SOME ASPECTS OF THE INFLUENCE OF ADDITIONS OF SURFACE-ACTIVE SUBSTANCES ON THE ELECTRODEPOSITION OF METALS

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UDC 621.357.7

The qualitative principles of the adsorption of surface-active substances on metal as a function of its potential, expressed in a reduced scale, are successively examined. The peculiarities of the behavior of various crystal faces distinguishing solid metals from liquid mercury are analyzed. The disruptions of adsorption equilibrium caused by the incorporation of adsorbed substances into the cathodic deposits and some of their consequences are considered as a function of the conditions of deposition.

It is known that addition of surface-active substances are widely and successfully used for the modification of many properties of cathodic deposits of various metals: luster, contour, hardness, etc., as well as for an intensification of electrodeposition processes.

The choice of the additives and the selection of their optimum concentration are performed almost exclusively empirically — by means of long, numerous, and painstaking experiments. The explanation for this should be seen in the fact that the action of additives depends on very many factors: on their nature and the nature of the metal, on the composition of the solution, the intensity of its movement, temperature, etc. It is extremely difficult to take all these factors into account. However, an attempt can be made to determine which of them are the most important and to consider the probable nature of their influence. The present article is devoted to an analysis of some of these questions.

Regardless of the mechanism of action of additives, their adsorption on the surface of the metal should be considered as a necessary intermediate step. In view of this, any method yielding any, even approximate information on the adsorption of additives on an interphase between a metal, especially a solid metal, and the medium is of interest. One of these methods is the method based on the concept of the reduced potential scale [1-3]. In this scale, the zero point of the metal is selected as the beginning of the reading. The value of the potential in the reduced scale is determined from the equation

$$\varphi=\varepsilon-\varepsilon_N, \tag{1}$$

where ε is the potential of the metal under the given conditions, while ε_N is its zero point, expressed in the same arbitrary scale, e.g., the hydrogen scale. The potential φ thus does not depend on the arbitrary scale used and represents an approximate measure of the charge relative to the solution under conditions corresponding to the potential ε.

A peculiarity of the reduced scale is the fact that it permits a comparison of the electrochemical and adsorption processes on different metals at approximately the same charges of the surface (φ potentials), i. e., under conditions of approximately equal manifestation of the forces of electrostatic interaction. This permits the use of data obtained on one metal for predicting the results that might be expected when analogous processes occur on another metal or metals in the same solutions, when definite conditions are observed. Thus, if we know the region of potentials within which adsorption of some compound from its aqueous solution of mercury is observed, we can calculate the region of potentials within which the same compound will be adsorbed on a different metal, let us say, on lead.

Let us assume that some surface-active compound R, at a volume concentration C_R^0, is adsorbed on mercury in the region of potentials from +2 to −0.5 V according to the hydrogen scale. Desorption of this compound occurs as a result of the fact that at the indicated potentials it is displaced from the double layer either by water molecules or by cations or anions of the electrolyte.

Kiev Polytechnic Institute. Translated from Zashchita Metallov, Vol. 14, No. 4, pp. 387-392, July-August, 1978. Original article submitted August 9, 1977.

The zero point in water is equal to −0.19 V according to the hydrogen scale; its value is rounded off to −0.2 V to simplify the calculations. Consequently, the positive potential of desorption $_{Hg}\varphi_d^+$ under the conditions selected will be

$$_{Hg}\varphi_d^+ = {}_{Hg}\varepsilon_d^+ - {}_{Hg}\varepsilon_N = +0.2 - (-0.2) = +0.4 \text{ V}, \quad (2)$$

and the negative potential

$$_{Hg}\varphi_d^- = {}_{Hg}\varepsilon_d^- - {}_{Hg}\varepsilon_N = -0.5 - (-0.2) = -0.3 \text{ V}. \quad (3)$$

As a first assumption, which, by the way, is extremely often justified [4, 5], it can be assumed that the desorption of a given compound from the surface of other metals will occur as a close value of the charge [2, 3, 6, 7], i. e., at approximately the same values of the φ potential. For lead, selected as such a different metal, we can consequently expect that the compound R will also be adsorbed in the region of φ potentials from +0.4 to −0.3 V.

$$_{Pb}\varphi_d^+ = {}_{Pb}\varepsilon_d^+ - (-0.7) = +0.4 \text{ V} \quad (4)$$

and

$$_{Pb}\varphi_d^- = {}_{Pb}\varepsilon_d^- - (-0.2) = -0.3 \text{ V}. \quad (5)$$

This region, however, will correspond to entirely different values of the potential along the hydrogen scale, since the zero points of mercury and lead differ. The zero point of lead is close to −0.7 V, and, consequently,

$$_{Pb}\varepsilon_d^+ = {}_{Pb}\varphi_d^+ + {}_{Pb}\varepsilon_N = 0.4 - 0.7 = -0.3 \text{ V}. \quad (6)$$

and

$$_{Pb}\varepsilon_d^- = {}_{Pb}\varphi_d^- + {}_{Pb}\varepsilon_N = -0.3 - 0.7 = -1.0 \text{ V}. \quad (7)$$

We can thus assert, on the basis of the data obtained on mercury, that the compound R should be adsorbed on lead between −0.3 and −1.0 V, and in this region of potentials (along the hydrogen scale) we should expect an influence of adsorbed particles of R on the processes that occur on the lead electrode, e. g., on the liberation of hydrogen, on the reduction of some substances, etc. This compound should not influence the deposition of lead from sulfate solutions, which occurs beyond the limits of the region $\varphi_d^+ - \varphi_d^-$.

Evidently such conclusions would be impossible without the use of the reduced potential scale. Therefore, its use substantially facilitates the selection of surface-active substances — luster formers, equalizing agents, condensers, and other additives — and introduces a definite rational element into it.

At the same time, it must be emphasized that the considerations outlined are only a first approximation, and the actual relationships are considerably more complex.

These complications arise primarily in connection with peculiarities distinguishing solid metals from liquid metals, i. e., from mercury, which was selected as the standard, since the phenomena of adsorption can most easily be investigated on it. The differences between solid metals and mercury are usually more appreciable, the more "rigid" the given metal, i. e., the higher its melting point and hardness. All solid metals can be arbitrarily divided into "soft" with melting points mp no higher than 350°C and hardness H no greater than 10 kgf/mm^2 and "hard" for which mp > 350°C, while H > 10 kgf/mm^2 [7]. The soft metals* include liquid metals, alkali and most of the alkaline-earth metals, as well as Bi, Cd, In, Sn, Pb, Tl, et al.; the hard metals include metals of the platinum and iron groups, Ag, Cu, Zn, et al. On the surface of all the hard polycrystalline metals, there will be facets of various symbols. The percent yield of these facets will differ substantially, depending on the history of the given metal sample, in particular, on the conditions of its preparation. On a soft metal these differences will gradually be leveled out (as a result of their relatively high fluidity), while on a hard metal they should be preserved for a long time. Facets of different symbols differ in density of packing and, consequently, in a number of other properties as well, in particular, in work function.

*We should note that the division into "hard" and "soft" metals [8] approximately coincides with the distribution of metals between electrochemical groups I and II, suggested earlier [1, 9]. Recently this division has also been used by other authors, only they call soft metals mercurylike [10].

It can be considered proven that the zero point is a function of the work function, which is rendered for aqueous solutions by the approximate equation [3, 7]

$$_{M}\varepsilon_{N} = \frac{1}{F}\omega_{e}^{M} - 4.7. \quad (8)$$

Each facet is therefore characterized by its own intrinsic value of the zero point, while the average value of the zero point of a polycrystalline sample of any metal should be a function of the fraction of the yield of facets of different symbols on its surface, i. e., a function of the history and prehistory of the sample. In this we can probably see one of the causes of the poor experimental reproducibility of the values of the work function and zero points of hard metals. Furthermore, since each facet possesses its own zero point, we should expect substantial differences in the behavior of the same substances in contact with liquid and solid metals. In the sequence from mercury to hard metals, the region of potentials within which adsorption of the same substance is possible should be expanded. Moreover, the adsorption of this substance and its influence on kinetics should be different on different facets, which can lead, e. g., to a change in the texture of the deposit.

Let us elucidate these questions for the example of such a typical hard metal as copper (mp = 1083°C, H = 40 kg/mm^2). Copper has a fcc lattice, and it is characterized by facets with symbols (011), (001), and (111). The ratio of the density of packing for these facets is 1:1.38: 1.65. The facet (001), which determines the texture of the copper deposit when it is isolated from sulfate electrolytes, is the most stable. It is believed that the electron work function decreases with increasing density of packing; therefore, its value should increase in the direction (111) (001) (011); according to Eq. (8), the positive value of the zero point should increase in the same direction. Usually the difference in the work functions for the facets (011) and (001) or (001) and (111) is 0.1-0.3 eV. Approximately this difference (0.15 ± 0.04 V) has been found, e.g., for the zero points of the octahedral (111) and cubic (001) facets of a single crystal of silver [11]. If we assume that the calculated value of the zero point of copper −0.2 V pertains to the facet (001), then the facet (111) can be assigned a value of −0.4 V, and the facet (001) a value of ± 0.0V.* For each of these facets, the widths of the region of adsorption of the substance R at a concentration of it in solution C_R^0 remains the same, i. e., will be bounded by $_{Cu}\varphi_d^+ = +0.4$ and $_{Cu}\varphi_d^- = -0.3$ V, while the regions of adsorption in the hydrogen scale will correspond, respectively, to

$$_{Cu(111)}\varepsilon_d^+ = +0.4 - 0.4 = \pm 0.0 \text{ V} \quad (9)$$

and

$$_{Cu(111)}\varepsilon_d^- = -0.3 - 0.4 = -0.7 \text{ V} \quad (10)$$

for the facet [111];

$$_{Cu(001)}\varepsilon_d^+ = +0.4 - 0.2 = +0.2 \text{ V} \quad (11)$$

and

$$_{Cu(001)}\varepsilon_d^- = -0.3 - 0.2 = -0.5 \text{ V} \quad (12)$$

for the facet [001];

$$_{Cu(011)}\varepsilon_d^+ = +0.4 \pm 0.0 = +0.4 \text{ V} \quad (13)$$

and

$$_{Cu(011)}\varepsilon_d^- = -0.3 \pm 0.0 = -0.3 \text{ V} \quad (14)$$

for the facet [011].

Thus, for a polycrystalline sample of copper, on the surface of which all three facets are present, the region of adsorption is expanded in comparison with a homogeneous surface of mercury and now encompasses not 0.7 V, but 0.4 − (−0.7) =1.1 V. However, it should be noted that primarily one facet is usually present on the surface of the metal, and therefore the expansion of the region of adsorption should not be so pronounced.

Under conditions of the occurrence of most electrochemical processes, the surface of the metallic electrode can be considered equipotential. However, inhomogeneity with respect to the value of the charge corresponds to this, since facets of different symbols have different zero points, and, consequently, according

* Direct measurements give values differing somewhat from those cited here, and the differences in the values of ε_N for different facets of the single crystal are smaller [12]; this, however, is of no vital importance.

to Eq. (1), their charge will differ at the same potential. The adsorption of the substance R should therefore proceed at different rates on regions of the electrode corresponding to facets at different symbols. Thus, let us assume that processes of deposition of copper from a sulfate solution containing the additive R in a concentration C_R^0 occur at a potential 0.3 V, i. e., at a comparatively low current density. At this potential, the adsorption of the additive R is possible only on the facet (011), which should lead to changes in the conditions of formation of the cathodic deposit in comparison with the pure solution. When the current density increases and a potential from 0.2 to 0.1 V is reached, adsorption of the additive R also becomes possible on the facet (001). When the potential is further displaced in the negative direction, adsorption of the additive proved impossible on the facet (011), and, on the contrary, is appreciable on the facet (001). Thus, a change in the current density (electrode potential) leads to a redistribution of the additive over the surface and to a corresponding change in the rates of growth of its various portions, i. e., to a change in the structure and texture of the deposit.

All these considerations are correct only if reversible adsorption of the additive is not disrupted in the course of the electrode process. This condition is observed in electrocapillary and capacitance measurements on mercury, but is not fulfilled during many electrochemical processes, including the electrodeposition of metals. Surface-active additives are either incorporated into the metal deposit or are subjected to electrochemical or chemical conversion. The decrease in the content of the additive in the layer near the electrode should be covered by its delivery from the depth of the solution. This is accomplished (against a background of a concentrated electrolyte solution) by diffusion and conversion. If the deviation from equilibrium is small, then the content of the additive close to the electrode decreases somewhat, e. g., to the value of C_R; a concentration gradient is created, which ensures the necessary rate of supply of the additive to the surface

$$_Ri_d=k(C_R^0-C_R). \tag{15}$$

Adsorption equilibrium is still preserved here, but the surface concentration of the additive already corresponds not to the initial volume concentration C_R^0, but to its concentration in the layer near the electrode, i. e., to a lower value of C_R. To establish the region of adsorption, we should now use the electrocapillary curve, taken in a solution not with concentration C_R^0, but in a solution with a lower concentration C_R, which leads to a narrowing of the region of potentials within which adsorption of the additive R is possible. With increasing deviation from equilibrium, the value of C_R, and, consequently, the region of adsorption will continuously decrease. * In the limit, the concentration of the additive in the layer near the electrode will approach zero, while the rate of its delivery to the surface of the electrode will approach the limit:

$$_Ri_l=kC_R^0. \tag{16}$$

In this case, roughly speaking, all particles of the substance R that have reached the cathode will be incorporated into the deposit or subjected to electrochemical conversion, if the electrode potential lies within the region of adsorption. Otherwise the action of the additive will cease, its concentration in the perielectrode layer will increase, until its adsorption on the facets where the values of the potential permit becomes possible. The distribution of the additive will therefore be nonuniform, both in the electrode-solution direction and along the surface of the electrode itself, which in turn leads to a change in the conditions of growth of the crystal, in particular, to the formation of laminar deposits.

The rate of delivery of a surface-active substance is determined, according to Eq. (16), by its volume concentration and the value of K. The value of K includes the coefficient $1/\delta$, where δ is the thickness of the diffusion layer

$$_Ri_l=k'\frac{1}{\delta}C_R^0. \tag{17}$$

The thickness of the diffusion layer δ and, consequently, K depend on the concentration of the basic components of the electrolyte and on the conditions of electrodeposition. The concentration of the basic electrolyte determines the permissible current density. In a stationary electrolyte, a convection flow arises at the cathode, directed from the bottom up and due to depletion of ions of the basic component in the perielectrode layer, copper ions in the example considered. This flow may be all the more intense, the higher the permissible current density, i. e., the higher the copper ion concentration. The existence of directed movement of the electrolyte at the electrode leads to a decrease in the thickness of the diffusion layer δ, i. e., to an increase

*Another general factor that might cause the lack of coincidence of the regions of adsorption of the same substance on different metals is their different hydrophilicity.

in the rate of delivery of the additive. Its action will therefore be more appreciable at the lower portion of the cathode and should be weakened with movement upward. The optimum concentration of the additive consequently is functionally dependent on the concentration of the basic electrolyte, the system of electrolysis, the geometry of the bath, and in particular, the height of its cathode, and should ensure a definite degree of coverage of the surface in a system of adsorption-diffusion or purely diffusion limitations. *

In the electrodeposition of copper, very often thiourea $S=C(NH_2)_2$ and its derivatives are used as additives. The surface concentration of thiourea, providing for the creation of a solid monomolecular layer, corresponds to $\approx 3.3 \cdot 10^{-8}$ g·mole/cm^2. At a current density of 2 A/dm^2, the average thickness of the diffusion layer in the usual sulfate electrolyte is about $2 \cdot 10^{-2}$ cm; the diffusion coefficient of thiourea is $\sim 2 \cdot 10^{-5}$ cm^2·sec^{-1}; consequently, at a concentration $C_R^0 = 5 \cdot 10^{-5}$ g·mole/liter or $5 \cdot 10^{-8}$ g·mole/cm^3, the rate of delivery will be equal to

$$_R i_l = \frac{\Delta}{\delta} C_R^0 = \frac{2 \cdot 10^{-5}}{2 \cdot 10^{-2}} 5 \cdot 10^{-8} = 5 \cdot 10^{-11} \text{ g·mole/cm}^{-2}\text{·sec}^{-1}.$$

Thus, the degree of coverage will correspond only to a fraction of a percent of the entire surface, while the decomposition of thiourea in a system of diffusion control is about 7.5 g·mole per 1000 kg Cu.

When thiourea and its derivatives are used, sometimes a deposit with vertical poles is formed. This is probably explained by the fact that, in view of some factors, e.g., the formation of incrustations at the lower margin of the cathode, the convection flow is disrupted, and a stagnant vertical zone appears, in which the value of δ will be greater, while the rate of delivery of the additives will be smaller than on neighboring regions. Naturally, the properties of the deposit will be different here, which leads to the appearance of poles. This defect can be eliminated either by purifying the electrode of chemical impurities or by the creation of intensive circulation, more effective than in natural convection flows.

Another particular type of defect is microroughness, when the copper deposit resembles emery paper, evidently due to too high a concentration of the additive, in which its delivery to the surface is not limited, and it is capable of exerting a specific action on facets of different symbols.

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* Problems of the action of surface-active substances under conditions of electrodeposition of metals are most completely discussed in connection with the equalizing effect of additives [13-15].