Structure of SnO$_2$-Ag coating formed on copper by electroexplosion

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Abstract. Studies of the phase and elemental composition of the surface layer of the copper electric contact of the KPV-604 contactor subjected to electro-explosive spraying of the composite SnO$_2$-Ag coating were carried out by means of transmission electron microscopy. The scale of elemental structure of the coating surface varies within a very wide interval after electro-explosive spraying – from hundreds of micrometers to tens of hundreds of nanometers. According to the morphological structure, two layers can be distinguished in the coating volume: the coating itself and the heat affected layer smoothly transferring into the bulk of the sample. A nanocrystalline structure was detected. The main phases of the coating are SnO$_2$, Ag$_3$Sn, Cu$_{10}$Sn$_3$, Cu$_2$Sn, Cu$_6$Sn$_5$, Ag$_4$Sn and CuO. The volume of copper adjacent to the coating has a fragmented structure indicating a high level of deformation of the sample surface layer under the electro-explosive formation of the coating.

1. Introduction
According to the data of the International Association “Interelectromash”, the share of failures in the operation of electrical equipment due to the failure of a contact instrument takes the first place among other problems and amounts to 26%. To restart the work, the contact must be replaced by the new one. A combination of different and incompatible requirements is typical for electric contact materials. These are high hardness, melting temperature, electrical and heat conductivity, electrocorrosion and corrosion resistance combined with the absence of welding and the formation of bridges. The application of powder metallurgy methods [1] enables to realize a diverse and contradictory set of properties that the electrocontact should have in one material. Nowadays, a large number of electrocontact materials are developed for application in various service conductions. Their composition includes, as a rule, a matrix of high electric conductivity and a high-melting component (filler) with high wear and electroerosion resistance [2]. Composite materials based on the silver, copper, copper-nickel, aluminum matrix and the high-melting filler are the most promising for the manufacturing of contacts. The following systems are among them: W-Cu, Mo-Cu, W-C-Cu, Mo-C-Cu, Ti-B-Cu, Ti-B-Cu, TiB$_2$-Cu, TiB$_2$-Al, W-Ni-Cu, Mo-Ni-Cu, Cr-C-Cu, Cr-Cu, CdO-Ag, SnO$_2$-Ag, W-Ag, Mo-Ag, W-C-Ag and Mo-C-Ag etc. [3-8].

One of the most advanced directions of condensed matter physics is the development of methods for enhancing the service characteristics of different materials. In this regard, the surface hardening of arc-resistant electric contacts is one of the most urgent problems in the development of modern technologies.
The aim of this work is to study the phase composition, the defect substructure and the phase morphology of the electroexplosion coating of the SnO$_2$-Ag system by means of transmission electron microscopy.

2. Materials and methods
The object of the study was the copper contacts of the KPV-605 contractor on the surfaces of which the coating of the SnO$_2$-Ag system was formed by the electro-explosive method [9]. 250 mg of silver foil was used as an electrical current conducting material, on the surface of which the charge of 50 mg of the SnO$_2$ powder was placed in the explosion area. The time of plasma impact on the sample surface was $\sim$ 100 $\mu$s, the absorbed power density on the jet axis was $\sim$5.5 W/m$^2$, the pressure in the shocked layer near the irradiated surface was $\sim$ 12.5 MPa, the residual gas pressure in the working chamber was $\sim$100 Pa; the plasma temperature on the nozzle cut was $\sim$10$^4$K, the thickness of the thermal affected zone was $\approx$ 50 $\mu$m. Elemental and phase composition, morphology and defect structure of the coating were analyzed by means of transmission electron diffraction microscopy (JEM – 2100F device, JEOL). Foils for the material testing were manufactured from thin ($\approx$100 $\mu$m) plates located in the sample cross section by the electron thinning method. It enabled to study the structure of the coating and the transition layer, which separates the coating from the substrate.

3. The results and discussion
A typical electron microscope image of a surface layer of copper subjected to an electro-explosive modification is shown in figure 1. It is clearly seen that the copper layer adjacent to the coating has a fragmentary structure, which indicates a high level of deformation of the sample surface during the formation of the coating.

![Figure 1.](image1.png)

**Figure 1.** Electron microscope image of the structure of the “coating/substructure” system formed on copper by the electro-explosive method. The arrows indicate: a coating layer adjacent to the surface of copper (1) and a copper layer adjacent to the coating (2).

Figure 2 shows the electron microscope image of the coating formed under the electro-explosive modification of the copper contact of the KPV-605 contactor. The obtained images indicate that the coating was formed has a nanocrystalline structure with a size of crystallites varying from 20 to 40 nm.

![Figure 2.](image2.png)

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

The elemental composition of a part of the coating surface layer (figure 3 b) was determined by means of the micro X-ray spectrum analysis. Energy spectra and conditions of the analysis are shown in figure 3 a. The results of the quantitative analysis of the elemental composition of the coating material are presented in table 1.
As a result of studies performed by this method, it was established that the analyzed coating appeared to be a multi-elemental material, the main metallic elements of which are copper, silver and tin. Consequently, a mix of elements of the substrate and the coating was observed as a result of electro-explosive coating.

Table 1. Results of the analysis of the micro X-ray spectrum of a part of the coating (figure 3 b) formed as a result of electro-explosive coating of modified copper.

| 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 (L)  | 2.984             | 39.18                |
| Sn (L)  | 3.443             | 16.76                |

Figure 4. Electron microscope image of a part of the coating formed on copper sample by the electro-explosive method (a) and the corresponding microelectron diffraction pattern (b). The arrows indicate the reflections in which the dark field images of the foil part (a) shown in figure 5 were obtained, namely reflection 1 – [004] Ag₃Sn; reflection 2 – [100] Ag₃Sn; reflection 3 – [002] Cu₄Sn₅; reflection 4 – [110] SnO₂.

The phase composition and the defect structure of the coating were analyzed by means of diffraction electron microscopy. Following the results shown before [10], it may be concluded that in the 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 oxide phases of the indicated elements in the coating should not be excluded.

A typical electron microscope image of the coating structure (figure 4 a) and the microelectron diffraction pattern corresponding to the structure (figure 4 b) 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 a class of nanocrystalline material. Taking into consideration the nonequilibrium conditions of transformation occurring during the electro-explosive formation of the coating and the possible presence of several phases in the analyzed part of the foil, the indication of microelectron diffraction patterns was done through determining the phase belonging of each of the five nearest diffraction rings separately.

The indication of the microelectron diffraction pattern shown in figure 4 b revealed reflections of the following phases: SnO$_2$, Ag$_3$Sn, Cu$_{10}$Sn$_3$, Cu$_3$Sn, Cu$_6$Sn$_5$, Ag$_4$Sn and CuO. When analyzing the results of studies of the phase composition of the coating, it may be noted that the particles of SnO$_2$ tin dioxide have a round shape and a size of particles varying within 15-40 nm. The particles of the Ag$_3$Sn, Ag$_4$Sn and Cu$_6$Sn$_5$ compounds are relatively coarser (20-50 nm) and they often form areas of 80-120 nm.

4. Conclusions
The study of the elemental and phase compositions, the defect substructure, and the morphology of the coating phases formed on the surface of copper samples was carried out by means of electron diffraction microscopy. The formation of a multi-elemental multi-phase coating of a nanostrystalline structure was determined. Through the indication of the microelectron diffraction pattern, it was stated that the main phases of the coating are SnO$_2$, Ag$_3$Sn, Cu$_{10}$Sn$_3$, Cu$_3$Sn, Cu$_6$Sn$_5$, Ag$_4$Sn and CuO. It was found that the volume of copper adjacent to the coating has a fragmentary structure, indicating a high level of deformation of the surface layer if the samples during the electro-explosive formation of the coating.

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