



A Physical Model of the Interphase Boundary of the Passivating Layer on the Metal in the Electrolyte Solutions

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ABSTRACT

The model of processes on the interphase boundary metal-passivating layer is proposed. The balance of ions upon the formation of the cells of oxide is examined. The velocity expressions of these processes are obtained.

Key words: Physical model, Passivity of metals, Electrolyte.

INTRODUCTION

The mechanism of processes on the interphase boundary of the passivating oxide layer PL has a fundamental value, whereas, the properties of the passivating layer are determined by them. In this paper a consistent model of the boundary metal-oxide MO is presented.

General stationary laws.

On the interphase boundary of metal with PL, the continuous dissolution of metal occurs. It disappears consecutively monolayer after a monolayer and the cells of oxide occupy its place. If at time Δt the layer of metal ΔM of thickness Δx disappears, then the plane MO displaces in its side with the speed v , equals

$$v = \Delta x / \Delta t = (i_b / zF) (\mu / \rho)$$

where i_b - total dissolution current; μ , ρ - the molar mass and density. The thickness of the oxide layer Δ_{ok} , substituting for the same time, is also equal.

Let us designate a quantity of ions in the initial layer ΔM of metal and its substituted layer of oxide Δ_{ok} by ΔN and ΔN_1 respectively. It is obvious, that $\Delta N_1 < \Delta N$, since the specific volumes, according to the metal ion, in ΔM and Δ_{ok} are different. Consequently, only ions ΔN_1 in a layer ΔM involved in the formation of oxide Δ_{ok} . The remaining part, equal $\Delta N_2 = \Delta N - \Delta N_1$, considered to be excess and must leave into the solution through the boundary MO and PL. Therefore, the balance of space in the layer of metal ΔM and the oxide Δ_{ok} is observed.

Thus, the surface MO serves as the source of ions M_{ok}^{z+} , and in the passivating layer, their intensive transfer by the mechanism of hopping migration in the strong electric field E should be occurred. Accordingly, the total current of the dissolution of metal is divided into the transfer current i_{bm} of the ions through the boundary MO in PL and the current i_{bo} of oxide formation on this boundary (subscripts indicate: b- boundary, m- metal, o- oxygen; the current i_{bo} determines a quantity of metal ions, which in 1cm^3 every second are connected in the layer ΔM with oxygen), such as

$$\Delta N_1 + \Delta N_2 = \Delta N, \quad \dots(2)$$

$$i_{bm} + i_{bo} = i_b.$$

The subsequent analysis confirms this conclusion. The total current must be equal

$$i_b = i_{bo} \exp(a_m \beta E), \quad \beta = \alpha_b z_m F / RT, \quad \dots(3)$$

$$E = (\varphi - \varphi_b) / \delta(\varphi), \quad \varphi_m = a_m E.$$

Where a_m - interatomic distance in the cationic sublattice, α_b - transfer coefficient on the boundary MO.

Equation(3) assumes, that an ion M , passing into the state of anion M_{ok}^{z+} , must overcome a potential jump $\varphi_m = a_m E$. Thus, the barrier of transition decreases to $\Delta W_m = a_b z_m \varphi_m$. The constant of transition speed is determined from the independent temperature measurements (for Fe, for example,).

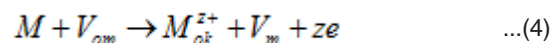
The total current i_b is the fundamental characteristic of stationary processes on the interphase boundary MO, and the micro scheme of the formation of cells M_2O_3 are ambiguous. They must consider a difference between the interatomic distances and the angular directions in the lattices of metal and oxide, and require the use of probabilistic methods for describing regrouping particles.

Further, it is interesting to detail a physical

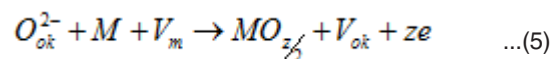
situation on a surface MO to calculate the currents i_{bm}, i_{bo} and the ratio between the values ΔN_1 and ΔN_2 . For this purpose let us proceed from general consideration to the specific models of processes on the boundary MO. The most simple and real vacancy model is presented below. It allows to open a better physical sense of the relations (3).

The vacancy model of MO boundary

Vacancy model proceeds from the idea about the fact that, for forming the new cell M_2O_3 , three ions O_{ok}^{2-} from the passivating layer must penetrate in the boundary monolayer of metal. This requires the presence of three vacancies V_m in it, which can arise only as a result of previous transition in the passivating layer of three ions of metal. These ions fill three vacancies V_{om} in the cation's sublattice of oxide. The transition scheme (V_m - vacancy in a metallic sublattice of oxide, - vacancy in the boundary layer of the metal ΔM)



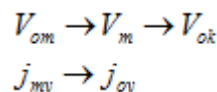
Transition (4) serves as the necessary condition for the subsequent penetration into the layer of oxygen ions



Where V_{ok} - vacancy in the oxygen sublattice in place passed into the metal ion O_{ok}^{2-} .

The opposite reactions (4), (5)- appear basic in the vacancy model. It is obvious, that the surface MO serves as a drain of cationic vacancy V_{om} , brought by their diffusive flow j_{mv} from solution. Simultaneously, it is the source of the vacancies V_{om} , which are discharged into the solution by their flow j_{ov} . Flows j_{mv} and j_{ov} appear, of course, as a result of the motion of ions M_{ok}^{z+} and O_{ok}^{2-} in the passivating layer by the mechanism of hopping migration in the strong field.

The transformation of vacancies and their flows occurs on the surface MO by the scheme.



in this transformation, the vacancies V_m are mediators, which connect processes (4) and (5). Their total quantity is determined by the withdrawal of metal ions and penetration in metal of the oxygen ions O^{2-}_{ok} , i.e. the relations of the speeds (4) and (5). In the stationary mode, the value of is invariable (see below).

The speeds of formation of oxide and cation transfer through the boundary MO.

Thus, processes On the boundary MO are characterized by the currents (speeds) i_{bm}, i_{bo} of reactions (4), (5) i_{bm}, i_{bo} and by the total current i_b of the metal dissolution. It is measured, and is primary value, and its determination (3) can be called extra-model. The calculation of currents i_{bm}, i_{bo} depends on model presentations. let us examine these values.

1) Transition current i_{bm} of ions M in the passivating layer and their further transfer to the solution depends on the electric field E and the boundary concentration $a_m N_{mv2}$ of vacancies V_{om} . Indeed, for transition into the passivating layer according to the scheme (4), ions M must cross the plane MO and move away from it on interatomic distance a_m of a cationic sublattice, having overcome potential jump $\varphi_m = \alpha_m E$. Transition barrier is reduced on $\Delta W_m = \alpha_b z_m a_m E$, its probability is proportional to a quantity of vacant places, i.e., the concentration $a_m N_{mv2}$ of vacancies V_m . As a whole the speed (4) is equal

$$\begin{cases} i_{bm} = \bar{i}_{bm}^{(0)} \exp(\beta \alpha_m E), & \beta = \alpha_b z_m F / RT, \\ \bar{i}_{bm}^{(0)} = \bar{i}_{bm} \alpha_m N_{mv2} N_{met}, & \bar{i}_{bm} \sim \exp(-W_b / KT), \\ E = (\varphi - \varphi_p) / \delta(\varphi), & \varphi_m = \alpha_m E, \end{cases} \quad (6)$$

α_b - transfer coefficient, N_{met} - concentration of atoms in metal, - \bar{i}_{bm} speed constant of reaction.

2) The current i_{bo} of ions M, which form oxide $MO_{z/2}$ according to the reaction (5), represents the speed of oxide formation on the Boundary MO. let us take it equal to (\bar{i}_{bm} - constant of speed, reverse current is neglected)

$$\begin{cases} i_{bo} = i_{bo}^{(0)} c_{met}^{z/2} (N_{z2} / N_{z0}) f(u) \exp(\beta \alpha_b E), \\ \beta = \alpha_b z_o F / RT, & i_{bo}^{(0)} = \bar{i}_{bo} N_{z0} \alpha_o^{z/2}, \\ c = N_{met} / N_{M}, & \varphi_o = \alpha_o E, & N_{z2} = N_{z0} - N_{z1} \end{cases} \quad \dots(7)$$

In the system (7), the dependence of current i_{bo} on the field E, the concentration c_{met} , the vacancies V_m and the probabilistic factor $f(u)$ are taken into account. the influence of field is regulated by the value of transfer coefficient α_b , and it is connected with the fact, that for the penetration into the metal through the plane MO, ion O^{2-}_{ok} must dislocate in the anion sublattice to the interatomic distance a_o , overcoming the potential jump $\varphi_o = \alpha_o E$. In this case, the barrier of penetration is reduced to the value $\Delta W_o = \alpha_b z_o a_o Z$. Influence on current i_{bo} of concentration c_{met} is considered with the fact, that without vacancies V_m , penetration can't occur (see (5)).

The Probability factor $f(u)$ in (7) takes into account the specific mechanism of formation of cells $MO_{z/2}$. If the penetration of ions and the structuring of cells occur in parallel, then it is not possible to exclude the deceleration necessary of regrouping of particles. The micro schemes of these processes can be different and random. Their possible influence on the speed of formation of oxide is described by probabilistic factor $f(u)$ in (7). Its calculation is an autonomous task.

If the penetration of ions O^{2-}_{ok} is limited and it is weakly dependent on the subsequent structuring, then . Within the limit of the passivating layer it can consist of the partially structure systems complexes M_2O_3 , the speed of formation of which is determined by (7) at $f(u)=1$. Structuring depends, in particular, on the noncoincidence of interatomic distances and angular orientations in the lattices of metal and oxide.

Transfer coefficients α_b and $\beta_b = b(1 - \alpha_b)$ in (6) and (7) characterize asymmetry barrier W, which overcome by ions during their motion on the units of crystal lattice in the direct and opposite directions. Depending on α and β , how much an electric field changes barrier W. In the case of an isotropic

homogeneous medium $\alpha_b \sim \beta_b \sim \frac{1}{2}$. However, in a thin passivating layer on the strange base layer, these values α_b and β_b are not proved. Furthermore, the current values α_b, β_b in the volume of the passivating layer, and its more disordered boundaries may differ, i.e. they depend on coordinate system. Apparently, in this respect, the boundary MO is isolated, on which exactly $\alpha = \alpha_b, \beta = \beta_b$. Then the jumps of the potential φ_m and φ_o overcome by ions M and O^{2-}_{ok} upon transition through the plane MO are equal respectively to $\varphi_m = a_m E$ and $\varphi_m = a_o E$.

Barriers(4) in the Boundary MO are reduced on $\Delta W_m = a_b z_m \varphi_m$ and. All this are taken into account in (6) and (7).

Using (6), (7) it is possible to calculate stationary concentration of vacancies. Actually, the withdrawal of ions M and the penetration of ions O^{2-}_{ok} are strictly compensated (for example, for formation M_2O_3 , three ions M have to leave metal and three ions O^{2-}_{ok} will penetrate in it).

for example, for forming , three ions must leave from the metal and three ions will penetrate in it. Therefore, speeds (6) and (7) are identical, i. e. $\frac{2}{3} i_{bm} = i_{bo}$ and, consequently (excluding small reverse currents)

$$c_{met} = \frac{2}{3} \frac{i_{bm}^{(0)} \exp\{E(\beta a_m - \beta a_o)\}}{i_{bo}^{(0)} (N_{o2}/N_{o0}) f(u)},$$

$$N_{o2} = N_{o0} - N_{vo}$$

3) total current in i_b the vacancy model is easy to relate with the values i_{bm} and i_{bo} taking into account, that the dissolution of the metal at the interface MO is faster oxide formation. Actually, according to the presented above, for the appearance of a cell M_2O_3 it is necessary for emergence of a cell, that: a) three ions of metal from a layer ΔM passed to PL by the scheme (4), composing the current i_{bm} ; b) three ions from a passivating layer entered into a layer according to the scheme (5); c) since, the cell M_2O_3 contains two ions M^{z+}_{ok} , then two ions of metal in the ΔM layer must be connected with three penetrating ions of oxygen O^{2-}_{ok} respectively, to form a complex M_2O_3 and to compose the current .

Thus, with the formation of each cell M_2O_3 ,

layer loses not two, but five ions of metal, from which three prove to be excess. Their departure from the layer ΔM implements balance of space, compensating for the difference in specific volumes for each metal ion in the lattice of a metal oxide. Therefore in the passivating layer the intensive transfer of cations M^{z+}_{ok} by the mechanism of hopping migration occurs. The surface MO is their intensive source, concentration of N_{mv2} vacancies V_{om} in (6) is small, the relation of stationary values of currents m and i_{bo} equal 3/2.

The total current is equal to the sum

$$i_b = i_{zm} + i_{zo} = \frac{2}{3} i_{zm} = \frac{2}{3} i_{zm} \text{ or, accordingly (6),(3)}$$

$$i_b = i_{bo} \exp(\beta a_m E), \quad \beta = \frac{\alpha_b z_m F}{RT},$$

$$i_{bo} = \frac{5}{2} i_{bm}^{(0)} = \frac{5}{2} \bar{i}_{bm} \alpha_m N_{mv2} N_{met} \quad \dots(8)$$

The current of the formation of oxide is equal $i_{bo} = \frac{2}{3} i_b$. Every second on 1 cm^2 of the plane MO there is a number of cells occurs, which at $z_m = 3$ be equal

$$n = \frac{i_{bo}}{2 z_m e} = \frac{1}{5} \frac{i_b}{z_m e}$$

If the stoichiometry of oxide is different than the previous one, then it will change numerical coefficients [2]. In the general case for the cell $M_A O_B$ we have

$$\begin{cases} i_{bo} = \frac{A}{A+B} i_b, & n = -\frac{1}{A+B} \left(\frac{i_b}{e z_m} \right), \\ i_{bo} = \frac{A+B}{B} i_{bm}^{(0)} \end{cases}$$

With the stated of the vacancy model boundaries MO, self processes at the interface with the opposite solution, considered in the following publications.

REFERENCES

1. Vetter, K. Z. *Electrochemist.* **1951**,55, 274; **1954**,58, 230-232
2. Popov, Y.A. *Electrochemist.***1985**,21, 1496; **1986**, 22, 762-764.