ON THE KINETICS OF ION EXCHANGE BETWEEN METAL AND SLAG

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Abstract

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ON THE KINETICS OF ION EXCHANGE BETWEEN METAL AND SLAG

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The rate of ion exchange between liquid metals (Fe–C, Fe–Si, Fe–P, Ag) and molten slags was studied by the method described earlier (^{1}). From the values found for the diffusion resistance R_d, the diffusion coefficients D of iron and silver ions were estimated using the relation (^{2}):

$$R_d = \frac{RT}{n^2F^2}\frac{1}{C}\sqrt{\frac{2}{D\omega}}, \tag{1}$$

where C is the concentration of the potential-determining ions in the slag, ω is the angular frequency of the current, R is the gas constant, T is the absolute temperature, F is Faraday' s constant, and n is the charge of the ion.

It turned out that, for slags containing 31% CaO, 54% SiO_2, and 15% Al_2O_3, the diffusion coefficients of iron ions at 1500°C lie in the range from 2.4 to $3.1 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$. The values obtained are close to that previously found ($D = 3.5 \cdot 10^{-6}$) at the same temperature by the radioactive-isotope method (^{3}).

The diffusion coefficient of silver ions in molten sodium borate (15% Na_2O, 85% B_2O_3) was found to be $0.6 \cdot 10^{-7}$ at 840° and $1.42 \cdot 10^{-7}$ $cm^2 \cdot s^{-1}$ at 940°. Hence the activation energy of the diffusion process, calculated from the usual exponential equation, is 23 kcal/g-atom. The smaller values of D_{Ag^+} compared with $D_{Fe^{2+}}$ are apparently due to the relatively high viscosity of the medium and the low temperatures.

From the values of the reaction resistance R_r, the exchange currents i_0 were calculated using the expression (^{2}):

$$i_0 = \frac{RT}{nF} \cdot \frac{1}{R_r}. \tag{2}$$

For iron alloys with carbon, silicon, and phosphorus, and for slags containing CaO, SiO_2, Al_2O_3, Na_2O, B_2O_3, P_2O_5, and small concentrations of FeO and Fe_2O_3, an almost rectilinear dependence was found between i_0 and the total percentage of iron oxides (see Fig. 1). A similar dependence, at low concentrations of potential-determining ions, has been observed for a number of metals in aqueous and organic solutions (^{2,4,5}). As is known (^{2}), this fact indicates that ion discharge is the stage determining the rate of exchange.

Introduction of Na_2O into the slag leads to an increase in the concentration of FeO in it and to an increase in the exchange current. This is consistent with previously obtained results, according to which the addition of Na_2O increases the density of negative charge on Fe—C and Fe—P electrodes (^{6}) and promotes a decrease in the interfacial tension at the boundary under consideration (^{7}).

Measurements carried out for liquid cast iron (4.3% C) and a slag with 31% CaO, 54% SiO_2, and 15% Al_2O_3 showed that, at a temperature of 1350°C and an iron-ion concentration of 0.36%, the exchange current was 22 ma/cm^2; at 1550°

and at a concentration of 0.52% it was 50 ma/cm^2. Hence, taking into account the linear dependence of i_0 on C, we find the activation energy of reaction (E_1):

$$\mathrm{Fe}\,(\text{cast iron}) = \mathrm{Fe}^{2+}\,(\text{slag}) + 2e, \tag{a}$$

equal to 23.5 kcal/g-at, and for the reverse process $E_2 = 13$ kcal/g-at. Such a relation between E_1 and E_2 is apparently due to the fact that the carbon of the metallic alloy creates sharply reducing conditions at the interphase boundary. The influence of changes in the potential jump with temperature and with the concentration of ions (^{8}) on the magnitude of the activation energy (^{9}) has not yet been investigated by us.

Electrolyte composition	t, °C	i_0, ma/cm^2	C, μF/cm^2
14.48% Na_2O,85.4% B_2O_3,0.12% Ag_2O	940	75	16.8
14.43% Na_2O,85.4% $B_2O_3$0.17% Ag_2O	840	46	16.8
30% CaO,70% P_2O_5,0.01% Ag_2O	1040	19	16.5

For a silver electrode in oxide melts, the results presented in Table 1 were obtained. They make it possible to estimate the activation energy for the direct (E_1)

Fig. 1. Dependence of the exchange current between iron alloys and slags on the concentration of iron ions in the slag

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$$\mathrm{Ag}\,(\mathrm{metal}) = \mathrm{Ag}^{+}\,(\mathrm{slag}) + e \tag{b}$$

and reverse (E_2) exchange processes. They are $E_1 = 12.8$ and $E_2 = 22.8$ kcal/g-at. Such a relation of the values E_1 and E_2 for silver seems unusual and requires further investigation. It is possible that it is caused by the strong bond of the Ag^{+} cations with the anions of the borate melt.

The values of the double-layer capacitance are approximately the same in all three cases and are close to those obtained earlier for Fe–C. This suggests that on the surface of silver in contact with borate there is also an excess of negative charge.

Fig. 1. Dependence of the exchange current between iron alloys and slags on the concentration of iron ions in the slag

It is noteworthy that, despite the high temperature and the relatively high concentration of potential-determining iron ions in the slag, the values of i_0 in the melts studied (Fe–C, Fe–Si, Fe–P) are close to those observed in aqueous solutions. Apparently, iron ions are bound to the slag more strongly than metal cations are to an aqueous solution. In addition, silicon, carbon, and phosphorus are concentrated at the interphase boundary (^{1}), which leads to depletion of the metal surface in iron atoms, i.e., to a kind of isolation of the latter from the slag. A similar effect of surface-active substances on the magnitude of the exchange current (a decrease in it) was observed in aqueous solutions (^{4}).

The foregoing is also supported by the extremely low resistance of the reaction between cast iron (4.3% C) and a slag containing calcium carbide (10.8% $\mathrm{CaC_2}$, 55% CaO, 19.8% $\mathrm{SiO_2}$, 3.6% $\mathrm{Al_2O_3}$, 10.8% MgO, and 0.143% Fe) at a temperature of about 1500°. Probably, in this case the potential is determined by the transition not of iron, but of carbon:

$$2\mathrm{C}\,(\mathrm{metal}) + 2E = \mathrm{C}_2^{2-}\,(\mathrm{slag}). \tag{c}$$

High concentrations of it in the surface layer of cast iron and slag promote rapid ionic exchange and sharply increase i_0. The capillary activity of $\mathrm{CaC_2}$ at such an interface follows from the fact of a decrease in the interphase tension (^{10}).

In this connection one may think that, for pure iron and other metals, the exchange current with the slag must be large at high temperatures. This is also indicated by a comparison of the values of i_0 for Ag and Fe–C. Their exchange currents are approximately the same, despite the lower temperature and the lower concentration of Ag^+ ions in the slag.

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