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## MULTIATOMIC ION MODELS FOR INTERDIFFUSION OF LIQUID SILICATES

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<u>Résumé</u>. - L'analyse a été faite des profils d'interdiffusion du système 40CaO·20Al<sub>2</sub>O<sub>3</sub>·40SiO<sub>2</sub> (% en poids) à 1.370-1.550°C à l'aide des modèles d'ion multiatomique; dans lesquels les espèces diffusives ont été décrites avec des paramètres de structure inconnus et la solution de l'équation de diffusion pour les systèmes ioniques multicomposants a été dérivée en fonction des coefficients d'autodiffusion des éléments composants. Les compositions des espèces diffusives inconnues ont été déterminées par la meilleure adaptation des profils de concentration calculés théoriquement à ceux déterminés expérimentalement. Afin de déterminer la composition de l'ion de silicate inconnu, une analyse similaire a été faite aussi pour le système l6Na<sub>2</sub>O·12CaO·72SiO<sub>2</sub> à 1.200°C.

<u>Abstract</u>. - Interdiffusion profiles of the system 40CaO·20Al<sub>2</sub>O<sub>3</sub>· 40SiO<sub>2</sub> (wt%) at 1,370-1,550°C were analysed using multiatomic ion models, in which diffusing species were described with unknown structure parameters and the solution of the diffusion equation for multicomponent ionic systems was derived in terms of self-diffusion coefficients of constituent elements. The compositions of the unknown diffusing species were determined by means of best fitting of the theoretically calculated concentrations to experimentally determined profiles. Similar analysis was conducted also for the system 16Na<sub>2</sub>O·12CaO·72SiO<sub>2</sub> at 1,200°C to determine the composition of the unknown silicate ion.

1. <u>Introduction</u>. - The complexity of the diffusion mechanism in liquid silicates comes from the fact that multiple diffusing species can exist for a single constituent element. To solve this problem, the interdiffusion equation was derived for multiatomic ion models [1].

In the interdiffusion equation, the unknown multiatomic ions were described using unknown structure parameters. Those parameters were determined through theoretical calculations of concentration distributions so as to give the best fit to the experimentally determined diffusion profiles.

The liquid silicate employed for the first analysis is the system  $CaO-Al_2O_3-SiO_2$ , in which self-diffusion coefficients of all the constituent elements have been already determined. The concentration distributions were determined by the electron probe microanalysis after interdiffusion of diffusion couples under given conditions.

For a simple demonstration of the logic of the present diffusion model, a single multiatomic ion was assumed for each cationic element in the diffusion equations in principle. The possibility of the existence of free oxygen ions was always provided in the present diffusion model. The oxygen self-diffusion coefficient determined by the tracer technique was interpreted as the average of the self-diffusion coefficients of the free oxygen ion and the oxygen species associated with the multiatomic ions. In describing the thermodynamical nonideality of the liquid silicate in the diffusion equation, an assumption was made that the nonideal system with respect to oxide components can be regarded as an ideal system when the actually diffusing species are taken as the components on the analogy of the interdiffusion in systems of alcohol and carbon tetrachloride [2].

A similar analysis was conducted also for the system Na<sub>2</sub>O-CaO-SiO<sub>2</sub>.

2. Theoretical. - The diffusion flux in a thermodynamically ideal ionic r-component system is described by Eq. (1).

$$J_{i} = -D_{i} \frac{\partial C_{i}}{\partial X} + C_{i} V + D_{i} c_{i} Z_{i} \frac{F}{RT} \epsilon \qquad (i=1,\cdots,r)$$
(1)

where  $J_{\rm i}$  is the flux density,  ${\rm D}_{\rm i}$  the self-diffusion coefficient,  ${\rm C}_{\rm i}$  the concentration,  ${\rm Z}_{\rm i}$  the valence of the ith species, x the distance, v Darken's mass flow velocity, and E the strength of electric field which results from different diffusivities of various diffusing species. Eq. (1) can be rewritten for conditions of the volume-fixed reference frame and no current flow in a general form as

$$J_{i} = -\sum_{j=1}^{r-2} M_{ij} \frac{\partial C_{j}}{\partial X} \qquad (i=1,\cdots,r-2) \qquad (2)$$

where  $M_{ij}$  are the coefficients described in terms of self-diffusion coefficients, valences, concentrations and molar volumes of the components. The concentration distributions for interdiffusion in a semiinfinite diffusion couple can be calculated using Eq. (2) for given conditions. The diffusing units and their self-diffusion coefficients in the silicate-aluminate ions model and the aluminosilicate ion model are listed in Table 1, where the asterisked D are tracer diffusion coefficients [3]. The unmarked are the assumed D for the unknown diffusing species.

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System 40C	$a0.20A1_{2}O_{3}.40SiO_{2}$ (wt%)		~	System 16Na20.12Ca0.72Si02 (wt%)			
Diffusion model	Diffusing unit	D		Diffusion model	Diffusing unit	D	
Silicate- Aluminate Ions Model	$Si_{p}O_{q}^{(2q-4p)-}$ Al <sub>m</sub> O <sub>n</sub> (2n-3m)- CaO <sub>s</sub> (2-2s)+ O <sup>2-</sup>	D <sub>si</sub> * D <sub>Al</sub> * D <sub>Ca</sub> * D <sub>F</sub>		Silicate Ion Model	$Si_{nr}O_{n(2r+1)}$ Na <sup>+</sup> Ca <sup>2+</sup> O <sup>2-</sup>	D <sub>S</sub> D <sub>Na</sub> * D <sub>Ca</sub> * D <sub>F</sub>	
Alumino- silicate Ion Model	$Si_u Al_v O_w^{(2w-4u-3v)}$ Al <sup>3+</sup> CaO <sub>r</sub> <sup>(2-2r)+</sup> O <sup>2-</sup>	D <sub>Si</sub> * D <sub>A</sub> D <sub>Ca</sub> * D <sub>F</sub>					

Table 1 : Diffusion parameters for multiatomic ion models.

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All the compositions of employed diffusion couples were so designed as to make the same average compositions, as shown in Fig. 1.



Fig. 1 : Diffusion paths on ternary diagram (1500°C). Diffusion couple 4-5 at 1445°C.

3. <u>Results.</u> - An example of the diffusion profiles is shown in Fig. 2 for the diffusion couple 6-7 interdiffused at 1500°C and 11 min. The CaO with no initial concentration gradient exhibits an "up-hill" diffusion, which is also described as a curved diffusion path in the ternary diagram in Fig. 1. The up-hill diffusion is satisfactorily described by the theoretical calculation on the basis of the silicatealuminate ions model, which is represented by the solid curve in Fig.2.



Table 2 summarizes the analyses by the two multiatomic ion diffusion models for the diffusion profiles of various diffusion couples for the slag system under various conditions. The results indicate that Ca and Al diffuse as free cations and a fraction of oxygens diffuses as free oxygen ions and that the number of Si atoms in the silicate ion is less than 10 according to both diffusion models.

Silicate-aluminate ions model						
Temp. Sip <sup>0</sup> q			A1 <sub>m</sub> 0 <sub>n</sub>		Ca0 <sub>s</sub>	02-
(°C)	р	q	m	n 🤇	S	N <sub>F</sub>
1370 1445 1450 1500 1550	9.68 2.11 3.85 9.71 5.37	21.4 6.26 9.96 21.5 12.8	1.00 1.00 1.00 1.00 1.00	0.668 0.607 0.433 1.20 0.174	0.00 0.00 0.00 0.00 0.00 0.00	0.342 0.157 0.281 0.261 0.372
Avg	6.14	14.4	1.00	0.616	0.00	0.283

Table 2 : Structure parameters and concentration of free  $0^{2-1}$  ion, for the system  $40Ca0 \cdot 20A1_2O_3 \cdot 40SiO_2$ .

A	Aluminosilicate ion model					
Temp. (°C)		Si <sub>u</sub> A1 v	/ <sup>0</sup> w w	Ca0 <sub>r</sub>	0 <sup>2-</sup>	
1370 1445 1450 1500 1550	9.85 5.40 6.55 9.75 6.57	$0.00 \\ 0.09 \\ 0.00 \\ $	21.7 13.0 15.2 21.5 15.2	0.00 0.00 0.00 0.00 0.00	0.443 0.391 0.413 0.442 0.415	
Avg	7.62	0.02	17.3	0.00	0.421	

Figure 3 shows the interdiffusion profiles for the diffusion couple of  $16Na_20.7Ca0.77sio_2 - 16Na_20.17Ca0.67sio_2$  determined at 1200°C and 4.00 h [4]. The solid curves in the figure represent the corresponding theoretical calculations by the silicate ion model which is described in Table 1. The results indicate that the silicate ion diffuses with self-diffusion coefficient  $1.8 \times 10^{-8}$  cm<sup>2</sup>/s and that 14% of the oxygen diffuses as free ions with self-diffusion coefficient  $7.5 \times 10^{-8}$  cm<sup>2</sup>/s.

The silicate ion in the system  $16Na_20 \cdot 12Ca0 \cdot 72SiO_2$  greater than that in the system  $40CaO \cdot 20Al_2O_3 \cdot 40SiO_2$  is interpreted to be due to the SiO<sub>2</sub> concentration higher in the former.



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