

STUDY OF ANODE PROCESSES DURING DEVELOPMENT OF THE NEW COMPLEX THIOCARBAMIDE-CITRATE COPPER PLATING ELECTROLYTE

O. Smirnova

PhD, Associate Professor*
E-mail: oleo1970@gmail.com

A. Pilipenko

PhD, Senior Lecturer*
E-mail: opilipenko1984@gmail.com

H. Pancheva

PhD, Senior Lecturer**

A. Zhelavskiy

V. N. Karazin Kharkiv National University
Svobody sq., 4, Kharkiv, Ukraine, 61022
E-mail: zhelavskyy97@gmail.com

K. Rutkovska

Postgraduate student*
E-mail: rutkovskaya9@gmail.com

*Department of technical electrochemistry***

Department of labor and environment protection*

***National Technical University
«Kharkiv Polytechnic Institute»

Kyrpychova str., 2, Kharkiv, Ukraine, 61002

Досліджено кінетику анодних реакцій на міді у тіокарбамідно-цитратних розчинах. Встановлено, що анодне розчинення металу приводить до появи комплексних сполук одновалентної міді. Тіокарбамід утворює з міддю комплекс катіонного типу. Лимонна кислота забезпечує кисле значення рН та сприяє активному розчиненню міді. Результати проведених досліджень показують, що анодне розчинення міді відповідає закономірностям дифузійної кінетики

Ключові слова: комплексні сполуки, анодна поляризація, лімітуюча стадія, дифузійна перенапруга, поляризаційна залежність

Исследована кинетика анодных реакций на меди в тиокарбамидно-цитратных растворах. Установлено, что анодное растворение металла приводит к возникновению комплексных соединений одновалентной меди. Тиокарбамид образует с медью комплекс катионного типа. Лимонная кислота обеспечивает кислое значение рН и способствует активному растворению меди. Результаты проведенных исследований показывают, что анодное растворение меди отвечает закономерностям диффузионной кинетики

Ключевые слова: комплексные соединения, анодная поляризация, лимитирующая стадия, диффузионное перенапряжение, поляризационная зависимость

1. Introduction

Copper plating is one of the most common processes for applying coatings in electroplating engineering. Excellent levelling and covering properties make copper an ideal substrate when other metals are applied.

To apply coatings to steel products, as well as to parts with complex shape, complex electrolytes of copper plating are used, the most common of which are the cyanide electrolytes.

Disadvantages of cyanide electrolytes (instability of composition and high toxicity) stimulate the development of other complex electrolytes for copper plating. Such electrolytes must meet the following requirements:

- 1) to ensure application of high-quality coatings with durable adhesion to the base;
- 2) to have a stable composition;
- 3) to be suitable for operational use and to be non-toxic;
- 4) preparation of the electrolyte must include widespread and cheap components.

There are known complex electrolytes for copper plating containing ammonia, potassium pyrophosphate, ethylenedi-

amine, trilon B, carboxylic acids. The most common of these electrolytes is the pyrophosphate electrolyte, which has two significant drawbacks:

- 1) high content of components predetermines their great losses as the solution is taken out of bath with parts;
- 2) complexity of purification of washing water from pyrophosphate ions, which when ingested in water cause intense algal blooms.

Other complex electrolytes are not applied in industry.

Thus, it is an important task to develop a new electrolyte for copper plating. The electrolyte should ensure acceptable technological parameters for a copper plating process and remain stable under operation conditions. Electrolyte components should be affordable and harmless for the environment.

2. Literature review and problem statement

Complex copper plating electrolytes with organic ligands are the insufficiently explored area of technical electrochemistry. Studying the kinetics of charge and the ionization of

complex particles in these systems could contribute to the development of a new copper plating electrolyte. There is a series of complex copper plating electrolytes based on organic ligands. It is a promising direction to develop electrolytes based on thiourea, which form strong complexes with copper. For example, authors of paper [1] examined effect of thiourea and chloride ions on the structure of electrodeposited copper. It is shown that introduction to a sulfate electrolyte of thiourea causes reduction of grain size of copper, which is associated with the adsorption of $\text{CS}(\text{NH}_2)_2$ on the cathode surface. However, influence of thiourea on the anodic dissolution of copper in a sulphate electrolyte was not studied.

Paper [2] addresses influence of the concentration of thiourea on the electrochemical deposition of copper. Increasing the concentration of $\text{CS}(\text{NH}_2)_2$ leads to a growth of polarization of the reduction process and contributes to obtaining fine-grained coatings. The process of complex formation at anode dissolution of copper in a given electrolyte was not shown.

The results of study [3] reveal that the introduction to electrolyte of $\text{CS}(\text{NH}_2)_2$ enables the formation of shiny compact copper coatings. The authors did not explore the anodic processes on a copper electrode.

Effect of additives of chloride ions and thiourea on the structure of cathode copper deposition was studied in article [4]. It was established that thiourea predetermines formation of compact copper deposition through the inhibition of growth of the most active places in the cathode. Influence of the anodic processes on the stability of electrolyte was not investigated in the article.

Authors of paper [5] investigated deposition of copper from baths containing sodium citrate and triethanolamine. It is shown that such electrolytes contain copper in mono- and divalent form. Effect of triethanolamine on the process of complex formation in the solution was not tackled. The anode process a given electrolyte was not addressed.

Study [6] aims to develop the electrolyte for copper deposition on microelectronics products. It was established that electrodeposition leads to the formation of plastic coatings. Influence of citrate ions on the course of anode dissolution of copper anode was not studied.

Authors of paper [7] investigated the morphology of copper coating from the proposed citrate electrolyte. The result of deposition process was the formation of compact coatings, which were characterized by the presence of small grain of the metal. Influence of the patterns of anode dissolution of copper on electrolyte stability was not considered.

Thus, the purpose of studies performed in this field was to explore the cathode process of copper deposition. There are almost no data on the kinetics of dissolution of copper in thiocarbamide-citrate electrolytes. It is thus impossible to assess the effect of anodic processes on the electrolyte stability and the constancy of composition of the plating bath. However, development of such electrolytes is a relevant task. Acid thiocarbamide-citrate electrolytes could enable rapid build-up of copper coatings by reducing a copper (I) complex.

3. The aim and objectives of the study

The aim of present study was to examine the anodic processes on a copper electrode in the acid thiocarbamide-citrate electrolyte. This would make it possible to optimize the

composition of a copper plating electrolyte and the mode of electrolysis.

To accomplish the aim, the following tasks have been set:

- to investigate the effect of electrolyte composition on the behavior of copper under conditions of anode polarization in solutions containing organic ligands;
- to determine the kinetic indicators and the nature of limiting stage of copper ionization in acid thiocarbamide-citrate solutions.

4. Procedure for conducting experimental research

To prepare the electrolyte, we used as a starting salt the copper (II) citrate, obtained by neutralizing citric acid with base copper carbonate. We used thiourea and citric acid as organic ligands. These reagents of qualification “pure for analysis” were dissolved in distilled water at a temperature of 25–35 °C. The electrolyte was filtered upon complete dissolution of components.

We used copper M00 as the anode during research. The surface of copper was degreased in an alkaline solution, activated in dilute H_2SO_4 and washed with warm and cold water.

Polarization measurements were performed using the potentiostat PI 50-1-1. In the research, we used a three-electrode cell with separated cathode and anode spaces. In the course of the experiment, the cell was thermostated. A smooth rod made of platinum, brand PI 99.9, was applied as an auxiliary electrode. Reference electrode was a silver chloride electrode, brand EVL-1M1.

5. Results of the study into kinetics of anodic processes on a copper electrode in thiocarbamide-citrate solutions

Kinetics of the copper anodic dissolution was examined by registering voltammograms. Voltammograms make it possible to establish the effect of electrolysis conditions through a graphical representation of the current density dependence on electrode potential in a given medium. Polarization dependences are acquired at a linear shift of the electrode potential from its value of stationary potential E_{st} .

Fig. 1 shows anodic polarization dependences of the dissolution of a copper electrode in the solutions of thiocarbamide, citric acid, and in a mixed solution. The dependences were acquired under conditions of the electrode potential sweep toward the region of positive values at a speed of $10 \text{ mV}\cdot\text{s}^{-1}$. The results obtained show that the anodic polarization of the copper electrode in 0.1 M solution of $\text{CS}(\text{NH}_2)_2$ is characterized by small current densities of copper dissolution (Fig. 1, Curve 1). The ionization of copper in a solution occurs with considerable inhibition. In 0.1 M solution of $\text{C}_6\text{H}_8\text{O}_7$, copper ionization proceeds without difficulties (Fig. 1, Curve 2).

Adding citric acid to the solution of thiocarbamide dramatically changes the character of anodic behavior of copper. Citric acid stimulates active dissolution of copper in the range of potentials (–0.25)–(+0.4) V. Analysis of dependence 3 allows us to isolate three typical sections on it. These sections correspond to the region of active dissolution, current density limit, and to the region of further electrochemical oxidation of copper to the ions of Cu^{2+} .

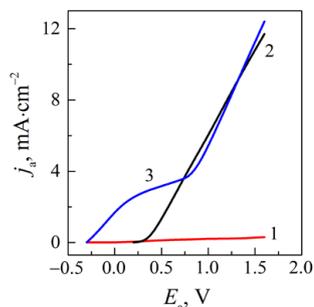


Fig. 1. Anodic polarization dependences of copper electrode in solutions containing 0.1 M $\text{CS}(\text{NH}_2)_2$ (1); 0.1 M $\text{C}_6\text{H}_8\text{O}_7$ (2); 0.1 M $\text{CS}(\text{NH}_2)_2$ +0.1 M $\text{C}_6\text{H}_8\text{O}_7$ (3). $t=25^\circ\text{C}$

The dependences shown are consistent with earlier findings for the anodic behavior of copper in $\text{CS}(\text{NH}_2)_2$ solutions and a mixture of $\text{CS}(\text{NH}_2)_2$ and $\text{C}_6\text{H}_8\text{O}_7$ [8]. The results are supplemented by the dependence acquired in a solution of citric acid.

The composition of a solution affects the value of stationary potential and the potential of copper electrode activation (Table 1). The difference between the values of potentials (Δ) between E_{st} and E_{act} in the solution containing only $\text{CS}(\text{NH}_2)_2$ or $\text{C}_6\text{H}_8\text{O}_7$ is 0.095–0.1 V. In solutions containing both components, $\Delta=0.005$ –0.01 V. Combined presence of $\text{CS}(\text{NH}_2)_2$ and $\text{C}_6\text{H}_8\text{O}_7$ in a solution leads to a significant activation of the copper electrode. Increasing the concentration of thiocarbamide results in the offset of copper potentials towards a negative region. Influence of $\text{C}_6\text{H}_8\text{O}_7$ is insignificant.

Table 1

Values of stationary potential (E_{st}) and activation potential (E_{act}) of copper

Composition of solution	E_{st} , V	E_{act} , V
0.1 M $\text{CS}(\text{NH}_2)_2$	-0.295	-0.2
0.1 M $\text{C}_6\text{H}_8\text{O}_7$	0.2	0.3
0.1 M $\text{CS}(\text{NH}_2)_2$ +0.1 M $\text{C}_6\text{H}_8\text{O}_7$	-0.3	-0.29
0.1 M $\text{CS}(\text{NH}_2)_2$ +0.1 M $\text{C}_6\text{H}_8\text{O}_7$ + +0.016 M Cu (met.)	-0.195	-0.19
0.25 M $\text{CS}(\text{NH}_2)_2$ +0.1 M $\text{C}_6\text{H}_8\text{O}_7$ + +0.016 M Cu (met.)	-0.36	-0.35

Potentials of copper that are given in Table 1 are consistent with those obtained by authors in [9]. They have the same sign, but differ slightly in absolute magnitude.

To determine the limiting stage in the process of copper dissolution, the dependences obtained were represented in the semi-logarithmic coordinates. This allowed us to establish the stage of an electrode reaction whose rate determines the total speed of the process.

Results of graphical processing are shown in Fig. 2. According to them, the electrode reaction of copper dissolution proceeds at diffusion control. This is indicated by the fact that the greatest linearization of polarization dependence is observed at its mapping in coordinates $\eta - \lg(1 - j/j_d)$, where η is the overvoltage of anodic reaction, $\eta = E_j - E_{\text{st}}$, V; j is the anodic current density, $\text{A}\cdot\text{cm}^{-2}$; j_d is the diffusion current density, corresponding to its mean magnitude on the section of current limit of curve 3 (Fig. 1), $\text{A}\cdot\text{cm}^{-2}$. In this case, there is a slow progress of the stage of removal of the anode reac-

tion products from the interface of phases into the volume of electrolyte.

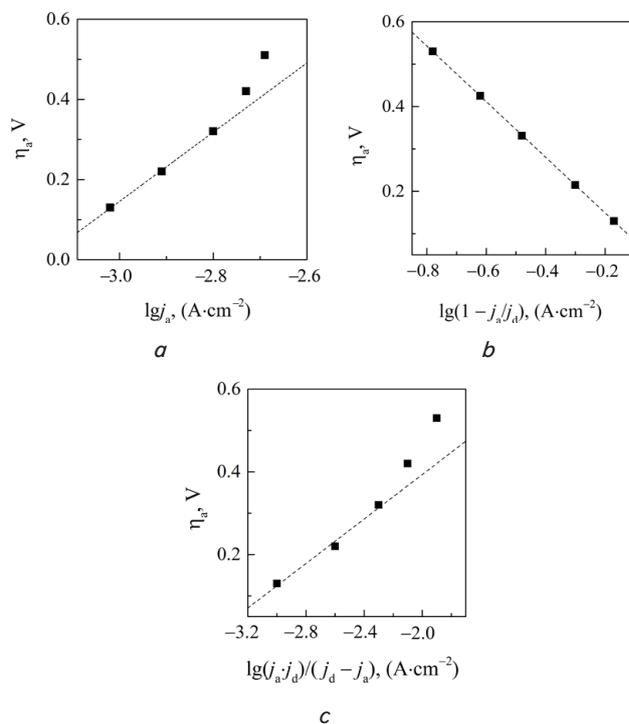


Fig. 2. Polarization dependence of anode dissolution of copper, mapped in coordinates: *a* – electrochemical kinetics; *b* – diffusion kinetics; *c* – mixed kinetics

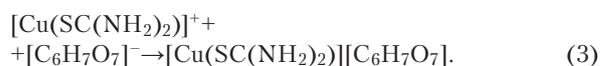
The anodic reaction overvoltage is 0.6–1 V at $j_a=0.5$ –3 $\text{mA}\cdot\text{cm}^{-2}$. The calculated values of certain kinetic characteristics: exchange current density $j_0=6.73\cdot 10^{-6}$ $\text{A}\cdot\text{cm}^{-2}$; charge transfer coefficient of anodic reaction $\beta=0.12$, the number of electrons participating in the ionization reaction $z=1$. This means that the complexes of univalent copper are formed in the solution:



At a potential of +0.8 V, a current maximum is reached for a given reaction; in this case, $j_a=3.6$ $\text{A}\cdot\text{cm}^{-2}$. A further rise in the current along curve 3 points to the progress of another oxidative reaction. Since the potential of oxygen isolation is not reached yet, this process implies the formation of copper (II) complexes:



The presence of $\text{C}_6\text{H}_8\text{O}_7$ in a thiocarbamide solution contributes to the formation of a complex compound of the mixed type:



Effect of thiocarbamide concentration on the rate of copper dissolution in citrate solutions was determined by establishing the order of reaction for $\text{CS}(\text{NH}_2)_2$. The results are shown in Fig. 3 in the form of a logarithmic dependence j_d of copper dissolution on the concentration of thiocarbamide.

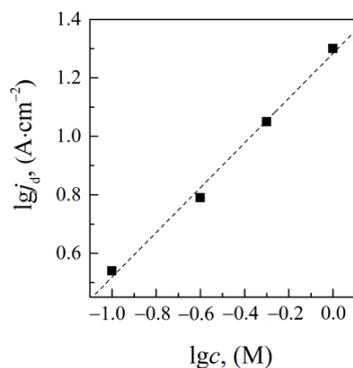


Fig. 3. Dependence of the rate of copper dissolution on the thiocarbamide concentration in 0.1 M solution of $C_6H_8O_7$. The range of change in the concentration of $CS(NH_2)_2$ is 0.1–1 M

The resulting dependence is rectilinear. The order of reaction for thiocarbamide is close to unity ($P=1$). Consequently, the reaction participates one molecule of thiocarbamide participates in the reaction with the formation of cation $[Cu(SC(NH_2)_2)]^+$. The formation of copper complexes is possible in the volume of electrolyte. with a large coordination number, for example, $[Cu(SC(NH_2)_2)_2]^+$, $[Cu(SC(NH_2)_2)_3]^+$ and $[Cu(SC(NH_2)_2)_4]^+$. A composition of the complex depends on the concentration of ligand. Increased concentration of $CS(NH_2)_2$ leads to an increase in the number of molecules, coordinated by the copper ion.

6. Discussion of results of studying the kinetics of anodic processes

Study of the kinetics of anodic process showed that active copper dissolution in the electrolyte occurs at a potential more positive than -0.36 V. The process is predetermined by the presence of two components – thiocarbamide and citric acid. Copper forms stable complexes with thiocarbamide, in which it has an oxidation degree of +1. In this case, the largest contribution to the total overvoltage of anodic reaction is provided by the diffusion overvoltage.

A confirmation of the diffusion control over copper dissolution is the influence of potential sweep rate v_p on polarization dependences (Fig. 4). A change in v_p from 5 to 100 $mV\cdot s^{-1}$ has no effect on E_{st} of copper electrode, but it leads to an increased current density due to the elimination of diffusional limitations. The range of potential values in which copper actively dissolves also extends. This indicates that the progress of reaction obeys the laws of diffusion kinetics.

Anodic process is characterized by uniform dissolution of copper anodes with no transition into the passive state. Anode current output is close to 100%. This is explained by the fact that copper forms with thiocarbamide and citric acid stable complex compounds [10–12]. The thiocarbamide complexes $[Cu(SC(NH_2)_2)_2(H_2O)]^+$, $[Cu(SC(NH_2)_2)_3]^+$, $[Cu(SC(NH_2)_2)_4]^+$ are known for univalent copper. Divalent copper forms cationic complexes with composition $[Cu(SC(NH_2)_2)_2]^{2+}$, $[Cu(SC(NH_2)_2)_3]^{2+}$, $[Cu(SC(NH_2)_2)_4]^{2+}$. The presence of copper (II) ions in the solution is unlikely since $CS(NH_2)_2$ reduces Cu (II) to Cu (I).

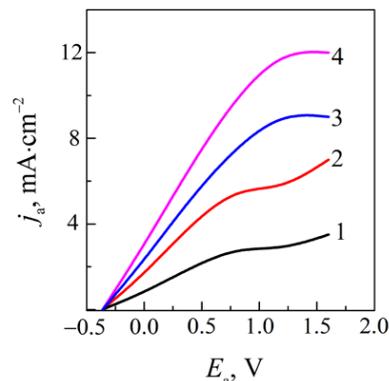


Fig. 4. Anodic potentiodynamic dependences of copper dissolution in electrolyte 0.25 M $CS(NH_2)_2+0.1$ M $C_6H_8O_7+0.016$ M Cu (met.). v_p , $mV\cdot s^{-1}$: 5(1); 10(2); 50(3); 100(4). $t=25$ °C

The evidence of stability of anodic process is the chronopotentiograms acquired on copper in the current density range of 2–8 $mA\cdot cm^{-2}$ [13]. There are no abrupt changes in potential on dependences, indicating copper dissolution with a uniform etching of boundaries and the volume of grain. Metal dissolution occurs evenly, without the formation of sludge. Anode passivation does not occur, which contributes to maintaining anodes in an active state. Anode current output is close to 100%, there is no oxygen evolution. Stable work of copper anodes enables a constant replenishment of the electrolyte with copper ions.

7. Conclusions

1. We have examined influence of the composition of a complex electrolyte on copper dissolution under conditions of anodic polarization. It was established that thiocarbamide contributes to the formation of stable complexes of copper (I) in a solution. Citric acid ensures acid pH value (2–4) of the solution, but it also affects active copper dissolution in the region of potentials $(-0.25)-(+0.4)$ V. Composition of the solution affects the values of E_{st} and E_{act} of the copper electrode. The difference in values between E_{st} and E_{act} in the solution containing only $CS(NH_2)_2$ or $C_6H_8O_7$ is 0.095–0.1 V. For solutions that contain both substances, $\Delta=0.005-0.01$ V. Joint presence of $CS(NH_2)_2$ and $C_6H_8O_7$ in the solution contributes to the copper electrode activation under conditions of anodic polarization. Increasing the concentration of thiocarbamide leads to a drastic shift in copper dissolution potentials towards the region of negative values.

2. Analysis of polarization dependences allowed us to establish that the dissolution of copper in a thiocarbamide-citrate electrolyte is controlled by the diffusion phase. This is confirmed by the results of graphical processing of polarization dependences in coordinates $\eta-\lg(1-j_a/j_d)$. An increase in potential v_p within 5–100 $mV\cdot s^{-1}$ causes an increase in j_d from 2.2 to 12.0 $mA\cdot cm^{-2}$, which indicates diffusion control over the process. The anodic reaction overvoltage is 0.6–1.0 V at $j_a=0.5-3$ $mA\cdot cm^{-2}$. Processing the dependences obtained made it possible to calculate the number of electrons involved in the reaction of ionization and the order of reaction for $CS(NH_2)_2$. The results obtained show that copper forms cationic complexes of the type $[Cu(SC(NH_2)_2)]^+$ in a thiocarbamide solution.

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