# The Effect of Organic Surface-Active Additives Upon the Kinetics of Electrodeposition of Ultrafine Copper Powder

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The influence of organic additives on the kinetics of electrodeposition of copper ions on the surface of the polycrystalline copper electrode from the mixed aqueous-organic solutions, the possibility of obtaining ultrafine powders of copper by electrolysis in a water-isopropanol solution of cupric nitrate in the presence of additives, polyvinyl alcohol and cationic amine containing polyelectrolyte VPK, are investigated in this work. It is shown that the organic surfactants can reduce the particle size of the copper powder and  increase the homogeneity with respect to fractional composition.

## 1.  Introduction

The study of electrocrystallisation parameters of copper to identify the formation conditions of ultrafine copper powders, and the influence of the nature of the electrolyte in the presence of surfactants in the electrodeposition are little-known regions. The obtainment, which is known from "Demeev et al. (2011, 2013) and Chulovskaya et al. (2006),  of copper powders from inorganic aqueous electrolytes based on "simple" copper salts, which contain monohydric organic alcohols, allows to synthesize fine powders. The empirically chosen monohydric organic alcohols (ethanol, propanol, etc.), change permittivity, viscosity, and adsorption at the electrode/solution phase boundary. It also changes physico-chemical properties of electrolytes. Danilov et al. (2000) and Demeev et al. (2012) have reported that adsorption of the surfactant changes the rate of nucleation and electrocrystallization on the metal surface. This leads to a change in properties of the obtained metal powders.

Research objects are the electrochemical behavior of copper ions in the aqueous-alcoholic solution of copper nitrate in the presence of surfactants, and the electrodeposition of ultrafine copper powders on copper and steel cathodes.

## 2.  Experimental

The research methods used in this study are potentiodynamic voltammetry experiments, which were carried out on an AUTOLAB PGSTAT 302N potentiostat/galvanostat (Netherlands) along with a computer control. Microscopic studies, which were carried out on Quanta 3D 200i scanning electron microscope (SEM), galvanostatic electrolysis, and microphotography.

Copper nitrate 0.1M solutions in aqueous alcoholic media were investigated in the absence and then in the presence of surfactants in the electrolyte.

Measurements were performed in potentiodynamic mode at different temperatures in  quiescent and stirred (300 rpm) electrolytes. Potential scan rate was 10 mV/s.

All electrodes mentioned above were mechanically polished to a mirror finish with absence of microscopically visible scratches (x100-200 magnification) by using sandpaper of varying grits and diamond powder ACM 5/3 micron with addition of distilled water. In order to remove oxide films the working electrode was held before the polarization measurements at a potential of -0.4 V (vs SCE).

Electrodeposition of copper powder was performed in galvanostatic mode in a temperature-controlled cell under constant stirring of the electrolyte. Steel electrode and cylindrical copper plate (Cu + Ag 99.997% mass) were used in electrolysis as a cathode  and an anode respectively.

As surfactants, known from Abramzon et al. (1979), next compounds were used: chemically pure grade of polyvinyl alcohol (PVA) with formula [-$CH_2$-$CH(OH)$-]$_n$, and a cationic amine-based polyelectrolyte VPK-101 with formula [-$CH_2$-$CH$-$C_6H_4$-$CH_2N^+(CH_3)_2$]$_n$$Cl^-$ (n=100-500).

Reagents of a "P.A." grade (Merck) and ultrapure water, purified by Milli-Q water purification system (Millipore, USA) with a specific resistivity of 18 mGoM/cm, were used to prepare solutions for experiments with polycrystalline electrodes, and with total amount of organic carbons TOC (organic impurities) less than 10 ppb. Methods for calculating the electrochemical parameters: current output, the exchange current «Io» and transfer coefficient «α» given in Rotinyan et al. (1981).

## 3. Results and Discussion

During the formation process of cathodic depositions of copper the crystal growth is complicated by indirect factors, e.g. the influence of surfactants adsorbed on the cathode. Typically, as a result of the discharge process of metal and hydrogen ions at the cathode hydroxides and basic salts of precipitated metals, which are formed in the *near-cathode electrolyte layer,* may play the role of surfactants. The presence of such surfactants can be due to the impurity of electrolyte components or anode material.

However, they are often added to the electrolyte intentionally. Depending on the nature and concentration of the solution, surfactants may improve the formation of particles with developed dendritic structure, or vice versa, may obstruct their growth by dispersing the precipitate. Study of the surfactants' influence on the formation stage and on the growth of new phase nuclei are considered in Demeev et al. (2012), Danilov et al. (1987) and Tarallo et al. (1999). Most researchers believe that the following effects take place in the adsorption of surface-active substances:

1) Change in the surface energy of the boundaries in a new phase of nucleus-electrolyte, boundaries in a new phase of nucleus–solid substrates, and in the nucleation work.
2) Blocking the active sites of the substrate.
3) Changes in the structure of the electric double layer. This leads to the change in the kinetics of ion discharge, in the nucleus growth, and in the shielding zones.

According to the dynamic model of development of dispersed sediment in galvanostatic conditions, the effect of additives of organic substances on the electrodeposition of loose copper deposits can be explained by using the basic principles of mixed kinetics. Kinetics of the development of the cathode deposit is mainly determined by the diffusion mode of the process which is characterized by the depletion factor $K = i_k / i_{dif}$, and electrochemical parameters of the electrode reaction, including exchange current $i_0$ and $α_k$, transfer coefficient. When adding additives into electrolyte they affect on the diffusion of discharging ions. This increases the depletion factor resulting in dispersing the powder particles, increases its dendricity, decreases its bulk density and fluidity. The additives inhibit discharge of copper ions, reduce $K_{dep}$, $i_0$ and $α_k$, and facilitate the production of small and less dendritic powder particles with enhanced bulk density and fluidity. It was found that all additives block the active centers of the substrate. This leads to a decrease in a stationary nucleation rate with increasing the concentration of surfactant. Figure1 high current efficiency is observed for small concentrations of alcohols (higher conductivity of the solution).

As it follows from the results shown in table 1,2 when increasing alcohol concentration in the electrolyte transfer coefficient α naturally decreases. This indicates that inhibition of the electron transfer reaction takes place. The values of the current output are different for different formulations of electrolytes.
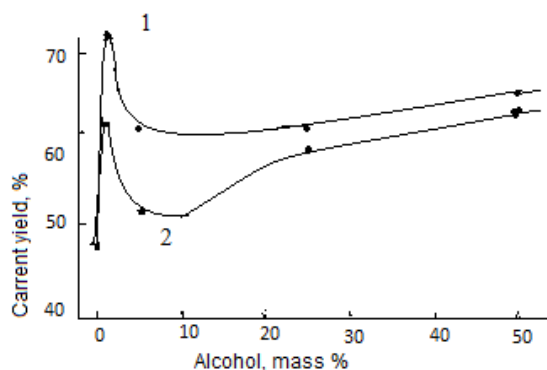


*Figure 1: Dependence of copper powder current yield on electrolyte composition. Concentration: 0.1 M $Cu(NO_3)_2$ + alcohol, temperature: $35^0C$, 1- ethanol, 2- isopropanol*

*Table 1: Dependence of transfer coefficients α on electrolyte composition at 25ºC.*

| Composition, water:alcohol, mass % | 99:1 | 99:5 | 75:25 | 50:50 |
|---|---|---|---|---|
| α   $(Cu(NO_3)_2 + C_2H_5OH)$ | 0,527 | 0,468 | 0,281 | 0,305 |
| α   $(Cu(NO_3)_2 + C_3H_7OH)$ | 0,404 | 0,386 | 0,292 | 0,252 |

*Table 2: Dependence of transfer coefficients α on electrolyte composition at 35ºC.*

| Composition, water:alcohol, mass % | 99:1 | 99:5 | 75:25 | 50:50 |
|---|---|---|---|---|
| α   $(Cu(NO_3)_2 + C_2H_5OH)$ | 0,401 | 0,474 | 0,339 | 0,295 |
| α   $(Cu(NO_3)_2 + C_3H_7OH)$ | 0,391 | 0,462 | 0,586 | 0,275 |

Inhibition of discharge reaction of $Cu^{2+}$ ions on the electrode in the presence of both alcohols is particularly noticeable at a ratio of 99:5 (exchange current values in this case are minimal, table 3). The observed reduction in α values is more significant for a system with isopropanol. At relatively low alcohol concentrations it points to the adsorption nature of the inhibition reaction.

*Table 3: Dependence of exchange current $i_0$ on electrolyte composition at 25ºC.*

| Composition, water:alcohol, mass % | 99:1 | 99:5 | 75:25 | 50:50 |
|---|---|---|---|---|
| $i_0$   $(Cu(NO_3)_2 + C_2H_5OH)$, A/м$^2$ | 9.527 | 1.166 | 7.69 | 5.48 |
| $i_0$   $(Cu(NO_3)_2 + C_3H_7OH)$, A/м$^2$ | 22.85 | 2.5 | 8.1 | 6.45 |

*Table 4: Dependence of exchange current $i_0$ on electrolyte composition at 35ºC.*

| Composition, water:alcohol, mass % | 99:1 | 99:5 | 75:25 | 50:50 |
|---|---|---|---|---|
| $i_0$   $(Cu(NO_3)_2 + C_2H_5OH)$, A/м$^2$ | 25.6 | 2.41 | 4.66 | - |
| $i_0$   $(Cu(NO_3)_2 + C_3H_7OH)$, A/м$^2$ | 38.81 | 4.46 | 4.25 | 14.42 |

Exchange currents in table 3 for systems with isopropanol are higher than with ethanol of same concentration at temperatures up to 35ºC. When increasing alcohol concentration the exchange current is increasing. The high values of exchange current are presumably due to the high conductivity of the solution, dielectric constant ε is lower. The increase in electrolyte temperature(table 4) leads to the activation of electrochemical processes, therefore, it leads to the removal of inhibition of the reactions of electroreduction by alcohols additives (increasing values of the coefficient of transfer and current exchange).

The growth of current of a single hemispherical nucleus can be calculated  Polukarov et al.(1982) and Fletcher (1983) as follows:

$$I(t) = (Ia + Ic) \times Ir \times (Ic + Ir)^{-1} + B$$

Where, $I(t) -$ is the velocity of nucleation,

$$Ic = io \exp(azFt / RT)$$ - cathodic current nucleation,

$Ir = \frac{zFDC}{r}$   , r- radius of a nucleus, changing in time.

It can be seen from the equations that when decreasing the exchange current and increasing overvoltage (decreasing α) the growth of current of a single hemispherical nucleus reduces in time. This is beneficial for the formation of fine metal powders.

Voltametric research results are presented in figure 2. The potentiodynamic polarization curves were obtained from 0.1M solution of copper nitrate at different concentrations of ethanol and isopropanol at $25^0C$ .

When stirring the electrolyte and increasing alcohol concentration the limiting diffusion current $i_d$ decreases; its lowest value corresponds to the composition of 50:50. This is due to the increase of adsorption of alcohols, viscosity of the electrolyte, and related diffusion limitations. In a quiescent electrolyte the value of limiting current in the presence of alcohols is higher than in "pure" electrolyte, since the conductivity of the solution in the presence of alcohols is higher (Figure 2, curve 2, 3) . When increasing alcohol concentration in the solution the limiting current value is decreasing due to the same reasons as in the case of stirring electrolyte.

Depending on the nature and concentration of the additives added, the effect of their action is different: some of them mainly affect on diffusion kinetics, others - directly on the discharge of copper ions. The effect of surfactants on the kinetics of copper ion discharge is clearly seen in Figure 3. The adsorption of additives is higher in a solution without isopropanol rather than in its presence. This explains the high polarization of the electrode.

Polyvinyl alcohol (PVA) - at low concentrations has almost no effect on the kinetics of the discharge of copper ions, and on the conditions for their diffusion to the cathode (Figure.3 curve 5).

In water-isopropanol solution of the limiting currents are significantly lower and the angle of polarization curves is much higher (Figure 4) than in pure nitric acid solution (Compare figures 3 and 4), that explains obtaining of copper powders in the nanometer size range. Ultrafine powders were obtained as a result of electrolysis in the presence of PVA+VPK (Figure 5).
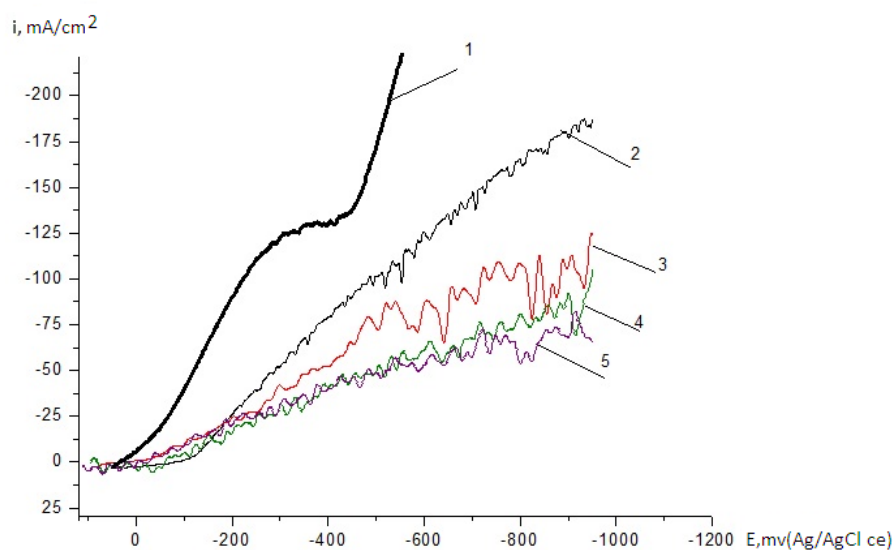


*Figure 2: Polarization curves of copper ions reduction in water-ethanol solutions. 0.1M solution of copper nitrate, water : alcohol ratio is equal respectively: 1 – 1:0, 2 -99:1, 3 – 95:5, 4 – 75:25, 5 – 50:50.  t=35 °C, quiescent electrolyte.*
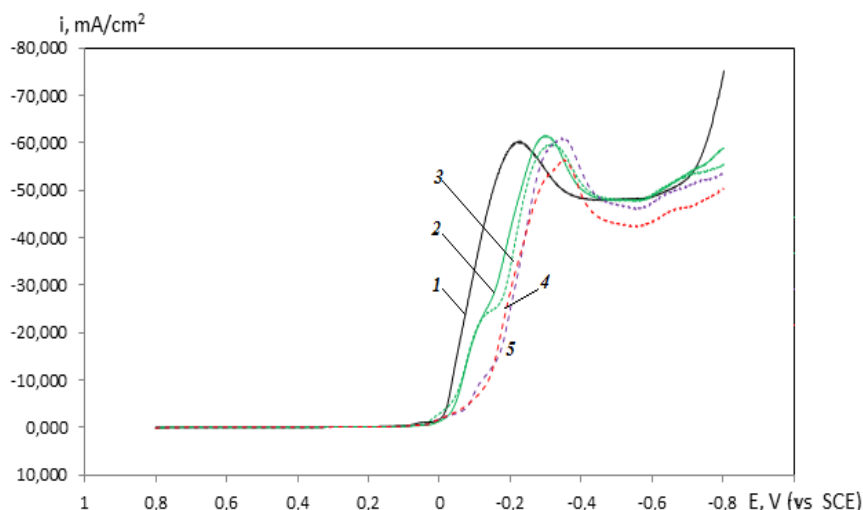


*Figure3. Polarization curves of copper ions reduction in an aqueous solution in the presence of polyvinyl alcohols (PVA) and  amine-based polyelectrolyte (VPK-101), mG /L: 1- 0; 2 – $C_{VPK}$=20; 3 - $C_{VPK}$ =60; 4 - $C_{VPK}$ =100; 5 - $C_{VPK}$ =100 + $C_{PVA}$ =20*
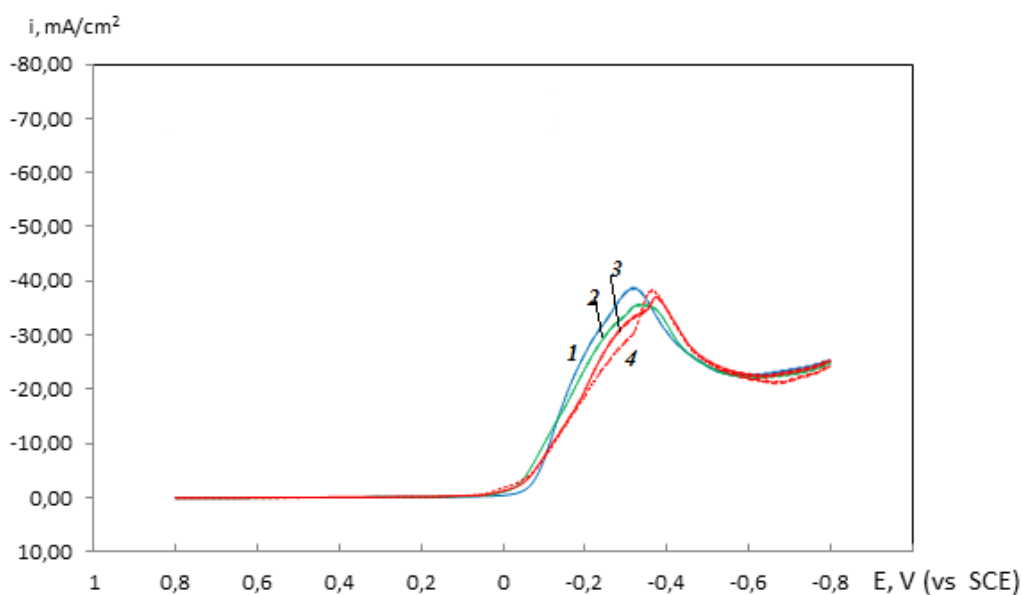
*Figure 4: Polarization curves of copper ions reduction in the mixed solution of water and iso-propanol in the presence of surfactant in mG/ L : 1- 0; 2 – $C_{VPK}$ =40; 3 - $C_{VPK}$ =60 + $C_{PVA}$ =1·10; 4 - $C_{VPK}$ =1·100 + $C_{PVA}$ =20*
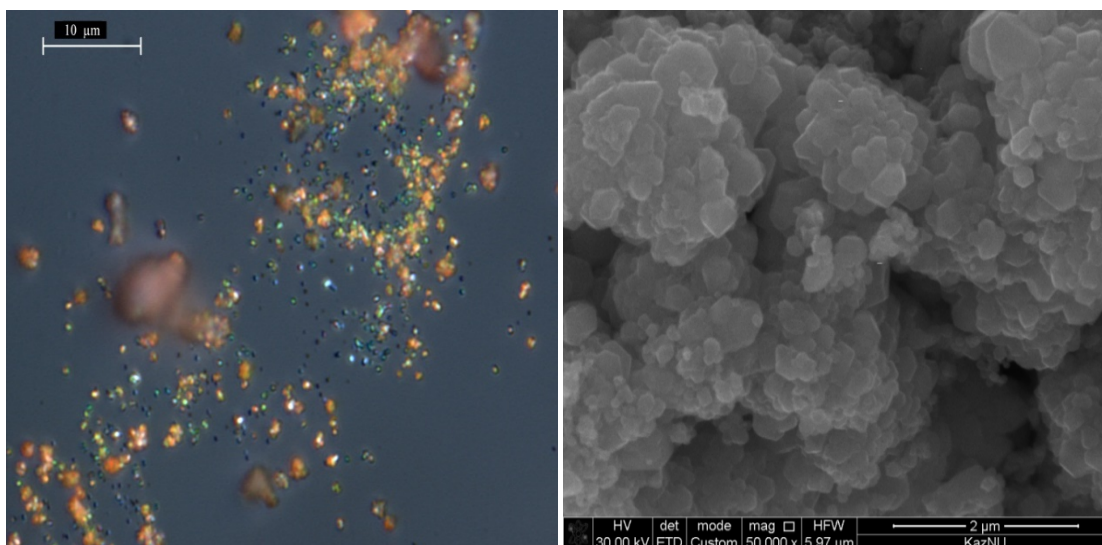


*Figure 5: Photomicrographs of copper powders obtained from aqueous iso-propanol with the addition of electrolytes 10 mg/ L  PVA  +  50 mG /L VPK at 25 $^{o}$C*

As seen from the photomicrograph (Figure 5), in the presence of PVA + VPK obtained powders are uniformly distributed on the fractional composition of the particles with the dimension of a nanometer range reaching about 200 nm

## 4.    Conclusions

In difference from known studies the alcohols and surface active additives are shown to change the kinetic parameters and properties of ultra dispersed powders electrodeposition due to their deposition on the electrode surface. Increasing the alcohol content in the solution leads to inhibition of the electrochemical reduction (reducing the amount of exchange current, the increasing of the slope of the polarization curves and reducing the maximal diffusion current). Copper powders which are obtained in an aqueous isopropanol solution, without surfactants introducing have size of the order of 0,6-1,0µm.

The best results on the fineness of the resulting copper powder the electrolyte composition Cu (NO3) 2 + i-C3H7OH + PVA + VPK containing 5-25% weight of isopropanol. The powder have spherical shape. Ultra dispersed copper powders are deposited from this electrolyte. The Most copper particles are closed to nanoparticles by their size (about 200 nm).

The series of experiments with additives of polyvinyl alcohol showed that the fractional composition homogeneity of the copper powder was enhanced in the presence of PVA in the electrolyte. Moreover, the percentage of the particles of the same size has been increased. Systems with branched alcohols (isopropanol and polyvinyl alcohol) resulted in powders with a narrower dispersion range (uniform particles of about the same size). Use of surfactants allows to produce the finest powders with the minimum particle sizes by prolonged electrolysis, 0.5 - 1hour.

The results show that the process parameters such as temperature, operating current density, electrolyte composition and especially a surfactant additive technology allows you to adjust the properties of the copper powder.

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