction patterns, we used the Match! 2003–2009 CRYSTAL IMPACT (Bonn, Germany) software package and American Mineralogist Crystal Structure Database (AMCSD) and Crystallography Open Database (COD).

IR spectra of Mg CH were studied with an FT-801 Fourier spectrometer (OOO NPF SIMMEKS, Novo-

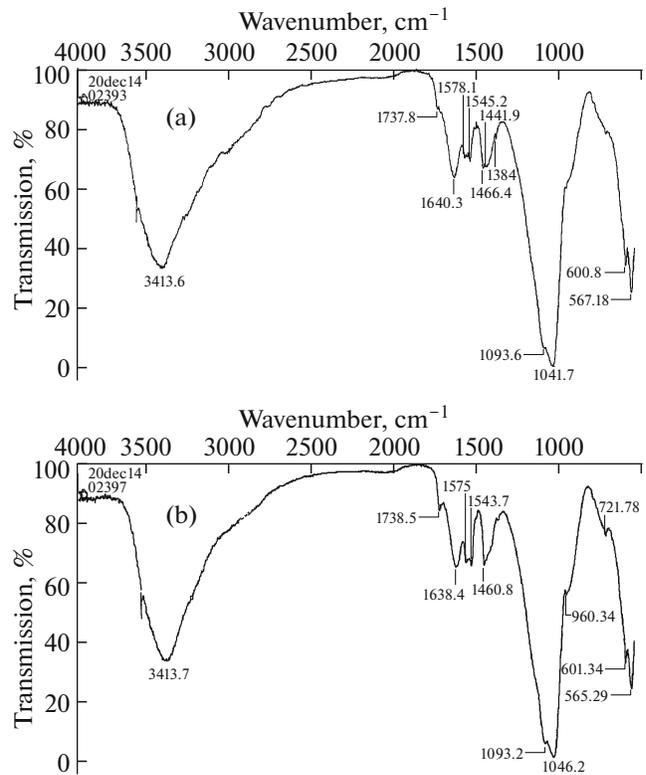


Fig. 2. IR spectrum of Mg CH (a) heat treated at 200 and (b) 600°C.

sibirsk) in the wavenumber range 500–4000 cm^{-1} using pellets with KBr.

The surface morphology of the samples was analyzed on a MIM-7 optical microscope with a Sony DSC-W710 digital photographic camera. The structure of coatings was examined on polished cross sections on an MIM-8 metallographic microscope.

The adhesion of a deposited coating was determined by the shear method (GOST 14759-69) using a universal IR 5082-100 (OOO IMPUL'S, Ivanovo) tensile-testing machine at a cross arm velocity of 0.5 mm/min.

XRD analysis showed that, in spraying, the initial magnesium-substituted CH powder decomposes in the following main phases: MgO (magnesium oxide) [8], $\text{CaMg}_3(\text{CO}_3)_4$ (huntite) [9], $\text{Ca}_{9.5}\text{MgP}_7\text{O}_{28}$ (whitlockite) [10], $\text{Ca}_3(\text{PO}_4)_2$ (β -tricalciumphosphate) [11], and $\text{Mg}_3(\text{PO}_4)_2$ (farringtonite) [12] (Fig. 1). In general, we can state that magnesium destabilizes the structure of CH. This fact is explained by the difference between the ionic radii of calcium and magnesium and is not in conflict with the results from [4].

IR analysis of the Mg CH samples heat treated at 200 and 600°C shows that the vibrational frequencies of main groups PO_4^{3-} , O–P–O, and OH mainly correspond to the synthetic CH sample (Figs. 2a, 2b).

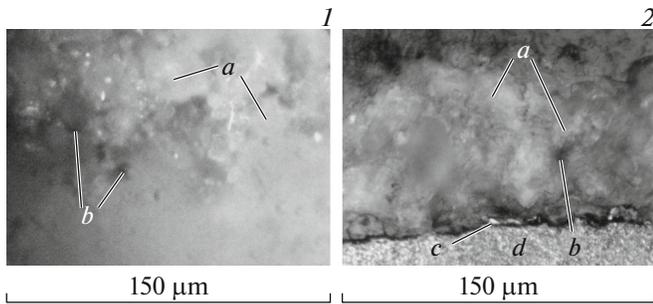


Fig. 3. (1) Surface morphology and (2) polished section of samples with a plasma-sprayed Mg CH coating: (a) plasma-sprayed Mg CH powder particles, (b) pores, (c) plasma-sprayed titanium sublayer, and (d) compacted titanium substrate.

When temperature changes from 200 to 600°C, the main absorption bands narrow, which indicates an increase in the degree of crystallinity of Mg CH samples.

To determine the adhesion of a coating according to the mode I shear method, sample pairs were glued on the side of coating. As a cohesive, we used ED-20 epoxy resin (specifications 2252-003-62517430-01) with a polyethylenepolyamine hardener, which can withstand specific mode I loads of 35–40 MPa. For high-quality adhesion, samples were pressed against each other with loads and stored at room temperature for 24 h.

Adhesion was determined as the average ratio of the average force of breakaway of the glued samples to the breakaway area (GOST 27890-88). The maximum force at which a sprayed coating was separated from the base was 5.4 kN. The adhesion of a plasma-sprayed Mg CH coating was 14.0–14.9 MPa, which is higher than the average adhesion characteristics of plasma-sprayed CH coatings (10–11 MPa) [3]. The increase in the adhesion is likely to be related to the formation of a more homogeneous structure in the plasma-sprayed Mg CH coating and the presence of β-tricalciumphosphate in the coating. It appears due to the magnesium-induced destabilization of the CH structure [4] and has higher adhesion characteristics as compared to CH coatings, according to the experimental data from [3].

Figure 3 (1) shows a micrograph of the surface of the sample coated with Mg CH. An analysis of such micrographs shows that the plasma-sprayed Mg CH coating is homogeneous over the entire surface. This coating consists of individual particles 20–40 μm in size and their agglomerates up to 100 μm in size, which corresponds to the characteristics of plasma-sprayed CH coatings formed under similar plasma spraying conditions [3]. An analysis of polished sections showed that the Mg CH coating thickness is 90–110 μm and the coating structure is homogeneous.

Individual melted close-packed Mg CH powder particles 20–50 μm in size are visible, and closed pores (voids) 10–15 μm in size are observed between them, which is comparable with the closed porosity of plasma-sprayed CH coatings (Fig. 3 (2)) [3].

An analysis of our experimental results demonstrates that the introduction of magnesium into the structure of hydroxyapatite does not exert a negative effect on the morphology of the plasma-sprayed coatings.

CONCLUSIONS

(1) Mg²⁺CH was synthesized by precipitation from aqueous solutions of calcium nitrate, magnesium nitrate, diammonium phosphate, and ammonium hydroxide, and its structure was studied by XRD and IR spectroscopy.

(2) Mg²⁺CH decomposes into the following phases during plasma spraying: MgO, CaMg₋₃(CO₋₃)₋₄, Ca_{9.5}MgP₇O₂₈, Ca₃(PO₄)₂, and Mg₃(PO₄)₂. This finding supports a destabilizing effect of magnesium on the CH structure.

(3) The morphology of the plasma-sprayed Mg CH coating was shown to be homogeneous over the entire surface. This coating consists of individual particles 20–40 μm in size and their agglomerates up to 100 μm in size. The internal structure has closed pores 10–15 μm in size. These characteristics are comparable with those of plasma-sprayed CH coatings.

(4) The adhesion of the plasma-sprayed Mg CH coating is 14.0–14.9 MPa, which is higher than the average adhesion characteristics of the CH-based composite coatings formed by plasma spraying by approximately 20%.

(5) Based on the obtained results and reported data, we conclude that the Mg CH coatings deposited by plasma spraying are promising for medicine, including dental implantology and traumatology, due to a homogeneous morphology, high adhesion–cohesion characteristics, and an osteointegration potential [5, 6]. We are now performing combined medical–biological in vitro and in vivo tests of the synthesized powders and related coatings according to GOST R ISO 10993-2009 Estimation of the Biological Action of Medicine Parts.

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