Cathodic transformation of bactericidal silver-containing bioceramic coatings for implants

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Abstract. In the article the micro- and nanostructures of the biocomposite coating on titanium VT1-00, cathodically transformed by silver, were studied by the method of scanning electron microscopy. There is given a brief characteristic of the structural state of the coating, depending on its chemical composition. It is established that in the structure there are evenly distributed micrometric sprayed particles of a bioceramic dust adhered to the surface. The structure of individual particles is characterized by nanometric elements with an average size of 40±10 nm, as well as single agglomerates of nanograins with an average size of 200 to 500 nm. The technology for obtaining high-performance coatings and the construction of an adapted electrochemical bath are proposed. Moreover, it is revealed that the concentration of the alloying silver additive in the coating is about 0.5–1.0%, which allows the increase of the percentage of engraftment of titanium implants with such bioceramic coatings.

1. Introduction
At present an actual problem of modern medical and technical products (implants) is to improve mechanical properties of the functional coatings [1-3] and to minimize their rejection. One of the reasons of the rejection is inflammation of the bone around the implant (perimplantitis), which is characterized by a gradual loss of bone tissue (resorption). An undesirable consequence of this disease is the rejection of the implanted structure. To prevent such a complication, it is advisable to use alloying additives (lanthanum, silver, copper and other elements) that impart antimicrobial and antiplatelet properties to the surface of intraosseous implants [4-8]. The most favorable condition for increasing the characteristics of biocompatibility will also be the formation of a biocompatible coating on the surface characterized by the presence of submicrometry and nano-sized elements of morphology [4,5]. The aim of the work is to determine the conditions for obtaining nanostructural characteristics of a biocomposite coating obtained by plasma spraying (PS) and following cathodic implantation of bactericidal silver-containing components.

2. Methodology
For electrochemical studies titanium plates VT1-00 with dimensions 10×10×2 mm were used as samples. On their surface calcium-phosphate coatings were formed. This technology provides ultrasonic degreasing of the titanium base of medical and technical products in distilled water and alcohol, air-abrasive treatment with electrocorundum, as well as the preparation of matrix coatings, which are subsequently subjected to cathodic modification. The cathode saturation of the pores of calcium-phosphate coating with silver deposited on the titanium base was carried out from an aqueous solution of 0.4 M AgNO₃ in a galvanostatic regime for 10 minutes at different cathode current densities (iₖ=0.2–0.5 mA/cm²) and the temperature of 20 °C. Electrochemical measurements were conducted on potentiostat P-5848 complete with self-recording potentiometer KSP-4 in a standard
glass three-electrode cell with a titanium auxiliary counter electrode and a nonaqueous silver-chloride comparison electrode. Non-current chronopotentiograms were recorded on electrodes before and after cathodic polarization.

Experimental investigations of the micro- and nanostructure of the obtained coatings were carried out using the method of scanning electron microscopy (SEM) with the possibility of conducting energy-dispersive X-ray fluorescence analysis (EDX).

3. Results
Potentiodynamic curves allow the registration of all possible processes that occur on the electrodes in the investigated interval of potentials most demonstrably. The presence of peaks and areas on \( i,E \)-curves allows the evaluation of the expected composition of products in the process of electrochemical transformations and their stability. The maximum residue limit (MRL) studies were carried out in the electrolyte of the intercalation in the potential range from -3 to +1 V with a linear sweep speed of 20 mV/s. \( E-t \) curves for Ti/HAp coatings are presented in Figure 1. Analysis of the \( E-t \) curves of Ti/HAp coatings covered with silver is quite definite. However, the value of non-current potential is affected by the value of the cathode current density. The value of the cathode process potential is monotonically shifted to a region of more negative quantity with increasing of the \( i_k \). This is also seen in the analysis of non-current chronopotentiograms. The values of the potentials of the investigated coatings absolutely correspond to the value of the potential of pure silver.

![Figure 1. E-t curves of Ti/HAp coatings when they are saturated with silver.](image)

The reconstruction of silver ions proceeds practically with a 100% current yield in the absence of nitrate ions. However, their presence reduces the current efficiency up to 80–90% due to the side processes of reconstruction of NO\(^-\) to ammonia and hydroxylamine. This allows the estimation of the approximate amount of silver in the pores of the nanostructured coatings. The values of the amount of silver in the nanostructured coatings are given depending on the penetration current density \( (i_k) \). From the analysis of the conducted experiments it is established that with the increase in the current density, silver is introduced more and more stable.
SEM data show that all titanium samples with the coatings are characterized by a typical microstructure formed at the PS [4]. In the structure there are evenly distributed micro-sized sprayed particles (splats) of the bioceramic powder adhered to the surface (Figure 2a). The structure of individual splats is characterized by nano-sized elements, which are evenly distributed over the surface with an average size of 40±10 nm, as well as single agglomerates of nanograins with an average size of 200 to 500 nm (Figure 2b).

EDX showed that, in addition to the main components of silver-containing PS coatings O, P and Ca with the corresponding content (40±15)%, (10±4)% and (25±15)%, there are additives of Ti, Cr, Fe and Ag. The concentration of the alloying silver additive in the coating is about 0.5–1.0%.

Based on the experimental and theoretical data obtained, we have developed a special galvanic bath construction for cathodic insertion of modifying additives (silver, lanthanum) into calcium-phosphate coatings (Figure 3).

Figure 2(a, b). SEM of the coating micro- (a); and nanostructure (b).

Figure 3. The construction of a cathodic introduction of lanthanum into the coatings of cylindrical titanium dental implants (explanations are in the text).
The bath consists of two cylindrical bodies of different diameters, made of polytetrafluoroethylene (PTFE) – an external 1 having a deepening in the middle of the base and an inner 2 with a special protrusion 3. The protrusion 3 of the body 2 provides its fixation inside the body 1 at some distance from its inner walls, which causes the formation of a water jacket 4, through which water circulates having a thermostatically set temperature. The circulation of water through the jacket takes place through the inbuilt in an external body inlet and outlet adapter sleeves 5 and 6, which are connected by plastic hose with the thermostat. The presence of the water jacket in this bath is necessary because the temperature of the water moving in it allows the control of the temperature of the electrolyte 7 inside the body 2. In the body 2, using bolts 8 made of titanium, a double cylindrical hollow titanium anode 9 is mounted, consisting of two annular anodes of different diameter, connected with each other by titanium conductors 10. This construction feature of the anode makes it possible to ensure uniformity of the embedding process. At the bottom of the body 20 a magnet 11 is located, sealed in a glass tube 12, isolating it from the chemical action of the electrolyte. The magnet rotating by means of a magnetic stirrer 13 allows the stirring of the electrolyte solution.

As a cathode electrode, a special cover-bracket 14 was developed, into which in which screws are twisted in a certain circumference 15, on which titanium blanks of dental implants are fixed with a threaded connection 16, which are serving as working cathode elements. The screw-cap system is made of titanium.

The required level of electrolyte should correspond to a special level mark applied to the outer wall of the housing 2. The bath cover 20 is made of Teflon and has symmetrical apertures coaxial with the cathode lid 14. An additional aperture 21 in the lid of the bath is designed for the output of the electrical whisker of the cover-cathode. In addition, the complex can be composed in both potentiostatic and galvanostatic variants.

4. Conclusions
As a result of the investigation, the possibility of cathodic introduction of the bactericidal component (silver) into the matrix plasma-sprayed coating of medical and technical function (implants) was established. Additional electrochemical impact, e.g. cathodic modification, allows the increase of the percentage of engraftment of titanium implants with bioceramic coatings.

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