Effect of Fluorine on Silicate Network for CaO–CaF₂–SiO₂ and CaO–CaF₂–SiO₂–FeOₓ Glasses

M. HAYASHI, N. NABESHIMA, H. FUKUYAMA and K. NAGATA

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552 Japan.

(Received on October 26, 2001; accepted in final form on December 28, 2001)

The chemical state of fluorine and the effect of fluorine addition on the degree of polymerization of silicate network have been investigated for the CaO–SiO₂–CaF₂ and CaO–SiO₂–CaF₂–FeOₓ glasses using the X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy measurements. The F1s XPS spectra indicate that the fluoride is dominantly coordinated with calcium rather than silicon. The O1s XPS spectra for the CaO–SiO₂–CaF₂ glasses and the values of Fe²⁺/Fe³⁺ obtained by Mössbauer spectra for the CaO–SiO₂–CaF₂–FeOₓ glasses indicate that CaF₂ addition does not depolymerize the silicate network for both systems.

KEY WORDS: chemical state of fluorine; polymerization; silicate network; X-ray photoelectron spectroscopy; Mössbauer spectroscopy.

1. Introduction

CaF₂ is widely used as an addition to steelmaking slags because of the strong fluxing power. Addition of CaF₂ lowers the liquidus temperature and the viscosity of slags, resulting in improvement of reactivity in slag–metal interface. It has been also reported that CaF₂ addition increases the sulphide capacity of slags having a constant CaO/SiO₂ ratio.¹ However, there has been growing recognition that fluoride has harmful influence both on the natural environment and on recycling of slags. Thus, it is desired to develop fluorine free steelmaking flux. For this purpose, it is essential, as a first step, to elucidate the mechanism for improving the physicochemical properties of slags by CaF₂ addition. Since the physicochemical property is relevant to the structure, it is of great importance to investigate the structure of slags containing CaF₂.

The structure of silicate glasses containing CaF₂ has been predicted from the data obtained by means of viscosity²–⁴ and cryoscopic measurements,⁵ and studied more directly using spectroscopic measurements such as infrared absorption,⁶–⁹ Raman,¹⁰,¹¹ X-ray photoelectron spectroscopy¹²,¹³ and ¹⁹F nuclear magnetic resonance spectroscopies.¹⁴,¹⁵ The conclusions deduced from the above reports can be classified into three conflicting views:

(i) The addition of CaF₂ to acidic silicate glasses leads to the depolymerization of silicate network owing to the formation of Si–F bonds. But in basic glasses fluorine is present as F⁻ and does not contribute to the breakage of Si–O bonds irrefpective of glass compositions.⁵,¹¹,¹³

(ii) Fluorine predominantly bonds with silicon for a CaF₂ concentration of less than about 10 mol%, and is present as F⁻ coordinated with Ca²⁺ for higher CaF₂ concentration.¹⁰,¹²

(iii) Fluorine is present as F⁻ coordinated with Ca²⁺ and does not contribute to the breakage of Si–O bonds irrespective of glass compositions.⁵,¹¹,¹³

Consequently, there is no consensus on the structure of silicate glasses containing CaF₂. In order to judge the above views, it is necessary to accumulate more reliable data for the structures of glasses having different compositions to determine the relationship between the structural role of fluorine and the glass composition.

The objective of this study is to measure the chemical state of fluorine and the effect of fluorine addition on the degree of polymerization of silicate network for the CaO–SiO₂–CaF₂ and CaO–SiO₂–CaF₂–FeOₓ glasses using the X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy measurements. In the XPS measurements, we have employed fresh surfaces of glassy samples fractured in ultrahigh vacuum (2×10⁻⁷ Pa) and optimum charge neutralization by flooding electrons to distinguish two chemical states of fluorine. The chemical compositions of glassy samples have been chosen so as to examine the effects of both CaO/SiO₂ ratio and CaF₂ concentration on the structural role of fluorine.

2. Experimental

2.1. Sample Preparation

Six series of glassy samples were prepared as follows:

Series 1. 95[(1+y)CaO–1/(1+y)SiO₂]–5CaF₂ (y=0.6, 0.7, 0.8, 0.9, 1.0)

Series 2. (50–x)CaO–50SiO₂–xCaF₂ (x=0, 5, 10, 15)

Series 3. (50–x/2)CaO–(50–x/2)SiO₂–xCaF₂
(x=0, 5, 10, 15, 20) 

Series 4. \(90(y/(1+y))\text{CaO}–1/(1+y)\text{SiO}_2–10\text{Fe}_2\text{O}_3\)  
\((y=0.6, 0.7, 0.8, 0.9, 1.0)\)

Series 5. \((45–x)\text{CaO}–45\text{SiO}_2–x\text{CaF}_2–10\text{Fe}_2\text{O}_3\)  
\((x=0, 5, 10, 15, 20)\)

Series 6. \((45–x/2)\text{CaO}–(45–x/2)\text{SiO}_2–x\text{CaF}_2–10\text{Fe}_2\text{O}_3\)  
\((x=0, 5, 10, 15, 20)\)

where the nominal compositions are represented in mol%.

Samples were prepared from reagent grade SiO2, CaF2, Fe2O3, and CaCO3 powders, the last being decomposed to CaO by heating at 1423 K for 24 h. Powders of SiO2, CaF2, and Fe2O3 were dried at elevated temperatures. The reagents were weighed to the desired compositions and mixed in an agate mortar. About 20 g of these mixtures were melted in platinum crucibles at 1783 K in air for 1 h for the samples of series 1–3 and for 3 h for the samples of series 4–6, respectively. It has been confirmed that the melting time of 3 h is long enough for the fraction of Fe3+ ions to the total iron ions to reach a constant value. Glassy samples were prepared by pouring the melts onto a water cooled copper plate in air. Samples for the XPS measurements were prepared by cutting the samples into rods of 4 mm in diameter and 16 mm in length, and washing them with acetone in an ultrasonic bath.

2.2. Measurements

X-ray diffraction studies were carried out with CuKα radiation to identify the crystal structure of the samples. The chemical compositions of the samples were analyzed by EPMA (electron probe micro analyzer). The F1s and O1s XPS spectra were measured using an X-ray photoelectron spectrometer (Perkin-Elmer PHI Model 5500) incorporating a spherical capacitor analyzer. A monochromatized AlKα radiation (1486.6 eV) was used as the X-ray source, which was operated at 300 W and 14 kV. The rod shaped samples were fractured in ultrahigh vacuum (\(2\times10^{-7}\) Pa). The surface charging was neutralized by flooding electrons. Pass energy and aperture size of the analyzer were 5.85 eV and 0.8 mm, respectively. Data were acquired with 0.025 eV steps. In order to correct the charging effects, the measured binding energies were calibrated using the binding energy of the adventitious C1s line assuming that the C1s core level is 284.6 eV.

Mössbauer spectroscopy measurements were carried out at room temperature using 30 mCi 57Co in Rh as the γ-ray source to determine the fraction of Fe3+ (or Fe2+) ions to the total iron ions. It has been reported that the fraction of Fe3+ (or Fe2+) ions to the total iron ions determined by Mössbauer spectroscopy and wet-chemical techniques are the same within these uncertainties. The Doppler velocity scale for the measurements was calibrated at room temperature using the spectrum of α-Fe foil.

3. Results

Table 1 shows the analyzed chemical compositions of the samples. The analytical uncertainty in the composition values is within 3%. The values of (mol%FeO)/(mol%Fe2O3) have been determined by Mössbauer spectroscopy measurements. The decreases of CaF2 and SiO2 concentrations and the increase of CaO concentration were observed during melting for the samples of series 1–3, probably owing to the vaporization of SiF4 and HF.

Figure 1 shows a typical X-ray diffraction profile of a glassy sample. As shown in Fig. 1, all the X-ray diffraction profiles only showed a broad peak around the diffraction angle 2θ of 30 deg except for that of the 40(mol%)CaO–40SiO2–20CaF2 sample. This is so-called halo pattern confirming that the samples are amorphous. Figure 2 shows the X-ray diffraction profile of the 40(mol%)CaO–40SiO2–
20CaF₂ sample, where Ca₅SiO₇F₁₂, 3CaO2SiO₂CaF₂, CaF₂ and 3CaO2SiO₂ were identified.

Figures 3 and 4 show the F₁s XPS spectra for the samples of series 2 and 5, respectively. The binding energies of CaF₂ crystal¹³,²⁰ and F-containing SiO₂ glass due to the vapor phase axial deposition method (VAD)¹³ are indicated in both figures. The spectra for all samples give symmetrical peaks and have been fitted with single Gaussian functions. Table 2 summarizes the binding energies at peak position (BE) and the full widths at half maximum intensity (FWHM) of the F₁s spectra for all samples.

Figures 5, 6 and 7 show the O₁s XPS spectra for the samples of series 1, 2 and 3, respectively. On the basis of the Gaussian functions the spectra have been deconvoluted into two peaks at about 530 eV and 532 eV. The fraction of the atoms having the same binding energy should be deduced from the ratio of the peak area to the whole spectrum area. However, we assume here that the intensity of the peak corresponds to the fraction because of less accurate deconvolution. It can be seen from Fig. 5 that the intensity ratio of the low binding energy peak to the high binding energy peak decreases with decreasing the value of y, i.e., basicity of (mol%CaO)/(mol%SiO₂). When CaF₂ is added as substitution for CaO, as shown in Fig. 6, the intensity ratio of the low binding energy peak to the high binding energy peak decreases with an increase in the value of x, i.e. CaF₂ concentration. On the other hand, when CaF₂ is added to the glasses with a constant value of (mol%CaO)/(mol%SiO₂), it is found from Fig. 7 that the intensity ratio of two peaks is almost identical irrespective of the value of x, i.e. CaF₂ concentration.
Figure 8 shows the O1s spectra for the samples of series 5. Only one asymmetry peak appeared probably because there are various chemical states of oxygen in the silicate glasses containing iron ions.

Figure 9 shows a typical Mössbauer spectrum of CaO–SiO2–CaF2–FeO\(_x\) glass samples. On the basis of Lorentzian function this spectrum has been deconvoluted into three symmetrical quadrupole doublets due to Fe\(^{2+}\) ions in octahedral symmetry and Fe\(^{3+}\) ions in octahedral and tetrahedral symmetries.\(^{16}\) The spectra for all samples of series 4, 5 and 6 have been deconvoluted. Table 3 summarizes the percentages of Fe\(^{2+}\) ions in octahedral symmetry and Fe\(^{3+}\) ions in octahedral and tetrahedral symmetries and values of isomer shift and quadrupole splitting.

4. Discussion

4.1. Chemical State of Fluorine for the CaO–SiO2–CaF2 and CaO–SiO2–CaF2–FeO\(_x\) Glasses

Table 2 indicates that the binding energies at peak posi-
tion of the F1s XPS spectra range from 683.4 to 684.9 eV. The binding energies are close to that of CaF₂ crystal (684.3 eV \textsuperscript{13}) 685.1 eV \textsuperscript{20}) rather than that of F-containing VAD SiO₂ glass (687.1 eV).\textsuperscript{20}) Consequently, it can be concluded that the fluorine is dominantly coordinated with Ca²⁺ in the present composition ranges of the CaO–SiO₂–CaF₂ and CaO–SiO₂–CaF₂–FeOₓ glasses.

### 4.2. Effect of CaF₂ Addition on the Degree of Polymerization of Silicate Network for the CaO–SiO₂–CaF₂ Glasses

The O1s XPS spectra for all samples shown in Figs. 5–7 are composed of two distinctive peaks. The low and high binding energy peaks are attributed to non-bridging oxygens (NBO) and bridging oxygens (BO), respectively.\textsuperscript{22}) Table 4 summarizes the fraction, the binding energies at peak position (BE) and the full widths at half maximum intensity (FWHM) of BO and NBO. Figure 5 gives the acceptable result that the fraction of non-bridging oxygens to the total oxygens decreases with a decrease in basicity of (mol%CaO)/(mol%SiO₂) when the CaF₂ concentration is constant. Fig. 6 indicates that an increase in the value of x leads to a decrease in the fraction of non-bridging oxygens to the total oxygens for the samples of series 2. Thus, the substitution of CaF₂ for CaO causes polymerization of the silicate network. It can be seen from Fig. 7, on the other hand, that the fraction of non-bridging oxygens to the total oxygens is constant regardless of the value of x for the samples of series 3. This result corresponds to the fact that CaF₂ addition to the samples with a given basicity (mol%CaO)/(mol%SiO₂)=1 does not affect the network polymerization. Based on the above results, it can be concluded that CaF₂ addition does not depolymerize the silicate network effectively in the composition ranges of the present study. This supports the conclusion derived from the F1s XPS spectra that the fluorine predominantly bonds with Ca rather than Si and does not break the Si–O–Si bonds.

### 4.3. Effect of CaF₂ Addition on the Oxidation States of Iron Ions for the CaO–SiO₂–CaF₂–FeOₓ Glasses

Figure 10 shows the ratio of the number of Fe²⁺ ions to that of Fe³⁺ ions (Fe²⁺/Fe³⁺) as a function of the value of (mol%CaO)/(mol%SiO₂) for the samples of series 4, 5 and 6. The values of (mol%CaO)/(mol%SiO₂) were obtained from the analyzed chemical compositions shown in Table 1. The value of Fe²⁺/Fe³⁺ decreases with increasing value of (mol%CaO)/(mol%SiO₂) and that the relations between the values of Fe²⁺/Fe³⁺ and (mol%CaO)/(mol%SiO₂) are identical irrespective of CaF₂ concentration in glasses. Mysen et al.\textsuperscript{23}) have proposed the following redox equilibrium model of iron ions involving the anionic structural units.

\[
4\text{SiO}_2 + 4\text{FeO}^2_2 + 4\text{Fe}^{2+} = 4\text{SiO}_3^{2-} + 4\text{Fe}^{3+} + 4\text{O}_2 \quad \ldots \ldots (1)
\]

with the equilibrium constant

\[
K = \frac{[\text{Fe}^{2+}][\text{SiO}^2_3]}{[\text{Fe}^{3+}][\text{SiO}_2]^{4}}f_{\text{O}_2} \quad \ldots \ldots (2)
\]

where the ratios of the number of non-bridging oxygens to that of silicon atoms for SiO₂, SiO₃⁻, SiO₂⁻ and SiO₄⁻ are 0, 1, 2, 3 and 4, respectively. FeO₂⁻ indicates a tetrahedrally coordinated Fe³⁺ ion and f_{O₂} is oxygen fugacity. This equation expresses that depolymerization of silicate network

---

**Figure 9.** A typical Mössbauer spectrum of CaO–SiO₂–CaF₂–FeOₓ glass samples.

**Table 3.** Mössbauer parameters for the samples of series 4, 5 and 6. P, IS and QS represent the mole percentage (%), the isomer shift (mm/s) and the quadrupole splitting (mm/s), respectively.

<table>
<thead>
<tr>
<th>Series</th>
<th>x</th>
<th>Fe²⁺(Oh) P</th>
<th>IS</th>
<th>QS</th>
<th>Fe²⁺(Oh) P</th>
<th>IS</th>
<th>QS</th>
<th>Fe²⁺(Td) P</th>
<th>IS</th>
<th>QS</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.6</td>
<td>22</td>
<td>1.05</td>
<td>1.98</td>
<td>37</td>
<td>0.32</td>
<td>0.90</td>
<td>41</td>
<td>0.31</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>23</td>
<td>1.06</td>
<td>1.99</td>
<td>40</td>
<td>0.33</td>
<td>0.90</td>
<td>37</td>
<td>0.31</td>
<td>1.44</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>17</td>
<td>1.05</td>
<td>1.97</td>
<td>41</td>
<td>0.32</td>
<td>0.90</td>
<td>42</td>
<td>0.31</td>
<td>1.42</td>
</tr>
<tr>
<td>7</td>
<td>0.9</td>
<td>16</td>
<td>1.04</td>
<td>1.99</td>
<td>42</td>
<td>0.32</td>
<td>0.90</td>
<td>42</td>
<td>0.31</td>
<td>1.45</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>10</td>
<td>1.05</td>
<td>2.00</td>
<td>43</td>
<td>0.32</td>
<td>0.90</td>
<td>47</td>
<td>0.30</td>
<td>1.45</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>10</td>
<td>1.05</td>
<td>2.00</td>
<td>43</td>
<td>0.32</td>
<td>0.90</td>
<td>47</td>
<td>0.30</td>
<td>1.45</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>16</td>
<td>1.03</td>
<td>2.00</td>
<td>45</td>
<td>0.32</td>
<td>0.92</td>
<td>39</td>
<td>0.31</td>
<td>1.45</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>17</td>
<td>1.07</td>
<td>2.03</td>
<td>44</td>
<td>0.33</td>
<td>0.90</td>
<td>39</td>
<td>0.32</td>
<td>1.44</td>
</tr>
<tr>
<td>12</td>
<td>15</td>
<td>25</td>
<td>1.06</td>
<td>2.00</td>
<td>45</td>
<td>0.33</td>
<td>0.90</td>
<td>30</td>
<td>0.32</td>
<td>1.44</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>22</td>
<td>1.05</td>
<td>2.08</td>
<td>33</td>
<td>0.33</td>
<td>0.81</td>
<td>45</td>
<td>0.32</td>
<td>1.36</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>10</td>
<td>1.05</td>
<td>2.00</td>
<td>43</td>
<td>0.32</td>
<td>0.90</td>
<td>47</td>
<td>0.30</td>
<td>1.45</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>8</td>
<td>1.05</td>
<td>1.96</td>
<td>45</td>
<td>0.31</td>
<td>0.91</td>
<td>47</td>
<td>0.30</td>
<td>1.46</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>12</td>
<td>1.05</td>
<td>2.02</td>
<td>36</td>
<td>0.33</td>
<td>0.84</td>
<td>52</td>
<td>0.31</td>
<td>1.39</td>
</tr>
<tr>
<td>17</td>
<td>15</td>
<td>14</td>
<td>1.05</td>
<td>2.00</td>
<td>42</td>
<td>0.32</td>
<td>0.90</td>
<td>44</td>
<td>0.30</td>
<td>1.44</td>
</tr>
<tr>
<td>18</td>
<td>20</td>
<td>12</td>
<td>1.08</td>
<td>1.89</td>
<td>51</td>
<td>0.33</td>
<td>0.86</td>
<td>37</td>
<td>0.32</td>
<td>1.41</td>
</tr>
</tbody>
</table>
correspond to a decrease in the ratio of the number of Fe\(^{2+}\) ions to that of tetrahedrally coordinated Fe\(^{3+}\) ions at a constant oxygen fugacity. In this study the ratio of the number of tetrahedrally coordinated Fe\(^{3+}\) ions to that of octahedrally coordinated Fe\(^{3+}\) ions is around unity for all samples as shown in Table 3. Thus, the value of Fe\(^{2+}\)/Fe\(^{3+}\) can be used as an indicator for the degree of polymerization of silicate network based on the above equation. Consequently, the identical relation between the values of Fe\(^{2+}\)/Fe\(^{3+}\) and \((\text{mol}\%\text{CaO})/(\text{mol}\%\text{SiO}_2)\) irrespective of CaF\(_2\) concentration presents that the degree of polymerization is not affected by CaF\(_2\) addition, which is consistent with the chemical state of fluorine obtained by F1s XPS spectra.

### 4.4. Mechanism for Lowering the Viscosities of Slags by CaF\(_2\) Addition

It is well known that addition of CaF\(_2\) lowers the viscosity of slags considerably\(^{2,4}\) and several structural models have been presented to explain the effect of CaF\(_2\)\(^{2,5,24}\) Baak and Olander\(^{31}\) and Bills\(^{2}\) reported the following structural models: In a pure silicate glasses the divalent calcium ions bind together the silicate anions by electrostatic forces.

When CaF\(_2\) is added, as shown in Fig. 11, the electrostatic bindings are broken because CaF\(^{+}\) ion pairs are added to the silicate anions. Since this reduces the resistance of flow due to the electrostatic bindings between the silicate anions through the divalent calcium ions, the viscosity is lowered. Our conclusion that fluorine is dominantly coordinated with calcium in the slag compositions of this study supports the hypothetical effect of CaF\(_2\) proposed by Baak and Olander\(^{31}\) and Bills\(^{2}\).

### 5. Conclusions

The chemical state of fluorine and the effect of fluorine addition on the degree of polymerization of silicate network have been investigated for \(95[\text{y}/(1+\text{y})]\text{CaO}-(1/1+\text{y})\text{SiO}_2-5\text{CaF}_2\) \((\text{y}=0.6, 0.7, 0.8, 0.9, 1.0)\), \((50-x)\text{CaO}-50\text{SiO}_2-x\text{CaF}_2\) \((x=0, 5, 10, 15)\), \((50-x/2)\text{CaO}-(50-x/2)\text{SiO}_2-x\text{CaF}_2\) \((x=0, 5, 10, 15, 20)\), \(90[\text{y}/(1+\text{y})]\text{CaO}-(1/1+\text{y})\text{SiO}_2-10\text{Fe}_2\text{O}_3\) \((\text{y}=0.6, 0.7, 0.8, 0.9, 1.0)\), \((45-x)\text{CaO}-45\text{SiO}_2-x\text{CaF}_2-10\text{Fe}_2\text{O}_3\) \((x=0, 5, 10, 15, 20)\) and \((45-x/2)\text{CaO}-(45-x/2)\text{SiO}_2-x\text{CaF}_2-10\text{Fe}_2\text{O}_3\) \((x=0, 5, 10, 15, 20)\) using the X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy. The obtained results are summarized as follows.

1. The fluorine is dominantly coordinated with calcium rather than silicon.
2. CaF\(_2\) addition to the samples having a constant value of \((\text{mol}\%\text{CaO})/(\text{mol}\%\text{SiO}_2)\) does not change the degree of polymerization.
3. An identical linear relation has been obtained between the values of Fe\(^{2+}/\text{Fe}^{3+}\) and \((\text{mol}\%\text{CaO})/(\text{mol}\%\text{SiO}_2)\) regardless of CaF\(_2\) concentration for the CaO–SiO\(_2–\text{CaF}_2–\text{FeO}_x\) glasses.
4. The above conclusions support the following hypothetical effect of CaF\(_2\) on the viscosities: CaF\(_2\) addition breaks the electrostatic bindings between the silicate anions through the divalent calcium ions because CaF\(^{+}\) ion pairs are added to the silicate anions. Since this reduces the resistance of flow, the viscosity is lowered.

### REFERENCES

20) B. Vincent Crist: SpecMaster XPS Database, XPS International.