

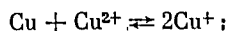
REASONS FOR THE REDUCTION IN CURRENT EFFICIENCY DURING THE ELECTRODEPOSITION OF COPPER FROM SULFURIC ACID SOLUTIONS

N. T. Kudryavtsev, E. A. Nechaev,
and V. A. Semenov

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It is difficult to study the reasons for the decrease in the current efficiency which occurs when the current density is reduced in a sulfuric acid copper-plating bath because there are two types of ions present (Cu^{2+} and Cu^+), and the electrochemical reactions may be accompanied by several chemical reactions, both at the electrode surface and in the bulk electrolyte.

The reasons which have been offered [1, 2] for the reduced current efficiency can be divided into three groups: (1) dissolution of copper through the disproportionation reaction



(2) incomplete reduction of divalent copper ions; (3) oxidation of copper by oxygen from the air with subsequent dissolution of the oxides in the sulfuric acid.

Other factors are evidently of a secondary nature, for they ultimately lead to changes in the rate of one of the three processes above.

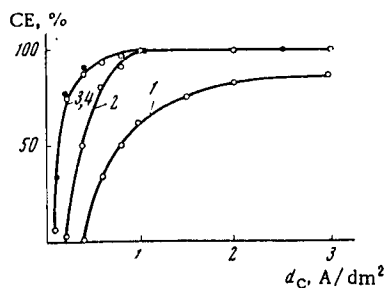


Fig. 1

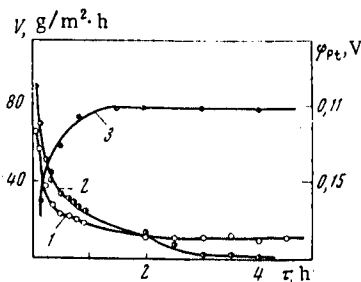


Fig. 2

Fig. 1. Dependence of the cathodic current efficiency on the current density for various electrolysis conditions. 1) No Cu^+ ions; 2) solution not purified, electrodes of type M-O copper; 3) purified solution, electrodes of "especially pure" copper; 4) solution not purified, electrodes of type M-O copper, hydrogen atmosphere.

Fig. 2. 1, 2) Dependence of the copper self-dissolution rate on the time the sample was held in the agitated electrolyte; 3) dependence of the microprobe potential on this time. 1) Type M-O copper; 2) "especially pure" copper.

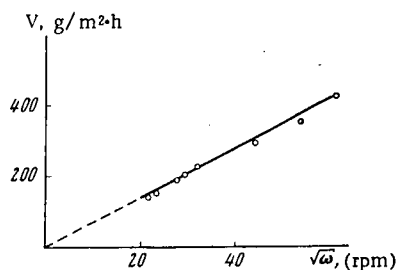


Fig. 3. Dependence of the rate of copper self-dissolution in an electrolyte without Cu^+ ions on the rotation velocity of a disc electrode.

oxygen was bubbled through the solution. The effects of oxygen from the air could be neglected because of its low solubility at the elevated temperature.

The experimental results were very reproducible and did not depend on whether the measurements were carried out in CO_2 , H_2 , or air.

The current efficiency did not reach 100% even with $d_c = 3 \text{ A/dm}^2$ (curve 1 in Fig. 1). Below 0.4 A/dm^2 no change in the mass of the copper sample could be detected at all, and the current efficiency became negative. Under these conditions, the reduction of the current efficiency is governed by copper self-dissolution through disproportionation, as was confirmed by the satisfactory agreement between the experimental and theoretical CE (d_c) curves (the latter calculated under the assumption that the self-dissolution rate corresponded to $d_c = 0.4 \text{ A/dm}^2$ and was independent of the electrode potential).

To evaluate the effect of incomplete reduction of Cu^{2+} ions on the current efficiency, we measured the latter in solutions saturated with Cu^+ ions. To determine whether similar solutions could be obtained, we studied the time dependence of the Cu^+ concentration in a solution of metallic copper.

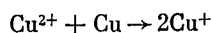
The Cu^+ concentration was monitored with a platinum microprobe; this concentration completely determines the potential

$$\varphi_{\text{Pt}} = \varphi_0 + \frac{RT}{F} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^+}},$$

since the Cu^{2+} concentration is large and essentially constant.

When copper is held in the solution, the probe potential (curve 3 in Fig. 2) shifts toward negative values, reaching a limiting value which depends on the immersed surface area of the copper plate. When the electrolyte is vigorously agitated, however, or when the copper sample is rotated, the probe potential takes on the value 0.1110 V, regardless of the sample area. In this case, the potentials of gold and mercury are 0.1104 and 0.1101 V, respectively.

If it is assumed that the rate of copper dissolution by the reaction



is governed by diffusion of Cu^+ ions into the bulk solution (Fig. 3), the electrolyte will presumably be saturated with Cu^+ ions under certain hydrodynamic conditions when there is a large-area copper plate in it.

The results show that the rate at which Cu^+ ions appear through reaction (1) is much greater than that at which they disappear in the bulk solution, so the Cu^+ concentration in the near-electrode layer is close to equilibrium.

When the solution is abruptly cooled from 90°C to 70°C , the value of Cu^+ does not change abruptly, but gradually; after a while, a metallic copper powder appears in the cell. Under certain conditions, therefore, electrolytes supersaturated with Cu^+ ions may exist. Experiments showed that the current efficiency exceeds 100% during electrolysis in such solutions, even at low current densities, although no change in the weight of the copper sample was observed under these conditions in the absence of a current.

It is quite probable that "supersaturated" solutions may also form during the anodic dissolution of copper. This could explain the dependence of the cathodic current efficiency on the anodic current density and on the separation between cathode and anode.

We attempt in this paper to evaluate each of these three factors.

Since the decrease in the current efficiency is much more noticeable at high temperatures, all the experiments were carried out at 90°C in a 100 cc cell in a constant-temperature bath. A copper coulometer was used to measure the current efficiency. The potentials were measured with respect to a saturated calomel halfcell connected to the test solution, made up to 250 g/liter $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50 g/liter H_2SO_4 .

To evaluate the effects of the disproportionation reaction on the current efficiency, we found the dependence of the latter on the current density (d_c) in an electrolyte free of the Cu^+ ions. To prevent the latter from appearing, we used insoluble anodes, shielded the samples carrying current, and changed the solution after each measurement. To prevent the oxidizing effects of oxygen, the anode compartment was separated by a diaphragm from the cathode compartment. Carbon dioxide purged of

With electrodes made of type M-O copper and electrolytes not subjected to special purification, the current efficiency at low current densities was below 100% (curve 2 in Fig. 1), while copper self-dissolution (curve 1 in Fig. 2) did not cease even when the solution was saturated* with Cu^+ ions.

After a thorough purification of the initial reagents [3] with a subsequent triple recrystallization of the copper sulfate, and when electrodes of "especially pure" copper are held in the solution for a long time (>3 h), self-dissolution is essentially stopped (curve 2 in Fig. 2) and the current efficiency is significantly increased (curve 3 in Fig. 1).

The effects of the purity on the copper self-dissolution rate are due to the occurrence of another cathodic process at inclusions in the copper. A possibility is the discharge of H^+ ions, forming adsorbed hydrogen atoms, which may be found on the surfaces of platinum-group metals† at extremely positive potentials [4].

At a very low hydrogen partial pressure in the external medium, the equilibrium potential of the hydrogen electrode is more positive than the copper potential in the test solution.

This assumption is supported by the increased current efficiency which results from the bubbling of gaseous hydrogen through the solution (curve 4 in Fig. 1). The $\text{CE}(\text{d}_\text{c})$ dependence is the same as that found during the use of the purified solutions and the "especially pure" copper.

Corrosion is apparently possible only when molecular hydrogen does not appear at impurity inclusions as the result of a cathodic process. Otherwise, the hydrogen partial pressure near the electrode increases, and the equilibrium potential of the hydrogen electrode becomes more negative than the copper potential. This is apparently related to the fact that copper does not self-dissolve in dilute H_2SO_4 solutions, even at relatively high temperatures.

The corrosion process continues in the presence of copper ions by means of one of the two reactions‡



or



To choose between these reactions, regions of platinum were deposited 1 mm apart on a copper sample by an electric-arc method, and the potential of a platinum probe 0.1 mm from the surface was measured. The probe potential with respect to the test electrode changed when the probe was moved parallel to the surface: near the platinum regions, it was found that $\text{Pt}/\text{Pt} = -0.0070 \pm 0.0012$ V, while away from them (near copper regions), it was found that $\varphi_{\text{Pt}} = -0.0093 \pm 0.0004$ V. Accordingly, the Cu^+ concentration near an inclusion is less than that at the pure copper surface, so reaction (4) is the more probable. At anodic regions, copper evidently dissolves, forming Cu^+ ions.

An electrochemical reaction – the incomplete reduction of Cu^{2+} ions – is probably the reason for the fact that the current density does not reach 100% at low current densities, even in solutions saturated with Cu^+ ions.

It is unlikely that the current efficiency would be reduced because of a disproportionation reaction in solutions saturated with Cu^+ ions.

If it is assumed that copper is electrodeposited through the discharge of Cu^{2+} ions, the disproportionation reaction will thus tend to form metallic copper.

If Cu^+ ions are assumed to discharge at low current densities, one of two copper atoms which discharge will again pass into the solution as a result of the disproportionation reaction, and thus the charge expenditure will be equivalent to the discharge of Cu^{2+} ions.

It should be noted that the conclusions we have drawn in this paper refer to high temperatures only: at room temperature, when the equilibrium concentration of Cu^+ ions is negligibly small, the mechanism may quite possibly differ from that described here.

* Conditions were arranged to keep the probe potential at a constant 0.1110 V during the experiment.

† Found as impurities in copper after electrolytic purification [2].

‡ Copper ions may be reduced by atomic hydrogen [5].

In sulfuric acid copper-plating electrolytes free of Cu^+ ions, the reduced current efficiency at low current densities is therefore due primarily to a disproportionation reaction.

In CuSO_4 solutions saturated with Cu^+ ions, the corrosion process may have an important effect on the current efficiency along with the incomplete reduction of Cu^{2+} ions.

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