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FEATURES OF THE STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF COPPER PRODUCED BY THE METHOD OF ELECTRON BEAM EVAPORATION AND CONDENSATION IN VACUUM

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ABSTRACT

The structure and physico-chemical properties of copper, produced by the method of electron beam evaporation and condensation in vacuum were studied. A substrate from steel of St3 grade heated to 700 ± 15 °C was used for metal deposition. An intermediate pool from Cu–Zr–Y alloy was applied in the experiments. Evaluation of the properties of condensed copper, compared to cast one, showed a small difference in the values of specific electric resistance, and a certain increase of the level of mechanical characteristics, that is, probably, associated with the differences in its intragranular block structure. A 1.5 times increase of the condensate hardness was found in the case, when the intermediate pool was used, which is related to Zr and Y microalloying. Gravimetric studies of condensed copper corrosion in water revealed a significant influence on this process of such factors as presence of hardness salts in tap water and high specific electric resistance of distilled water. The greatest changes in the sample weight were observed in the first 10 h of corrosion testing, and then process stabilization and monotonic decrease of sample weight took place. In tap water copper is characterized by the highest corrosion resistance, weight losses being two times higher under dynamic testing conditions than this value for static testing. Under dynamic conditions, the medium movement prevents salt deposition, and electric resistance increase becomes slower. Analysis of corrosion polarization diagrams confirmed the slowing down of corrosion processes in tap water, compared to distilled water. Results of measurement of surface electric resistance of the samples before and after testing showed that the initial corrosion period with a relatively fast weight change, is characterized by an abrupt increase of electric resistance of the sample surface, which points to a predominant formation of copper oxide (I); and reduction of the dynamics of electric resistance change in the next testing periods is due to stabilization of the processes of film growth with copper oxide formation (II).

KEYWORDS: electron beam evaporation, vacuum, copper, condensates, mechanical characteristics, corrosion resistance

INTRODUCTION

At present many composite materials (CM) are manufactured on copper base, which is due to its unique properties [1]. In particular, by its low values of specific electric resistance (at 20 °C it is equal to $1.724\text{--}1.80 \cdot 10^{-8}$ Ohm·m), copper is inferior only to silver. Due to that it is widely used in electrical engineering industry for manufacture of power cables, wires and other conductors.

Copper purity has a decisive influence on CM properties, as impurities abruptly lower the electric conductivity [2–4]. Modern methods of refining metals and alloys, in particular, vacuum-induction, plasma-arc and electroslag melting, ensure quite efficient cleaning from metal impurities, nonmetallic inclusions and gases. The most significant results on copper refining, however, were obtained at application of the technology of electron beam remelting [5, 6]. The advantages of this technology are a deeper refining of the metal due to fractional distillation, dehydra-

tion, flotation and coagulation, while the high specific surface power in the working spot and availability of vacuum, which prevents gas absorption during welding allow controlling the beam power in space and time. All this enables realization of diverse technological schemes of the process, which it is difficult or impossible to conduct by other methods of vacuum metallurgy [7, 8].

Comprehensive analysis of the chemical composition and structure of condensates based on copper for electric engineering purposes [9–13] showed that formation of the structure, electrotechnical characteristics, mechanical strength and corrosion resistance essentially depends on the purity of the initial materials, which, alongside the alloying components, has a significant influence on the above characteristics. In this connection, studying the structural features and properties of pure condensed copper is of considerable interest. It allows determination of the influence of alloying components added to copper, on CM properties.

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The objective of this work is studying the features of formation of the structure, mechanical characteristics and corrosion resistance of pure copper, produced by the method of electron beam condensation and evaporation in vacuum.

MATERIALS AND METHODS OF INVESTIGATION

Cast copper in ingots of MO DSTU 859:2003 grade was used as initial materials. Copper was evaporated in a multipurpose laboratory electron beam unit L-2. Its feature is the possibility of performance in one installation of the majority of typical technological processes, which are currently realized using diverse special-purpose electron beam units [14]. This unit is fitted with three hot cathode guns with strip cathode. The rated accelerating voltage is 20 kV. Vacuum in the working chamber, when producing the condensates, is on the level of 10^{-2} – $5 \cdot 10^{-3}$ Pa. The substrate for copper deposition was a plate from steel of St3 grade, heated to 700 ± 15 °C, on which a separation layer of CaF_2 was first deposited. A copper ingot of 70 mm diameter was placed into a copper water-cooled crucible, from which it was evaporated. The vapour flow deposition rate was 10–15 $\mu\text{m}/\text{min}$. Condensed copper sheets of 200×250 mm size and 1.0–1.2 mm thickness were produced as a result of conducting the evaporation-condensation process. Two series of experiments were performed. The second series differed from the first one by application of an intermediate pool from Cu–Zr–Y alloy during copper evaporation, which accelerated the copper evaporation rate 2–3 times [16]. The microstructure of the produced samples was studied by scanning electron microscopy, mechanical properties were determined at room temperature tensile tests of standard samples to DSTU ISO 6892-1:2019. Samples of initial cast copper of MO grade, DSTU 859:2003 after vacuum annealing for 2 h at 450 °C were also tested for comparison of the properties. Corrosion resistance was analyzed using gravimetric investigations, which were conducted with sample soaking in tap and distilled water for 100 h. Increase of the thickness of corrosion product films was controlled by measurement of electric resistance of the sample surface by the scheme shown

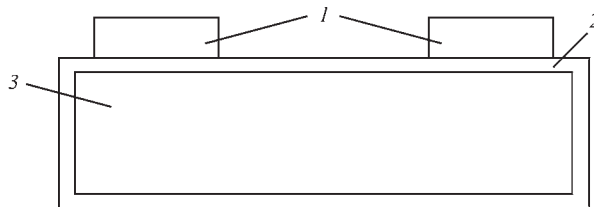


Figure 1. Scheme of contact application for measuring the electric resistance of the sample surface: 1 — put-on contacts; 2 — film; 3 — sample

in Figure 1. Control of the surface electric resistance was conducted after every 10 h of corrosion testing.

INVESTIGATION RESULTS AND THEIR DISCUSSION

Comparative evaluation of the properties of condensed copper and copper produced by the casting method, showed a slight difference of their values (Table 1). A slight increase of electric resistance of condensed copper, produced through an intermediate pool, is attributable to additional alloying by zirconium and yttrium in the total amount of 0.05–0.10 wt.%. Some changes in the level of mechanical characteristics of deposited copper, compared to cast metal, are associated with differences in its intragranular block structure, which forms under the conditions of physical deposition of copper in vacuum [16]. Moreover, increase of the condensate electric resistance and hardness (1.5 times) in case of application of an intermediate pool, is also associated with copper microalloying by zirconium and yttrium. Final conclusions on this issue require further detailed electron microscopy studies of the condensate microstructure.

Performed electron microscopy studies showed that pure copper condensates have a clearcut columnar structure with crystallite dimensions of approximately 35–40 μm (Figure 2).

Room temperature studies of copper condensate fractures demonstrated the tough fracture mode by the mechanism of microvoid coalescence with large plastic deformation preceding the fracture (Figure 3).

Cast copper and its alloys are prone to uniform corrosion, but here pitting, cavitation and intercrystalline types of corrosion, as well as corrosion cracking are observed [16]. Pure copper has satisfactory corrosion resistance under atmospheric conditions at room temperature. Here, the purer the copper, the higher is its

Table 1. Main physical and mechanical properties of condensed and cast copper

Copper	ρ (density), kg/m^3	R , $\mu\text{Ohm}\cdot\text{m}$	σ_p , MPa	σ_y , MPa	δ , %	HB , MPa
Condensed	$8.85 \cdot 10^3$	0.0181	210–220	55–60	53–55	500–600
Condensed through an intermediate pool	—»—	0.0183	215–225	56–61	50–53	520–630
Cast, annealed	$8.9 \cdot 10^3$	0.0178	200–240	70	40–50	350–400

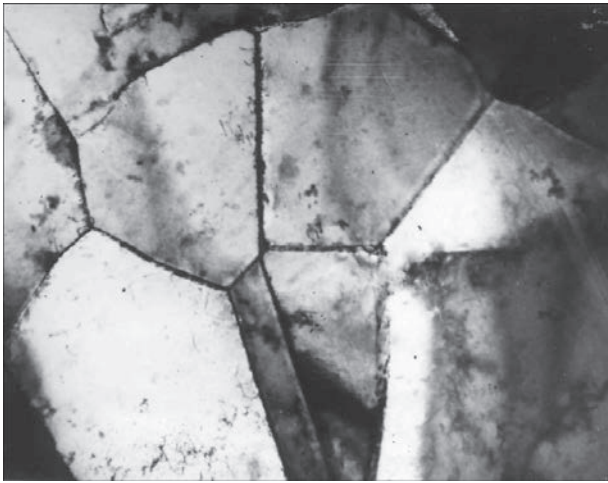
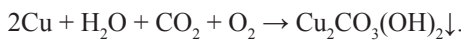


Figure 2. Microstructure of condensed copper in the cross-section, normal to vapour flow incidence ($\times 8000$)

corrosion resistance. Pure copper is resistant to atmospheric corrosion due to formation of a thin protective film of $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ composition on its surface. Fresh water and vapour condensate have practically no effect on copper. The corrosion rate of copper in sea water is also low. In humid air copper oxidizes, forming basic copper carbonate (II):



From the electrochemical point of view, the surface of copper condensate is microheterogeneous, which is determined by the presence of orientation of individual crystals, existence of grain boundaries, imperfections of the crystalline lattice as a result of dislocation formation and other violations of the fine structure. It leads to nonuniform overstress of the sample surface and, consequently, to running of the anode and cathode processes. Thus, copper corrosion in water environments proceeds by the electrochemical mechanism [17].

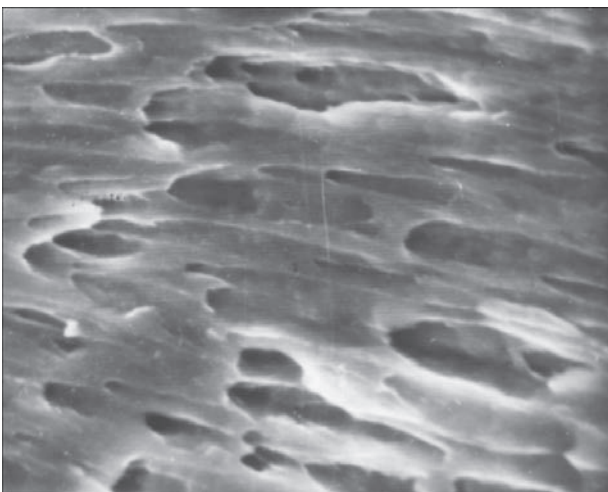


Figure 3. Electronic fractogram of copper condensate fracture ($\times 400$)

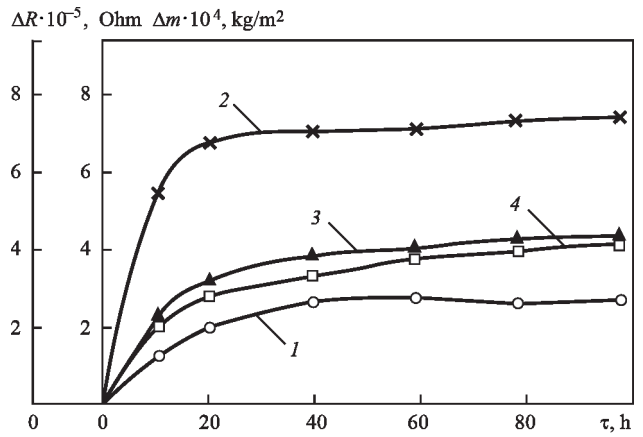


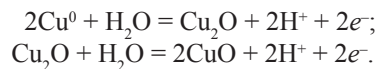
Figure 4. Change of sample weight (1, 2) and electric resistance of sample surface (3, 4) during corrosion testing under static (1, 3) and dynamic conditions (2, 4) in distilled water

The given data of gravimetric testing of copper condensates in the static and dynamic modes in distilled water showed that the greatest changes in the sample weight are observed in the initial period of corrosion testing (10–20 h) (Figure 4).

This is followed by stabilization of the corrosion processes and weight change is of a uniform nature, close to the linear one. Electron microscopy studies showed that corrosion runs uniformly over the entire sample surface. The main anode process consists in copper ionization with transition of double-charge cations into the solution;



This is confirmed by the results of chemical analysis of corrosive media after 100 h of testing (Table 2). Stabilisation of the corrosion process probably occurs due to formation on the sample surface of a thin layer of a mixture of copper oxides (I) and (II) having protective properties:



Application of the method of measurement of the sample electric resistance for evaluation of the corrosion processes was considered in two aspects: change of electric resistance due to formation of corrosion products on the sample surface and studying the selective dissolution of the electronegative component. As during measurement of the electric resistance the contact was made over the sample surface, and the distance between the contacts was small (6 mm),

Table 2. Chemical analysis of corrosive environments after 1000 h of testing in distilled water

Testing mode	Cu^{2+} ion content, mg/l
Before tests	0.09
Static	0.151
Dynamic	0.186

increase of the sample electric resistance can be attributed to a change of the surface layer thickness and chemical composition of the corrosion products, forming it. Electric resistance of the sample surface before corrosion testing was small and was taken to be zero. Copper oxides, particularly Cu_2O , differ by a much greater specific electric resistance, compared to pure copper. Thus, formation of protective oxide films on the sample surface is accompanied by increase in the total electric resistance of the samples.

Obtained values of measurement of the sample surface electric resistance can be used to calculate the oxide film thickness. The total electric resistance of the sample (R_{tot}) is expressed as follows:

$$R_{\text{tot}} = R_{\text{Me}} + 2R_f \quad (1)$$

where R_{Me} is the electric resistance of that part of the sample, which was not exposed to corrosion; R_f is the additional electric resistance, allowing for the presence of corrosion products film.

Electric resistance of uncorroded part of the sample, is found from the following formula:

$$R_{\text{Me}} = \rho_{\text{Me}} L / (a \cdot b), \quad (2)$$

where ρ_{Me} is the specific electric resistance of the sample material; L is the distance between the contacts; a , b is the sample thickness and width, respectively.

As for copper $\rho = 1.72 \cdot 10^{-8}$ Ohm·m, and the distance between the contacts was selected equal to 0.005 m, then at sample thickness of 0.005 m and width of 0.001 m, its electric resistance will be very small (approximately $1.7 \cdot 10^{-5}$ Ohm·m), compared to $2R_f$. With reduction of the sample cross-section in the corrosion process, resistance R_{Me} will change only slightly. The film electric resistance is equal to:

$$R_f = \rho_f h_f / S_c, \quad (3)$$

where ρ_f is the specific electric resistance of the film; h_f is the film thickness; S_c is the contact area.

As ρ_f has large values, and $S_c = 0.000005$ m², the electric resistance is mainly determined by film thickness. Having jointly solved equations (1) and (3) with respect to h_f , we get

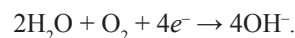
$$h_f = (R_{\text{tot}} - R_{\text{Me}}) S_c / 2\rho_f$$

Note that application of the derived equation is complicated for the case, when complex mixtures of corrosion products form on the sample surface, and it is impossible to assess ρ_f . Oxide film thickness calculated by this formula was equal to $3.7 \cdot 10^7$ m.

Results of measurement of the surface electric resistance agree well with gravimetric studies. Alongside a relatively fast change of weight, the initial period of corrosion is characterized by an abrupt increase of electric resistance of the sample surface, which confirms the postulate of predominant formation of copper oxide (I), having a high value of specific electric resistance.

Reduction of the dynamics of R_f change in the following testing periods points to stabilization of the film growth processes and the possibility of qualitative changes in it with formation of copper oxide (II).

Test results show that a greater reduction of the sample weight is observed under dynamic conditions, compared to the static conditions (Figure 3). Under dynamic conditions, due to greater aeration of the environment and better removal of the corrosion products, more favourable conditions are in place for running of the corrosion processes with oxygen depolarization



Increase of oxygen concentration in the water from 6.90 under static up to 7.34 mg/l under dynamic conditions promotes acceleration of the processes of formation of copper oxides (I) and (II), and sample movement in the environment eliminates the diffusion limitations. Increase of aeration also increases the content of CuO oxide in the film, which has higher electric conductivity, compared to Cu_2O . It is confirmed by lower values of surface electric resistance of the samples tested under the dynamic conditions, compared to static conditions.

Derived results agree with the measured values of pH and electric conductivity (κ) of environments, where corrosion tests were performed (Table 3). The given data confirm the conclusion about activation of the corrosion processes in the dynamic mode, which is indicated by higher content of copper ions,

Table 3. Change of pH and specific electric conductivity of the environments during corrosion testing

Testing mode	Characteristic	Values after τ , h			
		0	20	50	100
Static	pH	6.41	6.29	6.53	6.81
	κ , S/m	$6.24 \cdot 10^{-4}$	$6.74 \cdot 10^{-4}$	$7.88 \cdot 10^{-4}$	$9.34 \cdot 10^{-4}$
Static	pH	6.41	6.13	6.74	7.01
	κ , S/m	$6.24 \cdot 10^{-4}$	$8.17 \cdot 10^{-4}$	$9.07 \cdot 10^{-4}$	$1.92 \cdot 10^{-3}$

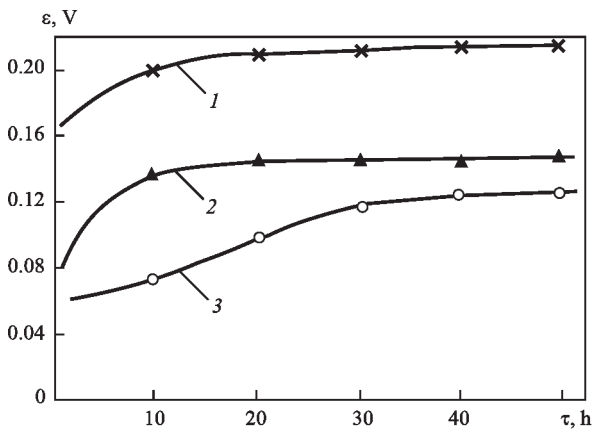


Figure 5. Influence of oxygen concentration $[O_2]$ in distilled water on the magnitude of stationary electrode potential of copper electrodes, mg/l: 1 — 8.95; 2 — 8.67; 3 — 14.29

which are gone into the solution, and which increased the specific electric conductivity of the environment, respectively.

An important characteristic, which allows judging the kinetics of the corrosion processes, is the magnitude of stationary electrode potential (Figure 5).

Results of investigations in environments with different oxygen content show that increase of oxygen concentration shifts the stationary potential into the positive region, as a result of facilitation of running of the cathode process of oxygen reduction.

NaCl addition to distilled water rather strongly shifts the stationary electrode potential ($\epsilon = 0.018$ V) to a more negative region, i.e. the corrosion processes run more intensively. It is demonstrated by the corrosion diagram for copper condensates, derived when taking the polarization curves in a potentiodynamic mode in 3 % NaCl solution (Figure 6).

The above data show that at copper condensate corrosion in a 3 % NaCl solution the controlling stage is the process of oxygen reduction running in the diffusion mode. The diffusion current under static con-

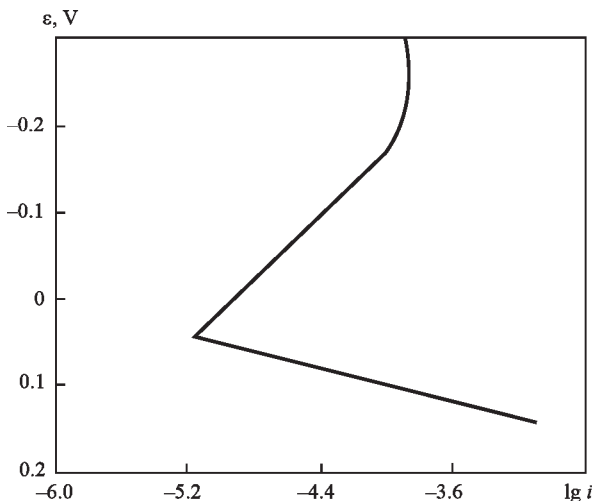


Figure 6. Corrosion polarization diagram for copper condensate in 3 % NaCl solution

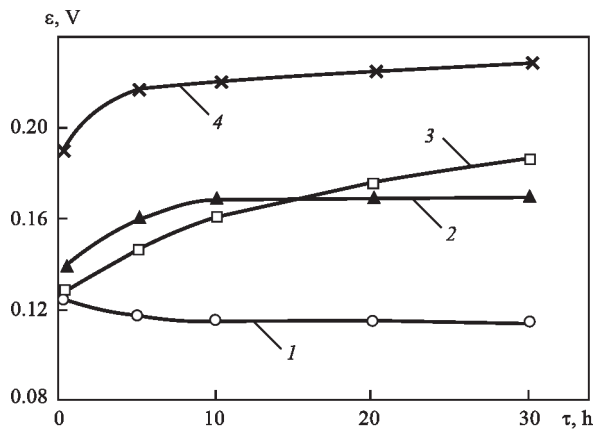


Figure 7. Influence of oxygen concentration $[O_2]$ in tap water on the value of stationary electrode potential in copper condensates, mg/l: 1 — 2.3; 2 — 3.1; 3 — 8.11; 4 — 16.07

ditions is equal to 0.631 A/m², and the general dissolution rate is 0.661 A/m² at corrosion potential of +0.04 V.

In tap water the stationary electrode potential of copper condensates largely depends on the time of water being in contact with atmospheric air. So, in fresh tap water Cu stationary potential has the highest negative value. During water settling dissolved oxygen concentration in it becomes higher, and part of the hardness salts precipitates. Here, the stationary electrode potential takes more positive values than those in the distilled water.

The influence of the above factors on the value of stationary electrode potential is given in Figure 7. Thus, increase of oxygen content in tap water, pH increase and reduction of the concentration of Ca²⁺ and Mg²⁺ ions promote shifting of the stationary electrode potential of vapour-phase condensates into the positive region.

Gravimetric studies showed that copper condensates are characterized by high corrosion resistance in tap water (Figure 8, curves 1, 2). However, under dy-

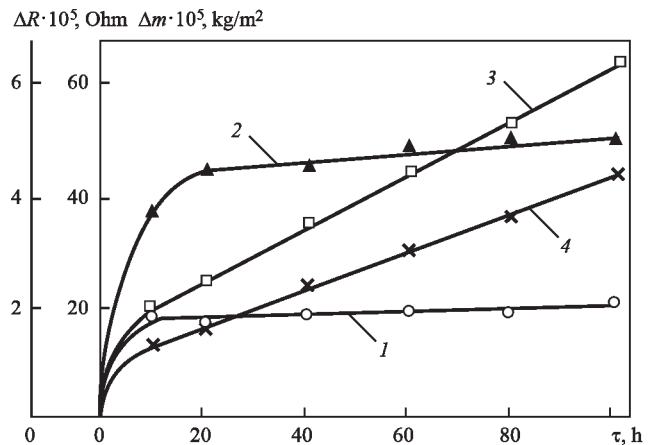


Figure 8. Change of weight (1, 2) and electric resistance of sample surface (3, 4) during corrosion testing under static (1, 3) and dynamic (2, 4) conditions in tap water

Table 4. Results of chemical analysis of tap water after 100 h of corrosion testing

Testing mode	Ion content in corrosive environment, mg/l		
	Cu ²⁺	Ca ²⁺	Mg ²⁺
Before tests	0.053	90.09	10.94
Static	0.113	86.90	10.24
Dynamic	0.162	88.01	10.73

dynamic test conditions weight losses exceed two times this value for static tests. The greatest weight changes are observed in the first 10 h of corrosion testing, and this is followed by process stabilization and monotonic reduction of sample weight. It follows from the layout of the curves of sample surface electric resistance that under static conditions ΔR grows more intensively, compared to dynamic conditions (Figure 8, curves 3, 4). This is attributable to precipitation of hardness salts on the sample surface in the absence of the environment movements, which have high values of specific electric resistance.

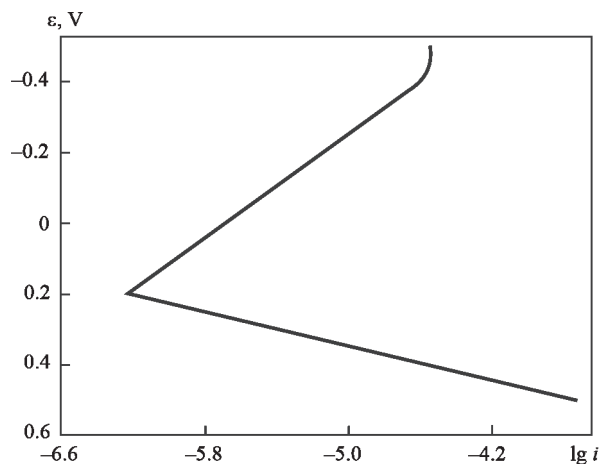
Under dynamic conditions, the environment movement prevents salt precipitation, and increase of electric resistance slows down. The results of electrochemical investigations, derived by taking polarization curves, confirmed deceleration of the corrosion processes in tap water, compared to distilled water (Figure 9). This is confirmed by corrosion currents, the values of which are smaller in tap water, than in distilled water, and are equal to $6.31 \cdot 10^{-3}$ A/m². The process of electrochemical corrosion runs in two environments with cathode control.

Gravimetric tests agree well with the data of chemical analysis of the environment after corrosion testing (Table 4).

Hardness salt content in the environment decreases in connection with formation of films on the sample surface, which include calcium and magnesium ions; copper ion concentration in the environment becomes higher, which is particularly pronounced for dynamic conditions.

CONCLUSIONS

1. Comparative studies of deposited copper, produced by electron beam evaporation and condensation and by the traditional casting method (MO grade), revealed a slight difference in electric resistance values. A certain increase in the level of deposited copper mechanical characteristic, compared to cast material, is, probably, associated with the differences in its intergranular block structure. A 1.5 times increase in hardness of condensate produced with application of


Figure 9. Corrosion polarization diagram of condensed copper in tap water

an intermediate pool, is associated with copper microalloying by zirconium and yttrium.

2. The influence of water environment on corrosion resistance of condensed copper was studied. It was found that copper corrosion in water environments proceeds by the electrochemical mechanism. Slowing down of the corrosion processes in tap water, compared to distilled water, is confirmed by gravimetric testing, data of chemical analysis of the environment after corrosion testing, and corrosion currents, the values of which are lower in tap water, than in the distilled one.

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