

EFFECT OF THE CONCENTRATION DEPENDENCE OF THE PHYSICAL PROPERTIES OF A SOLUTION OF THE RATE OF ANODE DISSOLUTION OF A METAL

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With the electrochemical dissolution (or deposition) of metals in the preelectrode region of a solution, a large concentration gradient of the solution may be set up. Under these circumstances, there arise corresponding changes in the ionic diffusion coefficients, the viscosity, and the density of the solution, which, in turn, has an effect on the rate of ionic mass transfer with the anode dissolution of a metal. In [1, 2] numerical solutions were obtained to the equations of ionic mass transfer near the surface of a rotating disk under conditions of an intense electrochemical process, leading to a sharp change in the preelectrode physical properties of the solution, as a result of a change in the local concentration of ionic reagents. However, the results of the above work related to only a few fixed volumetric concentrations of the electrolyte and concrete numerical values of the parameters characterizing the local physical properties of the solution. For verification of the postulates of the theory, determination of the parameters of the theoretical model, and an unambiguous interpretation of the experimental data, we require a knowledge of the analytical form of the dependence of the rate of dissolution of the metal on the concentration driving force, i.e., on the preelectrode gradient of the concentration of the ions transferred. An analytical dependence can be obtained if it is postulated that definite limitations are imposed on the concentration driving force. This article gives the derivation of such a dependence, taking account of the effect of the concentration on the diffusion coefficient, the viscosity, and the density of the solution for the case of the anode dissolution of a metal in a solution of its salt.

In [3] an equation was derived for the transfer of cations near the surface of a rotating metallic disk, under conditions of the dissolution of a metal in a concentration solution of its own salt (e.g., iron in a solution of FeCl_2). If no account is taken of the mass velocity of the flow of the solution at the surface of the anode (this velocity is due to the effect of mass transfer on the hydrodynamics, and must be taken into consideration with very high rates of the electrical processes), then, the transfer equation has the form:

$$\frac{M_3 D_2 (z_2 - z_1) v_0^{1/2}}{z_2 D_2 - z_1 D_1} \frac{d}{dy} \left(\frac{Cg}{\rho \bar{v}} \frac{dC_1}{dy} \right) - \frac{i(M_1 D_1 - M_2 D_2) v_0^{1/2}}{\bar{v}_0 \omega D_1^{1/2} F (z_2 D_2 - z_1 D_1)} \times$$

$$\times \frac{d}{dy} \left(\frac{C_1}{\rho} \right) + \frac{2a\rho_0}{\rho} \frac{dC_1}{dy} \int_0^y \int_0^{y'} \frac{\rho(y') \bar{v}_v(y') dy'' dy'}{\rho(y'') \bar{v}_v(y'')} = 0. \quad (1)$$

Here C_1 is the local concentration of the cations of the dissolving metal (everywhere in what follows the subscripts 1, 2, and 3 relate, respectively, to cations, anions, and molecules of the solvent); v and ρ are the local values of the kinematic viscosity and the density of the solution (the corresponding quantities with the subscript 0 relate to conditions in the depths of the solution); y is the dimensionless distance from the surface of the disk, referred to the effective thickness of the diffusional boundary layer:

$$y = \bar{v}_0 \left(\frac{v_0}{D_1} \right)^{1/2} \int_0^x \frac{dx'}{\bar{v}_v(\tau')}$$

where x is the true, dimensional distance; ω is the angular frequency of rotation of the disk;

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i is the density of the anode current; $C = C_1 + C_2 + C_3$ is the total molar concentration of the solution; M_c are the molecular masses of the components of the solution; z_c ($c = 1, 2$) is the valence of the ions; D_c are the ionic diffusion coefficients in an infinitely diluted solution; F is the Faraday number; α is a numerical coefficient, equal to 0.51; g is a function, describing the concentration dependence of the local activity coefficient:

$$g = 1 + \frac{d \ln \gamma_{12}}{d \ln (C_1/C_0)}.$$

Here γ_{12} is the mean activity coefficient of the electrolyte; C_0 is the concentration of electrolyte in the depths of the solution. This function is connected with the apparent ionic diffusion coefficients D_i^* by the relationship [3]

$$D_i^* = - \frac{(z_1 - z_2) D_1 D_2 C}{z_1 D_1 - z_2 D_2} \frac{M_1 M_2}{\rho} g.$$

The solution of Eq. (1) must satisfy the following boundary conditions:

$$\left(\frac{dC_1}{dy} \right)_s = - \frac{i \rho_s \sqrt{\omega} z_2}{z_1 F \sqrt{\omega} (z_2 - z_1) D_1^{1/2} M_2 C_s g_s} \text{ with } y=0; \quad (2)$$

$$C_1 = - \frac{z_2}{z_1} C_{20} \text{ with } y=\infty. \quad (3)$$

Here C_{20} denotes the concentration of anions in the depths of the solution; the subscript s denotes values at the phase interface.

To find the profiles of the concentrations $C_1(y)$, the form of the concentration dependences $v(C_1)$, $\rho(C_1)$ and $g(C_1)$ must be made concrete. The existing experimental data in the literature can be correlated in sufficiently general form using the following dependences [4-6]:

$$v = v_s \exp \left[\frac{n}{C_{20}} (C_1 - C_{1s}) \right]; \quad \rho = \rho_s \exp \left[\frac{m}{C_{20}} (C_1 - C_{1s}) \right]; \quad (4)$$

$$g = g_s \exp \left[\frac{-k}{C_{20}} (C_1 - C_{1s}) \right],$$

where n , m , and k are empirical constants. The numerical values of these constants for some substances are given in the literature (see, e.g., [5]).

We substitute expression (4) into Eq. (1) and, in the subsequent calculations, by C_c and $C = \sum_{c=1}^3 C_c$ we shall understand the dimensionless ratios corresponding local concentrations to

C_{20} . We introduce also the quantity $I = \frac{i v_0^{1/2} D_1^{-1/2}}{z_1 F C_{20} \sqrt{\omega}}$.

As a result of this statement, we obtain the following boundary-value problem:

$$\frac{d}{dy} \left\{ g_s C \exp \left[- \left(m + \frac{n}{2} + k \right) (C_1 - C_{1s}) \right] \frac{dC_1}{dy} \right\} + A \exp[-m(C_1 - C_{1s})] \int_0^y \int_0^{y'} \exp \left\{ \left(m + \frac{n}{2} \right) [C_1(y') - C_1(y'')] \right\} dy'' dy' - \quad (5)$$

$$- \chi B \frac{d}{dy} \{ \exp[-m(C_1 - C_{1s})] C_1 \} = 0$$

$$\frac{dC_1}{dy} = \chi \text{ with } y=0; \quad (6)$$

$$C_1 = -\frac{z_2}{z_1} = C_{10} \quad \text{with} \quad y = \infty, \quad (7)$$

where

$$A = \frac{2a\rho_0(z_2D_2 - z_1D_1)\sqrt{v_s}}{(z_2 - z_1)D_2M_3C_{20}\sqrt{v_0}}, \quad B = -\frac{z_1C_{20}g_sC_s(M_1D_1 - M_2D_2)}{\rho_s z_2 D_2}$$

$$\chi = z_1 I \sqrt{\frac{v_s}{v_0}} \frac{M_1D_1 - M_2D_2}{(z_2 - z_1)M_3D_2B}$$

In what follows we postulate that: 1) the relative concentration of the solvent C_s makes the principal contribution to the value of C , and does not change in the preanode space during the dissolution process: $C \approx C_s = \text{const}$ (the local density of the solution can nevertheless depend to a considerable degree on the spatial coordinate y , e.g., as a result of the large molecular mass of the metal M_1); 2) the parameter χ is small in comparison with unity; 3) the concentration of cations at the surface of the anode can be assumed to be a given quantity: $C_1 = C_{1s}$ with $y = 0$. Cases of given concentrations of the cations of the dissolving metal at the surface of the anode can, in practice, be realized under conditions of saturation of the preelectrode layer by these cations. This occurs, e.g., with the anode dissolution of iron, nickel, cobalt, and a number of alloys [7] in solutions of sodium chloride.

Equation (5) of convective diffusion was solved by the method of successive approximations. In the zero approximation, assuming that $\chi \rightarrow 0$, the solution of (5) can be written in the form

$$C_1 = C_{1s} + \chi \Phi(y); \quad \Phi(y) = \int_0^y \exp\left(-\frac{\alpha y'^3}{3}\right) dy'; \quad \alpha = \frac{A}{2C_s}. \quad (8)$$

Using expression (8), we can rewrite Eq. (5) in the first approximation with an accuracy to terms on the order of x^2 .

$$\frac{d^2C_1}{dy^2} = \frac{dC_1}{dy} \left\{ -\alpha y^2 + \chi \left(m + \frac{n}{2} + k \right) \frac{d\Phi}{dy} - \chi \alpha \left(\frac{n}{2} + k \right) \Phi(y) y^2 + \right.$$

$$\left. + 2\alpha \chi \left(m + \frac{n}{2} \right) [\Psi(y) - F(y)] + \frac{\chi B}{C_s g_1} \right\}; \quad (9)$$

$$\Psi(y) = \int_0^y dy' \int_0^{y'} \Phi(y'') dy'', \quad F(y) = \int_0^y y' \Phi(y') dy'.$$

Integrating Eq. (9), the dependence of the gradient (dC_1/dy) on the difference in concentrations $\Delta C = C_{1s} - C_{10}$ can be obtained in explicit form. After substitution of this dependence into Eq. (2), we obtain an expression for the flow of mass from unit area of the surface of the rotating disk

$$I = \lambda \Delta C \left\{ 1 - \left[0.418m + 0.091n + 0.272k + 0.561 \frac{B}{C_s g_1} \right] \Delta C \right\}, \quad (10)$$

where

$$\lambda = 0.778 \frac{M_3 D_2 B (z_2 - z_1)}{z_1 (M_2 D_2 - M_1 D_1)} \frac{\sqrt{v_0}}{\sqrt{v_s}} \alpha^{1/4}.$$

Thus, a theoretical analysis has shown that, under the above conditions, the current of the anode dissolution of a rotating metallic disk in a solution of its own salt is proportional

to $\frac{\rho_0}{\rho_s} \left(\frac{v_0}{v_s} \right)^{1/2} v_0^{-1/4}$. In accordance with the traditional [8] equation of convective diffusion

for a rotating disk electrode, the current is proportional to $v_0^{-1/6}$. Further, the current is not proportional to the concentration drop ΔC , as in the traditional theory, but contains higher powers of ΔC (the approximation which we have considered corresponds to taking account of square terms with respect to ΔC).

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EFFECT OF CHEMICAL AND PHASE INHOMOGENEITY ON FORMATION OF ELECTROPOLISHING DEFECTS IN NICKEL ALLOY

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There is a relatively small range of electrolyte constituent working concentrations for electropolishing dispersion-hardened nickel-based alloys in sulfuric-phosphoric acid electrolyte [1]. We discovered that smoothing out of initial microinequalities was accompanied by appearance of pits over the grain body with quenched alloy and also by pitting along the grain boundaries with aged alloy when KhN70MVTYuB nickel alloy* was polished in an electrolyte of normal composition ($8 \text{ N H}_2\text{SO}_4 + 27 \text{ N H}_3\text{PO}_4$) (Fig. 1).† When more than 10μ of metal are removed, this reduces the initial surface finish standard by 1-2 classes and affects the fatigue strength of components. According to published findings, the chemical and phase compositions of alloys affect the formation of electropolished surface microgeometry [2]. Metallographic investigations were carried out to find the causes of electropolishing defects in KhN70MVTYuB alloy; a study was also made of alloying element distribution in the grain boundary zone and near inclusions in the grain body. Specimens for metallographic and microanalytical studies ("Samesa" x-ray microanalyzer, localization of electron probe 1μ) were cut from KhN70MVTYuB alloy components on which electropolishing defects were clearly apparent. The prepared microsections were etched electrochemically [3] to reveal the microstructure (Fig. 2). The grain boundary sectors chosen for x-ray microspectral analysis were marked on a PMT-3 microhardness gauge. Since the depressions along the grain boundaries were unlike in nature, it was assumed that the alloy composition and the amount of segregated phases also altered, both in the direction perpendicular to the boundary and along the grain boundaries; the analysis was therefore made in several cross sections in various sectors of the boundaries (Fig. 3).

The metallographic findings led to the conclusion that continuous chains of carbide segregations formed on the grain boundaries in KhN70MVTYuB alloy in the process of aging (Fig. 2). They are cubic chromium carbide Cr_{23}C_6 and form minute globules measuring from 0.05 to 1μ .

* Alloy chemical composition (mass %) according to Technical Specifications: chromium 16-19, titanium 1.9-2.8, aluminum 1-1.7, molybdenum 1-6, tungsten 2-3.5, columbium 0.5-1.3, carbon ≤ 0.12 , remainder nickel.

† Heat treatment routine: 1) quenching 1200° , 5 h, cooling in air; 2) quenching 1070° , 8 h, cooling in air + aging 800° , 16 h, cooling in air.

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