ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 8, pp. 1396−1400. © Pleiades Publishing, Ltd., 2009.
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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Preparation and Properties of Ultradisperce Silver Powder

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Received December 29, 2008

Abstract—The ultrafine powders of silver are prepared by the method of electrochemical deposition on cathode from water–ethanol solutions. Distribution of particles by size and quality of the synthesized powders are determined. A comparative evaluation of antimicrobial activity of silver nano-sized particles and foil is performed.

DOI: 10.1134/S107042720908014X

In the recent years occurs continuously increasing stream of information related to the preparation of ultrafine powders of metals and application them in various fields, including science, medicine, biology and agriculture. This is due to the fact that at the transition to the nanometer range appear new qualities in the nano-sized objects themselves and in the materials produced from them [1–3].

In [4–6] has been shown a possibility of the synthesis of nano-sized copper powders from the water–isopropanol solutios of electrolytes by the method of electrochemical deposition on cathode. Correct choose of the synthesis conditions allows monitoring the physical and chemical parameters of the particles. The fine powders can be prepared at the limiting current density in the presence of surfactants. Electrolytic powders feature by high purity and well-developed specific surface.

Bactericidal and wound-healing properties of silver have long been known to medicine [7]. The basis of microbactericidal action of silver is the nonspecific binding to proteins of a protoplasm of microorganisms. The main advantage of silver as an antibacterial agent is its tolerance toward microorganisms, as well as the inability to develop resistance against it. Silver nano-powders with a large specific surface area have expanded contact with bacteria and viruses, that enhances significantly the bactericidal action of silver [8]. Thus, the use of silver as nano-disperse powder could allow hundreds times decrease the silver concentration, with retention of bactericidal properties. Taking into account that silver nanoparticles are able to maintain long-term biocidal properties, it is advisable to add them to paint, varnish, and medical dressings.

In this paper are considered features of formation of the silver ultrafine powders from water – ethanol solutions of electrolytes and is showed the applicability of the prepared silver powders for modifying the traditional medical materials to confer them enhanced biocidal properties.

EXPERIMENTAL

Electrodeposition of silver was carried out from the water–ethanol solution of silver nitrate in a glass electrochemical cell in potentiostatic mode at 295 K. The pH value of electrolyte in the process of electrolysis was approximately 3.0. As a cathode was used copper wire, on which was deposited silver from the electrolyte of the composition (g l^{-1}): Ag (metal, as $AgNO_3$) 25, KCNS 120, K_2CO_3 25, $K_4Fe(CN)_6$ 50. Anode is titanium support with deposited on it a layer of ruthenium dioxide RuO_2 and a layer of titanium dioxide TiO_2. To prepare the electrolyte were used the reagents of "chemically pure" grade.

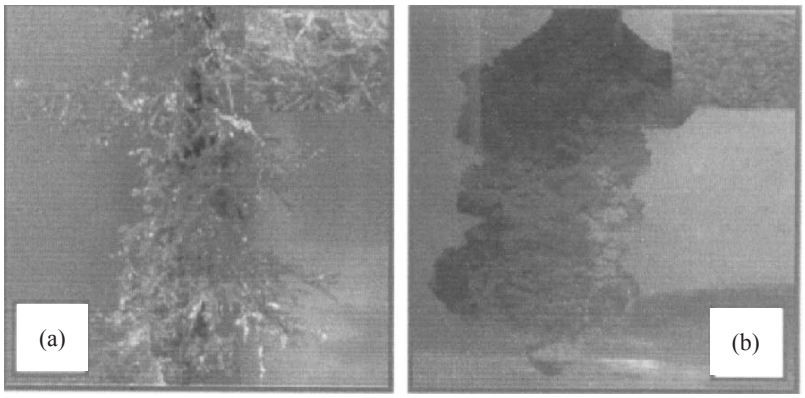

Fig. 1. Structure of silver precipitates: needle (a), foam (b).

The values of current needed for the electrochemical synthesis of ultrafine powders of silver were found from the polarization curves. Polarization measurements were performed using a stable voltage source PI-50-1 together with the PR-8 programmer, at a sweep rate of voltage 5 mV s^{-1}. As the working electrode served a copper disk, a subsidiary electrode was platinum, the reference electrode was saturated silver chloride electrode.

Particle size of silver was determined from the microphotographs obtained with a transmission electron microscope EMV-100 L in the high-resolution regime [9]. To construct histograms describing the dispersion of powders were prepared electronic microphotographies of different parts of the sample at different zoom values. X-ray images were obtained on a Dron-3M diffractometer using $Cu_{K\alpha}$ (λ = 0.154 nm) radiation. A qualitative composition of nanoscale powders of silver (YHGC) was determined by comparing the interplane distances in the diffractograms of the powder sample with the reference data [10].

Antibacterial effect of the material modified with silver nanoparticles and of silver foil with thickness 0.3 mm was studied on the gram-negative prokaryotes (gracilicutes) of the *Enterobacteriaceae genus Escherichia* family. As the test-microbe were used the species of the genus *Escherichia–Escherichia coli*, a representative of the normal microflora of the lower division of intestine associated with gastrointestinal diseases. In addition, *E. coli* is the primary cause of urinary tract infections and intrahospital infections, including septicemia and meningitis. In sanitary microbiology *E. coli* are used as an indicator of faecal contamination, as a sanitary demonstration microorganism for assessig the quality of drinking water and foodstuffs. The investigated powders

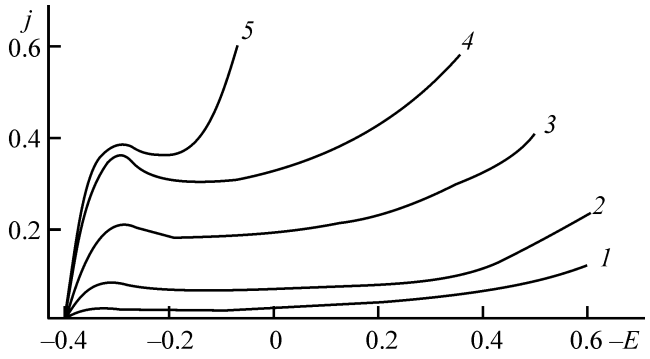

Fig. 2. Cathodic polarization curves at the electrolysis of water–ethanol solution of silver nitrate. Contents of C_2H_5OH 0.004 mol fraction, (*j*) is current density, A dm^{-2}; (*E*) is potential, mV AgCl. Concentration of silver nitrate, mol kg^{-1}: (*1*) 0.05, (*2*) 0.1, (*3*) 0.15, (*4*) 0.2, (*5*) 0.4.

were applied to the medical material from 1% alcohol suspensions by impregnation.

Preparation of strains for the study was carried out in accordance with methodological recommendations for the control growth media of biological indicators [11, 12]. The sowing working dose [1000 colony forming units (CFU) in 1 ml] was prepared by dilution of the standard culture of the tests-strains by physiological solutions.

Tests of the silver bactericidal nanoscale powders was carried out in two variants, on solid and liquid nutrient media.

(1) Sowing the bacterial lawn with the meat-peptone agar (MPA). To a Petri dish with the MPA and the test-culture of the bacteria *E. coli* in a sowing dose of 1000 CFU in 1 ml were placed the examined samples. The dishes were incubated 24 h in a thermostat at 37°C, and then observed the absence or presence of a zone of grow delay of the test bacteria around the studied samples.

(2) The sensitivity of microorganisms in a liquid nutrient medium. The test samples were placed in test tubes with meat-peptone broth (BCH) and test culture suspension of *E. coli* (the sowing dose 1000 CFU in 1 ml). The vials incubated for 24 h in a thermostat at 37°C and maintained for 1 day at room temperature. In order to confirm the availability of bactericidal properties against *E. coli* were determined transmittance and optical density of the solution of the studied samples on a photoelectric colorimeter KFK-2.

At the change of solution composition and the electrolysis parameters have formed sediments with different surface morphology, from needle with the branched structure to the sponge (Fig. 1). Silver in the form of a solid porous mass is allocated on the cathode surface after reaching the limit diffusion current, calculated with accounting of the electrode surface area.

Figure 2 presents the results of polarization studies of solutions with different concentrations of silver nitrate. The content of ethyl alcohol was 0.04 mol %. The choice of non-aquatic component is based on previously carried out studies and values of surface potentials of some organic solvents, calculated on the basis of the potential voltage differences [13, 14].

From the analysis of polarization curves follows that in the range of concentrations of silver nitrate 0.05–0.15 mol per 1 kg of solvent there is quite a long platform of limiting current, where the rate of supply of ions to the near-cathode region restricts the total process. This situation is one of the main causes for the formation of nano-sized silver powder. To carry out the synthesis of powders at the salt concentration 0.4 mol per 1 kg of solvent and higher is difficult because of unstable regime of electrolysis, since the rate of sedimentation of fine precipitate is low. When the concentration of $AgNO_3$ is 0.05 mol kg^{-1} and below the electrochemical deposition is not effective because of low deposition rate and the product yield. The optimal concentration providing a steady process of electrosynthesis of nanoscale silver particles is 0.05–0.15 mol kg^{-1} of $AgNO_3$.

Thus, based on the results of polarization studies are selected the optimal composition of the electrolyte and regimes for the effective conducting the process of electrodeposition of nanoscale powders of silver, j = 0.1 A dm^{-2}, 0.1 mol per 1 kg of $AgNO_3$, 0.04 mol. fraction of C_2H_5OH. With the used composition of the solution the yield of silver on the current is 95%. The silver powders synthesized under these conditions were used for further X-ray and biological research.

Analysis of micrographs of nano-sized silver powder is presented in the form of histograms in Fig. 3. The bulk (about 95%) of the total mass of the powder particles

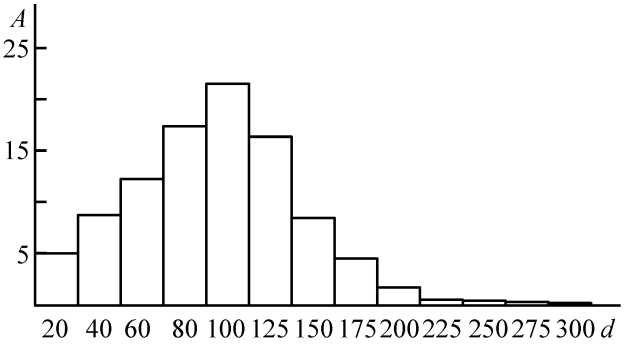

Fig. 3. Histogram of distribution of nano-sized silver particles in powder. (*A*) content, %, (*d*) particle size, nm.

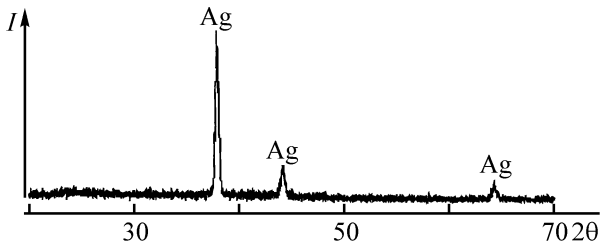

Fig. 4. Diffractogram of nano-sized silver powder synthesized by electrochemical method. (*I*) intensity, (2θ) angle of reflection (degrees).

Table 1. Iterplane distances and intensity

Intensity *I*, %	2θ, deg	*d/n*	
		calculated	reference data
37.91	37.92	2.37	2.36
44.09	44.12	2.05	2.04
64.39	64.15	1.45	1.44

Table 2. Bioactivity ad the values of the zones of inhibition of growth of bacteria by nanoscale particles of silver with respect to *E. coli*

Bioactivity	Growth of bacteria, mm		
	a	*b*	*c*
None	10		
Significant		15	
Strong			20

Table 3. Effect of nano-sized powders of silver on the survival of bacteria *E. coli* in liquid nutrient medium

Indicator	Sample			
	a	*b*	*c*	*k*[a]
Transmittance, %	72	90	94	73
Sown dose, CFU ml^{-1}	>1000	0	0	>1000

[a] *k* is sowing from the control tube containing sowing dose of 1000 and more microbial cells in 1 ml (without the sample).

comprises nanoparticles of the size from 20 to 150 nm. The maximum corresponds to the particle size of approximately 100 nm. A smaller portion (approximately 5%) corresponds to the larger forms (200 nm or more), composed of loosely coupled particles of small size.

Figure 4 provides X-ray diffractogram of the nanoscale silver powder synthesized by an electrochemical method. The calculated values of interplanar distances for a given value of the wavelength are presented in Table. 1. Values of the interplanar distances corresponding to different maxima at diffractogram are in good agreement with the reference data [10]. Thus, it is elucidated that the examined powder is composed mainly of Ag, while the amount of silver oxide is so little that can not be analyzed by this method.

The results of the study of bioactivity (Table 2) showed that the medical material (sample a), metallic silver (sample b) and the material modified with nano-sized silver powder (sample c) behave differently.

As shown in Fig. 5, the source material, the control sample (a), does not exhibit antimicrobial activity against the test-culture *E. coli*. Chemically pure metallic silver (b) although it displays expressed bioactivity, but the zone of suppression of bacteria growth in the test-sample is much less than that of the materials modified with nano-sized particles of silver, that is of higher bioactivity (c).

This variant of testing is considered as a model of developing an infectious process in its initial phase, adhesion, and the ability to inhibit this phase in order to prevent infection. In this regard, it should be noted that the advantage of the materials modified with the nanoscale particles of silver over the other decontamination reagents is that their bactericidal effect persists for a long time.

The action of silver on a microbial cell is carried out in 2 stages. Initially, occurs sorption of silver on the surface of cells, then it penetrates into the cell that leads to inactivation of enzymes, damage of nucleotides

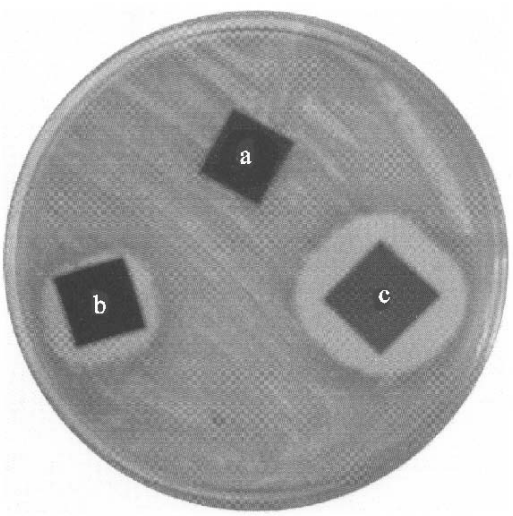

Fig. 5. Micrographs of the starting material (a), the silver foil (b) and the medical silver-containing material modified with nano-sized powder (c) after sowing the bacterial lawn with the strains of *E. coli* on solid nutrient medium.

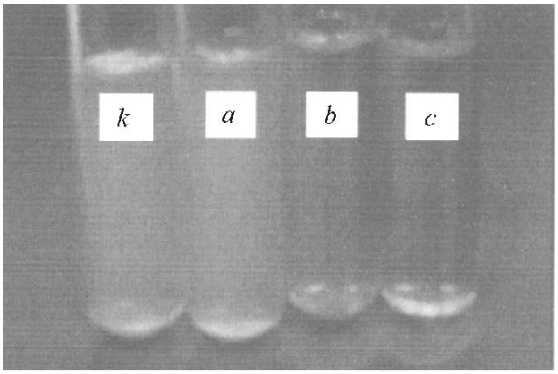

Fig. 6. Test (a, b, c) and control (k) samples for strains of *E. coli* in the liquid nutrient medium.

and lysis of the cells. Chemically pure silver metal has a pronounced anti-microbial activity, but the silver ions and ionogenic compounds of silver are more bioactive, and the activity of silver is higher when higher the concentration of its ions in solution.

The present study revealed prolonged bactericidal effect of the nano-sized silver. It was found that at the diffusion for 24–48 h into the nutrient agar from the samples of the material modified by silver nanoparticles the antimicrobial effect persists long time after removal the material, within 7–14 days. In the zone of delayed growth and on the site after the removal of the nano-samples no microbial growth occurs, while on the site of controls the nutrient agar rapidly becomes infected.

The results of microbiological analysis of modified bioactive materials in a dense nutrient medium are in good agreement with the results of the study bioactivity in a liquid nutrient medium (Table 3, Fig. 6).

As can be seen from the data presented, metallic silver (b) in liquid nutrient medium showed the same high bioactivity and complete suppression of growth of the test-culture, as the silver nanoparticles (c). Transmission coefficient in vitro with these samples was the maximum.

Thus, it is shown that with the application of this method are obtained more accurate results, confirming the complete loss of the test microbes in a liquid medium with nanosized particles of silver. This is very significant for the development of new antimicrobial drugs with the desired properties at the antibiotic-resistant pathogens. A mechanism of effects of silver ions on the microbial cells is proposed. In particular, compounds of silver induce in *Escherichia coli* lysis of cytoplasm, damage of nucleotide content in the cells and rejection of the cell content from cell envelope.

CONCLUSIONS

(1) Optimal conditions for the synthesis of nanoscale powders of silver by the electrolysis of water–ethanol solution of silver nitrate are elucidated.

(2) Large specific surface area of nano-sized powders of silver increases the contact area of silver with the microorganisms, improving bactericidal properties of silver.

(3) Significant difference in antimicrobial activity of metallic silver and the silver nano-sized particles reflects the possibility of the use of ultrafine metallic powders in medicine owing to their effective biocidal properties.

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