INFLUENCE OF A SECONDARY PROCESS ON COPPER DEPOSITION RATE IN NITRATE BATHS

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In a number of cases the electrodeposition process is accelerated when NO_3^- ions are added to the metal plating bath [1-5]. It is the special feature of these baths that the cathodic reduction of NO_3^- ions can occur in parallel with the basic reaction depositing the metal. This gives rise to changes in composition of the solution layer next to the electrode, which in turn can lead to the formation of complexes, faster or slower mass transport, and stirring by gaseous reaction products. In the present work we estimate the influence of the secondary reaction on mass transport but disregard complex formation.

It was the aim of the present work to study the accelerating effect of NO_3^- ion discharge on copper electrodeposition in acidic nitrate baths. To this end we experimentally determined the overall and partial reduction rates of the Cu^{2+} and NO_3^- ions in nitrate and sulfate baths, and we also performed a theoretical analysis of the possible reasons for the effects observed.

The partial polarization curves were calculated from the experimental overall polarization curves and the copper current yields found with the aid of a copper coulometer. In order to avoid dendrite formation and the potential changes in true surface area of the electrode associated with it we recorded the polarization curves using short galvanostatic pulses (≤ 5 sec). The values of potential are stated relative to a normal hydrogen reference electrode.

Sulfate and nitrate electrolytes having identical Cu^{2+} ion concentrations were investigated over the solution pH range from 2.8 to 0.8 (these values were controlled by adding the corresponding acid). "Chemically pure" substances were used to prepare the electrolytes.

The results obtained at pH of 2.8, 1.9, 1.3, and 0.8 show that the partial rates of copper electroreduction in nitrate baths at high current densities (including the limiting current density) are about 1.8 to 4.5 times higher than those in sulfate baths. This effect can be attributed to the influence of the migrational current component on copper ion mass transport. Considerations of migration phenomena in the diffusion layer show that in the absence of base electrolyte, the current of metal ion reduction is twice higher than the diffusion current in the case of 1:1 and 2:2 electrolytes, and three times higher in the case of 2:1 electrolytes [6]. On this basis the limiting currents in $Cu(NO_3)_2$ solutions should be 1.5 times higher than those in $CuSO_4$ solutions of the same concentration. One can see from Fig. 1 that approximately this ratio of the limiting currents is observed in the electrolytes discussed when working in weakly acidic solutions. But at higher bath acidities an appreciable increase in this limiting-current ratio is observed (Fig. 1). In sulfate electrolytes, the limiting current of copper deposition decreases with increasing sulfuric acid concentration, just as it should as a result of the suppression of migration by addition of a base electrolyte, but in nitrate electrolytes the limiting currents increase with increasing nitric acid concentration. One can suggest that this is due to the influence of NO_3–ion reduction occurring in parallel with copper ion reduction.

It was shown in [7-9] that in the reduction of cations, simultaneous reduction of cations of another type or of neutral molecules may lead to an exaltation of the limiting current. However, electroreduction of copper in nitrate solutions cannot unambiguously be interpreted in terms of exaltation, since in this case anions NO_3^- rather than cations are reduced in parallel to the primary metal. The mechanism of NO_3^- ion reduction depends on the electrode material, electrode potential, and solution pH [10]. According to literature sources [11-131], this process most probably proceeds according to one of the following reactions, in the copper nitrate solutions being examined:
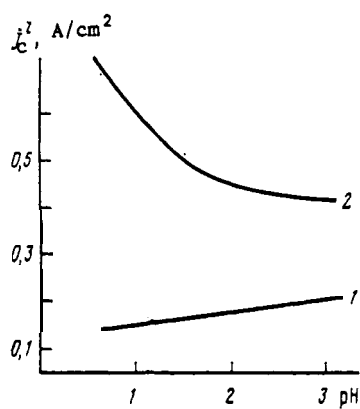
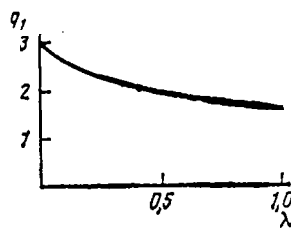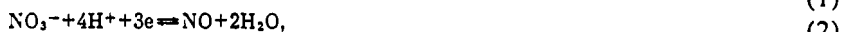Fig. 1   Fig. 2

Fig. 1. Limiting currents of copper deposition as functions of pH in 1 M $CuSO_4$ (1) and 1 M $Cu(NO_3)_2$ (2) solutions.

Fig. 2. Influence of acidity on the rate of copper deposition when accompanied by reaction (1).

$$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O, \tag{1}$$
$$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O, \tag{2}$$
$$NO_3^- + 2H^+ + e \rightleftharpoons NO_2 + H_2O, \tag{3}$$
$$NO_3^- + 2H^+ + 2e \rightleftharpoons NO_2^- + H_2O, \tag{4}$$
$$NO_3^- + 10H^+ + 8e \rightleftharpoons NH_4^+ + 3H_2O, \tag{5}$$
$$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-. \tag{6}$$

The electrode reactions (1) to (6) listed above can occur in parallel with the main reaction, i.e., electrochemical copper reduction:

$$Cu^{2+} + 2e \rightarrow Cu. \tag{7}$$

In order to determine the mutual influence of the two processes one must solve the corresponding systems of mass-transport equations while allowing for the diffusion and migration components. In particular, the system of electrodiffusion equations describing electrode processes (1) and (7) occurring in parallel is of the form of

$$D_1\left(\frac{dc_1}{dx} + 2c_1\frac{d\psi}{dx}\right) = \frac{j_1}{2F}, \tag{8}$$

$$D_2\left(\frac{dc_2}{dx} - c_2\frac{d\psi}{dx}\right) = \frac{j_2}{2F}, \tag{9}$$

$$D_3\left(\frac{dc_3}{dx} + c_3\frac{d\psi}{dx}\right) = \frac{3j_2}{2F}, \tag{10}$$

$$2c_1 + c_3 = c_2, \tag{11}$$

where $c_{1, 2, 3}$ and $D_{1, 2, 3}$ are the concentrations and diffusion coefficients of ions Cu^{2+}, NO_3^-, and H_3O^+, respectively,* $\psi = EF/RT$ is a dimensionless quantity where E is the electric potential, F the Faraday constant, R the gas constant, and T the absolute temperature, j_1 and j_2 are the cathodic current densities of reactions (7) and (1), and the current associated with the H_3O^+ ions is related to the current of the NO_3^- ions in accordance with the stoichiometry of reaction (1).

We assume that at $x = L$ (where L is the diffusion-layer thickness) the component concentrations and the potential are given as:

'In reactions (1) to (6), the nonhydrated proton H^+ has been written for the sake of simplicity.

$$c_1(L) = c_1{}^0, \quad c_2(L) = (\lambda+2)c_1{}^0; \quad c_3(L) = \lambda c_1{}^0; \quad E(L) = 0, \tag{12}$$

where parameter $\lambda \geq 0$ is the concentration ratio of the hydrogen and copper ions in the bulk solution. A calculation of the limiting currents, $j_{1\,\text{lim}}$ and $j_{2\,\text{lim}}$, which will be described in separate publications, leads to the following result

$$j_{1\,\text{lim}} = \frac{2FD_1c_1{}^0}{L} \frac{(3\eta-1)\lambda+6\eta}{(1+\eta)\lambda+2\eta}, \tag{13}$$

$$j_{2\,\text{lim}} = \frac{2FD_2c_1{}^0}{L} \frac{2\lambda(2+\lambda)}{\lambda(1+\eta)+2\eta}, \tag{14}$$

where $\eta = 3 D_2/D_3$. The first factors in Eqs. (13) and (14) are the limiting diffusion currents of reduction of the Cu^{2+} and $NO_3{}^-$ ions.

A calculation following Eqs. (13) and (14) shows that with increasing acidity j_1 decreases, while j_2 and the overall current increase. We shall introduce the parameter q_1, which is the ratio between the limiting current of copper deposition in the presence of a secondary reaction and the limiting diffusion current. The relation between q_1 and λ is shown in Fig. 2. When acid is not present ($c_3{}^0 = 0$, $\lambda = 0$) we have $q_1 = 3$, i.e., it coincides with the factor for the current in 2:1 electrolyte determined for solutions not containing a base electrolyte [14]. Quantity q_1 falls monotonically with increasing λ. Without presenting here the mathematical analysis for the cases involving parallel reactions (2) to (5) we point out that the results obtained are qualitatively analogous; the limiting current of reaction (7) is not increased on account of reactions (2) to (5).

Of particular interest is reaction (6). i.e., the reduction of $NO_3{}^-$ ions with water as the proton donor. An analysis of the corresponding electrodiffusion problem shows that here the connection between the current j_1 of copper deposition and the limiting current $j_{2\,\text{lim}}$ of $NO_3{}^-$ ion discharge is given by

$$j_1 = \frac{2FD_{Cu^{2+}} \cdot C_1^0}{L} \frac{3}{1-J} \left[1 - \left(\frac{1+\xi}{\xi} \right)^{\frac{2(J-1)}{3J}} \right]. \tag{15}$$

Here

$$\xi = 2D_{NO_3-}/D_{OH-}, \quad J = \frac{2j_{2\,\text{lim}}D_{Cu^{2+}}}{j_{1\,\text{lim}}D_{OH-}}.$$

Thus, according to the above analysis, nitrate ion discharge in acidic electrolytes leads to a decrease in the current of copper discharge relative to that in nonacidified solution. Hence the observed acceleration of copper deposition with solution acidification cannot be explained in terms of the effects of correlational exaltation. Complex formation in the system may, fundamentally, be the reason for the increase in limiting current observed experimentally. It had been shown in [15, 16] that complex formation in a number of cases leads to an increase in limiting current of the primary reaction. Moreover, the limiting currents can increase on account of the development of convective flows caused by gas evolution which accompanies nitrate ion reduction to more highly reduced products, e.g., NO.

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