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Abstract

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Change in the Microgeometry of a Surface during Anodic Dissolution of Metals

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In studies of the processes of electrochemical etching and polishing, considerable attention is paid to investigating the microgeometry of the surface of the metal being treated. This question is discussed in a number of works. There have been attempts at a quantitative approach to individual specific cases, for example: calculation of the diffusion mechanism of smoothing during electrochemical polishing ($^{1-3}$), etc. Of interest is a more general formulation and investigation of the problem of the change in the microgeometry of a metal surface during anodic behavior.

We shall proceed from the following assumptions. In a number of cases of anodic (and sometimes simply chemical) behavior of a metal, a homogeneous layer of electrolyte is formed at its surface, differing in composition and in certain other properties from the bulk of the solution, or a homogeneous phase film. Moreover, although the character of the conductivity of this layer is in general not known to us, it may be asserted that on protruding portions of the microprofile, for an electrochemically homogeneous metal, where the layer thickness is smaller, the dissolution current density is higher than in depressions. Let us consider the dissolution of an electrochemically heterogeneous surface with an average value of the deviations of the potentials of the portions ε and with an arbitrary microprofile under a layer of this kind (Fig. 1). In our reasoning we use the fact, known from practice, that the effective thickness of the layer formed, δ, as a rule exceeds the dimensions of the irregularities of the microprofile H, so that the outer boundary of the layer, facing the electrolyte, will be practically flat and will not reproduce the microrelief. Let the selected points 1 and 2, situated at a distance $2H$, be extreme points (1—the highest, 2—the lowest point of the profile). At these points the height of the irregularity H and the current densities i_1 and i_2 are normal to the profile surface.* It is easy to see that the rate of its change, on the basis of Faraday' s law, will be equal to:

$$-dH/dt = M(i_1 - i_2)/\rho n F, \quad (1)$$

where t is the electrolysis time; M, ρ, n are, respectively, the molecular weight, density, and valence of the dissolving metal.

If one takes into account that the overvoltage in the anodic process is, as a rule, very small, then, other conditions being equal, the current densities at the portions will be functions of their electrochemical potentials, associated with the crystalline and chemical structure of the constituents of the surface at these places, and of the distance between the metal surface and the outer boundary near-anode layer. We use the fact that a decrease in the thickness of the near-anode layer and an increase in the anodic potential each, taken separately and together, cause an increase in the current density, and conversely. This gives grounds for writing, for a protrusion, $i_1 = i(\delta - H, \varphi + \Delta\varphi_1)$, and for a depression, $i_2 = i(\delta + H, \varphi - \Delta\varphi_2)$, under the condition $\partial i/\partial\delta < 0$. Here $\Delta\varphi_1$ and $\Delta\varphi_2$ are, respectively, the deviations from the value of the electrode potential at the point O for the selected regions. In the general case, choosing the point O, equidistant from regions 1 and 2, does not yet mean equality of these deviations, so that $\Delta\varphi_1 \neq \Delta\varphi_2$.

Expansion of i_1 and i_2 in series under the condition that $\partial i/\partial\delta$ is negative gives:

$$i_1 = i(\delta, \varphi) + \frac{\partial i}{\partial \delta}H + \frac{\partial i}{\partial \varphi}\Delta\varphi_1 + \left\{\frac{\partial^2 i}{\partial \delta^2}H^2 + 2\frac{\partial i}{\partial\delta\,\partial\varphi}H\Delta\varphi_1 + \frac{\partial^2 i}{\partial\varphi^2}\Delta\varphi_1^2\right\} + \ldots,$$

$$i_2 = i(\delta, \varphi) - \frac{\partial i}{\partial \delta}H - \frac{\partial i}{\partial \varphi}\Delta\varphi_2 + \left\{\frac{\partial^2 i}{\partial \delta^2}H^2 + 2\frac{\partial i}{\partial\delta\,\partial\varphi}H\Delta\varphi_2 + \frac{\partial^2 i}{\partial\varphi^2}\Delta\varphi_2^2\right\} + \ldots \quad (2)$$

Substitution of (2), under the condition $H < \delta$ and $(\Delta\varphi_1 + \Delta\varphi_2) < \varphi$, gives, after discarding terms containing higher powers:

$$-\frac{dH}{dt} \cong \frac{2M}{\rho nF}\left[\left|\frac{\partial i}{\partial \delta}\right| H + \frac{\varepsilon}{2}\left(\frac{\partial i}{\partial \varphi}\right)\right] = \frac{2M}{\rho nF}\left[|a|\frac{H}{\delta} + b\frac{\varepsilon}{\varphi}\right], \quad (3)$$

where $\varepsilon = \Delta\varphi_1 + \Delta\varphi_2$, by assumption, is the mean value of the deviation of the anode potential; $|a| = \delta\,|\partial i/\partial\delta|$ and $b = 0.5\,\varphi\,(\partial i/\partial\varphi)$ are constants, and when using (3) explicitly it should be borne in mind that the sign before a has already been taken into account. Especially noteworthy is the particularly good convergence of (3) with respect to the degree H, since the terms containing even powers disappear. Taking into account that, in the notation adopted, H is half the protrusion, provided the values of the derivatives coincide or do not change too rapidly with increasing order, in practice expression (3) may be used for the ratio H/δ up to 0.25.

Since $2H$ in fact characterizes the average height of the irregularity of the microprofile, it is clear that the constants a and b will, respectively, be functions

- In the presence of gas evolution at the anode, i determines only the current density of metal dissolution.

of the mean effective value of the diffusion-layer thickness δ and of the electrode potential φ. Of course, in the dissolution process the potentials of particular regions may change discontinuously owing to the disappearance of one or another crystalline element of the surface; but if the uniform statistical distribution of inclusions in the bulk of the metal is taken into account, then, in a dimensionless form, expression (3) may be integrated over the limits from H_0 to H, considering ε constant:

$$H = H_0 e^{-\alpha\tau} + \frac{\beta}{\alpha}\left(e^{-\alpha\tau} - 1\right), \tag{4}$$

where $\alpha = 2M|a|/\rho nF\delta$, $\beta = 2Mb\varepsilon/\rho nF\varphi$.

Analysis shows that, for a negative cathodic value of ε, under the condition $\beta/\alpha < -H$, a further etching process occurs; for $-H < \beta/\alpha < 0$, partial suppression of etching takes place. In the case of a positive value of ε, the profile is first leveled (until the moment $\tau = \frac{1}{\alpha}\ln\left(\frac{\alpha}{\beta}H_0 + 1\right)$), and then a depression is formed in place of the protrusion. As in the preceding case, when $\beta/\alpha > H$ further dissolution will occur; when $0 < \beta/\alpha < H$, partial suppression of etching occurs. Complete suppression of etching is effected when $\beta = 0$, which is possible when either ε or $\partial i/\partial\varphi$ is equal to zero.

The physical picture is fairly simple to imagine if one takes into account that a positive value of ε indicates an increase in the anodic potential of the protrusion in comparison with the region in the depression. This leads to an additional increase in the dissolution rate of the protrusion. In the case of a negative (cathodic) value, on the contrary, a factor appears that retards the dissolution of the metal on the protrusion and leads to the predominance of ra-

dissolution of the metal in the depression. On the basis of (4) it is possible to estimate the possible scale of etching.

For $\tau \to \infty$, from (4), obviously, we shall have:

$$H_n = \frac{b}{|a|}\frac{|\varepsilon|}{\varphi_c}\delta_c. \tag{5}$$

Of course, the rate of change of the form of the microprofile may prove to be considerably less than the rate of dissolution of the anode metal, and this will lead to disappearance of the regions under consideration before the etching size stationary under the given dynamic conditions is established; however, taking into account the statistical character of the distribution of the crystalline constituents over the surface and into the depth of the metal, the indicated scale of etching is ultimately established.

In a number of works ($^{2-4}$) it was indicated that, under certain conditions, the current density on different parts of the microrelief ceases to be a function of their potentials (the limiting current on the $I\varphi$-curve). In this case conditions are created for smoothing the surface microprofile (polishing). Putting in (4) $(\partial i/\partial\varphi)=\beta=0$, we obtain

$$H=H_0\exp\left(-\frac{2M|a|\tau}{\rho nF\delta_c}\right). \tag{6}$$

Thus, the logarithmic character of smoothing of a rough surface during electrochemical polishing does not depend on the nature and character of the near-electrode layer.

With a certain specification of the character of the conductivity of the near-electrode layer, using the indicated method, one can obtain a number of dependences, some of which were obtained by us earlier by more complicated methods ([2,3,5]). Thus, for the case of concentration polarization we shall have: $(\partial i/\partial\delta)=nFD\left[d\left(\partial C/\partial y\right)/d\delta\right]$, but $(\partial C/\partial y)\cong(C_0-C_e)/\delta$ (where C_e is the concentration in the bulk of the solution). Differentiation gives:

$$a=-nFD(C_0-C_e)/\delta. \tag{7}$$

If, however, the layer has a character of conductivity close to ohmic, the estimate of a can be made in the following way. We have $i\sim\varphi/\delta$, $(\partial i/\partial\delta)\sim-\varphi/\delta^2$,

$$a=-i. \tag{8}$$

The value $b=0.5(\partial i/\partial\varphi)\varphi$ can be found from an estimate of the slope angle of the tangent at the given point of the polarization curve. Thus, we obtain the relation:

$$H=H_0\exp\left(-\frac{2Mi\tau}{\rho nF\delta}\right)+\frac{\varepsilon\delta}{2i}\left(\frac{\partial i}{\partial\varphi}\right)\left[\exp\left(-\frac{2Mi\tau}{\rho nF\delta}\right)-1\right]. \tag{9}$$

In the region of the limiting current $(\partial i/\partial\varphi)\cong0$, whence we shall have

$$H=H_0\exp\left(-\frac{2Mi\tau}{\rho nF\delta}\right). \tag{10}$$

We shall obtain the scale of etching by putting in (3) $dH/dt=0$

$$H_{\text{tr}}=\frac{|\varepsilon|\delta}{2i}\left(\frac{\partial i}{\partial\varphi}\right). \tag{11}$$

In conclusion I consider it my duty to express gratitude to V. P. Galushko for discussion of the question and to Yu. A. Chizmadzhev, who made valuable comments when reading the manuscript.

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