in turn determines the corrosion behavior of the nickel. In the former case there is active solution of nickel, accompanied (as in the case of copper) by activation of the surface; in the latter case the surface is smoothed out somewhat, and the nickel remains passive.

A comparison of the adsorption isotherms for polished copper 1 and nickel 3 surfaces shows that various amounts of adsorbate are retained on a unit of area at the same potentials. This is apparently due to differences in the degree of surface roughness in nickel and copper with identical preliminary preparation. It may be thought that the roughness factor in mechanical polishing is greater in copper, being softer than nickel [8], which leads to settlement of a larger amount of adsorbate on the copper surface.

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A ROTATING DISK—RING ELECTRODE STUDY OF COPPER CORROSION IN METHANOL (CASE OF METAL IONIZATION COUPLED WITH THE REDUCTION OF STABLE COPPER IONS)

A. N. Molodov, L. A. Yanov, and V. V. Losev

UDC 620.193.01

Certain metals immersed in solutions of their own stable ions dissolve [1, 2] with formation of ions of lower valence, according to the overall reaction

$$M+M^{2+}\rightarrow 2M^{+}. \quad (1)$$

The process continues until the equilibrium concentration of M^+ ions is established in the bulk. Accumulation of M^+ ions in a solution of large volume can require a long period of time and involve significant metal losses due to corrosion. Since the formation of low-valence ion occurs for several metals both in aqueous solutions and in organic solvents (Cu, In, Bi) as well as in melts (Bi, Pb, Cd, Cu, In, Ga, Al, Mg, Be, Na, etc.), cf., e.g., [1-10], it was of interest to determine the characteristics of this type of corrosion. The present paper is aimed at the establishment of the effects of bulk concentration of the M^{2+} oxidant and stirring on both the rate of metal self-dissolution i_c and the corrosion potential φ_c. The mechanism of reaction (1) considered here

$$M\rightarrow M^{+}+e \quad (2a)$$

$$M^{2+}+e\rightarrow M^{+} \quad (2b)$$

$$\overline{M+M^{2+}\rightarrow 2M^{+}}; \quad (2c)$$

is characteristic of metals which dissolve via the following consecutive steps [1, 11-19]:*

*Diagnostic mechanistic criteria for mechanism (2) are discussed in [2].

L. Ya. Karpov Scientific-Research Institute of Physical Chemistry. Translated from Zashchita Metallov, Vol. 12, No. 5, pp. 578-582, September-October, 1976. Original article submitted February 28, 1975.

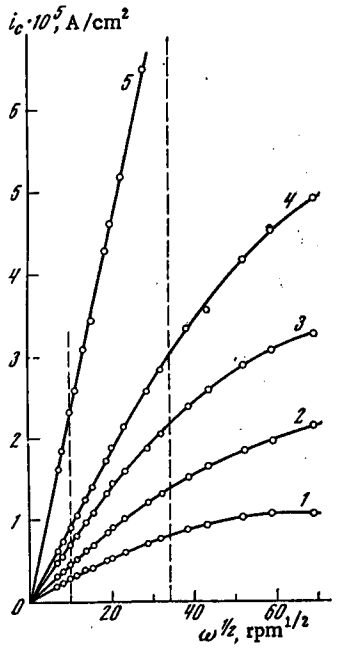

Fig. 1

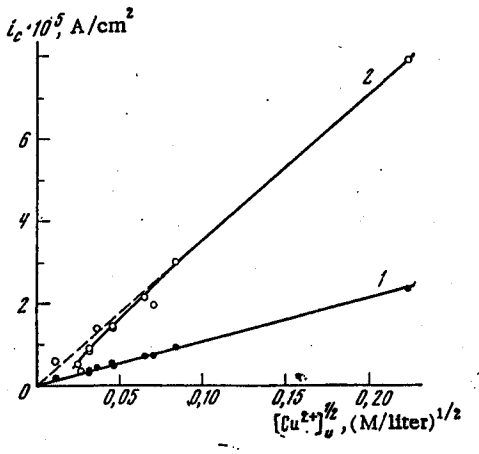

Fig. 2

Fig. 1. The dependence of i_c on $\omega^{1/2}$ for the following $CuSO_4$ concentrations (M/liter): 1) $1 \cdot 10^{-3}$; 2) $2.1 \cdot 10^{-3}$; 3) $4.2 \cdot 10^{-3}$; 4) $7 \cdot 10^{-3}$; 5) $5 \cdot 10^{-2}$.

Fig. 2. The dependence of i_c on $[Cu^{2+}]_{V1/2}$ for ω: 1) 100, 2) 1150 rpm.

$$M \overset{i_{01}}{\rightleftharpoons} M^+ + e, \tag{A}$$

$$M^+ \overset{i_{02}}{\rightleftharpoons} M^{2+} + e, \tag{B}$$

where i_{01} and i_{02} are the exchange currents. It is assumed that the metal is in contact with a stirred solution of infinite volume, in which $[M^+]_V = 0$ and $[M^{2+}]_V = \text{const}$ (consequently, the ψ_1-potential is also constant) throughout the solution [20]. It is also assumed that the solution components are not specifically adsorbed at the surface.

It follows from the stoichiometry of reaction (2c) that the rate of the metal corrosion is given by

$$i_c = 0.5 i_{d1}, \tag{3}$$

where $i_{d1} = (FD_1/\delta_1)[M^+]_S$ is the rate of diffusion of the corrosion products away from the surface, D_1 is the diffusion coefficient of M^+, δ_1 is the thickness of the diffusion layer, and $[M^+]_S$ is the concentration at the electrode interface. The presence in Eq. (3) of the factor 0.5, characteristic of the corrosion case considered, is due to the fact that only one-half of the M^+ flux is directly connected with metal corrosion, i. e., with the transfer of the metal from one phase to another.

It follows from Eq. (3) that the kinetics of metal dissolution should depend on the stirring rate and on the interfacial M^+ concentration. These dependences are conveniently studied using a disk—ring electrode for which $i_{d1} = k_1 \omega^{1/2} [M^+]_S$, where $k_1 = 0.62 FD_1^{2/3} \nu^{-1/6}$, ω is the angular velocity, and ν is the kinematic viscosity. When reaction (1) proceeds on the disk, the ring oxidation current I_R is given by [21]

$$I_R = k_1 S_R N \omega^{1/2} [M^+]_s, \tag{4}$$

where S_R is the ring surface area and N is the collection efficiency. Eliminating $[M^+]_S$ from (3) and (4) we obtain the following relation between i_c and I_R:

$$i_c = 0.5 I_R / S_R N = 0.5 i_R / N, \tag{5}$$

where $i_R = I_R / S_R$ is the ring current density. Thus, the disk corrosion rate can be calculated from the measured I_R value, and consequently the effects of various factors on i_c can be evaluated.

The dependence of i_c on $[M^{2+}]$ and ω will now be considered. From the two possible limiting cases: $i_{01} \gg i_{02}$ and $i_{02} \gg i_{01}$ we shall discuss the first one, as it is most frequently encountered [22]. In this case the metal potential is practically determined by the equation [1, 22]

$$\Delta\varphi = (RT/F) \ln([M^+]_s/[M^+]_e), \quad (6)$$

where $\Delta\varphi = \varphi_c - \varphi_e$, φ_e and $[M^+]_e$ are the equilibrium potential and concentration of M^+ ions for a given $[M^{2+}]_V$, respectively.

Eliminating $[M^+]_S$ from (3) and (6) we obtain

$$i_c = 0.5 i_{d_1}^0 \exp(\Delta\varphi F/RT) = 0.5 k_1 \omega^{1/2} K^{1/2} [M^{2+}]_V^{1/2} \exp(\Delta\varphi F/RT). \quad (7)$$

where $i_{d_1}^0 = (FD_1/\delta_1)[M^+]_e = k_1 \omega^{1/2} K^{1/2} [M^{2+}]_V^{1/2}$ is a quantity numerically equal to the limiting diffusion current of the reduction of M^+ ions at the metal (disk) under conditions of equilibrium concentration of M^+ in the solution and K is the equilibrium constant of reaction (2c). When δ_1 and K are known, the calculation of the corrosion rate from Eq. (7) requires only the measurement of $\Delta\varphi$.

It follows from Eq. (7) that i_c should increase with increasing $[M^{2+}]_V$ and ω. However, under the conditions described above, intensive stirring can result in a decrease of $[M^+]_S$ and a negative shift of φ_c [2, 19], and thus, a decrease of i_c. Furthermore, at constant ω, $\Delta\varphi$ decreases with increasing M^{2+} concentration [19]. Therefore, in order to express i_c as a function of ω and $[M^{2+}]_V$ only, one must know the dependence of φ_c on those paramters. For example, under conditions of weak stirring the M^+ concentration at the electrode hardly decreases and thus, $[M^+]_S = [M^+]_e$ [2, 19] and [cf. Eq. (6)], $\Delta\varphi = 0$, i. e., $\varphi_c = \varphi_e$. Consequently, the metal dissolves under equilibrium conditions, according to reaction (2). In this case it follows from Eq. (7) that

$$i_c = 0.5 i_{d_1}^0 = 0.5 k_1 K_p^{1/2} \omega^{1/2} [M^{2+}]_V^{1/2}, \quad (8)$$

i. e., the reaction order of the metal dissolution with respect to the oxidant equals 0.5. Usually, the corrosion rate is controlled by the stirring-dependent diffusion of the oxidant to the surface and i_c is proportional to the first power of the oxidant's concentration [23].

It should be mentioned that the determination of the i_c (and I_R) dependence on ω and $[M^{2+}]_V$ under equilibrium conditions allows the evaluation of D_1 and K [21], but it cannot lead to the establishment of the kinetic parameters of metal dissolution or the elucidation of the corrosion mechanism [2].

The validity of Eq. (8) [developed for the case of metal corrosion according to sequence (2)] has been tested in a study of the dissolution of copper electrolytically deposited on a platinum disk. The oxidation current of Cu^+ ions, I_R, was measured at a platinum ring ($r_1 = 0.25$, $r_2 = 0.27$, $r_3 = 0.387$ cm) for various values of ω and $[CuSO_4]$ in a methanolic 1 N H_2SO_4 solution (~1% H_2O) in an argon atmosphere at 25°. Under these conditions the coupled discharge—ionization process proceeds for copper according to the (A)—(B) mechanism [2] with formation of considerable amounts of Cu^+ ions [24, 25]. The i_c values were calculated from I_R using Eq. (5). The ring current I_R was measured at $\varphi_R = -0.100$ V (with respect to the aqueous Hg| Hg_2SO_4 reference electrode) which corresponds to the diffusion limiting current region of Cu^+ oxidation [25]. The background current I_B (0.8-4 μA) (corresponding to methanol oxidation [2]) has been taken into account in calculations of i_c. It was assumed that I_B is the same in the presence and absence of Cu^+ ions and remains constant during experiments. This assumption may be erroneous and cause, along with the commensurability of I_B and I_R values, the observed scatter of experimental data. The collection efficiency N = 0.47 was determined by interpolation of the data tabulated in [26].

Upon the introduction of copper ions into the solution the disk potential was found to equilibrate, i. e., to acquire values which obey the Nernst equation ($d\varphi_e/d\log[Cu^{2+}]_V = 32 \pm 2$ mV), at low angular velocities. The appearance of the ring current and its increase with ω shows that copper corrodes and that the corrosion rate increases with ω. Since the disk potential is independent of ω at low values, the corrosion process can be assumed to proceed under equilibrium conditions.

The dependence of i_c on $\omega^{1/2}$ is shown in Fig. 1 for various Cu^{2+} ion concentrations. At lower values the plots are linear and pass through the origin. This result agrees quantitatively with Eq. (8). The dependence of i_c on $[Cu^{2+}]^{1/2}$ at $\omega = 100$ rpm, i. e., under conditions of $\varphi_c \simeq$ const within < 1 mV, is also practically linear and passes through the origin, as predicted by Eq. (8) (Fig. 2, curve 1). Thus, the experimental data concerning copper corrosion in methanol under equilibrium conditions obeys the relationships derived above.

It can be seen in Fig. 1 that at higher ω values the i_c vs $\omega^{1/2}$ plots deviate from linearity. The deviation appears at the lower angular velocities the lower is the bulk concentration of cupric ions. Correspondingly the i_c vs $[Cu^{2+}]^{1/2}$ plots deviate from linearity for high ω values (Fig. 2). These effects are not caused by turbulence, since for a 0.05 M $CuSO_4$ solution the linearity of i_c vs $\omega^{1/2}$ plots is retained even at high ω values. The deviations are caused by the disrupted equilibrium of reaction (2c), as evidenced by a considerable potential change observed at high angular velocities (in our case the potential shifts in the negative direction with increasing ω [2]).

Thus, the rate of corrosion of a metal, whose dissolution is coupled with the reduction of the metal's stable ions and proceeds at a corrosion potential virtually equal to the equilibrium value, has been shown to be proportional to the square root of the oxidant concentration. In spite of this formal similarity to the usually encountered case of corrosion controlled by the rate of oxidant supply, the presently observed i_c vs $\omega^{1/2}$ dependence is due to the slow diffusion of the corrosion products away from the metal. It must be mentioned that the disruption of the equilibrium conditions (as indicated by the decrease of potential with increasing stirring intensity) changes the corrosion kinetics described above.

We express our gratitude to Academician Ya. M. Kolotyrkin for his valuable comments.

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