Evaluating Composition Dependence in Surface Tension of Si–Ca–Na–O–F Reciprocal Oxide–fluoride Melts

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Surface tension of molten ionic mixtures such as slag is an important physical property related directly to various surface or interfacial phenomena in high-temperature industrial processes. In particular, surface tension of oxide–fluoride melts is of interest to understand interfacial phenomena in continuous casting in steelmaking. However, the composition dependence of surface tension in reciprocal ionic melts has not been well understood because of its complexity related to the reciprocal reaction between input components in the melt. In this study, we measured the surface tension of reciprocal oxide–fluoride melts in a Si–Ca–Na–O–F multicomponent system, to evaluate its composition dependence. We used a maximum bubble pressure method to determine the surface tension of these melts with high accuracy. Our results indicate that (1) the surface tension of the SiO2–CaO melt decreases by NaF addition more steeply than by Na2O addition, and (2) the surface tension of the SiO2–CaO–CaF2 melt decreases with Na2O addition but depends on NaF formation because of the reciprocal reaction CaF2 + Na2O = CaO + 2 NaF. When this reaction is taken into account, the surface tension of the SiO2–CaO–CaF2–Na2O melt matches that of the SiO2–CaO–NaF melt with increased CaO concentration from the above melt composition.

KEY WORDS: surface tension; reciprocal ionic mixture; oxide–fluoride slag; composition dependence; maximum bubble pressure method.

1. Introduction

Knowledge of the surface tension of ionic melts such as molten slag is of importance to understand various surface or interfacial phenomena in high-temperature processes. Molten oxide slag that contains some fluoride is used as mold flux in continuous casting in steelmaking. In the casting process, this mold flux acts as a lubricant, which penetrates between the molten steel and the mold, helps the molten steel flow smoothly, shields molten steel from air, aids with heat-retention of molten steel during its moderate solidification, and so forth.1,2) The entrapment of molten slag into steel may be related to the interfacial tension between the molten steel and slag, and thus the surface tension of molten oxide–fluoride slag is key to understanding the interfacial phenomenon.3)

One of the authors investigated the surface tension of ionic mixtures by modifying Butler’s equation, which was applied successfully to predict composition dependence in the surface tension of molten alloy, but could not be applied directly for ionic mixtures.4–7) Recently, Tanaka et al. derived a semi-empirical model to estimate the surface tension of molten ionic mixtures by taking into account the ionic radii ratios of cations and anions,8) and this model was applied successfully to binary common alkali–halide systems and molten oxide slags.8–11) However, uncertainties still exist regarding the surface tension of reciprocal ionic mixtures such as oxide–fluoride melts, in particular its composition dependence.

We have measured the surface tension of reciprocal oxide–fluoride melts in a Si–Ca–Na–O–F system, to evaluate its composition dependence. SiO2, CaO, Na2O, CaF2, and NaF are considered fundamental initial components in this system; however, each component is distributed in the melt as the corresponding cation or anion. For Na2O addition to a SiO2–CaO–CaF2 melt, the following reciprocal reaction may be considered:12)

$$\text{CaF}_2 (\text{liq.}) + \text{Na}_2\text{O} (\text{liq.}) = \text{CaO} (\text{liq.}) + 2 \text{NaF} (\text{liq.})$$

$$\Delta G_{\text{f,723K}}^\circ = -91275 [\text{J/mol}]$$

Using FactSage thermodynamic computation software and the latest thermodynamic databases,13) the standard Gibbs energy change of the above reaction was found to be negative. Since pure NaF melt shows a very low surface tension compared with other molten pure components,9,10,14,15) NaF formation according to the reciprocal reaction (1) may affect the composition dependence of the surface tension of the Si–Ca–Na–O–F melt.

Among several methods used to measure the surface tension of high-temperature liquids, the maximum bubble
Pressure method is recognized as one of the most reliable to evaluate precise surface tension values of molten salt and oxide mixtures. In the maximum bubble pressure method, a capillary tube is immersed in the liquid sample and a bubble is formed on the edge of the capillary tube. The liquid surface tension is determined from the maximum pressure values where the bubble is removed from the capillary tube. When good wettability is achieved between the capillary tube and the liquid sample, the bubble is formed along the inner diameter of the capillary tube, which is related to precise surface tension measurements with low degree of scattering. However, for further lower degrees of scattering on the determined surface tension value, outer atmospheric pressure control is required so that the maximum bubble pressure can be kept almost constant.

In this study, we evaluated the composition dependence of the surface tension of molten Si–Ca–Na–O–F slag at constant temperature using the maximum bubble pressure method. A more accurate surface tension value was achieved by minimizing fluctuations in the outer furnace atmospheric pressure. The effect of NaF addition to decrease the surface tension of the SiO2–CaO melt was investigated, and the result compared with that decreased by Na2O addition. We examined the effect of Na2O addition on surface tension of the SiO2–CaO–CaF2 melt with various CaF2 concentrations. Unique composition dependences in the surface tension of SiO2–CaO–CaF2–Na2O melts are discussed based on the reciprocal reaction (1) related to NaF formation as a reciprocal component in the melt.

2. Experimental

2.1. Surface Tension Measurement by Maximum Bubble Pressure Method

The methodology to measure the surface tension of a liquid by the maximum bubble pressure method is described in this section. Figure 1 shows a schematic diagram of the experimental apparatus (electric furnace was fabricated by Mizugami Electric Works, Osaka, Japan), and bubble formation at the edge of the capillary tube immersed in liquid. When a bubble is formed at the edge of the capillary tube by static gas flow, the following relationship is obtained between bubble pressure \( P \), liquid surface tension \( \sigma \), and density \( \rho \):

\[
P - P_0 = \frac{2\sigma}{r} + \rho_L g (h + x)
\]

where \( P_0 \) is the outside pressure around the liquid, \( r \) is the curvature radius of the bubble, \( \rho_L \) is the gas density, \( g \) is the gravitational acceleration, \( h \) is the immersed depth of the capillary tube, and \( x \) is the vertical diameter of the bubble made in the liquid. If good wettability is achieved between the liquid and the capillary tube, a maximum bubble pressure \( (P_{\text{max}}) \) is obtained since the curvature radius of the bubble is equivalent to the inner diameter of the capillary tube \( (R) \). Then, the gas density \( \rho_G \) is generally so small that it is negligible compared with the liquid density \( \rho_L \). When the vertical size of the bubble \( x \) is adequately small compared with the immersed depth of the capillary tube \( h \), Eq. (3) is derived from Eq. (2):

\[
\Delta P_{\text{max}} = P_{\text{max}} - P_0 = \frac{2\sigma}{R} + \rho_L gh
\]

Equation (3) indicates that a linear relationship is obtained between \( \Delta P_{\text{max}} \) and the immersed depth of the capillary tube \( h \), and that the liquid surface tension is determined from the intercept of the linear relationship. To adjust the effect of bubble shape on surface tension determination, the following equation, including the Schroedinger coefficient \( K \), is used:

![Fig. 1. Schematic diagrams of (a) experimental apparatus for surface tension measurements, (b) bubble formation at the edge of capillary tube in a liquid.](image-url)
The actual immersed depth of the capillary tube is different from the operational depth because of liquid surface movement caused by immersing the capillary tube. We used the following equation to determine the actual immersed depth of the capillary tube:

\[ h = h_0 \left(1 + \frac{d^2}{D^2 - d^2} \right) \] ........................... (5)

where \( D \) is the inner diameter of the liquid container, \( d \) is the outer diameter of the capillary tube, and \( h_0 \) is the operational depth of the capillary tube.

In this study, a liquid container (25 cm\(^3\), outer diameter 30–32 mm, height 38 mm, thickness 1 mm) and capillary tube (outer diameter 2.0 mm, inner diameter 1.5 mm, height 70 mm) made of Pt–10% Rh were used as the contacting material with the liquid sample, because platinum has a good wettability with liquid oxide and fluoride slag. The outer and inner edges of the capillary tube were polished carefully with waterproof abrasive paper of different roughness, so that stable bubble formation was achieved along the inner diameter of the capillary tube. The outer and inner diameters of the capillary tube were measured using a horizontal optical microscope with ±1.0% uncertainty. At high temperature, the following thermal expansion coefficient of platinum \(^{17}\) was taken into account to determine the actual diameters of the capillary tube and the liquid container:

\[
\frac{\Delta L}{L} = 9.12 \times 10^{-6} (T - 293) + 7.467 \times 10^{-10} (T - 293)^2 + 4.258 \times 10^{-15} (T - 293)^3
\] ........................... (6)

Table 1 summarizes the chemical compositions of the slag samples investigated in this study. Twenty-three different slag compositions were prepared. A1 and B1 were selected to compare the composition dependences of the surface tension of the SiO\(_2\)–CaO slag (CaO/SiO\(_2\) mass ratio = 1.0) with Na\(_2\)O or NaF addition. A1, A2, and A3 were selected to investigate the composition dependence of the surface tension of the SiO\(_2\)–CaO–CaF\(_2\) slag with Na\(_2\)O addition under fixed mass ratios of SiO\(_2\):CaO:CaF\(_2\). Here, reciprocal reaction (1) was taken into account to consider the effect of NaF formation on surface tension. If one assumes that the reciprocal reaction (1) progresses fully to the right, the added Na\(_2\)O changes into NaF and the apparent CaO concentration increases. A2–4 and A3–4 were regarded as critical compositions where all CaF\(_2\) species in the slag react with added Na\(_2\)O to form NaF. The slag compositions of B2 and B3 were proposed to verify the agreement.

<table>
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<th>Category</th>
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<th>Initial composition (mass%)</th>
<th>Ionic concentration (mol%)</th>
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<td></td>
<td>SiO(_2)</td>
<td>CaO</td>
</tr>
<tr>
<td>A1</td>
<td>A1-1</td>
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<td></td>
<td>B3-3</td>
<td>31.8</td>
<td>43.2</td>
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between the surface tension of the SiO$_2$–CaO–CaF$_2$–Na$_2$O slag and that of the SiO$_2$–CaO–NaF slag with a mass ratio CaO/SiO$_2$ increase from 1.0. The mass ratios CaO/SiO$_2$ of B2 and B3 compositions correspond to those of A2–4 and A3–4, respectively.

The oxide–fluoride slag samples were prepared from silicon dioxide, calcium carbonate, sodium carbonate, calcium fluoride, and sodium fluoride (special grade purity, Wako Chemicals Co., Ltd.). CaCO$_3$ powder calcination was conducted at 1 223 K for 12 h in air to produce CaO powder. SiO$_2$, CaO, and Na$_2$CO$_3$ powders were mixed in a mortar, and the mixture was pre-melted at 1 873 K for 3 h in air and quenched to form SiO$_2$–CaO or SiO$_2$–CaO–Na$_2$O mother slag. The mother slag was crushed to powder, mixed with NaF or CaF$_2$, and pre-melted at 1 673 K for 1 h in dehydrated Ar (99.999% in purity) to achieve the desired slag compositions. We added these fluorides in the latter step to minimize the fluoride loss in slag caused by their volatilizing behavior.$^{18}$

To begin the surface tension measurement, 30 g pre-melted slag sample was inserted into a Pt–Rh crucible and set in the center position in the furnace tube (Fig. 1(a)), which was located in the soaking area at the investigated temperature (1 723 K) with ±2 K deviation. The furnace atmosphere was filled with purified Ar gas (dehydrated by silica gel and magnesium perchlorate, then deoxidized by flowing the gas into the preliminary furnace with magnesium tips at 823 K) to prevent possible reaction between water vapor and fluorides in slag to form HF gas. The furnace temperature was increased to 1 723 K and held for 1 h. Surface tension measurements were conducted as follows: a capillary tube that was suspended on the liquid sample was moved down slowly, and a change in pressure in the capillary tube was detected when the edge of the capillary tube touched the liquid surface. At 2, 4, 6, 8, and 10 mm immersed depths in the capillary tube, dehydrated Ar gas flowed in the capillary tube to form a bubble, and its maximum pressure was measured until it broke. A cathetometer with 0.01 mm accuracy was used to measure the immersed depth of the capillary tube. The Ar gas flow rate was adjusted manually (0.1–0.2 ml/min) so that every bubble was broken in approximately one minute intervals. It is generally believed that the gas flow rate should be set as low as possible to satisfy the relationship between bubble pressure and sum of surface tension and ascending force. Our preliminary studies conclude that the above gas flow rate was sufficient to achieve the relationship shown in Eq. (3) and to determine the surface tension of silicate slags. The pressure difference between the capillary tube and outer space was detected electrically by a differential pressure transmitter produced by the Yokogawa Electric Corp., and this electrical signal was transferred to the ADCMT 7351E digital multimeter at 0.1 s intervals. The relationship between inner capillary tube pressure and the electrical voltage detected in the differential pressure transmitter was calibrated by the following equation, which was predetermined using a distilled manometer filled with purified water at room temperature:

$$\Delta P / \text{Pa} = 593.7 \cdot V / V - 375.91$$ (7)

In addition, the outer pressure in the furnace tube, $P_0$ in Eq. (2), was obtained by measuring the pressure in the capillary tube in the furnace before immersion in liquid. This outer pressure should be stable during the maximum bubble pressure measurement, although it may fluctuate because of gas stagnation in the furnace tube. Therefore, it is necessary to prepare sufficient space for stabilized gas flow. We prepared sufficient space between the sample stage and inner edge of the furnace tube and an enlarged gas outlet as shown in Fig. 1(a). As a result, outer pressure fluctuations were minimized. The effect of outer pressure fluctuations on surface tension accuracy is discussed in Section 2.2.

The above maximum bubble pressure measurement was repeated several times at each immersed capillary tube depth, to verify its reproducibility with possible uncertainties. Finally, the surface tension of the liquid slag sample was determined from the linear relationship obtained experimentally between maximum bubble pressure and immersed capillary tube depth, according to Eqs. (3) and (4).

### 2.2. Source of Experimental Uncertainty

Major sources of experimental uncertainties in the surface tension measurement are the determination of (i) outer furnace pressure, (ii) maximum bubble pressure, (iii) inner capillary tube diameter, and (iv) immersed capillary tube depth. According to Eq. (3), these factors are indicated as $P_0$, $P_{\text{max}}$, $R$, and $h$, respectively, and deviations in these factors affect the accuracy in surface tension determination directly. Contributions of the above factors to total experimental uncertainty are summarized in Table 2, which demonstrates that each measurement had degrees of uncertainties in the above factors as indicated in the middle column, and the effects of these uncertainties on the accuracy in surface tension value were calculated individually, as indicated in the last column. Outer pressure and maximum bubble pressure measurements had higher comparative uncertainties, because the dynamic volatilizing behavior of fluorides from molten slag may partially affect these uncertainties. In this study, the total uncertainty in the determination of surface tension was evaluated to be less than 4%, and it was adequately small when the composition dependence in slag surface tension was discussed.

Although a change in slag composition because of fluoride vaporization may also affect the surface tension as occurs for its composition dependence, it could be compensated by analyzing the chemical composition of the slag sample after measurement, as discussed below.

### Table 2. Experimental uncertainties in determination of surface tension.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Uncertainty in determination</th>
<th>Uncertainty in surface tension</th>
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<tbody>
<tr>
<td>Outer pressure</td>
<td>$&lt; \pm 8 \text{ Pa}$</td>
<td>$\pm 1.2%$</td>
</tr>
<tr>
<td>Maximum bubble pressure</td>
<td>$&lt; \pm 12 \text{ Pa}$</td>
<td>$\pm 1.7%$</td>
</tr>
<tr>
<td>Inner capillary tube diameter</td>
<td>$&lt; \pm 0.015 \text{ mm}$</td>
<td>$\pm 1.0%$</td>
</tr>
<tr>
<td>Immersed capillary tube depth</td>
<td>$&lt; \pm 0.01 \text{ mm}$</td>
<td>$\pm 0.1%$</td>
</tr>
<tr>
<td>Total error</td>
<td>$&lt; \pm 4.0%$</td>
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</table>
2.3. Slag Composition Analysis

In addition to the slag surface tension values, slag compositions should be analyzed to evaluate accurately the composition dependence in slag surface tension. We detected the chemical compositions of the slag sample after surface tension measurement with X-ray fluorescence analysis. Several glass beads were prepared from the Li$_2$B$_4$O$_7$ solvent and predetermined amounts of SiO$_2$, CaF$_2$, and NaF powders, and melted at 1 223 K in air as standard specimens. Slag samples were also diluted using Li$_2$B$_4$O$_7$ solvent to satisfy the 10 mass% total amount of glass bead. Si, Ca, Na, and F concentrations in the prepared glass beads were measured by a Rigaku Supermini200 X-ray fluorescence analyzer with ±1% uncertainty. In relation to fluoride vaporization from the glass bead melts, BF$_3$, NaF and SiF$_4$ were specified as major fluoride gas species. The calculated result of phase equilibrium by the FactSage computation program and the latest thermodynamic databases of oxide and fluorides$^{13}$ indicated that BF$_3$ vapor pressure would have been in the order of 10$^{-3}$ atm, and NaF and SiF$_4$ vapor pressures would have been in the order of 10$^{-5}$ atm respectively, in the experimental condition to prepare the glass bead melts. Taking account of the inner volume of the furnace used for melting (W120 × D180 × H1110 mm), the fluoride loss in dissolving the slag sample into the Li$_2$B$_4$O$_7$ solvent at 1 223 K was estimated less than 5 % in maximum in total fluoride amounts. Therefore, based on the above thermodynamic calculation, this fluoride loss may have slightly affected F content determination in the slag sample.

3. Results and Discussions

3.1. Surface Tension and Composition Analysis Results

Table 3 shows results from the surface tension measurement of Si–Ca–Na–O–F slag at 1 723 K, and these composition analyses. The slag surface tension was evaluated by the maximum bubble pressure method with ±1–4% uncertainty. Several measurements were conducted for identical slag samples, and we confirmed that these surface tension values were reproduced within the above uncertainties.

The measured results indicate that the slag surface tension decreases as fluoride concentration increases, because pure CaF$_2$ and NaF melts exhibit a lower surface tensions compared with other pure components in the molten state.$^{11}$ Analytical results of the slag compositions reveal that the detected Na and F concentrations were lower than designed (Table 1), which probably indicates fluoride vaporization as NaF molecules from the molten slag.

3.2. Composition Dependence in Surface Tension of Si–Ca–Na–O–F Slag

The surface tension of the Si–Ca–Na–O–F slag is exhibited as a function of Na$^+$ molar fraction in total amount of cations in the melt (Si$^{4+}$ + Ca$^{2+}$ + Na$^+$) calculated from the analytical data shown in Table 3, to discuss its composition dependence when Na$_2$O or NaF is added in the molten slag.

3.2.1. Effect of Na$_2$O or NaF Addition on Surface Tension of SiO$_2$–CaO Slag

Figure 2 shows the measured surface tension of A1 and B1 slag as a function of Na$^+$ molar fraction in total amount of cations in the melt at 1 723 K, and indicates the effect of Na$_2$O or NaF addition on SiO$_2$–CaO slag surface tension (CaO/SiO$_2$ mass ratio was fixed as unity). Na$_2$O and NaF additions decrease the surface tension of the SiO$_2$–CaO slag. Furthermore, the SiO$_2$–CaO–Na$_2$O slag (B1) shows a lower surface tension than the SiO$_2$–CaO–Na$_2$O slag (A1) at identical Na$^+$ concentrations. This tendency may be related to the fact that pure NaF melt has a lower surface tension than pure Na$_2$O melt at 1 723 K.$^{14,15}$ Interestingly, a small NaF addition decreases the slag surface tension significantly, however, this decreasing tendency becomes moderate with increase in NaF concentration. This may be because the Na$^+$–F$^−$ bond willingly occupies the surface area of the molten slag to decrease the slag surface tension steeply, but the Na$^+$–F$^−$ bond fraction is saturated when the NaF concentration increases in the bulk slag.

3.2.2. Effect of Reciprocal Reaction on Surface Tension of SiO$_2$–CaO–CaF$_2$–Na$_2$O Slag

Figure 3 shows the surface tension of A1, A2, and A3 slag as a function of Na$^+$ molar fraction in total amount of cations in the melt at 1 723 K, and indicates the effect of Na$_2$O addition on the surface tension of SiO$_2$–CaO–CaF$_2$ slag where the CaO/SiO$_2$ mass ratio was set as 1.0, and the
CaF$_2$ concentration was varied between 0 and 20 mass%. When CaF$_2$ is not included in the slag, the surface tension decreases by Na$_2$O addition almost linearly and approaches that of pure Na$_2$O melt. The surface tension of the SiO$_2$–CaO–CaF$_2$ slag decreases more steeply with Na$_2$O addition than that of the SiO$_2$–CaO slag. Such uniquely decreasing behavior of surface tension becomes clear when the CaF$_2$ concentration in the slag is high. This behavior may be related to the reciprocal reaction expressed by Eq. (1) in the melt; when this reaction is taken into account, the apparent CaO/SiO$_2$ mass ratio increases from unity and NaF is formed in the melt. Therefore, the surface tension of the Si–Ca–Na–O–F slag may depend on NaF formation.

Figures 4 and 5 compare the surface tension of A2 and B2 slag, and that between A3 and B3 slag, respectively. The CaO/SiO$_2$ mass ratios of B2 and B3 slag each correspond to those of A2-4 and A3-4, respectively, where the reciprocal reaction (1) proceeds completely to the right. The result in Fig. 4 demonstrates that the surface tension of B2 slag (SiO$_2$–CaO–NaF system, CaO/SiO$_2$ mass ratio = 1.0) reproduces the surface tension value of A2-4 slag (SiO$_2$–CaO–10 mass% CaF$_2$–Na$_2$O system, CaO/SiO$_2$ mass ratio = 1.0). Similarly, Fig. 5 shows good agreement between the surface tension of B3 slag (SiO$_2$–CaO–10 mass% CaF$_2$–Na$_2$O system, CaO/SiO$_2$ mass ratio = 1.16) and A3 slag (SiO$_2$–CaO–20 mass% CaF$_2$–Na$_2$O system, CaO/SiO$_2$ mass ratio = 1.36).
system, CaO/SiO$_2$ mass ratio = 1.36) and that of A3-4 slag (SiO$_2$–CaO–20 mass% CaF$_2$–Na$_2$O system, CaO/SiO$_2$ mass ratio = 1.0). Thus, a series of surface tension measurements suggests that the surface tension of the Si–Ca–Na–O–F slag depends on NaF formation that may occur because of the reciprocal reaction CaF$_2$ (liq.) + Na$_2$O (liq.) = CaO (liq.) + 2 NaF (liq.) in the melt.

3.3. Comparison between Experimental Results and Predicted Surface Tensions

The experimental results of the slag surface tension were compared with the predicted values obtained using the semi-empirical model proposed by Tanaka $et al.$\textsuperscript{8–11}) This model requires ionic radii, molar volume, and surface tension data of pure components to calculate the surface tension of ionic melts including molten slag. In this study, these parameters were collected in the same way as in Ref. 11), where ionic radii data were from Shannon,$^{19}$ molar volume data were from Mills and Keene,$^{20}$ and the recommended surface tension values of pure components were taken from Nakamoto $et al.$\textsuperscript{9,10}) (CaO, Na$_2$O), NIST molten salt databases$^{14}$ (SiO$_2$,CaF$_2$), or Ogino $et al.$\textsuperscript{15}) (NaF).

**Figure 6** compares the experimental and predicted surface tension of SiO$_2$–CaO–NaF slag (B1–B3 in Table 1) and demonstrates that good agreement is achieved when experimental uncertainties are taken into account.

**Figure 7** compares the experimental and predicted surface tension of the SiO$_2$–CaO–CaF$_2$–Na$_2$O slag (A1–A3 in Table 1). When CaF$_2$ is not included in slag, good agreement is observed between the predicted and experimental results (Fig. 7(a)). The experimental surface tensions of the SiO$_2$–CaO–CaF$_2$–Na$_2$O slag exhibit obviously lower values than the predictions when the reciprocal reaction is not considered (Figs. 7(b) and 7(c)). However, the experimental surface tensions are reproduced by the predictions when the reciprocal reaction CaF$_2$ (liq.) + Na$_2$O (liq.) = CaO (liq.) + 2 NaF (liq.) is taken into account (dashed lines in Figs. 7(b) and 7(c)). If one assumes that this reaction proceeds com-
completely to the right, then the surface tension may vary with the generated NaF concentration up to A2-4 or A3-4 slag compositions, because all CaF₂ in the slag is reacted with the added Na₂O to form CaO and NaF at these compositions. When further Na₂O is added into A2 and A3 slag, the surface tension may simply vary with Na₂O concentration.

These agreements indicate that the above reciprocal reaction should be taken into account to reproduce the composition dependence in the surface tension of the Si–Ca–Na–O–F slag accurately. However, all components in the slag are distributed as corresponding cations and anions, and the surface tension (or surface free energy) should be determined from the total Gibbs energy minimization of the system, including the bulk liquid and surface area, in terms of ionic distributions. Therefore, future modeling is required to reproduce the unique composition dependence in the surface tension of the molten reciprocal oxide–fluoride slag.

4. Conclusions

The surface tension of the molten Si–Ca–Na–O–F slag was measured by the maximum bubble pressure method with an experimental uncertainty of ±1–4%. The slag compositions after measurements were examined by X-ray fluorescence analysis. This slag is composed of SiO₂, CaO, Na₂O, CaF₂, and NaF as initial components, although they are distributed as corresponding cations and anions in the melt. The composition dependence of the surface tension was evaluated by taking account of the reciprocal reaction CaF₂ (liq.) + Na₂O (liq.) = CaO (liq.) + 2 NaF (liq.). The following conclusions were obtained:

(1) Na₂O and NaF additions decrease the surface tension of the SiO₂–CaO slag for a fixed CaO/SiO₂ mass ratio. In particular, the SiO₂–CaO–NaF slag has a lower surface tension than the SiO₂–CaO–Na₂O slag in the molten state, at identical Na⁺ fractions for total cation amount.

(2) The surface tension of the SiO₂–CaO–CaF₂ slag (CaO/SiO₂ mass ratio = 1.0) decreases more steeply with Na₂O addition than that of the SiO₂–CaO slag where CaF₂ is not included. When the reciprocal reaction CaF₂ (liq.) + Na₂O (liq.) = CaO (liq.) + 2 NaF (liq.) is taken into account, the apparent CaO/SiO₂ mass ratio increases from 1.0 and the surface tension may depend on NaF formation. We have also measured the surface tension of the SiO₂–CaO–NaF slag (CaO/SiO₂ mass ratio = 1.16 or 1.36), and found that the surface tension of the SiO₂–CaO–CaF₂–Na₂O slag is reproduced by that of the SiO₂–CaO–NaF slag.

(3) These experimental results of the surface tension of SiO₂–CaO–CaF₂–Na₂O slag deviate negatively from its composition dependence from the predictions by Tanaka’s model where the reciprocal reaction CaF₂ (liq.) + NaO (liq.) = CaO (liq.) + 2 NaF (liq.) is not considered, although they agree with those where the above reciprocal reaction is assumed to proceed completely to the right. Therefore, the above reciprocal reaction should be taken into account to reproduce the composition dependence in the surface tension of the Si–Ca–Na–O–F reciprocal oxide–fluoride slag.

REFERENCES