

## Laws of interaction of alloys with aggressive electrolyte

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(Received: January 12, 2009; Accepted: February 22, 2009)

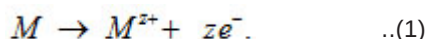
### ABSTRACT

The interaction of alloys with the ionic components of the electrolyte, in the metallic lattice of alloys, shows that the boundary layer with the changed composition presents, the interdiffusion of its components occurs, and plastic flow of atomic planes appears. The physical mechanism of these phenomena is examined.

**Key words:** Current density, electrolyte, alloys, potential, electrolyte.

### INTRODUCTION

As a result of interaction of the surface atoms of metal with the ions of electrolyte, the bond of these atoms with its lattice is weakened, and they depart to the electrolyte, i.e., they are dissolved according to the reaction



It is possible to show that the current density of their dissolution is equal

$$i = c_s \cdot q(\varphi), \quad \dots(2)$$

Where  $c_s$  - the concentration of surface atoms  $M$ , and  $q(\varphi)$  - the function of anodic (i.e. interphase) potential  $\varphi$ , determined by the kinetics of the transition (1).

Accordingly, surface translationally moves with the speed

$$V = \frac{i}{zF} \left( \frac{\mu}{\rho} \right),$$

$\mu$ ,  $\rho$  - molar mass and density of metal. In the elementary acts of dissolution, the activating anions of electrolyte participate, current density  $i$  depends on their surface concentration and, therefore, on their volume concentration  $C_0$ .

In the case of binary alloys, i.e. the basic construction materials, which consist of the metallic components  $M_1$  and  $M_2$ , the physical mechanism of their transitions into the electrolyte is complicated. They are dissolved with the unequal speed, i.e. the densities  $i_1$  and  $i_2$  of their currents are different. It is possible to show, that

$$\begin{aligned} i_1 &= c_{1s} \cdot q_1(\varphi) \\ i_2 &= c_{2s} \cdot q_2(\varphi) \\ q_1(\varphi) &\neq q_2(\varphi) \end{aligned} \quad \dots(3)$$

Therefore the values  $c_{1s}, c_{2s}$  of atom concentrations to the surface  $S$  and their volumetric values  $c_{10}, c_{20}$  in the general case can not coincide, i.e.

$$c_{1s} \neq c_{10}, \quad c_{2s} \neq c_{20} \quad \dots(4)$$

The regime of the uniform dissolution of the alloy, when the densities of the molar flows of its components are equal, is of practical use

$$J_1 = v \cdot c_{10}, \quad J_2 = v \cdot c_{20} \quad \dots(5)$$

The speed  $v$  of translational motion of the surface of alloy is determined by the kinetics of the transitions (1) of components. Moreover

$$J_1 \equiv \frac{i_1}{z_1 F}, \quad J_2 \equiv \frac{i_2}{z_2 F} \quad \dots(6)$$

We have accordingly (3), (5), (6):

$$\frac{i_1}{i_2} = \frac{z_1 c_{10}}{z_2 c_{20}}, \quad \frac{c_{1s}}{c_{2s}} = \frac{q_1(\varphi) \cdot z_1 c_{10}}{q_2(\varphi) \cdot z_2 c_{20}} \quad \dots(7)$$

From (7) it follows that the values,  $\frac{c_{1s}}{c_{2s}}$  and  $\frac{c_{10}}{c_{20}}$ , i.e., the relationships of the concentrations of the components of alloy in its volume and on the surface  $S$  in the general case do not coincide, which is also asserted above.

For the fulfillment of conditions of uniformity<sup>5</sup>, the surface concentration  $c_{1s}$  of rapid component must decrease, and the concentration  $c_{2s}$  of slow component increase, so that, the difference in the values of the kinetic values  $q_1(\varphi)$  and  $q_2(\varphi)$  would be compensated.

Accordingly, in the alloy, the boundary layer that is changed in comparison with volume, composition, and with the concentration gradients of the components, is formed. Their diffusion appears, to provide a shaping of steady-state boundary layer. The role of diffusion, therefore, is fundamental.

Assume that  $i_1 > i_2$ , i.e., component  $M_1$  is dissolved more rapid than the slow component  $M_2$ . During the dissolution in the time at  $dt$ , the external part of the boundary layer into the electrolyte pass into their masses  $dq_1$  and  $dq_2$ .

Value of  $dq_1$  is equal to the sum of the mass of rapid component which was being originally Contained in and entered in by the mechanism of diffusion.

It is analogous, value of  $dq_2$  is equal to a difference in the mass of the slow component, which was being originally contained in and moved out from the volume of alloy by means of the diffusion.

Consider some aspects of interdiffusion in the BL of alloys. It occurs via the vacancy mechanism, with nonequilibrium vacancies NV at a concentration of  $c_v = c_3$  being of primary importance. Vacancies appear on the surface as a result of metal ion transfer into electrolyte, from where they migrate into the BL lattice and further into the bulk of the alloy. The diffusion coefficients and of the components strongly depend on the concentration of vacancies

. As a result of the presence of NV, a plastic flow arises in the BL. The vacancies can be regarded as an independent subsystem (a third component of the lattice), with the gradient in the concentration of vacancies being predominantly localized within the BL.

The concentrations of the alloy components and the flux densities are the sought functions. They should satisfy the conservation laws

$$\begin{aligned} c_1(x, t) + c_2(x, t) + c_3(x, t) &= 1, \\ j_1(x, t) + j_2(x, t) + j_3(x, t) &= 0, \\ c_v(x, t) &\equiv c_3(x, t), \quad c_{vz}(x, t) \equiv c_{3z}(x, t), \end{aligned} \quad \dots(8)$$

Where  $c_3$  is the equilibrium concentration of vacancies. Adopting the conventional expression  $j_k = -D_k \partial c_k / \partial x$  for the flux densities, and using a standard diffusion scheme, we have the following system of incompatible equations for these functions:

$$\begin{aligned}\partial c_1 / \partial t &= D_1 \partial^2 c_1 / \partial x^2, \\ \partial c_2 / \partial t &= D_2 \partial^2 c_2 / \partial x^2, \\ \partial c_3 / \partial t &= D_3 \partial^2 c_3 / \partial x^2.\end{aligned}\quad \dots(9)$$

These equations ignore the effect described in<sup>1,2</sup>. Since the concentration of vacancies in the BL is high, they should disappear, being filled with diffusing ions present in the alloy. Thus, atomic planes as a whole migrate at a velocity of  $u=u(x,t)$ . Such so-called plastic flow of the lattice was first introduced by Darken<sup>1</sup> to explain the Kirkendall effect. Plasticity plays an important role in the anodic dissolution of alloys, because the concentrations of nonequilibrium and thermal vacancies differ by several order of magnitude. Nonequilibrium vacancies appear due to surface-electrolyte interaction, whose action is similar to that of an external force, which is absent in the Kirkendall effect. Since most of the NV are located in the BL. Plasticity maintains its integrity, precluding the formation of pores and other defects. From the microscopic point of view, plastic flow arises due to spatially separated processes of disassembling and assembling of atomic planes (formation and collapse of cavities).

However, theories taking into account NVs<sup>1-3</sup> do not consider them explicitly; i.e., the parameters of the system, including the velocity of viscous flow, are independent of the concentration of NVs. Actually, the velocity should be determined by the decay of vacancies [the density of sources is designated by  $\sigma=\sigma(x,t)$ ]. Solving this problem is equivalent to a generalization (improvement) of the Darken theory of interdiffusion.

In [3] a system of equations was obtained for the concentrations  $c_1(x)$ , and of the ionic component and NV diffusing in the BL. This system takes into account the above-mentioned factors and the movement of the alloy-electrolyte interface at the velocity . Under steady-state conditions, value is independent of time , and, hence , the concentration distribution travels inside the alloy at a velocity . In this case,

the equations take the form

$$\begin{aligned}D(c_3 \frac{dc_1}{dx} - c_1 \frac{dc_3}{dx}) + (v-u)c_1 &= v c_{1b}, \\ c_1(0) &= c_{1b},\end{aligned}\quad \dots(10)$$

$$\begin{aligned}D \frac{dc_3}{dx} + v(c_3 - c_{3b}) + (1-c_3)u &= 0 \\ c_3(0) &= c_{3b} \\ c_2 &= 1 - c_1 - c_3 \\ u(x) &= \int_x^{\infty} \frac{c_3(\xi) - c_{3b}}{L^2} d\xi, \quad L^2 \approx D\tau,\end{aligned}\quad \dots(11)$$

Where is the diffusion path covered by a NV within its average lifetime  $\tau$ .

Let us now take into account that the diffusion mechanism becomes more complex at high values of  $c_3(x)$ . according to<sup>3</sup>, if  $c_3(x)$  exceeds some critical value ( $c_{cr} \approx 10^{-4}$ ) during the anodic dissolution of an alloy, the diffusion of the components proceeds along so-called liquid filaments<sup>3</sup> ( the conventional vacancy mechanism is also operative, but its contribution is negligible). In BLs, a concentration as high as  $c_3(x) \leq 10^{-3}$  is achieved (see also)<sup>4</sup>, with the BL boundary and BL thickness being determined by the conditions  $c_3(x_{cr}) = c_{cr}$  and  $\delta_3 = x_{cr}$  respectively. Thus, the plane  $X = X_{cr}$  is the boundary between the alloy bulk and BL. The diffusion coefficient  $D$  in the BL is given by

$$D_0 = \bar{D}_0 \exp(-E/kT), \quad c_3 \geq c_{cr},$$

Where  $W$  is expressed in terms of the latent heat of melting of the alloy. Correspondingly, it is sufficient to consider Eq. (10) within the range

$$\begin{aligned}0 \leq x \leq x_{cr}, \quad x_{cr} &= \delta_3, \\ c_1(x_{cr}) &= c_{1b}, \quad c_3(x_{cr}) &= c_{cr}, \\ c_3|_{x=x_{cr}} &= c_{3b}\end{aligned}\quad \dots(12)$$

That is, within the BL. At high  $L$  values ( $L \rightarrow \infty$ ), when the rate of removal of vacancies is negligibly small, we find from Eq. (11)

$$c_1(x) = c_{1s} \exp(-ax), \quad 0 \leq x \leq \delta_1, \quad \delta_1 = c_{1s},$$

$$\delta_1 = -\frac{D_0}{v} \ln\left(\frac{c_{1s}}{c_{1b}}\right), \quad a = \frac{v}{D_0}, \quad \dots (13)$$

$$c_{1s} = c_1(0), \quad c_1(\delta_1) = c_{1s}$$

Hence, at  $v/D_0 \sim 10^3 \text{ cm}^{-1}$  (for example,  $v \sim 3.5 \times 10^{-6} \text{ cm/s}$  and  $c_{cr}/c_{3s} \sim 0.3$ , the BL thickness was evaluated at  $\delta_3 \sim 10^{-3} \text{ cm}$ . reducing Eq. (10) to the dimensionless form and taking into account Eq. (13) simplifies this equation:

$$\frac{dc_1(Z)}{dZ} + A(Z)c_1(Z) = \frac{a\delta_3}{c_3(Z)} c_{1b},$$

$$A(Z) = a\delta_3 \frac{[1 + c_3(Z)]}{c_3(Z)}, \quad c_1(0) = c_{1s},$$

$$Z = x/\delta_3, \quad 0 \leq Z \leq 1, \quad a = v/D_0$$

Let

$$c_1(Z) = Q(Z) \exp\left[-\int_0^Z A(y) dy\right],$$

$$c_1(0) = Q(0) = c_{1s},$$

$$Z = x/\delta_3, \quad 0 \leq x \leq \delta_3,$$

Where

$$Q(Z) = a\delta_3 c_{1b} J(Z) + c_{1s},$$

$$J(Z) = \int \frac{dy}{c_3(y)} \exp\left[\int_0^y A(\zeta) d\zeta\right]$$

It is easy to find that

$$J(Z) = \frac{1}{a\delta_3} \left[ \exp\left(\frac{e^{a\delta_3 Z} - 1}{c_{3s}}\right) - 1 \right]$$

Correspondingly,

$$c_1(Z) = c_{1s} \left\{ 1 - \left( 1 - \frac{c_{1s}}{c_{1b}} \right) \exp\left[ -\frac{1}{c_{3s}} (e^{a\delta_3 Z} - 1) \right] \right\}.$$

Approximately, we obtain

$$c_1(Z) \approx c_{1b} \left\{ 1 - \left( 1 - \frac{c_{1s}}{c_{1b}} \right) \exp\left[ -\frac{a\delta_3 Z}{c_{3s}} \right] \right\},$$

$$c_3(Z) = c_{3s} e^{-a\delta_3 Z}, \quad Z = \frac{x}{\delta_3}, \quad 0 \leq x \leq \delta_3.$$

The thickness  $\delta_1$  of the diffusion layer for the fast component is determined by the condition

$$c_1(\delta) = c_{1b} \left\{ 1 - \left( 1 - \frac{c_{1s}}{c_{1b}} \right) \exp\left[ -\frac{a\delta_1}{c_{3s}} \right] \right\},$$

hence

$$\left\{ \delta_1 = -\frac{c_{3s}}{a} \ln\left[ \frac{c_{1b} - c_1(\delta_1)}{c_{1b} - c_{1s}} \right] \right\}.$$

At  $[c_{1s} - c_1(\delta_1)]/(c_{1b} - c_{1s}) \sim 0.1/0.9$ , we have  $\delta_1 \sim 2 \times 10^{-6} \text{ cm}$ ; i.e., the diffusion approximation is valid

At finite values,  $c_3(Z) \ll 1$  and  $c_{3b} \ll c_3(Z)$ , system (15) yields

$$\frac{dc_1(Z)}{dZ} + \alpha c_3(Z) = \left( -\frac{\delta_3}{L} \right)^2 \int_Z^\infty [c_3(\xi) - c_{3b}] d\xi,$$

$$Z = \frac{x}{\delta_3}, \quad \alpha = v\delta_3/D, \quad 0 \leq x \leq \delta_3.$$

As a result, we find

$$c_1(Z) = e^{-\alpha Z} \left\{ c_{1s} + \left( \frac{\delta_3}{L} \right)^2 \int_0^Z d\xi e^{\alpha \xi} \int_\xi^\infty [c_3(y) - c_{3b}] dy \right\}.$$

Thus, this study of diffusion in the BL takes into account the main physical factors:

The plastic flow of the alloy lattice, which maintains its integrity; the presence of diffusing NVs

; and removal of NVs due to their excess concentration in the BL.

The average diffusive path of NVs depends on density and, hence, the structure of the alloy, its granularity, etc. the boundary layer, where the major part of the vacancies is localized, is separated from the alloy bulk, which is free of diffusion.

We believe that there is an analogy between the BL of binary alloys and the passivation layer PL on metals. The PL is known to be a barrier between the electrolyte and metal, which reduces the rate of anodic dissolution by several orders of magnitude. The BL barrier arises due to the enrichment of the BL in the slow component. In the steady state (fixed-rate dissolution), the level of BL enrichment necessarily approaches a level sufficient to satisfy the fixed-rate condition (see below). The slow component migrates into electrolyte, governing the dissolution kinetics of the fast component; it simultaneously diffuses into the alloy bulk and stabilizes the BL. However, the diffusion parameters affect only the BL thickness, while the surface concentrations of the components  $C_{1s}, C_{2s}$  (i.e. the values  $\Delta_1 = c_{1b} - c_{1s}$  and  $\Delta_2 = c_{2b} - c_{2s}$  are governed by the interaction with the electrolyte, a process that is controlled by diffusion). The same behavior is typical of passivated metals.

The stabilizing roles of the anionic (i.e.; oxygen) PL sub lattice and the slow component are evidently similar. However, the anionic sub lattice is in partial electrochemical equilibrium with the electrolyte; therefore, its composition remains constant to the uncertainty associated with the equilibrium exchange between the passivated metal surface and the electrolyte. Oxygen ions diffuse to the metal surface (i.e., support), generating new oxide cells and stabilizing the characteristics of the PL.

The interdiffusion process under study is of fundamental importance, because it supplies reactants for the alloy-electrolyte reaction. Indeed, in the main regime of fixed-rate dissolution (when components  $M_1$  and  $M_2$  steadily pass into electrolyte in amounts corresponding to the ratio of their bulk concentrations  $c_{1b}$  and  $c_{2b}$ ), the steady-state condition should be valid:

$$\frac{i_1(\varphi)}{i_2(\varphi)} = \frac{z_1 c_{1b}}{z_2 c_{2b}} = \frac{c_{1s} q_1(\varphi)}{c_{2s} q_2(\varphi)},$$

Where, as above  $C_{1s}, C_{2s}$  and  $C_{3s}$  are the concentration of NVs on the dissolving alloy surface  $s$ .

That is, the chemical composition in the bulk of the alloy and in its BL may be dissimilar. Their difference arises only in the presence of diffusion.

The main factor that determines the values of  $C_{1s}$  and  $C_{2s}$  is the mutual influence of components  $M_1$  and  $M_2$ , which manifests itself through changes in their kinetic properties (for the interaction of the alloy with an electrolyte) with respect to the properties of pure (individual) metal. This influence always appears in metal alloys due to differences in the bonds between the atoms and changes in the characteristics of these bonds caused by rearrangement in the electronic structure of these metals.

In an alloy of metals A and B, along with A-A and B-B bonds, A-B bonds are formed. The relative numbers of bonds of these depend on the alloy composition, i.e., on the concentrations of its components. As a result, the energies of bonding of the atoms at the lattice nodes change. Since these energies depend on the concentrations of the components, the characteristics of their mutual influence in the BL and in the alloy bulk differ. Correspondingly, the kinetic properties of the component change during the interaction with the electrolyte, which is a manifestation of their mutual influence.

## REFERENCES

1. Darken. L., Trans. AIME, **175**: 184 (1948).
2. Manning. I. R., Diffusion kinetics for atom in crystals, New York: Van Nostrand, 1968. translated under the title kinetika diffuzii atomov v Kristallakh. Moscow: Mir (1971).
3. Popov. Yu. A., Teoriya vzaimodeistviya metallov I splavov s korrozionno-aktivnoi sredoi (Theory of interaction of metals and alloys with Corrosive media), Moscow: Nauka, **1155**: 1975 (1995).
4. Pickering. H.W., Wagner. C.J., *Electrochem. Soc.* **114**: 698 (1967).