Original Article

Improvement of copper alloy properties in electro-explosive spraying of ZnO-Ag coatings resistant to electrical erosion

Denis Romanov\textsuperscript{a,b}, Stanislav Moskovskii\textsuperscript{b}, Sergey Konovalov\textsuperscript{a,c,*}, Kirill Sosnin\textsuperscript{b}, Viktor Gromov\textsuperscript{b}, Yuriy Ivanov\textsuperscript{d}

\textsuperscript{a} Wenzhou University Institute of Laser and Optoelectronic Intelligent Manufacturing, Wenzhou, 325024, China
\textsuperscript{b} Siberian State Industrial University, Department of natural science disciplines of Professor V. Finkel, Novokuznetsk, 654007, Russia
\textsuperscript{c} Samara National Research University, Samara, 443086, Russia
\textsuperscript{d} Institute of High Current Electronics of the Siberian Branch of the RAS, Tomsk, 634055, Russia

\textbf{ARTICLE INFO}

Article history:
Received 28 August 2019
Accepted 5 September 2019
Available online 26 September 2019

Keywords:
Composite coating
ZnO-Ag system
Structure
Electrical erosion resistance
Nanohardness
Young modulus

\textbf{ABSTRACT}

The electroerosion resistant coatings of ZnO-Ag system have been obtained for the first time on the surface of the electrical contact of the electromagnetic starter CJ20. The formation of the coatings of ZnO-Ag system was produced due to the processing of the electrical contact surface by plasma formed at electrical explosion of silver foil with the weighed sample of ZnO powder. The nanohardness, Young modulus, wear resistance, friction coefficient and electroerosion resistance of the formed coatings have been investigated. After the electroerosion spraying the wear resistance of the modified layer increases \approx 1.3 - fold as compared to the annealed copper. The nanohardness of the sprayed coating is \approx 3.8 - fold larger than that of the annealed copper. By the electroerosion resistance the coating is consistent with the requirements of standards. The investigation into the electroexplosion coating of ZnO-Ag system was done by the methods of scanning electron microscopy, transmission electron microscopy and atomic-force microscopy. The structure of the coating is formed by the cells of high-velocity crystallization. The cell dimensions vary within 150 nm–400 nm. The cells are separated by the interlayers of the second phase whose thickness varies within 15–50 nm. Bu the method of atomic-force microscopy the separate particles of ZnO of different shape with size of 10–15 nm located chaotically in the silver matrix were revealed as well as the spherical particles of ZnO with size of 2–5 nm. The total thickness of the coating amounts to 60 nm.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

As world experience shows the crisis phenomena in countries as a whole and in power engineering, in particular, affect negatively such an important indicator of energy efficiency of the transmission and distribution of electric energy as its losses in the electric networks [1,2]. The characteristic fact, in this case, is that the dependence of growth of losses in the electric networks and the crisis of economy take place not only in Russia and CIS countries but in other countries having entered into the period of transition from the centralized to market methods of management of economy [3,4]. It is connected, apparently, with the weakening of energy consumption control, the decrease in the paying capacity of the considerable part of the consumers, in the first place, the population, with the growth of energy misappropriations, the aggravation of problems through the imperfection of the traditional system of energy accounting. The supernormative losses of electric energy in electric networks are the direct financial losses of energy producers. The savings from the decrease in losses might be directed to the technical re-equipment of the networks, the increase in the personal wage, the improvement of the organization of the power supply and distribution, the increase in the reliability and quality of the consumers power supply, the decrease in power tariffs [5,6]. The decrease in power losses in electrical networks is a complex problem requiring the considerable capital investments needed for the optimization of electrical networks, the improvement of power accountings system, the introduction of new information technologies in power sale activity and control of network regimes, the personnel training and equipment by the check instrumentation of the power measurement devices [7,8]. One of the reasons of the electrical energy losses is the unreliable electrical contact in different switches and commutation apparatuses, first of all, the contacts of powerful electrical networks [9,10]. Nowadays, more and more scientists take interest in the problem of creating the protective coatings of different systems [11–14]. The application of such coatings will make it possible to protect effectively not only the electrical contacts [15] but also to recover the operating capacity of the contact after its failure. Among the numerous composite materials intended for the protection of the electrical contacts the special place belongs to the compositions based on ZnO-Ag system [16,17]. As stated in a “road map” [18] coating with different systems will be a developing branch in coming decades. The study [19], in particular, suggests a commercially, economically and technologically approved method of spraying heat-resistant, not fireproof coatings deposited by electrical explosion. The work [20] researches plasma coatings, formed on aluminum alloys and the influence of hydrogen on wear resistance of steels. Coatings of a system WC-Co-Cr to be formed according to technology HVOF [21] have a good erosion resistance. As seen in these literature data, research into coatings formed by different methods is a promising and efficient field of studies.

The purpose of the research was the formation of the electroexplosion coating of ZnO-Ag system on the surface of the copper electrical contact as well as the study of its structure, wear resistance, friction factor, nanohardness, Young modulus and electroerosion resistance.

2. Material and methods of investigation

The investigation was concerned with the copper electrical contacts of electromagnetic starter CJ20 on the contact surfaces of which the electroexplosion coating of ZnO-Ag system was formed by the electroexplosion method. The silver foil of 250 mg in mass on the surface of which in the area of explosion the weighed sample of ZnO powder of 80 mg in mass was placed was used as an electric current conducting material. The chemical composition of silver foil, at %: 99.90 Ag, 0.003 Pb, 0.004 Fe, 0.01 Sb, 0.02 Bi, 0.063 Cu. A thickness of silver foil is 20 μm. The chemical composition of a powder used for electroexplosion - CuO 99.44 at.%, Cu 0.25 at.%. A diameter of particles 5.0...20.0 μm. The time of plasma effect on the sample surface was ~100 μm, the power density being absorbed on the axis of jet ~5.5 GW/m², the pressure in shock-compressed layer near the surface being irradiated ~12.5 MPa, the residual gas pressure in the working chamber ~100 Pa; the temperature of plasma on the nozzle cut ~10⁴ K, the thickness of the thermal effect zone ~50 μm. A coefficient of utilization of the conductor material to be exploded is 0.95 for the specified parameters. The investigations into the elemental and phase composition, the state of the defect substructure of the surface layer formed as a result of electroexplosion spraying (EES) were performed by the methods of the scanning electron microscopy (device Carl Zeiss EVO 50 equipped by the microanalyzer EDAX), the transmission diffraction electron microscopy of thin foils (device JEOL JEM –2100F) and the atomic force microscopy (device Solver NEXT). The foils were manufactured by the methods of iron thinning of the plates cut in the plane located perpendicular to the surface of modification. The properties of the material were characterized by nanohardness and young modulus (nanohardness meter DUH-211S (Shimadzu, Japan), the indenter load ~30 mN). The atomic-force microscopy was carried out in the layer of the coating located at 10 μm distance from the surface of the coating as well as at the interface between the coating and copper substrate. The tribological studies (the determination of wear resistance and friction factor) were done using the tribometer Pin on Disc and Oscillating TRIBO tester (TRIBO technic, France) at the following parameters: the ball from VK6 solid alloy and 6 mm in diameter, the track radius ~3 mm, the indenter load ~3 N; the track length varied depending on the wear resistance level of the material under study. The electroerosion resistance tests of the coatings in the conditions of the arc erosion were performed on the contacts of electromagnetic starters CJ20 with the alternating current and the inductive load in accordance with the requirements of test regime AC-3 for commutation wear resistance in operation in three-phase circuit with the low voltage value of 400/230 V, the frequency of 50 Hz for the current to 320 A and cosφ = 0.35 and the commutation cycle number of (6000)
3. Results and discussion

The mechanical properties of the copper modified layer were characterized by nanohardness. Nanohardness and Young modulus were determined using the transverse metallographic sections when carrying out the indentation along the straight line located in parallel with the surface of modification at $\approx 15 \mu m$ distance from the surface of the processing. The results of the performed tests showed that the hardness of the electroexplosion coating varied within 750 MPa to 2250 MPa at the average hardness value of 1600 MPa, it increased the microhardness of the annealed copper by 3.8 times [22]. Young modulus of the electroexplosion coating varies within 56.1 GPa to 89.0 GPa at the average modulus value of 75.1 GPa. Note, that Young modulus of the annealed copper varies within 110–130 GPa, Young modulus of silver – 80 GPa [22].

EES of copper is accompanied by the insignificant ($\approx 1.1$-fold) increase in wear resistance of the modified layer; the friction factor, in this case, increases 1.3-fold. The change in the friction factor in the process of the tribological tests (Fig. 1) should be paid attention to. Namely, at the initial stage of the tests the friction factor of the modified surface (Fig.1, b) is substantially lower than that of the initial copper. This fact may be indicative of the fact that the hardened layer is thin and it loses quickly its wear resistance properties.

Let’s analyze the dependence of contact resistance ($R$) on the number of on/off cycles ($N$) when testing the coatings of ZnO-Ag system for electroerosion resistance in the conditions of arc erosion (Fig. 2). The initial values of the resistance for the phases L1, L2, L3 are equal to 5.6, 3.2, 4.5 $\mu$Ohm at the number of on/off cycles being 134, 152, 213, respectively. Later on the function of resistance increases. For L1 phase the resistance increases from 5.6 to 9.2 $\mu$Ohm at the number of on/off cycles from 134 to 2178. For L2 phase the resistance increases from 3.2 to 6 $\mu$Ohm at the number of on/off cycles from 152 to 2134. For L3 phase the resistance increases from 4.5 to 8.2 $\mu$Ohm at the number of on/off cycles from 213 to 1883. After it the drop of the resistance is observed. For L1 phase the resistance decreases to 6.3 $\mu$Ohm at the number of cycles of 3002. For L2 phase the resistance decreases to 5.4 $\mu$Ohm at the number of cycles of 3145. For L3 phase the resistance decreases to 4.7 $\mu$Ohm at the number of cycles of 3211. Then the resistance value increases again and reaches the maximum value. For L1 phase the resistance increases to 14.1 $\mu$Ohm at the number of cycles of 3990. For L2 phase the resistance to 12 $\mu$Ohm at the number of cycles of 4123. For L3 phase the resistance increases to 13 $\mu$Ohm at the number of cycles of 4207. It is indicative of the fact that at this stage of the experiment the intensive evaporation of the low melting silver matrix under the effect of the electric arc begins. The contact surface is enriched by the particles of ZnO powder possessing the lesser electrical
Fig. 3 – Structure of transverse metallographic section of copper electrical contact subjected to electroexplosion spraying. (1) surface layer; (2) transition layer; (3) thermal effect layer; (a) general view of the coating; (b) structure being formed on the boundary of the coating with the substrate; (c) electron microscope image of surface layer structure.

Fig. 4 – Distribution of silver atoms (curve 1) and copper (curve 2) in copper electrical contact subjected to EES of coating of ZnO-Ag system.

conductivity ($10^{-8} \text{ S/m}$) as compared to silver (62.5 MS/m) [23]. For this reason, the contact resistance increases at this part of the graph. At the end of the tests the resistance decreases again. For $L_1$ phase the resistance decreases to 6.3 $\mu$Ohm at the number of cycles of 5997. For $L_2$ phase the resistance decreases to 4 $\mu$Ohm at the number of cycles of 5983. For $L_3$ phase the resistance decreases to 5.7 $\mu$Ohm at the number of cycles of 6123. At the end of the test the resistance values for $L_1$, $L_2$, $L_3$ phases are equal to 6.3, 4, 5.7 at the number of on/off cycles of 5997, 5983, 6123, respectively. The performed tests have shown that the formed coatings of ZnO-Ag system satisfy the tests of starters for the commutation wear resistance [24].

The contacts CJ20 should ensure not only the long operation without the impermissible overheating in the conditions of the normal regime but also the required thermal and electrodynamic resistance in the regime of short circuit. The movable circuit-opening contacts should not fail under the action of the high temperature of the electric arc that forms at their opening and they should close safely without welding and melting at switching for short circuit. The operation of these electrical contacts consists of 4 stages – the opened state, closing, closed state and opening, each of which effects the reliability of contacting. In the opened state the environment influences the electrical contacts and as a result the films are formed on their surface. In the closed state when the contacts are pressed to each other and the electric current flows through them they heat and deform; under some conditions if the contacts overheat the welding may occur. At closing and opening of the contacts the bridge or discharge phenomena take place which are accompanied by the vaporization and the transfer of the contact metal, changing its surface. In addition, the mechanical wear of contacts is possible as a result of shocks and sliding on each other.

Thus, the increase in the electrical resistance as a part of the tests of the electroexplosion coatings of ZnO-Ag system for the commutation wear resistance is caused by the vaporization of the low-melting silver matrix under the effect of the electric arc and the enrichment of the coating material by ZnO particles. The electrical contacts hardened by the electroexplosive coatings of ZnO-Ag system are capable of the mechanical cleaning of the surface from ZnO particles. The formed coatings of ZnO-Ag system satisfy the tests of the starts for commutation wear resistance.

The defect substructure of the electroexplosive coating of ZnO-Ag system was studied by analyzing the transverse etched metallographic sections (Fig. 3). It has been stated that EES of copper is accompanied by the formation of the multilayer structure. The thickness of the surface layer (Fig. 3a, layer 1) having the submicrocrystalline (150–230 nm) structure (Fig. 3c) changes in wide limits and varies from 30 to 60 $\mu$m. The surface layer is separated from the thermal effect layer by
Fig. 5 – TEM structure of electroexplosion coating of ZnO-Ag system obtained on copper contact; (a, b) surface layer, (c) transition layer, (d) thermal effect layer.

Fig. 6 – Electron microscope STEM image (a) of electroexplosive coating structure of ZnO-Ag system obtained on copper electrical contact; (b) structural image of the portion obtained in characteristic X-ray radiation of silver atoms, (c) atoms of zinc; (d) atoms of oxygen.
the transition layer 1.0–1.3 μm thick (Fig. 3b, layer 2). It should be noted that the transition layer contains a large number of micropores (Fig. 3a, b). The phase composition of the coating is a silver matrix with ZnO inclusions in it.

By the methods of micro X-ray spectral analysis the investigations into the elemental composition of the modified layer of the copper electrical contact have been carried out. The results of the studies presented in Fig. 4 testify that silver is the main element of the surface layer. In the transition layer the silver atom concentration decreases fast and in the bulk of the copper electrical contact the silver atoms are found in the minimum quantity.

The phase and elemental composition, the defect substructure state of the copper electrical contact subjected to EES of the coating of ZnO-Ag system were analyzed by the methods of the transmission electron diffraction microscopy of thin foils. The performed studies show that in the surface layer up to 60 μm thick the structure of high-velocity cellular crystallization is formed independent of the distance to the surface of irradiation. Its characteristic electron microscopic images are shown in Fig. 4(a, b). The cells have a round shape (Fig. 5a). The cell size varies within 150–400 nm. The cells are separated by the interlayers (Fig. 5b) whose thickness varies within 15–50 nm. In the volume of the cells the dislocation substructure in the form of chaotically distributed dislocation (Fig. 5b) is revealed. The scalar density of the dislocation is \( \approx 2.1 \times 10^{15} \text{ cm}^{-2} \). The transition layer has the dendritic crystallization structure from the side of the electroexplosive spraying layer (Fig. 5c, layer 1) and the lamellar structure from the side of the thermal effect layer (Fig. 5c, layer 2). The thermal effect layer of the copper electric contact has a grain and subgrain structure (Fig. 5d). In the volume of copper grains, the dislocation substructure in the form of chaotically distributed dislocations (Fig. 5d) is observed. The value of scalar dislocation density amounts to \( \approx 1.3 \times 10^{15} \text{ cm}^{-2} \). In should be noted that a large number of the bend extinction contours \([25,26]\) (Fig. 5d) are present on the electron microscopic image of the thermal effect layer that is suggestive of the high curvature-torsion level of the material caused by the internal stress fields \([27]\).

---

**Table 1** – Relative content of chemical elements in surface layer of electroexplosive coating of ZnO-Ag system. Fitting coefficient: 0.1921.

<table>
<thead>
<tr>
<th>Element</th>
<th>E, keV</th>
<th>Mass %</th>
<th>Counts</th>
<th>Error, %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (L)</td>
<td>2.984</td>
<td>51.83</td>
<td>101179.97</td>
<td>0.01</td>
<td>63.89</td>
</tr>
<tr>
<td>Zn (K)</td>
<td>8.630</td>
<td>31.43</td>
<td>33371.70</td>
<td>0.01</td>
<td>22.82</td>
</tr>
<tr>
<td>O (K)</td>
<td>0.525</td>
<td>16.74</td>
<td>18340.04</td>
<td>0.26</td>
<td>13.29</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.00</td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** – Relative content of chemical elements in transition layer of copper modified by electroexplosion method.

<table>
<thead>
<tr>
<th>Element</th>
<th>E, keV</th>
<th>Mass %</th>
<th>Counts</th>
<th>Error, %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (K)</td>
<td>8.040</td>
<td>86.84</td>
<td>179363</td>
<td>0</td>
<td>91.4</td>
</tr>
<tr>
<td>Ag (L)</td>
<td>2.984</td>
<td>8.6</td>
<td>9663.6</td>
<td>0.01</td>
<td>5.33</td>
</tr>
<tr>
<td>Zn (K)</td>
<td>3.443</td>
<td>4.28</td>
<td>4812.1</td>
<td>0.01</td>
<td>2.41</td>
</tr>
<tr>
<td>O (K)</td>
<td>0.525</td>
<td>0.28</td>
<td>595</td>
<td>0.61</td>
<td>0.86</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Fig. 7** – Electron microscope STEM image (a) of electroexplosive coating structure of ZnO-Ag system obtained on the copper electrical contact; (b) image of the portion structure (a) obtained in characteristic X-ray radiation of copper atoms; (c) silver atoms; (d) zinc atoms.
Fig. 8 – 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.

The distribution of silver, zinc and oxygen atoms in the electroexplosive coating was studied by the methods of micro-X-ray spectral analysis of thin foils. The result of the studies are shown in Figs. 6 and 7. When analyzing the results presented in Fig. 5, one can conclude that in the structure of the high-velocity cellular crystallization being formed in the surface layer the volume of cells is formed mainly by the silver atoms (Fig. 6b), the atoms of zinc (Fig. 6c) and oxygen (Fig. 6d) are located chiefly along the cells boundaries, forming the extended interlayers.

The relative content of the atoms forming the surface layer of the sprayed electroexplosive coating is given in Table 1. When analyzing the results presented in Table 1 it can be noted that the main elements of the surface layer are silver, zinc and oxygen as was to be expected.

In the transition layer structure (the layer with dendritic crystallization) the atoms of silver and zinc are located mostly along the boundaries of dendrites (Fig. 7c, d). In the volume of copper grains forming the thermal effect zone the atoms of silver and zinc are revealed in the negligible quantity by the methods of micro-X-ray spectral analysis.

The relative content of the atoms forming the transition layer of the electroexplosive coating of ZnO-Ag system is shown in Table 2. When analyzing the results presented in Table 2 it may be noted that the concentrations of silver and zinc atoms in the transition layer is substantially lower that in the surface layer and that is in good agreement with the results of micro-X-ray spectral analysis obtained by the methods of scanning electron microscopy (Fig. 4).

The separate ZnO particles of the various shape and 10–15 nm in size, chaotically located in the silver matrix (Fig. 8a) have been revealed by the methods of the atomic force microscopy. The spherical particles of ZnO 2–5 nm in size have been detected as well. The fractions of the silver matrix, the coarse and fine particles of ZnO in the coating are estimated as 60, 15 and 25%. The relief asperity of the coating amounted to 550.6 nm, and that of the dent ~300.5 nm. On the coating – substrate interface the surface periodic structures with the average period of 3 nm (Fig. 9) are noted from the side of the coating.

The results obtained in the research suggest that the increase in the strength (nanohardness) and the tribological (wear resistance) properties and the electroerosion resistance of the cooper coating of ZnO-Ag system is caused by the formation of the multielemental multiphase submicronanodimensional state enriched by the atoms of different elements in the surface layer.
4. Conclusion

It has been shown that the surface spraying of the cooper electrical contact by the methods of the electric explosion of the current conducting silver foil with the weighed sample of zinc oxide powder located on its surface is accompanied by ≈1.1 - fold increase in the wear resistance of the modified layer; in this case, the friction factor increases ≈1.3 - fold. It has been established that the nanohardness of the sprayed coating is ≈3.8 - fold larger than that of the annealed copper. It has been found that the electroexplosion spraying of the copper electrical contact is accompanied by the formation of the multilayer structure of total thickness up to 60 μm. The phase composition of the coating is a silver matrix with ZnO inclusions. It has been revealed that the structure of the high velocity cellular crystallization is formed in the surface layer independent of the distance to the surface of modification. The cells’ dimension varies within 150-400 nm. The cells are separated by the interlayers of the second phase whose thickness varies within 15-50 nm. It has been shown that the transition layer has the structure of dendritic crystallization from the side of the surface layer and the lamellar-type structure from the side of the thermal effect zone. It has been established by the methods of micro X-ray spectral analysis that the cells’ volume of the surface layer structure is enriched by silver atoms, the atoms of zinc and oxygen are located mostly in the interlayers along the cells’ boundaries. It has been suggested that perhaps the increase in the strength (nanohardness) and tribological (wear resistance) properties and the electroerosion resistance of the copper electrical contact subjected to the electroexplosion spraying of the coating of ZnO-Ag system is caused by the formation of the multielemental multiphase submicro-nanodimensional structure in the surface layer. The application of such a coating makes it possible a 2-fold increase in the operation life of the copper electrical contacts.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

The present work was performed within Russian Science Foundation project no. 18-79-00013.

References


