DIFFUSION COEFFICIENTS OF IONS IN MOLTEN SLAGS

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Abstract

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Cathodic deposition of various elements from molten slags is accompanied by concentration polarization (^{1}). This makes it possible to use oscillography at a specified current strength ($^{2-5}$) to determine the diffusion coefficients (D) of ions in liquid slags. At a current density (i) greater than the limiting value, the concentration (C_0) of the substance being reduced at the cathode rapidly decreases and, after a certain time (t_0), becomes equal to zero, which causes a jump in the electrode potential. From the experimentally found value of t_0, for the selected C_0 and i, the value of D is calculated by the formula (^{2}):

$$D = \frac{4i^2 t_0}{\pi C_0^2 n^2 F^2}, \tag{1}$$

in which n is the number of electrons in the elementary act of discharge, and F is Faraday' s constant.

The slags studied, the electrolyzer, and the electrodes were the same as in the previous work (^{6}). The change in electrode potential with time was recorded with a loop oscillograph at several speeds of motion of the photographic film. An amplified signal was fed to the oscillograph. The amplifier, assembled with 6N9 and 6G7 tubes in a bridge circuit, made it possible first to compensate for the voltage drop caused by the ohmic resistance of the cell and to record the polarization of the electrode. To determine the dimensions of the surface of the working cathode (liquid copper), X-ray photographs were taken of it in contact with the slags studied at various temperatures (1350–1550°C) and current densities (0.13–0.40 A/cm^2). It turned out that the meniscus has the form of a hemisphere, the radius of which is close to that of the tube (3.25 mm). The working area of the cathode varied comparatively little with the conditions, from 0.60 to 0.66 cm^2, and averaged 0.63 cm^2.

To calculate the values of C_0 (g-ion/cm^3) from the atomic percentages (2%) of the additive, the density of the melts serving as the polarographic background was measured. The values found in this way were in satisfactory agreement with those available in the literature (^{7}).

The results of measurements of the diffusion coefficients of iron, cobalt, silicon, niobium, vanadium, titanium, and zirconium ions in aluminate slag (45% CaO, 47% Al_2O_3, 6% MgO, and 2% B_2O_3), as well as of nickel, iron, vanadium, and niobium ions in a silicate melt (40% CaO, 40% SiO_2, and 20% Al_2O_3), are presented in Fig. 1 in coordinates $\lg D, 1/T$. Unfortunately, there are no literature data for comparison, except for the values of D_{Fe} in silicate slag obtained by the radioactive-tracer method (^{8}). As follows from Table 1, both measurement methods give close values of D_{Fe}.

Fig. 1 shows that in each slag the ions are clearly divided into two groups. The diffusion coefficient of the modifiers (1st group—Fe, Co, Ni) at 1450° is approximately 20 times greater than that of the network-forming elements (2nd group—Si, Nb, V, Ti, Zr). Calcium, as is known, also belongs to the first. In accordance with this, the values D_{Ca}, found by another method ($^{8-10}$), are close to those for iron (D_{Fe}).

Table 1

Diffusion coefficients ($\mathrm{cm}^2 \cdot \mathrm{sec}^{-1}$) of iron and calcium ions, found by various experimental methods

T-ra, °C	D_{Fe}	$D_{\mathrm{Fe}}^{(8)}$	$D_{\mathrm{Ca}}^{(8)}$	$D_{\mathrm{Ca}}^{(9,10)}$
1360	$2.2 \cdot 10^{-6}$	–	–	$3.5 \cdot 10^{-7}$ (1350°)
1400	$2.7 \cdot 10^{-6}$	$1.1–1.9 \cdot 10^{-6}$	$0.7–1.3 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$ (1430°)
1460	$4.2 \cdot 10^{-6}$	–	–	$9.6 \cdot 10^{-6}$ (1450°)
1500	$5.1 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	$1.8 \cdot 10^{-6}$	$2–12 \cdot 10^{-6}$
1510	$6.6 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$ (1540°)

As is seen from Fig. 1, the dependence of the diffusion coefficient on temperature is described by the equation:

$$D = D^0 e^{-E/RT}. \tag{2}$$

In this case all values of D for each group of ions fall, for a given slag, approximately on a single straight line. Apparently this is connected with the fact that ions of the 1st group occupy octahedral cavities formed by oxygen anions, whereas ions of the 2nd group occupy tetrahedral ones. Since in the given slag the mean distances between the corresponding cavities and the energy barrier separating the latter are of the same order, one should expect the diffusion coefficients for ions of each group to be close. Thus there are altogether four straight lines ($\lg D, 1/T$), two parallel ones for each corresponding melt. At the same

Fig. 1

Figure 1: Fig. 1

time, the mean activation energy (E) for both groups of ions in silicate slag lies within 37-38 kcal/g-ion, and in aluminate slags within 47-48 kcal/g-ion.

Fig. 1. Dependence of the logarithm of the diffusion coefficients ($\lg D$) for various ions in liquid slags on $1/T$. 1—diffusion of Fe, 2—Co, 3—Ni, 4—Si, 5—V, 6—Ti, 7—Zr, 8—Nb.

The strong increase in the value of E is probably due to the greater strength of the bonds between the particles of the aluminate melt, which is confirmed by the elevated values of the surface tension of these slags in comparison with silicate slags ([7,11]).

Nevertheless, the diffusion coefficients in the aluminate (I) melt exceed those in the silicate (II) melt ($D_{\mathrm{I}} > D_{\mathrm{II}}$), which is reflected especially sharply in the values of D^0 for the 1st and 2nd groups of ions: $D_{\mathrm{I},1} = 4.85$; $D_{\mathrm{I},2} = 0.49$; $D_{\mathrm{II},1} = 0.23$ and $D_{\mathrm{II},2} = 0.014$.

According to the theory of absolute reaction rates ([12])

$$D^0 = e\lambda^2 \frac{kT}{h} e^{\Delta S^*/R}, \tag{3}$$

where λ is the distance between neighboring equilibrium positions of the diffusing particle, k and h are the Boltzmann and Planck constants, and ΔS^* is the entropy of activation.

If the applicability of equation (3) to both groups of ions is assumed, the products

$$\lambda_{i,j} e^{\Delta S^*_{ij}/2R} = \Pi_{ij}$$

are $\Pi_{I,1} = 22.2$ Å, $\Pi_{I,2} = 7.0$ Å, $\Pi_{II,1} = 4.8$ Å, and $\Pi_{II,2} = 1.2$ Å. Although the distance λ in aluminate slag is greater than in silicate slag, it hardly exceeds 3-4 Å ([13,14]). Therefore, the high values of the products for the aluminate melt are probably due to the larger entropy of activation ($\Delta S^*_I > \Delta S^*_{II}$).

However, the difference in the values of ΔS^* for the 1st and 2nd groups of ions ($\Delta S^*_{i,1} > \Delta S^*_{i,2}$) cannot explain the observed inequality of the corresponding products ($\Pi_{i,1} > \Pi_{i,2}$). The point is that ions of the 1st group, passing from one octahedral void to another, find themselves in the region of a tetrahedral void, where the number of neighbors is smaller. This decreases the thermodynamic probability of the transition state. Conversely, ions of the 2nd group, leaving a stable state in a tetrahedral void, temporarily enter octahedral coordination with a larger number of neighbors, which increases the number of possible ways of realizing the transition state. In this connection one should expect the opposite relationship for the entropies of activation, i.e. $\Delta S^*_{i,1} > \Delta S^*_{i,2}$.

Apparently, small network-forming cations move together with the large oxygen anion (6). In this case their diffusion is determined by displacement relative to the small (12) modifier cations, while the large complexes of the network-forming ion with the oxygen anion merely occupy the vacated sites. Naturally, the magnitude of such a displacement is small (0.6–0.7 Å) in comparison with the jump (2.7–3.5 Å) of a modifier ion from one equilibrium position to another. This is what accounts for the smaller value of D_2^0 in comparison with D_1^0.

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