OBTAINING SILVER BACTERICIDAL LAYERS ON SURFACE OF POROUS MATRIXES FROM ANODIC ALUMINA BY CHEMICAL DEPOSITION

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Abstract. Silver films due to such properties as high electrical and thermal conductivity, high corrosion resistance and antibacterial properties are now widely used in biomedical technique and biotechnology. At present work was investigated the processes of chemical deposition of silver nanoparticles into a porous matrix of anodic aluminum oxide with nanosize pores. According to the results obtained, the process of chemical deposition of silver particles on porous anodic alumina with preliminary impregnation of Sn (II) ions was proposed. The extended surface of the obtained nanocomposite film provides high bactericidal effect and can be used for water disinfection.

Keywords: Silver particles; bactericidal layer; porous anodic aluminum; chemical deposition; water disinfection.
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Introduction

Silver films due to such properties as high electrical and thermal conductivity, high corrosion resistance and antibacterial properties are now widely used in biomedical technique and biotechnology. Thin layers of silver are used to manufacture biomedical measuring electrodes. New designs of dry electrodes based on silver nanowires for electrocardiography have been proposed. The process of electrode manufacturing by including silver nanoparticles into the polymer matrix is described in [1]. The processes of obtaining and properties of silver nanoparticles are also intensively studied due to their wide range of biomedical properties: antimicrobial [2], antitumor [3], antifungal [4] and photocatalytic [5].

At present, various mechanisms have been proposed to explain the increased chemical activity of silver particles with respect to microorganisms contained in water. In [6] a catalytic mechanism of water disinfection by silver applied to the surface of aluminum oxide powder under ultraviolet irradiation is described. The adsorption mechanism of water disinfection with silver [7] has also been proposed. Cell membrane consists of special proteins - glycoproteins or polypeptides connected by amino acids. Silver, interacting with external peptidoglycans, inhibits their ability to transmit oxygen inside the bacterium cell, which leads to the death of the microorganism.

One of the applications of silver nanoparticles in medicine is the fabrication of composites based on them, allowing the use of the complex effect of a composite with inclusions of silver nanoparticles. It is known that disperse silver particles are the most effective for disinfection. A promising approach in this direction is to obtain silver particles by deposition of silver in nanoporous templates. Porous templates based on anodic aluminum oxide have a great advantage for this technology. It is known that porous anodic aluminum oxide films are characterized by a highly ordered porous structure and the possibility of controlled self-organized growth [8]. The introduction of metallic silver particles into porous channels leads to the formation of particles with dimensions determined by the nanopore diameter.

The aim of this work was to investigate the processes of chemical deposition of silver nanoparticles into a porous matrix of anodic aluminum oxide with nanosize pores.

Experimental

Aluminum foil (99.9% purity) with thickness of 100 microns was used for obtaining porous matrixes. Porous anodic alumina films were formed in galvanostatic anodizing mode with current density of 1 A/dm^2 in 20% aqueous solution of sulfuric acid at 15 °C during 50 min. The film thickness of the anodic alumina formed in this mode was 10±1 microns. Thickness was measured by means of eddy-current BT30N thickness meter. For chemical deposition of silver nanoparticles, a two-stage process was used. The first stage involved preliminary formation of catalytically active crystallization centers of Sn^{2+} on the surface of anodic aluminum oxide to induce precipitation of silver nanoparticles from solutions. The working solution was 0.33 M $SnSO_4$, processing time was one minute. At the second stage, chemical deposition of silver nanoparticles on activated surface of anodic oxide in a solution containing 7.2 g/l $AgNO_3$, 15.0 ml/l NH_4OH, 2.5 g/l Glucose and 1.0 ml/l formalin was performed. The pH of the solution was about 10. The reaction of silver deposition on tin (II) was initiated on such activated surface. The deposition time in experiments was varied from 5 to 30 min.

Specific surface resistance of silver precipitated layer on the surface of anodic alumina was measured by means of the four-probe method on ISO-3m. To assess the efficiency of silver nanoparticles deposi-

tion in different modes, the breakdown voltage between the metallized surface and the aluminum base was measured.

Results and discussion

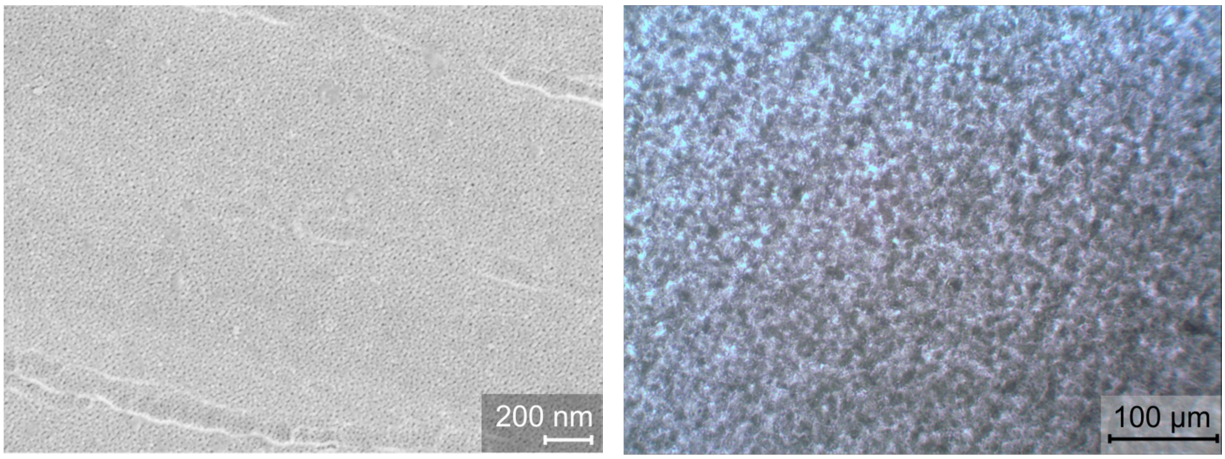
Due to its porous structure, anodic alumina has a highly developed surface. To initiate the deposition of silver nanoparticles by creating crystallization centers in the pores and on the surface of anodic aluminum oxide, tin ions from the working solution were previously deposited. Before that, several preparatory operations were performed. Immediately after anodizing, samples of porous anodic aluminum oxide films were washed in flow distilled water for 10 minutes. Then the samples were dried at reduced pressure and temperature 50 °C. For comparison, part of samples was treated without low pressure.

After the completion of preparatory operations, the samples were treated at 0.33 M $SnSO_4$ at reduced pressure for 3 min. Samples were washed by the following route: washing in cold distilled water, washing in acetone and air drying at temperature 50 °C at reduced pressure.

To deposition of silver nanoparticles, the processed samples were placed in a solution containing silver for from 5 up to 30 minutes. After that, the samples were air-dried at a temperature of 50 °C at reduced pressure.

The results obtained showed that without sample drying at reduced pressure, silver nanoparticles were mostly deposited on the open surface of anodic alumina. Taking into account the morphology of the porous layer, most of the silver was accumulated around the mouth of pores. After the samples were dried under reduced pressure during short-term chemical metallization, silver was applied to the pore walls to form nanotubes.

Figure 1 shows the photographs of the surface of porous aluminum oxide before (Figure 1a) and after (Figure 1b) deposition of silver particles. As you can see from Figure 1a, the initial porous aluminum oxide films had a pore diameter of about 10 nm. After exposure of the anodic films in a solution containing silver, the film surface was covered with a solid layer of silver for 30 minutes (Figure 1b).



a *b*

Fig. 1. Images of surface morphology of the samples with porous anodic alumina before (a) and after (b) silver deposition for 30 min

The curve characterizing change in silver layer specific surface resistance on exposure time in the processing solution is shown in Figure 2.

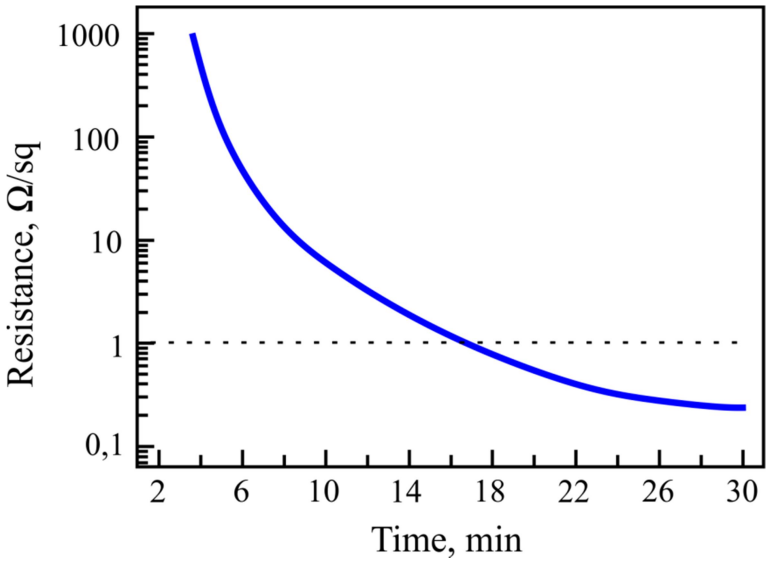


Fig. 2. Change in specific surface resistance of silver layer deposited on porous anodic alumina on exposure time in the processing solution

It is worth noting that after 10 minutes of exposure in the solution, the curve passes to the area of smooth resistance reduction over time. The weight of samples for the selected deposition time was determined by the weighing method. Then the values of mass increment were converted to the average specific thickness of the silver layer. The obtained curve characterizing change in silver layer thickness on exposure time in the processing solution is shown in Figure 3.

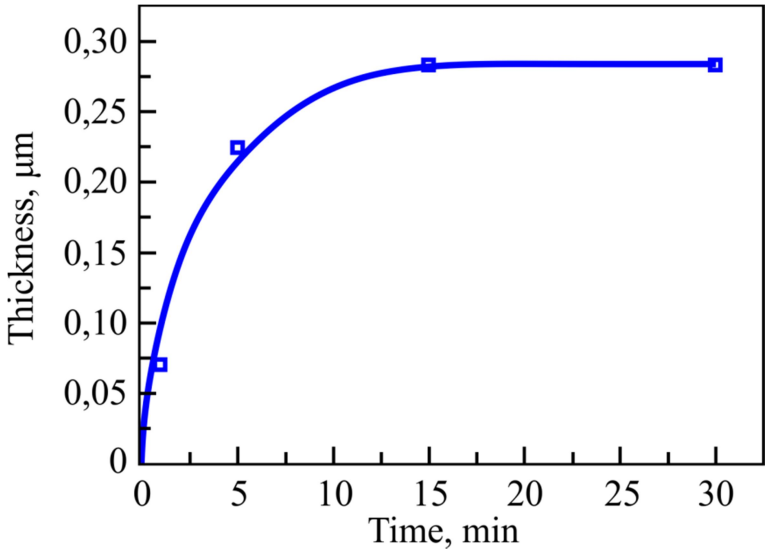


Fig. 3. Change in silver layer thickness on porous anodic alumina on exposure time in the processing solution

As can be seen from the Figure, after 10 minutes of exposure in solution, the thickness of the film has changed slightly from time to time. This behavior of the curve after 10 minutes indicates the completion of the processes of silver particles deposition in the pore channels and the beginning of deposition dominating on the open surface of aluminum oxide.

Table 1 shows the dependence of the breakdown voltage of anodic alumina films with a layer of silver particles on the processing conditions before deposition (under normal conditions or under low pressure). The data obtained show a significant reduction in the breakdown voltage in the case of low pressure treatment, which indicates a deeper penetration of silver particles into the pore channels.

Table 1. Change in the value of the breakdown voltage of anodic alumina films with deposited silver on the processing conditions

Processing conditions	Under normal conditions			Under low pressure		
Experiment number	1	2	3	1	2	3
Breakdown voltage, V	50	46	51	15	12	14

The data obtained show a significant reduction in the breakdown voltage in the case of under pressure treatment, which indicates deeper penetration of silver particles into the pore channels.

Conclusion

According to the results obtained, the process of chemical deposition of silver particles on porous anodic alumina with preliminary impregnation of Sn (II) ions was proposed. This process allows obtaining porous alumina films with a layer of silver particles. The ordered porous structure of anodic films with a pore diameter of 10-12 nm allows obtaining the specified dimensions of silver nanoparticles. The extended surface of the obtained nanocomposite film provides high bactericidal effect and can be used for water disinfection.

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Authors contribution

Vrublevsky I.A. – concept development, methodology development, general management.

Tuchkovsky A.K. – production of samples, preliminary analysis, processing of results.

Lushpa N.V. – production of samples, preparation of specialized software, writing a working version, editing and design of an article.

Tran D.L. – concept development, assessment of results, work with references, processing of results.

Pham G.V. – methodology development, assessment of results, work with references, processing of results.

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