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Technical Report

Features of The Electrolytic Copper Powder Deposition in the Presence of Polyols

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Results of the effect of polyols addition in the copper electrolysis process has been described and analyzed, particularly in reference to the dispersity of electrolytic copper powder. It is shown that the addition of polyols to electrochemical systems in the process of electrolysis has an impact on dendrite formation, size and shape of grains and colors of the resulting copper powder, which has an influence on its applications.

Keywords: electrolysis, electrolyte, polarization curve, copper powder, dendrites and dispersion of sediment

1. INTRODUCTION

It is well known that the composition of the electrolyte, along with the process parameter conditions of the electrolysis process, has a decisive role on dispersity and quality of the copper powder. Not only the acidity (pH) of the solution and the concentration of copper ions in the electrolyte, but also the presence of impurity elements, complex formations, and also organic compounds with well-developed molecular structure influence the physical characteristics of the deposit [1-4].

Thus, addition of organic compounds to the electrolyte contributing to the emergence of new copper crystallization centers during adsorption leads to a refinement of the powder particles and increase of its dendrite. Organic compounds that slow down the discharge of copper ions lead to the formation of larger and less dendritic powder particles.

The analysis of published data found that the surface-active substances affect not only the nature of the electrodeposition of copper, but also the structural characteristics of the resulting product. Organic substances of different classes, which depending on their structure and nature, may have the polar part - the hydrophilic components (functional groups-OH,-COOH,-SOOOH,-O-, etc., or, more often, their salts, ONa, SOONa-,-SOOONa, etc.) and non-polar (hydrocarbon) part - the hydrophobic component. Examples of surfactants that can serve the purpose are ordinary soap (a mixture of sodium salts of fatty carboxylic acids - oleate, sodium stearate, etc.) and detergents, as well as alcohols, carboxylic acids, amines, etc [5].

A number of publications have studied the effect of organic substances and organic origin surfactants to copper electrolytic deposition process from aqueous solutions of electrolytes [6,7], i.e. glucose [8] and sulfurous acid [9] and surfactants of organic origin [10,11].

Authors [12] investigated the behavior of JGB (Janus Green B) as the sole additive in acidic sulphate Cu electrodeposition baths. This study is based on cyclic voltammetry performed with an RDE and in-situ Raman spectroscopy. From cyclic voltammetry higher nucleation over potentials are found in the presence of JGB, related to the adsorption of the organic. JGB also causes an increase in the nucleation rate. JGB increases the exchange current density and decreases the cathodic Tafel slope, indicating a variation in the Cu^{2+}-reduction mechanism with respect to the additive-free system.

The study of PEG influence [13] shows its adsorption during Cu electrodeposition indicating a suppressor activity based on the data that exchange current density is decreased in the presence of PEG. Micrographs in the paper show that PEG gives rise to major grain refining effects (globular features are stabilized vs. faceted ones), favors renucleation onto growing crystallites, delays dendrite formation and stabilizes the growth of branched vs. smooth dendrites. Potentiostatic transients prove that PEG increases the critical overpotential and transition times to dendritic growth.

$[BMIM]HSO_4$ is found to be an efficient leveling additive in copper electro-deposition, leading to more leveled and fine-grained cathodic deposits. The presence of $[BMIM]HSO_4$ and thiourea in acidic sulfate solutions inhibit crystal growth and promote nucleation of copper, leading to finer grained copper deposits. Both additives increase the cathodic polarization of copper, through their adsorption on the cathodic surface and inhibit the kinetics of the Cu^{2+} reduction process. The strongest inhibition is observed in the presence of thiourea [14].

This study looks at the influence of polyols structure on the dispersion and structure of deposited electrolytic copper powder.

2. EXPERIMENTAL PROCEDURE

Studies of the polyols influence on the process of electrochemical deposition of copper from copper sulfate solution in the presence of sulfuric acid were carried out by potentiodynamic polarization methods. Voltage-amperometric system IPC-PRO M with automatic control and computer data entry has been used for potentiodynamic studies.

Measurements were carried out in a three-electrode cell with no separation of the electrodes. Reference electrode was a copper wire, 0.6 mm in diameter, pressed into the cork and immersed in the working solution. To prepare the auxiliary electrode, two copper strips 0.5 mm thick, with dimensions of 5 x 70 mm were used. The working electrode was a plate with thickness of 0.9 mm and 10 x 10 mm length and width. Polarization curves were taken consecutively three times for each electrolyte and are shown as line numbers 1, 2 and 3 on the Figures.

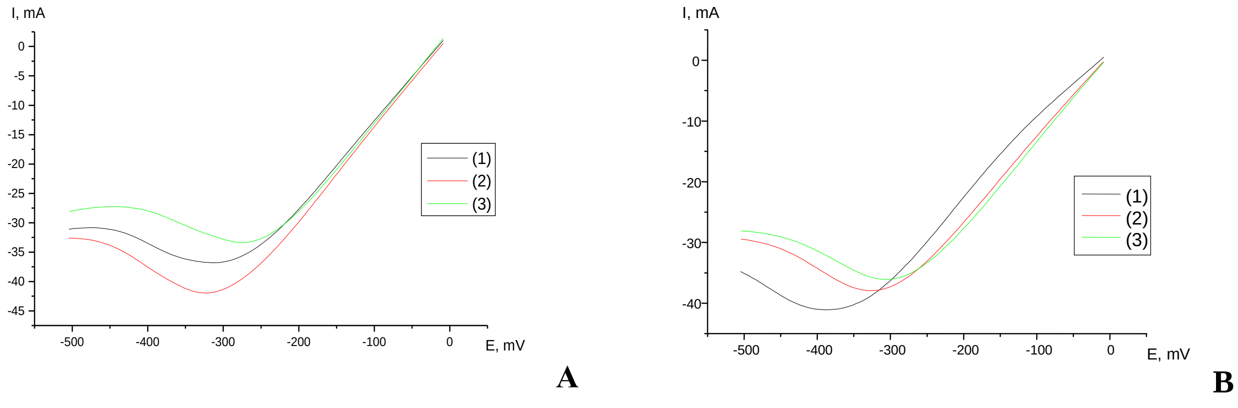
Copper sulfate solution was prepared with a copper content of 5 g/l and 20 g/l and the sulfuric acid was added at 10 g/l and 50 g/l, as electrolyte concentration variables. The polyols addition was made at 10-20 g/l of ethylene glycol $C_2H_4(OH)_2$ and 10-50 g/L glycerol $C_3H_5(OH)_3$, where an electrolyte without polyol additions was treated as the base.

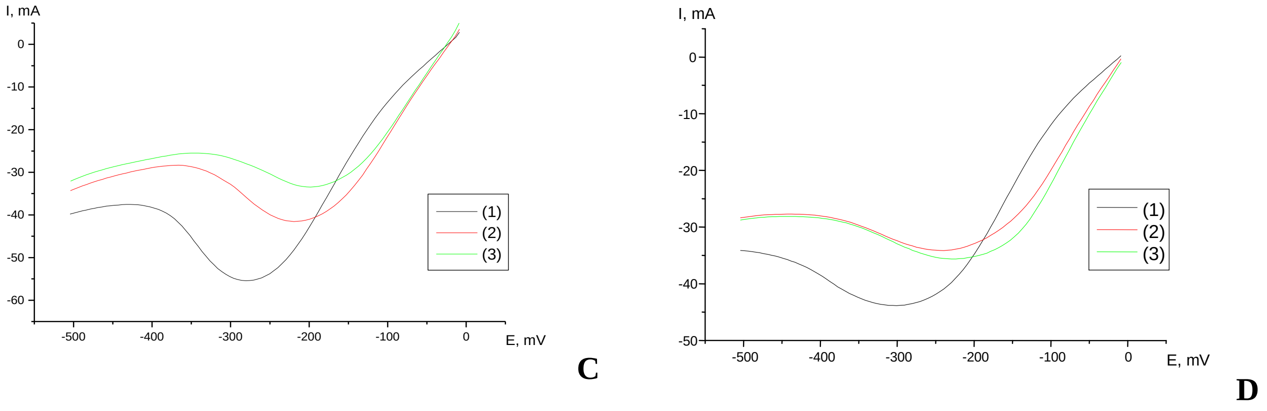
To determine the effect of organic compounds on the formation of copper deposits and the resulting change of color tone, low vacuum scanning electron microscope (Joel JSM-6490 LA) with energy dispersive X-ray microanalysis system has been used, which allows to reach a magnification of up to 300,000 and a resolution of 3 nm.

3. RESULTS AND DISCUSSION

Predominantly dense precipitates, with a yield of fine fraction of less than 70 %, were obtained in the electrolysis of a solution without organic additives. At first, there is a fairly intense hydrogen evolution, ceasing with the development of the electrode surface due to deposition of copper. Addition to the electrolyte of a viscous organic matter, for example, glycerol, leads to thickening of the electrolyte, which lowers the rate of ionic diffusion. As a result, the supply of copper ions to the cathode is hampered and as a consequence, the powder begins to precipitate at high current densities.

This effect is clearly visible by comparing the polarization curves in the diagrams *a* and *b* (Fig. 1). When the amount of glycerol is equal to 10 ml/l, limiting current for copper deposition is about 37 mA, while with the amount of glycerol at 50 ml/l, limiting current for copper deposition is more than 40 mA at the same concentrations of sulfuric acid and copper. In addition, formation of glycerol complexes with copper (glycerate) is possible, which also hinders the formation of powder. Therefore, we recommend the addition of glycerol in small amounts for effective deposition of copper.





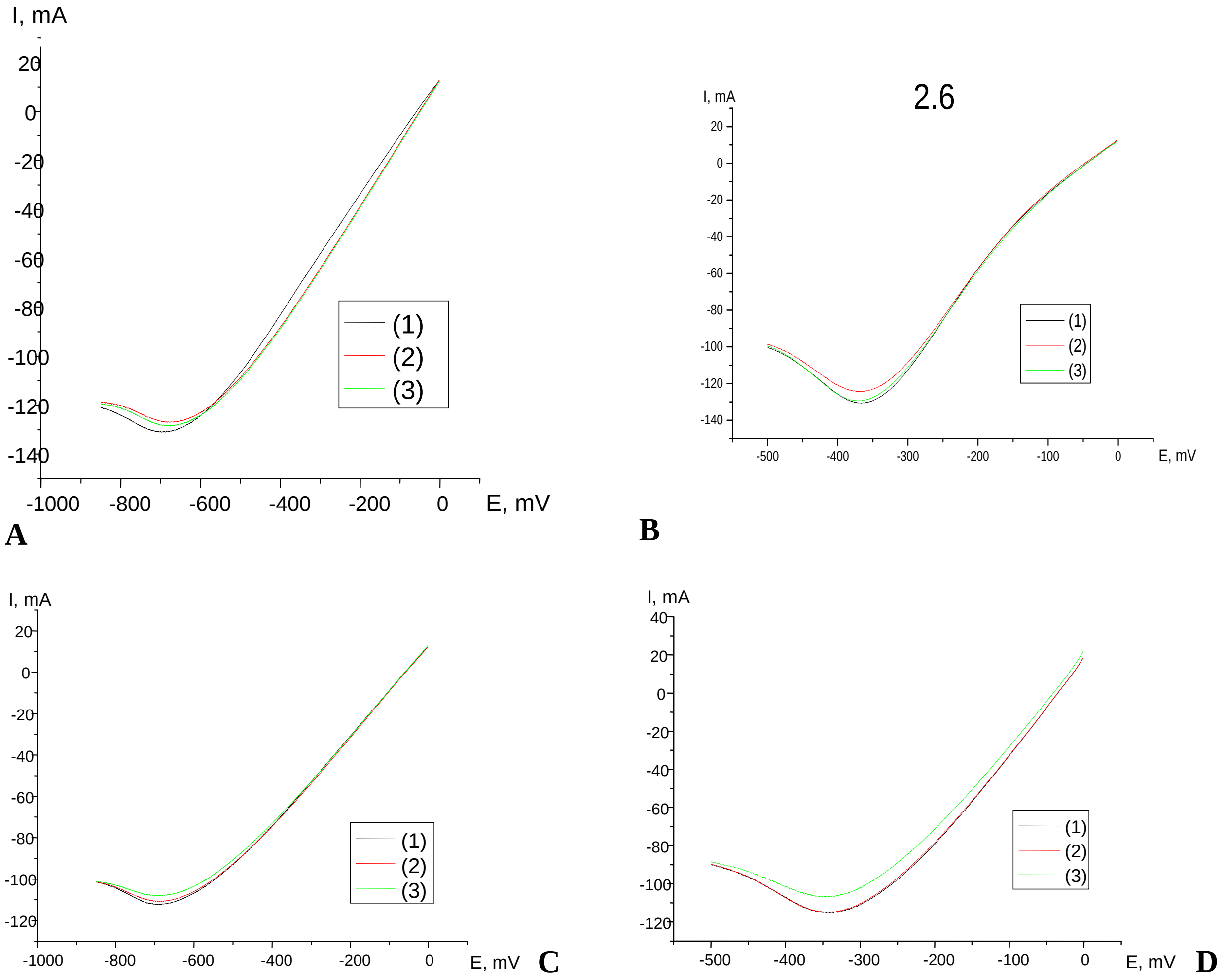
a – H_2SO_4 = 10 g/l; glycerol amount = 10 ml; *b* – H_2SO_4 = 50 g/l; glycerol amount = 10 ml;
c – H_2SO_4 = 10 g/l; glycerol amount = 50 ml; *d* – H_2SO_4 = 50 g/l; glycerol amount = 50 ml

Figure 1. Polarization curves for deposition of electrolytic copper powder (C_{Cu} = 5 g/l) when glycerol is added.

Injection of glycerin to the solution in an amount of 10 ml/l with copper concentration of 5 g/l and sulfuric acid of 10 g/l, leads to a significant change in the form of the polarization curve in comparison with the curve without glycerol. In particular, the injection of glycerin leads to a slight shift of peak potential in positive direction, and at the same time to a fall-off of the current peak value. Lowering of the current peak probably is related, as noted above, with a significant increase in viscosity. Shift of the peak potential is caused by the same process of viscosity change, because reducing current limit leads to earlier formation of the maximum rate of non-steady state process. Under these conditions, the formation of the maximum copper is determined by two components: the rate of copper ions supply and their electrochemical reduction.

More explicitly, this effect is noticeable when the concentration of sulfuric acid is increased to 50 g/l (Fig. 1b), because here, in spite of the increased viscosity, electrical conductivity increases, which eliminates the difficulty of ion transport through the dense part of the viscous surface layer at the electrode. It is seen (Fig. 1, b) that the withdrawal of the curves one after the other leads to a change in their form, i.e. a constant current peak reduction (Fig. 1b) and the potential shifts in the positive direction. It describes the state of the electrode surface, which is due to the strong adsorption of glycerol and formation of a viscous dense layer can lead to permanent recovery of the organic part with the copper complex ions. Additional influence on the reproducibility of the surface occurs due to the recovery of copper powder.

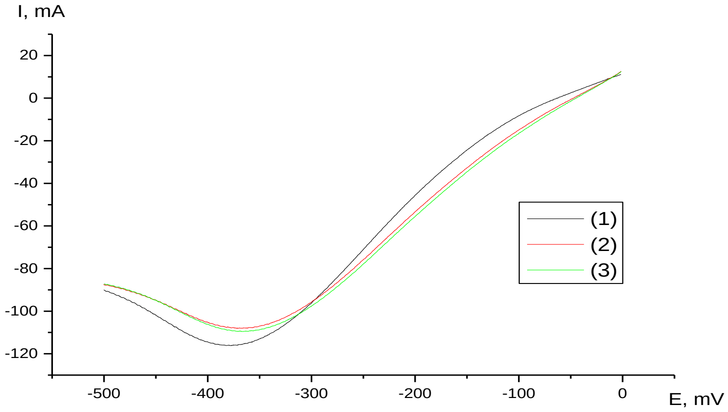
Increasing amount of glycerol to 50 ml exacerbates the process by increasing the viscosity of the electrolyte, an even greater shift of the potential takes place, as well as a decrease in the value of metal recovery current. An interesting fact can be seen that when concentration of sulfuric acid is increased from 10 to 50 g/l (glycerol amount is 50 ml) (Fig. 1: c, d) the current peak value remains virtually unchanged, although current potential peak is shifted by 100 mV. However, clear conclusion cannot be drawn regarding the influence of sulfuric acid, because again there is the imposition of a minimum of two processes that form the current peak for non-stationary flow, when on the one hand surface layer containing copper ions is developed, on the other hand a supply of this reagent from solution is carried. This effect has a stronger impact on the location of the current peak at large quantities of glycerol.



a – CH_2SO_4 = 10 g/l; glycerol amount = 10 ml; *b* – CH_2SO_4 = 50 g/l; glycerol amount = 10 ml;
c – CH_2SO_4 = 10 g/l; glycerol amount = 50 ml; *d* – CH_2SO_4 = 50 g/l; glycerol amount = 50 ml

Figure 2. Polarization curve for depositions from copper electrolytes (C_{Cu} = 20 g/l) when glycerol is added.

A further increase in the concentration of copper in this system with glycerol at a concentration of 20 g/l (Fig. 2a) also leads to a smoothing and the disappearance of elevated peaks. The transformation into a curve with maximum current, and an increase in acid concentration over the normal, forms transient deviation on the polarization curve (Fig. 2, b). With increasing of copper concentrations up to five times, the limiting current increase is roughly comparable, and the increase in glycerol concentration to 50 ml/l in these solutions did not significantly affect the limiting current density, and the process becomes more reversible at high concentrations of copper. Particularly during polarization there is no big difference between the first and subsequent cycles, indicating that the reversibility increases with increasing concentration of copper in solution (Fig. 2, c, d).



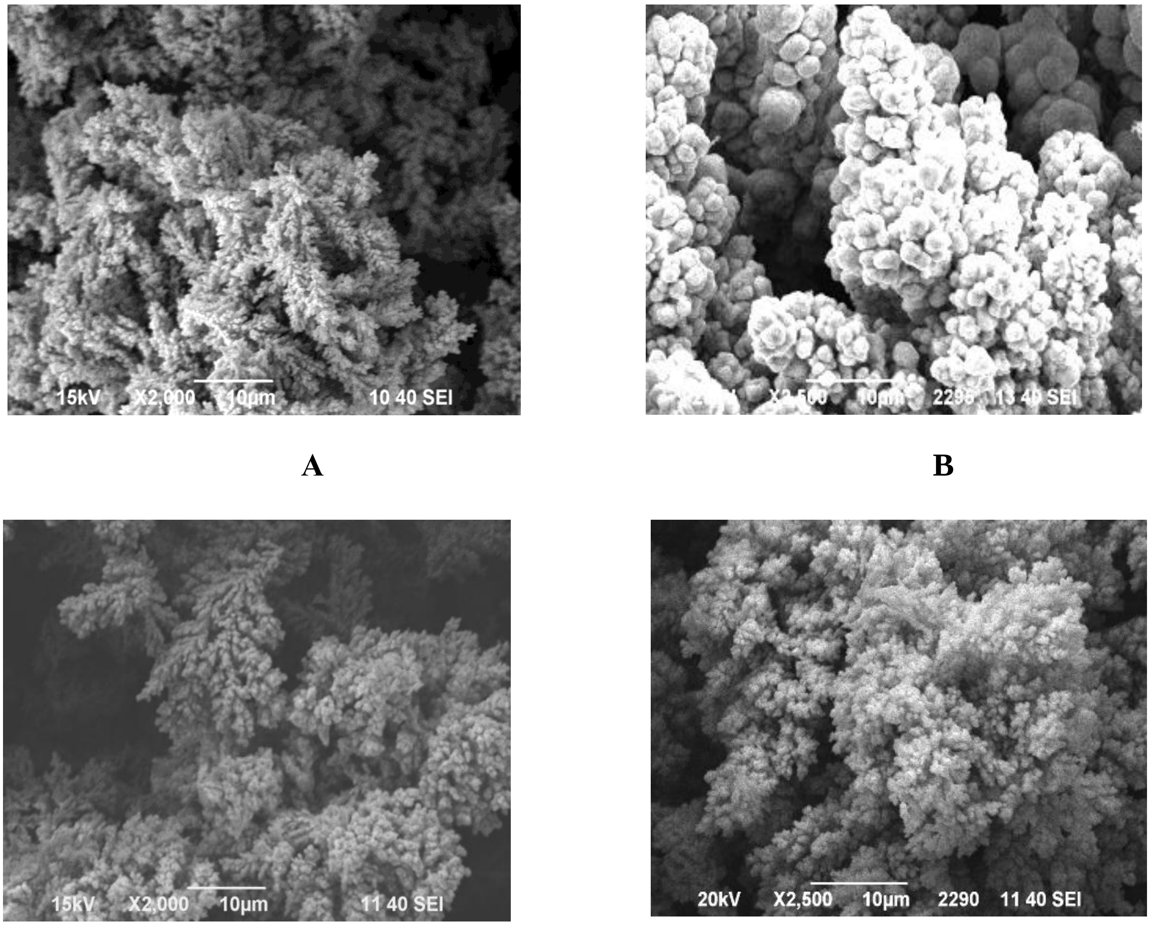
CH_2SO_4 = 20 g/l; CH_2SO_4 = 50 g/l; addition of ethylene glycol – 20 ml/l;

Figure 3. Polarization curve of copper deposition from electrolyte when added ethylene glycol

Replacement of glycerol to ethylene glycol leads to the expected result, where the polarization curves coincide in a sufficiently large extent, which in itself is natural, since the ethylene glycol properties are not so different from glycerol. This is clearly seen by comparing Fig. 2, b and Fig. 3. The results of polarization studies of the electrolyte (Fig. 3), which includes ethylene glycol showed that the limiting voltage and current values are close to the investigations with glycerol (Fig. 1, c). Therefore we had to evaluate the impact of ethylene glycol and glycerol on the quality of the deposited copper powder.

Copper powders obtained in the experiment were subjected to sedimentation analysis; the most representative results are presented in the Table 1. In the electrolysis of a solution without organic additives predominantly dense sediment was obtained. At first, there is a fairly intense hydrogen evolution, ceasing with the development of the electrode surface due to deposition of copper. It has been noticed that at an introduction of small fraction of glycerin, not much difference is noticed in comparison with the initial electrolyte, and the addition of ethylene was accompanied by an active allocation of hydrogen and low current efficiency.

Influence of organic substances on the quality of the copper powder was also studied by electron microscopy. Studies have shown that the addition of organic matter affects not only the dispersion of deposited copper powders, but also the shape and size of the grains. Thus, the addition of the glycerol to electrolyte lowers dendrite formation, followed by a pronounced orientation of the dendrite growth, and the injection of ethylene glycol to electrolyte contributes to refinement of individual dendrites, with the simultaneous development of dendritic structure and the formation of friable and more diffuse deposits (Fig. 4).



A **B**

C **D**

a – C_{Cu} = 5 g/l; *b* – C_{Cu} = 20 g/l

Figure 4. Micrographs of copper powders obtained by adding a solution of glycerin (50 ml), and from electrolyte (C_{Cu}= 5 g/l) without the addition of an organic compound (c) and when added 20 ml ethylene glycol to a solution (d).

Increasing the quantity of glycerol from 10 to 50 ml/l, the nature of the sample surface of copper does not change, but decreases the density of the sediment and increases its porosity. It should be noted that the influence of copper concentration in the electrolyte is to modify the surface of copper powder. With the increase in copper concentration from 10 to 20 g/l, powder surface is loose, but it forms large near-spherical shape aggregates and decreases the amount of fine particles. The copper surface is porous in nature (Fig. 4).

It should be noted that electrolytic copper deposition in the presence of organic compounds, such as paint sludge, is dependent on the concentration of copper:

– the copper powder is formed with homogeneous claret color in case of low concentration of copper in electrolyte in the presence of glycerin;

– increase in copper concentration in the electrolyte solution containing glycerol leads to the formation of dark maroon spotted with red.

Table 1. The influence of organic additives on the powder characteristics and the current efficiency in electrolysis with sulfuric acid electrolyte

The addition of organic reagent	Grain size classes	Output of fraction, %	i, A/cm^2	Current efficiency,%
Electrolyte without organic additives	+0.16	7.95	0.85	74.32
	-0.16 + 0.10	9.44		
	-0.10 + 0.074	7.31		
	-0.074 + 0.044	8.12		
	-0.044	66.18		
	-0.16 + 0.10	10.80		
	-0.10 + 0.074	4.44		
	-0.074 + 0.044	15.51		
	-0.044	62.93		
Glycerol. 50 g/l	+0.16	4.96	0.80	82.44
	-0.16 + 0.10	7.62		
	-0.10 + 0.074	5.02		
	-0.074 + 0.044	4.22		
	-0.044	78.18		
Ethyleneglycol, 20 g/l	+0.16	7.12	0.78	80.4
	-0.16 + 0.10	8.02		
	-0.10 + 0.074	6.96		
	-0.074 + 0.044	7.01		
	-0.044	70.89		
Note: The composition of the electrolyte - 50 g/l H_2SO_4, 5-20 g/l Cu, organic additives				

The color of copper powder is close to the color of the powder achieved from the pure sulfuric acid-based electrolyte, but has a lighter tone. The sediment color change is apparently due to formation of the spongy surface and the presence of spherical aggregates on it.

Copper powder, precipitated from the electrolyte solution with the addition of ethylene glycol, is tinted in a darker color with a dark crimson shade. That is, two samples of copper have similar structure. However, injection of ethylene glycol into the electrolyte forms more dendritic shape of copper. It is noted that the output of fines generated with addition of glycerol and ethylene glycol is small compared with the original electrolyte, but the addition of ethylene was accompanied by more active hydrogen evolution and lower current efficiency than in the presence of glycerol. Formation of powder with a darker color is also associated with increased oxidation of its surface. Donchenko et.al [15] have observed similar effects on copper morphology when approx. 10^{-3} g/L of decylpyridine chloride with oxyethylated phenol has been added. The crystal size of the copper powder has decreased along with a leveling effect. Increase of the additive concentration results in strong inhibition of copper ion discharge (100-150 mV increase in polarization) and crystallization of three-dimensional nuclei. Wang et. Al. [16] have shown that porous copper films can be successfully electrodeposited using a hydrogen bubble template, where the cationic surfactant cetyl trimethylammonium bromide, the anionic surfactant sodium dodecyl sulphate, the non-ionic surfactant alkylphenol polyoxyethylene and combined surfactants are used as additives to the electroplating baths. Results have shown that porous electrodeposited copper films have an obvious difference in the crystallinities in films derived from baths containing different surfactants. Field emission scanning electron microscopy micrographs revealed that both the size and morphology of the pore walls acutely depend on the type of surfactant.

4. CONCLUSION

Effect of polyols is primarily to increase the viscosity of the solution. An interesting fact is that at low concentrations of copper (5 g/L), almost regardless of the concentration of glycerin, we achieve a modified form of polarization curves, which indicates a passivation of the electrode surface at high concentrations of copper. However, changes in surface conditions from cycle to cycle are not observed. This situation may be due to the fact that the depleted solutions on copper observed a far greater contribution of hydrogen in the formation of the precipitate of copper, which causes the formation of oxide layers on the surface and, accordingly, the passivation of the surface.

Deposition achieved in the presence of alcohols, is characterized by looseness in comparison with powder obtained without addition of organic additives. In addition, supplements of organic matter affect the dispersion of produced copper powders, shape and size of the grains. Thus, the addition of the glycerol into electrolyte lowers dendrite formation, followed by a pronounced orientation of the dendrite growth, and the injection of ethylene glycol into electrolyte contributes to refinement of individual dendrites, with the simultaneous development of dendritic structure and the formation of friable and more diffuse deposits.

The increase of OH groups in the molecule of alcohol had little effect on the change of the surface of deposited copper powder. However, in the presence of two atomic alcohol (ethylene glycol) released sediment was painted in a darker tone compared to the copper powder obtained from glycerol containing (triatomic alcohol) electrolyte solution. Consequently, the decrease in the chain of alcohol and the CH-OH groups gives the crimson shade of copper precipitate in coloring. Change in color of copper powders is interconnected with their dispersion and structural changes, the depth of which is due to the nature of the organic additives.

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