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PLASMA-SPRAYED NANOSTRUCTURED COMPOSITE COATINGS BASED ON Cu-CONTAINING HYDROXYAPATITE

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The processing regimes of plasma spraying of composite coatings based on copper-containing hydroxyapatite are described. Properties of the initial powder and resulting coating are investigated by using the methods of transmission electron microscopy, optical microscopy, SEM, and others.

Introduction

In modern stomatology and orthopedy, implants whose intraosteal part, as a rule, is made of a compact material (titan, zirconium, tantalum, etc.) having high mechanical characteristics are being used extensively. To improve the biocompatibility of such implants, their surface is covered with composite coatings obtained by level-by-level deposition of powders of metals and bioactive materials, in particular, hydroxyapatite (HA).

A progressive technology of deposition of coatings of different purposes is the electroplasma spraying [1]. This method is rather promising owing to its high productivity and the possibility of manufacturing porous coatings with a developed morphology and high adhesion and cohesion characteristics, which is especially important for coatings on the surface of intraosteal implants [1].

Of special interest is the use of metal-substituted hydroxyapatites, in particular, copper-containing hydroxyapatite (Cu-HA), as spraying powders. The choice of this type of coating is explained by the fact that hydroxyapatite possesses expressed bioactive properties and copper is bactericidal; such a combination can give a synergetic effect [2-4].

The purpose of the present study is to investigate the electroplasma spraying of a Cu-HA powder and the physical and chemical properties of the initial powder and the resulting biocomposite nanostructured Cu-HA coatings.

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TABLE 1. Processing Regimes of Plasma Spraying of Cu-HA

Powder type	Arc current, A	Spraying distance, mm	Dispersity of powder, μm	Spraying time, s	Consumption of the plasma-forming gas (argon), l/min
Titanium	350	up to 150	100-150	5-7	20
Cu-HA	300	up to 50	up to 90	10-12	20

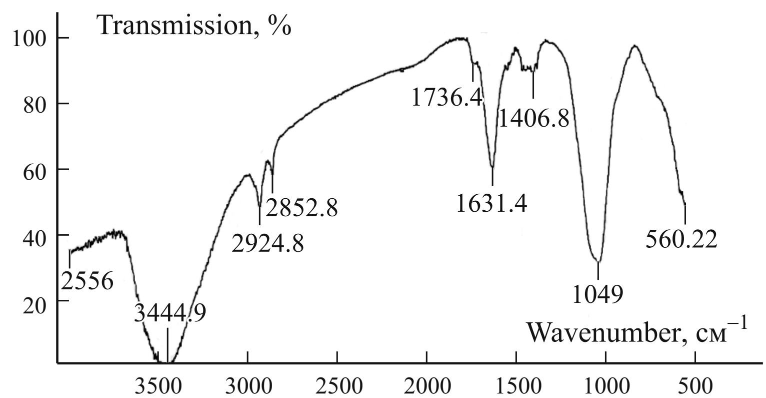

Fig. 1. IR spectrum of the Cu-HA powder.

1. Materials and Methods

The morphology and phase composition of the sprayed Cu-HA coating were investigated on titanium specimens of trademark VT1-0 in the form of cylinders of diameter 6.5 and height 1.5 mm; adhesion of the coating was examined on plane specimens of dimensions 10 × 20 × 2 mm.

Before spraying, surfaces of the specimens were first cleaned and degreased in a UZUMI-2 installation of ultrasonic treatment (Trim Ltd, Saratov) at a frequency of 18 kHz in a water solution of surface-active substances at a temperature of 30-35°C for 5 min, and then subjected to an 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 used. The regimes of plasma spraying are shown in Table 1.

The infrared (IR) spectra of Cu-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 morphology of specimen surface was examined by using an MIM-7 metallographic microscope and an AGPM-6M complex.

The morphology and elementary chemical composition of the surface were analyzed by a MIRA 2 LMU autoemission scanning electron microscope (Tescan company, Brno, Czechia) equipped with a system of energy-dissipation microanalysis, INCA Energy 350.

The adhesion strength of the plasma-sprayed coating was determined by the method of shear, according to GOST 14759-69, on an IR 5082-100 universal testing machine (IMPULS Ltd, Ivanovo) at a crosshead speed of 0.5 mm/min. To determine the adhesion strength, the specimens were glued together in pairs by their sprayed surfaces. As the adhesive, an ED-20 epoxy resin (TS 2252-003-62517430-01), with a polyethylenepolyamine hardener, capable of taking up specific rupture loads of 35-40 MPa was used.

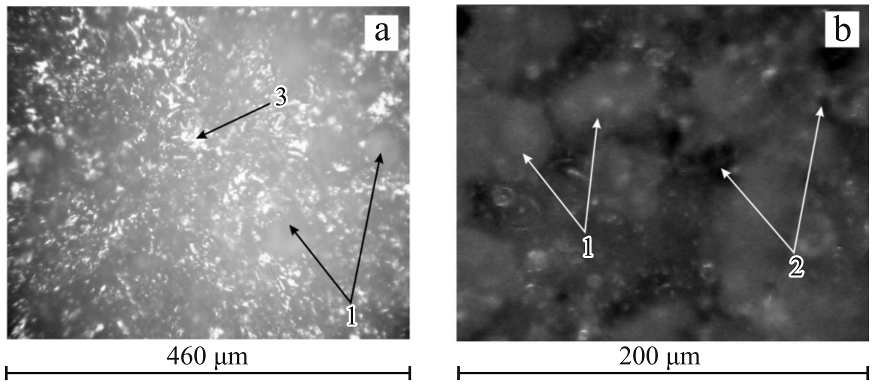

Fig. 2. Morphology of the Cu-HA coating: 1 — particles of sprayed powder, 2 — open pores, and 3 — titanium base.

TABLE 2. Elementary Composition of the Plasma-Sprayed Cu-HA Coating (wt.%)

Spectrum	O	P	Ca	Ti	Cu
1	45.21	16.84	26.00	2.22	9.72
2	47.41	18.44	24.76	0.28	9.11
3	43.59	17.93	26.05	1.26	11.18
4	43.36	18.97	26.05	-	11.62
5	25.00	10.47	31.26	1.21	32.05
Max	47.41	18.97	31.26	2.22	32.05
Min	25.00	10.47	24.76	0.28	9.11

2. Results and Discussion

An infrared analysis of the Cu-HA powder (Fig. 1) showed the presence of the characteristic lines of valence vibrations of absorbed water — 3415 cm^{-1}, valence vibrations v_3 of $(PO_4)^{3-}$ groups with a maximum of 1049 cm^{-1}, and the structured band of in-plane and out-of-plane deformation vibrations of PO_4^{3-} (O–P–O) with a maximum of 560 cm^{-1}. Lines determining the degree of monocrystallinity of HA (3415 and 560 cm^{-1}) were found too. According to the results of IR spectral analysis of Cu-HA, the specimen of the powder basically corresponded to that of the synthetic HA specimen.

Microphotos of the Cu-HA coating are presented in Fig. 2. The Cu-HA coating formed by the plasma spraying method consisted of powder particles about 60-100 μm in size (see Fig. 2b). They were uniformly distributed over specimen surface — both areas with densely accumulated particles and uncovered regions of substrate were observed (see Fig. 2a). The nonuniformity of the coating could be caused by caking of the Cu-HA powder during plasma spraying.

An analysis of the results obtained by the scanning electronic microscope showed that the surface of the plasma-sprayed Cu-HA coating consisted mainly of rounded particles (Fig. 3b) up to 100 μm in size. There existed powder nanoparticles with sizes of 60-100 nm uniformly distributed on the surface of larger particles (Fig. 3a), which could positively influence the osteointegration characteristics of the coating [5].

To analyze the elementary chemical composition of Cu-HA coatings, a sample of at least five points was taken on their surface (Fig. 3b). The results obtained showed that the plasma-sprayed Cu-HA coating consisted basically of oxygen, calcium, phosphorus, and copper (Table 2); the samples also contained some amounts of titan, which is explained by the nonuniform distribution of Cu-HA powder over the base. The copper was present on all investigated surface sites.

Adhesion tests of the coatings revealed that the maximum force at which the separation of the plasma-sprayed Cu-HA coatings occurred was 4.3 kN. The adhesion strength of the coating, calculated as the average ratio between the force of separation of glued specimens and the area of separation region, was found to be 14.3-14.6 MPa. These values exceed the

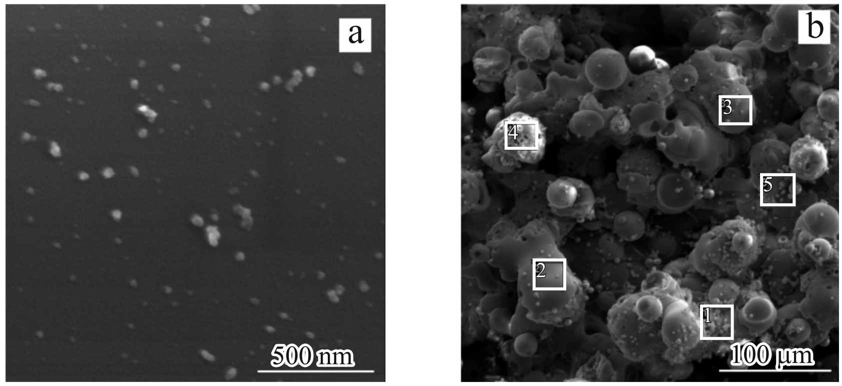

Fig. 3. SEM images of surface of the Cu-HA coating.

average indices of adhesion strength of plasma-sprayed HA coatings, equal to 10-11 MPa, but are comparable to those of HA with a high degree of crystallinity [1].

Summarizing the stated above, it can be concluded that Cu-HA coatings obtained by the method of electroplasma spraying are of significant interest for medicine, especially implantology. According to literature data, alongside with the osteointegration potential inherent in calcium phosphates, copper-containing hydroxyapatite possesses an antimicrobial effect due to the presence of copper. Moreover, coatings based on it are adhesively strong, which is especially important for intraosteal implants subjected to high sign-variable loads during functioning. Additional experimental investigations, including medical and biologic tests on cytotoxicity, antimicrobial and osteointegration potentials, etc., are required.

Conclusions

The structure of the initial Cu-HA powder is confirmed by the method of IR spectroscopy. It is shown that plasma-sprayed coatings on the basis of Cu-HA powder possess a developed morphology and are formed of macroparticles with sizes of up to 100 µm and nanoparticles of about 60-100 nm in size. The coatings contain such elements as oxygen, calcium, phosphorus, and copper. The adhesion strength of the coating obtained was 14.3-14.6 MPa, which exceeds the average adhesion strength of plasma-sprayed HA coatings.

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