

Study of Properties of Silver-Substituted Hydroxyapatite and Biocomposite Nanostructured Coatings Based on It

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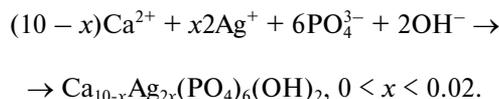
The goal of this work was to describe a method for the synthesis of silver-substituted hydroxyapatite powder. The technology and modes of plasma spraying of silver-substituted hydroxyapatite coatings are also described. Studies of the morphological and physicochemical parameters of the silver-substituted hydroxyapatite coatings using X-ray fluorescence analysis, infrared spectroscopy, transmission electron microscopy, optical microscopy, scanning electron microscopy, etc. are also discussed.

Introduction

Hydroxyapatite (HA) is one of the basic materials for bone implants. It is used for compensation of bone defects of various etiology and size. Hydroxyapatite is biocompatible and can be used as a component of composite materials and coatings on the surface of intrabone implants [1-3]. The ability to be chemically modified (cation substitution by metal ions) is an advantage of HA [1, 2, 4]. Modified HA (in particular, silver-substituted Ag-HA) is of particular interest because it has antimicrobial properties and is safe for living organisms [4, 5]. Coatings based on silver-substituted HA obtained by plasma spraying were studied in our previous works. However, in these studies, the powder was obtained by impregnation, which reduced the antimicrobial activity of the resulting product [5]. The goals of this work were synthesis and electro-plasma spraying of Ag-HA powder with further identification of products of its degradation. The physicochemical properties of plasma-sprayed nanostructured Ag-HA coatings were also studied.

Materials and Methods

Ag-HA powder was synthesized by sedimentation from aqueous solution at room temperature $t = 20^{\circ}\text{C}$, humidity 58%, and solution pH 9-12 [4]:



Pre-estimated volumes of solutions of calcium nitrate and silver were added into a beaker with stirring. Diammonium phosphate solution was added dropwise for 1 h. NH_4OH diluted 1 : 10 with water was added to maintain the required pH level. The resulting precipitate was stored for 24 h in the beaker, filtered on paper, dried at $90-95^{\circ}\text{C}$, and annealed at 200°C for 2 h to remove residual NH_4NO_3 . Then the precipitate was dried for 6 h at 600°C until crystallization was complete. The resulting powder was cooled for 2 h at room temperature and homogenized in a ceramic mortar for 15 min with a pestle. The powder was then fractionated with sieves.

The morphology and phase composition of the plasma-sprayed Ag-HA coating was tested using cylindrical titanium samples (VT1-0) 1.5 mm in height and 6.5 mm in diameter. The adhesion parameters were tested on flat titanium samples ($10 \times 30 \times 2$ mm).

Before spraying, the sample surface was cleaned and degreased using a UZUMI-2 ultrasonic apparatus (TRIMA, Ltd., Russia). The procedure was carried out in a surfactant aqueous solution at $35-40^{\circ}\text{C}$ and frequency 18 kHz for 3 min. Then samples were treated with an air-abrasive ASOZ 1.2 MEGA apparatus (VEGA-PRO, Ltd., Russia) using Belekt No. 25 electrocorundum powder (TU 9391-094-45814830-2003) with dispersion 250-300 μm for 5 min.

The plasma was sprayed using a UPN-28 semiautomatic apparatus (REMPASMA NPO, Russia). The spraying modes are given in Table 1.

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TABLE I. Plasma Spraying Modes

| Powder type | Arc current, A | Powder dispersity, μm | Plasma-forming gas run-off (argon), liter/min | Spraying distance, mm |
|-------------|----------------|----------------------------------|---|-----------------------|
| Titanium | 300 | 100-150 | 20 | Up to 150 |
| Ag-HA | 350 | Up to 90 | 20 | Up to 50 |

Ag-HA powder and samples with Ag-HA coating obtained by electro-plasma spraying underwent X-ray phase analysis in an Xcalibur/Gemini A diffractometer using an X-ray tube with copper anode ($\text{Cu-K}\alpha$ -radiation). Diffractograms were analyzed using Match! software (Crystal Impact, Germany). The American Mineralogist Crystal Structure Database (AMCSD) and Crystallography Open Database (COD) were used.

Infrared spectroscopy of Ag-HA was carried out using an FT-801 Fourier-spectrometer (NPF Simmex, Ltd., Russia) within the wave number range $500\text{--}4000\text{ cm}^{-1}$ (in KBr pellet). The Ag-HA powder was additionally tested using transmission electron microscopy in a Dual Atomizer Zeeman AA iCE 3500 spectrophotometer (Thermo Scientific Inc., USA). The morphology of the sample surface was tested using an MIM-7 metallographic microscope and Sony DSC-W710 digital photcamera.

The morphology and elemental and chemical composition of the surface were analyzed using an MIRA 2 LMU autoemission scanning electron microscope (Tescan, Ltd., Czech Republic) equipped with INCA Energy 350 system for energy-dispersive microanalysis. The resolution of the microscope was 1 nm; sensitivity of the INCA Energy detector, $133\text{ eV}/10\text{ mm}^2$. The tests were performed in vacuum ($\sim 10^{-2}\text{ Pa}$).

The adhesion parameters of the plasma-sprayed Ag-HA coating were tested by the shift method (GOST

14759-69) using the IR 5082-100 universal testing machine (Impuls, Ltd., Russia) at traverse movement rate $0.5\text{ mm}/\text{min}$. The coating adhesion was tested by the normal shift pull-off method using samples glued together pairwise with coated surfaces. The glue was epoxy resin ED-20 (TU 2252-003-62517430-01) with polyethylene polyamine hardener, which can withstand rupture loads up to $35\text{--}40\text{ MPa}$. Reliable gluing was achieved by load compression for 24 h at room temperature.

Results and Discussion

X-Ray structure phase analysis of the Ag-HA powder revealed typical peaks of HA and silver phases (Fig. 1a). The IR analysis of the Ag-HA powder (Fig. 1b) demonstrated the presence of the characteristic lines of valence oscillations of PO_4^{3-} , namely, an intense band of triple degenerate antisymmetric valency oscillations ν_3 with maximums 1044.8 , 1091.2 , and 960.87 cm^{-1} , as well as a structured band of deformation of intraplane and extraplane oscillations PO_4^{3-} (O–P–O) with maximums at 600.31 and 565.19 cm^{-1} , which basically correspond to synthetic HA. There are also bands with frequencies 3423.5 and 600.31 cm^{-1} that correspond to HA monocrystalline structure [3].

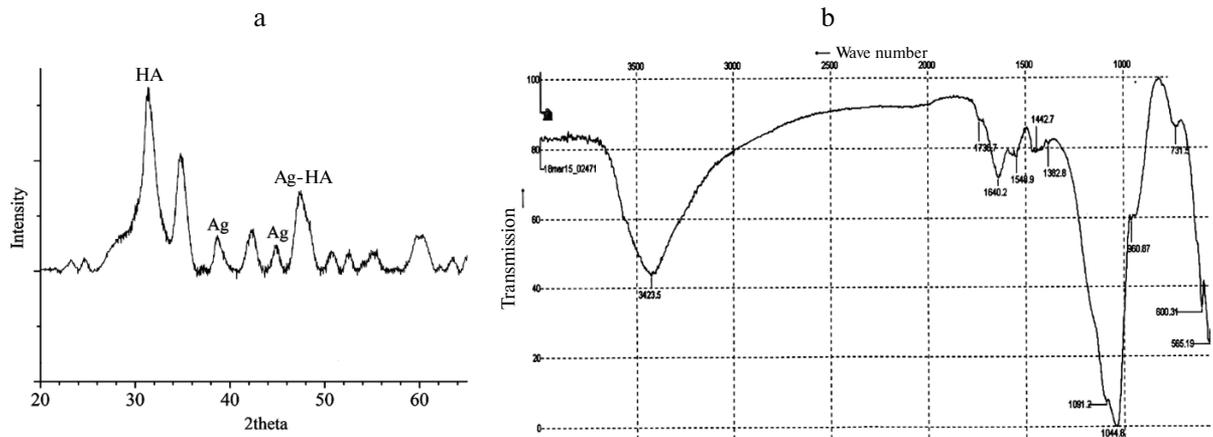


Fig. 1. Diffractogram of Ag-HA powder after electro-plasma spraying onto titanium substrate (a) and IR spectrum of the Ag-HA powder (b).

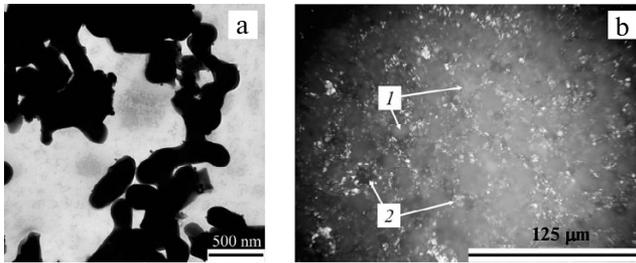


Fig. 2. Results of transmission electron microscopy of Ag-HA powder (a) and surface morphology of plasma-sprayed silver-substituted HA coating (b): 1) sprayed Ag-HA particles; 2) titanium sublayer.

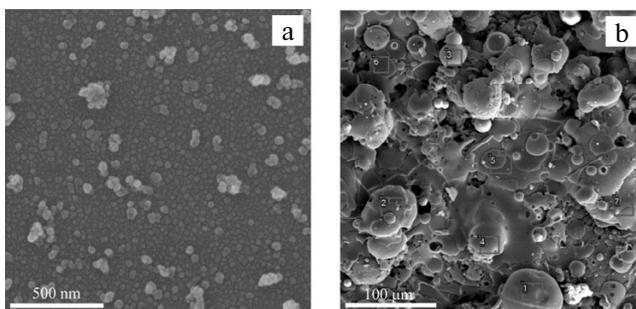


Fig. 3. a, b) Scanning electron microscopy images of the surface of the plasma-sprayed Ag-HA coating on titanium substrate.

According to the results of transmission electron microscopy, the size of the Ag-HA particles is 450–600 nm (Fig. 2a). The particles are of elongated cylindrical or spherical shape. Crushing and plasma spraying produces powder particle agglomerates, which is presumably due to fine fractionation.

A microphotograph of the surface of plasma-sprayed Ag-HA coating is shown in Fig. 2b. Analysis of images demonstrated that the coating is composed of individual powder particles 20–70 μm in size. The particles are homogeneously distributed over the sample surface. The resulting coating has less dense particle packing as compared to HA coatings obtained using similar modes of plasma spraying [3].

Scanning electron microscopy demonstrated that the surface of plasma-sprayed Ag-HA coating is composed of spherical particles (Fig. 3b) 50–100- μm in size, as well as 50–100 nm nanoparticles of sprayed powder distributed homogeneously over the surface (Fig. 3a).

The chemical and elemental compositions of the coatings were analyzed at six (or more) sites of the sample surface (Fig. 3b). The plasma-sprayed coating consisted

mainly of oxygen, calcium, phosphorus, and silver (Table 2). The presence of silver was observed in all tested surface segments, which is the evidence of homogeneous distribution of silver particles over the surface of the plasma-sprayed coating.

Adhesion was determined as the mean pull-off force-to-area ratio for glued samples (GOST 27890-88). The maximal pull-off force for plasma-sprayed coating was 1.8 kN. Adhesion of plasma-sprayed Ag-HA coating was 7.8–8.0 MPa, which is lower than mean values of adhesion of plasma-sprayed HA coatings [3]. It should be noted that the pull-off was observed mainly inside the coating, which is evidence of a decrease in the cohesion of the coating. This is presumably due to difficulties in obtaining a densely packed layer of sprayed particles.

We suggest that the plasma-sprayed Ag-HA coatings are promising for medical practice, including oral implantology and traumatology. However, the adhesion-cohesion parameters of the coatings should be improved by optimization of the spraying mode and thermo-mechanical treatment of the powder.

Conclusion

Ag-HA was synthesized from aqueous solutions of calcium nitrate and silver, diammonium phosphate, and ammonium hydroxide. Ag-HA structure was analyzed by X-ray fluorescence analysis and infrared spectroscopy. The size of the particles of silver-substituted HA was 450–600 nm. The plasma-sprayed Ag-HA coating was composed of individual powder particles 20–70 μm in size homogeneously distributed over the sample surface. Their packing density was lower than in plasma-sprayed HA

TABLE 2. Elemental Composition of Plasma-Sprayed Ag-HA Coating (wt. %)

| Spectrum | O | P | Ca | Ag |
|----------|-------|-------|-------|-------|
| 1 | 33.48 | 20.10 | 31.49 | 14.93 |
| 2 | 30.94 | 22.45 | 42.29 | 4.32 |
| 3 | 41.47 | 16.89 | 26.52 | 15.12 |
| 4 | 39.32 | 19.84 | 28.36 | 12.48 |
| 5 | 31.94 | 21.03 | 41.28 | 5.75 |
| 6 | 27.42 | 22.85 | 40.55 | 9.18 |
| 7 | 41.85 | 19.94 | 34.78 | 3.43 |
| Max | 41.85 | 22.85 | 49.74 | 15.12 |
| Min | 27.42 | 16.89 | 26.52 | 3.43 |

coatings, thereby causing a decrease in the adhesion-cohesion parameters of the Ag-HA coating as compared to the plasma-sprayed HA coating. It was demonstrated that the plasma-sprayed Ag-HA coating contained mainly oxygen, calcium, phosphorus, and silver. Particles of Ag-HA powder 50-100 nm in size were also observed. The particles are homogeneously distributed over the plasma-sprayed surface of the coating. Presumably, this increases the biological activity of the coatings.

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