Structure and Electrical Erosion Resistance of An Electro-
Explosive Coating of the ZnO-Ag System

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Abstract. For the first time, electroerosion-resistant coatings of the ZnO-Ag system were
obtained by electro-explosive spraying. The coating structure was investigated by atomic force
microscopy and scanning electron microscopy. The formed coating is a homogeneous composite
material consisting of a silver matrix and ZnO inclusions located in it. Tests of sprayed coatings
for electrical erosion resistance under arc erosion conditions were carried out. A formation
mechanism of hierarchical levels of the structure of electro-explosive coatings was 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 zinc oxide, the dependence of electrical contact resistance on the number
of on/off cycles in the process of testing for electrical erosion resistance is substantiated.

1. Introduction

Power systems safety, reduction of energy losses and saving material resources is mainly determined by
the reliability of electrical contacts. Reliability of electrical contacts determines the operation efficiency of
energy and industrial equipment, and by and large the global energy system. Due to poor-quality contacts, they are heated resulting in an increase of power losses and emergency situations. According to
the National Association of Rescue and Environmental Organizations, 50% of fires in industrial
enterprises and in the residential stock are caused by electrical equipment malfunction, while 50% of
electrical equipment fires are caused by electrical contact failures.

The use of powder metallurgy methods allows implementing in one material a diverse and
contradictory complex of properties that an electrical contact material should have [1]. Currently, a large
number of electro-contact materials have been developed for their use in various operating conditions.
As a rule, they include a matrix with high electrical conductivity and a high-melting component (filler)
with high wear and electro-erosion resistance. [2]. The most promising for manufacturing contacts are
composite materials based on silver, copper, copper-nickel, aluminum matrix and 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, ZnO-Ag, ZnO-Ag, W-Ag, Mo-Ag, W-C-Ag и
Mo-C-Ag etc. [3–8].

Since the destruction process of the material begins with its surface, for a number of practical
applications, for example, hardening the contact surfaces of medium and heavy-duty switches and
switching devices, the formation of protective coatings is promising, since in this case the electrical
erosion resistance of the contact surface, and not the entire volume, is important. It is economically and
technically reasonable to develop an approach to materials creation, which ensures the mechanical
strength of a component by the use of cost-efficient substrates, and the special surface properties are
provided by continuous or local formation of composite coatings, the properties of which correspond to
operating requirements. This approach can give 90% savings. Expert assessments confirm this trend.
One of the priority areas of condensed matter physics is the development of methods for improving the
operating characteristics of various materials. With this in mind, the hardening of the surface of arc-resistant electrical contacts is a crucial task for the development of contemporary technologies.

The aim of this work is to study the structure and the phase morphology of electro-explosive coating of the ZnO-Ag system, using scanning and atomic force microscopy, as well as conducting tests for electrical erosion resistance.

2. Materials and methods

The subject of research was copper contacts of the KPV-604 contactor, on the contact surfaces of which the ZnO-Ag system was formed by the electro-explosive method [9]. A 250 mg silver foil was used as an explosive conductive material on the surface of which a 50 mg CdO powder sample was placed in the zone of the explosion. The exposure time of plasma on the sample surface was ~100 μs, the absorbed power density at the jet axis ~5.5 GW/m², the pressure in the shock-compressed layer near the irradiated surface ~12.5 MPa, the residual gas pressure in the working chamber ~100 Pa; the plasma temperature at the nozzle exit ~104 K, the thickness of the heat affected zone ~50 μm. The structure and morphology of the coating and the adjacent substrate layer were analyzed by scanning methods (Carl Zeiss EVO50) with an EDAX X-ray spectrometer and atomic-force microscopy (Solver NEXT). Tests for electrical erosion resistance of coatings under conditions of arc erosion were carried out at the contacts of the CJ20 electromagnetic actuators with alternating current and inductive load in accordance with the requirements of the AC-3 test mode for switching wear resistance when operating in a three-phase circuit with a low voltage value of 400/230 V, frequency 50 Hz for currents up to 320 A and cosφ = 0.35 and the number of switching cycles 6000.

3. The results and discussion

The structure and elemental composition of the section of the coating/substrate system formed by the electro-explosive method were studied by scanning electron microscopy. A typical image of the cross-sectional structure of the ZnO-Ag composition is shown in Fig. 1.

The analysis of the results obtained shows that the formed coating is a homogeneous composite material (Fig. 1, a, b). According to the structural morphology and the etching contrast, the forming coating consists of a light silver matrix and dark ZnO inclusions with dimensions varying from 0.3 to 0.5 μm (Fig. 1, b). The elemental composition of the coating was analyzed by X-ray microanalysis methods. The research results are given in Fig. 1 c-e. Analyzing the results presented in Fig. 1 c-e, it can be noted that the concentrations of copper (Fig. 1 c), zinc (Fig. 1 d) and silver (Fig. 1 e) in the coating vary slightly in its thickness. This fact also indicates the structural homogeneity of the coating obtained.

Atomic force microscopy was performed in the coating layer located at a distance of 10 μm (Fig. 2) from the coating surface, as well as at the interface between the coating and the copper substrate (Fig. 3).

Since the electro-explosive coating is formed by a silver matrix and ZnO powder particles located in it, small particles of ZnO powder can be crumbled out of the matrix during the preparation of thin sections. In this case, pores, i.e. dark areas in Fig. 2, a, b 30 to 100 nm deep and 2 to 5 nm wide (Fig. 2, c) are formed at the site of fallen particles. ZnO particles are dispersed to 2...5 nm in the process of an electric explosion during the formation of a pulsed plasma jet of products of the electric explosion of conductors.

Separate large particles of various shapes with sizes ranging from 10 to 15 nm are also detected. These ZnO particles do not crumble out of the silver matrix during the preparation of the thin section; they are sharply highlighted in color, i.e. they are lighter than the matrix. They are randomly located in a silver matrix. As can be seen from Fig. 2, a, b large particles have a complex structure. They are composed of spheres (globules) with a diameter of 2 to 5 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. Taking into consideration the fact that large ZnO particles consist of smaller globular ZnO particles then the ratio of the silver matrix and the inclusions of ZnO powder is 0.6: 0.4. This ratio is proportional to the content of ZnO powder and silver foil used for electro-explosive coating. The average roughness of the surface profile of the ZnO-Ag system coating is 100 nm.
Figure 1. Structure of electro-explosive coating of the Cu-Ag system (a, b) and concentration profiles of copper (c), zinc (d) and silver (e) atoms along the line indicated on (a). The copper concentration is determined by the characteristic Kα₁ X-rays; zinc concentration is determined by Kα₁; silver concentration is determined by Lα₁.
Figure 2. The coating structure of the ZnO-Ag system, detected by atomic force microscopy
a – 3D distribution of uneven relief in height, b – secant position (top view), c – roughness distribution along the base length.

Thus, it was possible to identify an important structural element - the ZnO globule, i.e. a spherical particle with a diameter of 2 to 5 nm. There is a multi-level hierarchical structure of the ZnO-Ag coating system, which is based on uniform spherical ZnO particles with a diameter of 2 to 5 nm. The fact that the ZnO inclusions, located in the silver matrix are made of a single structural unit is a very important argument in favor of the fractal mechanism for the formation of an electro-explosive coating. Such particles constitute the first hierarchical level of the structure of the electro-explosive coating of the ZnO-Ag system. The second hierarchical level consists of globules - large particles of various shapes with sizes ranging from 10 to 15 nm, which, in turn, form the sediment of micron-sized particles of irregular shape, detected by scanning electron microscopy. At the boundary between the coating and the copper substrate (Fig. 3, a, b) there are visible dark depressions ranging in size from 10 to 15 nm. Aforementioned large ZnO particles crumbled out of them. In addition, surface periodic structures appear at the coating/substrate boundary in a silver matrix. The secant held perpendicular to these structural formations (Fig. 3, b, c) suggests 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 products of the electrical explosion of conductors on a substrate and cooling the surface, the induced relief is fixed in the form of surface periodic structures. They can be formed due to evaporation, melting of the surface and displacement of the melt by excess vapor pressure, thermocapillary phenomena and thermochemical reactions, thermal deformations, the emergence and development of various instabilities such as Rayleigh-Taylor [10], Kelvin-Helmholtz [11], Marangoni [12] and others. In general, the phenomenon is universal and is an example of self-organization in a system with no initially selected directions and structures [13]. The energy regimes for obtaining surface periodic structures correspond to heating the material to a temperature approximately equal to the melting point (lower limit), but not higher than the temperature of developed evaporation. [13]. This regime was used in electro-explosive coating in the present work.
Figure 3. Structure on the border of the ZnO-Ag coating with a copper substrate, revealed by atomic force microscopy
a – 3D distribution of uneven relief in height, b – secant position (top view), c – roughness distribution along the base length

Surface profilometry in Fig. 3a showed that the roughness parameter of the electro-explosive coating of the ZnO-Ag system is 73 nm. In this case, the maximum profile protrusion reaches 536.85 nm, and the depth - 497.5 nm. Comparing the roughness parameters at the electro-explosive coating/substrate boundary (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 photo is taken by the substrate and 65% -by the coating. It strongly suggests that the substrate roughness is lower than the coating roughness. This is natural since due to precipitations of ZnO inclusions from the silver matrix, the roughness parameter of the coating increases.

The assembly mechanism of such a complex multi-level ZnO in the silver matrix can be represented as follows. The uniform size r1 of spherical ZnO particles of the first hierarchical level the can be explained within the framework of the model of diffusion-limited aggregation by the mechanism of diffusion-limited aggregation “particle-cluster” [14]. Plasma components of a multiphase jet of products of the electrical explosion of conductors distributed in a certain effective volume on a certain effective interface space of the substrate of the same size are assembled into a cluster, which will then 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 hierarchical level takes place will depend on the composition of the explosive conductors and the temperature. The formation of ZnO clusters occurs only at the initial stage of the impact of a pulsed plasma jet on the substrate. At the next growth stage, the particle-cluster aggregation mechanism ceases to operate, but the cluster sizes increase. Growth begins simultaneously and ends synchronously when the ZnO is in a plasma state, the clusters are transformed into particles of almost the same size (under the conditions discussed, these are spheres with a diameter of 2 to 5 nm). Particle sizes are not large enough for gravity force to dominate. In other words, the spheres with a diameter of 2 to 5 nm are maintained in a suspended state mainly due to Brownian motion and intermolecular interaction forces with other components of the molten metal. Under the action of Brownian forces, the spheres continue the chaotic movement that stimulates their agglomeration. Self-assembly of particles of the first hierarchical level leads to the formation of a second
hierarchical level of globules with r2 size from 10 to 15 nm. The formation of this hierarchical level occurs mainly through the cluster-cluster mechanism. Further, such globular particles can be enlarged due to conglutinating into micrometer particles.

Let us analyze the dependence of the contact resistance (R) on the number of on / off cycles (N) when testing ZnO-Ag coatings for electrical erosion resistance under arc erosion conditions (Fig. 4).

![Figure 4](image)

**Figure 4.** The dependence of the contact resistance (R) on the number of on / off cycles (N) when testing electro-explosion coatings of the ZnO-Ag system for electro-erosion resistance under conditions of arc erosion.

At the beginning of the experiment, the value of R contacts is 11, 7.5 and 9.5 μOhm for phases L1, L2, and L3, respectively. After the first on / off cycles, R begins to decrease from the initial values in linearity to the following values.: for phase L1, the value of R is 6.3 μOhm with N = 3059; for phase L2, the value of R is 4.7 μOhm at N = 2956 and is the smallest among all phases; for phase L3, the value of R is 5.4 μOhm with N = 3211. A gradual decrease in R when N is varied from 0 to 3211 indicates that a gradual burn-in of contacts occurs on this test part, which results in a stable surface roughness. In the next section of the curve, with increasing N, R increases to maximum values: for the L1 phase, the value R is 15.6 μOhm at N = 5015; for phase L2, the value of R is 13.3 μOhm at N = 5123 and is the smallest; for the L3 phase, the value of R is 14.3 μOhm with N = 4967. This indicates that at the present stage of the experiment intensive evaporation of the fusible 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) if compared with silver (62.5 MS / m) [15]. For this reason, the contact resistance on this part of the graph increases. When the maximum values of R are reached on all three phases with a further increase in N, the electrical resistance decreases again. The reason is that at N ≈ 5000 due to the evaporation of silver, the contact surface is enriched with refractory ZnO particles with a low electrical conductivity. Upon reaching N ≈ 5000, mechanical accumulation of ZnO particles on the contact surface occurs. As a result, the electrical resistance decreases again, namely, for the L1 and L2 phases, the R values are 6.2 μOhm with N = 6023 and 4 μOhm with N = 5983, respectively. For L3, the value of R equals 5.7 μOhm with N = 6122. The tests have shown that the formed coatings of the ZnO-Ag system satisfy for switching wear testing [16].

Thus, the increase in electrical resistance during the tests of electro-explosive coatings of the ZnO-Ag system for switching wear resistance is caused by the evaporation of the low-melting silver matrix under the influence of an electric arc and the enrichment of the coating surface with ZnO particles. Electrical contacts, hardened by electro-explosive 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 for switching wear testing.
4. Conclusion

This work presents a mechanism for the formation of hierarchical levels of the structure of electro-explosive coatings of the ZnO-Ag system. By comparing the images of atomic force microscopy of the surface of layers of electro-explosive coatings of the ZnO-Ag system, the typical sizes of the first and second hierarchical levels of the structure were established, which, under the coating conditions used, were from 2 to 5 nm and from 10 to 15 nm, respectively. The mechanism of self-assembly of hierarchical nanostructures is based on theoretical concepts of the formation and evolution of fractal aggregates with diffusion-limited and cluster-cluster aggregations. Such electro-explosive coatings are used to create contacts of switches of high-power electrical networks.

Surface periodic structures with an average wavelength of 3 nm were found at the coating/substrate boundary. They represent the residual nano-relief of the surface, which appeared after the end of the impact of a pulsed plasma jet of products of the electrical explosion of conductors on a substrate and cooling of the surface. Formed coatings of the ZnO-Ag system satisfy the testing of contactors for switching wear resistance. The increase in electrical resistance during the tests of electro-explosive coatings of the ZnO-Ag system for switching wear resistance is caused by the evaporation of the low-melting silver matrix under the influence of an electric arc and the enrichment of the coating surface with ZnO particles. Electrical contacts, hardened by electro-explosive coatings of the ZnO-Ag system, are capable of mechanically cleaning the surface of ZnO particles.

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