



CORROSION RESISTANCE IN NEUTRAL SALINE FOG OF THE COMPOSITES Cu-Mo OBTAINED BY PVD METHOD

V.G. GRECHANYUC¹, N.I. GRECHANYUC¹, Lucica ORAC²

¹Kiev National University of Building and Architecture, Ukraine

²University "Dunarea de Jos" of Galati
email: lucia_orac@yahoo.com

ABSTRACT

The basic materials used for electrical contacts, which may be available economically, are the Cu-Mo based composites obtained by the method of electron flow at high temperatures under vacuum.

Cu-Mo (12% max. Mo) composite materials are produced by simultaneous evaporation from separate Cu and Mo crucibles with subsequent condensation of the vapor flow on an OL-37 steel layer of 15 to 20 mm thickness and 800 mm diameter. The surface of the disk-support on which condensation of the vapor flow takes place was machined until a roughness of $Ra = 0.63$ was obtained.

Analysis of chemical composition and structure of composites based on copper and molybdenum content allowed determination of the variation of these elements from layer to layer (of up to 20-25% to 4-5 mas.) and the distribution gradient of these elements in the layers.

The Cu-Mo composites produced by PVD method were introduced in the room and tested in neutral saline fog exposure time of 100h. Cu-Mo composites, obtained by PVD method, have a fairly good corrosion resistance, at Mo concentrations ranging from 8% to 12 % of the surface do not present oxides and the concentrations of Mo between 1,2 to 6% area are covered with oxide.

KEYWORD: PVD method, layer, corrosion, saline fog

1. Introduction

The paper describes reviews referring to determination of working parameters of the development processes of some composites in copper matrix, obtained by vapour-phase deposition method. The molybdenum was used as complementary phase.

Development of the multi-component coatings necessary to enhance the electro corrosive resistance of the electric contact of commutation devices represents one of the future applications of this technology.

An important scientific and practical interest represents the use of the vaporization method involving high rates of electron flows and metal & non-metal condensation, not only having in view the building of coatings on working surfaces of the contacts, but also for development of the massive condensates (MC) necessary for the electric contacts.

In order to obtain composite materials made from Cu-Mo, condensed in the vapor phase, the electron flow industrial system, type UE-189, designed by the Welding Institute of the Academy of Science of

Ukraine and updated by the Centre of Scientific Production "Gekont" (CSP "Gekont") was used.

The composite materials of Cu-Mo have been obtained by simultaneous vaporising, from separate crucibles, of copper and molybdenum followed by the vapor flow condensing on a steel OL-37 sub layer, preheated up to 700 ± 20 °C. Copper and molybdenum ingots have been used as initial materials obtained by vacuum electron flow remelting. The condensate obtained as plates of 0,7 ... 1,2 mm thickness have been used for the study of corrosion resistance [1].

The structure of Cu-Mo composites is under the form of blocks. For each block it is characteristic an arbitrary striped structure. The period of stripes repetition is 150 ± 3 mm.

2. Results and experimental researches

To obtain composite materials based on copper and molybdenum, copper, molybdenum and calcium fluoride powder have been used; their characteristics are presented in Table 1.

Table 1. Material marks that were used to obtain composite materials based on copper and molybdenum.

Materials	Mark	Standard
Cu	M0b, M00, M0, M1, M2	GOST 859-78
Mo	MCVP	TU 48-19-247-87
CaF ₂	c	GOST 7167-77

For evaporation, use is made of copper ingots of 100mm diameter and 70 mm diameter molybdenum. The ingots were blanked to 98.5, respectively 68.5 mm size to avoid their jam in the evaporation process [2]. Calcium fluoride powder was pressed with a press-type P-457 at a pressure of 240 to 300 MPa, in a number of pills of 30 mm diameter and 15 to 20 mm thickness.

The surface of the disk-support, where vapor flow condensation takes place, was processed up to the roughness of $R_a = 0.63$.

The ingots of blanked copper and molybdenum are subjected to degreasing with acetone and then they are installed in the crucibles 8 and 9 (Figure 1).

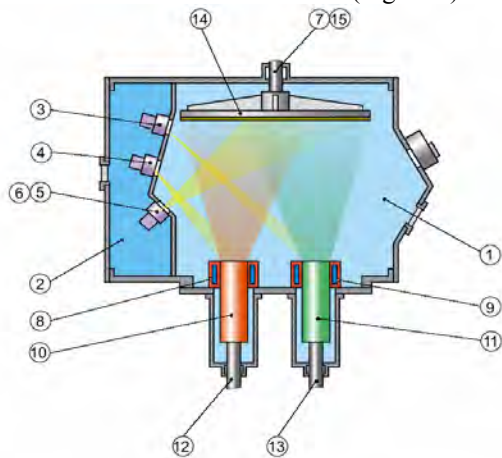


Fig 1. Electron flow installation

1-Technological working room; 2 - gun room, 3,4 (100kW),5,6(20 kW) - electron gun; 7- rod; 8($d=100mm$), 9($d=70mm$) – cooper crucible; 10,11- material; 12,13,14- assurance mechanisms to advance material,

$$T_{support} = 673 \dots 1073 \text{ K}$$

On the surface of the molybdenum ingot the CaF₂ pill with a weight of 4 ... 6 g is placed to form the separation layer on the surface of the support of OL-37. After installing and degreasing with acetone of the disc-support, the entire installation is vacuumed. Vacuum is done in 45 to 60 minutes and is $1.3 \dots 4 \cdot 10^{-2}$ Pa in the technological room and, $3 \cdot 10^{-2} \dots 6.6 \cdot 10^{-3}$ Pa – in the gun room.

When the needed vacuum pressure is achieved, it starts the disk-rotation mechanism and by means of the guns 5 and 6 heating is achieved up to temperatures of 923 ± 20 K.

The rotation speed of the disc-holder is 36 rpm.

On reaching the required temperature of the disc-support, the electron gun 4 starts and when a current flow of 0,2A and acceleration voltage of 20 kV are achieved, the pill CaF₂ is evaporated on the surface of the molybdenum ingot. In these process parameters the molybdenum ingot does not evaporate.

This technological process enables during one cycle to achieve deposition of the separation layer and to further obtain the composite material Cu-Mo without depressurization of the plant. After the separation layer deposition process is complete, between disc 14 and ingots a shutter is installed.

This prevents the vapor flow to reach the support surface with the process of reaching the technological regimes of evaporation of copper and molybdenum alloys.

The shutter being pulled down, the ingot of copper is heated (1.3 ... 1.5 A current flow). At the same time the ingot of molybdenum is heated as well. After completing the process of formatting the intermediate bath and heating the molybdenum ingot, the currents which flow on the ingot surface are brought to 3.2 ... 3.4 A for copper and up to 1.4 ... 1.8 A for molybdenum; the shutter opens and the technological process is performed to obtain the material concerned.

The composite material with a thickness of 0.8 ... 1.2 mm is achieved within 80 to 100 min. The duration of cooling the composite is 3.5 ... 4 h. After this, chamber 1 is depressurized and the composite detaches from the substrate.

The chemical composition of the condensates was determined by chemical-analytical methods [3].

The chemical composition was determined at the Electrotechnical Research Institute in Bucharest, according to STAS STAS 1706/1-85 and 1706/17-71 using spectrometric methods.

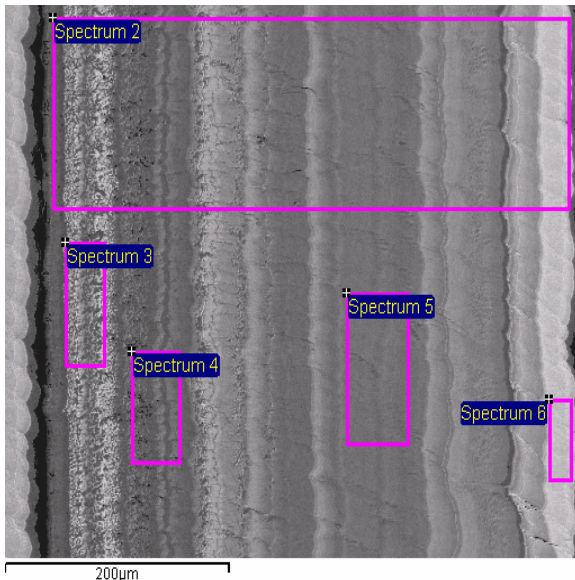
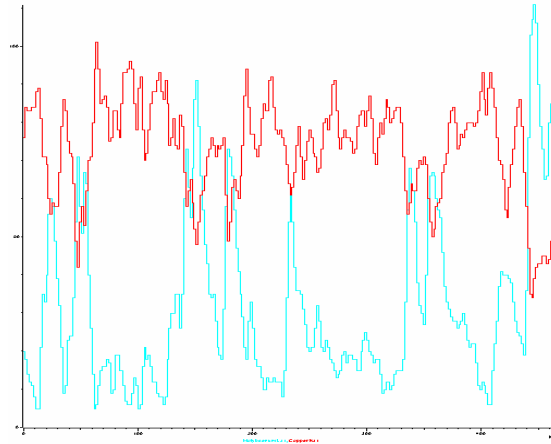
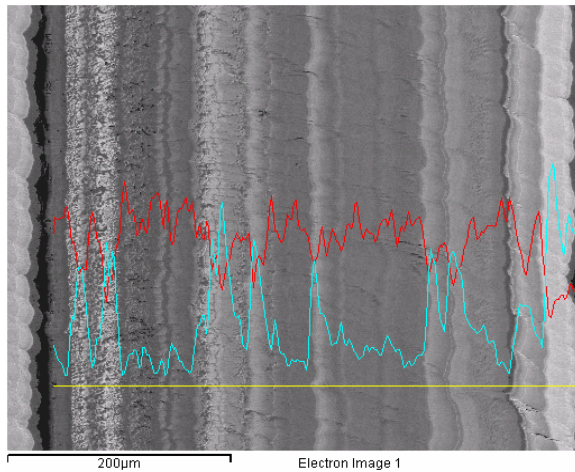
The result, which is the arithmetic average of tens of tests on samples with different thicknesses, is presented in table 2.

Table 2. Chemical composition of the composites

Sample code	Chemical composition, %	
	Cu	Mo
1	98.80	1.20
2	96.09	3.91
3	94.90	5.10
4	93.20	6.80
5	91.60	8.40
6	87.70	12.30

By electronic microscopy in cross –section and from the spot analyses EDX it could be noticed the

stratified distribution of both molybdenum and copper (Figure 2).



Processing option: All elements analysed (Normalised)
All results in weight%

Spectrum	Cu	Mo	Total
Spectrum 2	91.85	8.15	100
Spectrum 3	91.80	8.20	100
Spectrum 4	92.02	7.98	100
Spectrum 5	92.14	7.86	100
Spectrum 6	91.60	8.40	100

Fig. 2. Analyses EDX in cross section and spots for the stratified composite, Cu- Mo (8,4% Mo).

Analysis of the chemical composition and structure of composites based on copper and molybdenum allowed determination of these elements variation from layer to layer (of up to 20-25% to 4-5 mas.) and the gradient distribution nature of these elements in layers [4].

Composites obtained by physical vapor deposition increase, forming chains and conglomerates actually very important because thus increases the resistance to high temperatures [5].

Distribution of molybdenum concentration, upon evaporation from three crucibles, depends on the geometric arrangement of the crucibles. By changing the distance between the central axes of the crucibles an increased concentration of molybdenum in a particular sector of support can be obtained. Thin structure of the composites was investigated by

electronic microscopy method using electronic microscope. Metallographic attack was made with 20% HNO₃. For study purpose, samples of material based on copper and molybdenum, a molybdenum content of 12.3% (mas.), copper – remainder were considered. Specificity of the technology for obtaining composites Cu-Mo is a condition of the formation of a special laminated structure (Figure 3).

Composites were obtained in Cu-Mo micro layers with a structure sufficiently balanced by condensation at temperatures above the melting temperature to 0.3 than the melting temperature of the lowest fusible component (°C). Structure of Cu-Mo composites is under the form of blocks. For each block, it is characteristic an arbitrary periodic striped structure. The period of stripes repetition is 150 ±3 µm.

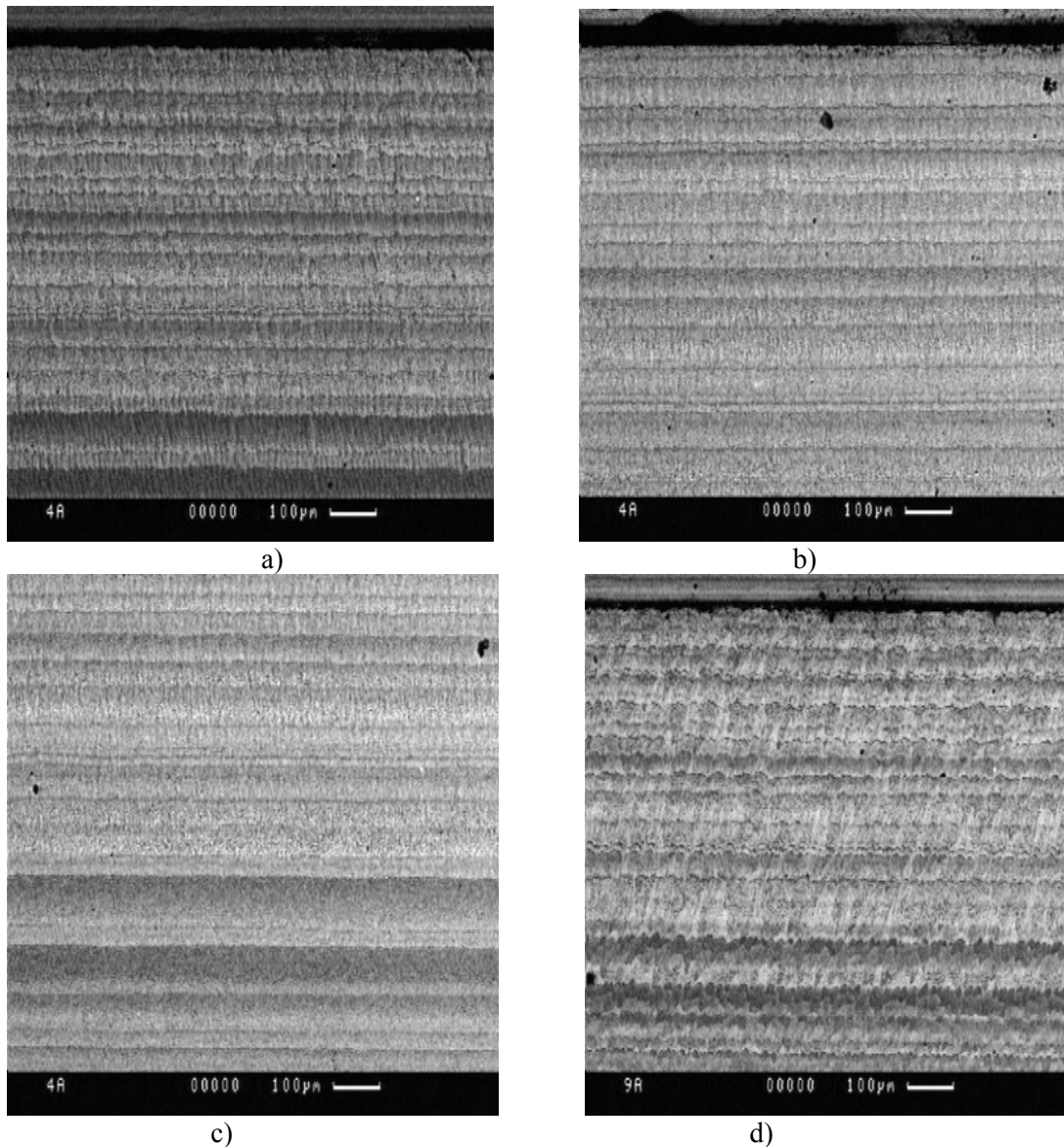


Fig. 3. Microstructures a) Cu – 3.91% Mo, b) Cu-5.1% Mo, c)-8.4% Mo, d) Cu-12.3% Mo magnification x 1000

Such a phenomenon is accounted for by the structure of this composite material which determines the corrosion process progress according to an electrochemical mechanism. In accordance with the Cu-Mo equilibrium state diagram, within the concentration interval, these are not miscible in liquid nor in solid state, and their reciprocal solubility at 900 °C is very low [6].

The corrosion test according to SR ISO 9227/1995, for a period of 100 hours at a temperature of 35°C. The purpose of the test was to detect discontinuities such as pores or other defects.

Initial samples were degreased with acetone, weighed on analytical balance with an accuracy of 0.01 mg and marked with a code. At the end of the test, samples were removed from the room and were left to dry for 30 minutes.

To determine the mass loss, the corrosion products were removed by etching in 50% hydrochloric acid solution (volumetric concentration), and the inhibitor was added 3.5g/L hexamethylene. Velocity values of corrosion and penetration indices when testing for corrosion in saline fog are given in Table 3.

Table 3. Behavior of Cu-Mo Composite obtained by PVD method, when tested in saline fog

Sample	Weight difference	Corrosion rate	Penetration index	Resistance group	Observations
	[g]	[g/cm ² ·h]	[mm/an]		
Cu – 1.2% Mo	0.0008	0.20	0.18	Rezistance	Non-adherent Oxide spots emergence on~80% of the area
Cu - 3.91% Mo	0.0006	0.15	0.12	Rezistance	Non-adherent Oxide spots emergence on~60% of the area
Cu – 5.1% Mo	0.0004	0.10	0.07	Rezistance	Non-adherent Oxide spots emergence on~10% of the area
Cu – 6.9% Mo	0.0004	0.10	0.07	Rezistance	

As shown in Figure 4, Cu-Mo composites, obtained by PVD method, have a fairly good corrosion resistance, at Mo concentrations ranging

from 1.2 to 5.1% area is covered with non adhering oxide and the concentrations of Mo between 6.8 to 12.3% of the surface do not present oxides.

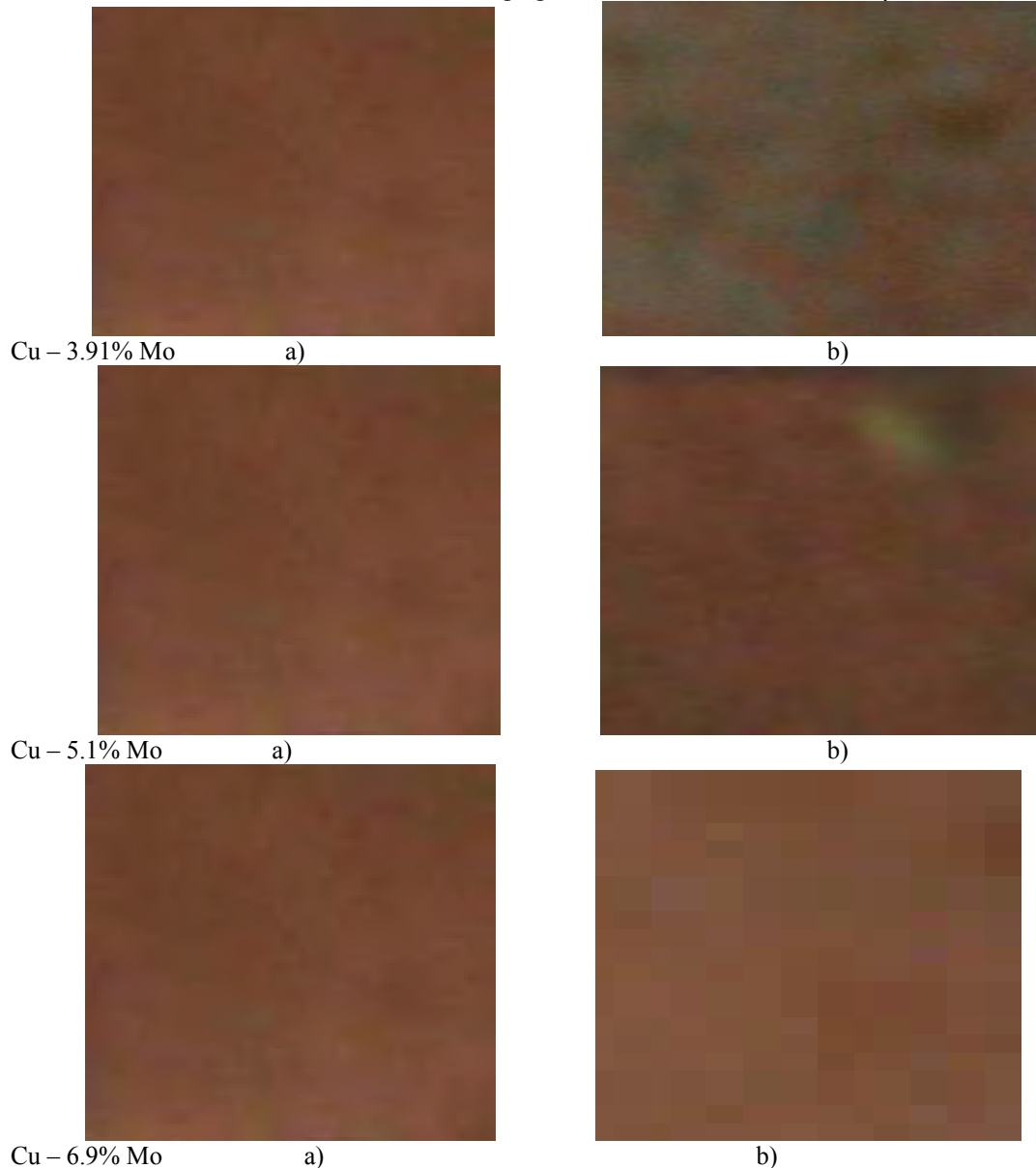


Fig. 4. Macrostructures of coatings: a) before corrosion, b) after corrosion, magnification x 50.



This is actually an adherent oxide coating, the penetration index remains unchanged. In saline fog, tests have shown that the corrosion resistance of the composites obtained by PVD method is higher than pure copper.

3. Conclusions

Analyses of chemical composition and structure of composites based on copper and molybdenum content allowed determination of the variation of these elements from layer to layer (of up to 20-25% to 4-5 mas.) and the distribution gradient of these elements in the layers. The composites obtained by physical vapor deposition increase, forming chains and conglomerates actually very important because they increase the resistance to high temperatures. Cu – Mo composites were obtained in micro-layers with a structure sufficiently balanced by condensation at temperatures above the melting temperature to 0.3 than the melting temperature of the component with the lowest fusibility (°C). In saline fog, tests have shown that the corrosion resistance of the composites obtained by PVD method is higher than pure copper.

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