

Research Article

Theory of Passivation Layer Formation on a Metal in Electrolyte Solutions

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The theory of the formation of the passivating layer (PL) on the surface S of the anodic dissolving metal is developed. It is formed as a result of the spontaneous production of the two-dimensional nucleus of the passivating oxide, which gradually fills the surface of metal S . The degree of filling is the growing function of anodic potential φ . It is found on the basis of the use of general principles of heterogeneous crystallization with the participation of the energy inhomogeneity of surface S . It is shown, that at the end of the active-passive transition the degree of filling approaches one, i.e., the continuous monolayer of oxide, which is completely passivating a surface S is formed.

Keywords: Formation, passivity of metals, repassivation electrolyte, oxide

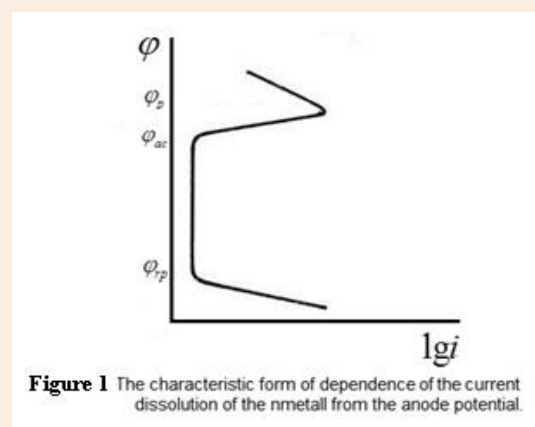


Figure 1 The characteristic form of dependence of the current dissolution of the metal from the anode potential.

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Introduction

The sequential theory of passivity of metal in the solution of electrolyte must include the problem about the formation of the passivating oxide layer (PL), which can be interpreted as the process of the passivation of metallic surface S . Along with the general laws of crystallization, the kinetics of passivation depends and on specific conditions (active dissolution of a surface S , the entering of components of oxide from various phases... etc.).

In the proposed model, the formation of the passivating layer (PL) begins from the heterogeneous production of the two-dimensional nucleus of oxide, definitely filling a surface S . The degree of filling $\theta_f(\varphi)$ and speed of nucleation $I_n(\varphi)$ are the functions of nature of metal, composition of solution, anodic potential φ and other parameters. Among them are essential binding energy of particles of oxide between themselves ψ and a substrate ψ_0 .

Nucleation -process is statistical. The specific probability of the appearance of a two-dimensional nucleus, which increases together with φ and which depends on the energies ψ, ψ_0 , corresponds to each value of potential. With a certain potential $\varphi \sim \varphi_{\text{int}}$ this probability and, therefore, the values $I_n(\varphi), \theta_f(\varphi)$ become noticeable. In this sense, it is possible to consider φ_{int} as the potential of the beginning of passivation.

Potential φ_{m} of a priori is unknown. It is natural to allow, without resorting to any restrictions, the possibility of its arrangement in the region of active dissolution. Apparently, already here spontaneously appear the centers of oxide, although it is not always easy to reveal experimentally this probabilistic process. Externally it can be manifested in the disturbance of the exponential (Tafel) dependence of anode current density i on the potential φ .

Thus, initially let us assume that in the Tafel's region along with the active anodic dissolution of metal, which has speed $i_a(\varphi)$, continues the competitor process of two-dimensional crystallization with speed $I_n(\varphi)$. It is important that the potentials $i_a(\varphi)$ and $I_n(\varphi)$ unequally depend on anode potential φ (as shown below). Active dissolution prevails at the small φ , and filling $\theta_f(\varphi)$ is small. However, with an increase in the velocity $I_n(\varphi)$, potential φ increases. With certain $\varphi = \varphi_p$, it is equalized with the speed $i_a(\varphi)$ of active dissolution, and it further exceeds it. The not monotony of a polarizing curve is also connected with it. The potential $\varphi = \varphi_p$ is the point of its maximum (figure). In the region $\varphi > \varphi_p$ the mass production of two-dimensional nucleus occurs, and current $i_a(\varphi)$ promptly falls, which is determined the region of active-passive transition (APT).

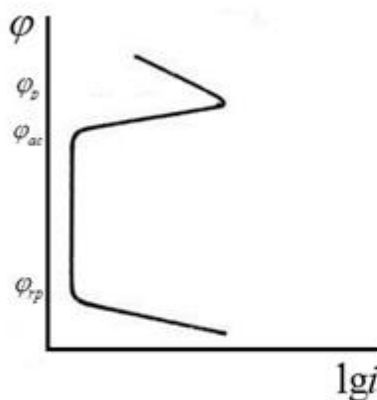


Figure 1 The characteristic form of dependence of the current dissolution of the metal from the anode potential.

On the section $\Delta\varphi$, having an order $0.1V$, total anode current i decreases, as it is known on 5–7 orders. This extraordinary sharp effect can be explained quantitatively, considering only the competition of processes of two-dimensional crystallization and active dissolution.

Thus, the effect of transition region is caused in our model by rapid growth of degree of filling $\theta_f(\varphi)$. By the site end of (APT), i.e., at the point $\varphi \sim \varphi_{ac}$ the filling is reached $\theta_f \sim 1$, i.e., the continuous monolayer of the two-dimensional passivating oxide appears, and the process of passivation comes to an end. Point $\varphi = \varphi_{ac}$ should be strictly considered as the beginning of passive region (called potential activation, flade-potential, ... etc.)

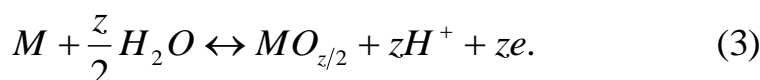
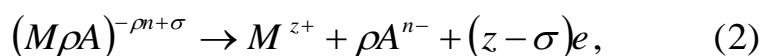
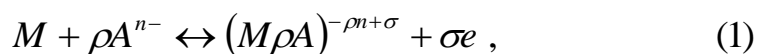
From stated, it is visible, that the potential of activation φ_{ac} is substantially different from the equilibrium potential φ_0 of formation of massive oxide. It depends on the composition of solution, method of the treatment of the surface of metal and others [1], and it can be found from the condition $\theta_f(\varphi_{ac})=1$.

At $\varphi > \varphi_{ac}$ on the first oxide monolayer the following monolayers are crystallized. Passivating oxide is thickened, coming under some influence of a metal substrate. However, as this region is strictly of passivity, we will pass to the following.

Now the immediate problem is consideration of passivated region, the determination of a functions $I_n = I_n(\varphi, \psi_0, \psi)$, $\theta_f = \theta_f(\varphi, \psi_0, \psi)$, the full density of current $i = i(\varphi)$ and calculation the polarizing curves on this basis.

Processes

We will present a physical picture on a surface S by the scheme of two main processes: active dissolution (1), (2) and two-dimensional crystallization (3):



During the first stage (1) of active dissolution, the chemical chemisorption of the activating ions A^{n-} with the formation of the intermediate surface complexes $(M\rho A)^{-\rho n + \sigma}$ occurs, where σ - partially transferred electronic charge, spent on the formation of chemisorbed bond. The activating anions, stimulating dissolution, could be OH^- , Cl^- and others. Also, molecules H_2O or the ions O^{2-} arise at the dissociation of being the adsorbing molecules H_2O .

Participation of anions in the elementary act (1) expresses influence of electrolyte on anode dissolution and therefore their account in (1) is necessary. The speed of formation of surface complexes $(M\rho A)^{-\rho n + \sigma}$ and the degree of the filling by them of surface S let us designate through $K_a(\varphi)$ and $\theta_a(\varphi)$. Both of them are functions of anode potential and other parameters.

At the second stage (2) of active dissolution, surface complexes are ionized with the transition of metal ions M^{z+} into the solution. We will designate the speed of ionization through $K_i(\varphi)$.

In the equation (3), the formation of two-dimensional nucleus of oxide M symbolizes a metal substrate (a source of metal ions M^{z+}). We will present, that the part of molecules of water of the dense part of electric double layer, focused by the oxygen end to metal and interacting with its surface S , dissociate, and ions O_{2-} appear in the adsorbed state. Fluctuating ions of metal are displaced in situation "between" the adsorbed oxygen. Their mutual arrangement is ordered in some sections of S , and with speed $I_n(\varphi)$ the two-dimensional nucleus of oxide (centers of passivation) are formed, which fill a surface S with the degree $\theta_f(\varphi)$.

Thus, process of passivation consists of several statistically independent stages, which are combined in acts of the nucleation. Its equation (3) is summary.

As a result of the main (basic) processes (1) – (3) on a surface S , the two competing fillings $\theta_a(\varphi)$ and $\theta_f(\varphi)$, through which density of total anode current $i(\varphi)$ is expressed are formed.

Basic Relations

For determining all functions we will consider that, the appearance of nucleus of oxide with $\varphi < \varphi_{ac}$ are in no equilibrium relative to solution and, therefore, they must be dissolved with a certain speed $I_k(\varphi)$. The absence of continuous monolayer characterizes the passivated region.

This representation will be coordinated with the general theory [2, 3] of the equilibrium of an ionic crystal $M_n A_m$ ($z_M n = z_A m$) with the electrolyte solution. Accordingly [2, 3] are simultaneously two necessary partial ionic equilibrium on each of the component. Potentials of equilibrium by ions of metal φ_{em} and ions (A^{n-}) φ_e have to coincide, which leads to expression of ionic product of solubility.

Imposing these conditions on the general equations of the currents of the ionic components i_M and i_A through the interphase boundary with the solution:

$$\begin{cases} i_M = \bar{k}_M \exp(\alpha_M z_M \varepsilon) - \bar{k}_M C_M \exp(-\beta_M z_M \varepsilon), \\ i_A = \bar{k}_A C_A \exp(\alpha_A z_A \varepsilon) - \bar{k}_A \exp(-\beta_A z_A \varepsilon), \\ \varepsilon = \frac{RT}{F} \varphi_b, \alpha + \beta = 1, \end{cases}$$

We find

$$\varphi_{em} = \frac{RT}{z_M F} \ln \left(\frac{\bar{k}_M}{\bar{k}_M} C_M \right), \quad \varphi_e = \frac{RT}{F} \ln \left(\frac{\bar{k}_A}{\bar{k}_A} \frac{1}{C_A} \right). \quad (4)$$

In an oxide nucleus $M_n O_m$ anion A^{n-} is traditionally considered oxygen O_{ox}^{2-} . Interphase potential on the surface of the nuclei $\varphi_b = \varphi - \Delta\varphi$, $\Delta\varphi$ - Potential jump on its thickness. As the source of oxide ions according to [4] serve the molecules H_2O , which are adsorbed and which dissociate on metal centers M_{ox}^{z+} of the nucleus ($H_2O \leftrightarrow O_{ox}^{2-} + 2H^+$).

In the passivated region $\varphi < \varphi_{ac}$ and, apparently, $\varphi_{em} \ll \varphi_b < \varphi_e$, i.e. none of the ionic components is located in the equilibrium with the electrolyte, not saturated by the ions M^{z+} . Therefore nuclei are dissolved with a speed $I_k(\varphi)$ of transition to solution of ions of oxygen O_{ox}^{2-} :

$$I_k(\varphi) = i_{ox} \left\{ \exp \left[-\alpha_k \frac{z_k F}{RT} (\varphi_b - \varphi_e) \right] - \exp \left[\beta_k \frac{z_k F}{RT} (\varphi_b - \varphi_e) \right] \right\}, \quad (5)$$

where the exchange current is

$$i_{ox} = \bar{k}_k C_w N_M \exp\left[\alpha_k \frac{z_k F}{RT} (\varphi_b - \varphi_e)\right] = \bar{k}_k C_H^2 N_k \exp\left[-\beta_k \frac{z_k F}{RT} (\varphi_b - \varphi_e)\right], \quad (6)$$

$$N_M = [M_{ox}^{z+}], N_k = [O_{ox}^{2-}], C_w = [H_2O], C_H = [H^+], \alpha_k + \beta_k = 1.$$

It is slightly more difficult to find the speed of nucleation $I_n = I_n(\varphi, \psi_0, \psi)$. Using a classical approach [5-7], it assumes that the speed of the appearance of nuclei is determined by the dynamics of increase and disintegration of the elements of two-dimensional structure, which spontaneously appear on the surface S , i.e. transitions from the two-dimensional nonequilibrium small crystals of the size a to $a \pm r_0$, where r_0 - the interparticle distance. If V_a - Speed of transitions, then in steady state it must be

$$V_{(a-r_0) \rightarrow a} + V_{(a+r_0) \rightarrow a} = V_{a \rightarrow (a+r_0)} + V_{a \rightarrow (a-r_0)},$$

i.e. the stationary distribution of small crystals according to the sizes (by the size) is kept constant (invariable). Hence the rate (speed) of formation of the small crystals:

$$\mathfrak{I}(a) = V_{(a-r_0) \rightarrow a} - V_{a \rightarrow (a-r_0)} = V_{a \rightarrow (a+r_0)} - V_{(a+r_0) \rightarrow a}.$$

At the critical dimension, $a = r$ the nucleus is called equilibrium, since, according to [5], the probabilities of attachment or detachment of a peripheral series of its particles at preservation of two-dimensional character are coincide:

$$P_{r \rightarrow (r+r_0)} = P_{r \rightarrow (r-r_0)},$$

$$V_{r \rightarrow (r \pm r_0)} = n(r) P_{r \rightarrow (r \pm r_0)},$$

$$\mathfrak{I}(r) = I_n(\varphi),$$

Where $n(r)$ - number of small crystals of the size r . In [8] it is shown, that

$$I_n = I_0 \exp\left[-\frac{2\psi^2/kT}{ze(\varphi - \varphi_0) + \psi_0 - \psi}\right], \quad (7)$$

Where φ_0 - Potential of formation of equilibrium, massive oxide ($\Delta G = zF\varphi_0$; in [9] it is obtained close to (7) expression). According to (7)

$$\varphi_{int} \sim \varphi_0 + \frac{1}{ze}(\psi - \psi_0), \quad (8)$$

Values in (5) and (7) determine the degrees $\theta_f(\varphi)$ and $\theta_a(\varphi)$ of the filling of surface S with two-dimensional nucleus and by the intermediate adsorptive complexes $(M\rho A)^{-\rho n + \sigma}$, which appear in the reactions of the active dissolution (1), (2). The steady-state equations for $\theta_f(\varphi)$ and $\theta_a(\varphi)$ adequate to the scheme (1), (2), take the form

$$(1 - \theta_a - \theta_f)K(\varphi) = \theta_a K_i(\varphi), \quad (9)$$

$$(1 - \theta_a - \theta_f)I_n = \theta_f I_k(\varphi),$$

Where $K_a(\varphi)$ and $K_i(\varphi)$ are speeds of adsorption of the activating anions A^{n-} and ionization of intermediate complexes $(M\rho A)^{-\rho n+\sigma}$, respectively,

$$K_a(\varphi) = k_a C_A^\rho \exp\left(\frac{\alpha_a \sigma F \varphi}{RT}\right), \quad (10)$$

$$K_i(\varphi) = k_i \exp\left(\frac{\alpha_i (z_M - \sigma) F \varphi}{RT}\right).$$

From (9) we find

$$\theta_f = \frac{I_n}{I_k + (1 - \theta'_a) I_n} (1 - \theta'_a), \quad \theta_a = (1 - \theta_f) \theta'_a, \quad (11)$$

$$\theta'_a = \frac{K_a(\varphi)}{K_a(\varphi) + K_i(\varphi)},$$

The current density $j(\varphi)$ of anode dissolution (transition of metal ions into the electrolyte) is equal

$$\begin{aligned} j(\varphi) &= \theta_a(\varphi) K_i(\varphi) + [I_k(\varphi) + i_k(\varphi_b)] \theta_f, \\ i_k(\varphi_b) &= i_0 \exp\left(\alpha \frac{z_M F}{RT} \varphi_b\right), \\ \varphi_b &= \varphi - \Delta \varphi. \end{aligned} \quad (12)$$

Formula (12) considers an account of all mechanisms in the total current $i(\varphi)$. The first composed in the right part corresponds to the active dissolution of metal (2). The second composed considers the direct dissolution of nucleus with a speed $I_k(\varphi)$, as a result of which ions M_{ox}^{z+} seem "painted" (nucleus on direct reaction (3) are formed). The third composed considers the transfer of ions of metal through nucleus into the solution (i.e. their migration through the passivating by two-dimensional oxide). According to previous, in the passive region $\varphi > \varphi_{ac}$ this composed is the main thing. Really, values are reached here $\theta_f = 1, \theta_a = 0, \varphi_b = \varphi_e$, and, therefore, $i(\varphi) = i_k(\varphi_b)$.

Energy surface inhomogeneity of metal

Formulas (5), (7), (10) – (12) for the unknown values $I_k(\varphi), I_n(\varphi), K(\varphi), \theta_f(\varphi)$ and $j(\varphi)$ represent the closed system of the connected relationships correlation. However, it is additionally necessary to consider, that one of the basic values $I_n(\varphi)$ (consequently, and other values) depends on energy of binding ψ_0 of oxide with the metallic base layer. This causes the essential dependence of the process of passivation on the properties of the surface S of metal and, in particular, on its energy inhomogeneity, i.e. the dissimilarity of energy ψ_0 in the different sections of S .

Let us represent a surface with the totality of the areas dS_i (as the sum of areas), in the limits of each of which the energy ψ_0 is constant and equals ψ_{0i} . The number i of area dS_i assigns the coordinate of its center. The total surface area of metal is [10]:

$$S = \sum_{(i)} dS_i,$$

and its important characteristic is the function $f(\psi_{0i})$ of the statistical distribution of areas dS_i in terms of the values of the energy ψ_{0i} . The determination of this function- is autonomous and difficult.

The distribution function $f(\psi_{0i})$ version valid for a so-called uniform and non-uniform surface ((leading, in particular, to the logarithmic isotherm of Temkina) is widely used. In this case all values of energy ψ_{0i} are concluded in the range from ε_{\min} to the ε_{\max} they all are equally probable.

Values ε_{\min} and ε_{\max} - are the boundaries of the energy spectrum of surface S , and $f(\psi_{0i})$ is called the function of spectral energy distribution ψ_{0i} . Analytically

$$f(\psi_{0i}) = \begin{cases} \frac{1}{\Delta\varepsilon}, & \text{if } \varepsilon_{\min} \leq \psi_{0i} \leq \varepsilon_{\max}, \\ 0, & \text{if } \varepsilon_{\min} > \psi_{0i} \text{ or } \varepsilon_{\max} < \psi_{0i}, \end{cases} \quad (13)$$

Moreover,

$$\Delta\varepsilon = \varepsilon_{\max} - \varepsilon_{\min}, \quad (13a)$$

$$\int_{\varepsilon_{\min}}^{\varepsilon_{\max}} f(\psi_{0i}) d\psi_{0i} = 1.$$

The accounting of statistical distribution of areas dS_i on the energies means transition to the local description of superficial processes. Values $\theta_f(\varphi)$, $I_n(\varphi)$ and $j(\varphi)$ become local, i.e. depending on the number of the areas. The system of formulas for these values follows from(7), (11) and (12):

$$\begin{aligned} \theta_{fi} &= \frac{I_{ni}(\varphi)}{I_k(\varphi) + (1 - \theta'_a)I_{ni}(\varphi)}, \quad \theta'_{ai} = (1 - \theta_{fi})\theta'_a, \\ \theta'_a &= \frac{K_a(\varphi)}{K_a(\varphi) + K_i(\varphi)}, \\ j_i &= \theta_{ai}(\varphi)K_i(\varphi) + [I_k(\varphi) + i_k(\varphi_b)]\theta_{fi}(\varphi), \\ I_{ni} &= I_0 \exp\left[\frac{2\psi^2/kT}{ze(\varphi - \varphi_0) + \psi_{0i} - \psi}\right]. \end{aligned} \quad (14)$$

In (14), φ_e , $i_k(\varphi)$, and $i_k(\varphi_b)$ are determined by formulas (4), (5), (10) and (12). The degree $\theta_f(\varphi)$ of the general filling with the two-dimensional nucleus of the passivating oxide of surface S and the total current density $i(\varphi)$ of dissolution are equal

$$\theta_f(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} d\psi_{0i} f(\psi_{0i}) \theta_{fi}(\varphi, \psi_{0i}, \psi), \quad (15)$$

$$i(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} d\psi_{0i} f(\psi_{0i}) j_i(\varphi, \psi_{0i}, \psi).$$

Further, we use the approximation of the fast ionization of intermediate adsorptive complexes, having accepted $K_i(\varphi) \gg K_a(\varphi)$, i.e. $\theta_a' \ll 1$. This assumption is not fundamental and only somewhat simplifies the calculations.

Then from (13) and (14) we obtain in the passivated region $\varphi < \varphi_{ac}$, the general filling of surface of the passivating oxide:

$$\theta_f(\varphi) = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} d\psi_{0i} f(\psi_{0i}) \frac{I_{ni}(\varphi, \psi_{0i})}{I_k(\varphi) + I_{ni}(\varphi, \psi_{0i})}. \quad (16)$$

Total anode current density taking into account the passivation

$$i(\varphi) = i_a(\varphi)[1 - \theta_f(\varphi)] + [I_k(\varphi) + i_k(\varphi_b)]\theta_f(\varphi), \quad (17)$$

$$i_a(\varphi) = \frac{K_i(\varphi)K_a(\varphi)}{K_i(\varphi) + K_a(\varphi)}.$$

According to its sense $i_a(\varphi)$ is the average current density of the active dissolution of the parts S , free from the passivating of two-dimensional nucleus.

Conclusion

Expression (17) taking into account (16) represents the general formula of the current of dissolution in entire range of potential change φ , in which the calculation of integral (16) leads to the agreement with the experiment.

In the passivated region $\varphi < \varphi_{ac}$ the main role is played by the behavior of functions $i_a(\varphi)$ and $\theta_f(\varphi)$. Calculations have shown that, up to a maximum of the polarization curve (i.e. at $\varphi < \varphi_p$) the main contribution in total current is making the process of active dissolution, since filling isn't enough and the value $i_a(\varphi)$ plays the main role. After a maximum, i.e. on a site of active - passive transition filling quickly increases, and active dissolution is displaced more by the process of the two-dimensional nucleation. At a point $\varphi < \varphi_{ac}$, the continuous monolayer is formed with $\theta_f \cong 1$ and the area of actually passivity $\varphi > \varphi_{ac}$ begins, considered in the following publication.

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