Comparative evaluation of silver-bearing and copper-molybdenum condensates

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Abstract. This work is devoted to the study of the corrosion and erosion resistance of composite materials based on copper and molybdenum, which are used as contact materials. It was investigated that the introduction of zirconium and yttrium into the Cu-Mo system (Cu – (10-12%)Mo – (0.2%)Zr,Y) contributes to an increase in corrosion resistance by 20%, and the corrosion depth is reduced to 0.02 g/(m^2·year). It is shown that the dependence of the change in contact temperature on the contact resistance is linear, the higher contact resistance leads to more intensively contact temperature increase. The dependence of the contact resistance of contacts made of Cu-Mo and Ag-CdO materials on the number of switching cycles is established. A comparative characteristic of contacts made of silver-containing materials and contact materials made of Cu-Mo is carried out and the advantage of last one is shown.

Keywords: composite materials, corrosion resistance, contact resistance, contact materials, Cu-Mo system.

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INTRODUCTION

One of the main reasons for limited use of electrical contact materials that do not contain silver or other noble metals is their rapid corrosion and erosion destruction during their use in oxidizing environments at high temperatures. Vapor-condensed composite materials (CCM) based on Cu-Mo have found wide application for the manufacture of electrical contacts and electrodes [1-6].

The corrosion and erosion resistance of electrical contacts is associated with the formation and destruction of films on their working surface and with material transfer. Films formation is facilitated by arc discharges during contact switching, but films can also occur on open contacts [7,8].

In air circuit breakers, electroerosive wear of contacts is accompanied by the interaction of the contact surface material with high-temperature ionized gas flows, especially strong when extinguishing the arc with compressed air. The flow of compressed air creates a sharp change in temperature and causes significant thermal stresses in the working layer of contacts, which lead to cracking, ejection and removal of solid detached particles of the surface from the molten and softened zones into the intercontact gap. In addition to the physical processes [9-13] that occur under the influence of an electric arc, chemical processes occur in the working layer on the contact surfaces and in the intercontact gap, which cause the appearance of new compounds - products of the interaction of the contact material and the environment. The conditions for the occurrence of chemical reactions in this case are special, because ionized gases that are part of the plasma of the arc column and in the surrounding space interact with the contact material in the vapor and condensed phases. The products of this interaction (oxides, nitrides, etc.) accumulate on the surface of the contacts, fuse with each other, and form more or less dense films, which leads to an increase in the contact resistance. In the absence of electric discharges, the mechanism of film formation is simple: molecules of surrounding gases and vapors are adsorbed by the contact surface. Metal ions are released from spatial lattices, interact with adsorbed gas ions, and form films that evenly cover the contact surface.

In the presence of electric discharges, the film formation mechanism becomes more complicated. Under the influence of high discharge temperatures, mixed oxides and nitrides appear, forming films of uneven thickness, localized near the discharge sites. Subsequent discharges can cause partial decomposition of the films and cleaning of the contact surface, but in most cases the rate of film formation is higher than the cleaning rate even on contacts made of noble metals.

Oxide films are close to insulators in terms of electrical properties. Thus, the electrical conductivity of Cu_2O and CuO oxides, which are formed during the operation of contacts on the working surface, is 1011 and 106 times lower than that of copper. Therefore, when contacts covered with such films are closed, current flow is possible as a result of electrical breakdown, fitting and mechanical crushing of the film. Crushing and destruction of such films is possible in the presence of hard metals, such as tungsten or molybdenum, which allow for greater contact pressure [14-18].

PURPOSE AND METHODS

To establish the possibility of operation of contacts made of Cu-Mo composite materials obtained by electron beam evaporation and condensation in vacuum, in the air environment in the off mode, corrosion resistance studies by the gravimetric method were presented [10].

The evaluation of contacts switching capacity was carried out using bench and field tests. Bench tests are usually carried out in conditions close to field conditions. Testing of materials Cu – (8-12% wt.)Mo – (0.2% wt.) Zr,Y [2] was carried out in the American company Ashurst Technology Group on a specially designed stand for this purpose.

RESULTS AND EXPLANATIONS

Studies of Cu-Mo composite materials operation in a neutral air environment in the on-off mode (130,000 cycles) at I = 20 A, U = 220 V in comparison with traditional systems gave positive results. Fig. 1 shows the surface topography of Ag-CdO and Cu-Mo samples after the corresponding tests.

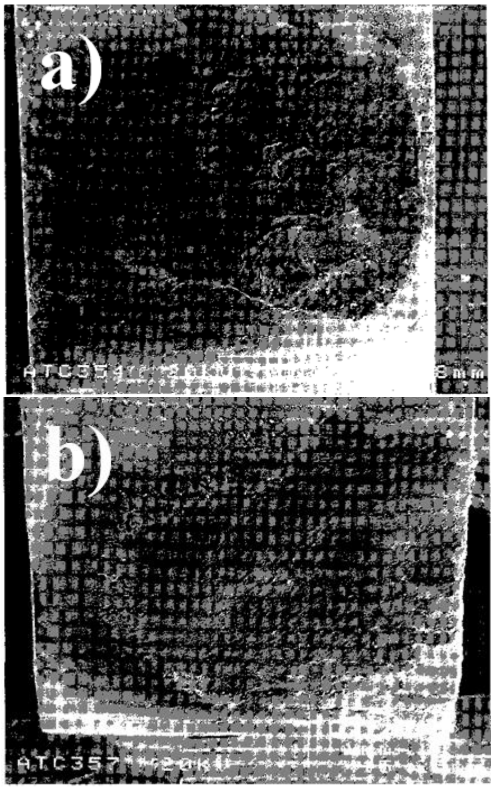

Figure 1. Surface topography after 130000 on-off cycles: a – Ag-CdO system, b – Cu-Mo composite material.

As can be seen from Fig. 1, the nature of the destruction of the surface layer observed in Cu-Mo composite materials obtained using electron beam technology and in Ag-CdO material obtained by powder metallurgy is similar. At the same time, the damage to the surface layer in the case of Ag-CdO is much greater, the photographs show quite large areas of silver flakes ejected from the contact surface.

During operation Cu-Mo contacts in air at temperatures above 300 °C, complex spinels $CuO \cdot MoO_3$ and $3CuO \cdot MoO_3$ are formed on the working surface. The $CuO \cdot MoO_3$ compound undergoes a polymorphic transformation at 550 °C, which occurs with a change in volume, which leads to their destruction and splitting from the working surface of the contacts, exposure of new areas and intensification of oxidation processes.

The negative effect of films is reduced if such compounds are unstable, easily evaporate, brittle and easily removed during contact pressing, when parts are pumped together or under the pressure of an air jet during arc extinguishing.

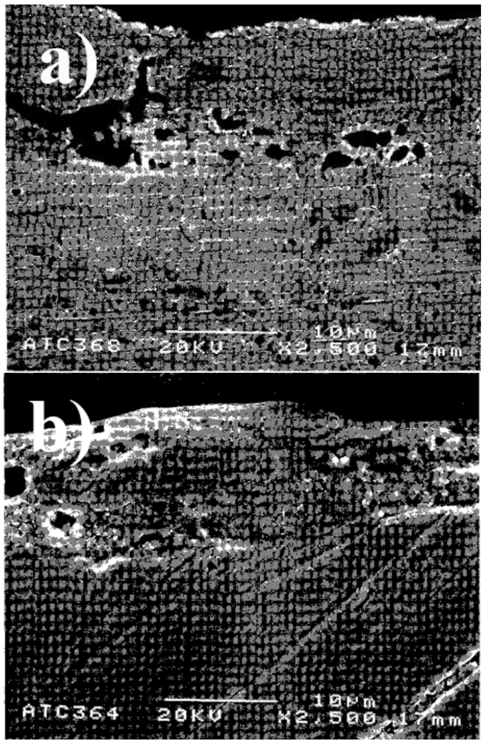

Figure 2. Electroerosion damage during operation of electrical contacts: a – Ag-CdO system, b – Cu-Mo composite material.

Fig. 2 shows the electroerosion wear of the Cu-Mo composite material and the traditional Ag-CdO system, which is observed during the operation of electrical contacts, due to the action of high-temperature ionized gas flows that arise when the arc is extinguished with compressed air.

The dark areas of the surface in the above electron-graphic structures of Cu-Mo composite material and Ag-CdO material obtained by the powder metallurgy method reflect corrosion damage, due to which the resistivity of the material in the contact area increases, which in turn also contributes to the destruction of the surface. If we compare the damage of Cu-Mo with the damage of contacts containing silver, it is clear that for the composite material Cu-Mo the formation of areas of corrosion destruction is significantly reduced, and their sizes are reduced. The occurrence of large defects is due, first of all, to the destruction of areas containing copper inclusions, which were formed as a result of droplet transfer of metal.

The different nature of the surface layer destruction is also evidenced by the depth and nature of the damage to the surface layer of the specified materials. For Ag-CdO samples, the formation of a brittle layer is characteristic, which is easily exfoliated from the surface of the material. The surface layer of condensed Cu-Mo materials has a denser structure and its exfoliation from undamaged areas is not so intense, which is probably due to differences in the structure of the specified materials.

The degree of surface destruction depends on the method of obtaining the materials from which the contacts are made. When using powder metallurgy methods to manufacture contacts from Ag-CdO material, during on-off cycles and the occurrence of an electric arc, evaporation of large particles of the fusible phase and the appearance of pitting corrosion defects are observed. Condensed materials, unlike materials obtained by traditional powder metallurgy methods, have a layered structure, which excludes the possibility of the material deep destruction. With the increase of molybdenum concentration, layers become more clearly defined (Fig. 3). It can be seen that at molybdenum concentration of 1%, the layers are almost not visually visible (Fig. 3.a) and the layers are more distinct at molybdenum concentration of about 20% (Fig. 3.b).

Gravimetric studies of Cu-Mo condensates have shown that the introduction of molybdenum up to 5 wt.% into the copper matrix has practically no effect on the corrosion resistance of the Cu-Mo composite material compared to pure copper. At higher molybdenum concentrations (up to 12%) there is a decrease in corrosion resistance to approximately 20%, which limits the use of Cu-Mo contact materials in an oxidizing environment (Fig. 4) [19,20].

a)
b)

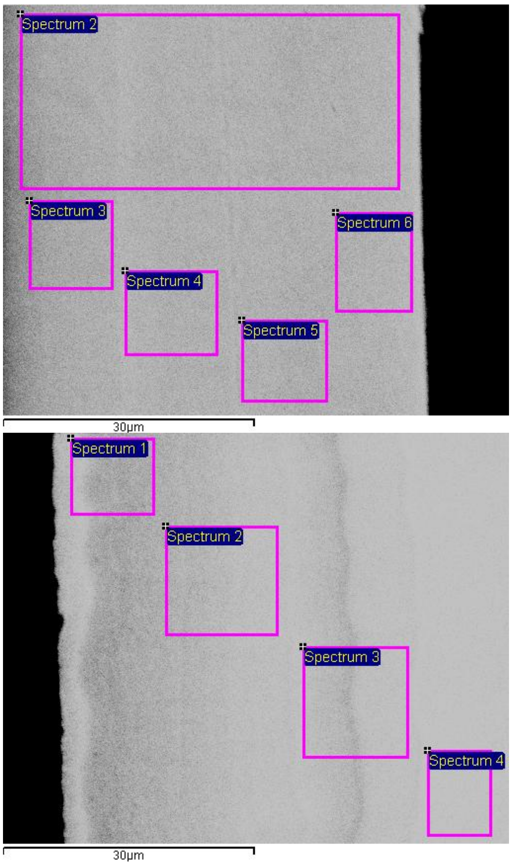

Figure 3. Surface microstructure of composite materials based on Cu-Mo with molybdenum concentration: a) up to 1%, b) up to 20%.

Corrosion and erosion processes are significantly inhibited by additional doping of Cu-Mo composite materials with other elements. From this point of view, the condensed Cu-Mo-Zr-Y (CMC) material proposed in this work is very promising for electrical contacts.

Gravimetric studies have shown that additional doping of the copper matrix with zirconium and yttrium in an amount of up to 0.2 wt. % of each component allowed to increase the corrosion resistance of composite materials by 20%. Addition of yttrium and zirconium to the material leads to the increase in corrosion resistance what can be associated with the shielding effect of yttrium and zirconium particles located at the crystallite boundary. In this case, the contact area of the anodic and cathodic zones decreases and corrosion processes that occur under the influence of the environment by the electrochemical mechanism are inhibited.

a)
b)
c)

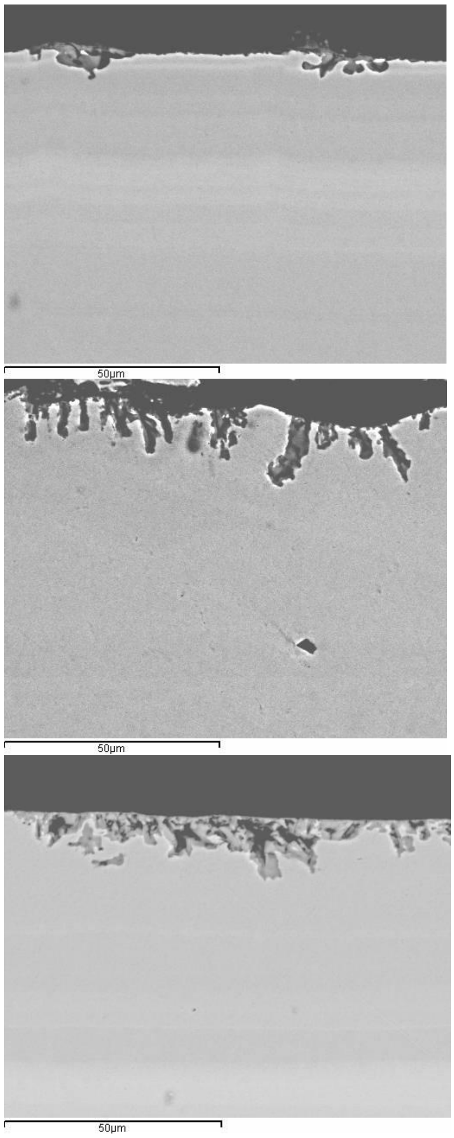

Figure 4. Electrocorosion damage of composite materials surface based on Cu-Mo with molybdenum concentration: a) up to 5%, b) up to 12%, c) up to 20%.

The composition of the oxide film that forms on the samples surface when the composite material is operated in an oxidizing environment changes: unlike Mo-Cu composites, in condensed materials containing zirconium and yttrium, films are formed on the basis of complex spinels of the type: $CuO{\cdot}MoO_3{\cdot}ZrO_2$, $CuO{\cdot}MoO{\cdot}ZrO_2{\cdot}Y_2O_3$, $CuO{\cdot}MoO_3{\cdot}ZrO_2{\cdot}Y_2O_3$. Such compounds do not have polymorphic transformations, are characterized by a quite high electrical conductivity and adhesion to the base material.

Based on the results of gravimetric studies, corrosion resistance indicators were calculated. The calculation of the corrosion depth was carried out according to the formula:

$$H = \frac{K_{mas}{\cdot}8.76}{\rho_{Me}}, \text{ mm/year,}$$

where: ρ – density of the material, K_{mas} – weight corrosion index.

$$K_{mas} = (m_0 - m_1) \cdot S_0 \cdot \tau,$$

where: m_0, m_1 – initial and final mass of samples, S_0 – surface area of samples; τ – time of corrosion tests in distilled water, as a more aggressive environment compared to tap water.

With the increase of molybdenum content from 1.1 to 14%, the depth corrosion index increases from 0.007 to 0.050 g/(m^2·year), and in the dynamic mode these changes are more pronounced (table 1).

When zirconium and yttrium are introduced into the Cu-Mo system in an amount of up to 0.2%, a significant increase in corrosion resistance in an aquatic environment is observed. The depth corrosion index for the Cu-(10-12%)Mo-(0.2%)Zr,Y system decreases to 0.020 g/(m^2·year). The structure of the surface layer practically does not change.

Table 1. Depth corrosion rates of CCM in distilled water.

Condensate composition				Corrosion depth index g/(m^2·year)	
Cu	Mo	Y	Zr	Static mode	Dynamic mode
100	0	0	0	0.007	0.017
98.9	1.1	0	0	0.077	0.021
97.7	2.3	0	0	0.008	0.023
94.6	5.4	0	0	0.0095	0.025
89.5	10.5	0	0	0.031	0.04
86	14	0	0	0.021	0.05
94.2	5.4	0.2	0.2	0.0075	0.018
89.2	10.5	0.2	0.2	0.008	0.02

The tests of the copper and molybdenum based CCM were carried out under the following conditions: current – 19 A, voltage – 208V, test cycle duration 3 seconds – on, 3 seconds – off.

Number of cycles was 130000. Tests were carried out at room temperature and humidity, which did not reach 65%. The dependence of changes in contact resistance on the number of cycles and the change in contact temperature depending on the contact resistance was determined.

Fig. 5 shows the dependence of the change in contact resistance of contacts made of material based on Cu-Mo system in comparison with standard contacts Ag-CdO, made by powder metallurgy methods.

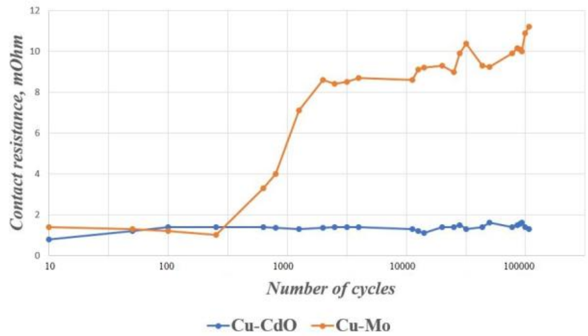

Figure 5. Dependence of the contact resistance of contacts made of Cu-Mo and Ag-CdO materials on the number of switching cycles.

As can be seen from Fig. 5, the initial contact resistance of contacts made of Cu-Mo material and Ag-CdO compositions is close. Comparable contact resistance values of contacts are observed only up to 400 test cycles. Then there is an increase in contact resistance from $1.4{\cdot}10^{-3}$ Ohm at 400 test cycles to $8{\cdot}10^{-3}$ Ohm at 3000 test cycles of contacts made of Cu-Mo material.

Further increase in the number of test cycles to 200000 leads to a slight increase in contact resistance to $10...11{\cdot}10^{-3}$ Ohm. At the same time, the contact resistance of Ag-CdO compositions during the entire test period remains practically unchanged at the level of $1.6...1.8{\cdot}10^{-3}$ Ohm.

The dependence of the change in contact temperature on the contact resistance is linear, as higher the contact resistance, then more intensively the contact temperature increases. Therefore, preparing technical recommendations for the use of Cu-Mo materials, it is necessary to take into account the maximum permissible contact temperature in switching devices.

A qualitatively similar dependence of contact resistance and contact temperature was obtained during testing electromagnetic relays IE-38U3. Rated operating current was 4A, voltage – 12V. The tests purpose was to assess the possibility of replacing contact materials based on silver with contact materials based on copper-molybdenum system.

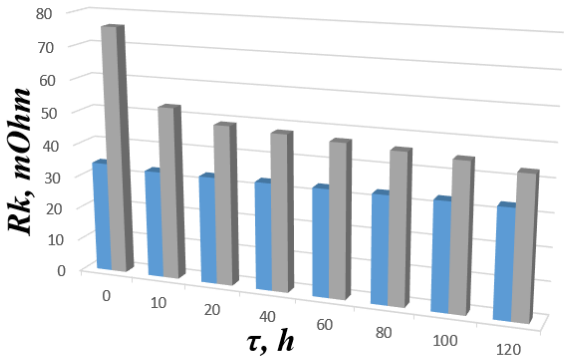

Figure 6. Dependence of the average resistance values of the opening contacts of the VS-43 time relay on the time elapsed after the relay was turned on at a current of 4 A: blue – silver Ag999; gray – Cu-(10-12%)Mo-(0,2%) Zr,Y.

Fig. 6 shows the curves of the dependence of the average values of the resistance of the opening contacts of the VS-43 time relay on the time elapsed after the relay was turned on at a current of 4 A. Contacts made of Ag999 material have a stable resistance value over time (blue columns), R = 33 mOhm. The average values of the opening contacts made of Cu-Mo material (gray columns) resistance decrease sharply in the first 10 hours of testing from 76 to 45 mOhm and subsequently practically do not change throughout the entire test period.

Qualitatively similar dependences were obtained during comparative tests of contacts made of silver Ag999 and Cu-(10-12%)Mo-(0,2%) Zr,Y in electromagnetic relays IE-38 (Fig. 7).

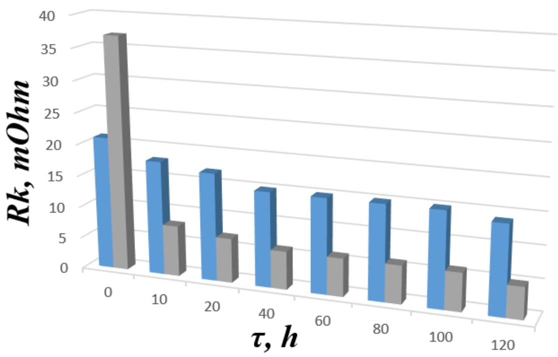

Figure 7. Dependence of the average resistance values of the opening contacts of the relay IE-38 on the time elapsed after the relay was turned on at a current of 4 A: blue – a pair of materials AgCdIn and Ag999; gray – Cu-(10-12%)Mo-(0,2%) Zr,Y.

The average resistance value of the contact pair made of AgCdIn and Ag999 materials (blue columns) decreased from 20 to 15 mOhm within 120 hours; the average resistance value of the contacts made of Cu-Mo material (gray columns) decreased from 25 to 7 mOhm within 120 hours. The Cu-(10-12%)Mo-(0,2%) Zr,Y – Cu-(10-12%)Mo-(0,2%) Zr,Y contact pair has almost two times lower resistance compared to AgCdIn – Ag999 pair. As shown by X-ray and electron microscopic studies, a fragile and porous film of molybdenum and copper oxides is formed on the surface of the contacts made of material based on Cu-Mo system, which is easily peeled off when the contact pair is turned on and off, i.e. self-cleaning of Cu-Mo composites from oxide films is observed.

Measurement of the contact overheating temperature at a nominal contact current of 4 A showed that the overheating temperature did not exceed 29 °C in all cases and was: material Ag999 – 7°C, material Cu-Mo – 13°C; material AgCdIn – Ag999 –29°C, material Cu-(10-12%)Mo-(0,2%) Zr,Y – 29°C.

The action of the discharge heat flux and contact with slip lead to the destruction of the initial structure, the formation in the working layer of a secondary structure and a set of new layered formations with boundaries enriched with molybdenum-based phases. This fragile layered structure is characterized by anisotropy of the layers with a major axis in the direction of contact slip. Under other conditions of contact and thermal action of the electric discharge, with an increase in the number of current switching cycles, the complete destruction of the layered structure of the condensate occurs, which is accompanied by crushing of the layers, their deformation, consolidation of particles in the layers, disruption of the continuity of the layers of the secondary structure as a result of vaporization and explosive destruction.

It should be noted the different nature of structural changes in the working layer of contacts during DC switching: on the surface of one - the formation of a crater and a layered "sandwich" of melt portions, on the surface of the other - almost uniform wear of the macrolayer with a thermally affected zone with a columnar structure limited to one level of the layer below.

Thus, based on the analysis of the features of changes in the structure morphology, it can be assumed that they are determined by the contacts polarity and the difference in processes caused by the action of a unipolar discharge. The insignificant, within one macrolayer up to 100 microns, zone of thermally affected discharge on the working layer with Cu-Mo-Zr-Y CCM indicates that this material can provide the necessary electroerosion resistance of the contact during current switching from 1 to 1000 A.

CONCLUSIONS

Based on this research work and taking into account features of obtaining CCM by electron beam technology, it can be concluded that Cu-Mo materials [7-9] have a number of advantages: they are obtained in one technological cycle; they are 1.5 ÷ 1.7 times cheaper than analogues obtained by powder metallurgy methods and significantly cheaper (2.5 ÷ 3 times) than silver-containing contacts; their operational reliability is not inferior to materials based on silver-containing compositions; they are well processed by cutting, stamping, grinding, drilling; they are easily soldered by known soldering methods using standard silver-containing solders and solders that do not contain silver.

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Порівняльна оцінка срібловмісних і купрум-молібденових конденсатів

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Олександра МАЦЕНКО

Анотація. В роботі розглянуто корозійну і ерозійну стійкість композиційних матеріалів на основі міді і молібдену, які використовуються в якості контактних матеріалів. Досліджено, що введення в систему Cu-Mo цирконію і ітрію (Cu-(10-12%)Mo-(0,2%)Zr,Y) сприяє підвищенню корозійної стійкості на 20%, а глибинний показник корозії знижується до 0,02 г/(м^2·рік). Показано, що залежність зміни температури контактів від контактного опору носить лінійний характер, чим вищий контактний опір, тим інтенсивніше зростає температура контактів. Встановлена залежність контактного опору контактів, виготовлених із матеріалів на основі Cu-Mo та Ag-CdO від кількості комутаційних циклів. Проведена порівняльна характеристика контактів із срібловмісних матеріалів і контактних матеріалів з Cu-Mo та показана перевага останніх.

Ключові слова: композиційні матеріали, корозійна стійкість, контактний опір, контактні матеріали, Cu-Mo система.