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ON THE CORROSION RESISTANCE OF Cu – Mo COMPOSITE MATERIALS OBTAINED BY PVD METHOD

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ABSTRACT

The Cu – Mo composite materials have been obtained by electron flow vaporizing followed by vapor –phase condensing. Researches have shown that corrosion resistance in wet environment varies with the content of molybdenum, working conditions and composition of the corrosion medium. The corrosion resistance of the composites has been studied by gravimetric method.

KEYWORDS: composite materials, PVD method, corrosion resistance, gravimetric method.

1. Introduction

One of the main causes of the limitation to the use of materials for electrical contacts free of Ag or other nobel matals, is the fast corrosive damage when operating in wet environment.

The composite materials of Cu-Mo have been obtained by simultaneous vaporising, from separate crucibles, of copper and molibden followed by the vapor flow condensing on a steel OL-37 sublayer, preheated up to 700 ±20 °C.

Copper and molibden ingots have been used as initial materials obtained by vaccuum 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 corrosion resistance is related to the formation and decay of the working surface films. Film formation is facilitated by the arc discharges when contacts are switched. The films formed on the contact working surface may be of organic or inorganic origin.

The main causes of film formation are the vapors and gases of organic and inorganic origin to be found in the environment, and the active chemical components of the contact material, which help the chemical reaction to take place with oxides and other combinations.

2. Experiment

The materials studied in this paper have been obtained at the Research and Production Center (CCP) „GEKONT”, Vinitza, with the device UE-189 manufactured by the Electrical Welding Institute E.O. Paton of the Ukranian ASS.

For the purpose of establishing whether the contacts made from Cu-Mo composite materials obtained by electron flow vaporising and vaccuum condensing in closed air environment are suitable, researches have been focused on the study of corrosion resistance by gravimetric methods.

The gravimetric researches of Cu-Mo condensates have shown that the corrosion resistance depends on the chemical composition of the condensate materials. Introducing up to 5% molibden in the Cu -matrix has no influence on the corrosion resistance of the Cu-Mo composite material as compared with the pure copper.

With higher Mo concentrations (up to 12%) a decrease in the corrosion resistance can be noticed (approx 20%), which will limit the use of materials for Cu-Mo electrical contacts in oxidating environment [2]. T

The corrosion resistance has been studied by gravimetric method on samples immersed into tap water and distilled water. Measurements have been made on 10 samples simultaneously, every 20 h, for 100 h.

3. Results and discussions

The researches on the corrosion resistance in neutral media/environments show that, with higher concentrations of molibden in Cu-Mo condensates, there is a considerable decrease in the sample weight, which implies a lower corrosion resistance (table 1).

Table 1. *Weight loss in Cu-Mo samples containing a variable Mo content after 100 h corrosion tests.*

Content of Cu	Content of Mo	Distilled water Dm	Tap water Dm
[%]		mg/m^2	
100	-	0,04	0,09
98,9	1,1	0,08	0,1
97,7	2,3	0,1	0,11
95	5,0	0,13	0,14
89	11	0,64	0, 49

As shown in the Table above, the most significant changes of weight take place with Mo concentration higher than 5 %.

Such a phenomenon is accounted for by the structure of this composite material which determines the corrosion process progress/development 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. The disperse phase fails to interact with the matrix or to produce solid solutions or chemical combinations, i.e, Cu-Mo compositions are heterogenous systems having the matrix made from the main material – copper- into which a hard dispersed allowance (molibden) which does not dissolve into matrix at normal and high temperatures, is introduced. In contact with the neutral electroconductive environment, such as water, a multi-electron system is formed, consisting of a Cu cathod and a Mo anode. Since molibden is an active metal, it passes into the medium, which results in lower sample weights. This is also confirmed by the corrosive medium analysis performed after 100 h corrosion tests. The Mo concentration in corrosion medium increases with higher concentrations of molibden in composites (table 2). The increase in the copper ion concentration in the corrosion medium is accounted for by the balanced progress of the processes.[3]

Table 2. *The analysis of the corrosion medium after 100 h tests*

Composition		Medium							
Cu	Mo	Tap water (initial state)		Tap water (after 100 h tests)		Distilled water (initial state)		Distilled water (after 100 h tests)	
		Content Mo^{3+}	Content Cu^{2+}	Content Mo^{3+}	Content Cu^{2+}	Content Mo^{3+}	Content Cu $^{2+}$	Content Mo^{3+}	Content Cu^{2+}
		[mg/l]							
98,9	1,1	0,31	3,22	0,35	5,45	0,16	1,29	0,22	2,58
97,7	2,3	0,31	3,22	0,38	5,37	0,16	1,29	0,37	2,57
95	5,0	0,31	3,22	0,47	5,39	0,16	1,29	0,77	2,55
89	11	0,31	3,22	0,78	5,38	0,16	1,29	1,33	2,61

The values of the corrosion weight indices, calculated from the gravimetric researches, increase with tap water from 0,008 g/(m^2 · an) for a Mo concentration of 1 % to 0,048 g/(m^2 · an) for Mo concentration of 11 %, which is confirmed by lower corrosion resistance of the latter.

Mention must be made, that for molibden 5 % concentration the values of the corrosin weight index, 0,0082 g/(m^2 · an) are slightly different from its values for the pure copper 0,0079 g/(m^2 · an).

The depth of the surface corrosion damage increases with higher Mo concentration in the system, especially at concentrations higher than 5 % Mo (fig. 1). Considerable variations can also be noticed in the thermal stability of the Cu-Mo condensates when the Mo content increases. Thus, at Mo concentrations of 11 % the oxidation process velocity reaches up to 0,51 mg/min, as compared with the pure copper – 0,16 mg/min., while the sample weight increases from 0,45 % for pure copper , up to 4,88 % for the condensates featuring a Mo content of 11 %.[4,5].

The increase in the oxidation velocity and sample weight because of high Mo concentration in the system results in lower thermal stability of the condensate (table. 3).

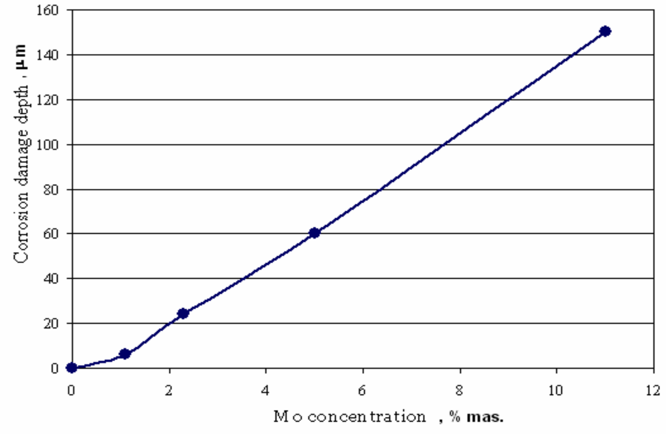

***Fig. 1.** Influence of Mo concentration on corrosion damage depth.*

***Table 3.** Thermal characteristics of the Cu-Mo condensate system*

Composition		Temperature of initial oxidation, stage 1	Temperature of initial oxidation, stage 2	Oxidation velocity stage 1	Oxidation velocity stage 2	Weight variation at 600 °C
Cu	Mo					
[%]		[°C]		[mg/min]		[%]
100	-	370	698	0,16	0,21	0,45
98,9	1,1	350	470	0,24	0,22	1,0
97,7	2,3	350	590	0,37	1,07	1,85
94,6	5,6	335	460	0,54	1,56	2,78
89,0	11	335	460	0,51	1,76	4,88

The researches carried out have shown that, after corrosion tests are perfomed in wet environment, on the surface of the Cu-Mo composite materials the line separating the sectors attacked by corrosion from perpendicular to the sublayer plan is a prevailing feature (fig. 2, *a*).

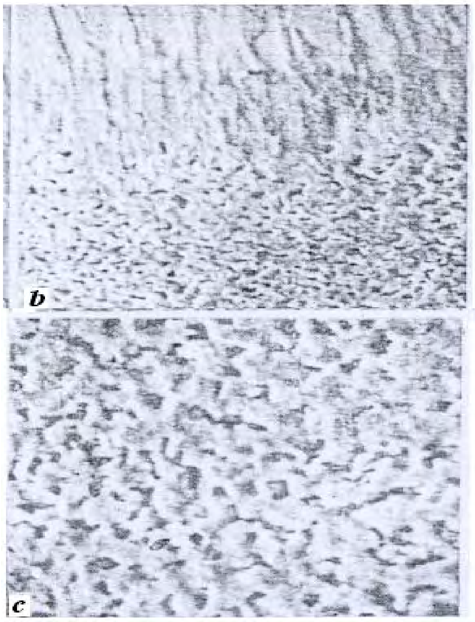

***Fig. 2.** Structure of the composite materials Cu-Mo: a – initial condensate; b – after the corrosion tests; c – corrosive layer.*

After performing the corrosion tests (fig. 2, *b*, *c*), the limit separating the condensate layer attacked by those free of corrosion becomes obvious (fig.2). For the initial Cu-Mo condensate material, the crystal lamelar pattern corrosion from the corrosion-free area can be clearly seen.

The pitting formation is related to the fact that in the Cu-Mo condensates, upon contact with the wet environment, the electrochemical corrosion takes place along with the dissolving of the more active metal – molibden. The latter has much more affinity to oxygen and that is why in liquid/wet medium higher oxides of MoO_2 and MoO_3, are formed, their existence being confirmed by x-ray method. These oxides have protection effect and the Mo oxidation process develops because it is more likely for MoO_3 to form than the cathod limit of the Mo passive state to occur. The corrosive attacks penetrate deeper into the samples. Upon getting far from the solution-surface layer separating limit, the Mo valence in its combinations with oxygen decreases [6,7].

Within the surface layers pitting sectors can be seen, and when the amount of Mo increases, the corrosion attack depth increases, too.

4. Conclusions

The researches have shown that in Cu-Mo condensate materials in neutral medium, the corrosion processes take place according to the electrochemical mechanism.

Condensates where Mo concentration does not exceed 5 % feature better corrosion resistance.

The thermal stability decreases when Mo is introduced into the copper matrix, and large variations are noticed with Mo concentrations over 5 %.

In order to use Cu-Mo condensate as electrical contacts, taking into account the anticorrosion research results and the thermal variations, it is but reasonable to recommend compositions of approx. 5 % Mo concentrations.

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