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S. I. Krichmar

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Abstract

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S. I. Krichmar

On the Theory of the Growth of Filamentary Crystals on the Cathode

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One of the most thoroughly studied processes of formation of galvanic deposits is the growth of filamentary silver crystals from solutions of simple salts, investigated in the works of K. M. Gorbunova, P. D. Dankov, and A. T. Vagramyan ([1], [2]). In ([1]) an attempt was made at a semi-quantitative approach to the phenomenon under consideration. A deeper theoretical analysis was given by Price et al. ([3]), who showed, in particular, that the current density to the end face of a growing filamentary crystal obeys the following dependence:

$$i \sim (C_e/R)^{1/3}, \tag{1}$$

where C_e is the concentration of the surface-active substance, and R is the radius of the filament. However, because of the considerable simplifications admitted, the analysis does not lead to the experimentally established fact that the current density is independent of the radius of the filament at large values of R ([1], [2]).

The theoretical calculation of this process given below is free of a number of shortcomings. We shall proceed from the idea that the growth of filamentary silver crystals is associated with the presence in the electrolyte solution of surface-active impurities. In ([4]) it was shown that the probability of formation of a two-dimensional nucleus w is related to the surface concentration of impurities σ by the relation

$$w = K \exp(-4r\sqrt{\sigma N}), \tag{2}$$

where r is the radius of the nucleus, N is Avogadro' s number, and K is a constant. If it is assumed that the growth of each subsequent layer begins with the formation of a nucleus, then substitution into (2) of the value of the mean frequency ν of formation of a new layer per unit time,

$$w \sim \nu = iM/\rho nFh_m \tag{3}$$

(where n, ρ, and M are respectively the valence, density, and molecular weight of the metal, and h_m is the size of its atom), gives

$$i = i_0 \exp(-4r\sqrt{\sigma N}); \tag{4}$$

here i_0 is the current to the same surface in the absence of surface-active substances.

The limiting possible diffusion current to a surface of considerable curvature, for which the tip of the growing filamentary crystal may approximately be regarded, will be:

$$i = nFD_mC_m/R, \tag{5}$$

where D_m is the effective diffusion coefficient of the metal ions, in the general case taking into account the migration of ions under the action of the electric field, and C_m is the concentration of metal ions.

The diffusion flux of impurity molecules f_1 to the tip of the growing filament may be written, in the first approximation for the case of a spherical surface, as follows:

$$f_1 = D_e(C_e - C_{es})/R \tag{6}$$

(D_e is the diffusion coefficient of the impurity molecules, C_e and C_{es} are the volume concentrations, respectively, in their bulk volume and at the metal surface). On the other hand, under steady-state conditions the rate of delivery of molecules to the growing surface is equal to the rate of their burial f_2. According to (3), the amount of contaminating substance adhering to a unit of growing surface per unit time, provided that the sizes of the metal atoms and impurity molecules are equal, is equal to $\sigma iM/\rho nFh_{\mathrm{M}}$. However, since the dimensions of the impurity molecules h_e may be greater than the thickness of a monoatomic layer of the metal, the rate of adhesion and, consequently, of their burial will evidently be

$$f_2 = (\sigma iM/\rho nFh_{\mathrm{M}})(h_{\mathrm{M}}/h_e) = \sigma iM/\rho nFh_e. \tag{7}$$

For small concentrations the adsorption isotherm has the form

$$\sigma = GC_{es}, \tag{8}$$

where G is the adsorption coefficient. Equating (6) and (7), taking (8) into account, we obtain:

$$C_e = \sigma \left(\frac{iMR}{nF\rho D_e h_e} + \frac{1}{G} \right). \tag{9}$$

The radius of a two-dimensional nucleus, as is known, is related to the overvoltage η by the relation

$$\eta = \theta M / \rho n F r, \tag{10}$$

where θ is the edge surface energy.

In the absence of surface-active substances, for small values of η the overvoltage is linearly related to the current density

$$i = b\eta. \tag{11}$$

Substituting expressions (9), (10), and (11) into (4), we finally obtain

$$i \ln \frac{i_0}{i} = \frac{4\theta M b}{\rho n F} \sqrt{\frac{C_{eNG}}{(iMGR/nF\rho D_e h_e) + 1}}. \tag{12}$$

Let us explain the physical meaning. According to the present concepts, preferential growth of the metal at one or several sites of the cathode is associated with the most favorable conditions for formation of a nucleus on the growing surface, owing to the larger area of surface free of contamination and to the decrease in the size of the nucleus, which is caused by the increased value of the overvoltage in the growth regions; this is observed at comparatively high current densities. At lower densities, when the rate of adsorption of impurity molecules predominates over the rate of their being embedded in the metal, only the second factor—the magnitude of the overvoltage—is of principal importance, since the character of the distribution of impurity molecules is then practically the same over the entire cathode surface.

At large values of i in the denominator of the expression under the radical one may neglect unity. Applying the iteration method to solve the transcendental equation (12), taking (5) into account, we find:

$$i \approx \frac{B_1 C_e^{1/3}}{R^{1/3} \left[\ln \left(\frac{nFD_{\mathrm{M}} C_{\mathrm{M}}}{B_1 R^{2/3} C_e^{1/3}} \right) \right]^{2/3}}, \tag{13}$$

where $B_1 = (16\theta^2 NMD^2_{eh_{eb}} / \rho n F)^{1/3}$. Comparison of the expressions obtained with formula (1) shows that at large current-density values both methods of calculation lead to close results, since the magnitude of the logarithm in the

denominator depends only very weakly on the change in the radius of the filament, all the more so because the current density varies over not very wide limits (on the order of several hundred times). The agreement of the available experimental data with dependence (1) is considered in detail in ([3]), and there is no need to present these data again.

Investigation of (12) at small values of i, i.e., of the surface concentration σ, leads to the expression

$$i \ln \frac{i_0}{i} = \frac{4\theta M b\,(GN\sigma)^{1/2}}{\rho n F}, \tag{14}$$

since in this case in (12) the first term in the denominator under the radical becomes much less than 1 and may be omitted. In this case, if i_0 remains greater than i, then, iterating (14), we find:

$$i \simeq \frac{B_2 C_e^{1/2}}{\ln\left(\dfrac{nF D_M C_M}{B_2 R C_e^{1/2}}\right)}, \tag{15}$$

where $B_2 = 4\theta M b\,(GN)^{1/2}/\rho n F$. As is evident from the last expression, at small i, and also C_e and G, the current density depends only very weakly on the radius of the filament. Thus, the constancy of the current density experimentally observed by a number of investigators for comparatively thick filamentary crystals is connected not only with the concentration of impurities, but also with their adsorption capacity (G) and with the character of the slope of the overvoltage curve of the depositing metal.

Table 1

Gelatin concentration, g/l	i, A/cm^2, experiment	i, A/cm^2, calculation	Filament growth rate, μ/min
0.095	0.8	1.7	50
0.22	1.7	1.9	100
0.52	2.5	3.4	150
0.75	4.2	4.2	250
1.00	6.2	4.6	380

In agreement with experiment we find, further, that at $C_e = 0$ one of the roots of (12) and (14) gives $i = i_0$ (the second root $i = 0$ has no meaning, since the current density under the given condition remains a finite quantity). Equation (15) gives a decreasing dependence between the current density and

the concentration of metal ions, which is confirmed by experimental data on the dependence of i on the concentration of $AgNO_3$ ([1]).

According to ([3]), for the case of a 1 N solution of $AgNO_3$ at 25°C, k (in our case b) is 80 A/cm$^2 \cdot$ V. Taking the magnitude of the edge energy in the formation of a two-dimensional nucleus as $\theta \approx 10^3$ erg/cm^2, the dimensions of the overvoltage molecules and their diffusion coefficient as, respectively, $h_e \approx 10^{-7}$ cm, $D_e \approx 10^{-6}$ cm^2/sec, the molar volume of silver $M/\rho \approx 10$ cm^3, the diffusion coefficient of its ions, with allowance for the migration effect, as $D_M \approx 2 \cdot 10^{-5}$ cm^2/sec, and substituting these quantities into (13), we shall have

$$i = 8 \left(\frac{C_e}{R} \right)^{1/3} \left[\ln \frac{2C_M}{BC_e^{1/2} R^{2/3}} \right]^{-2/3};$$

the coefficient obtained is close to the value found in work ([3]).

Unfortunately, at the present time data on the values of the adsorption coefficients are lacking; therefore, to estimate the results obtained from equation (15), we rewrite it in the form

$$i = B_2' \sigma^{1/2} \{ \ln(nFD_M C_M / B_2' R \sigma^{1/2}) \}^{-1}, \tag{15a}$$

where $B_2' = 4\theta MbN^{1/2}/\rho nF$. Substituting into (15a) the numerical values of the quantities entering it, we find

$$i \simeq 10^6 \sigma^{1/2} \left[\lg(3 \cdot 10^7 C_M / R\sigma^{1/2}) \right]^{-1}.$$

If, for example, we assume that the surface concentration σ is 10^{-2}% of the limiting value ($\sigma_{\lim} = 10^{-10}$ mol/cm^2), i.e., 10^{-14} mol/cm^2, $R \approx 10^{-3}$ cm, $C_M \approx 10^{-3}$ mol/cm^3, then i will be of the order of 10^{-1} A/cm^2, i.e., we obtain a quite realistic value. B_2 can also be calculated from experimental data using equation (15). Table 1 gives the results of comparison of the current density calculated from expression (15a) and found experimentally from the work of K. M. Gorbunova and A. I. Zhukova ([1]) during the growth of thick filaments (current strength 10^{-6} A, $C_{AgNO_3} = 1.5$ g-eqv, $B_2' = 4.7$).

In conclusion, let us consider the nature of the polarization in the growing filament. The concentration component, evidently, can be calculated from the known relation

$$\eta_k = -\frac{R_{kT}}{nF} \ln \left(1 - \frac{i}{i_0} \right) = -\frac{R_{kT}}{nF} \ln \left(1 - \frac{iR}{nFD_M C_M} \right). \tag{16}$$

For the case of thick crystals, the expression for the chemical polarization also has a comparatively simple form. Comparing (4) and (10), taking (15a) into account, we obtain:

$$\eta_x = \frac{40M\sqrt{\sigma N}}{\rho n F \ln(i_0/i)} = \frac{B_2\sqrt{C_e}}{b\ln(i_0/i)}. \tag{17}$$

For the case of growth of a filament of radius $4 \cdot 10^{-4}$ cm at $C_e = 0.5$ g/l gelatin in $1.5\,N$ $AgNO_3$, the total polarization will be

$$\Delta\varphi = \eta_k + \eta_x = \left[0.025 \ln\left(1 - \frac{1.7 \cdot 10^{-4} \cdot 4}{3 \cdot 10^{-3}}\right) + \frac{47(0.5)^{1/2}}{80 \ln 4.4}\right] = (5{+}25)\text{ mV} = 30\text{ mV};$$

experimentally determined, it was in this case about 25 mV. The low values of concentration polarization, and the predominance of chemical inhibition due to the delay in the formation of two-dimensional nuclei, which follow from relations (16) and (17), agree well with the experimental facts obtained in work ([1]).

Dneprodzerzhinsk Branch
of the State Institute of the Nitrogen Industry

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