MATERIALS FOR HUMAN LIFE SUPPORT AND ENVIRONMENTAL PROTECTION

Synthesis of Cobalt Ferrite/Piezoelectric Composite Particles for Use as Magnetoelectric Elements in Bone Implants

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Abstract—The issues of designing bone implants capable of creating an electrical stimulus for bone tissue regeneration under the influence of an external magnetic field are considered. A promising method for generating local electric fields is the use of magnetoelectric (multiferroid) micro- and nanoparticles that are polarized under the action of an external magnetic field and create electric fields comparable in amplitude to endogenous ones. Of practical interest are composite magnetoelectric particles consisting of a ferrimagnetic core and a piezoelectric shell brought into close mechanical contact. Modeling the magnetoelectric effect in a composite particle is carried out; composite particles with cobalt ferrite as a magnetostrictor are fabricated, and the issues of the chemical interaction of phases are discussed.

Keywords: bone implant, electrical stimulus, magnetoelectric composites, ferrimagnets, piezoelectrics, cobalt ferrite, barium titanate, potassium–sodium niobate, chemical interaction of phases **DOI:** 10.1134/S2075113322020393

INTRODUCTION

Solving the problems of bone tissue regeneration requires the design of new materials that could create a variety of stimuli affecting the growing bone. Among these stimuli, local electric fields are of particular interest; they can modulate the work of ion channels in cell membranes [1], in particular, by increasing the levels of intracellular Ca^{2+} and protein kinase C and stimulating the release of nitric oxide (NO) and prostaglandin-E2 (PGE2), which, in turn, act as anabolic regulators of bone growth [2, 3].

The use of magnetoelectric (multiferroid) microand nanoparticles, which are polarized under the action of an external magnetic field and create electric fields comparable in amplitude with endogenous ones, is considered a promising method for generating local electric fields [4–10]. Composite magnetoelectric particles consisting of dissimilar parts, for example, a ferrimagnetic core and a piezoelectric shell, brought into close mechanical contact, are of practical interest. Magnetoelectric particles are composites with the phase connectivity of the ferrimagnet and the piezoelectric type 0-3. Fibrous (1-3) and laminate (2-2)composites, although they demonstrate large values of magnetoelectric (ME) effect, have their drawbacks [11]. At the same time, composites of type 0-3 are easy to manufacture, have good electromechanical coupling between phases, and, in addition, allow minimizing leakage currents arising from the aggregation of particles of the ferrimagnetic phase and reducing the piezoelectric response [12]. Composites of type 0-3 can be made both by mixing and subsequent sintering of ferrimagnet and piezoelectric powders and by creating core—shell particles. Despite the noticeable advantages of the latter option (in particular, the possibility of achieving better electromechanical coupling), it should be noted that, owing to improved epitaxial phase matching at the interface, certain successes have recently been achieved in the implementation of the ME effect in composites obtained by mixing and sintering [13].

It is assumed that ceramic granules or particles with contacting phases of ferrimagnet and piezoelectric will be embedded in the macroporous matrix of the implant made of calcium phosphate ceramic or hydrogel by 3D printing [14]. The magnetoelectric response can be obtained both from particles encapsulated in the implant matrix and during their migration into the extracellular matrix after partial resorption of the implant. To achieve noticeable magnitudes of the ME effect, one should choose ferrimagnets with a large magnetostriction and piezoelectrics with a large piezomodule [11]; the cytocompatibility of the respective phases is equally important. From this point of view, cobalt ferrite $CoFe_2O_4$ and lead-free piezoelectrics, namely, barium titanate $BaTiO_3$, potassium–sodium niobate $Na_{0.5}K_{0.5}NbO_3$ (KNN), and bismuth ferrite $BiFeO_3$, which itself is a single-phase multiferroic, are of interest. In the manufacture of composite ME particles and their introduction into a ceramic calcium phosphate matrix, the issues related to the chemical compatibility of individual phases at temperatures of synthesis and sintering [12] (that is, interaction in cobalt ferrite/piezoelectric, cobalt ferrite/calcium phosphate, and piezoelectric/calcium phosphate pairs) are of great importance.

The purpose of this work is to simulate the magnetoelectric effect in a composite particle, select its design, fabricate composite particles with cobalt ferrite as a magnetostrictor, and study the chemical interaction of phases.

MATERIALS AND METHODS

Modeling the ME Effect in a Cobalt Ferrite/Piezoelectric Composite Particle

Modeling the operation of an ME element of the core-shell type was carried out for two types of composite spherical particles: (1) a cobalt ferrite core and a piezoelectric shell and (2) a piezoelectric core and a cobalt ferrite shell, in order to (a) substantiate the choice of particle design and (b) evaluate the efficiency of the ME element. Modeling was carried out in the COMSOL Multiphysics software environment. A spherical particle with a shell 100 nm in diameter (shell thickness 5 nm) was placed in a magnetic field with an induction of up to 3 T and in accordance with the constitutive equations (using a set of piezomagnetic and piezoelectric constants available in the COMSOL environment, as well as the data of the density functional theory (DFT) calculations [15]) of the magnetic and piezoelectric phases brought into a tight mechanical contact (ideal electromechanical bond); the fields of mechanical stresses created as a result of cobalt ferrite deformation in a magnetic field and the electric fields caused by these stresses as a result of deformation of a piezoelectric were calculated using the finite element methods. Cobalt ferrite was defined as an anisotropic material (the components of the elastic modulus tensor were taken from the Materials Project MP-36738 file). The components of the tensors of elastic constants and piezomodules of piezoelectrics, as well as the permeability, were taken from the Materials Project files [15] (as well as from [16– 18]): BaTiO₃ (MP-5777), BiFeO₃ (MP-23501), KNbO₃ (MP-4342), and NaNbO₃ (MP-4681).

Synthesis of Cobalt Ferrite/Piezoelectric Composites

Cobalt ferrite/barium titanate composites. The $CoFe_2O_4$ particles of various diameters were obtained by coprecipitation during mixing of 25 mL of 0.4 M

FeCl₃ \cdot 7.5H₂O and 25 mL of 0.2 M CoCl₂ \cdot 6H₂O in a medium of 25 mL of 3 M NaOH; 100 µL of oleic acid was also added to prevent in situ aggregation of particles. Then the mixture was stirred at 60°C for 1 h [19]. A BaTiO₃ coating solution was prepared as follows: 30 mL of an aqueous suspension of 0.029 g BaCO₃ and 0.1 g citric acid was added to 30 mL of an ethanol solution of 1 g citric acid and 0.055 mL of titanium butylate. The CoFe₂O₄ nanoparticles (0.1 g) were dispersed in 60 mL of a BaTiO₃ precursor solution under intense ultrasonic treatment. After prolonged sonication, the solution was evaporated to gelation at 60°C with stirring and then calcined at 780°C for 5 h to obtain CoFe₂O₄/BaTiO₃ nanoparticles [20].

Cobalt ferrite/potassium-sodium niobate composites. Potassium-sodium niobate was synthesized by photopolymerization of a solution of potassium and sodium nitrates and ammonium oxalatoniobate $(NH_4)[NbO(C_2O_4)_2] \cdot xH_2O$ in polyethylene glycol diacrylate (PEGDA-700; TPO-Li photoinitiator) and subsequent annealing of the hydrogel at 600°C. This method is novel and was applied by us for the first time both for the synthesis of the KNN powder and for the preparation of the cobalt ferrite/KNN composite of the core/shell type. In the latter case, cobalt and iron nitrates were also introduced into solution before polymerization. It should be noted that, in contrast to the Pechini method [21], the amount of residual carbon in such a powder after annealing at 600°C was rather small (a white powder was formed).

Study of the Chemical Interaction between Phases

We studied the chemical interaction of the following phases: (1) $Ca_3(PO_4)_2$ and $CoFe_2O_4$, (2) $Ca_3(PO_4)_2$ and $BaTiO_3$, (3) $Ca_3(PO_4)_2$ and $K_{0.5}Na_{0.5}NbO_3$ (KNN), (4) $Ca_3(PO_4)_2$ and $BiFeO_3$, (5) $CoFe_2O_4$ and $BaTiO_3$, (6) $CoFe_2O_4$ and KNN, (7) $CoFe_2O_4$ and $BiFeO_3$. The study of the interaction of phases was carried out in two ways, in powders and in contacting tablets: (a) the powder mixture (1:1 molar ratio) was investigated by the methods of thermogravimetric (TG) and differential thermal (DTA) analysis (TG/DTA); pressing from the same mixture was investigated by the method of dilatometry (the temperature of the onset of sintering was determined); annealing was carried out at a selected temperature for 6 h; the resulting powder was examined by X-ray diffraction (XRD) analysis; (b) the samples were separately compressed into tablets from each powder; the obtained samples were sintered; each pair of tablets was brought into contact under load and then subjected to thermal treatment at a selected temperature (in the range of 800–1200°C) for 6 h; the place of contact of the tablets was examined by scanning electron microscopy (SEM) and X-ray (EDX) microanalysis on a transverse section.

Thermal Analysis

TG/DTA of the samples was carried out on a STA 409 PC Luxx synchronous thermal analyzer with vertical loading of samples (Netzsch, Germany). The measurements were carried out in an air or argon atmosphere in the temperature range from 40 to 1300°C with heating rates of 2.5, 5, 10, and 20°C. Weighed portions of the samples (no more than 20 mg) were placed in alundum crucibles. To study the composition of exhaust gases during heating, we used an Aèolos QMS 403 C quadrupole mass spectrometer (Netzsch, Germany) with heating of the inlet capillary system.

Dilatometry

The linear shrinkage of the pressed OCF and zOCF samples was measured in a DIL 402 C horizontal dilatometer (Netzsch, Germany) in the mode up to 1200°C at a heating rate of 5° C/ min. The pressed samples were tablets 8 mm in diameter and 3 mm in height.

X-Ray Diffraction Analysis

X-ray diffraction studies were performed on a Rigaku D/Max-2500 diffractometer with a rotating anode. Registration was carried out in the reflection mode in the standard Bragg–Brentano geometry using Cu K_{α} radiation ($\lambda = 1.54183$ Å). The following registration parameters were chosen: angle interval $2\theta = 2^{\circ}-60^{\circ}$, 2θ step = 0.02°, registration rate of spectra of 5 deg/min. Qualitative analysis of the obtained X-ray diffraction patterns was carried out by the WinXPOW program using files from the ICDD PDF-2 database.

Scanning Electron Microscopy and X-Ray Microanalysis

The synthesized powders, as well as the microstructure of ceramic samples, were studied using a LEO SUPRA 50VP scanning electron microscope with a field emission source (Carl Zeiss, Germany). The samples were glued to a copper substrate using conductive carbon tape. The accelerating voltage of the electron gun was 1–20 kV. Images were acquired in secondary electrons at magnifications up to 100000 using SE2 and InLens secondary electron detectors. For X-ray microanalysis, we used an INCA microanalysis system (Oxford Instruments, UK).

Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed on a Libra 200 microscope (Carl Zeiss, Germany) with a thermal-field emission cathode at an accelerating voltage of 200 kV. Images were detected using an Ultra Scan 4000 CCD camera (Gatan, United States). Gwyddion free program was used for

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processing of obtained images. An Ω filter (Carl Zeiss, Germany) was used to record the characteristic electron energy loss spectra (EELS) and obtain images of characteristic losses. To carry out X-ray (EDX) microanalysis, we used an Aztec microanalysis system (Oxford Instruments, UK) for mapping and scanning along the selected directions.

RESULTS AND DISCUSSION

Study of Phase Interaction in Composite Particles

Ca₃(PO₄)₂ and BaTiO₃. On the dilatometric curve of the powder billet of a Ca₃(PO₄)₂ and BaTiO₃ mixture, we observed an inflection at \approx 1000°C, which is most likely associated with the formation of a new phase. According to XRD data, the phases of calcium titanate CaTiO₃, mixed barium–calcium phosphate Ba₂Ca(PO₄)₂, barium titanate Ba₄Ti₁₁O₂₆, and tricalcium phosphate β -Ca₃(PO₄)₂ doped with barium are formed as a result of the interaction.

The interaction is also confirmed by the X-ray microanalysis data from dense BaTiO₃ and Ca₃(PO₄)₂ tablets brought into contact and annealed for 6 h at 1200°C. There is a diffusion of barium and titanium toward Ca₃(PO₄)₂ and also, to a lesser extent, phosphorus toward BaTiO₃; the content of barium and titanium in the Ca₃(PO₄)₂ tablet is; 13 and 2 wt %, respectively, and the phosphorus content in the BaTiO₃ tablet is ≈ 1 wt %. By the depth of diffusion, taking into account the time of heat treatment, it is possible to estimate the effective diffusion coefficient *D* of the corresponding ions by the formula

$$D \approx \frac{\langle x \rangle^2}{2t},\tag{1}$$

where $\langle x \rangle$ is the average depth to which diffusion of the corresponding ion occurs, cm; and *t* is the exposure time at the synthesis temperature (6 h = 3600 s). The estimate gives the values $D \approx 2.3 \times 10^{-11}$, 3.7×10^{-8} , and 3.7×10^{-8} cm²/s for PO₄³⁻, Ba²⁺, and Ti⁴⁺, respectively.

Ca₃(PO₄)₂ and K_{0.5}Na_{0.5}NbO₃ (KNN). According to XRD data, at 900°C, mixed potassium–calcium phosphate Ca₁₀K(PO₄)₇, as well as the phase of calcium niobate Ca(NbO₃)₂, is formed. DTA and dilatometry also confirm the presence of interaction between the phases. According to the X-ray microanalysis data, there is practically no diffusion of calcium ions and phosphate anions into the potassium– sodium niobate tablet; the fractions of calcium and phosphorus are <0.5 wt %. At the same time, potassium diffuses into Ca₃(PO₄)₂ to a depth of about 100 µm (which corresponds to an efficient diffusion coefficient of $\approx 2.3 \times 10^{-9}$ cm²/s); its fraction at this depth is ≈ 2 wt %.

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Table 1. Distribution of mechanical stresses in a spherical ME element in a 1 T field (vertical direction)n)
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Composite type	Cobalt ferrite (core)/piezoelectr	ric Piezoelectric (core)/cobalt ferrite
Cobalt ferrite/barium titanate		2 The PROJECTION Languages multicle PHOL
Cobalt ferrite/bismuth ferrite		s) as the same, isotropic which as the interval isotropic which are the interval isotro
Cobalt ferrite/NaNbO ₃		All and the state state and the state and th
Cobalt ferrite/KNbO ₃		1000 1000 <t< td=""></t<>

 $CoFe_2O_4$ and $BaTiO_3$. In the $CoFe_2O_4$ -BaTiO₃ system, an interaction is observed, which, on the basis of the XRD data, leads to the formation of barium hexaferrite BaFe₁₂O₁₉. An endothermic peak associated with the onset of melting is observed on the DTA curve in the region of 1300°C. At the same time, the individual components of the mixture are melted at higher temperatures—1570°C for cobalt ferrite and 1670°C for tricalcium phosphate. This means the presence of a eutectic on the corresponding phase diagram. According to X-ray microanalysis data, mutual diffusion of calcium, phosphorus, cobalt, and iron occurs in the contact area of cobalt ferrite and barium titanate tablets. In the near-contact area in the cobalt ferrite tablet, up to 1.5 wt % Ba and up to 0.5 wt % Ti (the last value is at the error level) were observed; in a tablet of barium titanate, up to 2 wt % Fe and 1 wt % Co were observed.

 $CoFe_2O_4$ and $K_{0.5}Na_{0.5}NbO_3$ (KNN). Apparently, in this system, the phase interaction does not occur up to 1000°C, which is also confirmed by the X-ray micro-

analysis data. However, given the mobility of potassium, interactions should not be completely ruled out.

In the $Ca_3(PO_4)_2$ -BiFeO₃ system, double bismuth-calcium phosphate appears even at 800°C, and in the CoFe₂O₄-BiFeO₃ system, the interaction looks most pronounced: according to the X-ray microanalysis data, at 800°C, bismuth penetrates through the entire thickness of the CoFe₂O₄ tablet with the formation of a mixed cobalt-bismuth oxide phase.

Modeling the Magnetoelectric Behavior of a Cobalt Ferrite/Piezoelectric Composite Particle

The visualization of calculations is presented in Tables 1-4. The simulation results allow the following conclusions to be drawn:

(1) In a magnetic field, a transverse expansion of the magnetostrictor occurs, which causes mechanical stresses in the piezoelectric in contact with it. The voltage level is higher in the cobalt ferrite (core)/piezoelectric (shell) variant. The magnitude of stresses in various piezoelectrics is arranged in the fol-

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Table 2. Distribution of potential in a pie	ezoelectric as a result of its def	formation in cobalt ferrite/bar	ium titanate particles
in different fields (the outer surface of the	e particle is grounded)		-

Field, T	Cobalt ferrite (core)/t	oarium titanate	Barium titanate (cor	e)/cobalt ferrite
0.1				
0.5				
1.0				
3.0				

lowing order: cobalt ferrite > barium titanate > (potassium niobate > sodium niobate) (=KNN) (Table 1), which correlates with the rigidity of their lattices (with the exception of bismuth ferrite, where, apparently, the values of elastic moduli are overestimated).

(2) The electric field arising owing to the piezoelectric effect gives the following series in its magnitude: bismuth ferrite > barium titanate > (potassium niobate > sodium niobate) (=KNN) (Tables 2-4), which correlates with the rigidity of their lattices. However, from the point of view of the values of the d_{33} component of the piezomodule, the greatest effect should be observed for barium titanate (which probably indicates the need to correct the tensors of the elastic constants C and the piezomodule d for bismuth ferrite). The most important point is that only in the case of cobalt ferrite (core)/piezoelectric (shell) composite does the electric field "leave" the ME particle (Tables 2 and 3). This can be understood on the basis that. in the case of a piezoelectric (core)/cobalt ferrite (shell) particle, cobalt ferrite, as a more conductive material than a piezoelectric, actually shields the field induced by the core deformation. Thus, it is composite particles of the cobalt ferrite (core)/piezoelectric (shell) type that are of practical interest for the implementation of the ME effect.

(3) Grounding the piezoelectric shell (and placing it in a conductive medium), as expected, removes the electric field outside the particle. In this regard, it is necessary to understand how quickly the field will disappear when a particle is placed in an electrolyte solution (for example, a saline solution), since this will determine the protocol for the field impact on biological tissue containing such ME particles (constant field or alternating field of a certain frequency and strength).

(4) Taking into account the high reactivity of bismuth ferrite established above, the following composite ME particles are promising: cobalt ferrite (core)/barium titanate and cobalt ferrite (core)/KNN.

Structure of the Synthesized Cobalt Ferrite/Piezoelectric Composite Particles

Cobalt ferrite/barium titanate composites. The composite structure was investigated by TEM. To assess the distribution of the components, we used EEL spectroscopy (Fig. 1a) with registration of an image at the absorption edges of FeL and TiL

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Field, T	Cobalt ferrite (core)/barium titanate	Barium titanate (core)/cobalt ferrite
0.1		
0.5		
1.0		
3.0		

Table 3. Distribution of potential in cobalt ferrite/barium titanate particles placed in a dielectric (aluminum oxide)

 Table 4. Comparison of the potential distribution in cobalt ferrite (core)/piezoelectric particles placed in a dielectric (aluminum oxide) in a 1 T field

Composite	Cobalt ferrite/barium titanate	Cobalt ferrite/bismuth ferrite	Cobalt ferrite/KNbO ₃	Cobalt ferrite/NaNbO ₃
Potential distribution				

(Figs. 1b–1d). X-ray (EDX) microanalysis mapping was unsuccessful owing to the strong X-ray Fe*K* line signal from the steel parts of the microscope column (Fig. 1e). The images in the characteristic losses of iron and titanium suggest that this composite has in its structure a core containing iron (particle size no more than 30 nm) and a shell containing titanium and bar-

ium with a thickness less than 10 nm. The analysis of radial intensities reduced to ring electron diffraction patterns (Fig. 2) makes it possible to unambiguously identify the phases of cobalt ferrite and barium titanate.

Cobalt ferrite/KNN composites. The composite was obtained by photopolymerization of a PEGDA-



0 $0.01 \ 0.02 \ 0.03 \ 0.04 \ 0.05 \ 0.06 \ 0.07 \ \mu m$ 0

Ba L Ti K

Fig. 1. (a) EELS of cobalt ferrite/barium titanate composite particles; (b) TEM image of cobalt ferrite/barium titanate composite; (c) image of composite in characteristic FeL losses; (d) image in characteristic TiL losses; (e) EDX/TEM scanning along a selected line.

based hydrogel containing salts of all cations. According to TEM data, the composite has an inhomogeneous morphology characterized by the presence of relatively large (up to 200 nm) particles with light contrasting inclusions, as well as particles covered with an

amorphous layer, sometimes located separately by aggregates of small (less than 50 nm) particles (Fig. 3). Not in all cases it is possible to identify the KNN phase, which was obtained under similar conditions and gives small regular prismatic crystals (about 20 nm

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Fig. 2. (a) Electron diffraction patterns of cobalt ferrite/barium titanate composites; (b) phase identification by radial intensity distribution.

in size) with distinct diffraction and crystal lattice resolution (Fig. 4). The possible distribution of elements in composite particles was analyzed using X-ray (EDX) microanalysis in the mode of mapping and scanning along selected lines (Fig. 5). It can be seen that in some cases niobium is located not in the shell, but in the core. Thus, within the scope of the work, we managed to synthesize a cobalt ferrite/barium titanate composite of the core/shell type with a ferrite core size of about 30 nm and a barium titanate shell thickness of about 10 nm. Such particles can be considered satisfactory for use as ME composite particles. In the case of the cobalt ferrite/KNN composite, we failed to produce a



Fig. 3. TEM images and electron diffraction patterns of different parts of cobalt ferrite/potassium-sodium niobate (KNN) composite with identification of the constituent phases (bottom).

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Fig. 4. (a) Electron diffraction pattern and TEM image of the potassium–sodium niobate powder obtained from PEGDA hydrogel; (b) interpretation of the ring electron diffraction pattern and EELS.



Fig. 5. Distribution of elements in the cobalt ferrite/potassium–sodium niobate composite particles according to EDX/TEM data: (a) mapping, (b) scanning along the line.

satisfactory core/shell composite with a ferrite core. In general, it should be emphasized that it is necessary to develop a multipurpose procedure for the synthesis of cobalt ferrite/barium titanate and cobalt ferrite/KNN composites with isometric (spherical) cobalt ferrite cores and a piezoelectric shell uniform in thickness.

CONCLUSIONS

The results of modeling composite ME particles show that the level of mechanical stresses is higher in the cobalt ferrite (core)/piezoelectric (shell) variant. The electric field arising owing to the piezoelectric effect in its magnitude gives the series for particles with shells of bismuth ferrite > barium titanate > potassium-sodium niobate, which correlates with the rigidity of their lattices. The most important point is that only in the case of a cobalt ferrite (core)/piezoelectric (shell) composite is the electric field observed outside the ME particle. This can be understood on the basis that, in the case of a piezoelectric (core)/cobalt ferrite (shell) particle, cobalt ferrite, a more conductive material than a piezoelectric, actually shields the field induced during the core deformation. Thus, it is the composite particles of the cobalt ferrite (core)/piezoelectric (shell) type that are of practical interest for the implementation of the ME effect.

Grounding the piezoelectric shell (and placing it in a conductive medium) leads to the disappearance of the electric field outside the particle. In this regard, it is necessary to understand how quickly the field will disappear when a particle is placed in an electrolyte solution (for example, a saline solution), since this will determine the protocol for the action of the field on biological tissue containing such ME particles (constant field or alternating field of a certain frequency and strength).

Taking into account the high reactivity of bismuth ferrite, the following composite ME particles are promising for practical use: cobalt ferrite (core)/barium titanate and cobalt ferrite (core)/potassium sodium niobate. In the latter case, it is necessary to develop a reliable sol-gel procedure for building up a piezoelectric shell.

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