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Abstract

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ON THE JOINT DISCHARGE OF METAL IONS IN REAL CONJUGATE SYSTEMS

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The condition for the joint reduction of several kinds of metal ions is the equality of their discharge potentials:

$$\varphi_1^0 + \frac{RT}{nF}\ln a_1 - \eta_1 = \varphi_2^0 + \frac{RT}{nF}\ln a_2 - \eta_2, \tag{1}$$

where $\varphi_1^0, a_1, \eta_1; \varphi_2^0, a_2, \eta_2$ are, respectively, the normal potentials, activities, and overvoltages pertaining to the first and second kinds of metal ions. For simplicity, in the subsequent exposition we shall use the ion concentration instead of the activity.

We have shown ([1]) that electrochemical reactions occurring simultaneously at an electrode are conjugate; therefore equation (1) does not completely characterize the condition for joint discharge, namely, it does not take into account the mutual influence of the reducing ions, in particular: the change in the state of the electrode surface, the change in the concentration of discharging ions in the electrical double layer, and the change in the state of the ions in solution.

As is known, the rate of reduction of metal ions depends on the concentration of ions in the electrical double layer, and not in the bulk. For the case of discharge of hydrogen ions, A. N. Frumkin proposed ([2]) a relation establishing the connection between the surface and bulk concentration of ions,

$$[H_s] = [H]e^{-F\psi_1/RT}.$$

Naturally, in the joint discharge of metal ions, at a given polarization of the electrode the concentration of each kind of ion in the double layer will be reduced in accordance with the number of kinds of ions and their concentration, as a result of the partial displacement of some ions by others.

Taking into consideration that, during the joint reduction of metal ions, both the nature of the cathode substrate and its surface state (the degree of its passivation) change, one should take into account the overvoltage in the discharge of a given kind of ion on the alloy (η^{alloy}), and not the overvoltage in the separate

Fig. 1 and Fig. 2: polarization curves

Figure 1: Fig. 1 and Fig. 2: polarization curves

deposition of metals (η). To determine the conditions for the joint discharge of ions in real conjugate systems, it should be borne in mind that, when several kinds of ions enter the electrical double layer, the fraction of the polarization contributed by each kind of ion will be characterized by the fraction of ions entering the electrical double layer relative to the total number of ions responsible for the polarization. Denoting by C_i the concentration of each kind of ion, and by α the coefficient characterizing the ability of a given kind of ion to penetrate into the electrical double layer, the decrease in polarization due to the entry of other ions into the double layer can be expressed by the quantity

$$-\frac{RT}{nF}\ln\frac{\sum\alpha_i C_i}{\alpha_1 C_1}.$$

Accordingly, a change in the discharge rate of different ions will also occur.

Since equation (1) does not take into account the influence of the factors listed, the equation expressing the condition for the joint discharge of ions must be ···

it is necessary to write in the following form:

$$\varphi_1^0+\frac{RT}{nF}\ln C_1-\frac{RT}{nF}\ln\frac{\sum\alpha_i C_i}{\alpha_1 C_1}-\eta_1^{\text{all}}=\varphi_2^0+\frac{RT}{nF}\ln C_2-\frac{RT}{nF}\ln\frac{\sum\alpha_i C_i}{\alpha_2 C_2}-\eta_2^{\text{all}} \quad (2)$$

or

$$\varphi_1^0+\frac{RT}{nF}\ln\frac{\alpha_1 C_1}{\sum\alpha_i C_i}C_1-\eta_1^{\text{all}}=\varphi_2^0+\frac{RT}{nF}\ln\frac{\alpha_2 C_2}{\sum\alpha_i C_i}C_2-\eta_2^{\text{all}}. \quad (3)$$

Here it is not taken into account that the activity of each type of ion in the mixture will differ from the activity during their separate reduction.

Fig. 1. Dependence of the rate of reduction of iron and nickel ions on the electrode potential (N.C.E.). Total polarization curves: **1** –discharge of Ni^{2+} and H^+ from a 1 N solution of $NiSO_4$; **2** –discharge of Ni^{2+}, Fe^{2+}, and H^+ from a solution of 1 N $NiSO_4$ + 1 N $FeSO_4$; **3** –discharge of Fe^{2+}, H^+ from a 1 N solution of $FeSO_4$. Partial curves: **4** and **5** –discharge, respectively, of Ni^{2+} and H^+, obtained on the basis of curve **1**; **7** and **8** –discharge, respectively, of Fe^{2+} and H^+, obtained on the basis of curve **3**; **6**, **9**, and **10** –discharge, respectively, of Fe^{2+}, Ni^{2+}, and H^+, obtained on the basis of curve **2**.

Fig. 2. Dependence of the rate of reduction of Fe^{2+} and Ni^{2+} on the electrode potential (N.C.E.), pH 1.9. Total polarization curves: **1** –evolution of Ni^{2+}

and H^+; **2** –Fe^{2+}, Ni^{2+}, and H^+; **3** –Fe^{2+} and H^+. Partial curves: **4** and **5** –respectively Ni^{2+} and H^+, obtained on the basis of curve **1**; **6**, **7**, and **8** – respectively Ni^{2+}, Fe^{2+}, and H^+, obtained on the basis of curve **2**; **9** and **10** – Fe^{2+} and H^+, obtained on the basis of curve **3**.

In equation (3) it is assumed that, during alloy formation, the normal potentials of the metals do not change appreciably.

Allowing for the depolarizing action of the substrate during joint discharge was proposed by A. I. Krasovsky ([5]). It follows from equation (3) that, in the electrodeposition of two or more kinds of ions differing considerably in their normal potentials, a change in the concentration of the discharg-

···of the depositing ions, it is essentially impossible to bring their discharge potentials closer together. Therefore, the principal regulating factor may prove to be the magnitudes of the overvoltage. Since, during joint discharge, owing to a change in the nature of the substrate, the overvoltage changes both in the direction of increase and in the direction of decrease, the following cases are possible under real conditions of joint deposition of metals:

1. When

$$\eta_1^{\text{alloy}} + \eta_2^{\text{alloy}} \ll \varphi_1^0 + \frac{RT}{nF} \ln \frac{\alpha_1 C_1}{\sum \alpha_i C_i} C_1 + \varphi_2^0 + \frac{RT}{nF} \ln \frac{\alpha_2 C_2}{\sum \alpha_i C_i} C_2,$$

then the rate of deposition of the metal with the more positive reduction potential is greater than the rate of discharge of ions whose reduction proceeds at a more negative potential.

2. When

$$\eta_1^{\text{alloy}} > \eta_2^{\text{alloy}}, \quad \varphi_1^0 + \frac{RT}{nF} \ln \frac{\alpha_1 C_1}{\sum \alpha_i C_i} C_1 - \left(\varphi_2^0 + \frac{RT}{nF} \ln \frac{\alpha_2 C_2}{\sum \alpha_i C_i} C_2 \right) \ll \eta_1^{\text{alloy}} - \eta_2^{\text{alloy}},$$

then the rate of deposition of the metal with the more negative potential is greater than the rate in the case of the more positive ion.

Thus, in real coupled systems, owing to the influence of the nature of the substrate on the magnitude of the overvoltage, a change in the reduction rate of both the more positive and the more negative metal ions is possible over a wide range.

With a considerable decrease in the overvoltage of joint deposition (case 2), one should expect the opposite ratio of rates, i.e., the rate of reduction of ions with the more positive potential will exceed the rate of reduction of ions with the more negative potential.

To verify this proposition we studied the joint discharge of nickel and iron ions. The study was carried out from 1 N sulfuric-acid solutions of nickel and iron

with the addition of 30 g/l boric acid at pH 1.9 and at various temperatures, which were controlled with an accuracy of $±$0.5°. The method of investigation was described in previous papers ([1]).

Figure 1 presents the polarization curves for the joint and separate deposition of nickel and iron and the corresponding partial curves, obtained from the indicated solutions at $t = 25°$. As is seen from the curves, the reduction potential of nickel ions (4) during its separate deposition is much more positive than that of iron (7). However, during joint discharge the rate of reduction of nickel ions (9) is much lower than the rate of deposition of iron ions (6). Sometimes this "anomalous phenomenon" is explained by the fact that iron is deposited with depolarization because of alloy formation. It should be noted that in the case of depolarization the effect of lowering the potential should have occurred for both metals in accordance with their concentration in the alloy. As the experimental results show, such a lowering of the deposition potentials is absent for both metals; therefore the explanation given above is untenable.

As is known, in the electrodeposition of nickel, adsorption of hydroxides exerts a sharp inhibiting effect on the process of ion reduction, while in the electrodeposition of iron it is predominantly adsorption of hydrogen atoms ([3]). During the joint discharge of iron and nickel, a decrease in the overvoltage in the reduction of iron ions should be observed, owing to the fact that the alloy absorbs less hydrogen than when only iron is deposited. The increase in the overvoltage in the reduction of nickel ions during joint deposition with iron is due to the enhanced adsorption of hydroxides by the alloy surface compared with the separate deposition of nickel, because hydrate formation of iron begins in a more acidic region than for nickel.

During the electrodeposition of these metals at elevated temperature, the adsorption of both hydrogen and hydroxide decreases sharply, correspondingly···

···accordingly, the content of foreign particles in the deposit is considerably reduced. At the same time, the overvoltage accompanying the deposition of these metals is also sharply decreased.

Figure 2 presents the polarization curves for the separate and joint discharge of nickel and iron ions and, correspondingly, the partial curves in the same solutions, obtained at an elevated temperature of 95°. It is evident from these curves that, in contrast to the curves of Fig. 1, during electrodeposition of nickel and iron at high temperatures the rate of nickel deposition in the alloy is greater than that of iron. Obviously, with an increase in temperature and a decrease in the overvoltage during the deposition of these metals, the rate of ion reduction will be determined mainly by the quantity

$$\varphi_1^0 + \frac{RT}{nF} \ln \frac{\alpha C}{\sum \alpha_i C_i} C;$$

therefore the rate of deposition of a metal with a more positive normal potential

Fig. 3. Dependence of the reduction rate of Ni^{2+} (1) and Fe^{2+} (2) ions during joint discharge on temperature, and change in the electrode potential ϕ.

Figure 2: Fig. 3. Dependence of the reduction rate of Ni^{2+} (1) and Fe^{2+} (2) ions during joint discharge on temperature, and change in the electrode potential ϕ.

will be greater than that of one with a more negative potential, in accordance with condition (1).

Fig. 3. Dependence of the reduction rate of ions Ni^{2+} (1) and Fe^{2+} (2) during joint discharge on temperature, and change in the electrode potential ϕ.

Figure 3 shows the change in the discharge rate of nickel and iron ions during joint electrodeposition from the same solutions as in Fig. 2, as a function of temperature. As is evident from these curves, with increasing electrolyte temperature the rate of reduction of nickel ions increases, while that of iron decreases, and at temperatures above 90° the nickel content in the alloy is greater than that of iron.

The experimental results presented show that the theory of real coupled systems correctly takes into account the regularities of the joint discharge of metal ions.

The observed anomalously high rate of deposition of metal ions with a more negative reduction potential in comparison with more positive ones is associated with a change in the overvoltage of metal deposition during their joint deposition, owing to a change in the nature of the electrode substrate.

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Note: Figure translations are in progress. See original paper for figures.