

On the Structure and Electrical Erosion Resistance of the Electroexplosive Spraying of a ZnO–Ag-System Coating

D. A. Romanov^{a,*}, S. V. Moskovskii^{a,***}, V. E. Gromov^{a,**}, K. V. Sosnin^a, and A. D. Filyakov^a

^aSiberian State Industrial University, Novokuznetsk, 654006 Russia

*e-mail: romanov_da@physics.sibsiu.ru

**e-mail: gromov@physics.sibsiu.ru

***e-mail: psk-svm@yandex.ru

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Abstract—For the first time, electrical erosion-resistant coatings of the ZnO–Ag system are obtained by electroexplosive spraying. The coating structure is investigated by atomic force microscopy and scanning electron microscopy. The formed coating is a structurally homogeneous composite material consisting of a silver matrix and ZnO inclusions located in it. Surface periodic structures with an average wavelength of 3 nm are found at the coating/substrate interface. Tests of the sprayed coatings for electrical erosion resistance under arc erosion conditions are carried out. A formation mechanism of hierarchical levels of the structure of the electroexplosive coatings is suggested. The mechanism is based on theoretical concepts of the formation and evolution of fractal aggregates with diffusion-limited and cluster-cluster aggregations. Based on the electrical properties of silver and copper oxide, a dependence of the electrical-contact resistance on the number of on/off cycles in the process of testing for electrical erosion resistance is substantiated.

Keywords: composite coating, silver, zinc oxide, structure, electrical erosion resistance, properties, electrical contact

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INTRODUCTION

The safety of power-supply systems, reducing energy losses and saving material resources is largely determined by the reliability of electrical contacts. Their reliability determines the efficiency of the operation of power-generating- and industrial equipment and the global energy system as a whole. Due to poor-quality contacts, they heat up, energy losses increase, and critical emergencies occur. According to the National Association of Rescue and Environmental Organizations, 50% of fires in manufacturing facilities and in residential properties are due to the malfunction of electrical installations, while 50% of electrical equipment fires are caused by failures in electrical contacts.

The use of powder metallurgy methods makes it possible to realize in one material a diverse and contradictory set of properties that an electrical-contact material should possess [1]. At present, a large number of electrical-contact materials have been developed for use under a variety of operating conditions. They usually consist of a matrix with high electrical conductivity and a refractory component (filler) with high wear and erosion resistance [2]. The most promising for the manufacture of contacts are composite materials based on silver, copper, copper-nickel, and aluminum

matrices and a refractory filler. These include the following systems: W–Cu, Mo–Cu, W–C–Cu, Mo–C–Cu, Ti–B–Cu, TiB₂–Cu, TiB₂–Al, W–Ni–Cu, Mo–Ni–Cu, Cr–C–Cu, Cr–Cu, CdO–Ag, SnO₂–Ag, CuO–Ag, ZnO–Ag, W–Ag, Mo–Ag, W–C–Ag, and Mo–C–Ag, etc. [3–8].

Since the process of material destruction begins with its surface, for a number of practical applications, for example, hardening of the contact surfaces of medium- and heavy-loaded switches and switching devices, the formation of protective coatings is promising, since in this case the erosion resistance of only the contact surface, and not the entire volume, is important. It is economically and technically feasible to develop an approach for the creation of materials, where the mechanical strength of the part is ensured by the use of economical substrates and special surface properties are provided by the continuous or local formation of composite coatings on it, whose properties correspond to the operating requirements. Savings with this approach can reach 90%. Expert assessments confirm this trend. One of the focus directions of condensed matter physics is the development of methods for improving the operating characteristics of various materials. With this in mind, hardening the surface of

arc-resistant electrical contacts is an urgent task for the development of new modern technologies.

The purpose of this work is to study the structure and morphology of the phases of an electroexplosive coating of the ZnO–Ag system using scanning electron microscopy (SEM) and atomic force microscopy (AFM), as well as to conduct tests for electrical erosion resistance.

MATERIALS AND METHODS

The object of research was copper contacts of the KPV-604 contactor, on the contact surfaces of which the ZnO–Ag system was formed by the electroexplosive method [9]. A 250-mg silver foil was used as an explosive conductive material, on the surface of which a weighed portion of 120-mg ZnO powder was located in the explosion area. The time of plasma exposure to the sample surface is $\sim 100\ \mu\text{s}$, the absorbed power density on the jet axis is $\sim 5.5\ \text{GW}/\text{m}^2$, the pressure in the shock-compressed layer near the irradiated surface is $\sim 12.5\ \text{MPa}$, the residual gas pressure in the working chamber is $\sim 100\ \text{Pa}$, the plasma temperature at the nozzle exit section is $\sim 10^4\ \text{K}$, and the thickness of the heat-affected area is $\sim 50\ \mu\text{m}$. The structure and morphology of the coating and the adjacent substrate layer were analyzed by SEM (Carl Zeiss EVO50 device with an attachment for X-ray microanalysis) and AFM (Solver NEXT device) methods. Electrical-erosion-resistance tests of the coatings under arc erosion conditions were carried out on the contacts of CJ20 contactor starters with alternating current and inductive load in accordance with the requirements of the AC-3 test mode on commutation wear-resistance when working in a three-phase circuit with a low voltage value of 400/230 V, a frequency of 50 Hz, current of 320 A, and $\cos\varphi = 0.35$. The number of switching cycles was 6000.

RESULTS AND DISCUSSION

Scanning electron microscopy and X-ray microanalysis methods were used to study the structure and elemental composition of a cross section of the “coating/substrate” system formed by the electroexplosive method. A typical image of the cross-sectional structure of the coating of ZnO–Ag composition is shown in Fig. 1. An analysis of the results shows that the formed coating is a structurally homogeneous composite material (Figs. 1a, 1b). According to the morphology of the structure and the etching contrast, the formed coating consists of a light silver matrix and dark ZnO inclusions with sizes varying from 0.3 to $0.5\ \mu\text{m}$ (Fig. 1b). The elemental composition of the coating was analyzed by the X-ray microanalysis method. The research results are presented in Figs. 1c–1e. Analyzing the results presented in Fig. 1, it can be noted that the concentrations of copper (Fig. 1c), oxygen (Fig. 1d) and silver (Fig. 1e) in the coating vary

slightly over its thickness. This fact also indicates structural homogeneity of the resultant coating.

Atomic force microscopy was carried out in a coating layer located at a distance of $10\ \mu\text{m}$ (Fig. 2) from the coating surface, as well as at the interface between the coating and the copper substrate (Fig. 3). Since the electroexplosive coating is formed by a silver matrix and ZnO powder particles located in it, small particles of ZnO powder can break away from the matrix when preparing a thin cross section. In this case, pores are formed at the place of the lost particles (dark areas in Figs. 2a, 2b) with a depth of 30 to $100\ \text{nm}$ and a width of 2 to $5\ \text{nm}$ (Fig. 2c). ZnO particles are dispersed to sizes of 2– $5\ \text{nm}$ in the process of an electroexplosion, during the formation of a pulsed plasma jet of the electroexplosive products of conductors.

Separate large particles of various shapes with sizes from 10 to $15\ \text{nm}$ are also detected. These ZnO particles do not break away from the silver matrix when preparing the thin cross section; they stand out sharply in terms of color (they are lighter compared to the matrix). These particles are randomly arranged in a silver matrix. As can be seen from Figs. 2a and 2b, the large particles have a complex structure. The characteristic structural units of which they are composed are spheres (globules) with a diameter of 2 to $5\ \text{nm}$ (these are small spherical particles described above). The ratio of the silver matrix, large and small particles of ZnO powder is 0.6 : 0.15 : 0.25. If we take into account that large ZnO particles consist of smaller globular ZnO particles, then the ratio of the silver matrix and inclusions of ZnO powder will be 0.6 : 0.4. This ratio is proportional to the content of ZnO powder and silver foil used for electroexplosive spraying. The average roughness of the surface profile of the ZnO–Ag-system coating is $100\ \text{nm}$.

Thus, it was possible to identify an important structural element, i.e., the ZnO globule, which is a spherical particle with a diameter of 2 to $5\ \text{nm}$. There is a multilevel hierarchical structure of the ZnO–Ag-system coating, which is based on the same type of spherical ZnO particles with a diameter of 2 to $5\ \text{nm}$. The single structural unit, which is made of ZnO inclusions located in a silver matrix, is a very important argument in favor of the fractal mechanism for the formation of an electroexplosive coating. Such particles constitute the first hierarchical level of the structure of the electroexplosive coating of the ZnO–Ag system. The second hierarchical level is composed of globules: large particles of various shapes with sizes from 10 to $15\ \text{nm}$, which, in turn, form particles of micron sizes of irregular shape, detected by scanning electron microscopy.

At the interface between the coating and the copper substrate (Figs. 3a, 3b), dark depressions from 10 to $15\ \text{nm}$ in size are noticeable. Large ZnO particles, which were discussed above, broke away from them. In addition, surface periodic structures (SPS) occur at

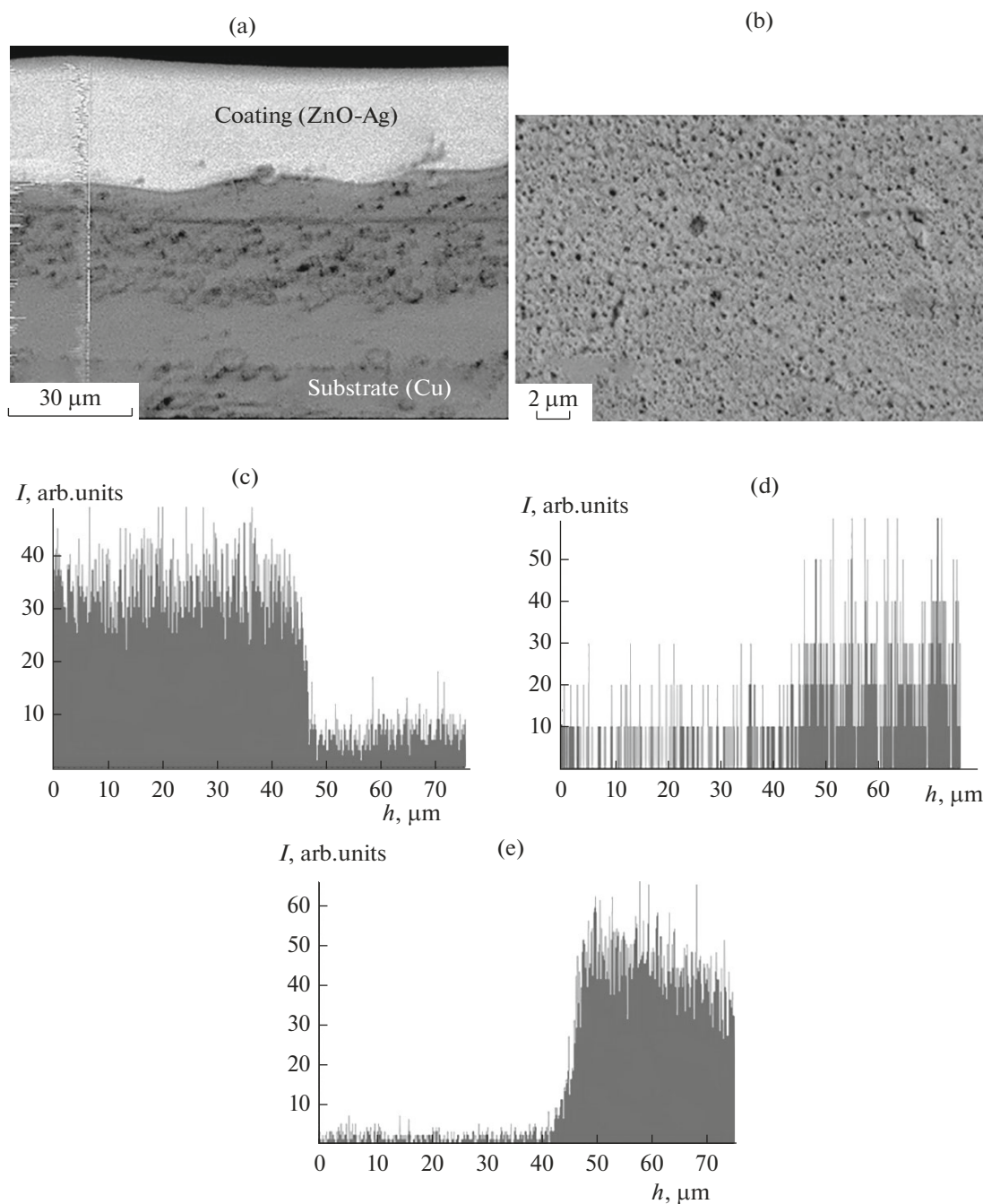


Fig. 1. Structure of the electroexplosive coating of the ZnO–Ag system (a), (b) and the concentration profiles of copper atoms (c), oxygen (d) and silver (e) along the line indicated on (a). The copper concentration is determined by the characteristic X-ray radiation $K_{\alpha 1}$; the oxygen concentration—according to $K_{\alpha 1}$; the silver concentration—according to $L_{\alpha 1}$.

the coating/substrate interface in the silver matrix. The secant line drawn perpendicular to these structural formations (Figs. 3b, 3c) gives grounds to assert that the wavelength in them is on average 3 nm. The structures are the residual nanorelief of the surface. After the end of the impact of a pulsed plasma jet of electroexplosive products of conductors on the substrate and cooling of the surface, the induced relief is

fixed in the form of SPS. The specific processes of their formation can be evaporation, surface melting and displacement of the melt by excessive vapor pressure, thermocapillary phenomena and thermochemical reactions, thermal deformations, the occurrence and development of various instabilities, such as Rayleigh–Taylor [10], Kelvin–Helmholtz [11], Marangoni [12] and others. In general, the phenome-

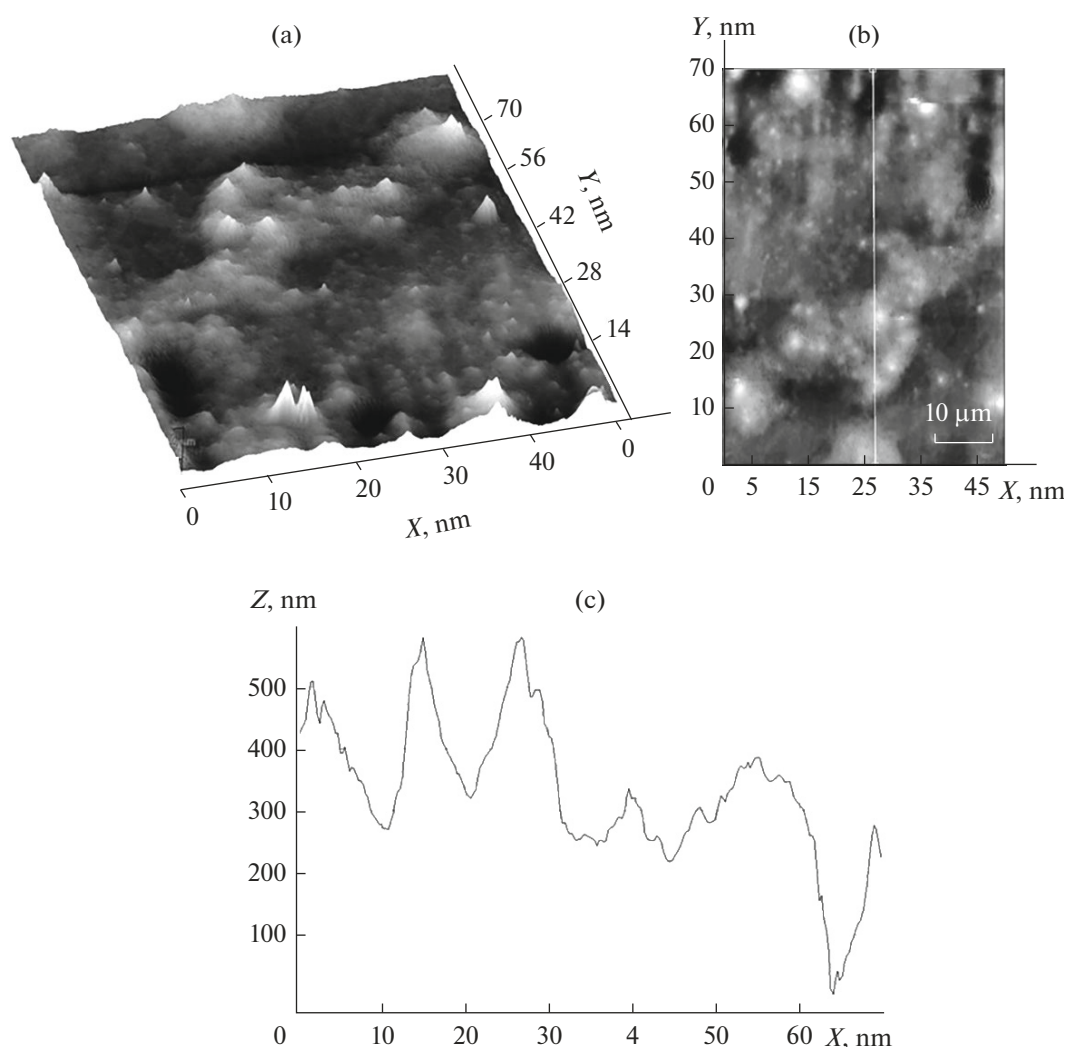


Fig. 2. The structure of the coating of the ZnO–Ag system obtained by atomic force microscopy: (a) distribution of the surface roughness in height in the 3D format, (b) position of the secant (top view), and (c) distribution of the roughness along the base length.

non is universal in nature and represents an example of self-organization in a system where initially there are no specified directions and structures [13]. The energy modes for the production of SPS correspond to heating of the material to a temperature approximately equal to the melting temperature (lower limit), but not higher than the developed evaporation temperature [13]. This is precisely the mode that was used in electroexplosive spraying in this work.

Profilometry of the surface shown in Fig. 3a, showed that the roughness parameter of the electroexplosive coating of the ZnO–Ag-particle system is 73 nm. The maximum protrusion of the profile in this case reaches a value of 536.85 nm, and the depression is 497.5 nm. Comparing the roughness parameters at the interface of the electroexplosive coating with the substrate (Fig. 3) with the roughness parameter in the coating layer located at a distance of 10 μm (Fig. 2), it

can be noted that they differ by 28%. In Fig. 3a 35% of the photograph is taken up by the substrate, and 65%, by the coating. This allows us to conclude that the roughness of the substrate is lower than the roughness of the coating. This is logical, because due to inclusions of ZnO which were lost from the silver matrix, the roughness parameter of the coating increases.

The mechanism of assembly of such complex multilevel ZnO in a silver matrix can be represented as follows. The uniform size r_1 of spherical ZnO particles of the first hierarchy level can be explained in the framework of the model of diffusion-limited aggregation by the mechanism of diffusion-limited “particle-cluster” aggregation [14]. The plasma components of a multi-phase jet of products of the electroexplosion of conductors distributed in a certain effective volume over some effective space of a substrate interface of the same size are assembled into a cluster, which will then

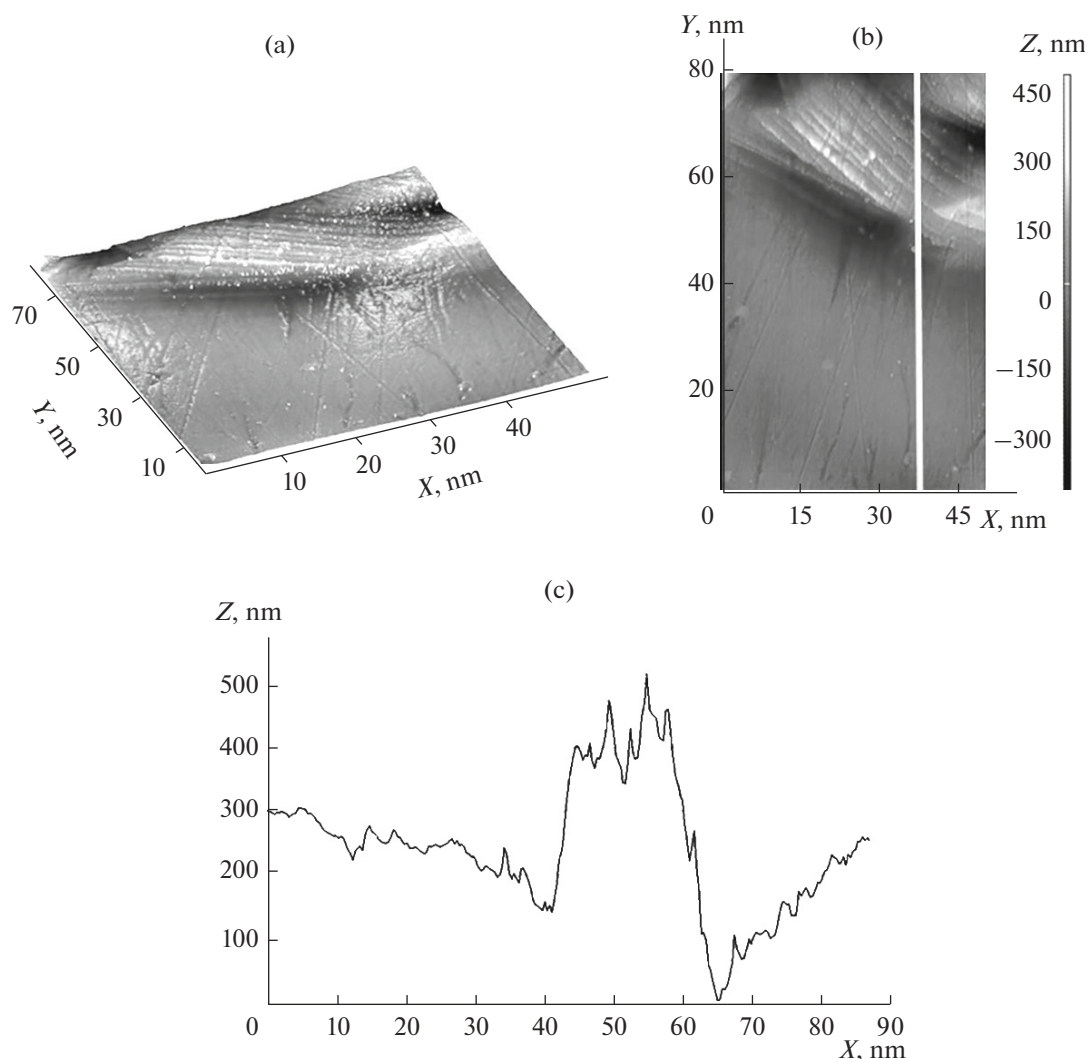


Fig. 3. Structure at the boundary of the ZnO–Ag coating with the copper substrate, obtained by atomic force microscopy: (a) distribution of the surface roughness in height in the 3D format, (b) position of the secant (top view), and (c) distribution of the roughness along the base length.

turn into a sphere with a diameter of 2 to 5 nm [14]. It should be noted that the size of the effective volume in which the formation of blanks of spherical particles of the first level of the hierarchy will depend on the composition of the exploding conductors and temperature. The formation of ZnO clusters occurs only at the initial stage of the action of a pulsed plasma jet on the substrate. At the next stage of growth, the “particle–cluster” aggregation mechanism ceases to act, but the cluster sizes increase. Growth begins simultaneously and ends synchronously after exhaustion of the presence of ZnO in the plasma state, the clusters turn into particles of almost the same sizes (under the discussed conditions, these are spheres with a diameter of 2 to 5 nm). The particle sizes are not large enough for gravitational forces to dominate. In other words, there is a metastable state in which spheres with a diameter of 2 to 5 nm are maintained in suspension mainly due to

Brownian motion and forces of intermolecular interaction with other components of the molten metal. Under the influence of Brownian forces, the spheres continue chaotic movement, which stimulates their agglomeration. The self-assembly of particles of the first hierarchy level leads to the formation of a second hierarchy level of globules with the size r_2 from 10 to 15 nm. The formation of this hierarchy level occurs mainly by the cluster-cluster mechanism. Further, such globular particles can be enlarged due to the agglomeration of particles in the micrometer range.

Let us analyze the dependence of the contact resistance R on the number of on/off cycles N when testing coatings of the ZnO–Ag system for electrical erosion resistance under arc erosion conditions (Fig. 4). The initial resistance values for the phases L_1 , L_2 , and L_3 are 5.6, 3.2, and 4.5 μOhm with the number of on/off cycles 134, 152, and 213, respectively. Subsequently,

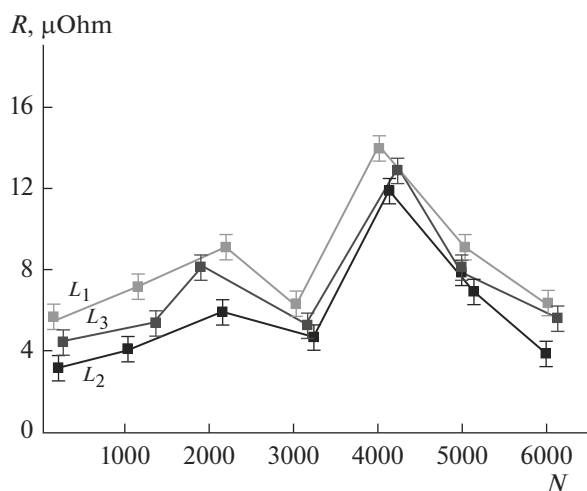


Fig. 4. The characteristic dependence of the contact resistance R on the number of on/off cycles N when testing electroexplosive coatings of the ZnO–Ag system for electrical erosion resistance under arc erosion conditions.

the resistance function increases. For phase L_1 , the resistance increases from 5.6 to 9.2 μOhm with the number of on/off cycles from 134 to 2178. For phase L_2 , the resistance increases from 3.2 to 6 μOhm with the number of on/off cycles from 152 to 2134. For phase L_3 , the resistance increases from 4.5 to 8.2 μOhm with the number of on/off cycles from 213 to 1883. Then a decrease in the resistance is observed. For phase L_1 , the resistance decreases to 6.3 μOhm with the number of cycles 3002. For phase L_2 , the resistance decreases to 5.4 μOhm with the number of cycles 3145. For phase L_3 , the resistance decreases to 4.7 μOhm with the number of cycles 3211. Then the resistance rises again and reaches its maximum value. For phase L_1 , the resistance increases to 14.1 μOhm with the number of cycles 3990. For phase L_2 , the resistance increases to 12 μOhm with the number of cycles 4123. For phase L_3 , the resistance increases to 13 μOhm with the number of cycles 4207. This indicates that at the present stage of the experiment, intense evaporation of the low-melting silver matrix begins under the influence of an electric arc. The contact surface is enriched with particles of ZnO powder, which has a lower electrical conductivity (10^{-8} S/m) compared to silver (62.5 MS/m) [15]. For this reason, the contact resistance in this section of the graph increases. At the end of the test, the resistance decreases again. For phase L_1 , the resistance decreases to 6.3 μOhm with the number of cycles 5997. For phase L_2 , the resistance decreases to 4 μOhm with the number of cycles 5983. For phase L_3 , the resistance decreases to 5.7 μOhm with the number of cycles 6123. At the end of the test, the resistance values for phases L_1 , L_2 , and L_3 are 6.3, 4.0, and 5.7 with the number of on/off cycles 5997, 5983, and 6123, respectively. The

tests showed that the formed coatings of the ZnO–Ag system satisfy the tests of the starters for commutation wear-resistance [16].

Thus, an increase in the electrical resistance during testing of the ZnO–Ag system of electroexplosive coatings for commutation wear-resistance is caused by the evaporation of a low-melting silver matrix under the influence of an electric arc and enrichment of the coating surface with ZnO particles. Electrical contacts hardened by electroexplosive coatings of the ZnO–Ag system are capable of mechanically cleaning the surface of ZnO particles. The formed coatings of the ZnO–Ag system satisfy the tests of starters for commutation wear-resistance.

CONCLUSIONS

A mechanism is proposed for the formation of hierarchy levels of the structure of electroexplosive coatings of the ZnO–Ag system. By comparing the images of atomic force microscopy of the surface of layers of electroexplosive coatings of the ZnO–Ag system, the typical sizes of the first and second hierarchy levels of the structure were determined, which, under the used spraying conditions, varied from 2 to 5 nm and from 10 to 15 nm, respectively. The self-assembly mechanism of hierarchical nanostructures is based on theoretical concepts of the formation and evolution of fractal aggregates in diffusion-limited and cluster-cluster aggregations. Such electroexplosive coatings are used to create switch contacts of high-power electrical networks.

At the coating/substrate interface, surface periodic structures with a wavelength of 3 nm on average were detected. They represent the residual surface nanorelief which arose after the end of the action of a pulsed plasma jet of electroexplosion products of conductors on the substrate and cooling of the surface.

The formed coatings of the ZnO–Ag system satisfy the tests of the starters for commutation wear-resistance. An increase in the electrical resistance during testing of the ZnO–Ag system of electroexplosive coatings for commutation wear-resistance is caused by the evaporation of a low-melting silver matrix under the influence of an electric arc and enrichment of the coating surface with ZnO particles. Electrical contacts hardened by electroexplosive coatings of the ZnO–Ag system are capable of mechanically cleaning the surface of ZnO particles.

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