CORROSION KINETICS OF AN ALLOY IMMERGED INTO A LIQUID METAL MELT CONTAINING OXYGEN

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Corrosion kinetics of a metal in metallic coolant containing oxygen is considered. The corrosion rate is found. The oxide film growth kinetics at moderate and high over-saturations of the oxygen content in coolant is considered. A mechanism of the oxide film growth blocking is described.

1. INTRODUCTION

The interest toward the liquid metal heat coolant in the form of the lead melt or eutectic *Pb-Bi* (PBE) is connected first of all with their use in the nuclear power plants of the next generation. These melts can also be used as the targets for neutron generation by means of the accelerators in the reactors that are destined for utilization of the depleted nuclear fuel and weapon plutonium. The advantage of these melts is their high thermal conductivity and relative safety in case of an accident but their negative feature is an ability to dissolve the contacting structural materials. The latter property prevents the utilization of these coolants without special corrosion protection of the structural material. The corrosion is meant the material components dissolution in the molten coolants.

The solubility of the metal in a melt increases with temperature and becomes particularly large when the formation of intermetallic compounds consisting of any of the components of the material and *Pb* or *Bi* atoms becomes possible. It is known that the protective oxygen film on the surface of an alloy contacting with Pb melt can suppress corrosion (see [1,2] and the literature cited therein). The protective effect of an oxide consists in the separation of the melt and the alloy which is further referred to as "metal". The metal solubility limit in the melt over the oxide is lower than that of unoxidized metal. Besides, the metal covered by the oxide film can be dissolved only after diffusional transportation through the oxide film.

The considerable amount of the experimental data on corrosion of iron and alloys on its basis (steels) in *Pb* and PBE is accumulated. The peculiarities of the growth kinetics of the oxide film being in contact with the melt saturated with oxygen and the kinetics of metal dissolution in the melt are not completely clear. The found thermodynamic values and, in particular, the constants of the thermodynamic equilibrium [1,2] indicate to which of the contacting subsystems metal-oxide-melt will this or that element be transferred if the equilibrium is broken. Still this is not enough for the description of the corrosion kinetics which depends not only on the thermodynamic relations but also on the transportation mechanisms and the reaction rates.

When describing the corrosion kinetics at the conditions of the oxide layer growth we should recon the diffusional transport of the oxygen from the melt into the oxide and the alloy and also transport of the alloy components both to the oxide layer and through this layer to the melt. Besides, the influence of the irradiation on the diffusion and chemical kinetics should be taken into account. To simplify the description we will only consider the one-component melt (e.g. lead) containing oxygen, and one-component structural material, e.g. $\alpha - Fe$.

It is considered that in an oxide as well as in a metal the atoms diffuse by vacancy mechanism. It should be taken into account that there are two sub-lattices in an oxide – metallic and oxygen one – and thus the two types of vacancies, oxygen and metallic ones. Due to the tight chemical bonds of the atoms of metal and oxygen the compositional disorder may be neglected, i.e. we can set the probabilities of finding the atom of oxygen in a metallic sub-lattice and the atom of metal in an oxygen one equal to zero. We will not dwell upon the formation process of the continuous oxide layer on the metal surface (it can also be obtained due to previous oxidation of the metal in the oxygen atmosphere). The metal oxidation and corrosion process will be described under conditions when the continuous oxide layer has been already formed. It is natural that in the limit of negligibly small layer thickness we should obtain the description of metal corrosion without an oxide film.

The reaction of oxidation is heterogeneous and proceeds at the boundaries of an oxide and a melt and at the interphase boundary metal-oxide. The objective of this work is to explore the rule of oxide layer boundaries movement and to find the flux of atoms of the metal, i.e. the rate of dissolution of metal in the melt.

The structure of the paper is as follows. First the equilibrium condition of the system melt-oxide-metal is described, in particular the equilibrium thickness of the oxide is found at a given amount of oxygen in the system. In the following sections the magnitude of the metal flow into the melt is found in case when the melt has metal concentration lower than the equilibrium one. Later on (section 3) the kinetics of growth of the oxide film is described under condition that the oxygen concentration in the melt is higher than the equilibrium one. In section 4 the case of relatively large oxygen over-saturation of the melt is considered. It is also shown that in this case the nuclei of the film growth are blocked and a heterophase structure containing great number of com-

114

ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2005. №.4.
Серия: Физика радиационных повреждений и радиационное материаловедение (87), с. 114-119.

plex oxides, which include the atoms of the melt, forms on the melt-oxide surface. In section 5 we give a brief review of such phenomenon as the modified Kirkendall effect caused by metal dissolution in the melt and also the oxide formation at grain boundaries in metal.

2. THE EQUILIBRIUM THICKNESS OF AN OXIDE

Let us start with considering the equilibrium oxide film contacting the melt and from the other side the metal. To describe the nonequilibrium kinetics we should know the parameters of the equilibrium system. Let us denote the thickness of the melt, oxide and metal by L_{Pb}, L_{ox}, L_M correspondingly and consider that there are N_0 atoms of oxygen in the system. Let us determine the equilibrium thickness L of the oxide. The geometry of the system is considered to be planar. At first we neglect the dissolution of oxygen in metal. It is obvious that the following condition of the balance of the oxygen amount should be satisfied

$$S[L_{Pb}c_0^{Pb} + L_{ox}c_0^{\tilde{o}x}] = N_0 a^3, \tag{1}$$

here c_0^{Pb} is the concentration of oxygen in the melt, $c_0^{\tilde{o}x}$ is its concentration in the oxide, S is the area of the system intersection, a^3 is the volume corresponding to an atom that is considered constant in all subsystems in order to avoid cumbersome expressions.

Let us find the equilibrium thickness L of the oxide from this relation

$$L = \frac{N_0 a^3}{S c_0^{\tilde{o}x}} - L_{Pb} \frac{c_0^{Pb}}{c_0^{\tilde{o}x}} . \tag{2}$$

The concentration of oxygen in oxide $M_x O_y$ is equal to

$$c_0^{\tilde{o}x} = \frac{y}{x+y} \tag{3}$$

The equilibrium concentration of oxygen in the melt over the oxide film is

$$\overline{c_0^{Pb}} = K_0^{ox,Pb} c_0^{\tilde{o}x}, \quad K_0^{ox,Pb} = \exp\left(\frac{\mu_0^{ox} - \mu_0^{Pb}}{T}\right), \tag{4}$$

where μ_o^{Pb} and μ_o^{ox} are the chemical potentials of oxygen in the melt and oxide respectively. Substituting this relation for the oxygen concentration in the melt to the formula for the equilibrium thickness L of the oxide we derive

$$L = L_{ox}^{\max} - K_0^{ox,Pb} L_{Pb}, \quad L_{ox}^{\max} = \frac{N_0 a^3}{S c_0^{\tilde{o}x}} \tag{5}$$

Here $L_{ox}^{\max}$ is the maximal thickness of the film obtained when all oxygen is in the oxide.

The deduced relations reveal the growth (dissolution) criterion of the oxide film contacting the melt. At

$$c_0^{Pb} > \overline{c_0^{Pb}} = K_0^{ox,Pb} c_0^{\tilde{o}x}, \tag{6}$$

or $L_{ox} < L$, the film growth takes place. Otherwise the film is dissolving. When writing these relations we neglected the oxygen solubility in metal.

Taking into account the oxygen dissolution in metal let us denote the equilibrium constant of oxygen in the system oxide-metal as $K_0^{ox,M}$:

$$K_0^{ox,M} = \exp\left(\frac{\mu_0^{ox} - \mu_0^M}{T}\right), \tag{7}$$

where μ_0^M is the chemical potential of the oxygen in metal. It is not hard to find that the equilibrium thickness of the oxide, $\overline{L}$, in this case is equal

$$\overline{L} = L_{ox}^{\max} - K_0^{ox,Pb} L_{Pb} - K_0^{ox,M} L_M, \tag{8}$$

where L_M is the thickness of metal.

3. DISSOLUTION OF METAL IN THE MELT

The protective effect of the oxide film appears in the fact that the transport of the metal to the melt through it is hindered. It is useful to clarify the dependence of the dissolution rate of the metal in the melt upon the kinetic properties and upon the structural properties of metal, melt and oxide.

In the equilibrium the concentration of the metal in oxide $M_x O_y$ is constant

$$\overline{c_m^{ox}} = \frac{x}{x+y}. \tag{9}$$

The equilibrium concentration of metal in the melt is determined from the condition of the thermodynamic equilibrium

$$\overline{c_m^{Pb}} = c_m^{\tilde{o}x} K_m^{ox,Pb}, \quad K_m^{ox,Pb} = \exp\left(\frac{\psi_m^{ox} - \psi_m^{Pb}}{T}\right). \tag{10}$$

Here ψ_m^{ox}, ψ_m^{Pb} is the free energy per atom of the metal in oxide and in lead.

Provided that the balance is broken and the concentration of metal in the melt is lower than the equilibrium one, $c_m^{Pb} < \overline{c_m^{Pb}}$, the atoms of metal from the oxide surface will be transferring into the melt. Under such conditions the excess vacancies are forming in the metallic sub-lattice of an oxide. Let us consider that the probabilities of transition of an atom of metal to the oxygen sub-lattice and the oxygen atom to the metallic sub-lattice are negligible. In this case, the excess vacancies will diffuse deep into the oxide and then into the metal. As a result there appears the counter-current flow of the atoms of metal which is equal in magnitude to the vacancy current $\vec{j}_{vm}^{ox}$ but opposite in sign

$$\vec{j}_m^{ox} = -\vec{j}_{vm}^{ox}. \tag{11}$$

115

ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2005. №.4.
Серия: Физика радиационных повреждений и радиационное материаловедение (87), с. 114-119.

Let us calculate this current. The kinetic equations for the vacancies of atoms of metal in the surface layer ($x=l_1$) are as follows:

$$\frac{\partial c_v}{\partial t} = \frac{c_m^{ox}}{\tau_m}\delta(x-l_1) + div\, j_v \, . \qquad (12)$$

$$\frac{\partial c_m^{ox}(l_1)}{\partial t} = -\frac{1}{\tau_M}c_m^{ox}(l_1) + R_{vm}c_{vm}^{ox}(l_1)c_m^{Pb}(l_1). \qquad (13)$$

$$\frac{\partial c_m^{Pb}}{\partial t} = \frac{1}{\tau_m}c_m^{ox}\delta(x-l_1) + div\, \vec{j}_m^{Pb}. \qquad (14)$$

$$j_{vm} = -D_{vm}^{ox}\partial c_{vm}/\partial x \, ,$$
$$\tau_m^{-1} = v_0 \exp T^{-1}(\psi_m^{ox} - \psi_m^{Pb} - \psi_{vm}^{ox}). \qquad (15)$$

Here τ_m is the time required for an atom of metal to transfer to the melt and generate a vacancy with free energy ψ_{vm}^{ox} at the surface, v_0 is the "frequency of attempts" which approximately equals to Debye frequency, R_{vm} is the recombination constant, and D_{vm}^{ox} is the is the diffusion coefficient of the metallic atom in the oxide. The recombination constant R_{vm} determines the response rate of fusion of an atom of metal from the melt with the metallic vacancy, i.e. the rate of transition of an atom of metal from the melt into the oxide,

$$R_{vm} = D_m^{Pb}v_0 r^2 \, , \qquad (16)$$

D_m^{Pb} is the diffusion coefficient of metal atom in the melt. The trapping radius r is comparable to the interatomic distance.

Taking into account (10) and (16) the equation (13) can be presented as

$$\frac{\partial c_m^{ox}(l_1)}{\partial t} = -v_0 c_m^{\overline{Pb}}c_{vm}^{\overline{ox}} + R_{vm}c_{vm}^{ox}(l_1)c_m^{Pb}(l_1). \qquad (17)$$

In the conditions of thermodynamic equilibrium $c_{vm}^{ox}(l_1) = c_{vm}^{\overline{ox}}$, $c_m^{Pb}(l_1) = c_m^{\overline{Pb}}$ and $\partial c_m^{ox}(l_1)/\partial t = 0$. This implies $R_{vm} = v_0$.

The case when the nonequilibrium concentration of metal in the melt is sustained permanently is practically interesting. Such nonequilibrium arises for example due to the temperature inhomogeneity along the cooling loop. It is seen from (10) that the equilibrium concentration of metal in the melt decreases in the lower temperature areas. There the excess metal deposits on the walls and the depleted melt will enter the hot part of the loop. The flow of the melt in the loop is not laminar so that the fast convective transfer rapidly balances the concentration of metal in the melt. This fast convective transfer does not extend to the thin wall layer near the oxide.

The thickness of this layer, L_m, is determined by the roughness of the oxide surface and the properties of the turbulent flow (see e.g. [3]). There is a diffusional transport of the metal atoms in the wall layer. Note that in the laminar flow $L_m = L^{Pb}$. In the turbulent flow, the concentration of the dissolved metal can be considered constant due to the fast turbulent mixing. Let us denote this quantity as c_m^{i}. Taking this into account the transport equation (14) should be supplemented by the boundary condition

$$c_m^{Pb}\big|_{l_1+L_m} = c_m^{i}. \qquad (18)$$

As for the metallic vacancies they diffuse through the coating into the metal and there go to sinks in the absence of high capacity sinks in the oxide. Dislocations, grain boundaries and pore surfaces are the sinks for them. Usually the density of such sinks in not small in real metals so that the mean distance from the interface oxide-melt to the sink of the metallic vacancies is approximately equal to the thickness of the oxide, $L_v \approx L^{ox}$. In the vicinity of sinks the concentrations of the vacancies are equal to the equilibrium values. Considering these arguments, the boundary condition for the equation (12) (at the interface metal-oxide) is as follows:

$$c_{vm}^{ox}\big|_{l_1-L_{ox}} = c_{vm}^{\overline{ox}}. \qquad (19)$$

In order to find the boundary conditions for $c_{vm}^{ox}(l_1), c_m^{Pb}(l_1)$, let us refer to the equations (11-17). We are interested in the quasi-stationary case when the changes in time of the required magnitudes can be neglected. In this case from (12), (14), (17-19) we have:

$$c_m^{\overline{Pb}}c_{vm}^{\overline{ox}} = c_{vm}^{ox}(l_1)c_m^{Pb}(l_1) \, ; \qquad (20)$$

$$|j_v^{ox}| = \frac{D_{vm}^{ox}\left(c_{vm}^{ox}(l_1) - c_{vm}^{\overline{ox}}\right)}{L_v}, \quad |j_m^{Pb}| = \frac{D_m^{Pb}\left(c_m^{Pb}(l_1) - c_m^{i}\right)}{L_m}. \qquad (21)$$

Subject to (21) the condition of the equality of the fluxes (11) is:

$$\frac{D_{vm}^{ox}\left(c_{vm}^{ox}(l_1) - c_{vm}^{\overline{ox}}\right)}{L_v} = \frac{D_m^{Pb}\left(c_m^{Pb}(l_1) - c_m^{i}\right)}{L_m} \, . \qquad (22)$$

It is easy to find magnitudes $c_{vm}^{ox}(l_1)$ and $c_m^{Pb}(l_1)$ from the equations (20-21) and along with them the value of the flux of metal to the melt which we are interested in. Let us introduce this solution in the most interesting case when $c_{vm}^{ox}(l_1) \gg c_{vm}^{\overline{ox}}$, $c_m^{Pb}(l_1) \gg c_m^{i}$. It is clear that otherwise the flux of metal will be negligible. As a result of simple transformations of expressions (20-22) we obtain

116

ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2005. №.4.
Серия: Физика радиационных повреждений и радиационное материаловедение (87), с. 114-119.

$$|j_m^{Pb}|=\sqrt{\frac{D_{vm}^{ox}\,\overline{c}_{vm}^{ox}}{L_v}\frac{D_m^{Pb}\,\overline{c}_m^{Pb}}{L_m}}\left[1-\frac{c_m^{\dot\iota}}{c_m^{Pb}(l_1)}\right]=$$

$$\sqrt{\frac{D_{vm}^{ox}\,\overline{c}_{vm}^{ox}}{L_v}\frac{D_m^{Pb}\,\overline{c}_m^{Pb}}{L_m}}\left[1-c_m^{\dot\iota}\sqrt{\frac{D_m^{Pb}\,L_v}{4D_{vm}^{ox}\,L_m}}\right].$$

(23)

This is finally the required expression for the magnitude of the corrosion current. Note that its value is in inverse proportion to the square root of the thickness of the oxide film and the thickness of the diffuse layer in the melt and is proportional to the square root from the value of the equilibrium concentration of metal in the melt. In (23) we kept the correction $\sim c_m^{\dot\iota}$ in order to see when it is required. The correction $\sim \overline{c}_{vm}^{ox}/c_{vm}^{ox}(l_1)$ is neglected.

4. DIFFUSION KINETICS OF THE OXIDE GROWTH

The description of the process of the oxide film growth at the conditions of over-saturation of melt with the oxygen is of interest. The oxidation of metal may take place in two ways:

1) the atoms of metal diffuse through the film and interface melt-oxide and there form a stochiometric compound M_xO_y with oxygen from the melt;

2) the oxygen atoms diffuse through the oxide and interface metal-oxide and there form the oxide.

These two processes are not independent if the atoms of metal diffuse only on the metal sub-lattice and the oxygen atoms diffuse on the oxygen one. The departure of atoms from metal to the interface melt-oxide causes accumulation of vacancies at the interface metal-oxide. These excess vacancies can move to sinks in the metal or along the oxygen sub-lattice to the interface melt-oxide. Thus the fluxes of atoms (and vacancies) of metal and oxygen are connected and this connection should generally be taken into account.

Since the conditions of the balance of fluxes, the equation of transport for vacancies and their solutions are simple we will start with the description of the boundary conditions for $c_{vm}^{ox}, c_{vo}^{ox}, c_{vm}^{M}$ at both interfaces. We have denoted the concentrations of oxygen vacancies in the oxygen sub-lattice and vacancies in metal as c_{v0}^{ox}, c_{vm}^{M} .

At the interface melt-oxide ($x=l_1$) the atoms of metal combining with the oxygen from the melt form new oxide cells. The vacancy in the metallic sub-lattice is formed when an atom of metal goes to the surface and from the condition of the thermodynamic equilibrium of reaction

$$O^{Pb}+M^{ox}\leftrightarrow O^{ox}+V_m+M^{ox} ,$$

(24)
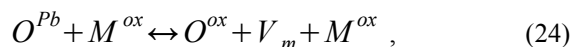
we obtain an equation

$$\psi_o^{Pb}+T\ln c_0^{Pb}(l_1)=\psi_o^{ox}+\psi_{vm}^{ox}+T\ln c_{vm}^{ox}(l_1)$$
.

(25)

Hence on repeating the calculations similar to the ones given in section 3 we obtain

$$c_{vm}^{ox}(l_1)=c_o^{Pb}(l_1)\frac{\overline{c}_{vm}^{ox}}{\overline{c}_o^{Pb}} .$$

(26)

As for the concentration of the oxygen vacancies at this interface it should be set equal to the equilibrium value

$$c_{vo}^{ox}(l_1)=\overline{c}_{vo}^{ox}=\exp(-\psi_{vo}^{ox}/T) .$$

(27)

The thermodynamic equilibrium of the oxygen sublattice is reached at this magnitude of c_{vo}^{ox} . In order to simplify the calculations we will pass over the consideration of oxygen transport in the diffusional layer of the melt. We can do this by using the fact that according to the equation of type (22)

$$c_o^{Pb}(l_1)\approx \overline{c}_o^{Pb}$$

(28)

because the diffusion coefficient of oxygen in the melt is usually much larger than D_{vm}^{ox}.

In order to find the values we are interested in at $x=l_1+L_{ox}\equiv l_2$ let us use the equation of balance of vacancies flows

$$|j_{vm}^{ox}|=|j_{vm}^{M}|+|j_{vo}^{ox}|,$$

(29)

where

$$j_{vm}^{ox}=\frac{D_{vm}^{ox}}{L_{ox}}[c_{vm}^{ox}(l_1)-c_{vm}(l_2)] ;$$

(30)

$$j_{vo}^{ox}=\frac{D_{vo}^{ox}}{L_{ox}}[c_{vo}^{ox}(l_2)-c_{vo}^{ox}(l_1)] ;$$

(31)

$$j_{vm}^{M}=\frac{D_{vm}^{M}}{L_{vm}^{M}}[c_{vm}^{M}-\overline{c}_{vm}^{M}].$$

(32)

Here c_{vm}^{M}, L_{vm}^{M} is the equilibrium concentration and the mean distance to the sink of vacancies in the metal.

Besides from the condition of thermodynamic equilibrium of vacancies in the oxide and metal we obtain

$$c_{vm}^{M}=K_v^{M,ox}c_{vm}^{ox}(l_2), c_{vo}^{ox}(l_2)=K_v^{ox}c_{vm}^{ox}(l_2).$$

(33)

where

$$K_v^{M,ox}=\exp[(\psi_{vm}^{ox}-\psi_o^{M})/T$$
$$\dot\iota$$
$$\dot\iota K_v^{ox}=\exp\{(\psi_{vm}^{ox}-\psi_o^{ox})/T\}.\dot\iota\dot\iota$$

(34)

It is not hard to find the solutions of the equations (29-24). But in order to escape the cumbersome expressions let us consider only the limiting cases that are of practical interest.

1). Thin oxide films. The flux of vacancies to the sink in the metal can be neglected if

$$|j_{vm}^M| << |j_{vm}^{ox}|, |j_{vo}^{ox}| .$$ (35)

As follows from (30) - (32) this condition is satisfied if the thickness of the oxide is small enough so that

$$\frac{D_{vm}^{ox}}{L_{ox}}[c_{vm}^{ox}(l_1) - c_{vm}^{ox}(l_2)] >> \frac{D_{vm}^M}{L_{vm}^M} c_{vm}^M(l_2) .$$ (36)

In this case

$$c_{vm}^{ox}(l_2) \approx \frac{D_{vm}^{ox}}{D_{vm}^{ox} + D_{vo}^{ox} K_v^{ox}} c_{vm}^{ox}(l_1) ;$$ (37)

$$|j_m^{ox}| = |j_o^{ox}| = \frac{D_{vm}^{ox} D_{vo}^{ox} K_v^{ox} c_{vm}^{ox}(l_1)}{L_{ox}(D_{vm}^{ox} + D_{vo}^{ox} K_v^{ox})} = \frac{\tilde{D}}{L_{ox}} c_{vm}^{ox}(l$$ (38)

and for the rate of the film growth we have the following expression

$$\partial L_{ox}/\partial t = V_{ox} = |j_m^{ox}| + |j_o^{ox}| = 2|j_m^{ox}| = 2 \tilde{D} c_{vm}(l$$ (39)

As is obvious in this case

$$L_{ox}(t) = 2 \sqrt{\tilde{D} c_{vm}(l_1)t}, \tilde{D} = \frac{D_{vm}^{ox} D_{vo}^{ox} K_v^{ox}}{D_{vm}^{ox} + D_{vo}^{ox} K_v^{ox}}$$ (40)

i.e. the parabolic law of film growth with the effective transport coefficient which equals $2\tilde{D}$ takes place.

2). Thick oxide films. In this case, when the thickness of the film is large and the distance to the sinks of vacancies in the metal is small, the inequality opposite to (36) is valid. In this case $|j_{vm}^{ox}| \approx |j_v^M|$, so that $c_{vm}^{ox}(l_2) \approx c_{vo}^{\overline{ox}}$,

$$c_{vm}^{ox}(l_2) \approx \frac{L_{vm}^M D_{vm}^{ox}}{L_{ox} D_{vm}^M K_v^{M,ox}} c_{vm}^{ox}(l_1)$$ (41)

$$|j_m| = \frac{D_{vm}^{ox}}{L_{ox}}[1 - \frac{L_v^M D_{vm}^{ox}}{L_{ox} D_{vm}^M K_v^{M,ox}}] c_{vm}^{ox}(l_1) \approx D_{vm}^{ox}$$ (42)

With that the oxide film grows only at the interface metal-oxide

$$\partial L_{ox}/\partial t = |j_m|$$ (43)

and on substituting the expression (42) in the right hand side and on subsequent integrating we obtain

$$L_{ox}(t) \approx \sqrt{D_{vm}^{ox} c_{vm}^{ox}(l_1)t} .$$ (44)

As it is clear, the thick films also grow according to the parabolic law but when comparing (40) and (44) we can see that in this case the square of thickness grows with another rate and the relation of these rates is

$$\frac{4 \tilde{D}}{D_{vm}^{ox}} = \frac{4 D_{vo}^{ox} K_v^{ox}}{D_{vm}^{ox} + D_{vo}^{ox} K_v^{ox}} .$$ (45)

It is determined by value K_v^{ox} . If $3D_{vo}^{ox} > D_{vm}^{ox}$, then the thin films grow faster than the thick ones.

5. A POSSIBLE MECHANISM OF BLOCKING THE GROWTH OF THE OXIDE FILM

The ability of the oxide film to suppress the corrosion of metal nonmonotonously depends on the concentration of oxygen in the melt. In the paper [2] the $\alpha-$ iron was taken as the tested metal and the lead with oxygen dissolved in it was taken as the melt. It turned out that at first the rate of corrosion deceases with increase of concentration. But upon reaching the minimum at some value c_o^{Pb} the rate of corrosion starts increasing fast. Upon that the abrupt increase of concentration of atoms of the melt is noticed both in the oxide and in the surface layer of the metal. An analogous dependence of the rate of corrosion on the concentration of oxygen is also observed for steels.

As it is clear from (26), (40), (44), the flow of the metal into the melt $j_m \sim 1/\sqrt{L_{ox}}$ decreases with increase of the thickness of oxide whose growth rate is proportional to $c_o^{Pb}/c_o^{\overline{Pb}}$. Apparently the experimental data at $c_o^{Pb} >> c_o^{\overline{Pb}}$ are not described by these relations. This implies that the found dependence of the film growth rate on c_o^{Pb} becomes invalid and that at $c_o^{Pb} >> c_o^{\overline{Pb}}$ some mechanism of suppression of the growth of film $M_x O_y$ and the degradation of its protective characteristics take place. We will describe the possible mechanism of blocking the growth of the protective oxide film which develops at comparatively large concentration of oxygen in the melt.

Let us study the kinetics of the oxide film growth in more detail. The systems $M_x O_y$ forming at its surface diffuse and upon reaching one of the centers of growth of the film they are embedded into it. The centers of growth are the kinks on the growth steps which constitute the edges of uncompleted planes. Let us denote the concentration of the kinks, i.e. their number falling at one cell of the oxide at the surface, as c_g . We will consider that the structure of the surface is changing a little while growing so that c_g can be taken as a constant. A kink may be blocked by the complex *PbO*. In this case it is converted to the centre of growth of the complex oxide *M-O-Pb* which violates the structure and the properties of the oxide film. In order to find the part of the kinks which are blocked by the com-

118

ВОПРОСЫ АТОМНОЙ НАУКИ И ТЕХНИКИ. 2005. №.4.
Серия: Физика радиационных повреждений и радиационное материаловедение (87), с. 114-119.

plexes *PbO* we have to find the probability of formation of the complex on a kink. On denoting the free energies of atoms of lead and oxygen in the complex *PbO* on the film as $\psi_{Pb}^{\iota}, \psi_o^{\iota}$ and the free energy of atoms of lead in the melt as ψ_{Pb} we obtain the following equilibrium equation for the probability of formation of the complex on a kink w^{ι}

$$\psi_{Pb}^{\iota} + \psi_o^{\iota} + T \ln w^{\iota} = \psi_{Pb} + \psi_o^{Pb} + T \ln c_o^{Pb} + T \ln \tag{46}$$

The addends $\ln w^{\iota}, \ln(1 - w^{\iota})$ describe the mixing entropy of blocked and free kinks respectively. From this equation it follows that

$$w^{\iota} = \frac{c_o^{Pb} \exp(\Delta\psi/T)}{1 + c_o^{Pb} \exp(\Delta\psi/T)}, \tag{47}$$

where $\Delta\psi = \psi_{Pb} + \psi_o^{Pb} - \psi_{Pb}^{\iota} - \psi_o^{\iota}$.

As for the part of the free kinks it is equal to

$$1 - w^{\iota} = 1/[1 + c_o^{Pb} \exp(\Delta\psi/T)]. \tag{49}$$

From this relation it is clear that the oxide film becomes substantially heterogeneous at

$$c_o^{Pb} \exp(\Delta\psi/T) \geq 1 . \tag{50}$$

When the cells M_xO_y and *M-O-Pb* vary greatly the incoherent phase boundaries which are the paths of easy diffusion of metal and hence suppress the protective properties of the oxide coating are formed. If $c_o^{Pb} \exp(\Delta\psi/T) << 1$ then the few cells *M-O-Pb* are immured in the oxide film of the stochiometric composition M_xO_y and do not affect its protective properties much.

6. DISCUSSION

The relaxation kinetic processes arise when the system deviates from equilibrium. These processes become particularly significant in the open systems whose nonequilibrium is supported from the outside. In this case the stable stationary and quasi-stationary states with nonzero fluxes of the complexes may set in. As a rule such states have the heterogeneous phase structure whose evolution is of interest. The regarded system melt-oxide-metal relates to these very objects. Since there are normally many ways of relaxation of the nonequilibrium system then the choice of the fastest process, i.e. the preliminary estimation of the rates of the most probable reactions and transport mechanisms, is of major importance. We consider the violation of the stochiometry of the oxide which is a compound with covalent bonds to be connected with the large increase of the free energy and this phenomenon is not regarded here. As a result the transport of atoms of metal and oxygen occurs by the vacancy mechanism in the different sub-lattices of the oxide. The validity of this assumption can be checked experimentally. In case when it is unjustified we should build a more complicated model of transport of the components in the oxide. It is obvious that this will cause the change of structure of the coefficients in the found expression for the growth

rate of the thickness of oxide and the flux of atoms of metal into the melt.

As the thickness of the oxide layer in [4,5] increased, the intergranular oxidation of an alloy under the continuous film of the oxide Fe_3O_4 was observed. We refrained from describing the kinetics of dissolution of oxygen in metal and formation of the oxide M_xO_y along the grain boundaries though this phenomenon has been observed experimentally. The model of the kinetics of dissolution of oxygen and the growth of the oxide along the boundaries is similar to those used in the description of the oxide film growth. The growth of the oxide along the grain boundaries is determined by the flux of oxygen dissolved in metal to the boundaries and proceeds until the chemical potential of oxygen in the boundary layer becomes equal to its chemical potential in the metal and the oxide film.

The papers [1,2] suggested the mechanism of destruction of the oxide film, namely the reaction of combination of lead with Fe_3O_4 resulting in the formation of the pure iron (in the melt) and the lead oxide. The kinetics of this process may be described in the framework of the model similar to those given in this paper provided that the required thermodynamic parameters are known.

The expressions for the concentration of vacancies in the metal (37), (41) show that it is excessive at the interface metal-oxide. The excessive vacancies may form the vacancy orthorhombic dislocation loops or pores. Both loops and voids are the sinks for vacancies. Therefore the nucleated voids will grow as the atoms of metal are dissolved in the melt or depart to the interface melt-oxide at the growth of the film. The development of porosity due to the nonrefundable flux of atoms through the interface of the contacting solid bodies is the Kirkendall effect. In our case the modified Kirkendall effect in the three-layered system is realized. In [4,5] it is reported on the development of porosity in the metal under the oxide film.

The built models of metal dissolution and growth of the oxide layer which contacts the melt should be modified allowing for the influence of irradiation on these processes. Under irradiation the transport rate (due to the point defects formation) and the reaction rates (due to the transfer excess energy to the systems of atoms) undergo alternation. Besides, the cascade-generating irradiation causes mixing of the atoms in the the cascade region. Analysis of these processes is beyond this communication and will be done elsewhere.

7. CONCLUSIONS

We have found the conditions of equilibrium of the conservative system melt-oxide-metal and have suggested the models of the relaxation kinetics in the nonequilibrium system. The expressions which describe the dissolution rate of metal in the melt and the growth of the oxide layer have been deduced. When the solution is moderately over-saturated by the oxygen, the film thickness growth obeys the parabolic law but the growth rates of the square of thickness for thick and thin films are different.

In the case when the melt is highly over-saturated by oxygen, at $c_o^{Pb} >> c_o^{Pb}$, the formation of the complex oxides of the type *M-O-Pb* on the kinks of the film growth steps becomes possible. This results in blocking of the growth of the oxide M_xO_y and formation of the

heterophase structure of the oxide at the interface melt-oxide.

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КИНЕТИКА КОРРОЗИИ СПЛАВА, ПОГРУЖЕННОГО В ЖИДКИЙ МЕТАЛЛИЧЕСКИЙ РАСПЛАВ, СОДЕРЖАЩИЙ КИСЛОРОД

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Рассмотрена кинетика коррозии металла в металлическом охладителе, содержащем кислород. Найдена скорость коррозии. Рассмотрена кинетика роста оксидной пленки при умеренной и высокой пересыщенности охладителя кислородом. Описан механизм блокирования роста оксидной пленки.

КІНЕТИКА КОРОЗІЇ СПЛАВА, ЗАНУРЕНОГО В РІДКИЙ МЕТАЛІЧНИЙ РОЗПЛАВ, ЯКИЙ МІСТИТЬ КИСЕНЬ

О.С. Бакай, Л.В. Танатаров

Розглянута кінетика корозії метала в металічному охолоджувачі, який містить кисень. Знайдена швидкість корозії. Розглянута кінетика роста оксидної плівки при помірній та високій пересиченості охолоджувача киснем. Описаний механізм блокування роста оксидної плівки.

120

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