

## DYNAMICS OF REDOX PROCESSES IN THE ELECTROLYTE FOR ELECTRODEPOSITION OF Cu-Sn ALLOY

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One of the serious problems of copper-tin alloy plating from non-cyanide electrolytes is the instability of solutions. It is caused by redox processes in the joint presence of ions of alternating valence. The results of the study of redox processes dynamics in the tetrafluoroborate electrolyte for bronze deposition are presented, based on analysis of cathodic polarization dependencies obtained at various stages of electrolyte storage. It is shown that the equilibrium of oxidation-reduction processes in the electrolyte is reached within a day. The opportunity of stable functioning of tetrafluoroboric electrolyte in the presence of EDTAcetat<sup>2-</sup> is found out. The cathodic polarizing curve, obtained for a copper electrode in this electrolyte after the establishment of redox balance, has voltammetric minimum in the field of potentials of the beginning of tin and copper codeposition. Copper is deposited at potentials of the first rise of a current on the polarizing curve, bright copper-tin alloy coatings by «yellow bronze» are deposited after the minimum. Potentiodynamic dependencies obtained in the working bronze electrolyte after equilibrium was established and in the electrolyte after a year of storage differ insignificantly. The electrolyte works stably, that is the constancy of the electrolyte composition ensures the constancy of the composition of the precipitated alloy.

“Yellow bronze” and “white bronze” coatings, depending on their composition, are used as antifriction, protective-decorative coatings, hard solders, for the restoration of worn bronzed parts, for corrosion protection of steel in hot water, for metal mirrors production, etc. The Cu–Sn alloy electrodeposition baths are classified as cyanide [1, 2] or non-cyanide ones. Sulfate [3, 4], tetrafluoroborate, pyrophosphate [5], citrate [6], tartrate [7], and other electrolytes are proposed to replace poisonous cyanide electrolytes. As a rule, alkaline electrolytes of bronze deposition have a low rate of coatings deposition, and acid electrolytes do not usually allow obtaining high-quality coatings by copper-tin alloy of sufficient thickness. For example, tetrafluoroborate electrolytes have a high rate of coating deposition. However, tetrafluoroborate electrolytes are mentioned in literature only as electrolytes for "white bronze"

electrodeposition. High speed of contact displacement of copper ions by tin interferes deposition of "yellow bronze". The modification of the tetrafluoroborate electrolyte with ethylenediaminetetraacetate ions [8] makes it possible to reduce the contact extrusion in the copper-tin system significantly [9, 10].

Additionally, the results of studies of copper and tin codeposition in either freshly prepared solutions or with separation of cathode and anode spaces, can be found in literature. There are indications of poor stability of electrolytes. Meanwhile, electrolytes for bronze deposition are complex systems containing copper and tin ions of various oxidation numbers, i.e. these are the systems that tend to change their qualitative and quantitative composition over time. The studies that would reflect these changes are extremely rare in the literature [7].

The aim of the present study is to evaluate the chemical stability of the tetrafluoroborate electrolyte for bronze deposition [8] during storage.

### **Research methodology**

Polarization curves were obtained at a potential sweep rate of  $1 \text{ mV s}^{-1}$  using a PI-50-1.1 potentiostat. The samples of copper were used as working and counter electrodes. The surface area of the working electrodes was  $1 \text{ cm}^2$ . The samples were cleaned successively by carbide-silicone paper of №№ 500, 100, 2000, 3000 grit, degreased in acetone, and then washed with distilled water. We used saturated silver chloride electrode and the mentioned potentials were recounted with respect to the standard hydrogen reference electrode (SHE).

The initial solution contained 0.85 M of copper tetrafluoroborate in 42% tetrafluoroborate acid solution.

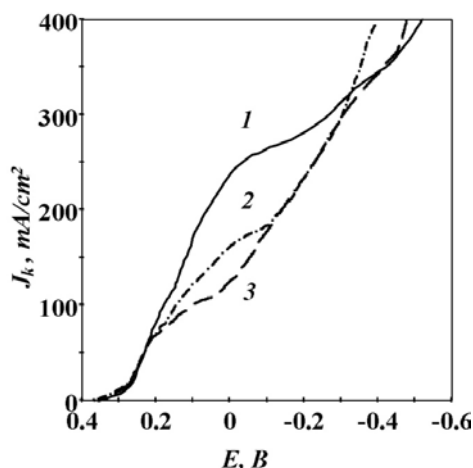
### **Results and Discussion**

The chemical stability of the electrolyte for bronze deposition was determined by an indirect method: we analyzed changes in cathodic polarization dependencies obtained at different stages of electrolyte storage. These dependences reflect the dynamics of redox processes in the electrolyte.

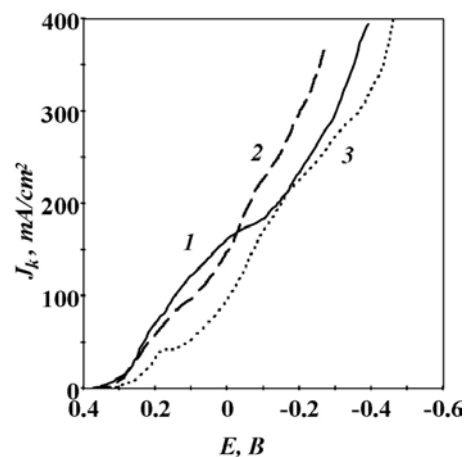
The cathodic polarization curve in an electrolyte containing 0.85 M copper tetraborftorborate has the shape of classical curve for copper electrodeposition from acid solutions. This curve has a plateau of limiting current (Fig. 1, curve 1), and it is not possible to obtain a compact copper coating at the corresponding potentials. Tin ions were added by contact displacement of a part of copper ions from the electrolyte with a tin powder. The addition of tin ions leads to decreasing copper deposition rate in the first region of the polarization curve and to the second limiting current for copper and tin codeposition appearance (curve 2):



The deposit forms at the limiting current of copper deposition, so the quality copper-tin alloy coating cannot be obtained. With further increase in tin ions concentration by reducing copper ions concentration in the electrolyte decreases the limiting currents of both copper and alloy deposition (curve 3).



**Fig. 1.** The cathodic polarization curves on copper (1) and copper-tin alloy (2, 3).  
The content of  $\text{Sn}^{2+}$ , M:  
2 - 0.29; 3 - 0.36



**Fig. 2.** Cathodic polarization curves in electrolyte for bronze deposition.  
The content of  $\text{Sn}^{2+}$  is 0,36 M.  
Storage time, h: 1 - 0.3; 2 - 1,2; 3 - 24.

Redox processes occur in electrolyte after preparation. The part of cupric ions reduces to the ions with an oxidation number of +1:



and oxidation of part of tin ions to Sn (IV) compounds

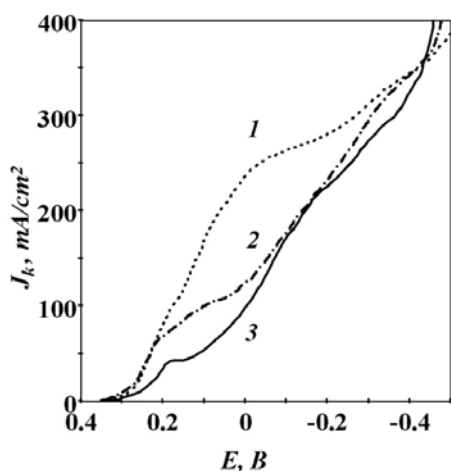


These processes are accompanied by a consequent reduction at the height of wave of copper deposition and codeposition of copper and tin (see Fig 2, curves 2 and 3) according to reactions (1, 2) and inhibition of the cathode reaction by products of interaction (curve 3).

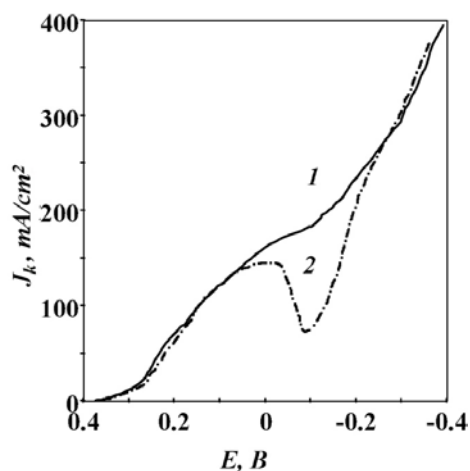
With increasing storage time, the difference between the value of the limiting current of alloy deposition and value of limiting current of copper deposition decreases (compare Fig. 3 and Fig. 1).

EDTA<sup>2-</sup> addition leads to the great decrease in the rate of cathode process in the potential range 0.5 ... -0.25 V in the limiting current of copper deposition and its codeposition with tin (Figure 4). This allows producing compact coating of copper-tin alloy. At the same time, it is revealed that “yellow brass” alloy deposits at more positive

potentials than tin, and less positive than copper. Shift of the potential of more electronegative component is caused by the reduction of partial molar free energy during the alloy formation, which may occur during the formation of the solid solution or intermetallic compounds [11].



**Fig. 3.** The cathodic polarization dependences of copper (1) and alloy (2, 3) deposition after 24 hours of storage. The tin content, M: 1 - 0; 2 - 0.29; 3 - 0.36.



**Fig. 4.** Cathodic polarization dependences of alloy deposition in the presence of EDTAcetate<sup>2-</sup>. The content of Na<sub>2</sub>EDTA, g/dm<sup>3</sup>: 1- 4; 2 - 30.

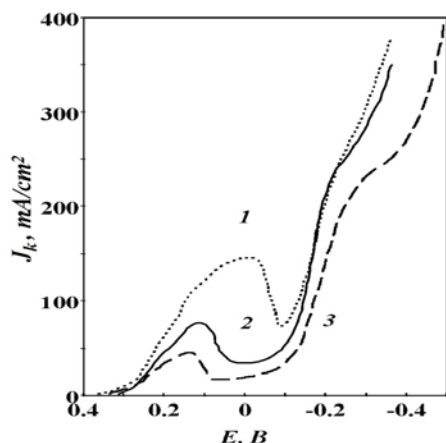
During the day, the inhibitory effect of EDTAcetate<sup>2-</sup> is amplified as a result of slow oxidation-reduction processes in solution (Figure 5). It leads to electrodeposition of not only compact coating, but also bright coatings of copper-tin alloys, and the coating becomes more fine-crystalline. The maximum possible rate of bronze coating deposition slightly decreases with time, while the range of current density values of alloy deposition expands. A similar effect of insertion of the additives was observed in, e.g., sulfuric acid electrolyte for bronze deposition [4].

Copper anodes were mainly used, as "yellow bronze" alloy contains only 10-15% of tin. Using copper anodes leads to the accumulation of copper ions in the electrolyte and the lack of tin ions. We studied the possibility of periodical use of tin anodes. As a result of exposure of tin anode in the electrolyte in galvanostatic regime, the stannous ion content increases (Fig. 6), and copper ions concentration reduces due to its preferential discharge at the cathode.

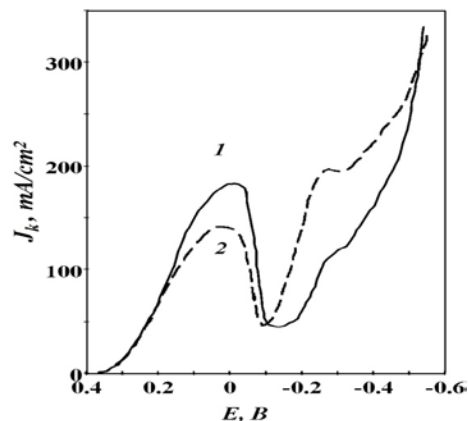
The degree of inhibition of the cathode process in the operating range of potentials does not change significantly with addition of Na<sub>2</sub>EDTA in the electrolyte with long term of operation (Fig. 7), compared to initial solution (curve 1 and 2). Further addition of Na<sub>2</sub>EDTA (curve 3) leads to a negative effect as the rate of bronze coating deposition reduces.

Despite the fact that chemical equilibrium in the electrolyte after its preparation is set for a long time (Fig. 2), equilibrium can still be

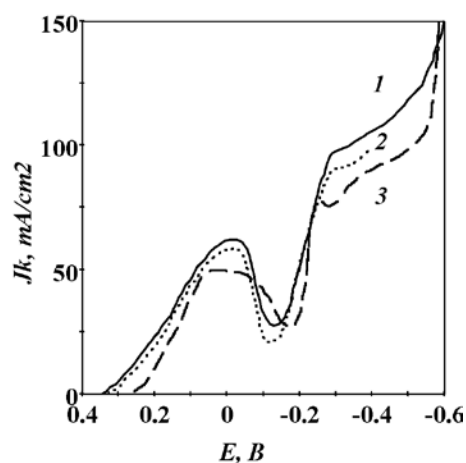
achieved. Potentiodynamic curves obtained in the working electrolyte for bronze deposition [8], containing additionally cobalt compound after equilibrium is established (Fig. 8, curve 1), and in the electrolyte after one year of storage (curve 2) differ slightly. The electrolyte is stable in operation, i.e. the constancy of electrolyte composition provides constant composition of the deposited alloy.



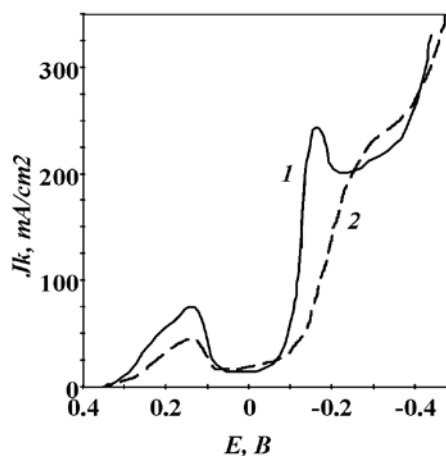
**Fig. 5.** Changing the cathodic polarization curves in alloy deposition in the presence of  $30 \text{ g/dm}^3$  of  $\text{Na}_2\text{EDTA}$  electrolyte due to storage. Storage time, h 1 - 0.3; 2 - 4; 3 - 24



**Fig. 6.** Cathodic polarization dependences alloy deposition before (1) and after electrolysis with tin anode (2)



**Fig. 7.** Effect of EDTAcetat on cathodic polarization curves in electrolyte after prolonged operation.  $\text{Na}_2\text{EDTA}$  content,  $\text{g/dm}^3$ : 1 - 0; 2 - 3; 3 - 5.



**Fig. 8.** Cathodic polarization curves in the electrolyte after 1 year of storage (1) and after 1 day (2)

## Conclusions

The study of dynamics of redox processes in the tetrafluoroborate electrolyte for bronze deposition shows that the rate of redox reactions in the electrolyte volume is significant during the first hour after its preparation. The equilibrium is reached in the electrolyte a day later. The cathode polarization dependences obtained in the working electrolyte have a minimum. Copper is deposited at potentials of the first rise of a current on the polarizing curve, bright copper-tin alloy coating of "yellow

bronze” is deposited after the minimum. The potentiodynamic dependencies obtained in the working tetrafluoroborate electrolyte after equilibrium is established and in the electrolyte after storage for a year differ insignificantly. This is one of the factors ensuring the constancy of composition of Cu-Sn alloy under deposition.

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