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STRUCTURE AND CORROSION PROPERTIES OF COPPER- AND TUNGSTEN-BASED COMPOSITE MATERIALS, PRODUCED BY HIGH-RATE EVAPORATION-CONDENSATION

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ABSTRACT

Structure, corrosion resistance, and mechanical properties of Cu–W composite materials used for various-purpose electric contacts were studied. Shown is the influence of tungsten concentration in Cu–W composite material on these properties. Gravimetric dependencies of Cu–W composite materials with different tungsten content are given and composition of the corrosive environment before and after corrosion testing is determined.

KEY WORDS: structure; corrosion resistance; mechanical properties; composite materials; tungsten; copper

INTRODUCTION

In economic terms, the main materials for electric contacts of various purposes are available, for example, those used in construction machines and devices (elevators, building cranes, lifting machines, cutoff switches, etc.). They are based on copper and alloys and have high strength characteristics. Such contacts are made either of cast as well as of rolling materials (plates, sheets, rods, wires), or from materials produced by the methods of powder metallurgy. Cast alloys have a number of significant drawbacks, such as low strength characteristics, stability to bridging, arc-extinguishing properties, etc. Contacts made by the methods of powder metallurgy, are characterized by high strength characteristics and higher electric contact properties, but their significant disadvantage is the complexity of their manufacturing technology, which includes several operations: producing powders of the required composition; compacting these powders; sintering or their gas-static pressing at high temperatures in a controlled environment; formation of required sizes, etc. [1].

In producing condensed composite materials for electric contacts, it is economically substantiated to use the method of a high-rate electron beam evaporation and condensation of metals and nonmetals in vacuum [2–7]. The technological advantages of this method consist in the fact that by evaporation of simultaneously several substances, by mixing of their steam flows and condensation on the substrate, such ratios of components can be obtained and such structures can be created that are very difficult or almost impossible to be produced by traditional ways.

A great importance in the development of means of switching high-power currents, especially in high-voltage switches belongs to composite materials based on copper and refractory metals — tungsten or molybdenum. For copper-tungsten contacts, such properties are typical as refractoriness, hardness, arc resistance, resistance against welding-on, mechanical strength at room and elevated temperatures, good heat removal and electric conductivity [8]. Today, the information about the structure and mechanical properties of contacts from composite materials based on copper and tungsten is available [9–11]. However, the information about the corrosive stability of composite Cu–W materials (CM) and its relation with the structure is not available at all.

Proceeding from the abovementioned, the aim of this work is to study the structure, physico-mechanical properties and corrosion resistance of copper-tungsten composite materials for electric contacts of various purposes, produced by the method of electron beam evaporation-condensation in vacuum.

PROCEDURE OF INVESTIGATIONS

Composite Cu–W materials were produced on a stationary substrate manufactured of St3, 250×220×10 mm in size at 900 ± 30 °C (temperature remained unchanged for all experiments) by electron beam evaporation and subsequent condensation in vacuum [2–5].

Corrosion resistance of condensates was investigated by gravimetric method [12]. After preliminary treatment, the specimens with an area of 100 mm² were immersed in a corrosive environment (water)

Table 1. Chemical composition of CM copper-tungsten, used for investigations, wt.%

Specimen	W	Cu
1	0.64	Rest
2	3.57	
3	8.27	
4	15.23	
5	20.39	
6	32.98	

per 100 h. The control of the change in the mass of the specimens was carried out every 20 h. The investigations were carried out in a static mode. To study the structure of the produced condensates, macro- and microstructural analyses by optical and electronic scanning microscopy were used [13].

The corrosion resistance and structure of copper-tungsten condensates were studied for six compositions of specimens with a tungsten content from 0.64 to 32.98 wt.% (Table 1).

RESULTS OF INVESTIGATIONS

The carried out investigations of microstructure of Cu–W condensates showed that the structure of the latter varies from homogeneous at a concentration of tungsten to 1 % to laminated with an increase in tungsten concentration in composite materials to 32.98 wt.%.

It should be noted that the higher the concentration of tungsten in the specimens, the lamination appears to be more expressive. For example, let us consider a structure of CM at a concentration of tungsten in it being 20.39 wt.% (Figure 1).

With the increase of tungsten content in the condensate, its distribution in layers is nonuniform (Figure 2).

For composite Cu–W materials, the predominant morphological type of layer structure is polygonal (equi-axial grains). For layers enriched with copper, near the substrate a column structure is characteristic (Figure 3).

Such a nonuniform nature is manifested in the form of concentration clusters, which, as can be assumed, are nuclei for the formation of a new column structure. In the composites with tungsten content of up to 20.39 wt.%, these columns have a conical shape and spheroidal apexes. With an increase in tungsten content, in the condensate with the mass of up to 32.98 wt.%, they become continuous, their share in the section of the specimens grows, and the height is comparable with the thickness of macrolayers.

According to the experimental data [14], electric conductivity of the specimens with an increase in tungsten content in them naturally falls, for example, with a tungsten content of about 10 wt.%, it amounts to 80 % of the electric conductivity of a pure copper.

Mechanical properties during tests of the condensate on tension are also changing. The yield and tensile strength are growing, the characteristics of ductility decrease with an increase in tungsten content in composite materials (Figure 4).

As is seen from Figure 4, the dependence between the tensile (σ_t) and yield strength ($\sigma_{0.2}$), as well as relative elongation (δ) from the concentration of tungsten, have a monotonous nature. An increase in the values

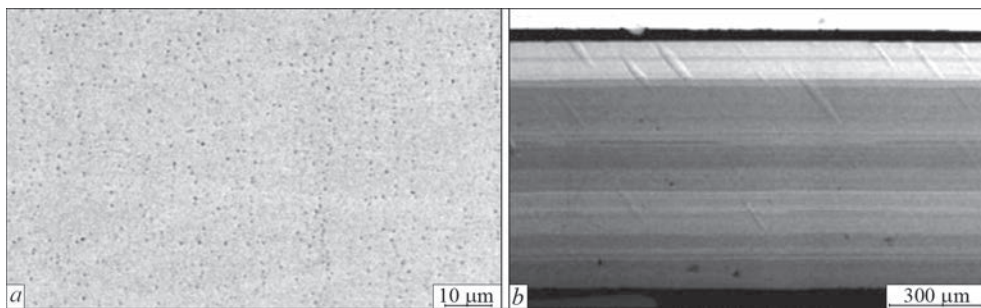


Figure 1. Microstructure of composite Cu–W materials at a concentration of W, wt.%. a — 0.64; b — 20.39

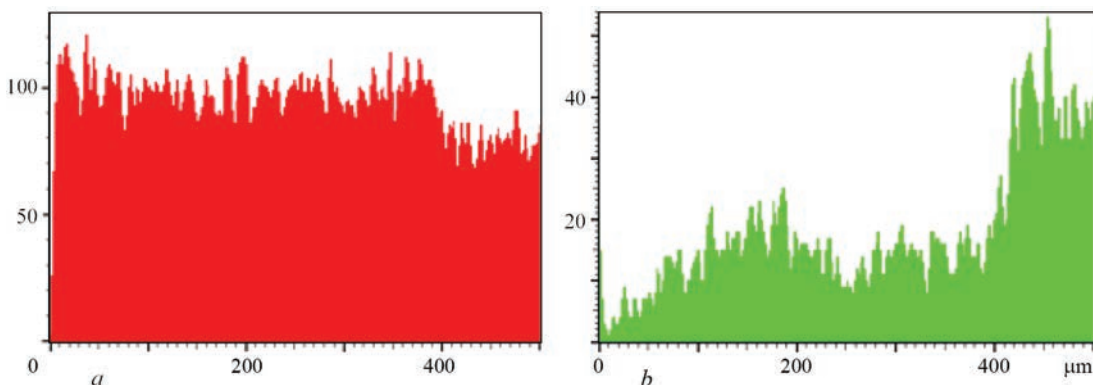


Figure 2. Distribution of copper (a) and tungsten (b) components in CM Cu — 20.39 % W

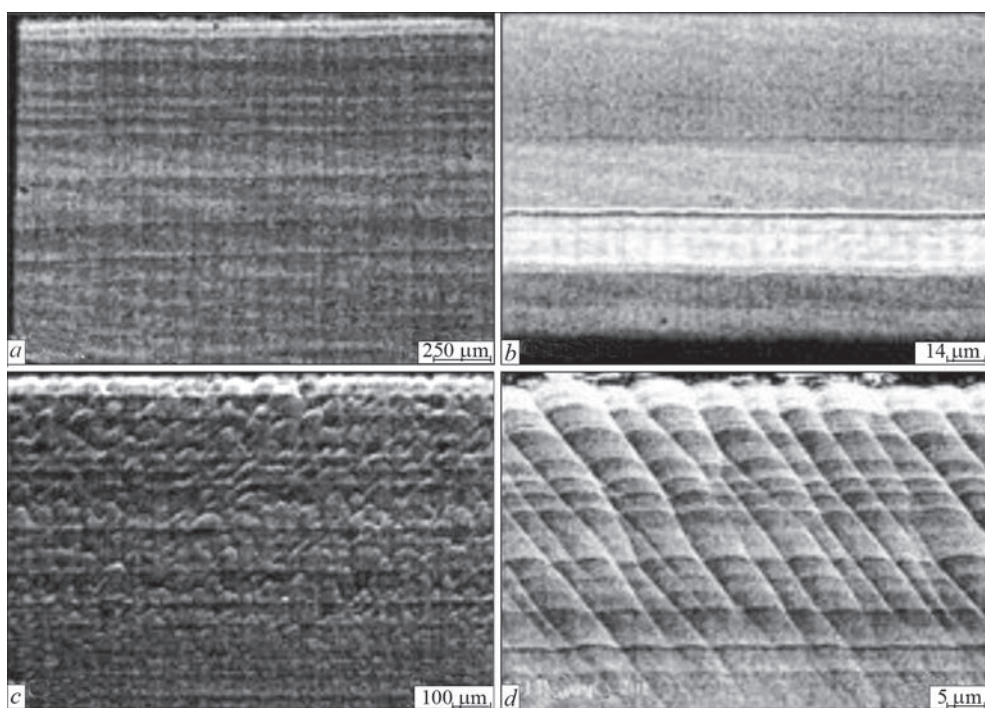


Figure 3. Structure of CM Cu–W specimens with different content of tungsten, wt.%: *a* — laminated (3.57); *b* — laminated with traces of local enrichment (8.27); *c* — cone-shaped (15.23); *d* — column (32.98)

of σ_t and $\sigma_{0.2}$ with an increase in the content of W and a reduction in δ from 30.2 to 2.2 % at a concentration of the latter being 32.98 wt.% is observed. Reducing the ductility, which is observed for the specimens with a significant tungsten content, is predetermined by the influence of defects of “rods” type, which penetrate the entire thickness of the condensate, as was shown in preliminary studies [14].

The fall in ductility with an increase in tungsten content (above 20.39 %) correlates with the peculiarities of the structure of condensates. A macrolayer enriched in copper, formed on the substrate, on which vapours of metals are condensed, is subjected to viscous fracture. The change in properties affects also by weakened impurities of the boundary interface of macrolayers and rods, that serve either as origins of fracture, or determine the direction of a fracture movement [14].

Since the fracture of contacts occurs not only during operation in switching on/off mode, but also in the non-working condition at the action of the environment, gravimetric corrosive studies of composite materials copper-tungsten in water, simulating 100 % moisture in accordance with GOST 25927–81 were carried out.

X-ray analysis showed that for the process of corrosion of Cu–W composites in the atmospheric conditions, on the surface copper and tungsten oxides are formed.

According to the results of previous studies it is known that in case of using the contacts of the Cu–W system, the oxidation products are most often WO_3 and Cu_2O oxides. The study of the surface before and after corrosion tests showed the presence of oxygen content from 10 to 31 % on the surface of condensates

after corrosion tests. At the same time, the presence of oxygen on the surface of the specimens before corrosion tests was not recorded.

The mechanism of electrochemical corrosion consists in arising of short-circuited microgalvanic elements with different micro-EMF (electromotive force) values on the surface of metals, which arises as a result of the difference in electrode potentials of copper and tungsten. The areas of surfaces of metals are characterized by different potentials not only in the presence of different electrode potentials of metals, but also as a result of various concentrations of structural defects, various treatments (roughness) of the surface, concentrations of impurities, thickness of adsorbed moisture films, dissolved oxygen concentrations in moisture films, etc. Therefore, for composite materials copper-tungsten, the presence of microgalvanic couples between copper and tungsten in areas

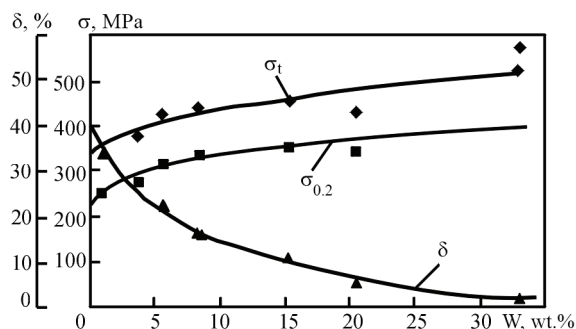


Figure 4. Dependence of tensile strength (σ_t), yield strength ($\sigma_{0.2}$) and relative elongation (δ) of Cu–W composites from tungsten content (after vacuum annealing 1173 K, 1 h) at a temperature of 293 K

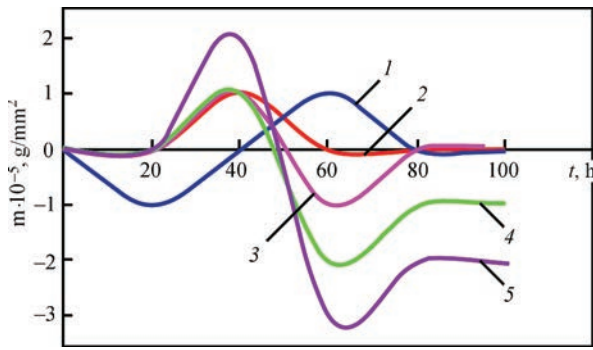


Figure 5. Gravimetric dependencies of Cu–W composites with a different content of tungsten, wt.%: 1 — 0.64; 2 — 8.27; 3 — 15.23; 4 — 20.39; 5 — 32.98

enriched with tungsten is possible. In this case, an anode ionization of more active metal — tungsten occurs. On the rest of the surface areas, formation of galvanic couples between copper with copper ionization and the transition of its ions into a solution is possible. This is evidenced by the analysis of the environment carried out before and after corrosion tests (Table 2).

As is seen from the given data, in the corrosive environment, ions of copper and tungsten are present.

With an increase in the content, in the Cu–W composites of tungsten, the concentration of tungsten ions in the environment increases and that of copper ions remains approximately the same. As it should be expected, the highest concentration of copper is present in the solution at a lower content of tungsten in the specimens.

Gravimetric studies showed that in the initial moment of corrosion tests, a slight decrease in the mass of the specimens occurs regardless of their composition, which is predetermined by ionization and transition to the solution of copper and tungsten ions. After 20 h of tests, an increase in the mass of the specimens begins. With an increase in the concentration of tungsten in the Cu–W composites, the process becomes more intense (Figure 5).

This is connected with the impossibility of the unlimited increase in the concentration of metal ions in the solution in connection with the formation of soluble compounds — copper and tungsten oxides.

Table 2. Composition of corrosion environment before and after the corrosion tests

Composition of composites, wt. %		Content of components in water after corrosion investigations, mg/l	
W	Cu	Cu	W
0.64	Rest	1.299	0.003
3.57		0.924	0.006
8.27		0.788	0.014
15.23		0.687	0.016
20.39		0.704	0.018
32.98		0.750	0.209
Initial water — 0.014			0

In addition, with an increase in the concentration of tungsten in the composites, also the formation of low-soluble salts of copper tungstates is possible.

Thus, the growth of the film formed from low-soluble compounds becomes more intense with an increase in the concentration of tungsten in the composites and the weight of the specimens respectively becomes higher. The formed film shields the metal surface, diffusion limitations of anode reaction in this case are deepened and the rate of corrosion is reduced. During the fracture of metals in natural atmospheric conditions, an oxygen depolarization reaction proceeds on the cathode. Taking into account a small solubility of oxygen in water (approximately 0.008 g/l), diffusion limitations occur during this reaction. Therefore, the rate of corrosion with oxygen depolarization is limited by the rate of supply of oxygen molecules to the surface of the corroded metal. This is also one of the reasons for inhibiting the corrosion process.

Reduction in the rate of running corrosion processes is indicated by studying the structure of the specimens with different tungsten content before and after corrosion tests (Figure 6).

The nature of fracture of the composites with molybdenum content of up to 3.57 wt.% is the same for all the specimens. The corrosion processes are observed mainly in those regions where structural defects are present. At the concentrations of tungsten being 15.23–32.98 wt.%, corrosion was not recorded (Figure 6, b).

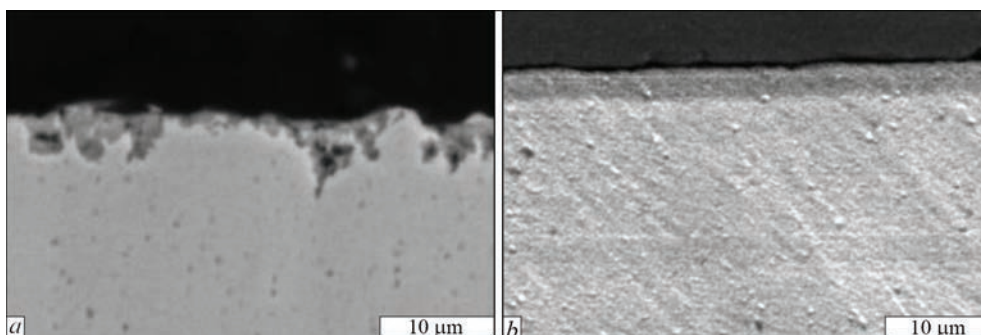


Figure 6. Destruction of composites with different content of tungsten, wt.%: a — 3.57; b — 15.23

CONCLUSIONS

1. The study of chemical composition, structure and properties of composite materials copper-tungsten, produced by the method of electron beam evaporation-condensation in vacuum, was carried out.

2. It was shown that copper-tungsten condensate is a laminated gradient material, the morphological features of which vary with an increase in tungsten content in it (from 0.63 to 32.98 wt.% in it).

3. Characteristics of the condensate strength during the test on tension are increased, and ductility decreases from 30.2 to 2.2 % with an increase of tungsten content from 0.63 to 32.98 wt.% in it.

4. Gravimetric analysis and microscopic examinations revealed that corrosion resistance of composite materials based on copper and tungsten is increased with an increase in tungsten concentration in the specimens from 0.63 to 32.98 wt.%.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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