THE SURFACTANTS INFLUENCE ON THE COPPER ELECTRODEPOSITION PROCESS IN NITRATE SOLUTIONS

M.I.Donchenko, O.G.Sribna, R.M.Redko,
V.V. Yudina
National Technical University of Ukraine “Kiev Polytechnic Institute”
37/4, Pr. Pobedy, 03056, Kiev, Ukraine

In the nitric copper plating electrolytes, collateral processes of reduction of nitrate-ions and nitric acid derivatives - hydroxylamine, nitrous acid, etc., accompany the cooper ions discharging. In this case, the additives of organic and inorganic substances are being entered [1 - 3], for suppression of collateral processes, formation of smooth nonporous coatings, increasing of throwing power (TP) in electrolytes. In the case copper electrodeposition on steel, inorganic oxo-anions are being added for steel base passivation and suppression of a pair copper - steel cementation [4].

In the present work decylpyridine chloride and oxyethylated phenol (NL) have been studied, among the surfactants, essentially influencing morphology of copper coatings. The introduction of these additives in small concentrations (about 10^{-3} g/l) causes decrease of the crystal sizes of electrodeposited copper and appearing of leveling effect. Increase of the additive concentration results in strong inhibition of cooper ions discharge (polarization raises on 100 - 150 mV), and crystallization begins as three-dimensional nuclei only on the separate active centers of the surface. The study of deposits morphology with the help of raster electron microscopy has shown, that the sizes and the number of nuclei grows up to the certain limit, and then the deposit represents the chaotically located crystals with legible facets. The layered growth of crystals frequently is often noticed. The form and the sizes of crystals essentially depend on electrolysis conditions. With the direct current, fine-crystalline deposit is formed with separate spherical outgrowths. With the pulse current the similar outgrowths is settled down as chains. The reversible current results in formation of fibrous branched dendrites, which are regulary distributed on a surface perpendicularly to it. Dendrites consist of large dissymetric crystals. Increasing of the crystal sizes at copper deposition by the reversible current in comparison with the direct current will be coordinated to the appropriate decreasing of cathode process polarization. The researches executed on the rotating disk electrode testify, that copper ions diffusion limitations did not play a determining role in formation of a deposit dendrite structure.

Recommended value of a solution pH is 1 - 2. While electrolyte service, not containing the buffer additives, pH of solution raises, as the reduction of nitrogen containing components proceeds with participation of hydrogen ions. The current copper yield is reduced with reduction of copper salt concentration and a solution pH. Increasing of cathode current density accelerates the basic process in the greater degree, than collateral. It results in growth of current copper yield, but causes deterioration of electrolyte throwing power. The additives of chlorine anions, organic surfactants, decreasing of copper ions concentration, application of the reversible current promote increase of the TP and interval of working current density.

Electrocapillary curves, received on mercury in nitric acid solutions (Fig), have shown, that the NL additive has high surface activity and poorly expressed cationic properties. The presence of two peaks on capillary curves, probably, is connected to the NL ability to various orientations on the metal surface depending on a mark of surface charge. The mobility of adsorbed molecules at current reversal can be one of the reasons of more uniform structure of copper deposits, received in the reversal conditions in a comparison with the direct or monopolar pulse current. The comparison of potentials area of copper ions deposition with adsorption potentials of NL in Antropov φ-scale has been shown, that dendrite structures forming near to the potentials of non-charged copper surface.

The coatings generated in the reversible electrolysis conditions, on appearance are similar to a fibrous fabric, however have mechanical strength and strong coupling with a basis. The high capillary properties caused by presence of branched volumetric pore system are characteristic for them. Such coatings can be used for increase of heat-conducting properties of the surface, creation of catalysts, filters and electrodes with the branched surface, composite materials. The coatings with 100 - 500 microns thickness can be copper plated in high-speed nitric electrolytes with 70 -120 microns / hour speed.

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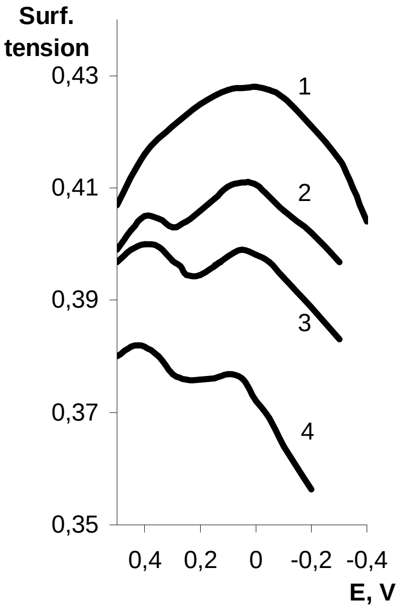

Electrocapillary curves on mercury in nitric acid solution in presence of NL (g/l): 1-0; 2- 0,015; 3-0,02; 4-0,03.