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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Abstract

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G. A. Toporishchev, O. A. Esin, V. N. Kalugin

STUDY OF THE KINETICS OF HIGH-TEMPERATURE ELECTRODE PROCESSES BY THE GALVANOSTATIC METHOD

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The dependence of the polarization η on the time t at a given current density i makes it possible, under known conditions, to find the exchange current i_0, the double-layer capacitance C, and also the diffusion coefficients D_1 and D_2 determining the potential of the substances (^{1}). The galvanostatic method was used by us to study, at temperatures of 1320–1420°, the behavior of the interfaces of melts: I Fe–C_{sat}–Si (0.29%), II Fe–C_{sat}–Mn (0.043%), and III Fe–C_{sat}–S (0.025%), with liquid aluminosilicates ($40\%\,\text{CaO}, 40\%\,\text{SiO}_2, 20\%\,\text{Al}_2\text{O}_3$, with and without the addition of $1\%\,\text{CaS}$) and aluminates ($44\%\,\text{CaO}, 48\%\,\text{Al}_2\text{O}_3, 6\%\,\text{MgO}$, and $2\%\,\text{MnO}$).

Fig. 1. Dependence of anodic polarization on time for the melt interface II Fe–C_{sat}–Mn (0.043%) with aluminate at $t = 1320°$ and $i = 0.16$ A/cm^2. a–rise curve, b–decay

Fig. 2. Dependence of η on t (a) and of η on $t^{1/2}$ (b) for anodic polarization of the boundary Fe–C_{sat}–Si (0.29%) with an aluminosilicate melt at $t = 1350°$ and $i = 0.01$ A/cm^2

The curves η, t were photographed from the screen of an S1-19 oscillograph, which makes it possible to record 2 mV in 10^{-7} s. The procedure for carrying out the measurements was analogous to that described previously (^{2},^{3}). Some of the curves obtained are shown in Figs. 1–3.

If the polarization is due to a slow discharge and diffusion, and if $\eta \ll 0.1\,RT/nF$, then, according to (^{4}), the dependence of η on t has the form

$$\eta = \frac{i}{C(A-B)} \left\{ \frac{A}{B^2} \left[\exp(B^2 t)\ \mathrm{erfc}(B t^{1/2}) + 2B \left(\frac{t}{\pi}\right)^{1/2} - 1 \right] - \frac{B}{A^2} \left[\exp(A^2 t)\ \mathrm{erfc}(A t^{1/2}) + 2A \left(\frac{t}{\pi}\right)^{1/2} - 1 \right] \right. \tag{1}$$

where

$$B\,(A) = \frac{i_0}{2nF} \left(\frac{1}{D_1^{1/2} C_1} + \frac{1}{D_2^{1/2} C_2} \right) (+) \left[\frac{i_0^2}{4n^2 F^2} \left(\frac{1}{C_1 D_1^{1/2}} + \frac{1}{D_2^{1/2} C_2} \right)^2 - \frac{nFi_0}{RTC} \right]^{1/2}; \tag{2}$$

C_1 and C_2 are the concentrations of particles in the oxidized (oxide melt) and reduced (metal) forms.

For very short ($10^{-6} \div 10^{-7}$ s) times t_m satisfying the condition

$$t_m \ll \frac{2m}{110\,AB}, \tag{3}$$

where m is the error in determining C, in percent; the Faradaic current may be neglected. Then (^{4,5})

$$\eta = \frac{it_{\mathrm{m}}}{C}. \tag{4}$$

For our conditions, at $m = 10\%$, the value of $t_{\mathrm{m}} = (0.3 \div 3)\, 10^{-6}$ sec. This made it possible, from the initial ($t = 10^{-7}$ sec) slope of the curve of the rise of anodic polarization a in Fig. 1 (for $i = 0.16$ A/cm^2) and expression (4), to estimate the double-layer capacitance $C = 6$ μF/cm^2 at the interface of melt II with aluminosilicate. An analogous calculation from curve b of the decay of η gives $C = 8$ μF/cm^2. In the first case the capacitance refers to equilibrium conditions, while in the second the value of C is determined for the given potential.

Table 1

Dependence of capacitance on polarization at the interface Fe–C_{sat}–Si (0.29%) with aluminosilicate at $t = 1420^\circ$

Anodic process	Anodic process	Anodic process	Cathodic process	Cathodic process	Cathodic process
i, A/cm^2	η, V	C, μF/cm^2	i, A/cm^2	η, V	C, μF/cm^2
0.0	0.0	6.0	0.0	0.0	6.0
0.005	0.1	8.0	0.032	0.23	12.0
0.02	0.2	14.0	0.065	0.50	40.0

Fig. 3

Figure 2: Fig. 3

Table 1 gives, for various values of η, the capacitances calculated from the curves of polarization decay at the interface of melt I with aluminosilicate. At $\eta = 0$, the double-layer capacitance (6 μF/cm^2) is noticeably lower than in the preceding experiments (^{6}), apparently because of the lower temperature. As in those experiments (^{6}), and in experiments in molten salts (^{7}), the value of C increases (to 10 and 14 μF/cm^2) with increasing cathodic and anodic polarization ($\eta = \pm 0.2$ V).

Fig. 3. Decay of anodic polarization as a function of time (curves a and b) for the interface Fe–C_{sat}–Si (0.29%) with an aluminosilicate melt at $i = 0.041$ A/cm^2 and $t = 1320°$. Rise of cathodic polarization (curves v and g) for the interface Fe–C_{sat}–S (0.025%) with aluminosilicate containing 1% CaS at $t = 1420$°C and $i = 0.02$ A/cm^2.

At $t_k > 50/B^2$, which corresponds to $10^{-4} \div 10^{-5}$ sec under our conditions, equation (1) is considerably simplified (^{4}):

$$\eta = \frac{2RTit^{1/2}}{\pi^{1/2}n^2F^2}\left(\frac{1}{D_1^{1/2}C_1} + \frac{1}{D_2^{1/2}C_2}\right) - \frac{RTi}{nF}\left[\frac{RTC}{n^3F^3}\left(\frac{1}{C_1D_1^{1/2}} + \frac{1}{C_2D_2^{1/2}}\right)^2 - \frac{1}{i_0}\right]. \tag{5}$$

If, moreover, the inequality $C_1D_1^{1/2} \gg C_2D_2^{1/2}$ is satisfied, then from the tangent of the slope of the straight line plotted in the coordinates $\eta, t^{1/2}$, one can determine the diffusion coefficient of the potential-determining element in the metal, D_2, and from the intercept η_{int}, the exchange current, when the double-layer capacitance is known.

Figure 3 shows curve g of the rise of cathodic polarization ($i = 0.01$ A/cm^2) and the corresponding straight line v in the coordinates $\eta, t^{1/2}$ for the interface of melt III with aluminosilicate. It was assumed that, in this case, cathodic dissolution of sulfur occurs,

$$S + 2e \to S^{2-},$$

and that its concentrations in both phases were chosen so that ($C_{S^{2-}} = 1\%$, $C_S = 0.025\%$) $D_{S^{2-}}^{1/2}C_{S^{2-}} \gg D_S^{1/2}C_S$. Taking $C \cong 10$ μF/cm^2, we find from the value of η_{int} that the exchange current is $i_0 = 1.3$ A/cm^2. The diffusion coefficient of sulfur D_S in the melt Fe–C_{sat}–S, calculated from the slope of straight line v, is $1.2 \cdot 10^{-5}$ cm^2 sec^{-1} and is close to the values reported in the literature (^{8}).

If at the boundary of melt I with the aluminosilicate the potential-determining process is the dissolution of silicon $\mathrm{Si} = \mathrm{Si}^{2+} + 2e$, then one has to reckon with two diffusion coefficients: D_{Si} in the metal and $D_{\mathrm{Si}^{2+}}$ in the silicate $^{(3)}$. Therefore, from the slope of the straight line $\eta, t^{1/2}$, corresponding to curve a for the rise of anodic polarization (see Fig. 2), at $i = 0.01$ A/cm^2 one can find only the sum

$$\left(\frac{1}{D_1^{1/2} C_1} + \frac{1}{D_2^{1/2} C_2}\right).$$

But, knowing C_{Si} and D_{Si} $^{(3)}$ and taking $D_{\mathrm{Si}^{2+}} = 3 \cdot 10^{-6}$ cm$^2 \cdot$ sec^{-1}, it is easy to estimate $C_{\mathrm{Si}^{2+}}$, which is found to be $2 \cdot 10^{-6}$ g-mol/cm^3. The latter value is apparently not very far from the true one, since the ratio $C_{\mathrm{Si}^{2+}}/C_{\mathrm{Si}^{4+}}$ calculated from it in the aluminosilicate is of approximately the same order as the ratio $C_{\mathrm{Al}^{+}}/C_{\mathrm{Al}^{3+}}$ in fluoride melts $^{(9)}$.

It follows from equation (3) $^{(4,5)}$ that the exchange current can be found from the relation:

$$\eta_c = \frac{RT}{nF} \frac{i}{i_0}, \tag{6}$$

in which η_c is the polarization corresponding to the time t_c, determined from the expression

$$t_c^{1/2} = \frac{\pi c}{4i} \frac{d\eta}{d\left(t^{1/2}\right)}. \tag{7}$$

According to the experimental data presented in Fig. 2, $C_{\mathrm{Si}} = 0.29\%$; $i = 0.01$ A/cm^2 and $d\eta/d(t^{1/2}) = 1.4$ V/sec. Taking $C = 6.5$ μF/cm^2, we find from equation (7) that $t_c^{1/2} = 0.9 \cdot 10^{-3}$ sec$^{1/2}$, $\eta_c = 0.9$ mV. Hence the exchange current is $i_0 = 0.8$ A/cm^2.

The value of i_0 can also be determined from the decay of anodic polarization at the same boundary. A sufficiently short decay time ($< 10^{-5}$ sec) ensures a minimal influence of diffusion retardations. This makes it possible to use the expression

$$\ln\left(\frac{d\eta}{dt}\right) = -\frac{\alpha nF}{RT} + \ln\frac{i_0}{C},$$

derived in $^{(10,11)}$ only for a delayed discharge.

As is seen from Fig. 3, the points of curve b (for 0.29% Si, $i = 0.04$ A/cm^2, $t = 1320°$), if plotted in coordinates $\lg \frac{d\eta}{dt}, t$, fall on the straight line a. From the intercept it cuts off on the axis lg $\frac{d\eta}{dt}$, we find the value lg $\frac{i_0}{C}$, and from the initial portion of the decay of η we estimate the capacitance ($C = 15$ μF/cm^2). From these data we obtain $i_0 = 0.78$ A/cm^2, close to that calculated by formula (6) and the curve of the rise of η (Fig. 2).

Summarizing the above, we see that the galvanostatic method can be successfully used to estimate the exchange current, the diffusion coefficient, and the capacitance of the double layer not only in molten salts (5), but also in high-temperature (1320-1420°) metallurgical systems (Fe—C—X, CaO—Al_2O_3—SiO_2).

Ural Polytechnic Institute
named after S. M. Kirov

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Note: Figure translations are in progress. See original paper for figures.