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Abstract

Full Text

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Approximate Calculation of the Leveling Effect in the Electrochemical Deposition of a Metal

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Recently, reports have appeared on the possibility of leveling the microprofile in the process of galvanic production of metallic coatings (^{1}). This phenomenon is to a certain extent similar to smoothing during electrochemical polishing (^{2}). It has been established that the effect is associated with the preferential adsorption of molecules of surface-active substances on the protruding regions of the microprofile (^{3}).

If one takes into account that the rate of diffusion of molecules of surface-active substances through the diffusion layer to the protruding parts of the microprofile is greater than to the depressions, then the reason for their preferential accumulation on the protrusions is clear. On the other hand, it is known that an increase in the concentration of adsorbed molecules of surface-active substances produces a certain additional obstacle to the discharge of metallic ions. Thus, despite the fact that the transport of metal ions through the near-electrode diffusion layer to the protruding regions of the microprofile is greater than to the depressions, passivation of the former due to enhanced adsorption of foreign molecules can not only reduce the relative growth rate of a microprotrusion, but under certain conditions lead to inversion of the process.

For a quantitative estimate of this phenomenon, let us turn to the device used by us earlier to describe the mechanism of smoothing during electrochemical polishing (^{4}). The rate of change of the microprofile dH/dt will, obviously, in this case also be proportional to the difference between the current densities of metal dissolution* at the highest i_Λ and lowest i_ν points of the surface. And since at the upper and lower points of the microprofile the directions of the current vectors coincide with the normal to the plane of the electrode, the tangential components of these vectors are equal to zero, and therefore one may write

$$\frac{dH}{dt} = \frac{M}{\rho n F}(i_\Lambda - i_\nu), \tag{1}$$

where M, ρ, n are respectively the molecular mass, density, and valence of the metal; i_Λ, i_ν are the normal components of the current vector at the extreme points, equal to their vectors at these points.

Let us consider the case in which the height of the protrusion $H < \delta \ll a$ (δ is the effective mean thickness of the diffusion layer, a is the base of the protrusion). In the presence in the electrolyte of foreign molecules adsorbing on the electrode surface, the current density, other conditions being equal, will be a function of the distance from the given surface point to the outer boundary of the diffusion layer and of the surface concentration of foreign molecules s. For a protrusion and for a depression we shall have, respectively:

$$i_\Lambda = i(\delta - H,\, s + \Delta s); \qquad i_\nu = i(\delta + H,\, s - \Delta s). \tag{2}$$

Expanding in a series, we obtain:

$$i_\Lambda = i(\delta_1 s) - \frac{\partial i}{\partial \delta} H + \frac{\partial i}{\partial s} \Delta s - \ldots; \qquad i_\nu = i(\delta_1 s) + \frac{\partial i}{\partial \delta} H - \frac{\partial i}{\partial s} \Delta s + \ldots \tag{3}$$

Substituting (3) into (1), we shall have

$$\frac{dH}{dt} = \frac{2M}{\rho n F} \left[\left(\frac{\partial i}{\partial s} \right) \Delta s - \left(\frac{\partial i}{\partial \delta} \right) H \right]. \tag{4}$$

According to what was said above, $(\partial i / \partial \delta) < 0$ and $(\partial i / \partial s) < 0$; therefore, in the case

$$|(\partial i/\partial \delta) H| < |(\partial i/\partial s)\Delta s|$$

the profile is leveled, and conversely.

For the case of concentration polarization, under the condition $a \gg \delta$, one may put [^4]

$$(\partial i/\partial \delta) \simeq -i/\delta, \tag{5}$$

Let us proceed to estimate the second term in equation (4). First we shall find $(\partial i/\partial s)$. We shall assume that the current density during crystallization is proportional to the probability of nucleus formation. For this case it has been shown [^5,^6] that it depends on the concentration of surface-active substances:

$$i = i_0 \exp\left(-4 r_0 \sqrt{sN}\right), \tag{6}$$

where r_0 is the radius of the nucleus, i_0 is the current density in the absence of surface-active substances, and N is Avogadro' s number. Differentiating (6), we obtain

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* In cases of gas evolution, the current efficiency should be taken into account.

$$(\partial i/\partial s) = -2r_0 N^{1/2} s^{-1/2}. \tag{7}$$

We shall find the quantity Δs in the following way. The flux of the surface-active substance f to the metal surface is equal to

$$f = D_e(\partial c_e/\partial y)_{y=0} \simeq D_e(c_e - c_e^*)/\delta, \tag{8}$$

where c_e and c_e^* are the bulk concentrations of molecules, respectively, in the bulk electrolyte and at the metal surface, and D_e is the diffusion coefficient of the molecules of the surface-active substance. For not too large values of c_e, the adsorption isotherm equation, giving the relation between the bulk and surface concentrations, may be written in the form

$$c_e^* = Gs, \tag{9}$$

where G is the adsorption coefficient. Substituting (9) into (8), we obtain

$$f = D_e(c_e - Gs)/\delta. \tag{10}$$

The rate of "burial" of molecules in the deposit, f_1, under stationary conditions is

$$f_1 = isM'/\rho nFh \tag{11}$$

(where h is the linear size of foreign molecules) and is equal to their supply rate f. Comparison of expressions (10) and (11) gives the relation between s and c_e:

$$s = c_e/(G + \mu i), \tag{12}$$

where $\mu = M\delta/\rho nFD_{eh}$.

It is obvious that the sum of the molecular fluxes to the depression and to the protrusion is equal to twice the mean flux to the metal surface, i.e., $f_v + f_\lambda = 2f(\delta, s)$. Expanding the left-hand side of this equality in a Taylor series in powers of H and Δs and retaining terms up to the second degree, we obtain

$$\frac{\partial^2 f}{\partial s^2}(\Delta s)^2 - 2H\Delta s\frac{\partial f}{\partial s}\frac{\partial f}{\partial \delta} + \frac{\partial^2 f}{\partial \delta^2}H^2 + ... = 0, \tag{13}$$

whence, on the basis of (10), $(\partial^2 f/\partial s^2) = 0$, $(\partial f/\partial s\,\partial\delta) = GD_e/\delta^2$, and $(\partial^2 f/\partial\delta^2) = 2D_e(c_e - Gs)/\delta^3$, which after substitution into (13) gives

$$\Delta s = H(c_e - Gs)/G\delta. \tag{14}$$

Comparing (14) and (12), we obtain

$$\Delta s = c_{eH}\mu i/\delta G(G + \mu i). \tag{15}$$

Substituting relations (5), (8), (15) into (4), with account taken of (12), we obtain

$$\frac{dH}{dt} = \frac{2MiH}{\rho nF\delta}\left(1 - \frac{2r_0\mu i}{G}\sqrt{\frac{Nc_e}{G+\mu i}}\right) = \frac{2iM}{\rho nF\delta}\alpha H. \tag{16}$$

Equation (16) admits integration, as a result of which we obtain

$$H = H_0 \exp(-2Mi\alpha t/\rho nF\delta). \tag{17}$$

The latter, just as in the case of electropolishing ⁽²⁾, has an exponential form and differs only in the value of the quantity α.

Equation (17) satisfies the following conditions: 1) at $i = 0$, $dH/dt = 0$; 2) at $c_e \to 0$, $dH/dt > 0$, and in this case smoothing regions do not exist for any values of i; 3) if $c_e > 0$, then at $0 < i < i_{\mathrm{n}}$ there lies the region of profile distortion ($dH/dt > 0$). Taking into account that, as the current density increases, the radius of the two-dimensional nucleus must decrease, at $i_{\mathrm{n}} < i < \infty$ there lies the smoothing region ($dH/dt < 0$), where i_{n} is the second root of equation (16), corresponding to the inversion point.

In order to carry out a more complete analysis of the relation obtained, let us estimate the order of magnitude of some of the quantities entering into it. Let us determine the order of $\mu = M\delta/\rho_{nFD_{eh}}$. Since $M/\rho \simeq 10$ cm^3, $\delta \simeq 10^{-2}$ cm, $D_e \simeq 10^{-5}$ cm$^2 \cdot$ cm^{-1}, $h \simeq 10^{-7}$ cm, then $\mu \simeq 10^6$ cm^{-1}/a. It may be assumed that the adsorption coefficient G has a value of $10^6 - 10^4$ cm^{-1}. Thus, the product μi reaches the value G at a current density of 0.1—1.0 a/cm^2. Therefore, for values of G of the order of 10^6—10^4 cm^{-1} and $i < 1$ a/cm^2, expression (16) may be simplified:

$$\frac{dH}{dt} = \frac{2MiH}{\rho nF\delta}\left(1 - 2r_0\mu i\sqrt{\frac{Nc_e}{G^3}}\right). \tag{18}$$

Let us turn to the investigation of the dependence of the expressions obtained on the current density. The magnitude of the two-dimensional nucleus, as is known, is related to the overvoltage η by the relation

$$r_0 = \theta M/\rho n F \eta, \tag{19}$$

where θ is the peripheral energy. Taking $\theta \simeq 10^3$ erg/cm, $M/\rho = 10$ cm^{-3}, we obtain $r_0 \simeq 10^{-8}/\eta$ (where η is measured in volts). Since the overvoltage for the case of deposition of most metals at low densities is proportional to i, then

$$r_0 = 10^{-8}/k_1. \tag{20}$$

Thus, for small current densities

$$\frac{dH}{dt} = \frac{2MHi}{\rho n F \delta}\left[1 - \frac{10^{-8}\mu}{k_1}\sqrt{\frac{Nc_e}{G^3}}\right]. \tag{18a}$$

Taking the overvoltage at current densities of the order of 10^{-4}—10^{-5} a/cm^2 to be equal to 10 mV, we obtain $k_1 = 10^3$—10^2 Ω. Then the second term in brackets is equal to 10^{-2}—10^{-3}. Therefore, at low current values in the electrodeposition process only profile distortion is possible. On the other hand, at considerable current densities the dependence of η on i is

$$\eta = k_2 \lg bi \tag{21}$$

(where k_2 and b are empirical constants). For the case of deposition of nickel from a sulfate electrolyte, one may take $k_2 = 10^{-1}$ V, $\lg b = 10$ (7). Substituting (20), we estimate the magnitude of the second term in (18) for this case. We obtain

$$\left(\frac{\partial i}{\partial s}\right)\Delta s = \frac{10^{-8}\cdot 10^6(6\cdot 10^{23})^{1/2}}{10^{-1}(10+\lg i)}\frac{c_e^{1/2}}{G^{3/2}}.$$

Table 1 gives the values of i_{n} at which $dH/dt = 0$ (transition region) for different values of $(c_e G^3)^{1/2}$. The range of variation of the latter quantity was investigated for the range of changes in c_e from 10^{-1} to 10^{-4} mol/cm^3 and G from 10^3 to 10^6 cm^{-1}.

Table 1

$(c_e G^3)^{1/2}$	10^{11}	10^{10}	10^9	10^8	10^7
i, a/cm^2	10.3	$8.2\cdot 10^{-1}$	$7.2\cdot 10^{-2}$	$6.4\cdot 10^{-3}$	$6.1\cdot 10^{-4}$

As is seen from Table 1, real values for i are obtained at $(c_e/G^3)^{1/2}$ of the order of 10^8 and lower, which corresponds to high concentrations c_e ($> 10^{-4}$ mol/l) and high adsorbability ($G \ll 10^3$ cm^{-1}).

In conclusion, we note that, as the calculations show, the exponential character of the dependence of the mean height of a microprofile irregularity on the electrolysis time is general in character for most cases of anodic and cathodic behavior of metals.

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REFERENCES

1. D. Whitwhan, P. Lelong, *Metaux*, **33**, No. 391, 101 (1958); S. S. Kruglyshev, N. T. Kudryavtsev et al., *ZhPKh*, **35**, No. 4 (1962).
2. S. I. Krichmar, *DAN*, **100**, No. 3, 48 (1955); *ZhFKh*, **31**, No. 7, 1598 (1957).
3. S. E. Beacom, B. J. Riley, *Studies on the Influens of Organic Addition Agents on the Electrodeposition of Nickel*, Michigan, 1961.
4. S. I. Krichmar, *DAN*, **144**, No. 4, 833 (1962).
5. Erdey–Gruz, Volmer, *Zs. Phys. Chem.*, **157**, 165 (1931).
6. S. I. Krichmar, *ZhFKh*, No. 1 (1962); *DAN*, **151**, No. 3 (1963).
7. V. I. Lainer, N. T. Kudryavtsev, *Fundamentals of Electroplating*, 1, Moscow, 1953, p. 419.

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