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Multiatomic Ion Model for Interdiffusion in the System Na_2O-CaO-SiO_2

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Concentration distributions after interdiffusion at 1200 °C were analysed for the diffusion couple of average composition $16Na_2O\cdot 12CaO\cdot 72SiO_2$ (wt%) in terms of self-diffusion coefficients of constituent elements. Theoretical calculation was conducted using a multiatomic ion model assuming that Si migrates with oxygens as a silicate ion. The composition of the silicate ion was estimated by determining the parameters in the diffusion equation so as to provide the best fit of the theoretical calculations to the experimental concentration profiles.

In spite of its scientific and technological importance,[1,2] the interdiffusion mechanism of liquid silicates has not been thoroughly clarified because of the structural complexity of ionic solutions. Another reason is due to insufficient thermodynamic and self-diffusion data necessary for the analysis of interdiffusion. With respect to the diffusion data, a system CaO–Al_2O_3–SiO_2 is the only multioxide liquid for which tracer diffusion coefficients of all the constituent elements are known.[3] For the present system Na_2O–CaO–SiO_2, tracer diffusion coefficients of sodium,[4] calcium,[5,6] and oxygen[7] are known but that of silicon has not been determined as yet.

In Wakabayashi and Oishi's analysis of liquid-state interdiffusion in the system Na_2O–CaO–SiO_2,[8] simple application of the monoatomic diffusion model did not satisfactorily describe the concentration distribution but the assumption of two different oxygen species with different diffusivities gave theoretically calculated concentration distribution agreeable with the experimental results. They interpreted that the fast and slow oxygen species correspond to the non-bridging and bridging oxygens, respectively. A non-bridging-oxygen controlled mechanism was also discussed for dissolution of solid SiO_2 in liquid $Na_2O\cdot 3SiO_2$ by Barklage-Hilgefort and Frischat.[9] In these two papers, the diffusion coefficient of the fast, not the whole, oxygen is assumed to be equal to that obtained by the tracer technique. In the tracer technique, however, the oxygen diffusion coefficient was calculated on the assumption that all the oxygen atoms are equally capable of undergoing isotope exchange. This contradiction is dissolved in the present work by interpreting the tracer diffusion coefficient as the average of self-diffusion coefficients of the fast and slow oxygen species.[10] This interpretation implies that the constituent element N of compound M_mN_n diffuses not only as monoatomic ion N^{m-}, but also as neutral undissociated molecule M_mN_n or as ion pair $M^{n+}N^{m-}$; tracer diffusion coefficient $D_N{}^*$ is expressed as the weighted average of the self-diffusion coefficients of those diffusing species, as described by Eq. 1,

$$D_N{}^* = y_1 D_{N_1} + y_2 D_{MN} + y_3 D_0, \tag{1}$$

where y_1, y_2, and y_3 represent the single-atomic fractions of element N, shared by N^{m-}, $M^{n+}N^{m-}$, and M_mN_n, respectively, and D_{N_1}, D_{MN}, and D_0 the self-diffusion coefficients of diffusing species N^{m-}, $M^{n+}N^{m-}$, and M_mN_n, respectively.

In the analysis[10] of the interdiffusion in liquid system CaO–Al_2O_3–SiO_2, theoretical calculation of the diffusion profiles showed good agreements with the experimental results in the case where the oxygen tracer diffusion coefficient defined as Eq. 1 was employed for a multiatomic ion model, in which the composition of the silicate ion was described in terms of unknown structure parameters. This analytical procedure was used in the present work to examine its applicability to the liquid interdiffusion of the system Na_2O–CaO–SiO_2. Since the Si self-diffusion coefficient in the system Na_2O–CaO–SiO_2 has not been determined, though those of three other elements are known, the self-diffusion coefficients of the fast and slow oxygens can not be determined only from the structure parameters of the silicate ion, as was the case in the system CaO–Al_2O_3–SiO_2. Consequently, the self-diffusion coefficient of the fast oxygen was also described with the aid of a new unknown parameter in the theoretical calculation of the diffusion profiles.

The flux density equation necessary for analysis of the present interdiffusion was derived in terms of self-diffusion coefficients of the constituent ions from Nernst-Haskel's equation modified with the mass flow term as defined by Darken.[11] The system Na_2O–CaO–SiO_2 is understood to be thermodynamically nonideal with respect to oxide components. However, instead of describing the non-ideality in terms of the thermodynamic factor, the present analysis of interdiffusion was conducted on the assumption that a nonideal system with respect to oxide components can be treated as an ideal system with respect to actually diffusing units.[10]

Theoretical

Multicomponent Diffusion Equation for Ionic Systems. The flux density of the i th ion can be described as Eq. 2 for chemical diffusion in a thermodynamically ideal ionic multicomponent system,

$$J_i = -D_i \frac{\partial C_i}{\partial x} + C_i v + D_i C_i Z_i \frac{F}{RT} \varepsilon, \tag{2}$$

where J_i is the diffusion flux density, D_i the self-diffusion coefficient, C_i the concentration, Z_i the valence of the ith diffusing species, x the diffusion distance, v the mass flow velocity, F the Faraday constant, R the gas constant, T the absolute temperature, and ε the strength of the electric field resulted from differing diffusivities of various diffusing ions. The conditions of the volume-fixed frame and no electric current resulted are described by Eqs. 3 and 4, respectively,

$$\sum_{i=1}^{r} V_i J_i = 0 \tag{3}$$

$$\sum_{i=1}^{r} Z_i J_i = 0, \tag{4}$$

where V_i is the molar volume of diffusing species i, and r denotes the number of components. Conditions of the electrical neutrality and a constant molar volume of each component with Eqs. 3 and 4 allow to rewrite Eq. 2 in a general equation as Eq. 5,

$$J_i = -\sum_{i=1}^{r-2} M_{ij} \frac{\partial C_j}{\partial x} \qquad (i = 1,2,\cdots, r-2) \tag{5}$$

where the coefficient M_{ij} is given as Eq. 6 as a function of self-diffusion coefficients, concentrations, valences, and molar volumes of the components,

$$\begin{aligned} M_{ij} = D_i\delta_{ij} - & \frac{C_i}{(Z_{r-1}V_r - Z_rV_{r-1})\sum_{k=1}^{r} C_kZ_k{}^2D_k} \\ & \times \{(Z_{r-1}V_r - Z_rV_{r-1})[Z_iZ_jD_i \\ & + \sum_{k=1}^{r} C_kZ_kD_k(Z_kV_j - Z_jV_k)] \times D_j \\ & + (Z_rV_j - Z_jV_r)[Z_iZ_{r-1}D_i \\ & + \sum_{k=1}^{r} C_kZ_kD_k(Z_kV_{r-1} - Z_{r-1}V_k)] \times D_{r-1} \\ & + (Z_jV_{r-1} - Z_{r-1}V_j)[Z_iZ_rD_i \\ & + \sum_{k=1}^{r} C_kZ_kD_k(Z_kV_r - Z_rV_k)] \times D_r\}, \end{aligned} \tag{6}$$

where δ_{ij} is Kronecker's δ.

Diffusing Units and Their Self-diffusion Coefficients.

The self-diffusion coefficient of sodium[4] is greater than those of calcium[5] and oxygen,[7] in the system Na_2O–CaO–SiO_2, and the activation energy for sodium[4] is half of those for calcium[5] and oxygen.[7] These facts suggest that the diffusing unit of sodium is the single-atomic Na^+ ion. The self-diffusion coefficient of calcium is greater than that of oxygen in this system and similar to that of calcium[12] in the system CaO–Al_2O_3–SiO_2 in which the diffusing unit of calcium is interpreted to be the single-atomic Ca^{2+} ion.[10] Based on these facts, the diffusing unit of calcium in this system is assumed to be the single-atomic Ca^{2+} ion. For a simple demonstration of the present diffusion model, a single multiatomic silicate ion is assumed to be the diffusing unit of silicon as the average of various silicate ions which may actually exist in the liquid silicate.[13–15] Since the composition of the present system is rich in SiO_2, the structure model of the silicate ion is described as discrete ion as proposed by Bockris *et al.*[16] Table 1 summarizes the diffusing units and their self-diffusion coefficients assumed in this study. Here, the structure of the silicate ion is described as n-membered r-fold rings of SiO_4 tetrahedra joined at apices. The oxygens composing this silicate ion are the slower oxygen species and the remainders are the faster species, where the concentrations of the two kind of oxygens are given by Eqs. 7 and 8 from the requirement of the number conservation of the total oxygen atoms.

TABLE 1. DIFFUSING SPECIES AND THEIR SELF-DIFFUSION COEFFICIENTS

Diffusing species	Self-diffusion coefficient
Na^+	$D_{Na}{}^*$
Ca^{2+}	$D_{Ca}{}^*$
$Si_{nr}O_{n(2r+1)}{}^{2n-}$	D_S
O^{2-}	D_F

$$C_{Sl} = C_{Si}\left(2 + \frac{1}{r}\right) \tag{7}$$

$$C_F = C_O - C_{Sl} \tag{8}$$

where C_{Si} represents the concentration of Si atoms and C_{Sl}, C_F, and C_O represent concentrations of the slow, the fast, and the total oxygen atoms, respectively.

In Table 1 star-marked self-diffusion coefficients are those determined by the tracer technique, while the self-diffusion coefficients with no mark are defined as follows: The tracer diffusion coefficient of oxygen, $D_O{}^*$, is the weighted average of self-diffusion coefficients of the slow and fast oxygen species, as described by Eq. 9,

$$D_O{}^* = \frac{C_{Sl}}{C_O} D_S + \frac{C_F}{C_O} D_F \tag{9}$$

where D_S is the self-diffusion coefficient of the slow oxygen, which is the same as that of the silicate ion, and D_F is that of the fast oxygen.

Determination of Parameters for Diffusing Units.

The diffusion couples in the present work were designed with relatively small concentration differences (10 wt%) so that the self-diffusion coefficients of all the diffusing species may be regarded as composition-independent. Consequently, coefficient M_{ij} in Eq. 6 is also regarded as constant and calculated for the average composition of the diffusion couple where the valences of diffusing species are read from Table 1. The molar volumes are so defined that the volume of the system is determined only by the volume of the oxygen atoms, as described by Eq. 10,

$$\left| \begin{array}{l} V_{Na^+} = V_{Ca^{2+}} = 0 \\ V(Si_{nr}O_{n(2r+1)})/V_{O^{2-}} = n(2r+1) \end{array} \right. \tag{10}$$

Self-diffusion coefficients of the constituent elements, $D_{Na}{}^*$,[4] $D_{Ca}{}^*$,[5] and $D_O{}^*$[7] are taken from the literature.

Applying the continuity equation to Eq. 5, the analytical solution can be derived as Eq. 12 for the initial and boundary conditions described by Eqs. 11,

$$\left| \begin{array}{ll} C_i = C_{i,A} & x<0,\ t = 0 \\ C_i = C_{i,B} & x>0,\ t = 0 \\ C_i = C_{i,A} & x = -\infty,\ t>0 \\ C_i = C_{i,B} & x = +\infty,\ t>0 \end{array} \right. \tag{11}$$

where $C_{i,A}$ and $C_{i,B}$ denote the initial concentrations of diffusing species i in the left and right sides of the diffusion couple, respectively.

$$C_i = C_{i,B} + \frac{1}{2}\sum_{j=1}^{r-2}\sum_{k=1}^{r-2} S_{ik}R_{kj}(C_{j,A} - C_{j,B})\,\mathrm{erfc}\left(\frac{x}{2\sqrt{\lambda_k t}}\right), \tag{12}$$

where S_{ij}, R_{ij}, and λ_i are the constants given by Eq. 13,[10]

$$\left|\begin{aligned}
\lambda_1 &= \{(M_{11}+M_{22}) + Q\}/2 \\
\lambda_2 &= \{(M_{11}+M_{22}) - Q\}/2 \\
S_{11} &= (M_{11}-M_{22}) + Q \\
S_{12} &= (M_{11}-M_{22}) - Q \\
S_{21} &= S_{22} = 2M_{21} \\
R_{11} &= 1/2Q \\
R_{12} &= \{-(M_{11}-M_{22})+Q\}/4M_{12}Q \\
R_{21} &= -1/2Q \\
R_{22} &= \{(M_{11}-M_{22})+Q\}/4M_{12}Q \\
Q &= \{(M_{11}-M_{22})^2 + 4M_{12}M_{21}\}^{1/2}.
\end{aligned}\right. \qquad (13)$$

Theoretical concentration distributions were repeatedly calculated using Eq. 12 for various magnitudes of the parameters until the best fitting to the experimental distributions are attained. The best fitting was carried out by minimizing the objective function F given by Eq. 14,

$$F = [\sum_{i=1}^{3} \sum_{j=1}^{N_i} \{W_i^{e}(x_j) - W_i^{c}(x_j)\}^2/3N_i]^{1/2}, \qquad (14)$$

where $W_i^{e}(x_i)$ and $W_i^{c}(x_j)$ represent the experimentally determined and calculated concentrations (in wt fraction) of oxide component i at diffusion distance x_j, respectively, and N_i denotes the number of the measurements for oxide component i. The experimental concentration distributions were taken from Wakabayashi and Oishi's paper.[8]

Results and Discussion

Figure 1 shows the theoretical concentration distributions (solid curves) calculated by Eq. 12 for the diffusion couple $16Na_2O\cdot 7CaO\cdot 77SiO_2$–$16Na_2O\cdot 17CaO\cdot 67SiO_2$ (wt%) at 1200 °C for diffusion time 4.00 h so as to best fit to the experimental results determined by Wakabayashi and Oishi[8] (plotted). The theoretical calculation is in good agreement with the experimental results. The experimentally determined "up-hill diffusion" of the component Na_2O which had no initial concentration difference has been satisfactorily described by the theoretical calculation of the present diffusion model. The solid curves for theoretical calculations in Fig. 1 were obtained for the self-diffusion coefficient of fast oxygen species, $D_F = 7.54 \times 10^{-8}$ cm²/s, which determined the self-diffusion coefficient of silicate ion as $D_S = 1.37 \times 10^{-8}$ cm²/s.

The theoretical calculation of the diffusion profiles was carried out also for the second diffusion couple $21Na_2O\cdot 7CaO\cdot 72SiO_2$–$11Na_2O\cdot 17CaO\cdot 72SiO_2$, for which Wakabayashi and Oishi determined the diffusion profiles experimentally at 1200 °C for diffusion time 2.00 h. The second diffusion couple was designed with no initial concentration difference in SiO_2 so as to have the same average composition as and a different compositional direction from the first diffusion couple.

The theoretical calculation for the second diffusion couple gave concentration distributions (solid curves) close to the experimental results (plotted), as shown in Fig. 2. However, with respect to the structure parammeter n, its magnitude could not be successfully optimized within the reasonable magnitude range. This seems to be due to composition-dependences of the self-diffusion coefficients, the thermodynamical nonideality, or/and the size distribution of the silicate ions, which is suggested by the asymmetrical diffusion profiles.

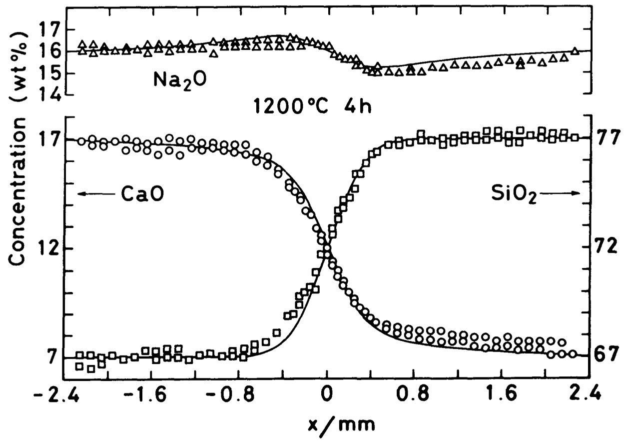

Fig. 1. Theoretical and experimental concentration distributions for the diffusion couple $16Na_2O\cdot 7CaO\cdot 77SiO_2$–$16Na_2O\cdot 17CaO\cdot 67SiO_2$ (wt%).

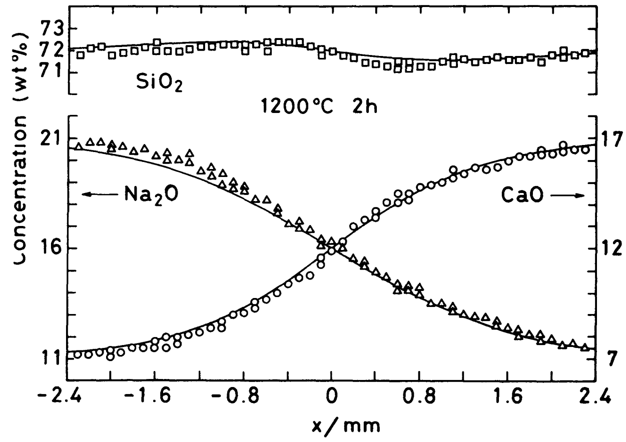

Fig. 2. Theoretical and experimental concentration distributions for the diffusion couple $21Na_2O\cdot 7CaO\cdot 72SiO_2$–$11Na_2O\cdot 17CaO\cdot 72SiO_2$ (wt%).

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