Note

The Coordination of F Ions around Mg and Ca Ions in Molten CaO–CaF₂–MgO–SiO₂ System at 1 873 K

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In the previous papers,^{1,2)} the effect of F ions on the structure of molten CaO–CaF₂–Al₂O₃–SiO₂ system has been investigated by using molecular dynamics simulation. It has been found that loosely bound Ca–2F complexes are formed in the melts. It means that the addition of CaF₂ to CaO–SiO₂ or CaO–Al₂O₃–SiO₂ melts does not influence the relative distribution of silica network units in the melts.^{1,2)}

Steelmaking slags always contain small amount of MgO. The ionic diameter of Mg²⁺ ion is rather small than that of Ca²⁺ and the structures of CaF₂ and MgF₂ crystal are different. These infer that the coordination structure of F around Ca and Mg may not be the same. Consequently, it is not certain whether loosely bound Mg–2F complexes can exist or not. If the loosely bound Mg–2F complexes are existed, the addition of CaF₂ to CaO–MgO–SiO₂ melts may influence the relative distribution of silica network units in the melts since the total amount of network modifiers will change by the formation of Mg–2F complexes. In the present study, the structures of CaO–CaF₂–MgO–SiO₂ systems with various F contents have been investigated by using molecular dynamics simulation to evaluate the effect of F ions on the structure of molten CaO–CaF₂–MgO–SiO₂ systems.

For the molecular dynamics simulation of the melts, the MXDORTHO program³⁾ was used. The pair potential used was the Busing approximation of the Born–Mayer–Huggins form⁴⁾:

$$U_{ij}(r) = Z_i Z_j e^2 / R_{ij} + f_0 (b_i + b_j) \exp((a_i + a_j - R_{ij}) / (b_i + b_j)) \dots (1)$$

where R_{ij} is the distance between ions i and j , Z_i is the charge of ion i , and f_0 is equal to 6.9472×10^{-11} N. a_i and b_i are potential parameters that are related to the size and softness of the i th atom, respectively. The reliability of the parameter sets for the Born–Mayer–Huggins potential was sufficiently discussed by Sangster and Dixon.⁵⁾ The values of the parameter set used in this calculation are shown in Table 1.

For the calculation, three-dimensional periodic boundary conditions were applied to basic cells containing about 5 000 atoms. The long-range Coulombic forces were calculated by the Ewald summation⁵⁾ within an uncertainty of 0.01%. The equation of motion was integrated by the Verlet

algorithm⁵⁾ using a time step of 2.0 fs. The calculation was carried out at a constant pressure of 101 kPa. The initial temperature was set to 3 273 K to agitate the atoms and eliminate the effect of the initial distribution on the final structure. The temperature was then decreased to 2 773, 2 273 and finally 1 873 K, and the calculation at each temperature was carried out for 10 000 steps. The temperature decreasing rate was set to 1 K per 10 steps. The calculated structural data were accumulated at each temperature. On the basis of these calculated data, the cumulative coordination numbers (CCNs), average distances between atoms, pair correlation functions (PCFs), and silicate anionic structural unit distributions were calculated. The compositions of the CaO–CaF₂–MgO–SiO₂ system in the present study are presented in Table 2 and Fig. 1.

Silicate melts are well known to consist of mixtures of five distinct types of structural units that have NBO/Si=0, 1, 2, 3, and 4 (NBO/Si: nonbridging oxygen per silicon).⁶⁾ In terms of a stoichiometric expression, these units are described as SiO₄⁴⁻ (monomer), Si₂O₇⁶⁻ (dimer), Si₂O₆⁴⁻ (chain unit), Si₂O₅²⁻ (sheet unit), and SiO₂ units. In the terminology commonly employed in NMR spectroscopy, these structures are referred to as Q⁰, Q¹, Q², Q³, and Q⁴, where the superscript refers to the number of bridging oxygen

Table 1. Parameter set used in the molecular dynamics calculation.

	Z	a (10 nm)	b (10 nm)
Si	4	1.102	0.080
Al	3	1.064	0.080
Na	1	1.260	0.080
Ca	2	1.414	0.080
F	–1	1.565	0.085
O	–2	1.626	0.085

Table 2. Investigated compositions of the CaO–CaF₂–MgO–SiO₂ systems.

		(mol%)				
		CaO	CaF ₂	MgO	MgF ₂	SiO ₂
A	5CaO·5SiO ₂	50.0	0.0	0.0	0.0	50.0
B	4CaO·MgO·5SiO ₂	40.0	0.0	10.0	0.0	50.0
C	3CaO·CaF ₂ ·MgO·5SiO ₂	30.0	10.0	10.0	0.0	50.0
D	2CaO·2CaF ₂ ·MgO·5SiO ₂	20.0	20.0	10.0	0.0	50.0
E	5CaO·MgF ₂ ·5SiO ₂	40.0	0.0	0.0	10.0	50.0

Fig. 1. Investigated compositions of the CaO–CaF₂–MgO–SiO₂ and CaO–MgF₂–SiO₂ systems. A: 5CaO·5SiO₂, B: 4CaO·MgO·5SiO₂, C: 3CaO·CaF₂·MgO·5SiO₂, D: 2CaO·2CaF₂·MgO·5SiO₂, E: 4CaO·MgF₂·5SiO₂.

atoms in a given structural unit.

The calculated distributions of Q^i in the $5\text{CaO} \cdot 5\text{SiO}_2$ system and $4\text{CaO} \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K are shown in **Fig. 2**. Their distributions of Q^i are essentially the same. It means that the replacement of Ca ions by Mg ions has negligible effects on the relative distribution of silica network units in the melts. Namely, the network modifying ability of Mg ions is almost the same as that of Ca ions. Stebbins *et al.*⁷⁾ mentioned that ^{29}Si NMR separate peaks are not resolvable in $\text{CaO} \cdot \text{SiO}_2$ system, although they span the known chemical shift ranges for at least the Q^1 , Q^2 , and Q^3 , and perhaps even Q^0 and Q^4 species. Thus, the calculated results of Q^i distribution may not be compared with their measured NMR peaks. However, Mysen *et al.*⁸⁾ measured Raman spectra of $\text{CaO} \cdot \text{SiO}_2$ system and their Q^i distributions estimated from the spectra are well agreed with the present calculated result. This agreement strongly supports the reliability of the present MD calculation.

The effect of replacement of CaO by CaF_2 in $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ melts at 1873 K is shown in **Fig. 3**. It is found that the fractions of Q^3 and Q^4 are increased by the substitution of F for O. Namely, it enhances the polymerization in the melts. The mechanism of the enhancement of the polymerization in the $\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ systems due to the substitution of F for O were already discussed and confirmed. Namely, due to the formation of the loosely bound Ca–2F complexes in those melts, the number of Ca ions available to the network modifier is decreased so that the degree of the polymerization of Si units in the melts is increased.

The enhancement of the polymerization in the $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ systems due to the substitution of F for O can be explained not only by the formation of the loosely bound

Fig. 2. Calculated distribution of Q^i in the $\text{CaO} \cdot \text{SiO}_2$ and $4\text{CaO} \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K.

Fig. 3. Calculated distribution of Q^i in the $4\text{CaO} \cdot \text{MgO} \cdot 5\text{SiO}_2$, $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ and $2\text{CaO} \cdot 2\text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K.

Ca–2F complexes but also possibly by the formation of the loosely bound Mg–2F complexes since the network modifying ability of Mg ions is found to be almost the same with that of Ca ions. To understand the details of the effect of F on the polymerization process of $\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot \text{SiO}_2$ melts, the coordination numbers of F around the Ca and Mg ions in the molten $\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot \text{SiO}_2$ system must be evaluated.

Information for F coordination around the Ca and Mg ions in the $\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot \text{SiO}_2$ melts can be obtained from the PCF value between ions i and j , $g_{ij}(r)$, and the running coordination number (RCN) curve, $N(r)$; $g_{ij}(r)$ and $N(r)$ are given by⁹⁾

$$g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \frac{\langle n_{ij}(r) \rangle}{4\pi r^2 \Delta r} \quad \text{.....(2)}$$

$$N(r) = 4\pi\delta_j \int_0^r r^2 g_{ij}(r) dr \quad \text{.....(3)}$$

where N denotes the number of ions in the box; V , the volume of the box; r , the distance between ions i and j ; n_{ij} , the number of ions j about ion i in the shell within distances $r \pm \Delta r/2$; $\langle \rangle$, the time average; and δ , the particle density of the ion. The PCF value represents the probability density of finding a pair of atoms at distance r apart, relative to the probability expected for a completely random distribution at the same density. RCN is a coordination number at the particular distance and the cumulative coordination number (CCN) is defined as the RCN value at the distance at which PCF has the minimum value. The equilibrated bond length is defined as the distance between the ion pairs where the PCF has the maximum value. The details of the calculation can be obtained from other studies.^{6,9)}

The PCF and RCN curves for the Ca–F and Mg–F pairs in the $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K are shown in **Fig. 4**. The equilibrated bond length of the Ca–F pair is found to be 0.234 nm and that of Mg–F pair is 0.204 nm. This difference can be attributed to the different ionic diameters of Ca and Mg ions. The cumulative coordination number (CCN) is defined as the RCN value at the distance at which PCF has the minimum value. The CCNs for Ca–F and Mg–F are 2.6 and 0.89 respectively. The PCF curves for Ca–F and Mg–F pair have long tails as shown in **Fig. 4**. It means that the Ca–F or Mg–F bonding in the tail

Fig. 4. PCF and RCN curves for the Ca–F and Al–F pairs in the $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K.

Fig. 5. PCF and RCN curves for the Ca-F and Mg-F pairs in the $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system at 1873 K.

area is not tight enough to retain F ions around Ca or Mg ions, and some F ions can move out easily from the influential area of Ca or Mg ion's Coulombic force. Namely, calculated CCNs include the number of F ions that are not essentially belonged to the cations. Despite of their including of the tail area, the CCN for Mg-F pair is still less than unit. If we assume tight binding between F ions and cations or neglect the tail effect, the RCN for F around Ca is about 2.0 and 0.6 for F around Mg. The assumed tight binding PCF curves are indicated by broken lines in Fig. 4. This value of 0.6 strongly suggests that Mg-2F complexes are not formed in the $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system.

To confirm the no-existence of loosely bound Mg-2F complexes, the structure of liquid $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system is simulated. The PCF and RCN curves for the Ca-F and Mg-F pairs in the $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system at 1873 K are shown in Fig. 5. The PCF curves are slightly different from those in the $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system, but the RCN curves are essentially the same as those in $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system. The CCN for Mg-F and Ca-F pairs in the $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system are found to be 0.81 and 2.87 respectively. These values simply indicate that F ions are mainly coordinate to Ca ions but not Mg ions. Namely the F ions initially associated with Mg ions are finally most coordinated to Ca ions. If so, the molten structure of $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system could be the same as that of $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system. The cal-

Fig. 6. Calculated distribution of Q^i in the $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ and $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system at 1873 K.

culated distributions of Q^i in the $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ system and $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ system at 1873 K are shown in Fig. 6. Just as expected, the distributions of Q^i of both systems are essentially the same, although there are small differences in Q^3 and Q^4 units' distribution. As shown in Fig. 4, a small amount of F ions is still coordinated to Mg ions. This F coordination to Mg ions may cause the small differences in the amount of Q^3 and Q^4 units between $4\text{CaO} \cdot \text{MgF}_2 \cdot 5\text{SiO}_2$ and $3\text{CaO} \cdot \text{CaF}_2 \cdot \text{MgO} \cdot 5\text{SiO}_2$ systems. The agreement between the two systems simply means that the F ion has a strong preference to coordinate to Ca ions but not Mg ions in the molten CaO-CaF₂-MgO-SiO₂ system.

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