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Preparation and *in vitro* apatite-forming ability of hydroxyapatite and β -wollastonite composite materials

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ABSTRACT

This paper provides a one-step method of preparation of the ceramic powders, containing various amounts of hydroxyapatite (HA) and β -wollastonite (WT), based on the salt coprecipitation and subsequent thermal treatment of the synthesis products at 1000 °C. Aqueous solutions of $\text{Ca}(\text{OH})_2$, H_3PO_4 and Na_2SiO_3 were used as precursors of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\beta\text{-CaSiO}_3$, as a minimal amount of by-product is formed during such an interaction of reagents. Variation of the concentration of the initial reagents allows the preparation of ceramic powders containing from 0 to 100 wt% of apatite. All composites were examined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), laser diffraction analysis and an adsorption method (BET). Degradability of composite powders was analyzed in the Tris-HCl buffer solution. The apatite-forming ability of synthetic composites was investigated by soaking composite ceramics in a simulated body fluid (SBF). The results that were obtained reveal an increase in the dissolution rate of powders with wollastonite addition. Soaking of the composite ceramics in SBF leads to the formation of a bone-like apatite spherical particle layer on their surfaces, which become thicker while the content of $\beta\text{-CaSiO}_3$ in the samples increases.

1. Introduction

In the field of medical materials science, there is a concept according to which stoichiometric hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is considered the ideal substance for the restoration of bone defects [1], as this synthetic salt is the closest to the mineral component of human hard tissues [2]. Bioactivity and the absence of negative reactions from the organism side during the apatite implantation caused its wide expansion. However, low solubility of HA ($-\log(K_{sp})^{25^\circ\text{C}} = 116.8$ [3]) and an extremely low rate of *in vivo* resorption, which hinders osseointegration, has led to studies in the direction of modifying the salt composition as a way of adjusting its properties. As a result, various forms of substituted apatites containing natural impurities of bone tissue (Na^+ , K^+ , Mg^{2+} , Sr^{2+} , CO_3^{2-} , F, Cl, and SiO_3^{2-} [4,5]) have been proposed for biomedical applications, increasing the defectiveness of the HA structure and its solubility.

At the same time, calcium phosphates (CPs) with the different form $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, stoichiometric composition ($\alpha\text{-}/\beta\text{-Ca}_3(\text{PO}_4)_2$, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6\cdot 5\text{H}_2\text{O}$, $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$, $\text{Ca}_4(\text{PO}_4)_2\text{O}$, $\text{Ca}_2\text{P}_2\text{O}_7$ [6–12]) and higher resorption rate were also considered biomaterials. Later, based

on the salt materials mentioned previously, CPs have been used in a number of applications in traumatology, orthopedics, maxillofacial surgery, and dentistry [13,14].

Investigations of the application of abiogenic substances in medical practice have shown that calcium salts that do not contain phosphate ions (for example, CaCO_3 , CaSO_4 , $\text{Ca}(\text{OH})_2$, and CaSiO_3) also have been proven to have bioactivity [15–18]. This effect is due to the ability of the calcium salts to gradually dissolve in contact with biological fluids and serve as a source of Ca^{2+} ions, which are involved in the process of formation of a hard tissue mineral component to provide the bone-structure formation *de novo*. A combination of HA with substances mentioned previously has been suggested in numerous works. CaCO_3 [19], $(\text{Ca,Mg})_3(\text{PO}_4)_2$ [20], $\beta\text{-CaSiO}_3$ [21–24], or CaSO_4 [25] can be the second component. In the general case, varying the additive amount allows the changing of the resorption rate of materials over a wide range, while addition of calcium silicates (CSS) to $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ also increases the strength characteristics and biocompatibility of the composites [21]. The latter is due to the formation of silanol groups (Si-OH) on the interphase boundary “synthetic material – biological liquid”, acting as active centers in the process of bioapatite formation [26].

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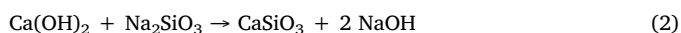
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The participation of silicate ions in the osseointegration processes [27,28] provides the prospect of biomedical use of composites containing $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in mixtures with $\beta\text{-CaSiO}_3$ (β -wollastonite, WT). The search for simple methods for the production of such materials is relevant. Mechanical mixing of HA and WT [21], sol-gel synthesis of apatite in the presence of natural CS particles [22], WT deposition in a suspension of previously obtained $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [23], and a two-step salt crystallization [24,29] are described in the literature. In this paper, the method of preparing mixtures with different HA and WT content by co-precipitating salts in an aqueous solution and following calcination is proposed, and the results of an investigation of the behavior of the synthetic composites in Tris-HCl buffer solution and the synthetic biological fluid (SBF) are described.

2. Materials and methods

2.1. Powder synthesis

The HA/WT composites with different weight ratios were synthesized by the method of chemical coprecipitation of salts with low solubility from water solutions. All reagents were analytical grade and used for synthesis without further purification. $\text{Ca}(\text{OH})_2$, H_3PO_4 , and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ were chosen as the initial reagents to minimize the amount of by-products and impurities in the solid phase formed during precipitation. All syntheses were carried out in plastic vessels. The theoretical amount of HA in powders varied from 0 to 100 wt%. The concentrations of the solutions of the initial reagents were calculated to prepare 2 g of powder using the reactions (1) and (2), as shown in Table 1.



First, the vessel with the appropriate concentration of $\text{Ca}(\text{OH})_2$ suspension was placed on a magnetic stirrer ("Big squid white", IKA) and mixed for 1 min with 1250 rpm speed to uniform $\text{Ca}(\text{OH})_2$ distribution in the fluid volume. Solutions with appropriate concentrations of H_3PO_4 and Na_2SiO_3 were gradually added into the reaction vessel one by one. After the complete addition, the pH of the reaction systems was adjusted to 12.0 by adding 20% NaOH solution. The exposition time was 22–24 h. White precipitate was filtered, washed on the filter by three portions of distilled water (100 ml each), dried at 90 °C to constant weight and ground in a porcelain mortar to a powdery state. The HA/WT composites were obtained by calcining the precipitate at 1000 °C for 2 h in the porcelain crucibles in the muffle furnace "SNOL 6.7/1300" (SNOL-TERM). In this study, each experiment was carried out in triplicate.

2.2. Bioceramics fabrication

The HA/WT composite powders were used as raw materials to prepare bioceramics. Powders (350 mg) were pressed using a manual hydraulic pellet press "Carver 4350. L" under a pressure of 4 metric tons for 5–10 s in a steel press form. The resultant tablets were 2 cm in diameter and 1 mm in height.

Table 1

Concentrations (mol/L) of reagents used for synthesis of 2 g composites HA and WT with different weight ratios.

Reagent Concentration, mol/L	Composite Ratio (HA/WT, wt%)						
	100/0	80/20	60/40	50/50	40/60	20/80	0/100
H_3PO_4	0.060	0.048	0.036	0.030	0.024	0.012	–
Na_2SiO_3	–	0.017	0.034	0.043	0.052	0.069	0.086
$\text{Ca}(\text{OH})_2$	0.100	0.097	0.094	0.093	0.092	0.089	0.086

2.3. Powder characterization

All the resulting precipitates were examined by X-ray diffraction (XRD), FT-IR spectroscopy (FTIR), scanning electron microscopy (SEM), the laser diffraction method and the adsorption method (BET).

Powder diffraction investigations (phase identification and scattering domains (CSD) measurements) were carried out with the diffractometer "XRD-7000" (Shimadzu) at 40 kV and 30 mA using $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation as an X-ray source in the 2θ range from 10° to 60° , where almost all significant peaks of HA/WT composites appear. X-ray patterns were recorded with a 0.05° scan step and scanning speed of $4^\circ/\text{min}$. Identification of the crystalline phases was carried out in the "Sieve+" software package using the PDF-4 database. CSD lengths were calculated with the Debye-Scherrer formula using the reflex at 25.8° for HA and 29.9° for WT.

FTIR spectra were scanned on an IR spectrometer "FT-801" (Simex) using the KBr pellet technique for the range of $500\text{--}4000 \text{ cm}^{-1}$ with 4 and 32 times scanning resolution. The program "ZaIR 3.5" was used to obtain and process the spectra. The results were interpreted according to the literature data [11,30–32].

Scanning electron microscopy (SEM) analysis of the samples was carried out using a "JCM-5700" microscope (JEOL) equipped with an energy dispersive X-ray spectrometer "JED-2300" in a high vacuum mode. The SpotSize parameter was selected as 10, 20 and 50, with the accelerating voltage value from 10 kV to 20 kV and magnification from $500 \times$ to $10000 \times$.

The powder particle size distribution was determined by a laser diffraction method on the laser diffraction particle size analyzer "SALD-2300" (Shimadzu). The complex refractive index for the measurements was equal to $1.65 \pm 0.00i$. Differential curves of the particle distribution by the dimensions were obtained for both average and modal particles, determined using the software package "WingSALD II" (Shimadzu).

The texture characteristics of the powders were determined by the adsorption method using nitrogen adsorption-desorption isotherms at 77.4 K obtained on the analyzer "Gemini VII" (Micromeritics Instrument Corporation). Before adsorption measurements, the samples were trained in a vacuum at 140 °C for 10–12 h. The specific surface area of the powder was determined by the BET method [33].

2.4. Chemical analysis of liquids

The chemical analysis of pure liquids separated from precipitates was carried out. The pH was measured using the pH-meter "pH-150MI" with a combined pH-electrode and thermal sensor. Residual Ca^{2+} , PO_4^{3-} and SiO_3^{2-} concentrations in solution were determined by the photometric method on the spectrophotometer "UV-1200" (EcoView). Calcium was defined by the reaction with Arsenazo III in an alkaline medium. The UV method of phosphate amount determination is based on the interaction between PO_4^{3-} and ammonium molybdate in an acidic medium and a molybdophosphoric heteropolyacid formation. Silicates were detected in a yellow form of molybdosilicic acid, which forms because of the interaction of monomeric-dimeric forms of silicic acid and silicates with ammonium molybdate in an acidic medium. The composition of the precipitates was established as the difference between initial and residual ion concentrations in the mother liquor.

2.5. Investigation of the powder resorption in the Tris-HCl buffer solution

The resorption of HA/WT composite powders was determined by a change in the time of pH and Ca^{2+} , PO_4^{3-} and SiO_3^{2-} concentrations in the Tris-HCl buffer solution. Powder fractions with average diameters of 40–70 μm were prepared for experiments by passing samples through a laboratory sieve. The composites were soaked in the Tris-HCl buffer solution with a powder/liquid ratio equal to 1/200 g/ml, at 22 °C, under static conditions. Plastic containers were used for all Tris-HCl

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