The Coordination of F Ions around Al and Ca Ions in Molten Aluminosilicate Systems

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The structure of CaO–CaF₂–Al₂O₃–SiO₂ systems with various F/O ratios has been investigated by using molecular dynamics simulation to evaluate the effect of F ions on the polymerization of melts. F ions in the melt are found to be mainly coordinated to Ca ions but not to Al ions. The formation of loosely bonded Ca–2F complexes in the CaO–CaF₂–Al₂O₃–SiO₂ melts is confirmed since the cumulative coordination number for F around the Ca ion at around the equilibrated bond length is approximately 2. Due to the formation of Ca–2F complexes, Ca ions available to the network modifier are decreased so that the degree of the polymerization of Si units in CaO–CaF₂–Al₂O₃–SiO₂ system is increased. The amount of aluminate tetrahedra embedded in silicate three-dimensional network unit is gradually decreased by the substitution of F ions for O ions because the amount of the silicate three-dimensional network unit is increased due to the decrease of Ca ions available to the network modifier.

KEY WORDS: F ions; aluminosilicate; polymerization; molecular dynamics simulation; running coordination number.

1. Introduction

It is well known that aluminum as well as silicon ions in aluminosilicate melts occur in tetrahedral coordination under most conditions.1) However, whether or not Al³⁺ can be tetrahedrally coordinated depends on the availability of metal cations for the electrical charge balance. Aluminum differs from silicon in that it exists as a trivalent cation in the melts. Therefore, to maintain the electrical neutrality, the electrical charge balance of tetrahedrally coordinated Al³⁺ must be compensated in order to obtain an effective electrical charge of +4. This charge balance can be obtained using alkali metals or alkaline earths.1)

The structure of aluminosilicate melts is best discussed by subdividing the system into three groups.1) These are the tectosilicate melts where the abundance of metal cations in the system is the exactly that required to charge-balance Al³⁺ in tetrahedral coordination. The second group will be referred to peralkaline aluminosilicate melts. In such melts, the abundance of metal cations exceeds that required for charge-balance of tetrahedrally coordinated Al³⁺. The third group is the peraluminous aluminosilicate melts where there are insufficient metal cations available for electrical charge-balance. In peraluminous melts, some Al³⁺ ions are in octahedral coordination. Simulated melts in the present study are peralkaline aluminosilicate melts so that all Al³⁺ can be tetrahedrally coordinated.

Mysen and Virgo2) studied the fluorine solubility in alkali aluminosilicate (NaAlO₂–SiO₂) melts. They confirmed that fluorine is dissolved by forming either aluminum fluoride or sodium fluoride complexes or mixtures of both. The proportion of Na⁺ and Al¹⁺ in the fluoride complexes is a function of both the total fluorine content and Al/(Al+Si) ratio of the melt.2) It is presumed that the interaction of aluminum with fluorine results in an equivalent amount of charge-balancing cations becoming a network modifier. Consequently, the highly polymerized aluminosilicate melts would become depolymerized as fluorine is dissolved. On the other hand, the interaction of a metal cation with fluorine in depolymerized melts results in an equivalent amount of charge-balancing cations being eliminated from the network modifier, and the polymerization of melts is enhanced. Thus, depending on the degree of polymerization, the role of the F ions will change.

A similar behavior of the F ions may be expected in alkaline earth aluminosilicate melts as well as alkali aluminosilicate melts. However, there are distinctive differences between the behavior of alkaline earth aluminosilicate melts and alkali aluminosilicate melts.1) Thus, the behavior of F in alkaline earth aluminosilicate melts may differ from that in alkali aluminosilicate melts.

In the present study, the structure of CaO–CaF₂–Al₂O₃–SiO₂ systems with various F/O ratios is investigated by using molecular dynamics simulation to evaluate the effect of F ions on the polymerization of melts.

2. Molecular Dynamics Simulation Method

For the molecular dynamics simulation, the MXDORTHO program3) was used. The pair potential used was the Busing
approximation of the Born–Mayer–Huggins form:\(^1\):

\[
U_{ij}(r) = ZZ_i e^2 / R_{ij} + f_0(b_i + b_j) \exp((a_i + a_j - R_{ij})(b_i + b_j))
\]

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 \(6.9472 \times 10^{-11}\) 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 has been 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 3000 atoms. The long-range Coulombic forces were calculated by the Ewald summation\(^6\) using a time step of 2.0 fs. At the start of the calculation, the distribution of the constituent atoms in the basic cells was statistically random. The calculation was carried out at a constant pressure of 101 kPa. The initial temperature was set to 3273 K to agitate the atoms and eliminate the effect of the initial distribution on the final structure. The temperature was then decreased to 2773, 2273, and finally 1873 K, and the calculation at each temperature was carried out for 10000 steps. The temperature decreasing rate was set to 1 K per 10 steps. The 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 anionic structural unit distributions were calculated. The calculated compositions of the \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\) melts, the summation of cells parallel to the diagonal corresponds to the percentage of each structural unit with different NBO/T ratios or \(Q^i\), where the superscript refers to the number of bridging oxygen atoms in a given structural unit. The same notations are also used for the aluminate units.

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

<table>
<thead>
<tr>
<th></th>
<th>(Z)</th>
<th>(a \times 10^{-10})</th>
<th>(b \times 10^{-10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4</td>
<td>1.102</td>
<td>0.080</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>1.064</td>
<td>0.080</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>1.260</td>
<td>0.080</td>
</tr>
<tr>
<td>Ca</td>
<td>2</td>
<td>1.414</td>
<td>0.080</td>
</tr>
<tr>
<td>F</td>
<td>-1</td>
<td>1.565</td>
<td>0.085</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>1.626</td>
<td>0.085</td>
</tr>
</tbody>
</table>

Table 2. Investigated compositions of the \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\) system.

<table>
<thead>
<tr>
<th></th>
<th>(\text{CaO})</th>
<th>(\text{CaF}_2)</th>
<th>(\text{Al}_2\text{O}_3)</th>
<th>(\text{SiO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40.0</td>
<td>10.0</td>
<td>0.0</td>
<td>50.0</td>
</tr>
<tr>
<td>B</td>
<td>40.0</td>
<td>10.0</td>
<td>10.0</td>
<td>40.0</td>
</tr>
<tr>
<td>C</td>
<td>30.0</td>
<td>20.0</td>
<td>10.0</td>
<td>40.0</td>
</tr>
<tr>
<td>D</td>
<td>20.0</td>
<td>30.0</td>
<td>10.0</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Fig. 1. Investigated compositions in the \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\) system. A: \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{5SiO}_2\), B: \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\), C: \(3\text{CaO}\cdot\text{2CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\), D: \(2\text{CaO}\cdot\text{3CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\).

Fig. 2. Calculated linkage distribution between Si and Al tetrahedra in the \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\) melts.

<table>
<thead>
<tr>
<th>Si</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.50</td>
<td>2.05</td>
<td>3.45</td>
<td>1.40</td>
<td>1.25</td>
</tr>
<tr>
<td>1</td>
<td>2.83</td>
<td>9.70</td>
<td>9.25</td>
<td>3.83</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>10.77</td>
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<td>6.70</td>
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</tr>
<tr>
<td>3</td>
<td>12.60</td>
<td>9.65</td>
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<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3. Calculated linkage distribution between Si and Al tetrahedra in the \(4\text{CaO}\cdot\text{CaF}_2\cdot\text{Al}_2\text{O}_3\cdot\text{4SiO}_2\) melts.
cates tetrahedral Si or Al.

As shown in Table 4, the amount of Q^4 for Al tetrahedra units is about 2 times larger than that of Si tetrahedra units. Namely Al^{3+} ions have a preference to enter the three-dimensional network structure. This preference is generally found in aluminosilicate systems and is known as Loewenstein's rule. Thus, Q^4 distribution may represent the characteristics of aluminosilicate melt.

The calculated distributions of Q^4 for the Si and Al tetrahedra in the CaO–CaF_2–Al_2O_3–SiO_2 system (A, B, C and D in Table 2) are shown in Fig. 2 as a function of the CaF_2 fraction. The Q^4 unit for the Si tetrahedra increases with an increase in the CaF_2 fraction, but that for the Al tetrahedra decreases. In other words, the substitution of F for O enhances the polymerization for the Si tetrahedra units and depolymerizes the Al tetrahedra units.

3.2. Coordination of F Ion around Al and Ca Ions

To understand the details of the effect of CaF_2 on the polymerization process of CaO–CaF_2–Al_2O_3–SiO_2 melts, the coordination numbers of F around the Ca and Al ions in the molten CaO–CaF_2–Al_2O_3–SiO_2 system were calculated by varying the CaF_2/CaO ratio using constant amounts of Al_2O_3 and SiO_2.

Information regarding F coordination around the Ca and Al ions in the CaO–CaF_2–Al_2O_3–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 by

\[ g_{ij}(r) = \frac{V}{N_i N_j} \sum_j \frac{n_j(r)}{4\pi r^2 \Delta r} \quad (2) \]

\[ N(r) = 4\pi \delta \int_0^r g_{ij}(r) dr \quad (3) \]

where N denotes the number of ions in the box; V, the volume of the box; n_j(r) the number of ions j about ion i in the shell within distances r±Δr/2; ⟨⟩, 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 for which the value of PCF is maximum. The details of the calculation can be obtained from other studies.7,9

The PCF and RCN curves for the Si–O and Al–O pairs in the 4CaO·CaF_2·Al_2O_3·4SiO_2 system are shown in Fig. 3. The equilibrated bond lengths of the Si–O and Al–O ion pairs are 0.162 nm and 0.176 nm, respectively. Their PCF curves are almost symmetric and show negligible tails. RCN for Si–O and Al–O pairs can be calculated from the area under each peak of the PCF and are both about 4. Namely, the development of the Si and Al tetrahedral structures is clearly identified from the RCN curves.

The PCF and RCN curves for the Al–O and Al–F pairs in the 4CaO·CaF_2·Al_2O_3·4SiO_2 system are compared in Fig. 4. The equilibrated bond length of the Al–O pair is shorter than that of the Al–F pair since the Coulombic interaction of the Al–O pair is stronger than that of the Al–F pair.

| Table 4. Q^i for Si and Al tetrahedra (i=0 to 4) in the 4CaO·CaF_2·Al_2O_3·4SiO_2 system. |
|---------------------------------|---------------------------------|
| Si tetrahedra | Al tetrahedra |
| Q^0 | 0.50 | 0.00 |
| Q^1 | 4.88 | 2.60 |
| Q^2 | 23.92 | 12.95 |
| Q^3 | 43.5 | 40.9 |
| Q^4 | 27.21 | 44.55 |

Fig. 2. Calculated distribution of Q^4 for Si and Al tetrahedra in the CaO–CaF_2–Al_2O_3–SiO_2 system as a function of the CaF_2 fraction.

Fig. 3. PCF and RCN curves for the Si–O and Al–O pairs in the 4CaO·CaF_2·Al_2O_3·4SiO_2 system.

Fig. 4. PCF curves for the Al–O and Al–F pairs in the 4CaO·CaF_2·Al_2O_3·4SiO_2 system.
The PCF and RCN curves for the Al–F pair in the 4CaO·CaF₂·Al₂O₃·4SiO₂ system are shown in Fig. 5 using a magnified scale. The PCF curve has a long tail. In contrast to the RCN curves for the Si–O and Al–O pairs, the RCN curve for the Al–F pair shows a gradual increase. The coordination number of F around Al for lengths nearly equal to the equilibrated bond length is extremely small of less than 0.2. This implies that the coordination number of F around Al can be negligible. This small value of RCN for the case of F around Al is also observed for another composition in the present study. Thus, it is confirmed that the stable F coordinated alumina complex such as AlO₃F₄/tetrahedra unit is not formed in the investigated melts.

The PCF and RCN curves for the Ca–F and Ca–O pairs in the 4CaO·CaF₂·Al₂O₃·4SiO₂ system are shown in Fig. 6. The equilibrated bond length of the Ca–F pair is almost identical to that of the Ca–O pair. The PCF curve of Ca–F pair has about two times large value than that of Ca–O curve. This implies that the degree of accumulation of the F ions around the Ca ions relative to a completely random distribution is approximately twice that of the O ions around the Ca ions. In other words, the F ions associate with the Ca ions to a greater degree than the O ions.

Differed from the case of Si–O pair, the PCF curve for Ca–F pair has a long tail as shown in Fig. 6. It means that the Ca–F binding is not tight enough to retain F ions around Ca ion, and some F ions can move out from the influential area of Ca ion’s Coulombic force. Namely, Ca–F pairs are rather loosely bonded. The PCF curve for Ca–F pair is reproduced in Fig. 7. In Fig. 7, the assumed PCF curve for the case of tight binding Ca–F pair is presented by the out line of hatched area. The coordination number of the assumed tight binding Ca–F pairs can be calculated from the hatched area and is about 2. The contribution of F ions in the tail area for the formation of Ca–F bonding can be negligible since the Coulombic force between the Ca ion and F ions in the tail area can be very small. Thus, the coordination of number of the loosely bonded Ca–F pairs can be reasonably close to that of the assumed tight binding Ca–F pairs and will be approximately around 2. Thus, it can be said that Ca and F ions form loosely bonded Ca–2F complexes in the melts. The existence of Ca–2F complexes in the CaO–CaF₂–SiO₂ and CaO–CaF₂–Na₂O–SiO₂ melt were also confirmed in a previous study.¹²,¹³)

### 3.3. Effect of F Ions on the Polymerization of Aluminosilicate Melts

The priority role of Ca ions in aluminosilicate melts is the compensation of the electrical charge for Al³⁺ ions.¹ If Ca ions are still remained after the coordination to Al³⁺, the remained Ca ions can work as network modifiers. As already discussed, Ca and F ions in aluminosilicate melts form the Ca–2F complex. A Ca ion in the Ca–2F complex cannot work as a charge compensator and/or network modifier. In the present melts, Ca ions are more than enough for the full compensation of the electrical neutrality even after the formation of Ca–2F complexes. Namely all Al³⁺ ions are fully compensated and all of them are tetrahedrally coordinated. It means that the total number of Al tetrahedra does not change by the introduction of F ions to the melt in this study.

The number of Ca ions required for the full compensation of the electrical neutrality is determined by the melt composition. On the other hand, the Ca ions for network modifiers must be decreased by the formation of Ca–2F complexes so that the polymerization of the melts is enhanced. The framework of network in the melts can be mainly constructed by the Si tetrahedra, and Al teterahedra are embedded in the Si tetrahedra network since the number of Si tetrahedra is 2 times larger than that of Al tetrahedra. Thus, the increase of Silicate Q₄ units by the substitution of 2F for O ions, as shown in Fig. 2, can be attributed to the decrease of Ca ions for network modifiers due to the formation of the Ca–2F complexes.

The total amount of Al tetrahedra in the melt is constant although the amount of silicate Q₄ unit is increased by the introduction of F ions into the melt. Thus, the relative amount of aluminate tetrahedra embedded in silicate Q₄...
unit can be expected to decrease with increase of the total amount of Ca–2F complexes. This tendency is qualitatively well presented in Fig. 2.

4. Conclusions

The effect of F ions on the structure of molten CaO–CaF₂–Al₂O₃–SiO₂ systems is investigated by using molecular dynamics simulation, and the following conclusions are drawn:

1. The stable F coordinated alumina complex such as AlO₄F⁴⁻ tetrahedra unit is not formed in the investigated CaO–CaF₂–Al₂O₃–SiO₂ melts since the coordination number of F around Al is found to be small—less than 0.2.

2. Ca–2F complexes are confirmed to be formed in the CaO–CaF₂–Al₂O₃–SiO₂ melts since the RCN for F around the Ca ion corresponds to the zone where Coulombic force is highly influential is approximately 2.

3. The substitution of CaF₂ for CaO with constant amounts of Ca, Al, and Si ions in the CaO–CaF₂–Al₂O₃–SiO₂ melts increases the number of Q⁴ units for Si since the amount of Ca ions required for network modifiers are decreased.

4. Due to the formation of Ca–2F complexes, Ca ions available to the network modifier are decreased so that the degree of the polymerization of Si units is increased.

5. The amount of aluminate tetrahedra embedded in silicate Q⁴ unit is gradually decreased by the introduction of F ions into the melt because the amount of the silicate Q⁴ unit is simultaneously increased due to the decrease of Ca ions available to the network modifier.

REFERENCES