Surface Tension Calculation of Molten Slag in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO--'FeO'--'Fe}_2\text{O}_3$ Systems Based on a Statistical Modelling Approach

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A calculation model for surface tension of molten slags in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ systems, based on a statistical modelling approach, was further extended to $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO--'FeO'--'Fe}_2\text{O}_3$ multi-component systems. A total number of 1493 surface tension data reported in literatures, including 661 iron-containing data in this study, have been collected and critically reviewed for optimizing model parameters. The model achieves an excellent agreement with literature values for iron-containing melts with an average error of 4.9% and overall absolute error of 29.75 mN/m. Moreover, the dependence of surface tension on composition and temperature the composition has been discussed using the present model. The results show that the surface tension always obviously decrease with the increment of SiO_2 content and substitution of CaO or Al_2O_3 by MgO will cause a decrease in the surface tension. In case of silica-free ternary systems such as the $\text{Al}_2\text{O}_3\text{--CaO--'Fe}_2\text{O}_3$ and $\text{CaO--MgO--'Fe}_2\text{O}_3$, the surface tension decreases with increasing ' Fe_2O_3 ' concentration with constant Al_2O_3 and CaO level respectively, indicating the network former role of ' Fe_2O_3 ' in these studied systems. Temperature coefficient is closely related with the melt composition and positive values for high ' FeO ' and ' Fe_2O_3 ' contents in the melts were found.

KEY WORDS: surface tension; statistical modeling approach; iron-containing molten slag.

1. Introduction

A large volume of iron oxides were found to be presented in molten slag both in the steelmaking and non-ferrous metallurgical processes. Iron-bearing melts are of great importance in the field of metallurgy. As one of the most fundamental physical properties of molten slag, the surface tension plays a key role in many unit processes of pyrometallurgy, including slag-metal emulsion, slag foaming, thereby influencing the kinetics of slag-metal reactions. However, it is often not possible to access to all surface tension data particularly over a wide composition and temperature range, and the available experimental data for a system even under the same conditions are often scattered. It is, therefore, indispensable to estimate the surface tension values of molten slags by developing a reliable model.

Various types of surface tension models have been published in literatures over the years. These models can be described by the concept of additive mode,^{1,2)} neural

network model,^{3,4)} excess surface tension model,^{5–7)} mass triangle model^{8,9)} and Butler model.^{10–16)} Some of these models were reported successfully applied to FeO_x containing systems, including additive mode of Boni¹⁾ and Mills,²⁾ neural network model of Nakamoto,⁴⁾ mass triangle model from Wang *et al.*⁹⁾ and Butler model from Tanaka.¹⁶⁾ These surface tension models can generally meet the demands of process controlling and optimization. However, existing surface tension models for FeO_x -containing systems are either optimized in relatively narrow composition ranges, showing limited accuracy (*i.e.* error higher than 8–10%), or too complex to be conveniently used. In addition, for ferrous (FeO) and ferric (Fe_2O_3) iron oxides existing melts, the above mentioned models always treat all iron oxides as ' FeO ', while the presence of Fe_2O_3 has not been considered, so that these models show a poor accuracy for high Fe_2O_3 content in melts. Thus simple and accurate and surface tension model for FeO_x containing systems are still needed to meet the growing requirements of precise numerical simulations.

The present authors¹⁷⁾ had already established a surface

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tension model for $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ multicomponent systems based on a statistical modelling approach. In this study, the model will be further extended to FeO_x -containing systems by utilizing the most reliable literature data.

2. Method

2.1. Experimental Data

The variation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, to a large extent, is a complex function of oxygen pressure, melt composition, and temperature. Thermodynamic calculation for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is highly sophisticated. In the present work, the ‘FeO’ and ‘ Fe_2O_3 ’ contents were calculated instead of calculating the exact $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. The calculation methods for the ‘FeO’ and ‘ Fe_2O_3 ’ contents used in this work were summarized in **Table 1** and the details could be available in a previous study about iron-containing density model.¹⁸⁾ To obtain model parameters, a large number of surface tension data were critically reviewed through published literatures. A summary of the references together with the brief experimental details was presented in **Table 2** in which a total of 661 iron-containing surface tension data were used to calibrate the model parameters.

2.2. Model Description

The same surface tension model¹⁷⁾ successfully developed for $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ systems was expanded to FeO_x -containing systems in this study. The surface tension of molten slag was calculated on the basis of Eq. (1).

$$\sigma = \sum X_i \sigma_i(T) + \sigma^{\text{EX}} \quad \text{..... (1)}$$

where σ and X_i represent the surface tension of molten slag and the mole fraction of component i , $\sigma_i(T)$ represents the partial molar surface tension of component i , and σ^{EX} represents the excess surface tension.

Accordingly, the $\sigma_i(T)$ and σ^{EX} are expressed by Eqs. (2) and (3), respectively.

$$\begin{aligned} \sigma_i(T) &= \sigma_{i,R} + \frac{\partial \sigma_i}{\partial T}(T - T_R) \\ &= \sigma_{\text{SiO}_2} + \frac{\partial \sigma_{\text{SiO}_2}}{\partial T}(T - T_R) + \sigma_{\text{Al}_2\text{O}_3} + \frac{\partial \sigma_{\text{Al}_2\text{O}_3}}{\partial T}(T - T_R) \\ &\quad + \sigma_{\text{CaO}} + \frac{\partial \sigma_{\text{CaO}}}{\partial T}(T - T_R) + \sigma_{\text{MgO}} + \frac{\partial \sigma_{\text{MgO}}}{\partial T}(T - T_R) \\ &\quad + \sigma_{\text{FeO}} + \frac{\partial \sigma_{\text{FeO}}}{\partial T}(T - T_R) + \sigma_{\text{Fe}_2\text{O}_3} + \frac{\partial \sigma_{\text{Fe}_2\text{O}_3}}{\partial T}(T - T_R) \\ &\quad \text{..... (2)} \end{aligned}$$

$$\begin{aligned} \sigma^{\text{EX}} &= \sum_{i < j} a_{ij} X_i X_j \\ &= a_{12} X_{\text{SiO}_2} X_{\text{Al}_2\text{O}_3} + a_{13} X_{\text{SiO}_2} X_{\text{CaO}} + a_{14} X_{\text{SiO}_2} X_{\text{MgO}} \\ &\quad + a_{15} X_{\text{SiO}_2} X_{\text{FeO}} + a_{16} X_{\text{SiO}_2} X_{\text{Fe}_2\text{O}_3} + a_{23} X_{\text{Al}_2\text{O}_3} X_{\text{CaO}} \\ &\quad + a_{24} X_{\text{Al}_2\text{O}_3} X_{\text{MgO}} + a_{25} X_{\text{Al}_2\text{O}_3} X_{\text{FeO}} + a_{26} X_{\text{Al}_2\text{O}_3} X_{\text{Fe}_2\text{O}_3} \\ &\quad + a_{34} X_{\text{CaO}} X_{\text{MgO}} + a_{35} X_{\text{CaO}} X_{\text{FeO}} + a_{36} X_{\text{CaO}} X_{\text{Fe}_2\text{O}_3} \\ &\quad + a_{45} X_{\text{MgO}} X_{\text{FeO}} + a_{46} X_{\text{MgO}} X_{\text{Fe}_2\text{O}_3} + a_{56} X_{\text{FeO}} X_{\text{Fe}_2\text{O}_3} \\ &\quad \text{..... (3)} \end{aligned}$$

where $\sigma_{i,R}$ represents partial molar surface tension of component i at reference temperature T_R , and $\partial \sigma_i / \partial T$ represents the temperature coefficient of component i , a_{ij} represents the interaction factor between components i and j .

The values of fitting parameters were obtained by minimization of the function.

$$\sum_{i=1}^N \frac{(\sigma_{\text{mea}} - \sigma_{\text{cal}})^2}{\sigma_{\text{mea}}} \quad \text{..... (4)}$$

where σ_{mea} and σ_{cal} represent the measured and calculated surface tension, respectively.

All surface tension data were equally used for the calibration of model parameters based on the Levenberg–Marquardt algorithm using non-linear least-squares fitting, as shown in **Tables 3** and **4**. The parameter values of the components SiO_2 , Al_2O_3 , CaO and MgO had been optimized for $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ multicomponent systems in a previous study.¹⁷⁾ Considering the effects of iron oxides on melt structure, the parameter values of the components SiO_2 , Al_2O_3 , CaO and MgO were optimized using iron-containing surface tension data in this study and no obvious changes was found compared with the parameter values obtained in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ multicomponent systems in a previous study. In view of the universality of model parameters, the parameter values of the components SiO_2 , Al_2O_3 , CaO and MgO obtained in a previous study would be accepted in the present model, thus only the parameters related with the ‘FeO’ and ‘ Fe_2O_3 ’ systems were optimized in this study.

3. Results and Discussions

3.1. Model Performance

The accuracy of the model was represented by the average relative error (Δ), for N measurements, which was calculated according to following equations

Table 1. Methods for calculation of ‘FeO’ and ‘ Fe_2O_3 ’ contents in FeO_x -containing melts.

Situations	‘FeO’/(‘FeO’ + ‘ Fe_2O_3 ’)	‘ Fe_2O_3 ’/(‘FeO’ + ‘ Fe_2O_3 ’)
Equilibrium with metallic Fe	1	0
Air	0	1
$P_{\text{O}_2} \leq 10^{-8}$ atm	1	0
$P_{\text{O}_2} \geq 10^{-0.68}$ atm (or 0.21 atm)	0	1
Inert atmosphere (Ar, N_2 , etc)	$\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3)$	$\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$
$\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3) \leq 0.05$	1	0
$\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3) \geq 0.80$	0	1
Other situations	$\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3)$	$\text{Fe}_2\text{O}_3/(\text{FeO} + \text{Fe}_2\text{O}_3)$

Table 2. Summary of selected experimental data of surface tension in FeO_x containing melts from various references.

System	Reference	Temperature (K)	Number	Method*	Condition
'FeO'–'Fe ₂ O ₃ '	Kawai, <i>et al.</i> (1976) ¹⁹⁾	1 673	1	MBP	Fe Sat (Ar)
	Kidd and Gaskell (1986) ²⁰⁾	1 683	1	Padday's cone technique	Fe Sat
	Popel, <i>et al.</i> (1969) ²¹⁾	1 673	1	MBP	Fe Sat (He)
	Wu, <i>et al.</i> (1963) ²²⁾	1 693 to 1 723	4	MBP	Assumed Fe Sat (Ar)
	Kozakevitch. (1949) ²³⁾	1 688 to 1 700	5	CD	Fe Sat
	Popel and Esin (1956) ²⁴⁾	1 673	6	MBP	N ₂ , Ar
	Hara, <i>et al.</i> (1991) ²⁵⁾	1 873 to 1 913	5	MBP	Air, CO ₂
SiO ₂ –'FeO'–'Fe ₂ O ₃ '	King, T. (1951) ²⁶⁾	1 573 to 1 748	24	RD	Fe Sat (N ₂)
	Kawai, <i>et al.</i> (1976) ¹⁹⁾	1 673	4	MBP	Fe Sat (Ar)
	Yu and Mukai. (1995) ²⁷⁾	1 673	5	/	Fe Sat (Ar)
	Fadeev, <i>et al.</i> (1980) ²⁸⁾	1 573 to 1 673	2	/	/
	Popel, <i>et al.</i> (1963) ²⁹⁾	1 673	1	MBP	Fe Sat (He)
	Popel, <i>et al.</i> (1969) ²¹⁾	1 563 to 1 813	24	MBP	Fe Sat (He)
	Popel and Esin (1956) ²⁴⁾	1 673	17	MBP	N ₂ , Ar
	Holeczy, <i>et al.</i> (1972) ³⁰⁾	1 285 to 1 320	23	RD	Fe Sat (N ₂)
	Vanyukov and Utkin (1958) ³¹⁾	1 523 to 1 673	4	MBP	/
	Kidd and Gaskell (1986) ²⁰⁾	1 683	7	Padday's cone technique	Fe Sat
	Karakash and Ternovoi (1977) ³²⁾	1 483	1	/	/
	Kozakevitch. (1949) ²³⁾	1 669 to 1 716	16	CD	Fe Sat
CaO–'FeO'–'Fe ₂ O ₃ '	Kawai, <i>et al.</i> (1976) ¹⁹⁾	1 673	8	MBP	Fe Sat (Ar)
	Kidd and Gaskell (1986) ²⁰⁾	1 683	9	Padday's cone technique	Fe Sat
	Kozakevitch. (1949) ²³⁾	1 652 to 1 690	6	CD	Fe Sat
	Sumita, <i>et al.</i> (1983) ³³⁾	1 573 to 1 823	30	RD	Air
	Hara, <i>et al.</i> (1991) ²⁵⁾	1 673 to 1 873	16	MBP	Air, CO ₂
	Vadász, <i>et al.</i> (2006) ³⁴⁾	1 623	6	MBP	Air
	Gulyaeva, <i>et al.</i> (1990) ³⁵⁾	1 473 to 1 873	40	MBP	Air
	Karakash and Ternovoi (1977) ³²⁾	1 493	1	/	/
	Vadasz, <i>et al.</i> (2000) ³⁶⁾	1 573	2	MBP	Air
SiO ₂ –Al ₂ O ₃ –'FeO'–'Fe ₂ O ₃ '	Yu and Mukai. (1995) ²⁷⁾	1 673	5	/	Fe Sat (Ar)
	Elliott and Mounier (1982) ³⁷⁾	1 473	16	MBP	Fe Sat (Ar)
	Fadeev, <i>et al.</i> (1980) ²⁸⁾	1 573 to 1 673	8	/	/
SiO ₂ –CaO–'FeO'–'Fe ₂ O ₃ '	Kawai, <i>et al.</i> (1976) ¹⁹⁾	1 673	12	MBP	Fe Sat (Ar)
	Skupien and Gaskell (2000) ³⁸⁾	1 573 to 1 708	16	CD	Assumed Sat
	Vanyukov and Utkin (1958) ³¹⁾	1 473 to 1 673	30	MBP	/
	Karakash and Ternovoi (1977) ³²⁾	1 403 to 1 433	3	/	/
	Hara, <i>et al.</i> (1991) ²⁵⁾	1 723 to 1 883	27	MBP	Air, CO ₂
	Vadasz, <i>et al.</i> (2000) ³⁶⁾	1 573	35	MBP	Air
	Daněk, <i>et al.</i> (1985) ³⁹⁾	1 723	6	MBP	Air
	Popel, <i>et al.</i> (1963) ²⁹⁾	1 673	10	MBP	Fe Sat (He)
SiO ₂ –MgO–'FeO'–'Fe ₂ O ₃ '	Yuan, <i>et al.</i> (1988) ⁴⁰⁾	1 673 to 1 773	3	MBP	Fe Sat (Ar)
	Toropov and Bryantsev (1966) ⁴¹⁾	1 623 to 1 823	5	/	/
Al ₂ O ₃ –CaO–'FeO'–'Fe ₂ O ₃ '	Vadasz, <i>et al.</i> (2000) ³⁶⁾	1 573	32	MBP	Air
	Zielinski and Sikora (1977) ⁴²⁾	1 723 to 1 923	25	MBP	Air
CaO–MgO–'FeO'–'Fe ₂ O ₃ '	Vadász, <i>et al.</i> (2006) ³⁴⁾	1 623	17	MBP	Air
SiO ₂ –Al ₂ O ₃ –CaO–'FeO'–'Fe ₂ O ₃ '	Schmetterer and Masset (2011) ⁴³⁾	1 505 to 1 773	13	SD	Fe Sat (Ar)
	Elliott and Mounier (1982) ³⁷⁾	1 473	7	MBP	Fe Sat (Ar)
	Pavlov, <i>et al.</i> (1980) ⁴⁴⁾	1 473 to 1 773	10	/	/
	Muraveva and Kaplun (1984) ⁴⁵⁾	1 394 to 1 623	14	/	/
SiO ₂ –CaO–MgO–'FeO'–'Fe ₂ O ₃ '	Yuan, <i>et al.</i> (1988) ⁴⁰⁾	1 673 to 1 773	50	MBP	Fe Sat (Ar)
	Popel, <i>et al.</i> (1963) ²⁹⁾	1 673	7	MBP	Fe Sat (He)
	Toropov and Bryantsev (1966) ⁴¹⁾	1 673	4	/	/
SiO ₂ –Al ₂ O ₃ –MgO–'FeO'–'Fe ₂ O ₃ '	Toropov and Bryantsev (1966) ⁴¹⁾	1 623 to 1 823	27	/	/

*: SD: sessile drop method; MBP: maximum bubble pressure; CD: cylinder detachment method; RD: ring detachment method.

$$\delta_i = \frac{|\sigma_{i,cal.} - \sigma_{i,mea.}|}{\sigma_{i,mea.}} \dots\dots\dots (5)$$

$$\Delta = \frac{1}{N} \sum_{i=1}^N \delta_i \times 100\% \dots\dots\dots (6)$$

The root mean square error (RMSE) was also calculated by the following expression.

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (\sigma_{i,cal.} - \sigma_{i,mea.})^2}{N}} \dots\dots\dots (7)$$

Table 3. Optimized parameter values of $\sigma_{i,R}$ and $\partial\sigma_i/\partial T$.

Component	$\sigma_{i,R}$ (1 773 K) (mN·m ⁻¹)	$\partial\sigma_i/\partial T$ (mN·m ⁻¹ ·K ⁻¹)
SiO ₂ *	293.93	-4.55×10^{-3}
Al ₂ O ₃ *	759.12	-277.27×10^{-3}
CaO*	672.09	-264.93×10^{-3}
MgO*	1 177.56	-789.32×10^{-3}
'FeO'	571.02	132.16×10^{-3}
'Fe ₂ O ₃ '	563.96	164.03×10^{-3}

*: The parameter values have been optimized separately for SiO₂–Al₂O₃–CaO–MgO systems in a previous study.¹⁷⁾

Table 4. Optimized parameter values of interaction coefficient for excess surface tension.

Parameter value a_{ij} (mN·m ⁻¹)	System
a_{12}	68.24 SiO ₂ –Al ₂ O ₃ *
a_{13}	–97.27 SiO ₂ –CaO*
a_{14}	–1 229.35 SiO ₂ –MgO*
a_{23}	–350.59 Al ₂ O ₃ –CaO*
a_{24}	–60.68 Al ₂ O ₃ –MgO*
a_{34}	–857.40 CaO–MgO*
a_{15}	–183.01 SiO ₂ –'FeO'
a_{25}	–425.46 Al ₂ O ₃ –'FeO'
a_{35}	–308.34 CaO–'FeO'
a_{45}	–400.43 MgO–'FeO'
a_{16}	–51.32 SiO ₂ –'Fe ₂ O ₃ '
a_{26}	–920.17 Al ₂ O ₃ –'Fe ₂ O ₃ '
a_{36}	–102.75 CaO–'Fe ₂ O ₃ '
a_{46}	–169.41 MgO–'Fe ₂ O ₃ '
a_{56}	–12.44 'FeO'–'Fe ₂ O ₃ '

*: The parameter values have been optimized separately for SiO₂–Al₂O₃–CaO–MgO systems in a previous study.¹⁷⁾

There is well agreement between the measured and calculated surface tension values, with an overall accuracy of 4.9% and the average absolute error of 29.75 mN/m for FeO_x-containing data within the selected composition ranges, as shown in Fig. 1(a). Together with the SiO₂–Al₂O₃–CaO–MgO systems reported earlier, the present model achieves a high accuracy with relative error of 4.85% and the average absolute error of 28.86 mN/m for 1 493 literature data in full SiO₂–Al₂O₃–CaO–MgO–'FeO'–'Fe₂O₃' systems, as shown in Fig. 1(b). For most of the iron-containing subsystems, the present model also provides reasonable deviation, as shown in Fig. 2. By comparison, the two previously reported additive models which all iron oxides were approximated as 'FeO' were also employed to predict the surface tension, but have a less satisfactory prediction performance. As shown

Fig. 2. Performances of present model in surface tension calculation for each system (S, A, C, M and F represent SiO₂, Al₂O₃, CaO, MgO, FeO_x respectively). (Online version in color.)

Fig. 1. Performance of present surface tension model: (a) FeO_x-containing systems (b) full SiO₂–Al₂O₃–CaO–MgO–'FeO'–'Fe₂O₃' systems. (Online version in color.)

Fig. 3. Prediction of surface tension of molten slag using previously similar models: (a) Boni model (b) Mills model. (Online version in color.)

in Fig. 3, the mean deviation are 8.26% and 19.11% for Boni model¹⁾ and Mills model²⁾ respectively. Especially, the model prediction by Mills²⁾ always show a large positive deviation with respect to literature data. This mainly result from a bigger partial molar surface tension of 'FeO' than that of Boni model¹⁾ and the present model.

3.2. Composition and Temperature Dependences of Surface Tension for 'FeO'-containing Systems

3.2.1. Unary System

Most of surface tension measurements of 'FeO' were conducted by using maximum bubble pressure method in equilibrium with metallic iron within narrow temperature ranges and there are some disagreements between the different sources. As shown in Fig. 4, The surface tension increases with increment of temperature. In fact, the influence of temperature on surface tension being more complicated than of viscosity. The attraction between particles is weakened with increasing temperature, giving rise to a decrease in the surface tension. Meanwhile, the increases of temperature also weaken the Si–O bond and depolymerized silica anionic unites, eg. $\text{Si}_2\text{O}_5^{2-}$, $\text{Si}_2\text{O}_6^{4-}$, $\text{Si}_2\text{O}_7^{6-}$ and SiO_4^{4-} , resulting in an increases in the surface tension. It is believed that the temperature coefficient of surface tension have a closed relationship with compositions in FeO_x -based melts. For most of the slag systems, temperature coefficient is abnormal in having positive values for high iron oxides level in the present model and a positive value of pure 'FeO' ($0.132 \text{ mNm}^{-1} \text{ K}^{-1}$) was found, showing a small differences with results ($0.0984 \text{ mNm}^{-1} \text{ K}^{-1}$) derived from Nakamoto, *et al.*¹⁰⁾ In Fe_xO melts, increasing temperature results in a decrease in Fe_2O_3 content, thus it is possible that the positive temperature coefficients observed are the result of significant decreases in the Fe_2O_3 content of the melts. It is indicated that, provided there is a significant change in the Fe_2O_3 content during heating process, the temperature coefficients of surface tension of the based- Fe_xO systems are probably positive.

Surface tension data for iron oxide melts is usually considered to be complicated due to the presences of Fe^{3+} ions in the melt. It is known that Fe_2O_3 is surface active compared to FeO , and the actual content present in the melts produce a significant impact on the surface tension.²⁾

Fig. 4. Temperature dependence of surface tensions of 'FeO'. (Online version in color.)

Since the FeO – Fe_2O_3 equilibrium depends on the melt composition, partial oxygen pressure of oxygen as well as temperature, it is difficult to accurately determine the Fe_2O_3 content. Consequently, additional diversity is introduced into the measured results. And also, determination of the temperature coefficient of surface tension of 'FeO' melts is not easy, because the Fe_2O_3 equilibrium level is temperature sensitive. For example, Lee and Gaskel⁴⁶⁾ carried out measurements of temperature coefficient for 'FeO' in the temperature range from 1 408 to 1 563°C, and found a small negative value ($0.047 \text{ mNm}^{-1} \text{ K}^{-1}$). By contrast, Kawai *et al.*¹⁹⁾ obtained a large positive temperature coefficient ($1.303 \text{ mNm}^{-1} \text{ K}^{-1}$) within a smaller temperature range from 1 370 to 1 430°C. It must be noted that both these measurements were conducted on melts with Fe_2O_3 contents around 8%.

3.2.2. Binary Systems

The effect of composition and temperature on surface tension for the SiO_2 –'FeO' and CaO –'FeO' are shown in Fig. 5. It was found that the calculated values of the SiO_2 –'FeO' agree well with the measurements and reveal a constant feature that increasing SiO_2 content could significantly decrease the surface tension. In cases of CaO –'FeO' system, as presented in Fig. 5(b), the surface tension decreases initially and then increases with the increases of

Fig. 5. Composition dependences of surface tension for binary systems: (a) SiO_2 - FeO ; (b) CaO - FeO . (Online version in color.)

CaO concentration. Furthermore, it should be noticed that the compositional dependence of surface tension shows a similar trend with the experimental results by Kozakevitch²³⁾ at 1 680 K. This behavior may be attributed to the fact that differences in the Fe_2O_3 levels could cause significant differences in the surface tension for the binary FeO_x - CaO system. Research from Allen and Snow⁴⁷⁾ indicates that, under equilibrium conditions with Fe, the amount of Fe_2O_3 in the liquid increases as the CaO content increases from 0 to 28 wt%, at which level the Fe_2O_3 content arrives a maximum value of 18–20 wt%. As the CaO content is further increased, the quantity of Fe_2O_3 in the system is progressively reduced.

In addition, temperature has an opposite effect on the surface tension in different ' FeO ' ranges. As mentioned above, the temperature coefficient was affected by melt compositions. According to Pavlov *et al.*,⁴⁴⁾ the surface tension has a positive temperature coefficient for above 38 wt% ' FeO ' content, and a negative one for below 25 wt% ' FeO ' content. In the present model, positive temperature coefficients for higher ' FeO ' content up to 55 wt% were found, and negative values for below 55 wt% ' FeO ' in the ' CaO - FeO ' system.

3.2.3. Ternary Systems

The iso-surface tension curves are calculated at 1 673 K using the model and compared with the measured values for SiO_2 - Al_2O_3 - FeO , SiO_2 - CaO - FeO and SiO_2 - MgO - FeO systems, respectively. As shown in Fig. 6, the surface tension consistently decreases with increment of SiO_2 content for silicate systems. As a surface-active component, the increase of SiO_2 content will effectively increase the polymerization degree of silicate melts, thereby decreasing the surface tension of silicate melts. Moreover, it is noted that the SiO_2 shows more effective role on surface tension for SiO_2 - MgO - FeO system compared with SiO_2 - Al_2O_3 - FeO and SiO_2 - CaO - FeO systems. In addition, substitution of Al_2O_3 by CaO results in a slight increase in the surface tension in lower SiO_2 region, while replacing Al_2O_3 or CaO with MgO will produce an effective decrease in the surface tension in higher SiO_2 region.

3.2.4. Quaternary Systems

Most of the experimental data for SiO_2 - Al_2O_3 - CaO -

FeO , SiO_2 - CaO - MgO - FeO and SiO_2 - Al_2O_3 - MgO - FeO systems were compared with the estimated values by the present model, as presented in Fig. 7. For the SiO_2 - Al_2O_3 - MgO - FeO , temperature coefficient of surface tension obtained by Toropov and Bryantsev⁴¹⁾ is abnormal in having a positive value which is inconsistent with the model prediction. The reason for this is largely due to experimental error. For example, the measurements obtained in a graphite crucible were often found to have large experimental uncertainties due to the reaction between graphite and molten slag. In addition, some surface tension measurements were carried out below the liquid temperature of the slag, which may also cause a large error because of the presence of the solid particles in molten slag. Because only a set of experimental data from Toropov and Bryantsev⁴¹⁾ was found in the SiO_2 - Al_2O_3 - MgO - FeO system, it is difficult to evaluate the predictive ability of the model to the system. Further experimental study may be needed.

The iso-surface tension curves for quaternary systems of SiO_2 - Al_2O_3 - CaO - FeO , SiO_2 - CaO - MgO - FeO and SiO_2 - Al_2O_3 - MgO - FeO with constant 10% Al_2O_3 , 10% MgO and 10% MgO content respectively are plotted at 1 673 K, as shown in Fig. 8. It was found that the SiO_2 - Al_2O_3 - CaO - FeO system in Fig. 8(a) shows a decreasing trend in the surface tension with a substitution of 10% Al_2O_3 by 10% MgO in SiO_2 - CaO - MgO - FeO system. A comparison of surface tension for the SiO_2 - CaO -10% MgO - FeO and SiO_2 - Al_2O_3 -10% MgO - FeO systems indicates an increase in the surface tension with a replacement of Al_2O_3 by CaO and showing a bigger positive effect on surface tension with the continuous lower of SiO_2 concentration.

3.3. Composition and Temperature Dependences of Surface Tension for ' Fe_2O_3 '-containing Systems

3.3.1. Unary System

The only one group of surface tension of the ' Fe_2O_3 ' system was measured by Hara, *et al.*²⁵⁾ using maximum bubble pressure method in air condition, as shown in Fig. 9. It can be observed that there is a linear relationship between the surface tension and temperature, the surface tension increasing gradually with increasing temperature, showing a same behavior with ' FeO '.

Fig. 6. Composition dependences of surface tension for several ternary systems: (a) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{'FeO'}$; (b) $\text{SiO}_2\text{-CaO-'FeO'}$; (c) $\text{SiO}_2\text{-MgO-'FeO'}$. (Online version in color.)

Fig. 7. Composition and temperature dependences of surface tension for several 'FeO'-containing quaternary systems: (a) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-'FeO'}$; (b) $\text{SiO}_2\text{-CaO-MgO-'FeO'}$; (c) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-'FeO'}$. (Online version in color.)

Fig. 8. Iso-surface tension curves for quaternary systems: (a) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-FeO}$; (b) $\text{SiO}_2\text{-CaO-MgO-FeO}$; (c) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-FeO}$. (Online version in color.)

Fig. 9. Temperature dependence of surface tensions of Fe_2O_3 . (Online version in color.)

Fig. 10. Composition dependences of surface tension for $\text{CaO-Fe}_2\text{O}_3$. (Online version in color.)

3.3.2. Binary System

Surface tension measurements of $\text{CaO-Fe}_2\text{O}_3$ system were performed by Sumita *et al.*³³⁾ and Gulyaeva *et al.*³⁵⁾ as presented in Fig. 10. The surface tension increases with increasing CaO content over the ranges studied. According to the experimental data from Gulyaeva *et al.*, temperature coefficient of surface tension tend to show an increases with increasing CaO content which in line with that of the present model. And it was seen from the present model that there is an opposite change in the temperature coefficient, through

positive to negative with the increases of CaO, showing a similar trend with CaO-FeO system.

3.3.3. Ternary Systems

The iso-surface tension curves for the ternary systems of Fe_2O_3 -containing ternary systems were plotted using the present model and are compared with the measured values within different surface tension ranges, as shown in Fig. 11. For the silica-free ternary systems of $\text{Al}_2\text{O}_3\text{-CaO-Fe}_2\text{O}_3$ and $\text{CaO-MgO-Fe}_2\text{O}_3$ in Figs. 11(b)-11(c), the

Fig. 11. Composition dependences of surface tension for 'Fe₂O₃'-containing ternary systems: (a) SiO₂-CaO-'Fe₂O₃'; (b) Al₂O₃-CaO-'Fe₂O₃'; (c) CaO-MgO-'Fe₂O₃'. (Online version in color.)

surface tension always decrease with increasing 'Fe₂O₃' content with constant Al₂O₃ and CaO level, respectively. According to the modeling results, it is clearly shown that the 'Fe₂O₃' overall acts as a network former in the investigated systems. The only other data available in literature for Al₂O₃-CaO-'Fe₂O₃' system was from Zielinski and Sikora.⁴²⁾ The variation in surface tension with 'Fe₂O₃' content at 1 600°C indicates a linear decrease with increasing 'Fe₂O₃' under equal amounts of Al₂O₃ and CaO. Zielinski and Sikora⁴²⁾ also investigated the change in surface tension with temperature for different 'Fe₂O₃' levels, suggesting a negative temperature coefficient of 0.14 mNm⁻¹ K⁻¹ with a reasonable agreement with the present model. In addition, it was also seen in Fig. 11(b) that the surface tension increases at first and then decreases with the increment of Al₂O₃ and there is a maxima at 0.2–0.3 mass fraction of Al₂O₃. This could be interpreted by the fact that, at less than 0.2 mass fraction of Al₂O₃, the mass fraction of 'Fe₂O₃' is high. Myson⁴⁸⁾ and Dingwell and Virgo⁴⁹⁾ investigated the structural behavior of ferric and ferrous iron in glass using Mossbauer spectroscopy at 1 450–1 500°C in equilibrium with air and drawn a consistent conclusion that ferric iron occurs in tetrahedral coordination with oxygen, acting as the network former. Thus, many ferric irons would combine with oxygen ion, resulting in low amount and activity of free oxygen ion. In this case, Al₂O₃ plays a role of network modifier which modify the Fe–O bonds, increasing the surface tension of melt. On the other hand, at more than 0.3 mass fraction of Al₂O₃, the melt contains relatively lower

'Fe₂O₃', while the amount of free oxygen ion is high, and consequently, Al₂O₃ behaves as a network former which decreases the surface tension of melt.²⁾

4. Conclusions

A surface tension model in SiO₂-Al₂O₃-CaO-MgO systems was extended to iron-bearing multi-component systems and a total of 661 iron-containing surface tension data were used for optimizing the model parameters in this study. The main conclusions are as follows:

- (1) The present model can be applied to estimate the surface tension of iron-containing melts with high accuracy of 4.9% and overall absolute error of 29.75 mN/m, showing superior performance to the existing model.
- (2) On a mass percent basis, substitution of CaO or Al₂O₃ by MgO will produce a decrease in the surface tension in 'FeO'-containing systems. In case of silica-free ternary systems of Al₂O₃-CaO-'Fe₂O₃' and CaO-MgO-'Fe₂O₃', the surface tension always decrease with increasing 'Fe₂O₃' concentration with constant Al₂O₃ and CaO level, respectively.
- (3) Temperature coefficient have a more closed relationship with melt compositions in FeO_x-based melts and positive values for high 'FeO' and 'Fe₂O₃' concentration in melts could be found.

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