Structure of SnO2-Ag coating formed on copper by electroexplosion method

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Abstract. The studies of the phase and elemental composition of the surface layer copper electric contact of KPV-604 contactor subjected to electroexplosion spraying of the composite SnO2-Ag-system coating were done by the method of transmission electron microscopy. The scale of the elemental structure of the coating’s surface varies within a very wide interval after the electroexplosion spraying – from hundreds of micrometers to tens of hundreds of nanometers. According to the morphological feature two layers may be distinguished in the coating’s volume: the coating proper and the thermal effect layer smoothly transferring to the bulk of the sample. The nanocrystalline structure was detected. The main phase of the coating are SnO2, Ag3Sn, Cu10Sn3, Cu3Sn, Cu6Sn5, Ag4Sn and CuO. The volume of copper adjacent to the coating has a structure indicative of the high level of deformation of the sample’s surface layer in the electroexplosion method of the coating’s formation.

1. Introduction
On evidence derived from the International association “Interelectromash” the segment of failures in the work of electroequipment for the reason of contact instrument failure ranks first among the other troubles and it amounts to 26%. To reestablish the work the contact is substituted for the new one. The combination of various and simultaneously incompatible requirements are characteristic of the electric contact’s materials. For example, they need to have a high hardness, the melting temperature, electro- and heat conductivity, electrocorrosion and corrosion resistance combining with the absence of welding and bridge-formation. The application of the powder metallurgy methods [1] enables to realize in one material the diverse and contradictory complex of properties that should be possessed by the electrocontact material. Nowadays, a large number of electrocontact material are developed for application in different service conductions. Their composition includes, as a rule, a matrix possessing a high electric conductivity and a high-melting component (filler) with high wear-and electroerosion resistance [2]. The composite materials based on silver, copper copper-nickel, aluminum matrix and a high melting filler are the most promising ones for the manufacture of contacts. The following systems belong to them: W-Cu, Mo-Cu, W-C-Cu, Mo-C-Cu, Mo-C-Cu, Ti-B-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, W-C-Ag and Mo-C-Ag and others [3–8].
According to the expert estimates the volume of the word composite, materials market in 2016 amounted to nearly 17 million tons. In the structure of the word consumption of the composite materials and products from them according to the sectors of economy share of the composite materials consumed by electronics and power industry amounts to 21% among other fields of industry and it is the main driver of growth. The volume of domestic production of arc-resistant electric contacts from the composite materials amounts of 18 billion rubles. If it is remembered that in fact, the wear of the contact before its failure and substitution for the new one does not exceed 50% then nearly 9 million rubles are spend in vain only in the Russian Federation.

As the process of the material’s failure begins with its surface, for a number of practical applications, for example, the hardening of contact surfaces of medium and heavy duty switches and commutation apparatuses, it is promising to from the protective coating because in this case it is important to have electroerosion resistance only on the surface of the contact instead of bulk. Economically and technically practical to develop the approach to the creation of the materials wherein the mechanical strength of the part is achieved by the use of the economic substrates and the special properties of the surface – by the continuous or local formation of the composite coating on it whose properties correspond to the service requirements. The economy in this approach may reach 90%. The expert estimates substantiate tendency. One of the primary directions of condensed state physics is the development of the methods of the increase in the service characteristics of different materials. With regard to it, the surface hardening of arc-resistant electric contacts in the topical problem of development of the new modern technologies. The purpose of the research is to study the phase composition, defect substructure and phase morphology of electroexplosion coating of SnO$_2$-Ag system by means of the transmission electron microscopy.

2. Materials and methods
The object of the studies was the copper contacts of KPV-605 contactor on whose contact surfaces the coating of SnO$_2$-Ag system was formed by the electroexplosion method [9]. The 250 mg silver fail, ion whose surface the weighed portion of SnO$_2$ powder of mass 50 mg was placed in the region of explosion, was used as the electric current conducting material. The time of plasma effect on the sample’s surface was $\sim$100 $\mu$s, the absorbed power density on the jet axis $\sim$5.5 W/m$^2$, the pressure in the shock-pressed layer near the irradiated surface $\sim$12.5 MPa, the residual pressure of gas in the working chamber $\sim$100 Pa; the plasma temperature on the nozzle cut $\sim$10$^4$ K, the of thermal effect zone $\approx$50 $\mu$m. The elemental and phase composition, morphology and defect structure of the coating were analyzed by the methods of transmission electron diffraction microscopy (device JEM – 2100F, JEOL). The foils for the material’s study were manufactured by the electron thinning method of thin ($\approx$100 $\mu$m) plates located in the cross section of the sample. It enabled to study the structure of the coating and the transition layer separating the coating and the substrate.

3. The results and discussion
The characteristic electron microscope image of the copper surface layer subjected to electroexplosion modification is shown in figure 1. It is clearly seen that the copper layer adjacent to the coating has a fragmentary structure that is indicative of the high level of deformation of the sample’s surface in the formation of the coating.

The electron microscope image of the coating being formed in electroexplosion modification of copper contact of KPV-605 contactor is shown in figure 2. The obtained images are indicative of the fact that coating being formed has a nanocrystalline structure with the size of crystallites varying 20–40 nm.

The elemental composition of the portion of the coating surface layer (figure 3b) was determined by the methods of micro X-ray spectrum analysis. The energy spectra and the conditions of the analysis are shown in figure 3a. The results of the quantitative analysis of the elemental composition of the material’s coating are presented in table 1.
Figure 1. Electron microscope image of the “coating/substructure” system structure formed on copper by electroexplosion method. The arrows designate: the layer of the coating adjacent to the copper surface (1) and the copper layer adjacent to the coating (2).

Figure 2. Electron microscope image of the coating structure formed on copper contact of KPV-605 contactor by electroexplosion method.

Figure 3. Energy spectra (a) of the coating portion (b) revealed in micro X-ray spectrum analysis foil.
As a result of the studies performed by this method it is established that the coating being analyzed is the multi-elemental material whose main metallic element are copper, silver and tin. Consequently, the mixing of substrate and coating elements is observed in electroexplosion formation of the coating.

**Table 1.** The elemental composition of the material’s coating.

| Element | Excitation energy | Fractional content % |
|---------|-------------------|----------------------|
| Al (K)  | 1.486             | 1.83                 |
| Ti (K)  | 4.508             | 0.8                  |
| Cr (K)  | 5.411             | 0.56                 |
| Fe (K)  | 6.398             | 0.34                 |
| Ni (K)  | 7.471             | 1.24                 |
| Cu (K)  | 8.040             | 39.3                 |
| Ag (K)  | 2.984             | 39.18                |
| Sn (K)  | 3.443             | 16.76                |

The phase composition and defect structure of the coating were analyzed by the methods of diffraction electron microscopy. Following the results shown in the papers [10–13] it may be concluded that in Ag-Sn-Cu system the compounds based on Ag-Sn and Sn-Cu can be formed; the presence of silver, tin and copper based solid solutions is possible as well. The presence of the oxide phases of the indicated elements in the coating should not be excluded.

**Figure 4.** Electron microscope image of the coating portion formed on the copper sample by electroexplosion method (a) and the corresponding microelectron diffraction pattern (b). The arrows designate the reflections in which the dark field images of the foil’s portion (a) shown in figure 5 were obtained, namely reflection 1 – [004] Ag₃Sn; reflection 2 – [100] Ag₄Sn; reflection 3 – [002] Cu₄SnS; reflection 4 – [110] SnO₂.

The characteristic electron microscope image of the coating structure (figure 4a) and the microelectron diffraction pattern corresponding to the structure (figure 4b) are shown in figure 4. It is clearly seen that the microelectron diffraction pattern has a circular structure as evidenced by the
essential quality of the coating as class of nanocrystalline materials [14–16]. Taking into consideration the nonequilibrium conditions of the transformation taking place in electroexplosion formation of the coating and possible presence of several phases simultaneously on the foil’s portion being studied the indexing of microelectron diffraction patterns were done by the determining of phase belonging of each from five nearest diffraction rings separately.

The indexing of the microelectron diffraction pattern shown in figure 4b revealed the reflections of the following phases: SnO₂, Ag₃Sn, Cu₁₀Sn₃, Cu₃Sn, Cu₆Sn₅, AgₓSn and CuO. Figure 5 shows the dark field images of the phase the most often detected in the coating being studied. When analyzing the results of the studies of the coating’s phase composition it may be noted that the particles of tin oxide SnO₂ whose image is shown in figure 5d have a round shape and the size of the particles vary within 15–40 nm. The particles of the compounds Ag₃Sn, AgₓSn and Cu₆Sn₅ (shown in figure 5a – c respectively) are relatively coarser (20–50 nm) and they often form the regions with size 80–120 nm.

![Figure 5](image_url)

**Figure 5.** Electron microscope dark field images of the coating’s portion whose light field is shown in figure 4a. The dark fields are obtained in the reflections designated by the arrows in microelectron diffraction pattern figure 4 b: (a) – [004] Ag₃Sn; (b) – [100] AgₓSn; (c) – [002] Cu₆Sn₅; (d) – [110] SnO₂.
4. Conclusion
The studies of the elemental and phase composition, the defect substructure and the morphology of the coating’s phases formed on the surface of copper samples by the electron diffraction microscopy methods. The formation of multi-elemental multi-phase coating having a nanostraylline structure was determined. By the indexing of microelectron diffraction pattern it is stated that the main phases of the coating are SnO₂, Ag₃Sn, Cu₁₀Sn₃, Cu₃Sn, Cu₆Sn₅, Ag₄Sn and CuO. It was found that the volume of copper adjacent to the coating has a fragmentary structure that may be indicative of the high level of deformation of the sample’s surface layer in electroexplosion method of the coating’s formation.

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