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MULTIATOMIC ION MODELS FOR INTERDIFFUSION OF LIQUID SILICATES

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Résumé. - L'analyse a été faite des profils d'interdiffusion du système $40\text{CaO}\cdot 20\text{Al}_2\text{O}_3\cdot 40\text{SiO}_2$ (% en poids) à $1.370\text{--}1.550^\circ\text{C}$ 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 $16\text{Na}_2\text{O}\cdot 12\text{CaO}\cdot 72\text{SiO}_2$ à 1.200°C .

Abstract. - Interdiffusion profiles of the system $40\text{CaO}\cdot 20\text{Al}_2\text{O}_3\cdot 40\text{SiO}_2$ (wt%) at $1,370\text{--}1,550^\circ\text{C}$ 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 $16\text{Na}_2\text{O}\cdot 12\text{CaO}\cdot 72\text{SiO}_2$ at $1,200^\circ\text{C}$ to determine the composition of the unknown silicate ion.

1. Introduction. - 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 $\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$, 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 $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$.

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

$$J_i = -D_i \frac{\partial C_i}{\partial x} + C_i V + D_i C_i Z_i \frac{F}{RT} \mathcal{E} \quad (i=1, \dots, r) \quad (1)$$

where J_i is the flux density, D_i the self-diffusion coefficient, C_i the concentration, Z_i the valence of the i th species, x the distance, V Darken's mass flow velocity, and \mathcal{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

$$J_i = - \sum_{j=1}^{r-2} M_{ij} \frac{\partial C_j}{\partial x} \quad (i=1, \dots, r-2) \quad (2)$$

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 semi-infinite 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.

Table 1 : Diffusion parameters for multiatomic ion models.

System $40\text{CaO} \cdot 20\text{Al}_2\text{O}_3 \cdot 40\text{SiO}_2$ (wt%)			System $16\text{Na}_2\text{O} \cdot 12\text{CaO} \cdot 72\text{SiO}_2$ (wt%)		
Diffusion model	Diffusing unit	D	Diffusion model	Diffusing unit	D
Silicate-Aluminate Ions Model	Si_pO_q $(2q-4p)^-$	D_{Si}^*	Silicate Ion Model	$\text{Si}_{nr}\text{O}_{n(2r+1)}^{2n-}$	D_{S}
	Al_mO_n $(2n-3m)^-$	D_{Al}^*		Na^+	D_{Na}^*
	CaO_s $(2-2s)^+$	D_{Ca}^*		Ca^{2+}	D_{Ca}^*
	O^{2-}	D_{F}		O^{2-}	D_{F}
Alumino-silicate Ion Model	$\text{Si}_u\text{Al}_v\text{O}_w$ $(2w-4u-3v)^-$	D_{Si}^*			
	Al^{3+}	D_{A}			
	CaO_r $(2-2r)^+$	D_{Ca}^*			
	O^{2-}	D_{F}			

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

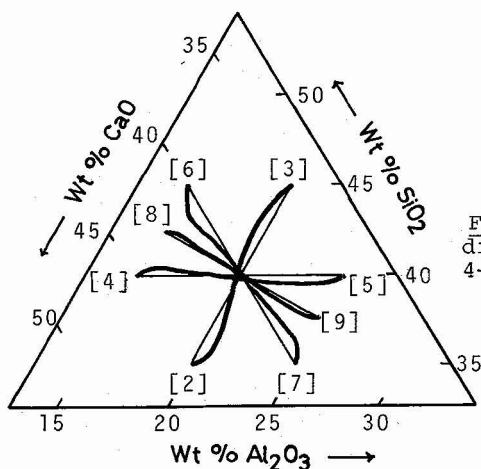


Fig. 1 : Diffusion paths on ternary diagram (1500°C). Diffusion couple 4-5 at 1445°C.

3. Results. - 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 silicate-aluminate ions model, which is represented by the solid curve in Fig.2.

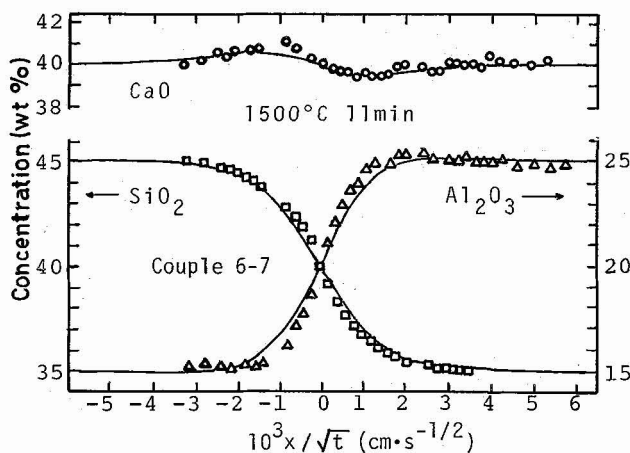


Fig. 2 : Normalized concentration distributions for diffusion couple 6-7 at 1500°C.

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.

Table 2 : Structure parameters and concentration of free O^{2-} ion, for the system $40CaO \cdot 20Al_2O_3 \cdot 40SiO_2$.

Silicate-aluminate ions model							Aluminosilicate ion model					
Temp. (°C)	Si_2O_p		Al_2O_m		CaO_s	$O^{2-}_{N_F}$	Temp. (°C)	Si_u	Al_v	O_w	CaO_r	$O^{2-}_{N_F}$
	p	q	m	n	s		u	v	w	r		
1370	9.68	21.4	1.00	0.668	0.00	0.342	1370	9.85	0.00	21.7	0.00	0.443
1445	2.11	6.26	1.00	0.607	0.00	0.157	1445	5.40	0.09	13.0	0.00	0.391
1450	3.85	9.96	1.00	0.433	0.00	0.281	1450	6.55	0.00	15.2	0.00	0.413
1500	9.71	21.5	1.00	1.20	0.00	0.261	1500	9.75	0.00	21.5	0.00	0.442
1550	5.37	12.8	1.00	0.174	0.00	0.372	1550	6.57	0.00	15.2	0.00	0.415
Avg	6.14	14.4	1.00	0.616	0.00	0.283	Avg	7.62	0.02	17.3	0.00	0.421

Figure 3 shows the interdiffusion profiles for the diffusion couple of $16Na_2O \cdot 7CaO \cdot 77SiO_2$ - $16Na_2O \cdot 17CaO \cdot 67SiO_2$ determined at $1200^\circ C$ 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 $1.8 \times 10^{-8} \text{ cm}^2/\text{s}$ and that 14% of the oxygen diffuses as free ions with self-diffusion coefficient $7.5 \times 10^{-8} \text{ cm}^2/\text{s}$.

The silicate ion in the system $16Na_2O \cdot 12CaO \cdot 72SiO_2$ greater than that in the system $40CaO \cdot 20Al_2O_3 \cdot 40SiO_2$ is interpreted to be due to the SiO_2 concentration higher in the former.

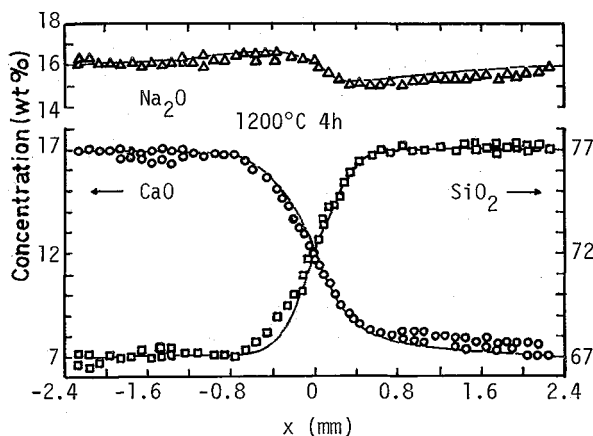


Fig. 3 : Concentration distributions for diffusion couple $16Na_2O \cdot 17CaO \cdot 67SiO_2$ - $72 \cdot 16Na_2O \cdot 7CaO \cdot 77SiO_2$ at $1200^\circ C$.

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