NANOTECHNOLOGIES AND NANOMATERIALS

Synthesis of Nanosized Powders and Coatings of Calcium Phosphates

M. A. Medkov, D. N. Grishchenko, N. I. Steblevskaya, I. V. Malyshev, V. S. Rudnev, and V. G. Kudryavyi

Institute of Chemistry, Far East Branch, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia
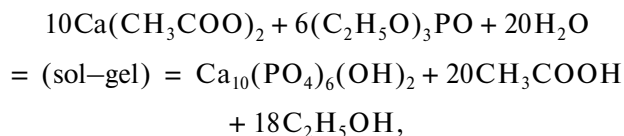*e-mail: medkov@ich.dvo.ru*

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Abstract—Hydroxyapatite powders with a particle size of nearly 100 nm, i.e., rather close to bone crystals shaped as $60 \times 20 \times 5$-nm flattened prisms, were synthesized by the pyrolysis of a solution of calcium oleate in tributylphosphate. The possibility of synthesizing hydroxyapatite coatings on different ceramic materials was demonstrated. The pyrolysis of a solution of strontium oleate in tributylphosphate was established to produce the $Sr_{10}(PO_4)_6(OH)_2$ compound isotypical to hydroxyapatite, which in turn creates prospects for synthesizing materials based on hydroxyapatite with some calcium atoms substituted by strontium.

In recent years, the search for biocompatible materials is conducted all over the world with the purpose of using them in traumatology, orthopedics, and stomatology. This is first of all associated with the growing interest in improving the quality and duration of human life. In particular, the achievement of this purpose implies, the creation of materials for artificial organs and tissues. The materials based on hydroxyapatite and other orthophosphates find wide application in medical practice, including stomatology, traumatology, and orthopedics. The ceramic materials based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and tricalcium phosphate $Ca_3(PO_4)$ are closest to the mineral component of bone tissue. Calcium phosphates are most often synthesized from aqueous solutions using the processes of hydrolysis and precipitation. In practice, the difficulty of the simultaneous monitoring of a great number of control parameters in the synthesis of hydroxyapatite by precipitation from aqueous solutions (pH, composition and concentrations of reagents and admixtures, regime and speed of stirring, temperature, time) may result in the poor reproducibility of the composition and morphology of particles [1]. Some shortcomings are also inherent in the other methods, such as high-temperature solid-phase synthesis ($CaO-P_2O_5$ systems) and sol-gel technology. The solid-phase method requires a prolonged annealing at high temperatures and results in the synthesis of coarse-crystalline materials. The sol-gel methods [2–4] realized, e.g., by the scheme

$$10Ca(CH_3COO)_2 + 6(C_2H_5O)_3PO + 20H_2O$$
$$= (sol-gel) = Ca_{10}(PO_4)_6(OH)_2 + 20CH_3COOH$$
$$+ 18C_2H_5OH,$$

are usually characterized by multiple stages. For this reason, increasing attention is currently focused on hydroxyapatite synthesis methods.

The objective of our work is to develop a method for synthesizing hydroxyapatite and hydroxyapatite-based coatings.

EXPERIMENTAL

Calcium chloride, sodium oleate, oleic acid, and tributylphosphate (TBP) were used as the initial compounds for the synthesis of calcium phosphates. Aqueous solutions of sodium oleate $C_{18}H_{33}O_2Na$ and calcium chloride $CaCl_2 \cdot 4H_2O$ were mixed at a molar ratio of 2 : 1. The mixtures were stirred for 10 min at room temperature to provide the formation of water-insoluble calcium oleate. The calcium oleate precipitate was filtered out, washed with water, and dried for 24 h at room temperature. After being analyzed for the content of calcium, calcium oleate was dissolved in benzene at a temperature of 50°C. The calculated amounts of a benzene solution of TBP were added to the solution of calcium oleate in benzene. The Ca : TBP molar ratios in these mixtures were 1.5–1.7 : 1. After being distilled from the solvent, the mixtures were heated for 1 h at a temperature of 200°C, calci-
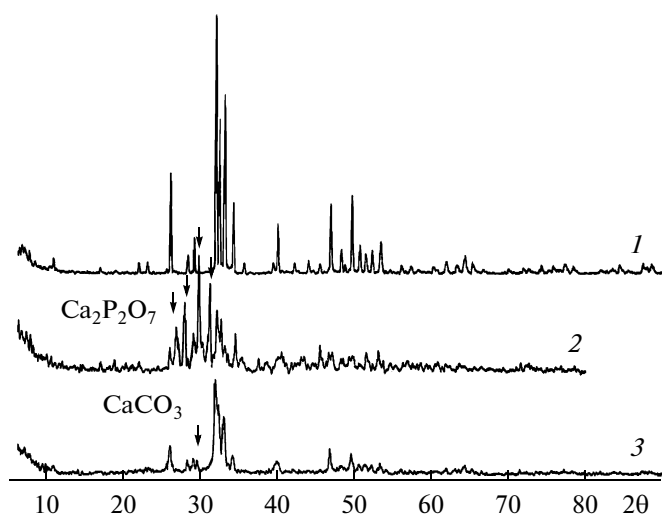
Fig. 1. X-ray diffraction patterns of calcium phosphates: (*1*) hydroxyapatite, (*2*) hydroxyapatite–$Ca_2P_2O_7$, and (*3*) hydroxyapatite–$CaCO_3$ composites.

nated in a muffle furnace up to the temperature of 600°C at a heating rate of 10°C/min, and then cooled down to the room temperature immediately in the furnace.

Hi-Nicalon fiber and ZrO_2–TiO_2/Ti undercoating layer were used as substrates for hydroxyapatite coatings. A ZrO_2–TiO_2/Ti coating was formed electrochemically in $Zr(SO_4)_2$, an aqueous electrolyte, for 10 min at a current density of 8 A/dm². The X-ray diffraction patterns of powder and coating samples were taken on a DRON-2.0 diffractometer in CuK_α radiation. The thickness of films was measured with a VT-201 thickness gauge. The elemental composition of coatings (depth of analysis was ~2–5 μm) was determined on a JXA-8100 electronic X-ray spectral microanalyzer (Japan). The phase composition was determined on a D8 ADVANCE X-ray diffractometer (Germany) in CaK_α radiation. The X-ray diffraction patterns were analyzed using the EVA retrieval software with the PDF-2 database.
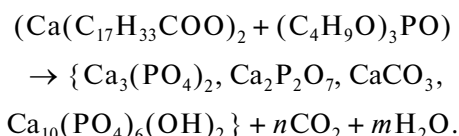
RESULTS AND DISCUSSION

The most widespread substituent in the crystal lattice of bioapatite is carbonate, which attains 2–8% of the total mass of the bone mineral [5]. Along with calcium phosphate and carbonate, the bone mineral contains a large number of other elements, such as sodium, magnesium, strontium, zinc, copper, iron, chlorine, and fluorine in different amounts [6]. It is known that these elements have an effect on the characteristics of the bone mineral, such as crystallinity, destruction behavior, and mechanical properties. The bioeffects of inorganic compounds on the bone-formation processes that are important for the therapy of the

diseases and destruction of bones are also described. An example of this therapy is the clinical application of strontium ranelate to cure osteoporosis [7].

The introduction of doping inorganic compounds that are either present in bone or able to produce some effect on its development into hydroxyapatite is attractive for curing the diseases associated with the injury of bones, so a number of calcium phosphate bone substitutes with such an inorganic dopants as copper, zinc, strontium carbonate, and others are currently developed. In our earlier work [8], it has been shown that the pyrolysis of metal extracts results in the formation of metal phosphates, if TBP is used as an extragent. It was of interest to synthesize calcium phosphates, in particular hydroxyapatite doped with different metals, using the extraction pyrolytic method [9].

Calcium is most efficiently extracted from acidic solutions with 100% TBP in the form of rhodanide complexes [10]; however, in this case, TBP will always have an excess concentration with respect to calcium in the organic phase, which leads to the formation of pyrophosphate during pyrolysis (Fig. 1). If TBP is diluted with an inert solvent, the distribution coefficients of calcium drop sharply. A mixture of TBP with a carboxylic acid also poorly extracts calcium.

In our opinion, a convenient method for obtaining organic solutions with a specified TBP : Ca ratio is the dissolution (liquid/solid-phase extraction) of calcium carboxylate in a diluted solution of TBP. After the solvent for the synthesis of calcium phosphate is distilled out, the pyrolysis of, e.g., calcium oleate, is performed at 700°C by the following scheme:

$$(Ca(C_{17}H_{33}COO)_2 + (C_4H_9O)_3PO)$$
$$\rightarrow \{Ca_3(PO_4)_2, Ca_2P_2O_7, CaCO_3,$$
$$Ca_{10}(PO_4)_6(OH)_2\} + nCO_2 + mH_2O.$$

Depending on the TBP : Ca ratio in an inert solvent, it is possible to synthesized different phosphates, such as tricalcium phosphate, calcium pyrophosphate, and hydroxyapatite. Moreover, this method of synthesis allows us to obtain hydroxyapatite partially substituted, in particular, by the carbonato group and also to introduce doping elements, such as magnesium, strontium, zinc, copper, iron, etc. in the from of carboxylates. In particular, when the TBP : Ca ratio in the organic phase is decreased, a hydroxyapatite–calcium carbonate mixture is formed as a result of pyrolysis (Fig. 1).

Here, we should note that elements such as copper, zinc, and iron are convenient to introduce into hydroxyapatite organic solutions in the form of extracts. Another advantage of the proposed method is the possibility and simplicity of film deposition, in particular films of hydroxyapatite, onto inert ceramic materials, such as titanium and aluminum oxides and Hi-Nicalon fiber-based materials (Fig. 2).

A true solution without suspended particles is formed upon the dissolution of calcium carboxylate in a TBP–organic solvent mixture. In particular, this is an advantage of the proposed method over the sol-gel technique. To obtain coatings, porous ceramic is impregnated with the above-mentioned solution. This is followed by the stages of the removal of a solvent and the calcination at a temperature of 700°C. All operations in synthesizing of powders and coatings using calcium oleate as an initial compound take nearly 2 h, which is another advantage compared to the sol-gel method [2–4]. The phase composition and morphology of the synthesized samples of powders and coatings were studied by X-ray powder diffraction analysis and scanning electron microscopy (SEM) (Figs. 3–5).

We have also verified the possibility of depositing hydroxyapatite onto systems close to real titanium implants. A ceramic-like coating representing a mixture of zirconium and titanium oxides (ZrO_2–TiO_2/Ti system) was preliminary deposited onto a $2 \times 2 \times 0.5$-cm sheet VT1-0 titanium (>99% Ti) specimen by the plasma-electrolytic oxidation (PEO) method [11, 12]. The ZrO_2–TiO_2/Ti coating was formed electrochemically in $Zr(SO_4)_2$, an aqueous electrolyte, for 10 min at a current density of 8 A/dm^2. The features of the treatment and some properties of the coatings are described in [12]. It should be noted that the PEO method allows the synthesis of oxide systems with various compositions, including the introduction of both oxides and compounds of many metals of the Periodic Table into the formed coatings, and may be of interest from the medical viewpoint in the long term.

Some characteristics of the used titanium-based oxide coating are given below:

Thickness, ~6 μm;

Concentrations, at %:

Zirconium, 13.1;

Titanium, 9.9;

Oxygen, 52.3;

Carbon, 24.6.

The data on elemental analysis were obtained by X-ray spectral microprobe analysis (microprobe) and averaged over a surface area of 200–300 μm^2. The surface layer was analyzed to a depth of 2–5 μm (the electron penetration depth in analysis depends on a material). The measurement error for the studied coatings is ~10%. The composition of ZrO_2–TiO_2 coatings with the zirconium-enriched upper layer, the thickness of which is 6–9% of the total thickness of a coating, is up to 40 at % [12].

The presence of carbon in coatings is presumably caused by its insertion from an electrolyte containing the carbonic acid hydrolysis products under the action of spark electric discharges due to the absorption of carbon dioxide from the atmosphere (plasma-electrolytic oxidation, anodizing in electrolytes at spark and
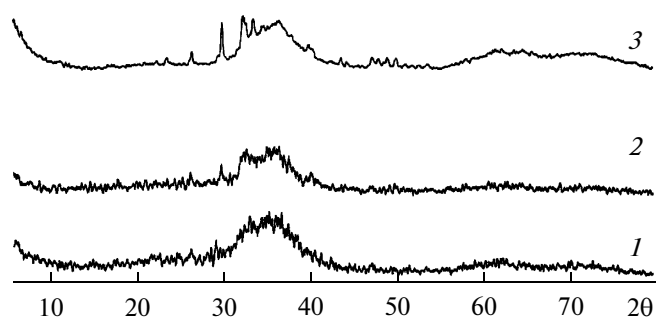

Fig. 2. X-ray diffraction pattern of Hi-Nicalon fiber coated with (*1*) 1, (*2*) 3, and (*3*) 6 hydroxyapatite layers.
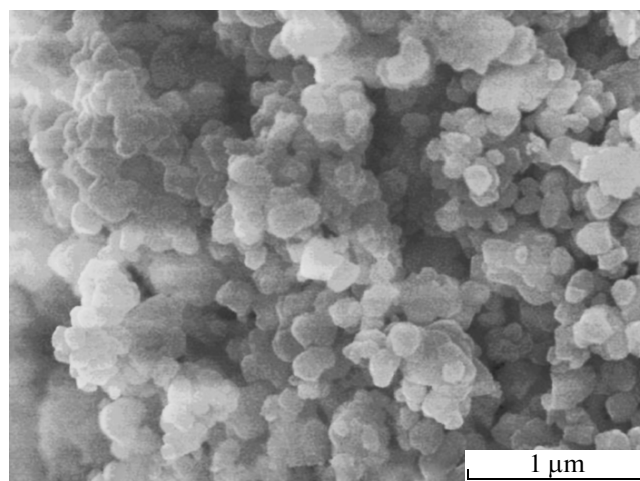

Fig. 3. SEM photo of hydroxyapatite.

microarc voltages). There are some grounds (data of high-resolution scanning electron microscopy, energy dispersion analysis, and X-ray photoelectron spectroscopy) for believing that carbon is present in coatings in the form of nanosized carbon formations, as well as in the structure of metal carbides.

Using the given instrument, we also obtained the photos of the surfaces of coatings in reflected electrons before (Fig. 5a) and after (Fig. 5b) their impregnation and calcination with the formation of calcium phosphates. It can be seen that the treatment of ZrO_2–TiO_2/Ti composites under the above-described conditions modifies the relief of the initial coating. The relief becomes rougher, the differences between the heights of protrusions and depressions are increased, and the fine initial morphology of the surface becomes undistinguishable. From our viewpoint, the given transformations are due to the formation of the surface crust of Ca(II) phosphates. This conclusion is confirmed by the X-ray powder diffraction analysis data shown in Fig. 6.

The monoclinic and tetragonal ZrO_2, TiO_2 (anatase, rutile) and Ti reflections can be seen in the X-ray
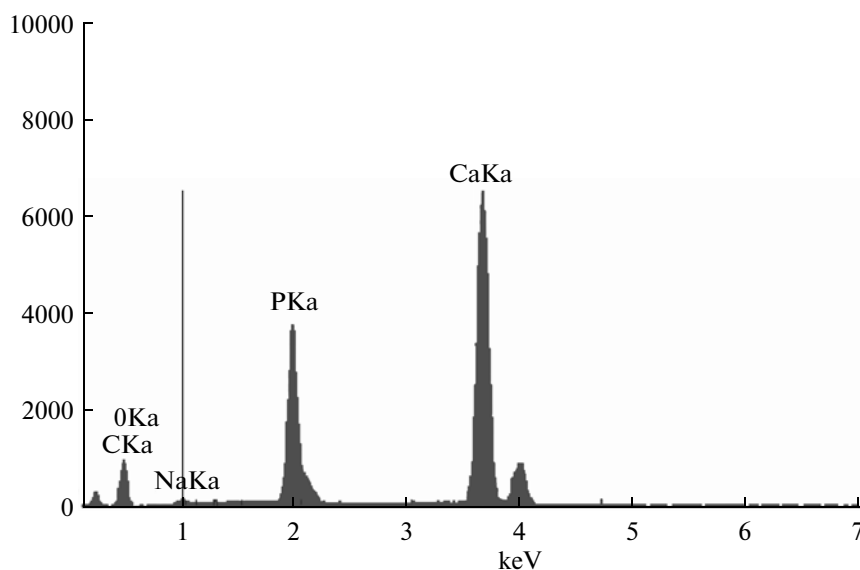
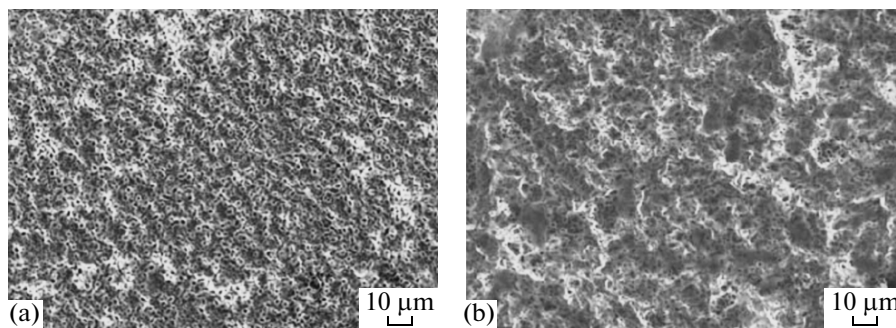**Fig. 4.** Energy dispersion spectrum of the hydroxyapatite−CaCO$_3$ composite.

Fig. 5. Amplitude SEM photos of (a) the initial and (b) additionally modified coatings of calcium phosphates.

● ZrO$_2$-monoclinic
○ ZrO$_2$-tetragonal
■ TiO$_2$-anatase
□ TiO$_2$-rutile
△ Ca$_3$(PO$_4$)$_2$
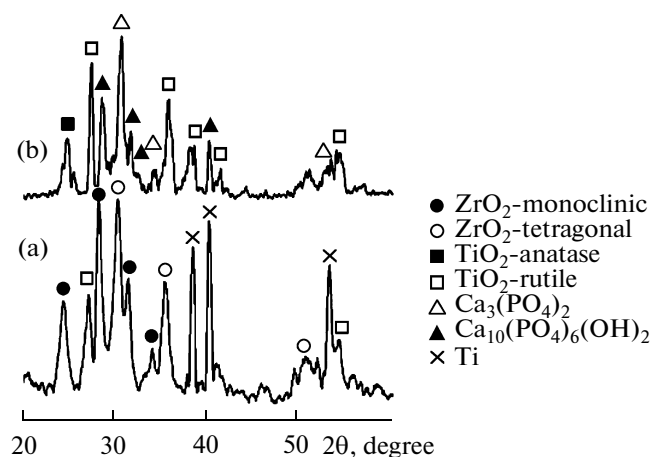▲ Ca$_{10}$(PO$_4$)$_6$(OH)$_2$
× Ti

Fig. 6. X-ray diffraction patterns of (a) the initial ZrO$_2$–TiO$_2$/Ti composite and (b) the same composite after the deposition of calcium phosphates.

diffraction pattern of the initial composite. The signals that correspond to the crystalline phosphates Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and Ca$_3$(PO$_4$)$_2$ additionally appear after extraction-pyrolytic treatment. The systems of hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, tricalcium phosphate Ca$_3$(PO$_4$), and ZrO$_2$ on a titanium implant may have good prospects in medical practice. While, as noted above, the developed approaches even better allow the additional introduction of compounds of some necessary elements of the Periodic Table into the composition of powders and coatings.

As can be seen from Fig. 3, the size of particles of hydroxyapatite synthesized by the pyrolysis of a solution of calcium oleate in TBP is nearly 100 nm; i.e., they are rather close to bone crystals shaped as 60 × 20 × 5-nm flattened prisms, whereas the solid-phase methods allows the synthesis of only coarse-crystalline hydroxyapatite samples.

The compound Sr$_{10}$(PO$_4$)$_6$(OH)$_2$ isotypical to hydroxyapatite is formed in the pyrolysis of a solution

of calcium oleate in TBP. Hence, the proposed method is very convenient for the synthesis of materials based on hydroxyapatite, in which some calcium atoms are substituted by strontium.

CONCLUSIONS

A simple method for the synthesis of hydroxyapatite via the reaction of calcium oleate and TBP solutions has been developed. The method allows the synthesis of nanosized hydroxyapatite powders and coatings doped with the admixtures that make up an integral part of the bone tissue. The possibilities of the method have been exemplified by the deposition of hydroxyapatite onto systems that are close to real titanium implants.

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