THE ROLE OF ELECTROPHORETIC DEPOSITION METHOD IN THE CREATION OF A BIOCOMPOSIT BASED ON HYDROXYAPATITE LAYERS AND SILVER NANOPARTICLES

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РОЛЬ МЕТОДА ЭЛЕКТРОФОРЕТИЧЕСКОГО ОСАЖДЕНИЯ В СОЗДАНИИ БИОКОМПОЗИТА НА ОСНОВЕ СЛОЕВ ГИДРОКСИАПАТИТИ И НАНОЧАСТИЦ СЕРЕБРА

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Аннотация. *Работа посвящена созданию многофункционального биокомпозита, состоящего из покрытия на основе гидроксиапатита (ГА) и наночастиц серебра с использованием высокотехнологичных методов обработки поверхности. Высокочастотное магнетронное распыление использовалось для получения слоев ГА покрытия с различной толщиной и структурой на титане и наночастицах серебра. Для получения антибактериального слоя наночастиц серебра использовался метод электрофоретического осаждения. Наночастицы серебра имели сферическую форму с диаметром 70 ± 20 нм и ζ -потенциалом -20 мВ. Дифракционные картины биокомпозитов выявили пики кристаллического ГА и серебра (Ag). Так же установлено, что наночастицы серебра являются кристаллическими с размером кристаллитов 14 нм.*

Introduction. Metals have a long history in the treatments of dentistry, dental and orthopedic treatment. The number of implants placed in the jaws is constantly increasing due to promoting development of novel materials and techniques based on collective clinical experience. It is commonly known that the foreign objects implanted in human body may be rejected due to different reasons such as wide range of local tissue reactions, in particular, inflammation, giant cell formation and fibrosis [1]. Silver nanoparticles (Ag-NPs) have been widely used for the disinfection and prevention of pathogenic bacteria. A major factor that determines the success of dental implantation is osseointegration, which is a stable anchorage of an implant in living bone achieved by direct bone-to-implant contacts [1, 2]. Consequently, the task of biomedical materials scientists is the formation of biocompatible and antibacterial implant surfaces for medical purposes. Our strategy is therefore based on the layer-by-layer preparation of coatings based on hydroxyapatite that contain internal silver nanoparticles as an antibacterial agent. The radio-frequency (RF) magnetron sputtering method was used to deposit the HA coatings [3]. The first and third HA layer were deposited for 8 and 2 h onto a titanium substrate and layer of Ag-NPs, respectively. Electrophoretic deposition (EPD) method was used to deposit the layer of Ag-NPs. Researchers developed several methods for depositing various metallic and semiconducting NPs onto the sample surfaces

using chemical reduction [4], radiation [5], electrochemical deposition [6], ion beam assisted deposition, pulsed laser ablation, and chemical vapor deposition [7]. Among all these methods, electrophoretic deposition has been largely used for the preparation of some metallic layers due to the versatility, low cost, and controllable processing of this method.

Materials and methods. To deposit the HA coatings a commercially available apparatus with an RF (13.56 MHz, COMDEL) magnetron source was used. The first and third HA layers were deposited for 8 and 2 h onto a titanium substrate and layer of Ag-NPs, respectively. Electrophoretic deposition method was used to deposit the layer of Ag-NPs. The coating of HA was deposited at an RF power level of 500 W in an argon atmosphere at the pressure of argon 0.4 Pa for either 8 or 2 h, which resulted in a layer thickness of 900 ± 100 or 150 ± 30 nm, respectively. The negatively charged Ag-NPs were synthesized by wet chemical reduction method of silver nitrate using glucose as a reductant and polyvinylpyrrolidone (PVP) as a stabilizer. PVP-stabilized Ag-NPs had a spherical shape with a diameter of the metallic core of 70±20, ζ- potential of -20 mV, and polydispersity index of –0.195, indicating the absence of large agglomerates and presence of a monodisperse system. The total amount of silver in the coatings after EPD was determined by atomic absorption spectroscopy (AAS) after the complete dissolution of all layers in concentrated aqueous HNO_3 (65 wt%); the results of the study are shown in figure 1. Variable parameters in the EPD process were: deposition time (t), working voltage (U), concentration of working solution (c) and distance between the anode and cathode (d).

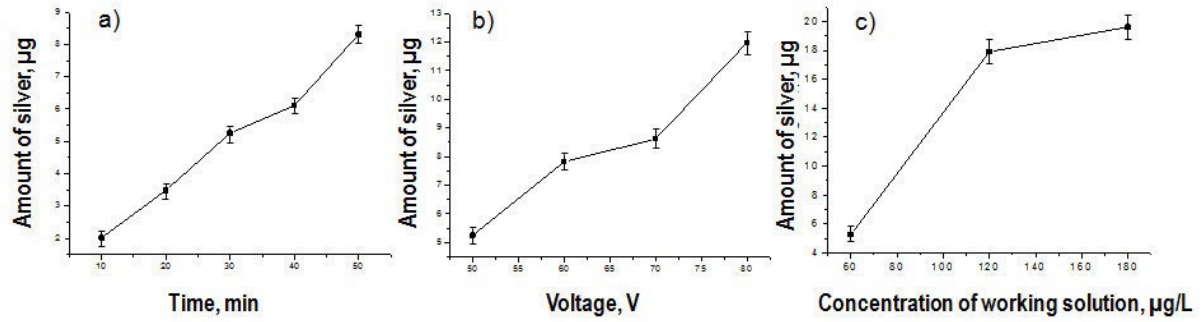

Fig. 1. Dependence of the silver amount at the surface of HA coating (thickness of 900 ± 100 nm) deposited by RF-magnetron sputtering during 480 min on the following EPD parameters: a) deposition time (U=50 V, d=1.5 ± 0.5 mm, c= 60 mg / l); b) working voltage (t=30 min, d=1.5 ± 0.5 mm, c= 60 mg / l); c) concentration of working solution (U=50 V, t=30 min, d=1.5 ± 0.5 mm).

Results. Figure 1 suggests that after 30 minutes in case a) the amount of silver reaches a value of 5.3 ± 0.2 µg, while in case b) with an increase in the working voltage to 80 V, the amount of silver reaches a value of 12.1 ± 0.7 µg, as in case c) the increase in the concentration of working solution up to 180 µg / L leads to an increase in the amount of silver, which attain a value of 19 ± 1 µg. Nevertheless, there are limitations associated with the electrical conductivity of the working solution, working voltage, and concentration of the working solution. Therefore, it is not always possible to use a high working voltage for the working solution containing the water. On the other hand, a gradual increase in the concentration of the working solution with time leads to its oversaturation. In the same way, using a long period of Ag-NPs deposition is not advantageous from an economic point of view. The results of AAS showed a high content of silver on the HA coating surface with distance between anode and cathode of 1 mm which amounts to 5.714 µg / cm^2, while for 3 mm this value

amounts to 0.761 μg / cm^2. Thus, choosing the minimum distance between the anode and the cathode is the most effective to form a monolayer of Ag-NPs on the surface of the HA coating. The final step in the formation of the Ag-HA biocomposite was a thin HA coating deposition on the surface of the Ag-NPs layer, the deposition time was 2 h, the thickness of the deposited HA coating was 150 ± 30 nm.

Conclusion. In this study, multilayer Ag-HA biocomposites were produced in three sequential steps. The first step was the preparation of a nanocrystalline 900 ± 100 nm thick HA coating by RF magnetron sputtering on the titanium substrates. Next step was the EPD of Ag-NPs onto the HA-coated titanium. The final step was the deposition of the HA layer 150 ± 30 nm thick on top of the Ag-NPs layer. The negatively charged Ag-NPs were synthesized by wet chemical reduction method. PVP-stabilized Ag-NPs had a spherical shape with a diameter of the metallic core of 70±20, ζ- potential of -20 mV. EPD method was largely used for the preparation of some metallic layers due to the versatility and controllable processing of this method.

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