Tracer Diffusivity of Ca\textsuperscript{45} and Electrical Conductivity in CaO-SiO\textsubscript{2} Melts

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The tracer diffusivity of Ca\textsuperscript{45} has been measured in CaO-SiO\textsubscript{2} melts in the temperature range 1500 to 1700\textdegree C. In addition the electrical conductivity has been determined. Both properties decrease with increasing silica content. The activation energies (\textasciitilde 30 kcal g\textsuperscript{-1} atom\textsuperscript{-1}) are of the same order of magnitude. The electrical conductivity as computed from the diffusivity on the assumption that the total current is transported exclusively by divalent calcium ions and that the usual Nernst-Einstein relationship is valid, is somewhat lower than the measured electrical conductivity with the difference increasing with increasing silica content.

The rate of many slag/metal reactions is controlled by transport in the slag, and in order to compute the rate of such reactions the mechanism of transport in the slag must be understood. Slags are multicomponent oxide mixtures which are dissociated into ions and which usually contain considerable amounts of silica. Only few and contradictory data are available on the mobilities of the various ions in the technically important slags. Usually, it is assumed that the silicate melts are cation conductors. This, however, is not in keeping with the self-diffusivity of oxygen which is reported to be in the same order of magnitude or higher than that of calcium.\textsuperscript{1-8} Also the self-diffusivity of silicon is, although lower than that of the cations, still rather high.\textsuperscript{114} Hence, the transport mechanism is not well understood and it is not clear how the electrical transport properties and diffusivities are interrelated and how flux equations should be formulated.

In order to improve this situation, self-diffusivities, chemical diffusivities, transference numbers and electrical conductivities should be measured, using the best experimental techniques available, to obtain sets of data as complete as possible for specific slag systems. The present authors have started such an investigation on CaO-SiO\textsubscript{2} melts. This system is the binary bounding system for most slags in iron and steelmaking. In the following paper the results will be reported on the tracer diffusivity of Ca\textsuperscript{45} and on the electrical conductivity. A subsequent paper will deal with the tracer diffusion of Si\textsuperscript{31}.

EXPERIMENTAL TECHNIQUE

The diffusivity of Ca\textsuperscript{45} was determined in the temperature range 1500 to 1700\textdegree C using the capillary technique. Active and inactive rods of the same chemical compositions and of 1.2 cm length were placed in a capillary over each other. The capillaries were machined from molybdenum and had internal diam of 2 mm. In order to avoid convection the capillaries were suspended in the lower half of the hot zone of the furnace during the diffusion experiment.

The slags were prepared from high purity calcium carbonate (Merck, Darmstadt) and silica (Koch-Light, Colnbrook). The mixture was first annealed at 1200\textdegree C for 12 h and then melted at 1600\textdegree C in a platinum crucible. In order to ensure homogenization the melt was stirred with a platinum-rhodium rod at regular intervals. Subsequently, the melts were vacuum degassed. The rods were prepared by sucking the melt into graphite tubing of 2 mm ID. The tubes were then quenched in a copper block. The rods could easily be pushed out of the bore. Pieces 1.2 cm in length were cut off, and the transverse surfaces of their extremities were ground and polished to obtain perfectly flat surfaces for joining the diffusion couples. The radioactive rods were made, in the same way, from the same starting mixture by adding "carrier free" Ca\textsuperscript{45} tracer. The tracer was purchased in the form of an aqueous Ca\textsuperscript{45}Cl\textsubscript{2} solution. After the addition to the slag mixture, concentrated ammonia was added and the mixture was heated to drive off the chlorine as ammonium chloride. In some experiments oxalic acid was added to convert the calcium chloride to calcium oxalate. There was no difference in the diffusivities as obtained with the rods prepared by these two procedures.

The diffusion experiments were carried out in a molybdenum wound tube furnace. Forming gas (95\% N\textsubscript{2}, 5\% H\textsubscript{2}) was used as atmosphere. In some experiments the forming gas was passed through a mixture of oxalic acid and oxalic acid anhydrate, held at 20\textdegree C in a thermostatically controlled bath to obtain a defined H\textsubscript{2}O/H\textsubscript{2} ratio and oxygen pressure. These experiments yielded the same results. The temperature of the furnace was controlled electronically within \textpm 1\textdegree C.

At the end of the diffusion run the sample was drawn into the cold top of the furnace. The capillary was embedded in mounting material and a longitudinal section of the sample was prepared by grinding and polishing. The concentration profile was determined with a measuring device which was built in this laboratory (Fig. 1). It consisted of a support table with a slit, the sample holder which could be moved over the slit with a micrometer and a methane counter with a gold window which was placed under the slit. The width of the slit was chosen at 0.5 mm. The \(\beta\)-radiation passing through the slit was measured in the samples each 0.5 mm.

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The activity \( A \) of \( \beta \)-radiation at distance \( x \) is given by:

\[
A = \frac{A_0}{2} \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right)
\]  

[1]

where \( A_0 \) is the unchanged activity at the end of the radioactive rod, \( D \) the diffusion coefficient of \( \text{Ca}^{45} \) and \( t \) the diffusion time. By plotting the ratio \( A/A_0 \) against distance on probability paper, straight lines are obtained and the diffusivity is computed from the slopes.

During solidification and cooling the samples contract.