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BIOCOMPOSITE PLASMA-SPRAYED COATINGS BASED ON ZINC-SUBSTITUTED HYDROXYAPATITE: STRUCTURE, PROPERTIES, AND PROSPECTS OF APPLICATION

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The method of synthesis of a zinc-substituted hydroxyapatite powder is presented, and the technology of creating coatings by its spraying is described. The results of studies on the morphological, physical, and chemical parameters of a zinc-substituted hydroxyapatite coating by using X-ray analysis, infrared spectroscopy, transmission electron microscopy, optical microscopy, SEM, and other methods are given.

1. Introduction

To increase the osteointegration potential of intraosteal medical implants, their surface is covered with bioactive coatings [1-3]. The use of the method of plasma spraying for manufacturing such coatings is explained by its high efficiency, the possibility of obtaining porous coatings with a developed morphology and regulation of parameters of the spraying process, sufficiently high adhesive-cohesive characteristics, and ecological purity [1].

Most frequently, hydroxyapatite (HA) is employed as the basic component of biocomposite coatings of implants. To impart special properties to the coatings, of interest is the use of a metal-substituted powdered HA, in particular, zinc-substituted HA (Zn-HA). According to literary data [4], the antimicrobial activity of Zn-HA twofold exceeds that of the silver-substituted HA, which can be employed in dental implantology and traumatology to prevent peri-implantal infections.

The purpose of the study is an investigation into the electroplasma spraying of a Zn-HA powder with the subsequent identification of products of its decomposition and the study of physical and chemical properties of the resulting nanostructured Zn-HA biocomposite coatings.

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1. Materials and Methods

The synthesis was carried out by the method of sedimentation from water solutions at room temperature (T = 20°C) and air humidity of 58% (pH of the solution was held at a level of 9-12) according to the reaction [4]

$$(10\text{-}x)Ca^{2+} + xZn^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10\text{-}x}Zn_x(PO_4)_6(OH)_2,\ 0 < x < 0.02.$$

The calculated amount of solutions of calcium and zinc nitrates was placed in a beaker with a mixer, and a solution of diammonium phosphate was added to it drop by drop for one hour. To maintain the pH of the solution, NH_4OH dissolved in water 1:10 was added. The deposit obtained as a result of synthesis was left to mature for 24 h in the Bunsen beaker, filtered through a filter paper, dried at a temperature of 90-95ºC and for 2 h at 200ºC to remove the remains of NH_4NO_3, and then annealed at 600ºC for 6 h so that to impart a crystalline structure to it.

The resulting powder was cooled at room temperature for 2 h, then ground in a stamp ceramic mortar for 10 min, and fractioned with the use of sieves (to 90 μm).

The morphology and phase structure of the sprayed Zn-HA were examined on VT1-0 titan specimens 6.5 mm in diameter and 1.5 mm in height; the adhesion of the coating was investigated on 10 × 20 × 2-mm plane specimens.

Before plasma spraying, the specimens were cleaned and degreased in a UZUMI-2 installation of ultrasonic treatment (Trim Ltd, Saratov) at a frequency 18 kHz in a water solution of a surface-active substance at T = 30-35ºC for 5 min, with a subsequent air-abrasive treatment on an ASOZ 1.2 MEGA unit (VEGA-PRO Ltd, Ekaterinburg) by a Belekt No. 25 electrocorundum powder (TS 9391-094-45814830-2003) of dispersity 250-300 μm for 10 min.

For the plasma spraying of coatings, a UPN-28 semi-automatic installation (SPA "REMPLAZMA," Moscow) was employed at the following spray regimes: arc current — 350 A, dispersity of the titan powder — 100-150 μm, dispersity of the Zn-HA powder — to 90 μm, consumption of plasma-forming gas (argon) — 20 l/min, the spraying distance of the titan powder — to 150 mm, and that of the Zn-HA powder — to 50 mm.

The infrared (IR) spectra of Zn-HA were investigated on an FT-801 Fourier spectrometer (SIMMEKS SPC Ltd, Novosibirsk) in the interval of wavenumbers of 500-4000 cm^{-1}; tablets with KBr.

The properties of the powder were studied by the method of transmission electron microscopy (TEM) on a Dual Atomizer Zeeman AA iCE 3500 spectrophotometer (Thermo Scientific Inc., USA).

The morphology of specimen surface was examined by using a MIM-7 metallographic microscope and a Sony DSC-W710 digital camera.

The morphology and chemical elementary composition of the surface were measured by a MIRA 2 LMU autoemission scanning electron microscope (manufactured by the Tescan company) equipped with a system of energy-dissipation microanalysis, INCA Energy 350. The resolution of the microscope reached 1 nm, and the sensitivity of the INCA Energy detector — 133 eV/10 mm^2. The investigations were carried out by the energy dissipation (EDS) method in the regime of vacuum of order 10^{-2} Pa.

The adhesion of the plasma-sprayed coating was determined by the method of shear, according to GOST 14759-69, 27890-88 on an IR 5082-100 universal testing machine (IMPULS Ltd, Ivanovo) at a crosshead speed 0.5 mm/min. To determine the adhesion of the coating by the method of normal separation in shear, the specimens were glued together in pairs by their sprayed surfaces. As the adhesive, we used an ED-20 epoxy resin (TS 2252-003-62517430-01) with a polyethylenepolyamine hardener, which takes up specific rupture loads of 35-40 MPa. To improve the quality of adhesion, the specimens were pressed against each other with the help of weights and held at room temperature for 24 h.

2. Results and Discussion

An infrared analysis of the powder of zinc-substituted hydroxyapatite (Fig. 1) showed that the specimen basically corresponded to that of the synthetic HA, namely: the characteristic lines of valence vibrations of PO_4^{3-} with maxima of 1041.9, 1079.4, and 987.01 cm^{-1} and the structured band of deformation in-plane and out-of-plane vibrations of PO_4^{3-} (O-P-O) with maxima of 603.56 and 555.00 cm^{-1} were observed. The lines determining the degree of monocrystallinity of HA (frequency 3426.6 and 603.56 cm^{-1}) [4] were observed, too.

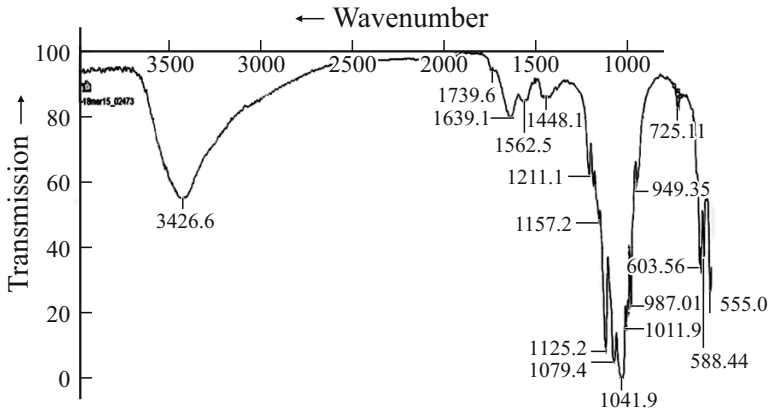

Fig. 1. IR spectrum of the Zn-HA powder.

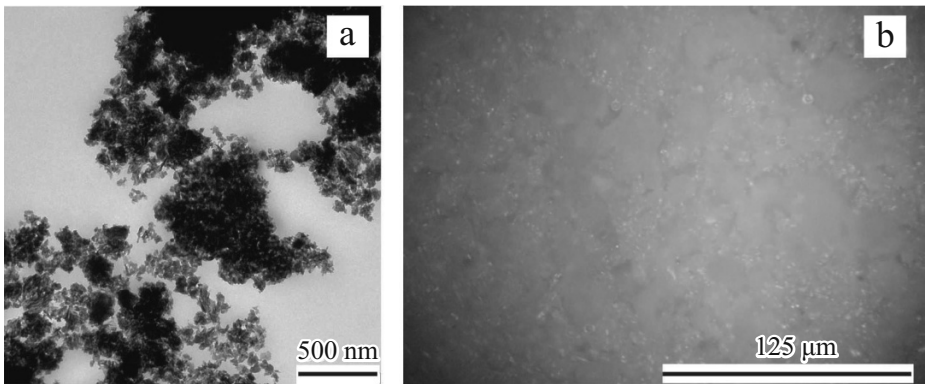

Fig. 2. TEM data of the Zn-HA powder (a) and surface morphology (b) of the plasma-sprayed zinc-substituted hydroxyapatites coating.

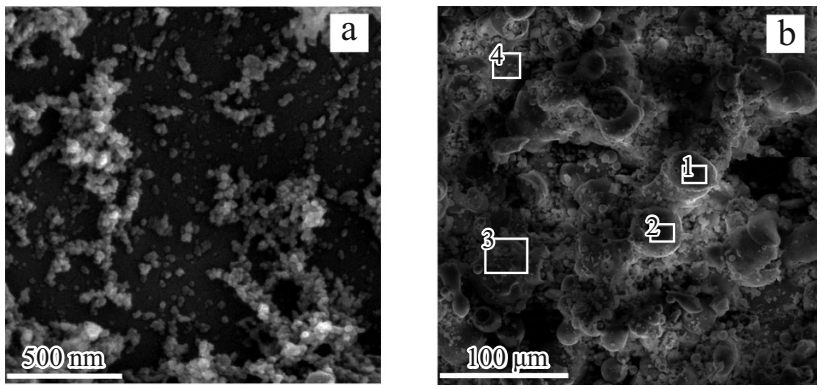

Fig. 3. SEM images of surface of the plasma-sprayed Zn-HA on a titanic substrate.

According to the data of TEM, the size of zinc-substituted HA particles was of order 50-100 nm (Fig. 2a). The particles had an extended rod and needle form. During grinding in the mortar, powder particles did not stick to the pestle and the powder was free-flowing, similar to the powder of HA synthesized by an identical method.

An analysis of microphotos of the coatings (Fig. 2b) showed that the plasma-sprayed Zn-HA coating consisted of densely packed powder particles of size about 10-30 μm, forming agglomerates up to 100 μm in size, uniformly distributed over the entire surface of specimens, which were comparable to the corresponding values for plasma-sprayed HA coatings [1].

TABLE 1. Elementary Composition of a Plasma-Sprayed Zn-HA Coating (wt.%)

Spectrum	O	P	Ca	Zn
1	38.54	20.92	32.14	8.40
2	33.10	23.36	37.01	6.54
3	40.18	15.70	30.92	6.90
4	47.39	19.67	28.41	4.52
Max	47.39	23.36	37.01	8.40
Min	33.10	15.70	28.41	4.52

As a result of SEM analysis, it was found that the surface of the plasma-sprayed Zn-HA coating consisted mainly of rounded particles (Fig. 3b) with sizes of up to 60 μm. Also, the presence of powder nanoparticles (about 50 nm in size) located on the surface in the form of particle aggregates (Fig. 3a) was registered, which can positively influence the osteointegration characteristics of the coating.

The chemical elementary composition of the coatings showed (see Fig. 3b) that the plasma-sprayed Zn-HA coatings consisted mainly of oxygen, calcium, phosphorus, and zinc (Table 1). We should point to the presence of zinc at rather small mass fluctuations on all the surface sites investigated, which confirms the presence of zinc particles in the plasma-sprayed coating and the uniformity of their distribution over the surface.

The maximum force at which the separation of the plasma-sprayed Zn-HA coating occurred was 2.3 kN at adhesion of 9-10 MPa, which agrees with average indices of adhesion for plasma-sprayed HA coatings [2].

Based on the results of our investigations and literary data, we may conclude that the zinc-substituted hydroxyapatite coatings obtained by the method of electroplasma spraying are rather promising for application to the medical practice, including osteoplastic surgery [4, 5]. However, further comprehensive medical and biologic tests *in vitro* and *in vivo* of the resulting powders and coatings on their basis are required.

Conclusions

The synthesis of Zn^{2+}-HA by the method of sedimentation from water solutions of nitrates of calcium and zinc, diammonium phosphate, and ammonium hydroxide has been performed, and its structure is confirmed by the method of IR spectroscopy. It is found that the coatings contain such elements as oxygen, calcium, phosphorus, and zinc. The coating consisted of densely packed powder particles of about 10-30 μm in sizes, which formed agglomerates to 100 μm uniformly distributed over the entire surface of the specimen. The plasma-sprayed Zn-HA coating contained powder nanoparticles of size 50 nm, which, according to literary data, can render positive influence on the osteointegration potential of the coating [5]. The adhesion of the resulting coating corresponded to the average adhesion indices of HA coatings and was equal to 9-10 MPa.

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