Reports of the Academy of Sciences of the USSR

S. I. KRICHMAR

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 122, No. 3

PHYSICAL CHEMISTRY

S. I. KRICHMAR

ON THE SCALES OF STRUCTURAL ETCHING DURING ELECTROCHEMICAL POLISHING OF METALS

(Presented by Academician A. N. Frumkin, 17 V 1958)

In a number of works (^{1,2}) it has been shown that, despite the high degree of perfection of the metal surface after electrochemical polishing, in a number of cases it possesses an etching structure. G. S. Vozdvizhenskii (^{2}) showed that even in those cases when the etching structure cannot be detected by direct microscopic examination, its existence can be demonstrated by a number of other methods (the maximum-gloss method (^{3}), etc.).

Electropolishing processes, like other processes of anodic dissolution, are directly connected with the destruction of the faces of the crystals of which the surface being treated is composed. The electrochemical inhomogeneities of these faces, depending on the circumstances, may appear in the form of microstructural etching to a greater or lesser degree. As is known, during electrochemical polishing, etching of the surface, as a rule, is not observed under microscopic examination. We have shown that in this case conditions are created that favor the suppression of ordinary structural etching (^{4}). However, the possibility is not excluded that revelation of the crystalline structure of the metal may occur on finer, submicroscopic scales, at which the influence of factors restraining etching is considerably weaker.

As is evident from the data presented in (^{4}), during electrochemical polishing the smoothing of the microrelief of the surface of a pure metal after etching does not differ from the smoothing of traces of mechanical working. This gives grounds to suppose that, in the present case, conditions are realized that not only favor smoothing but also, at certain scales, hinder the manifestation of the individual features of the separate crystalline components of the surface. As was noted in (^{4}), these conditions are most often realized in the limiting-current region, where, owing to the formation of a saturated layer of reaction products,

Fig. 1. Schematic distribution of the concentration of reaction products at the surface of an etching anode (deformed layer removed)

Figure 1: Fig. 1. Schematic distribution of the concentration of reaction products at the surface of an etching anode (deformed layer removed)

and sometimes the formation of a solid film, the volt-ampere characteristics of different structural elements converge.

However, when considering a dissolving anode it is necessary to take into account that, near very small crystalline inclusions, regions of supersaturation will exist. This should lead to an increase in the concentration gradient and, consequently, in the current density in these regions. Dissolution here will proceed more intensively until the gradient is equalized through an increase in the distance between the surface of the anode in this region and the outer effective boundary of the diffusion layer. In the case of the formation of solid films on the anode surface, mass transfer occurs through pores in them. The presence at the surface of regions with elevated concentration should in this case also cause more intensive dissolution of the metal in these regions. It follows from what has been set forth that electrochemical polishing of metals cannot prevent decrystallization

crystalline formations, the dimensions of which have a noticeable influence on the increase in the solubility of the metal.

Let us estimate the scales of etching. We shall consider the simplest case of the behavior of an anode made of a pure metal in an electrolyte that does not form passive films in the range of potentials under consideration. For small potentials, the current densities—at different parts of the anode (i_1) and averaged over the anode (i)—may be represented by the following equations:

$$i_1 = nFD\,\mathrm{grad}\,C_1, \tag{1}$$

$$i = nFD\,\mathrm{grad}\,C = nFD\left(\frac{\partial C}{\partial x}\right)_{x=0} \simeq nFD\frac{C_\Gamma - C_0}{\delta}, \tag{2}$$

where D is the effective diffusion coefficient, δ is the effective mean thickness of the diffusion layer at the anode, and δ_1 is that at a surface element. Evidently, on most surface elements it is possible to find extremal points where $\left(\frac{\partial C_1}{\partial y}\right) = \left(\frac{\partial C_1}{\partial z}\right) = 0$* (Fig. 1). Therefore, with a known approximation one may write:

Fig. 1. Schematic distribution of the concentration of reaction products at the surface of an etching anode (deformed layer removed)

$$i_{1\mathrm{extr}} \simeq nFD\frac{C_1 - C_0}{\delta_{1\mathrm{extr}}} = nFD\frac{C_1 - C_0}{\delta + H}, \tag{3}$$

where H is the magnitude of the deviation from the plane of the anode, determining the scales of etching; C_Γ and C_1 are, respectively, the concentrations: averaged over the anode and at surface elements. With sufficiently prolonged dissolution, the current densities at different regions become equalized. Equating (2) and (3), we obtain:

$$H = \delta(C_1 - C_0)(C_\Gamma - C_0)^{-1}. \tag{4}$$

The value C_1, as indicated above, depends on the deviation of the potential of a region from the mean potential of the anode in connection with the individual crystalline features of the regions (ε_a) and on the influence of the sizes of the crystals on the increase in solubility (ε_r). We have:

$$\varepsilon = \pm\varepsilon_a + \varepsilon_r, \tag{5}$$

where ε is the total deviation of the potentials of the regions from the mean statistical potential of the electrode. For ε we have:

$$\varepsilon = \frac{RT}{nF} \ln \frac{\gamma_1 C_1'}{\gamma_\Gamma C_\Gamma'}, \tag{6}$$

where C_Γ, C_1 and γ_Γ, γ_1 are, respectively, the ionic concentrations and activity coefficients of the reaction products. For most cases of electrochemical polishing the reaction products are weakly dissociated. Taking into account the first degree of dissociation, we obtain:

$$\varepsilon = \frac{RT}{2nF} \ln \frac{C_1}{C_\Gamma}. \tag{7}$$

For ε_r one may write:

$$\varepsilon_r = 2\sigma M(nF\rho r)^{-1}, \tag{8}$$

where σ is the surface tension at the metal-solution boundary, r is the effective radius of the crystalline inclusion.

Combining (5), (7), and (8), we obtain, for small ε:

$$C_1 \simeq C_r \left[1 \pm 2nF\varepsilon_a(RT)^{-1} + 4\sigma M(RT\rho r)^{-1}\right]. \tag{9}$$

After substituting (9) into (4), we shall have:

---

* It is meant that there are no traces of mechanical treatment on the surface (the deformed layer has been removed).

$$H = \delta C_r (C_r - C_0)^{-1} \left[4\sigma M (RT\rho r)^{-1} \pm 2nF\varepsilon_a (RT)^{-1}\right]. \tag{10}$$

The unlimited increase of H with a corresponding decrease of r is impeded by the sizes of the crystals. Therefore one may speak of maximum crystal sizes whose etching is not retarded by suppressing factors. Denoting the effective radius of such a crystal by r_0 and substituting r_0 for H in (10), we obtain:

$$r_0 = \frac{\delta C_r}{RT(C_r - C_0)} \left[\sqrt{(nF\varepsilon_a)^2 + \frac{4\sigma MRT(C_r - C_0)}{\rho\delta C_r}} \pm nF\varepsilon_a\right]. \tag{11}$$

At low current densities, if ε_a is sufficiently large, the first term in (10) may be neglected. Then

$$r_0 = H = \pm 2nF\delta C_r \varepsilon_a (RT)^{-1} (C_r - C_0)^{-1}. \tag{12}$$

Since δ is of the order of 10^{-2} cm (for the case of natural convection (^{5},^{6})), and the difference in the dynamic potentials of the faces of one and the same crystal reaches tenths of a volt (^{7}) (for example, for copper), according to (12) we obtain $r_0 \approx 10^{-1}$ cm. In reality r_0 is considerably smaller, since the treated surface is, as a rule, textured by preliminary mechanical treatment and therefore proves to be formed mainly by the same faces of the crystals (^{8}). Here ε_a is of the order of millivolts, and r_0, accordingly, is $10^{-2} \div 10^{-3}$ cm, which is confirmed by experiment.

On approaching the limiting current, in individual most electropositive regions of the surface the concentration of reaction products reaches saturation. A further increase in the electrochemical potential of these faces becomes impossible. Under these conditions ε_a decreases, and in the region of the limiting-current plateau it even becomes zero. In this case

$$r_0 \simeq 2 \left[\delta\sigma M C_r (C_r - C_0)^{-1} (\rho RT)^{-1}\right]^{1/2}. \tag{13}$$

As is evident from (13), here etching proceeds at the expense of the increased solubility of small crystals.

The considerations discussed are equally acceptable for the case in which the surface is covered by a thin passivating layer, since such a layer practically completely reproduces the microrelief of the metal surface, and at the boundary solid film–electrolyte the same concentration relations are established as when the solution is in contact with a clean metal surface.

For the case of dissolution of copper in H_3PO_4 we have $\delta = 10^{-2}$ cm (^{5}), $\sigma = 2 \cdot 10^3$ dyn/cm (^{9}), $M = 64$ g/mol, $\rho = 8$ g/cm^3, $C_r/(C_r - C_1) = 1$ (the case when $C_0 = 0$). For r_0 we obtain an order of 10^{-4} cm. An increase in temperature and a decrease in the thickness of the diffusion layer favor further suppression of etching. The linear dimensions of the etching figures in the case under consideration are so small that their detection by ordinary microscopic methods is almost impossible. However, as was indicated above, this submicrostructure can be detected by other methods. For example, electron-microscopic studies of an electrochemically polished aluminum surface (18000×) have shown that the surface has a cellular structure ([10]), the cell dimensions not exceeding tenths of a micron.

As for the upper limit of smoothing in electrochemical polishing, it is determined by the ratio of the dimensions of the irregularities to the thickness of the diffusion layer in cases of weak passivity or its complete absence, and, in cases of formation of thick passive layers (of the order of several microns and higher*), by the ratio of the dimensions of the irregularities to the thickness of this layer. If the dimensions of the irregularities are so large that the outer boundary of the diffusion layer or of the thick passive layer repeats the surface relief, smoothing will not occur. Most probably, this will take place when H is of the same order as δ. Since the values of δ under natural convection are of the order of 10^{-3}–10^{-2} cm, the upper limit will be of the same order.

It follows from the foregoing that electrochemical polishing may be regarded as a process that hinders structural etching and smooths irregularities of the microrelief only on certain scales—from 10^{-3} to 10^{-5} cm.

Received
15 X 1956

REFERENCES CITED

1. G. S. Vozdvizhenskii, DAN, **58**, 1587 (1948); G. S. Vozdvizhenskii, G. N. Deziderev, V. A. Dmitriev, ZhFKh, **25**, 547 (1951).
2. G. S. Vozdvizhenskii, G. N. Deziderev, V. A. Dmitriev, DAN, **65**, 697 (1949).
3. G. Tammann, *Metallovedenie*, Moscow–Leningrad, 1955, p. 118.
4. S. I. Krichmar, V. P. Galushko, ZhFKh, **30**, 577 (1956).
5. S. I. Krichmar, DAN, **100**, 481 (1955).
6. V. G. Levich, *Physicochemical Hydrodynamics*, Publishing House of the Academy of Sciences of the USSR, 1952, p. 106.
7. G. S. Vozdvizhenskii, V. A. Dmitriev, E. V. Rzhevskaya, ZhFKh, **29**, 280 (1955).

8. G. S. Vozdvizhenskii, A. Sh. Valeev, V. A. Dmitriev, Proc. Conf. on Electrochemistry, Publishing House of the Academy of Sciences of the USSR, 1953, p. 151.
9. S. I. Krichmar, DAN, **101**, 237 (1955); *Handbook of the Metallurgist for Non-Ferrous Metals*, **1**, 1940.
10. P. V. Shchigolev, ZhFKh, **29**, 682 (1955).
11. A. T. Vagramyan, A. P. Popkov, DAN, **102**, 297 (1955).

* For example, in the electropolishing of silver in cyanide baths (11).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.