*FRENCH-UKRAINIAN JOURNAL OF CHEMISTRY (**2017**, VOLUME **05**, ISSUE **02**)*

Citric acid influence on electroreduction processes in low concentrated $Cu(NO_3)_2$ solutions

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Keywords: *copper electrodeposition, citric acid, influence of pH, electroreduction of nitrate ions.*

Physico-chemical regularities citric acid influence on processes of copper and nitrate-ions reduction in low concentrated nitrate solutions were established. An influence of pH value on inhibitor action of low concentrations of the additive according to cathode reduction reaction of nitrate-ions, on kinetics of copper electrodeposition, on structure of the precipitates obtained was shown. Polarization measurements show us changes of copper electrodeposition at introduction of citric acid in $Cu(NO_3)_2$ solution. By the methods of traced elements and extraction into aqueous phase the reversible inclusion complexes into electrolytic copper, was established that proves participation of complexes in cathode process.

Introduction

In modern radioelectronic technique, instrumentation, mechanical engineering, attention is paid to creation and introduction to industry of the new progressive technologies, that supply an increase of covering quality, decrease of energetic consumption and materials expense, pollution of the environment, labor costs. To achieve these purposes an optimization of technological processes should be done. The important directions of optimization of copper electrodeposition are: transfer to electrolytes of thinning with low concentrations of low- and non toxic components; intensification of production of electrolytic copper precipitates at saving of high quality of covering, supplement of cathode copper deposition equality precipitates despite on its thickness [1].

Ecological danger of the modern galvanic manufacture lead us to the necessity of creation of electrolytes of new generation – low concentrated solutions with reproduction of electrodeposition of covering not lower than in corresponding high saturated electrolytes without additive energy expenses on solutions pumping and without necessity of galvanic equipment change [2]. From this point of view prospective are could be nitrate electrolytes of thinning because of limited cathode current of copper in $Cu(NO_3)_2$ solution is in 1,5 times more than analogical one in $CuSO_4$ solution [3].

But reactions of reduction of nitrate-ions (1-3) in these solutions it take place simultaneously with discharge of copper ions (4):

$NO_3^- + 2\ H_3O^+ + 2\ e^- \rightarrow NO_2^- + 3\ H_2O,$ (1)

$NO_3^- + 10\ H_3O^+ + 8\ e^- \rightarrow NH_4^+ + 13\ H_2O,$ (2)

$HNO_2 + 7\ H_3O^+ + 6\ e^- \rightarrow NH_4^+ + 9\ H_2O,$ (3)

$Cu^{2+} + 2\ e^- \rightarrow Cu^o,$ (4)

break the process of copper electrocrystallization. Investigation of the influence of nitrate ions on the copper electrodeposition processes was done out earlier in various acidic [4–5] and alkaline [6] electrolytes. A positive effect of nitrate ion additives on the process of electrodeposition of copper and silver from ammonia, pyrophosphate, ethylenediamine and cyanide electrolytes was noted in a number of works [7–8]. Additions of nitrate ions improve the distribution of metal on the cathode, and their ability to easily recover at the cathode allows us to expand the limits of the permissible current densities during the electrodeposition of metals from these electrolytes. But the reduction reactions of nitrate ions, which occur in $Cu(NO_3)_2$ in parallel with the discharge of copper ions, disrupt the process of electrocrystallization of copper. In addition, upon contact of metallic copper with an aqueous $Cu(NO_3)_2$ solution, a reversible Cu^+ formation reaction occurs (which is confirmed by qualitative reactions in the analysis of solutions after electrolysis):

$Cu^0 + Cu^{2+} \leftrightarrow 2Cu^+.$ (5)

The disproportionation of Cu^+ ions leads to the formation on the cathode deposit of a plaque in the form of copper powder. Acceleration of this reaction occurs by the presence in the solution of compounds oxidizing Cu^+ to Cu^{2+} [3]. In the system under study such oxidizing agents are nitrate ions:

$NO_3^- + 2Cu^+ + 3H^+ \rightarrow HNO_2 + 2Cu^{2+} + H_2O$ (6)

The course of all these processes leads to the liberation of the metal in an oxidized form with a deposit of finely dispersed copper powder [9]. Evidently, avoiding extraction of dense layers of copper from nitrate solution is possible at condition of avoiding parallel reactions of nitrate-ions reduction. It can be reached by introduction into solution of supplement small amounts, adsorbed on cathode and replaced nitrate-ions from electrical double layer, also by connection of copper ions into more stable complexes, than nitrate ones.

The purpose of our work is to study the mechanism and kinetic dependencies of electrodeposition of copper layer from low concentrated nitrate electrolytes with citric acid supplement.

Experimental part

The working solutions contained (mol/dm^3): 0,125 $Cu(NO_3)_2$ and nitric acid of the following concentrations: 0,25 (for pH 0,9) and 0,01 (for pH 1,7). In these solutions, the following compounds were introduced as additive citric acid ($C_6H_8O_7$) in the quantities ranging from 0,005 to 0,25 mol/dm^3. Solutions of additive were prepared from the reagents of the grade “chemically pure” or “pure for analysis”. All solutions were prepared using bidistilled water.

Current-voltage characteristics were obtained on a potentiostat PI-50-1 with the programmer PR-8 in the thermostabilized cell YSE-2 at the temperature + 293 K. The dependence of the current on the potential was registered with a two-coordinate recorder PDA-1. The electrode was subjected to mechanical polishing and degreased with alcohol before experiments. The electrode with the surface of 0,01 dm^2 was used for the polarization investigation. Methodic of the experiment was like in [10, 11].

Results and discussion

At choose of the additive we took into consideration the next of its properties: nontoxicity, availability, low price, formation with metal quite stable complexes, also use of this additive in industrial electrolytes. Citric (2-hydroxi-1,2,3 propanecarbonic) acid, widely used in galvanic industry, possess properties of polybasic carbon acids, formed 3 types of salts and esters (citrates) on carboxyl groups. It is a tribasic oxicarbon acid, possess buffer properties and can form with copper ions protoned citrate complexes [12]. In acidic media complex formation is described by scheme:

$$Cu^{2+} + H_3Cit \leftrightarrow CuH_2Cit^{+} + H^{+},\quad K = 5{,}17 \cdot 10^{-29} \tag{7}$$

$$Cu^{2+} + H_2Cit^{-} \leftrightarrow CuHCit + H^{+}.\quad K = 5{,}18 \cdot 10^{-23} \tag{8}$$

Investigated by us media is low concentrated and acidic. Therefore, fraction of Cu^{2+} ions in solution in complexes with ligand will be low. In the work [13] was shown, that chemical formula of Cu^{2+} in nitrate solution is complex of particles $\{Cu(H_2O)_n(NO_3)_y\}^{(2-y)+}$, and equilibria concentration of [Cu^{2+}] is a sum:

$$[Cu^{2+}] = \Sigma_{x,y\geq 0} |\{Cu(H_2O)_n(NO_3)_y\}^{(2-y)+}|. \tag{9}$$

It is widely known [3] that in nitrate system such particles are $[Cu(H_2O)_6]NO_3^{+}$. Evidently these particles are competitors of copper complexes with additive under absorption and in followed process of electroreduction on cathode surface.

As a result of carried out investigations it was established that citric acid is universal additive to nitrate system. At pH 1,7 of the solution it supplied obtainment of matt layers of copper, and at pH 0,9 – shined ones. As we can see from figure 1 cathode yields on current (CY$_к$ Cu) vary in two times. We should point out that matt copper coatings form from nitrate solutions at total exception of side processes (curve 2), and shined at part one (curve 1).

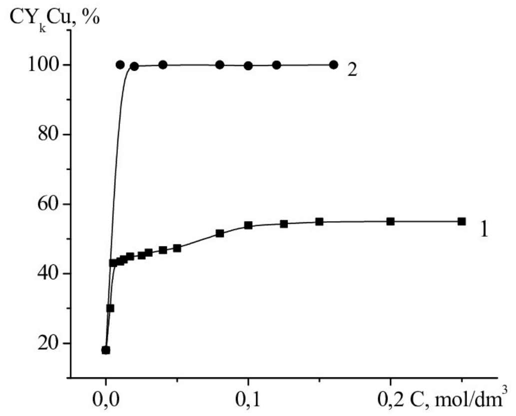

Figure 1. An influence of citric acid concentration on $CY_{к}$ Cu in solution of the composition (mol/dm^3): 0,125 $Cu(NO_3)_2$ + HNO_3 + citric acid: 1 – pH = 0,9; 2 – pH = 1,7.

We have calculated equilibria concentrations of particles in the system 0,125 mol/dm^3 $Cu(NO_3)_2$ + x HNO_3 + citric acid for various concentration of the additive at pH values 0,9 and 1,7. It can be seen from table 1 that at pH = 1,7 concentration of the additive in molecular form is lower by an order of magnitude, but in form of charged particles higher than at pH = 0,9. Formed at the process charged complex of particles of copper with citric acid take part in migration to cathode. Therefore, delivery of the additive in solution with pH=1,7 occurred faster than pH = 0,9 because it proceed not only by diffusion and convection like discharged particles, but also like migration. In more acidic solution migration takes place more slowly because of lower concentration of charged complex particles and $CY_{к}$ of Cu in this solution twice less than in solution with pH = 1,7.

Table 1. Composition of nitrate electrolyte of copper plating in volume of solution depends on additive concentration and initial pH of solution 0,125 mol/dm^3 $Cu(NO_3)_2$ + x HNO_3 + citric acid

№	The considered compound	0,005 mol/dm^3 citric acid		0,015 mol/dm^3 citric acid	
		pH = 0,9	pH = 1,7	pH = 0,9	pH = 1,7
		Concentration of the considered compound, mol/dm^3			
1	Cu^{2+}	$1{,}24\cdot10^{-1}$	$1{,}23\cdot10^{-1}$	$1{,}23\cdot10^{-1}$	$1{,}17\cdot10^{-1}$
2	L^{3-}	$2{,}09\cdot10^{-14}$	$5{,}38\cdot10^{-11}$	$8{,}93\cdot10^{-14}$	$9{,}49\cdot10^{-11}$
3	HL^{2-}	$2{,}56\cdot10^{-9}$	$3{,}24\cdot10^{-7}$	$1{,}10\cdot10^{-8}$	$8{,}58\cdot10^{-7}$
4	H_2L^-	$1{,}43\cdot10^{-5}$	$8{,}91\cdot10^{-5}$	$6{,}19\cdot10^{-5}$	$3{,}54\cdot10^{-4}$
5	H_3L	$2{,}66\cdot10^{-3}$	$8{,}12\cdot10^{-4}$	$1{,}15\cdot10^{-2}$	$4{,}84\cdot10^{-3}$
6	$CuHL$	$8{,}39\cdot10^{-7}$	$1{,}05\cdot10^{-4}$	$3{,}58\cdot10^{-6}$	$2{,}64\cdot10^{-4}$
7	CuH_2L^+	$3{,}25\cdot10^{-4}$	$1{,}99\cdot10^{-3}$	$1{,}39\cdot10^{-3}$	$7{,}55\cdot10^{-3}$
8	CuL_2^{4-}	$6{,}83\cdot10^{-21}$	$4{,}48\cdot10^{-14}$	$1{,}24\cdot10^{-19}$	$1{,}33\cdot10^{-13}$
9	$Cu_2L_2^{2-}$	$1{,}07\cdot10^{-16}$	$6{,}93\cdot10^{-10}$	$1{,}93\cdot10^{-15}$	$1{,}96\cdot10^{-9}$

Evidently at pH = 1,7 the additive occupied the surface of cathode faster. It can be seen from high increase of $CY_{к}$ Cu up to 100 % at introduction of small amounts of citric acid (Fig. 1, curve 2). Complex particles replace nitrate-ions from electrical double layer, a lot of crystallization centers form on cathode, and coating become matt. The additive moves more slowly to cathode in the solution with pH = 0,9 and charged outer spherical complexes $[Cu(H_2O)_6]NO_3^+$ are absorbed and reduced on cathode surface. Due to these processes cathode current yield of copper is about 50 % and obtained coatings are of another quality.

Because of side reactions of nitrate-ions reduction in the investigated solution with pH = 1,7 are avoided totally, the products of these reactions-ions of NO_2^- and NH_4^+ should be absent after electrolysis. Spectrophotometric analysis of these solutions after an electrolysis prove this consideration (Table 2, samples 7–8). An introduction of citric acid in nitrate solution with pH=0,9 lead us to two times increase of CYк Cu in comparison with solution without additives and approximately equal decrease of quantity of the product of reduction of nitrate ions in the solution after electrolysis and on precipitates of copper (Table 2, samples 1–4). The investigations, carried out by spectrophotometric, show us an absence of nitrate-, nitrite- and ammonia-ions in the obtained layers of copper at CYк Cu = 100 % (Table 2, samples 5–8).

Table 2. Dependence of quantity of the products of reduction of nitrate-ions after electrolysis and quantity of inclusions in copper precipitates from pH of electrolyte and thickness of covering. Solution composition: 0,125 mol/dm³ $Cu(NO_3)_2$ + HNO_3 + additive, j_k = 2 A/dm², 1-4 – pH=0,9; 5-8 – pH=1,7.

№	Additive, mol/dm³	δ, μm	Concentration in solution, mol/dm³		Number of inclusions in the precipitate, mol/cm²		
			NO_2^-	NH_4^+	NO_2^-	NH_4^+	CuL
1	–	3,3	$5{,}6\cdot10^{-3}$	$9{,}6\cdot10^{-4}$	$3{,}2\cdot10^{-8}$	$14{,}0\cdot10^{-8}$	–
2	–	5,4	$6{,}9\cdot10^{-3}$	$1{,}2\cdot10^{-3}$	$0{,}5\cdot10^{-8}$	$19{,}0\cdot10^{-8}$	–
3	0,005	2,9	$1{,}0\cdot10^{-3}$	$4{,}1\cdot10^{-4}$	$1{,}1\cdot10^{-8}$	$1{,}5\cdot10^{-8}$	$1{,}0\cdot10^{-8}$
4	0,005	5,9	$2{,}1\cdot10^{-3}$	$9{,}6\cdot10^{-4}$	$3{,}0\cdot10^{-8}$	$5{,}0\cdot10^{-8}$	$3{,}0\cdot10^{-8}$
5	0,005	2,7	none	$1{,}1\cdot10^{-6}$	trace quantity	trace quantity	$2{,}7\cdot10^{-8}$
6	0,005	5,5	trace quantity	$5{,}0\cdot10^{-7}$	trace quantity	trace quantity	$5{,}2\cdot10^{-8}$
7	0,015	2,8	none	none	none	trace quantity	$5{,}1\cdot10^{-8}$
8	0,015	5,4	none	none	none	none	$1{,}1\cdot10^{-7}$

An influence of pH of solution on number of inclusions in copper coating of citric acid can be seen from the results of radiometric investigation of the system (Figure 2). A number of inclusions in the coating, obtained from the solution with additive at pH = 0,9 (Figure 2, curve 4) by an order of magnitude higher than the coating, deposited from the solution with pH = 1,7 and the same concentration of citric acid (Figure 2, curve 1). Consequently, number of inclusions of citric acid in shined coatings is higher than in matt ones.

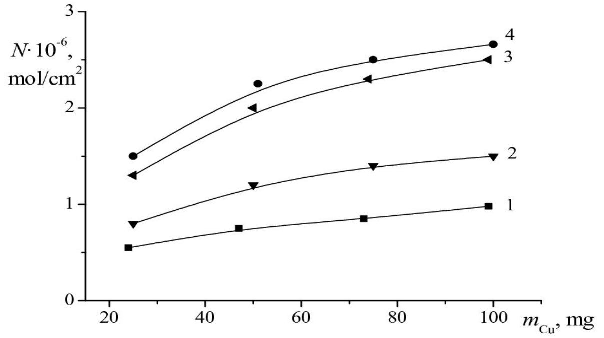

Figure 2. Dependence of number of included anions from copper mass, electrodeposited from the solution of composition (mol/dm^3): 0,125 $Cu(NO_3)_2$ + x HNO_3 + x_1 citric acid: 1,4 – 5,0·10^{-3}; 2 – 1,0·10^{-2}; 3 – 1,5·10^{-2}; 1–3 – pH = 1,7; 4 – pH = 0,9.

The results of galvanostatic measurements show us an acceleration of electrodeposition of copper from nitrate solutions at increase of pH. At discussion of CY$_{К}$ Cu was shown, that main part of current, passing through cathode, supply electrochemical reduction reactions of nitrate ions. Therefore of an influence of citric acid on the electrodeposition process of copper can be demonstrated by the partial curves of deposition of copper from nitrate solutions (Figure 3–4).

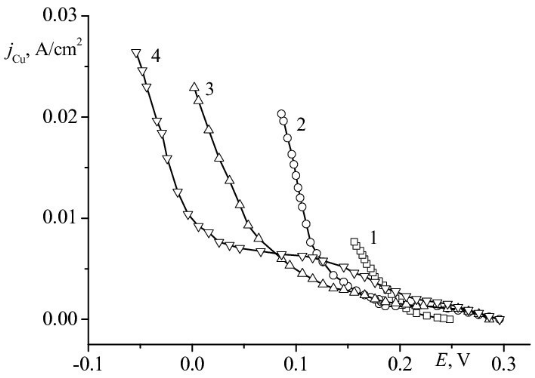

Figure 3. Partial curves of cathode polarization of copper in solution of composition (mol/dm^3): 0,125 $Cu(NO_3)_2$ + 0,25 HNO_3 + 1KNO_3 + x citric acid: 1 – without supplements; 2 – 0,005; 3 – 0,01; 4 – 0,015; pH = 0,9.

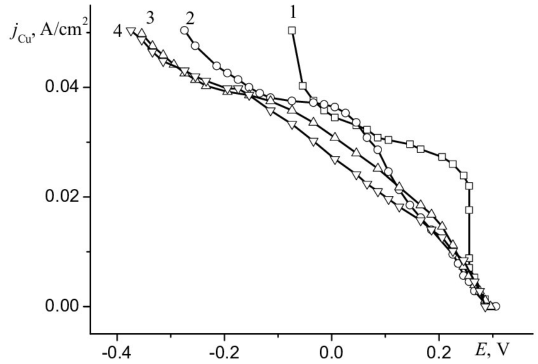

Figure 4. Partial curves of cathode polarization of copper in solution of composition (mol/dm^3): 0,125 $Cu(NO_3)_2$ + 0,01 HNO_3 + 1KNO_3 + x citric acid: 1 – without supplements; 2 – 0,005; 3 – 0,01; 4 – 0,015; pH = 1,7.

An introduction of citric acid in nitrate solution changes kinetic of electrodeposition of copper in electrolyte: at pH = 0,9 on curves 2–4 of Figure 3 an area of limited current appear, it is absent in pure solvent (curve 1), potential removes in the area of negative values. At pH = 1,7 an area of limited current become more visible (Figure 4, curves 2–4), and potential is getting negative values. From these facts, we can come to conclusion that increase of pH value and concentration of citric acid in the solutions investigated move potential in the area of negative values and increase value of limited current. An increase of cathode polarization with increase of concentration of the additive can be connected with increase of degree of filling of cathode surface by absorbed particles, because such dependence (an increase of inclusion of the additive with increase of its concentration) was observed at radiometric investigation of citric acid inclusion in copper coating (Figure 2). Described change in behavior of polarization curves of electrodeposition of copper in presence of citric acid can be explained by change of ψ'-potential at absorption of the additive or by formation in electrical double layer intermediate Cu^{2+} complexes with citric acid anions, which are bridge ligands and supply electron transfer.

Conclusions

As a result of carried out experiments it was established that citric acid makes different influence on side reactions of nitrate ions reduction, depending on pH of nitrate solution, at pH = 0,9 removes it partially, pH = 1,7 – totally. Decrease of partial rate of reaction of nitrate-ions reduction by citric acid introduction lead to the increase of cathode current yield of copper and to the improvement of quality of coatings: from more acidic copper deposited like shined layers, from less acidic like matt ones. By the methods of extraction in aqueous phase and radioactive indicators, reversible inclusion of complexes in electrolytic copper was established. The fact prove the conception about participation of complexes in the cathode process.

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