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Evaluation of Surface Tension of Molten Slag in Multi-component Systems

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A thermodynamic model for determining the surface tension of molten ionic mixtures, derived by considering the ionic radii of the components, was extended to multi-component slag systems. The composition dependence of the surface tension in 6-component systems of the type $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ was evaluated with the present model using information based on the surface tension and molar volume of the pure oxide components, and on the anionic and cationic radii. The evaluated results for the surface tension agree well with literature data.

KEY WORDS: surface tension; molten slag; mold flux; ionic radius.

1. Introduction

The surface tension of molten slag is one of the most important parameters for controlling the various interfacial phenomena in the refining or continuous-casting process of steelmaking. However, it is not often possible to find appropriate data on the surface tension of molten slag targeted for specific purposes, because molten slag is usually a multi-component oxide, sulfide, and fluoride system, where the effects of these components on the surface tension is very complicated, and not all the data (particularly over a wide temperature and composition range) have been reported. It is, therefore, indispensable to develop a prediction system for determining the surface tension of multi-component molten slag.

Tanaka *et al.* developed a predicting model[1–3] for determining the surface tension of molten oxide mixtures, thermodynamically-based on Butler's equation[4] and on the procedure proposed by Speiser *et al.*[5] Recently, Tanaka *et al.* modified this model by using the ratio of the cation to anion radius as a model parameter.[6] This improved model is characterized by the simplicity with which it can be extended to multi-component systems, particularly since the calculations are conducted only with respect to information based on the surface tension and molar volume of the pure components, and on the ionic radii of the components in the system. This model has previously been applied to the evaluation of binary silicate melts.[6] At that time, the modified model included certain hypotheses regarding the selection of the surface tensions of molten pure oxides below their melting points (especially in the case of CaO, MgO *etc.* which have high melting points), and on the ratio of the cation to anion radius of SiO_2.

Recently, further improvements were applied to the modified model based on the above hypotheses.[7] First, the temperature dependence of the surface tension was evaluated for pure oxides not only in their liquid region, but also below their melting points. Second, the minimum unit of SiO_2 was considered to be SiO_4^{4-}, and the radii ratio of Si^{4+} to SiO_4^{4-} was experimentally determined to be 0.5. These improvements allowed the modified model to be extended to evaluations for ternary molten slags, which includes not only such oxides as SiO_2, Al_2O_3, CaO, FeO, MgO and MnO, but also surface-active components such as Na_2O, B_2O_3 and CaF_2.[7,8]

In this work, a still further extension of the above modified model was attempted for determining the surface tensions of the more complex 6-component slag systems. The resulting calculated surface tensions were compared with the experimental data obtained from the multi-component system, and the effects of the addition of Al_2O_3, MgO and Na_2O on the surface tension of $CaO–SiO_2–CaF_2$ system were discussed.

2. Model for Estimation of the Surface Tension of Molten Slag

A model derived by the authors for the estimation of the surface tension of ionic mixtures was applied to the 6-component molten slag in the $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ system, which is common to general mold fluxes for continuous casting.

The surface tension σ of the 6-component molten slag is calculated from Eqs. (1)–(6):

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{SiO_2}} + \frac{RT}{A_{\mathrm{SiO_2}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{SiO_2}}}{M^{\mathrm{Bulk}}_{\mathrm{SiO_2}}} \quad \text{..................(1)}$$

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{CaO}} + \frac{RT}{A_{\mathrm{CaO}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{CaO}}}{M^{\mathrm{Bulk}}_{\mathrm{CaO}}} \quad \text{..................(2)}$$

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{Al_2O_3}} + \frac{RT}{A_{\mathrm{CaO}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{Al_2O_3}}}{M^{\mathrm{Bulk}}_{\mathrm{Al_2O_3}}} \quad \text{.................(3)}$$

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{MgO}} + \frac{RT}{A_{\mathrm{MgO}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{MgO}}}{M^{\mathrm{Bulk}}_{\mathrm{MgO}}} \quad \text{.................(4)}$$

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{Na_2O}} + \frac{RT}{A_{\mathrm{Na_2O}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{Na_2O}}}{M^{\mathrm{Bulk}}_{\mathrm{Na_2O}}} \quad \text{.................(5)}$$

$$\sigma = \sigma^{\mathrm{Pure}}_{\mathrm{CaF_2}} + \frac{RT}{A_{\mathrm{CaF_2}}} \ln \frac{M^{\mathrm{Surf}}_{\mathrm{CaF_2}}}{M^{\mathrm{Bulk}}_{\mathrm{CaF_2}}} \quad \text{.................(6)}$$

where

$$M_i^{\mathrm{P}} = \left(\frac{R_{\mathrm{A}}}{R_{\mathrm{X}}} \cdot N_i^{\mathrm{P}}\right) \Bigg/ \left(\frac{R_{\mathrm{Si^{4+}}}}{R_{\mathrm{SiO_4^{4-}}}} \cdot N^{\mathrm{P}}_{\mathrm{SiO_2}} + \frac{R_{\mathrm{Ca^{2+}}}}{R_{\mathrm{O^{2-}}}} \cdot N^{\mathrm{P}}_{\mathrm{CaO}} + \frac{R_{\mathrm{Al^{3+}}}}{R_{\mathrm{O^{2-}}}} \cdot N^{\mathrm{P}}_{\mathrm{Al_2O_3}} + \frac{R_{\mathrm{Mg^{2+}}}}{R_{\mathrm{O^{2-}}}} \cdot N^{\mathrm{P}}_{\mathrm{MgO}} + \frac{R_{\mathrm{Na^{+}}}}{R_{\mathrm{O^{2-}}}} \cdot N^{\mathrm{P}}_{\mathrm{Na_2O}} + \frac{R_{\mathrm{Ca^{2+}}}}{R_{\mathrm{F^{-}}}} \cdot N^{\mathrm{P}}_{\mathrm{CaF_2}}\right) \quad \text{..................(7)}$$

Subscript i refers to the following components: SiO_2, CaO, Al_2O_3, MgO, Na_2O or CaF_2. Subscripts A and X refer to the cations and anions of component i, respectively. Superscripts "Surf" and "Bulk" indicate the surface and bulk, respectively. R is the gas constant, T is the absolute temperature, σ_i^{Pure} is the surface tension of the pure molten component i, which is treated as a model parameter. $A_i = N_0^{1/3} \cdot V_i^{2/3}$ corresponds to the molar surface area in a monolayer of pure molten component i (N_0: Avogadro's number, V_i: molar volume of the pure molten component i). N_i^{P} is the mole fraction of the component i in phase P (P=Surf or Bulk). R_{A} is the radii of the cation, and R_{X} is the radii of the anion. For example:

$$R_{\mathrm{A}} = R^{4+}_{\mathrm{Si}},\ R^{2+}_{\mathrm{Ca}},\ R^{3+}_{\mathrm{Al}},\ R^{2+}_{\mathrm{Mg}},\ \text{or}\ R_{\mathrm{Na}} \quad \text{..............(8)}$$

$$R_{\mathrm{X}} = R^{4-}_{\mathrm{SiO_4}},\ R^{2-}_{\mathrm{O}}\ \text{or}\ R^{-}_{\mathrm{F}} \quad \text{.........................(9)}$$

where SiO_4^{4-} is considered to be the minimum anionic unit in SiO_2, and the value of $R^{4+}_{\mathrm{Si}}/R^{4-}_{\mathrm{SiO_4}}$ was experimentally determined to be 0.5.[7)]

The above Eqs. (1)–(6) have been derived on the basis of Butler's equation[4)] by considering the following assumptions [1] and [2][6)]:

[1] It has been known that molten ionic mixtures readily undergo surface relaxation due to spontaneous changes in the ionic distance at the surface, which causes the energetic state of the surface to approach that of the bulk state. Thus, the contribution from excess Gibbs energy terms is neglected in Butler's equation.

[2] In ionic substances, it is well known that their ionic structures depend upon the ratio of the cation to anion radii. In order to evaluate the ionic structures and physico-chemical properties of ionic materials, the cation to anion radii ratio should be considered.

Table 1. Radii of the cationic and anionic ions.[9)]

Ion	Radii (Å)
Si^{4+}	0.42
Ca^{2+}	0.99
Al^{3+}	0.51
Mg^{2+}	0.66
Na^{+}	0.97
O^{2-}	1.44
F^{-}	1.33

Table 2. Molar volumes of the pure components.[10)]

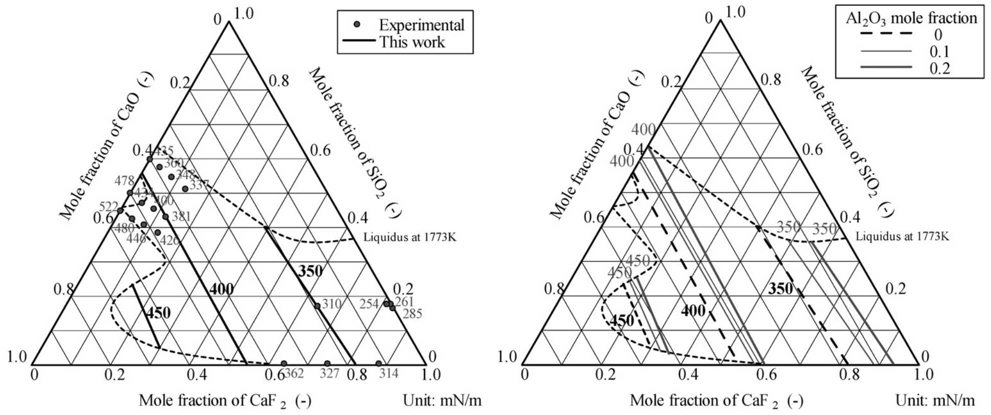
Oxide	Temperature (K) dependence of molar volume (m^3/mol)
SiO_2	$27.516\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$
CaO	$20.7\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$
Al_2O_3	$28.3\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$
MgO	$16.1\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$
Na_2O	$33.0\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$
CaF_2	$31.3\{1+1\cdot10^{-4}\cdot(T-1773)\}\cdot10^{-6}$

Table 3. Temperature dependence of the surface tensions of pure components.

Oxide	Temperature (K) dependence of surface tension (mN/m)
SiO_2	243.2 + 0.031T
CaO	791 - 0.0935T
Al_2O_3	1024 - 0.177T
MgO	1770 - 0.636T
Na_2O	438 - 0.116T
CaF_2	1604.6 - 0.72T

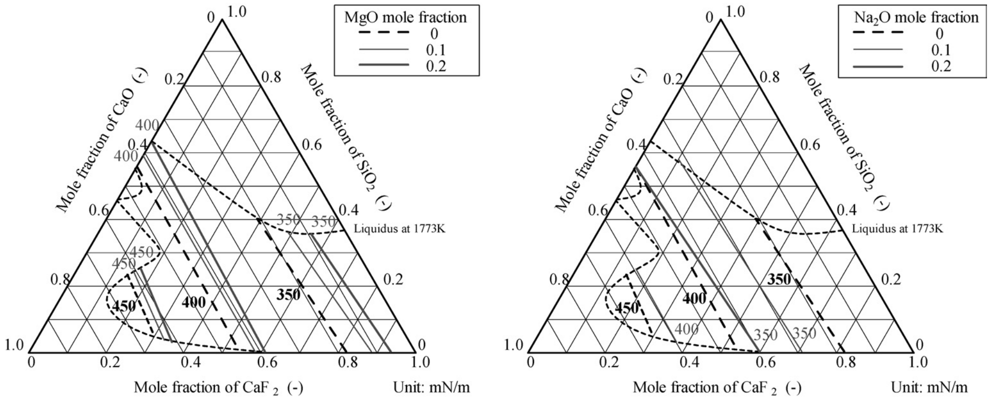
Data on the ionic radii were obtained from Shannon,[9)] and the molar volumes of the pure oxides recommended by Mills and Keene[10)] were used in the present model. These values are listed in **Tables 1** and **2**, respectively.

Regarding the temperature dependences of the surface tensions for pure SiO_2 and CaF_2, those recommended by NIST[11)] were used for the calculations in this study. The temperature dependences of the surface tension for pure CaO, Al_2O_3, MgO and Na_2O were evaluated in previous work[7,8)] and used in the current study. The equations for determining the temperature dependences of surface tension are listed in **Table 3**.



(a) CaO-SiO$_2$-CaF$_2$ system[8)12)]

(b) CaO-SiO$_2$-CaF$_2$-Al$_2$O$_3$ system



(c) CaO-SiO$_2$-CaF$_2$-MgOsystem

(d) CaO-SiO$_2$-CaF$_2$-Na$_2$O system

Fig. 1. Effect of the addition of a fourth component on the surface tension of molten slag of CaO–SiO$_2$–CaF$_2$ at 1 773 K.

3. Results and Discussion

3.1. Quaternary System

The surface tension of molten slag for the CaO–SiO$_2$–CaF$_2$ system was evaluated in the previous work.[8)] Based on these results,[8)] the effects of Al$_2$O$_3$, MgO or Na$_2$O addition on the surface tension of the above ternary system were evaluated in this study. The calculated results for the surface tension are shown in **Fig. 1**. Figure 1(a) is based on the results obtained for the CaO–SiO$_2$–CaF$_2$ system reported by Nakamoto *et al.*[8)] The three lines in this figure indicate the calculated results for the iso-surface tensions 350, 400 or 450 mN/m respectively. The experimental values were quoted from literature results.[12)] Some of the experimental values, which exist near the CaF$_2$ apex in this figure, are lower than the calculated values. Especially, there were such experimental values as lower than 300 mN/m near CaF$_2$. The reason on the low value of the experimental results is not evident, but these values might be evaluated too low under some specific experimental conditions. Except for this point, the calculated results reproduced the experimental values. Figure 1(b) shows the effect of Al$_2$O$_3$ addition on the surface tension of the ternary system shown in Fig. 1(a). Here, Al$_2$O$_3$ was supposed to be added in mole fractions of 0.1 or 0.2 while, the liquidus, which is expected to shift due to Al$_2$O$_3$ addition, was not considered here. With the addition of Al$_2$O$_3$, the three iso-surface tension lines shifted toward the SiO$_2$–CaF$_2$ line, thus the surface tension was found to increase in the whole composition range of the system. Figure 1(c) shows the effect of MgO addition on the surface tension of the CaO–SiO$_2$–CaF$_2$ system. Similar to the case of Al$_2$O$_3$ addition shown in Fig. 1(b), the surface tension increased through the whole composition range of the system. Figure 1(d) shows the effect of Na$_2$O addition on the surface tension of the CaO–SiO$_2$–CaF$_2$ system. Contrary to the cases of Al$_2$O$_3$ and MgO addition, the three iso-surface tension lines shifted toward the CaO apex with Na$_2$O addition. Thus, Na$_2$O is found to cause a decrease in the surface tension through the whole composition range of the system.

The effect of the addition of Al$_2$O$_3$, MgO and Na$_2$O on the surface tension is summarized in **Fig. 2**. This figure shows the relation between the mole fraction ratio of CaO to SiO$_2$ (CaO/SiO$_2$: basicity) and the surface tension at 1 773 K, where the surface tension increased with increasing basicity. Here, the basic composition refers to the composition in which the mole fractions of CaO and SiO$_2$ are both 0.4 and that of CaF$_2$ is 0.2. For example, in the case where the basicity increases from 1.0 to 1.2, the surface tension increases from 388 to 397 mN/m, accordingly. An increase in the surface tension ($397-388=9$ mN/m) can be obtained by the addition of Al$_2$O$_3$ or MgO with 0.09–0.10 mol fractions, rather than the effect of basicity.

3.2. System with 4–6 Components

The surface tension of molten slag with 4 to 6 components is evaluated and compared with the literature data.

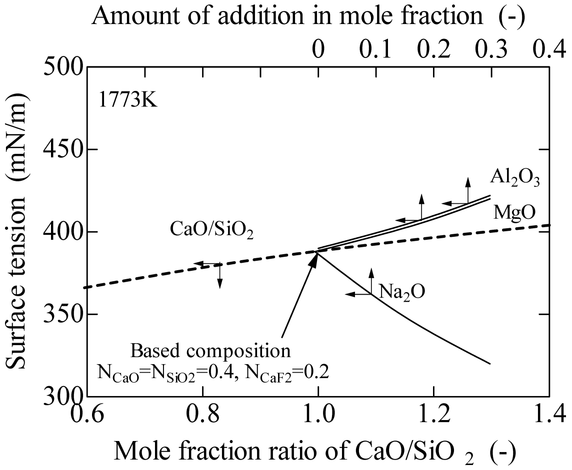


Fig. 2. Effects of CaO/SiO_2 mole fraction ratio and the addition of Al_2O_3, MgO or Na_2O on the surface tension of molten slag formed by the $CaO–SiO_2–CaF_2$ system.

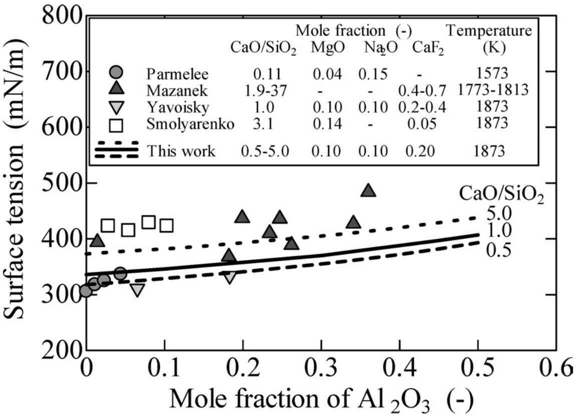


Fig. 3. Relation between the mole fraction of Al_2O_3 and the molten slag surface tension of the $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ system. Comparison between the evaluated results and the literature data.

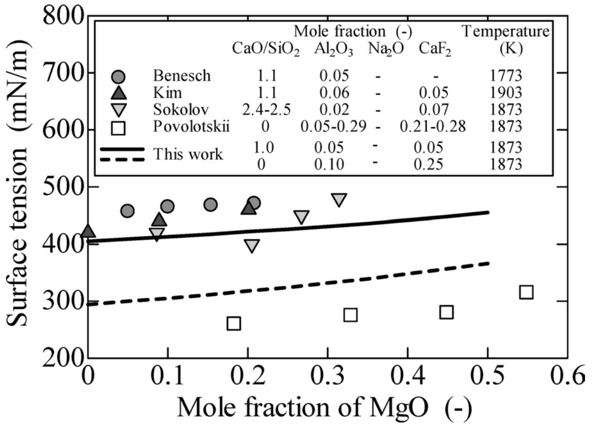


Fig. 4. Relation between the mole fraction of MgO and surface tension of molten slag of $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ system. Comparison between the evaluating results and the literature data.

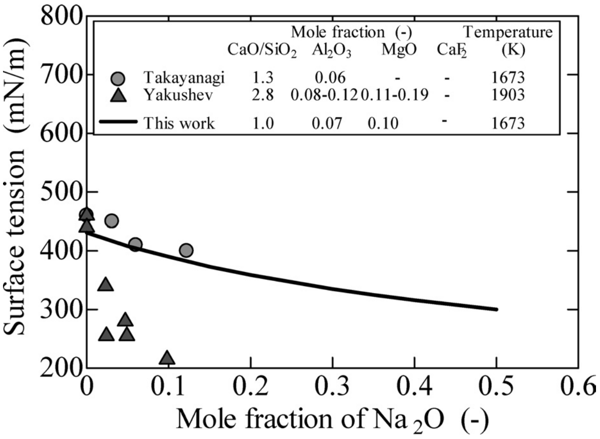


Fig. 5. Relation between the mole fraction of Ma_2O and surface tension of molten slag of $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ system. Comparison between the evaluating results and the literature data.

Figure 3 shows the relation between Al_2O_3 content and the surface tension of the molten slag. We selected here the literature data, which were measured at almost the similar composition range to the condition of the present calculation. The experimental values are different from each other, but the present model reproduced the dependency of the surface tension on Al_2O_3 content. Literature data[13–16] were selected so as not to cause large changes in the content of the other components. The present model reproduced well the literature data for the surface tension and composition dependence with Al_2O_3 addition.

Figure 4 shows the relation between MgO content and the surface tension of the molten slag. Similar to the case of Al_2O_3, as shown in Fig. 3, the present model also reproduced the surface tension results, and the evaluated results agreed well with the literature data.[17–20]

Figure 5 shows the relation between Na_2O content and the surface tension of the molten slag. Here, there is a large difference between the calculated results and the data reported by Yakushev *et al.*[21] Referring the other data on Na_2O in binary or ternary systems including Na_2O,[12] it seems to be difficult to make the surface tension decrease down to about 200 mN/m with Na_2O addition of only 0.1 mol fraction. Furthermore, the data by Yakshev was evaluated under the condition of higher basicity range at higher temperature than the present calculation. The calculated result agreed well with the data of Takayanagi *et al.*[22]

3.3. Reproducibility

Figure 6 shows a comparison between the evaluated results and surface tension literature data for the molten $CaO–SiO_2–Al_2O_3–MgO–Na_2O–CaF_2$ slag system. Here, the literature data are the same as those in Figs. 3–5. The reproducibility was evaluated as the average error defined as Eq. (10). The average error of the present model was 17.5%.

$$\text{Average error} = \frac{1}{N}\sum_{1}^{N}\left|\frac{\sigma_{\text{Calc}}-\sigma_{\text{Expe}}}{\sigma_{\text{Expe}}}\right|\times 100 \quad (\%) \qquad \text{..(10)}$$

In Fig. 6, the plots indicated with (*) correspond to the data for the $CaO–SiO_2–Al_2O_3–MgO–Na_2O$ system reported by Yakushev *et al.*,[21] which are positioned slightly offset from the broken line. In their data, the surface tension shows a large dependence on Na_2O content. The present model shows that the dependence of the surface tension on Na_2O content is not much larger than that reported by

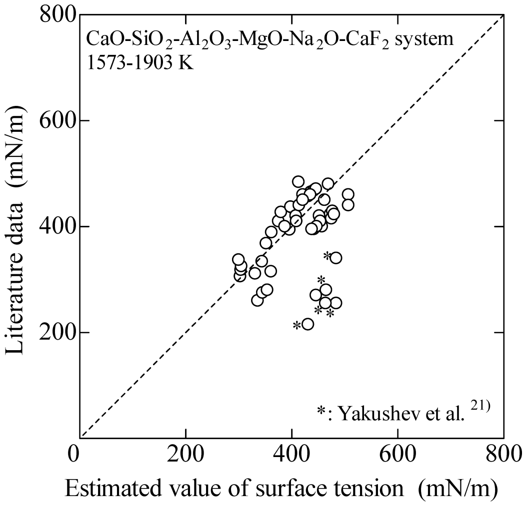


Fig. 6. Comparison of the evaluated surface tension results obtained for the molten slag of CaO–SiO$_2$–Al$_2$O$_3$–MgO–Na$_2$O–CaF$_2$ with the literature data.

Yakushev *et al.* By removing the literature data (Yakushev *et al.*) from the data plots, the average error in Eq. (10) is reduced to 10.3%.

4. Conclusions

A thermodynamic model for evaluating the surface tension of molten ionic mixtures by considering their ionic radii was extended to molten slags of multi-component systems including CaO, SiO$_2$, Al$_2$O$_3$, MgO, Na$_2$O and CaF$_2$. The calculated results obtained using the present model reproduced well the surface tension composition dependence of the molten slag in a 6-component system.

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