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The Phenomenological Model of Iron Oxidation in Pb Melt

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1. Introduction

Lead is considered as a coolant for innovative nuclear systems, while iron is a base component of steels - candidate structural materials for reactor active zones [1]. The *in-situ* formation of a protective oxide layer on the iron surface prevents the dissolution of iron into the melt. However the oxidation mechanism of Fe-based materials in lead melt containing oxygen has not been elucidated yet. To reflect the experimental results on kinetics of oxidation of Fe-based alloys in lead melts the Wagner's theory is used usually [2]. This theory is based on the hypothesis that at the phase boundaries the thermodynamic equilibrium is being set immediately and the concentrations of the reactants do not change with time. At the same time the experimental results testify that the phase and elemental composition of scale are being changed and the defects are being accumulated in the scale with time [3]. To reproduce analytically the oxidation process the kinetics of phenomena at the phase-boundaries and the defectiveness of formed structures should be taken into account. The aim of the present work is to describe the oxidation of iron in the lead melt saturated by oxygen at 550°C with taking into account the kinetics of phenomena at the phase-boundaries.

2. Analytical description

The growth of magnetite on the surface of iron contacting with Pb[O] was simulated in the framework of reaction diffusion (Fig. 1 a). The growth of scale is defined by the total flow (j_{Fe}) of bivalent and trivalent iron cations. Therefore, the diffusion of iron cations can be described by the following differential equations system:

$$D_1 \Delta C_1 = \partial C_1 / \partial \tau + k_1 C_1 - k_2 C_2 \ , \ D_2 \Delta C_2 = \partial C_2 / \partial \tau - k_1 C_1 + k_2 C_2 \ . \quad (1)$$

Here $C_i = C_i(x, \tau)$ and D_i – concentrations and diffusivities of bivalent (i=1) and trivalent (i=2) iron cations; k_1 and k_2 – coefficients, which characterize the direct and back reactions $Fe^{+2} \leftrightarrow Fe^{+3}$. Assuming that $C = C_1 + C_2$ is the total concentration of cations, it is obtained that the system of equations (1) get similar to the Fick`s equation. Here, the effective diffusivity of cations (D_{eff}) depends on both the time (τ) and the spatial value (x) in the scale. Assuming that the local dynamic equilibrium between bivalent and trivalent iron cations exists ($C_1 / C_2 = C_1^{eq} / C_2^{eq} = k_2 / k_1 = const$), it is obtained that:

$$D_{eff} \Delta C = \partial C / \partial \tau \ , \text{ here: } D_{eff} = (D_1 k_2 + D_2 k_1)/(k_1 + k_2) = const \, . \quad (2)$$

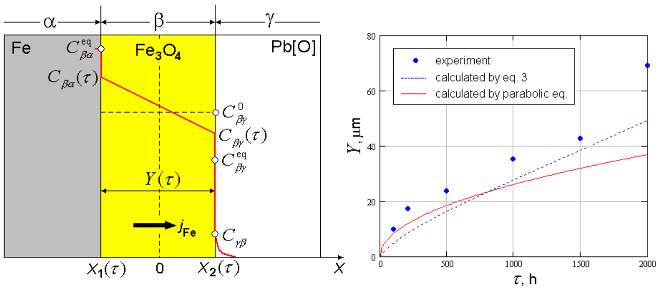
With time, the defects filled in liquid metal are accumulated in the magnetite scale. To describe the diffusion of iron in this oxide the system of Eq. (1) or Eq. (2) can be used. In this case the diffusion occurs by means of two ways: by slow bulk diffusion with diffusivity D_1 and by fast diffusion along the paths containing liquid-metal with diffusivity D_2. The oxygen concentration on these paths is C_1 and C_2, respectively, while the total concentration is C. For simplification, the linear distribution of iron in the oxide was used and the diffusion dissolution of iron in the lead melt was neglected. However, the kinetics of phenomena at the phase boundaries is taken into account.

Under the non-stationary conditions of mass exchange at the phase boundaries the thickness of scale $Y(\tau)$ can be determined according to the following equation [4]:

$$\left(Y(\tau)\right)^2/(2D_{eff})+Y(\tau)/H=F(\tau), \qquad (3)$$

here: $F(\tau)=\int_{\tau_0}^{\tau}\frac{C_{\beta\alpha}^{\mathrm{eq}}-C_{\beta\gamma}(\tau)}{C_{\beta\gamma}(\tau)-C_{\gamma\beta}}d\tau$, $C_{\beta\gamma}(\tau)=C_{\beta\gamma}^{\mathrm{eq}}-(C_{\beta\gamma}^{\mathrm{eq}}-C_{\beta\gamma}^{0})\exp(-k_{\gamma}(\tau-\tau_0))$.

The coefficient of mass transfer H in the Eq. 3 allows to take into account the kinetic barrier (the accumulated pores) for mass exchange at the $x = X_1$ interface. The parameter k_γ characterizes the time dependence of iron concentration at the outer $x = X_2$ interface. This dependence is caused by the generation of non-equilibrium cation vacancies and accumulation of the liquid metal components near $x = X_2$.



a

b

Fig. 1: Scheme of kinetic processes in the Fe / Pb[O] system (a) and the scale thickness (Y) versus time (τ) (b) formed on the surface of Fe after exposure to Pb melt (10^{-3} wt%O) at 550°C.

Fig. 1 b shows the kinetics of growth of the oxide layer (Fe$_3$O$_4$). The dotted line was plotted according to the proposed Eq. 3. The solid line represents the parabolic law of scale growth according to the Wagner's model. The curves are plotted using the following parameters: $D_{\mathrm{eff}} \approx 10^{-12}$ cm^2/s; $D_{\mathrm{eff}}/H = 0.5$ cm; $k_\gamma = 2\cdot10^{-4}$ s^{-1}; $C_{\beta\gamma}{}^{0}/C_{\beta\alpha}{}^{eq}=0.9$; $C_{\beta\gamma}{}^{eq}/C_{\beta\alpha}{}^{eq}=0.5$; $C_{\gamma\beta}/C_{\beta\alpha}{}^{eq}=0.1$.

It is evident from Fig. 1 b that the curve, calculated by Eq. 3, reflects qualitatively the experimental data obtained after exposure of Armco-Fe to Pb melt (10^{-3} wt% O, 550°C, 2000 h). It is shown that in the comparison with parabolic dependence (solid line) an accounting of the physical-chemical phenomena at the phase-boundaries changes substantially the kinetic curve of the oxide growth (dotted line) and reflects more adequately the experimental data. Thus, the difference in the trend of curves at the initial stages is caused by the existence of kinetic barrier at the interface $x = X_1(\tau)$, while at the later stages - by the increasing of defectiveness of outer oxide with time.

References

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