(steel Kh25T), iron 0.0087 (steel Kh17N13M3T), copper 0.0006 (steel 0Kh21N6M2T), iron 0.0032 (aluminum). For the other impurities (including vanadium), the rate of transfer is less than $2 \cdot 10^{-5}$ g/m$^2 \cdot$ h.

The rate of inflow of impurities into a real apparatus, calculated from our experimental data, revealed that all these structural materials can be used to obtain a specially pure product at an ammonium nitrate concentration of 50 g/liter and 20°C.

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USE OF A DISK ELECTRODE WITH A RING TO STUDY THE LAWS OF CORROSION OF COPPER WITH THE CONJUGATE NONEQUILIBRIAL REACTION OF REDUCTION OF Cu(II) IN METHANOL

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In a previous article [1] we investigated the laws of corrosion of copper in methane according to the overall reaction $Cu + Cu^{2+} \rightarrow 2Cu^{+}$, when the equilibrium of the reaction is practically undisturbed. This reaction appears to be a combination of two conjugate electrochemical reactions [2], as follows:

$$Cu \rightarrow Cu^{+} + e \quad (1)$$

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

$$Cu + Cu^{2+} \rightarrow 2Cu^{+} \quad (3)$$

where the exchange current of the first reaction, i_{e1}, is much greater than the exchange current of the second reaction, i_{e2}. If there is a constant high concentration of Cu^{2+} and a rapid diffusive removal of the corrosion product (i_{d1}), the equilibrium of the slow reaction (2), and consequently that of the overall reaction (3), is disturbed, and the metal dissolves in nonequilibrial conditions [1, 2]. This means that the concentration of univalent ions at the metal surface is less than their concentration for an equilibrial reaction (2), the corrosion potential φ_c is shifted toward the negative ($\varphi_c < \varphi_e$) away from the equilibrium value φ_e for the system Cu^{2+}/Cu, and the corrosion rate i_c increases with the stirring rate more slowly than if reaction (2) were at equilibrium [1, 2].

In [3] we made a quantitative analysis of the laws of solution of metal by scheme (1)-(3) when the reduction of oxidant (stable metal ions) occurs in nonequilibrium conditions. At a rotating disk electrode with a ring, with $i_{e1} \gg i_{e2}$ and $|\Delta\varphi| = |\varphi_c - \varphi_e| \ll RT/F$, the corrosion potential and the current I_R to the ring (proportional to the corrosion rate of the disk [1]*) are given [3] by the following equations:

*The following misprint occurs in [1]. Equations (4) and (5) ought to read

$$I_R = k_1 S_D N \omega^{1/2} [M^+]_s \quad (4)$$

and

$$i_c = 0.5 I_R / S_D N = (0.5 i_R N)(S_R / S_D), \quad (5)$$

where S_R and S_D are the surface areas of the ring and disk and N is the efficiency factor [4].

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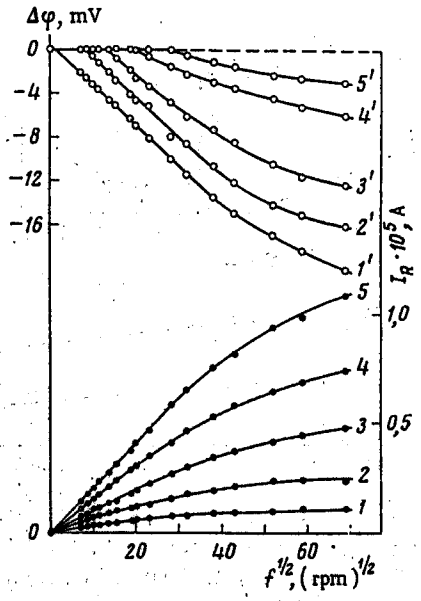

Fig. 1. Graphs of I_R (1-5) and $\Delta\varphi$ (1'-5') vs electrode rotation rate for the following concentrations of Cu^{2+} in moles per liter: 1, 1') $7 \cdot 10^{-4}$; 2, 2') $1 \cdot 10^{-3}$; 3, 3') $2.1 \cdot 10^{-3}$; 4, 4') $4.2 \cdot 10^{-3}$; 5, 5') $7 \cdot 10^{-3}$.

$$\Delta\varphi = -\frac{RT}{4F}\frac{k_1}{{}^0i_{o2}}K_e^{\beta_2/2}\omega^{1/2}[M^{2+}]^{-\beta_2/2}, \tag{4}$$

$$I_R = S_D N k_1 K_e^{1/2}\omega^{1/2}[M^{2+}]^{1/2} \times \left(1 - \frac{k_1}{4\,{}^0i_{o2}}K_e^{\beta_2/2}\omega^{1/2}[M^{2+}]^{-\beta_2/2}\right), \tag{5}$$

where for the stated conditions the relation between I_R and $\Delta\varphi$ is given [1-3] by the equation

$$I_R = S_D N k_1 K_e^{1/2}\omega^{1/2}[M^{2+}]^{1/2}\left(1 + \frac{\Delta\varphi F}{RT}\right). \tag{6}$$

Here ω is the angular rotation frequency, $k_1 = 0.62FD_1^{2/3}\nu^{-1/6}$, D_1 is the diffusion coefficient of M^+, ν is the kinematic viscosity, ${}^0i_{e2}$ and β_2 are the standard exchange current and transport coefficient of reaction (2), K_e is the equilibrium constant of overall reaction (3), and $[M^{2+}]$ is volumetric concentration of the oxidant.

Obviously, if the solution of copper in methanol follows scheme (1)-(3) and if the equilibrium of reactions (2) is disturbed by rapid stirring of the solution [1, 2], then the laws of corrosion of copper must follow Eqs. (4)-(6). With the aid of a rotating disk electrode with a ring, we have further justified mechanism (1)-(3) and have experimentally verified Eqs. (4)-(6).

We measured the zero-current potential φ_c of copper electrolytically deposited on a platinum disk (about 7 μ) and the limiting diffusion current of oxidation of Cu^+ on a platinum ring, I_R, in methanol solution of 1 N H_2SO_4 (~1% H_2O) with an electrode rotation frequency f = 0-4760 rpm and a concentration $[CuSO_4]$ of between 10^{-4} M and 0.1 M in an atmosphere of argon at 25°C. The method was described in detail in [1].

From Fig. 1 we see that at low values of f, the potential of the copper disk practically coincides with the equilibrium potential ($\Delta\varphi = 0$), and the current to the ring rises linearly with $f^{1/2}$ in accordance with Eq. (6) for the case $\Delta\varphi = 0$. This result agrees with the data in [1, 2] on the corrosion of copper in equilibrium conditions. At high values of f, also in agreement with the data in [1, 2] and Eqs. (4)-(6), we observe a shift in the corrosion potential toward the negative ($\Delta\varphi < 0$) and a deviation of the graph of I_R vs $f^{1/2}$ from linearity toward lower values of I_R.

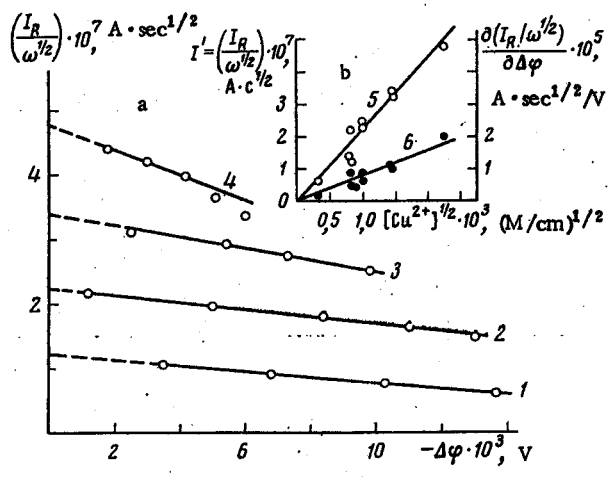

Fig. 2. a) Graphs of $I_R/\omega^{1/2}$ vs $\Delta\varphi$ for the following values of $[Cu^{2+}]$ in moles/liter: 1) $7\cdot 10^{-4}$; 2) $1\cdot 10^{-3}$; 3) $2.1\cdot 10^{-3}$; 4) $4.2\cdot 10^{-3}$; b) graphs of I' (5) and p (6) vs $[Cu^{2+}]^{1/2}$.

As required by Eq. (6), deviation of φ_c from φ_e and deviation of the graph of I_R vs $f^{1/2}$ from linearity occur at the same electrode rotation rate, not only at high values of $[Cu^{2+}]$ but also at low ones (see Fig. 1). In accordance with (4)-(6), the lower the concentration of divalent copper ions, the lower are the values of f at which these deviations set in. Our results show that the criterion for an electrochemical mechanism of formation of univalent ions [2] is satisfied for all $[Cu^{2+}]$, and consequently, for any concentration of divalent ions in the range under study, solution of copper occurs by scheme (1)-(3), and, judging by the direction of the shift in potential, the slowest reaction is (2), the equilibrium of which is also disturbed [2, 5].

In conformity with Eq. (4), at small deviations of the potential its shift with increase of $f^{1/2}$ is linear and its slope is the smaller, the higher is $[Cu^{2+}]$ (Fig. 1). At high concentrations of Cu^{2+} the length of the linear part of the $(\Delta\varphi, f^{1/2})$ graph becomes small (Fig. 1, curve 5'). This is apparently due to violation of the condition $i_{e1} \gg i_{e2}$. Polarization measurements showed that at high concentrations of Cu^{2+} the exchange current of reaction (2) becomes comparable with i_{e1}. For this reason, in the further work the data obtained at high concentrations of Cu^{2+} were not used.

From Eq. (6) it follows that the nonequilibrial parts of curves 1-4 (Fig. 1) for which $i_{e1} \gg i_{e2}$ should become straight lines when plotted as graphs of $I_R/\omega^{1/2}$ vs $\Delta\varphi$; this is confirmed experimentally (Fig. 2a). From Eq. (6) it also follows that the slopes of these lines, $p = \partial(I_R/\omega^{1/2})/\partial\Delta\varphi$, and their intercepts on the axis of ordinates, $I' = (I_R/\omega^{1/2})_{\Delta\varphi=0}$, should be proportional to $[Cu^{2+}]^{1/2}$. This is so within the experimental error (Fig. 2b, curves 5 and 6). The ratio of the slopes of curves 5 and 6 is equal to 0.027 V, i.e., close to the theoretical value of RT/F. According to (6), the value of I' is in fact identical with the slope of the equilibrial linear part of the $(I_R, \omega^{1/2})$ curve. This method of finding the slope of the equilibrial parts of the $(I_R, \omega^{1/2})$ curves from the value of I', i.e., by processing the nonequilibrial parts of these curves, can be useful when we need to study the equilibrium [6], while the experimental $(I_R, \omega^{1/2})$ curves have practically no linear parts even at very low values of ω (Fig. 1, curves 1 and 2).

Putting the value $I' = (I_K/\omega^{1/2})_{\Delta\varphi=0} = S_D N k_1 K_e^{1/2}[M^{2+}]^{1/2}$ into Eq. (5), after some transformations we get

$$I' - (I_R/\omega^{1/2}) = S_D N k_1^2 (4^0 i_{02})^{-1} K_p^{(1+\beta_2)/2} \omega^{1/2} [M^{2+}]^{(1-\beta_2)/2}. \quad (7)$$

From Eq. (7) it follows that at constant concentration of Cu^{2+} the graph of $[I' - (I_R/\omega^{1/2})]$ vs $\omega^{1/2}$ must be a straight line passing through the origin. This is also the case.

In connection with our earlier results [1, 2], these data lead us to the conclusion that the corrosion of copper in a solution of sulfuric acid in methanol containing ions of divalent copper with slow stirring occurs in equilibrium conditions [1], but if the stirring is rapid, in nonequilibrium conditions, according to scheme (1)-(3) with (2) as the slow reaction, and that relations (4)-(6), derived in [3], correctly represent the laws of this type of corrosion. We can suppose that when current is passing, the processes of anodic solution and cathodic deposition of copper in methanol also involve successive one-electron stages.

As already remarked [3], from the experimental data with the aid of relations (4)-(6) we can calculate the kinetic parameters of slow reaction (2) and the equilibrium constant of the overall reaction (3). However, quantitative calculations are rendered difficult by the marked scatter of the experimental data* (see Fig. 2) and the lack of literature data concerning the values of D_l and ν for the solutions used in our work.

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*This scatter is apparently due to the difficulty of eliminating traces of oxygen, which distort the value of I_R, and of maintaining a constant amount of water, formed by the esterification reaction, in the methanol.

ACOUSTIC EMISSION DURING EXFOLIATION CORROSION OF ALUMINUM ALLOYS

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The acoustic emission which arises in materials during deformation [1-3] has been observed also during stress corrosion cracking [4-7]. We have detected and investigated acoustic emission accompanying exfoliation corrosion.

Exfoliation occurs in intermediate products of aluminum alloys with marked deformation textures, linearly textured cathodic inclusions, continuous segregations of the anodic components of the matrix, and high alloying and impurity component contents, especially Mn, Zr, Cr, and Fe. It has been suggested [8] that exfoliation and the roles of the alkali effect and internal stresses have an electrochemical mechanism; however, there is no direct proof that internal stresses take part in corrosive exfoliation.

Following Okada et al. [6], we assumed that the occurrence of acoustic emission (AE) during exfoliation must mean that internal stresses take part in the process, whereas the absence of emission must mean that the corrosion mechanism is purely electrochemical.

The electrical signal from a piezotransducer attached to the specimen was led to a low-noise preamplifier located close to the piezotransducer in order to reduce the signal-to-noise ratio. The active element in the piezotransducer was PTS-19 ceramic with a resonance frequency of 600 kHz. The signal was then amplified by a DUK-66 defectoscope which was used as the main signal amplifier, and was processed by an AÉZ unit, which is a modification of the well-known AÉ2 apparatus [9]. The processing consisted in normalizing the pulse amplitude and measuring the intensity of the AE in analog form. The voltage output from the AÉZ unit was proportional to the AE intensity, i.e., to the number of pulses per unit time; it was fed to a PDP-002 two-coordinate potentiometer for plotting as a diagram. Time sweep along one coordinate of the potentiometer was effected by means of the linear sweep unit of a P5827 potentiostat. At the same time we registered the total number of normalized pulses by means of a Ch3-33 frequency meter. Special care was taken to eliminate extraneous noises registered by the apparatus and to keep down the level of electromagnetic interference.

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