

STRUCTURAL-PHASE STATE OF THE SYSTEM “CdO-Ag COATING / COPPER SUBSTRATE” FORMED BY ELECTROEXPLOSIVE METHOD

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The study on phase and elemental composition of the surface layer of copper electrical contact of contactor KPV-604, subjected to the electroexplosive deposition of the composite coating of the CdO-Ag system, was carried out by the method of Transmission electron microscopy (TEM). The scale of the elements of coating surface structure after electroexplosive deposition varies in a very wide range – from hundreds of micrometers to tens and hundreds of nanometers. According to the morphological characteristic two layers can be distinguished in the volume of coating: the coating itself and the heat affected layer smoothly transiting into the main volume of the sample.

Key words: coating, silver, cadmium oxide, electro-explosive spraying, structure-TEM

INTRODUCTION

According to the data of International Association “Interelectromash” the share of electrical equipment breakdowns due to the contact device failure ranks first among other faults and is 26 %. To restore the contact to operational condition it is replaced with a new one. The combination of different and simultaneously incompatible requirements is typical for the materials of electrical contacts. For example, they should possess high hardness, melting point, electrical and thermal conductivity, electroerosion and corrosion resistance combined with the absence of welding and bridging. The use of powder metallurgy methods allows a diverse and contradictory set of properties, that an electrical contact material must have, to be implemented in a single material [1]. At present a large number of electrical contact materials have been developed to be applied in a variety of operating conditions. Their composition includes, as a rule, a matrix with high electrical conductivity and a high-melting component (filler) with high wear and erosion resistance [2].

The most promising for making contacts are composite materials based on silver, copper, copper-nickel, aluminum matrix and high-melting filler. They include the following systems: W-Cu, Mo-Cu, WC-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, W-Ag, Mo-Ag, WC-Ag and Mo-C-Ag, etc. [3–8].

According to expert estimates the volume of the world market of composite materials for 2016 amounted to approximately 17 million tonnes. In the structure

of world consumption of composite materials and products from them by sectors of economy the share of composite materials consumed in electronics and power industries is 21 % among other industries and it is the main growth factor. The volume of domestic production of arc-resistant electrical contacts from composite materials is 18 billion rubles. If to take into account the fact that the contact wear before its failure and replacement with a new one does not exceed 50 % then about 150 million USD is wasted only in the Russian Federation.

Since the process of material destruction begins from its surface for a number of practical applications the formation of protective coatings is very promising, for example, for hardening of the contact surfaces of medium- and heavy duty circuit breakers and switching devices, because in this case the erosion resistance of the contact surface is important but not the entire volume. It is economically and technically expedient to develop an approach to the creation of materials which ensures the mechanical strength of a component by the use of cost efficient substrates, and the special surface properties are provided by the continuous or local formation of composite coatings on it, the characteristics of which correspond to operational requirements. Savings under this approach can reach 90 %. Expert assessments confirm this trend. One of the priority areas of condensed matter physics is the development of methods for improving the performance characteristics of various materials. Taking it into account the surface hardening of arc-resistant electrical contacts is an urgent task of developing new modern technologies.

The purpose of this work is to study the phase composition, defect substructure and the phase morphology of electroexplosive coating of the CdO-Ag system by means of transmission electron microscopy.

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MATERIAL AND METHODS OF RESEARCH

The subject of research was copper contacts of contactor KPV-604, on the contact surfaces of which the CdO-Ag system was formed by the electroexplosive method [9]. A silver foil 250 mg in weight was used as an explosive conductive material on the surface of which in the zone of explosion a sample of CdO powder weighing 50 mg was placed. The time of plasma action on the sample surface was $\sim 100 \mu\text{s}$, the absorbed power density at the jet axis $\sim 5,5 \text{ GW/m}^2$, the pressure in the shock-compressed layer near the irradiated surface $\sim 12,5 \text{ MPa}$, the residual gas pressure in the working chamber $\sim 100 \text{ Pa}$; the plasma temperature at the nozzle exit $\sim 10^4 \text{ K}$, the thickness of the heat affected zone $\approx 50 \mu\text{m}$. The phase composition, morphology and defect substructure of the coating and the adjacent substrate layer were analyzed by transmission electron diffraction microscopy (microscope JEM-2100F, JEOL). The foils for the study of material by the methods of transmission electron diffraction microscopy were made by ion thinning of thin plates ($\approx 100 \mu\text{m}$) located in the cross section of the sample. This allowed the structure of the coating and the transition layer that separates the coating and the substrate to be investigated. Ionic thinning of the plates was performed by means of Ion Slicer EM 09100IS.

THE STUDY RESULTS AND THEIR DISCUSSION

The typical electron microscopic image of the coating and the layer of copper adjacent to the coating is provided in Figure 1.

The coating of the CdO-Ag system formed on the surface of the copper contact of contactor KPV-604 by the electroexplosive method has a nanocrystalline struc-

ture (Figure 1, a, b). The crystallite size varies from 20 nm to 50 nm. The layer of copper adjacent to the coating has a polycrystalline structure. The size of crystallites varies from 200 nm to 400 nm (Figure 1, c). It can be assumed that the submicrocrystalline grain structure of the copper layer adjacent to the coating was formed as a result of high-speed crystallization as well as the process of dynamic recrystallization initiated by the thermal and mechanical action of the plasma flow generated by the conductor electrical explosion on the surface of the copper sample [10].

As the distance from the interface between the coating and the substrate increases, the defect substructure of copper significantly changes (Figure 2). In the layer located at a distance $\approx 90 \mu\text{m}$ from the boundary with the CdO-Ag coating a fragmented substructure typical for a strongly deformed copper is observed in the grain volume (Figure 2, a). In the volume of fragments a dislocation substructure, formed by randomly distributed dislocations, is found. The scalar density of dislocations is $0,8 \cdot 10^9 \text{ cm}^{-2}$. A band dislocation substructure and disoriented cellular substructure are observed in the layer located at a distance $\approx 170 \mu\text{m}$ (Figure 2, b). As the distance from the interface of the system "CdO-Ag coating / copper substrate" increases to $\approx 220 \mu\text{m}$, a cellular dislocation substructure (Figure 2, c) and the substructure of orientational chaos (Figure 2, d) are observed in the volume of copper grains. According to the results presented in the works [11-13] it can be stated that the electroexplosive formation of the coating of CdO-Ag composition is accompanied by a significant deformation effect on the sample surface. As the distance from the surface of the sample increases, the degree of material deformation decreases.

The phase composition of the material was analyzed by diffraction electron microscopy using the dark-field microscopy and the indexing of electron microdiffrac-

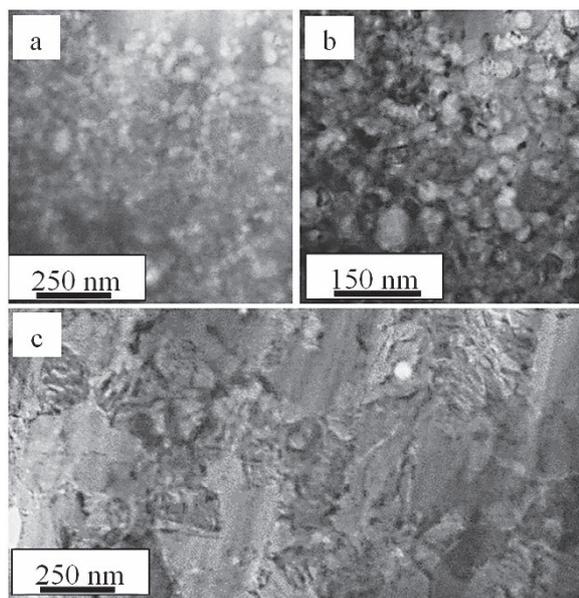


Figure 1 The structure of the CdO-Ag coating (a, b) and the copper layer adjacent to the interface between the coating and the substrate (c)

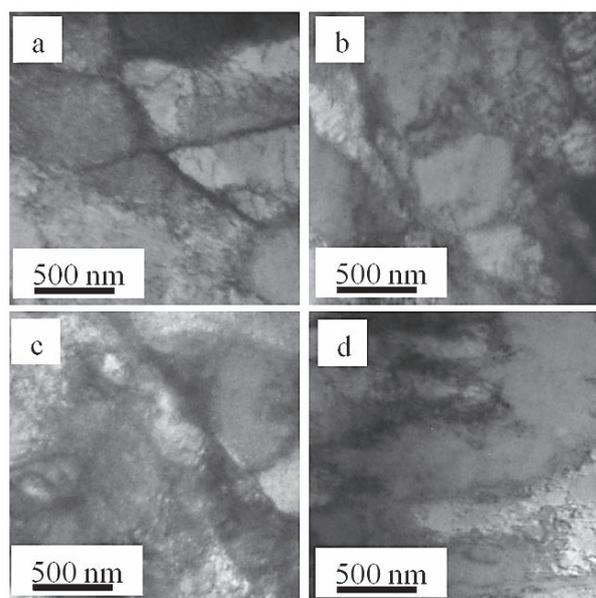


Figure 2 The structure of the copper substrate in the layers located at a distance $\approx 90 \mu\text{m}$ (a); $\approx 170 \mu\text{m}$ (b); $\approx 220 \mu\text{m}$ (c, d) from the boundary with the CdO-Ag coating

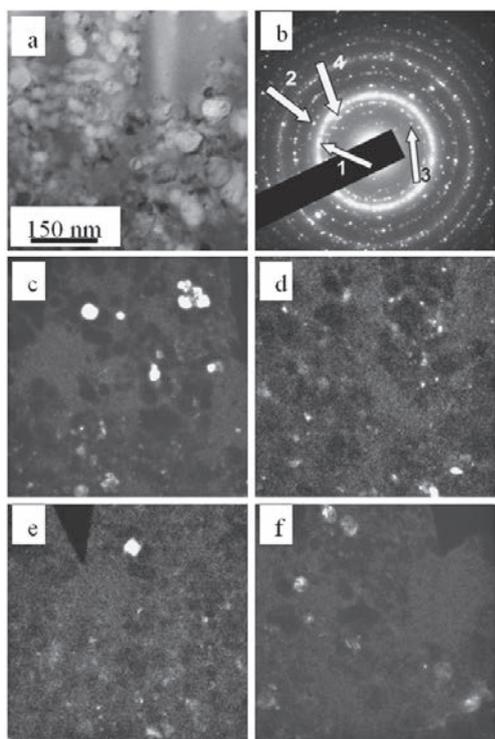


Figure 3 The structure of the CdO–Ag coating, formed on the copper surface by the electroexplosive method; a – bright field; b – electron microdiffraction pattern, the arrows indicate the reflexes in which dark fields are obtained (c-f), respectively; c-f – dark fields obtained in reflexes (111)Cu + (973)Cd₃Cu₄ (reflex 1), (002)Cu + (151)Ag₂O₃ (reflex 2), (200)CdO₂ (reflex 3), (953)Cd₃Cu₄ (reflex 4), respectively

tion patterns. In Figure 3 the results of electron microscopic microdiffraction analysis of the coating phase composition, formed on copper by the electroexplosive method, are provided. It can be clearly seen that the electron microdiffraction pattern (Figure 3, b) obtained from the coating section, the electron microscopic image of which is given in Figure 3, a, is annular, that confirms the above conclusions about the nanocrystalline structure of the coating [14 – 16].

Indexing of the electron microdiffraction pattern (Figure 3, b) shows that the coating is multiphase. The electron microdiffraction pattern reveals the reflexes of the following phases: Cu; Cd₃Cu₄, Ag₂O₃, CdO₂ and also CuO. The method of dark-field microscopy made it possible to determine the shape and sizes of the crystallites of the identified phases. It is established that the crystallites of phases have a predominantly round (globular) shape; the sizes of copper crystallites vary from 20 nm to 50 nm; the sizes of Cd₃Cu₄ inclusions are within (30 – 40) nm; the sizes of CdO₂ inclusions are within (15 – 50) nm; the dimensions of Ag₂O₃ inclusions are within (5 – 10) nm.

The copper layer adjacent to the coating is also multiphase (Figure 4). The indexing of the electron microdiffraction pattern (Figure 4, b), obtained from the given volume of material, made it possible to reveal the reflexes of the following phases: Cu; Ag₅Cd₈ and Cd₃Cu₄. The size of copper crystallites varies from 200 nm

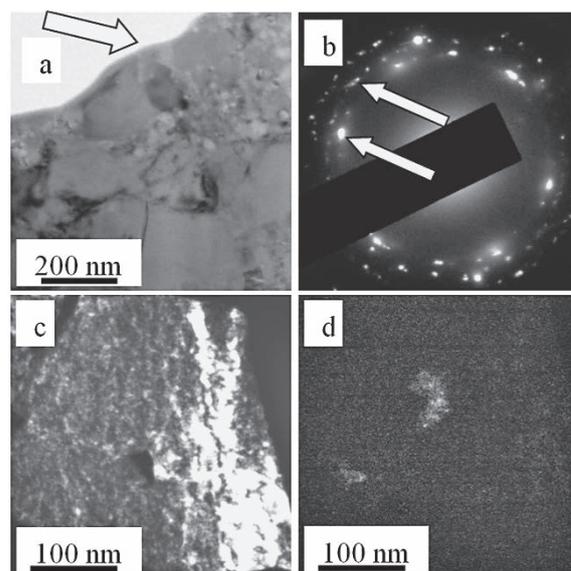


Figure 4 The structure of the copper substrate located at the boundary with the CdO–Ag coating; a – bright field; b – electron microdiffraction pattern, the arrows indicate the reflexes in which dark fields are obtained (c, d), respectively; c, d – dark fields obtained in reflexes (111)Cu (reflex 1), (600)Ag₅Cd₈ + (11 11 1)Cd₃Cu₄ (reflex 2), respectively; in (a) the arrow indicates the area of coating adjacent to the substrate

to 400 nm (Figure 4, a, c). Inclusions of particles of the second phases are located mainly along the boundaries of copper grains and have a globular shape or the shape of thin interlayers (Figure 4, d). The sizes of such inclusions vary from 40 nm to 60 nm. Inclusions that have a lamellar (needle) shape are much less frequent (Figure 4, d). Inclusions of this type are detected in the volume of copper grains and are located at the grain boundaries (they apparently grow from the grain boundaries).

A typical electron microscopic image of the structure of copper volume located at a distance (15 – 20) μm from the boundary with CdO–Ag coating. The dark-field microscopy shows that this layer of material is also multiphase. The indexing of the corresponding electron microdiffraction pattern made it possible to reveal the reflexes of copper, cadmium, CuO and Ag₅Cd₈.

Inclusions of the second phases have a globular shape and are located mainly along the boundaries of copper grains. The sizes of inclusions vary from 20 nm to 60 nm. It should be noted that in the volume of grains of the copper layer adjacent to the coating (Figure 4), a dislocation substructure is found mainly in the form of chaotically distributed dislocations. The scalar dislocation density is $0,5 \cdot 10^9 \text{ cm}^{-2}$. The low density of dislocations is most likely due to the processes of high-speed crystallization [10] and dynamic recrystallization [17 – 19] taking place in this layer of copper.

CONCLUSION

By the methods of transmission electron microscopy the study on phase and elemental composition, defect

substructure and morphology of phases of the "CdO-Ag coating / copper substrate" system, formed on the surface of copper electrical contacts of contactor KPV-604 by the electroexplosive method, was carried out. The formation of a multi-element multiphase coating having a nanocrystalline structure was revealed. It was established that the main phases of the coating are Cu, Cd₃Cu₄, Ag₂O₃, CdO₂, Cd₃Cu₄. It was found that the volume of copper adjacent to the coating has a submicrocrystalline grain structure, which can indicate the occurrence of high-speed crystallization in this layer as well as the dynamic recrystallization process. The dispersion hardening effect of the copper layer adjacent to the coating, caused by the generation of nanoscale phases of Ag₅Cd₈, Cd₃Cu₄, Cd and CuO composition, was revealed. It is shown that the electroexplosive deposition of the coating of CdO-Ag composition is accompanied by the thermal deformation effect on the surface of copper contacts of contactor KPV-604 with the formation of a gradient of dislocation substructures. It was found that as the distance from the sample surface increases, the degree of material deformation decreases.

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REFERENCES

- [1] A.F. Ilyushchenko, 50 years of powder metallurgy in Belarus. History, achievements, prospects, SSI "Institute of Powder Metallurgy", Minsk, 2010, 632 p.
- [2] F. Gerard, Advances in condensed matter and materials research, Nova Science Publishers, New York, 2005, 253 p.
- [3] K. A. Taiasov, V. P. Isupov, B. B. Bokhonov. Formation of nanosized metal particles of cobalt, nickel and copper in the matrix of layered double hydroxide, Journal of Materials Synthesis and Processing 8(2000)1, 21327.
- [4] Russell, A.M. Structure-property relations in nonferrous metals / A. M. Russell, K. L. Lee – Hoboken: John Wiley & Sons, 2005. – 501 p.
- [5] N. M. Talijan. Electrical contact materials based on silver, Zastita Materijala 52(2011)3, 173-180.
- [6] A. H. Qureshi, S. M. Azhar, N. Hussain. The effect of cobalt addition on sintering and microstructural behaviour of silver–tungsten (Ag–W) composite, Journal of Thermal Analysis and Calorimetry 99(2010), 203-209.
- [7] V. Bukhanovsky, M. Rudnytsky, M. Grechanyuk, R. Minakova, C. Zhang. Vapour-phase condensed composite materials based on copper and carbon, Materials and technology 50(2016)4, 523-530.
- [8] L.A. Timofeeva, V.S. Morozov. An arc-resistant electrocontact material based on copper for electrical equipment of traction rolling stock, Information-control systems in railway transport (2015)6, 37-41.
- [9] V.E. Panin, V.E. Gromov, D.A. Romanov, E.A. Budovskikh, S.V. Panin. The physical basics of structure formation in electroexplosive coatings, Doklady Physics 62(2017)2, 67–70.
- [10] N.A. Koneva, E.V. Kozlov. The nature of substructural hardening, Izvestiya vuzov Fizika (1982)8, 3-14.
- [11] N.A. Koneva, E.V. Kozlov. Physics of substructural hardening, Bulletin of TSUAB (1999)1, 21–35.
- [12] E.V. Kozlov, V.A. Starenchenko, N.A. Koneva. Evolution of dislocation substructure and the thermal dynamics of plastic deformation of metallic materials, Metals (1993)5, 152–161.
- [13] G. Thomas, M.J. Gorindzh. Transmission electronic microscopy of materials. – Moscow: Nauka, 1983. – 320 p.
- [14] Yu. F. Ivanov, A.V. Paul, N.A. Koneva, E.V. Kozlov. Electron microscopic analysis of nanocrystalline materials, The Physics of Metals and Metallography (1991)7, 206-208.
- [15] Yu.F. Ivanov, A.V. Paul, E.V. Kozlov, L.N. Ignatenko. Electron microscopic diffraction analysis of ultradispersed materials, Factory laboratory (1992)12, 38-40.
- [16] S.S. Gorelik, Recrystallization of metals and alloys, Metallurgy, Moscow, 1978, 568 p.
- [17] F. Hessner, Recrystallization of metallic materials Metallurgy, Moscow, 1982, 352 p.
- [18] L.N. Larikov, E.E. Zasimchuk, Study of defects in the crystal structure of metals and alloys, Naukova Dumka, Kiev, 1966, pp. 70-84.
- [19] L.N. Larikov, Physical basics of strength and plasticity of metals, Metallurgizdat, Moscow, 1963, pp. 255-322.

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