Surface Tension of FeS-Cu₂S-Ni₃S₂ Matte Systems

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A thermodynamic model for determining the surface tension of ionic system by considering the surface tension and molar volume of the pure sulfide components and their ionic radii was extended to the molten FeS-Cu₂S-Ni₃S₂ matte system. The temperature dependence of the surface tensions for pure FeS, Cu₂S and Ni₃S₂ have been determined and the calculated surface tensions based on the present model are in good agreement with the experimental values. The maximum error and the average error are 10.11 and 5.02 %, respectively.

Keywords: Thermodynamics model, Surface tension, Ionic radii, Molar volume, FeS-Cu₂S-Ni₃S₂ matte.

INTRODUCTION

The surface tension of molten slag is a key parameter in industrial processes at high temperatures for controlling the various surface and interfacial phenomena[1-3] in metallurgical processes. It is well known that the Ni₃S₂-FeS-Cu₂S molten mattes play an important role in Cu and Ni smelting and converting process. Surface tension of molten mattes is one of the basic properties for a better understanding of the process of metal extraction from sulfide ores. However, the surface tension data of molten Ni₃S₂-FeS-Cu₂S mattes are scarce and scattered because of the complexity of the phases involved and the difficulties encountered in performing experiments at elevated temperatures. Recently, the surface tensions of molten Ni₃S₂-FeS-Cu₂S mattes and its pseudo-binary boundary systems at 1473 K have been measured by Kucharski *et al.*[4] with the maximum bubble pressure method. But only 9 surface tension values of different compositions for the Ni₃S₂-FeS-Cu₂S ternary system were reported which were not enough for studying the surface and interfacial phenomena for the whole system. Therefore, it is necessary to develop a prediction model for determining the surface tension of molten Ni₃S₂-FeS-Cu₂S system.

Some models[5,6] have been developed for evaluating the surface tension of molten Ni₃S₂-FeS-Cu₂S system. Based on the assumption that the surface tension behaviour of the Ni₃S₂-Cu₂S pseudo-binary is approximately ideal, Ip and Toguri[7] used equations presented by Fujisawa *et al.*[8] to predict surface tension behavior of the Ni₃S₂-FeS-Cu₂S pseudo-ternary mattes from the surface tension data of the Ni₃S₂-Cu₂S and Ni₃S₂-FeS pseudo-binaries measured by themselves using the sessile drop

technique[9-11]. But the calculated iso-surface tension contours for the Ni₃S₂-FeS-Cu₂S pseudo-ternary mattes at 1473 K were not in good agreement with experimental data measured by Kucharski *et al.*[4]. In order to obtain more surface tension information of molten Ni₃S₂-FeS-Cu₂S mattes, different geometric models were developed, including a general solution model developed by Chou *et al.*[12] to calculate the surface tensions of molten Ni₃S₂-FeS-Cu₂S mattes from those of the pseudo-binary boundary systems as well as calculated surface tensions based on Butler's equation[13] with great attention to the model parameter, β values. However, the Kohler, Toop, Chou and Butler's equation[5] are all limited by the excess Gibbs free energy. Tanaka *et al.*[14] have developed a new model for evaluating the surface tension of molten silicates, which takes into consideration the ionic radii of the components. This particular model can be readily applied to many kinds of molten ionic mixtures and molten slag, because the surface tension of silicate melts can be calculated using the information on the surface tensions and molar volumes of pure oxides, as well as the cationic and anionic radii of the component oxides in the system. This model has already been applied to the calculations of surface tension for several ternary silicate melts[15] comprising SiO₂, Al₂O₃, CaO, FeO, MgO or MnO. Nakamoto *et al.*[16] applied this model to evaluate the surface tension of silicate melts containing the following surface-active components, B₂O₃, CaF₂ or Na₂O. Hanao *et al.*[17] have studied the composition dependence of the surface tension in 6-component systems of the type CaO-SiO₂-Al₂O₃-MgO-Na₂O-CaF₂ with the thermodynamic model.

In this work, another further extension of the above modified model was developed for determining the surface tensions

of the Ni_3S_2-FeS-Cu_2S molten matte systems. The obtained results reproduced the composition dependence of the surface tension in a wide range of ternary system.

EXPERIMENTAL

Model of surface tension evaluation for the molten ionic mixtures: The model for the evaluation of the surface tension of ionic mixtures was applied to the Ni_3S_2-FeS-Cu_2S molten matte systems based on the Butler's equation. The surface tensions of the 3-component molten slag are calculated from eqns. 1-3:

$$\sigma = \sigma_{FeS}^{Pure} + \frac{RT}{A_{FeS}} \ln \frac{M_{FeS}^{Surf}}{M_{FeS}^{Bulk}} \quad (1)$$

$$\sigma = \sigma_{Ni_3S_2}^{Pure} + \frac{RT}{A_{Ni_3S_2}} \ln \frac{M_{Ni_3S_2}^{Surf}}{M_{Ni_3S_2}^{Bulk}} \quad (2)$$

$$\sigma = \sigma_{Cu_2S}^{Pure} + \frac{RT}{A_{Cu_2S}} \ln \frac{M_{Cu_2S}^{Surf}}{M_{Cu_2S}^{Bulk}} \quad (3)$$

where $M_i^P = \left(\frac{R_A}{R_X} \cdot N_i^P\right) / \left(\frac{R_{Fe^{2+}}}{R_{S^{2-}}} \cdot N_{FeS}^P + \frac{R_{Ni^{2+}}}{R_{S^{2-}}} \cdot N_{Ni_3S_2}^P + \frac{R_{Cu^+}}{R_{S^{2-}}} \cdot N_{Cu_2S}^P\right)$ (4)

Subscript i refers to the following components: Ni_3S_2, FeS, Cu_2S. 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:

$$R_A = R_{Fe^{2+}}, R_{Cu^+}, R_{Ni^{2+}} : R_X = R_{S^{2-}} \quad (5)$$

where the valence of cation Ni in is considered to be +2. The above eqns. 1-3 have been derived on the basis of Butler's equation by considering the following assumptions[14-17] (1) and (2):

(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.

Data on the ionic radii[18], the molar volumes and surface tensions of the pure sulfides used in previous studies[5,6,19] were adopted in the present model. These values are listed in Tables 1 and 2.

Surface tension data: The chemical compositions and experimental surface tensions[4] of matte samples for the evaluation of the Ni_3S_2-FeS-Cu_2S ternary system were listed in Table-3.

TABLE-1
RADII OF THE CATIONIC AND ANIONIC IONS

Ion	Radii (Å)
Fe^{2+}	0.61
Ni^{2+}	0.69
Cu^+	0.77
S^{2-}	1.84

TABLE-2
MOLAR VOLUMES AND SURFACE TENSIONS OF THE PURE COMPONENTS AT 1473 K

Sulfide	Density (g/cm³)	Molar volume (cm³/mol)	Surface tension (mN/m)
FeS	3.81	23.07	326
Ni_3S_2	5.17	46.60	494
Cu_2S	5.28	30.31	389

TABLE-3
CHEMICAL COMPOSITIONS AND EXPERIMENTAL SURFACE TENSIONS OF MATTE

Sample No.	FeS (mole %)	Ni_3S_2 (mole %)	Cu_2S (mole%)	Surface tension, mN/m
1	0.80	0.20	0	348
2	0.50	0.50	0	401
3	0.20	0.80	0	442
4	0.20	0	0.8	354
5	0.50	0	0.5	333
6	0.80	0	0.2	328
7	0	0.80	0.2	421
8	0	0.50	0.5	403
9	0	0.20	0.8	396
10	0.16	0.20	0.64	385
11	0.10	0.50	0.40	398
12	0.04	0.80	0.16	424
13	0.40	0.20	0.40	366
14	0.25	0.50	0.25	409
15	0.10	0.80	0.10	433
16	0.64	0.20	0.16	357
17	0.40	0.50	0.10	409
18	0.16	0.80	0.04	443

RESULTS AND DISCUSSION

Binary systems: The calculated surface tensions of the binary systems based on the present model reproduced the experimental values (Fig. 1). Taking account of experimental[4] accuracy ± 2.5 %, the calculated results are in good agreement with the experimental data. For FeS-Ni_3S_2 system, the surface tension increases along with the addition of the higher surface tension (Table-2) FeS, Ni_3S_2. The increase of the FeS content can result in the decrease of the surface tension of the binary FeS-Cu_2S system. As for the Ni_3S_2-Cu_2S system, similar to the case of FeS-Cu_2S system. It is easy to find that the calculated results have a positive deviation from the measured data and the reason may be due to the assumption[1] that the contribution of the excess Gibbs energies was neglected in the present model.

Ni_3S_2-FeS-Cu_2S ternary system: Fig. 2 shows the calculated iso-surface tension curves of the Ni_3S_2-FeS-Cu_2S ternary molten matte system, showing that the calculated surface tensions of the ternary systems based on the present model reproduced the experimental values. But the surface tensions

of molten Ni_3S_2-FeS-Cu_2S mattes at the Ni_3S_2-rich corner in Fig. 2 are not in good agreement with the calculated results and the reason may result from that the calculated surface tensions of the Cu_2S-Ni_3S_2 and the FeS-Ni_3S_2 binary systems have a large deviation from the experimental values in the Ni_3S_2-rich domain (Fig. 1).
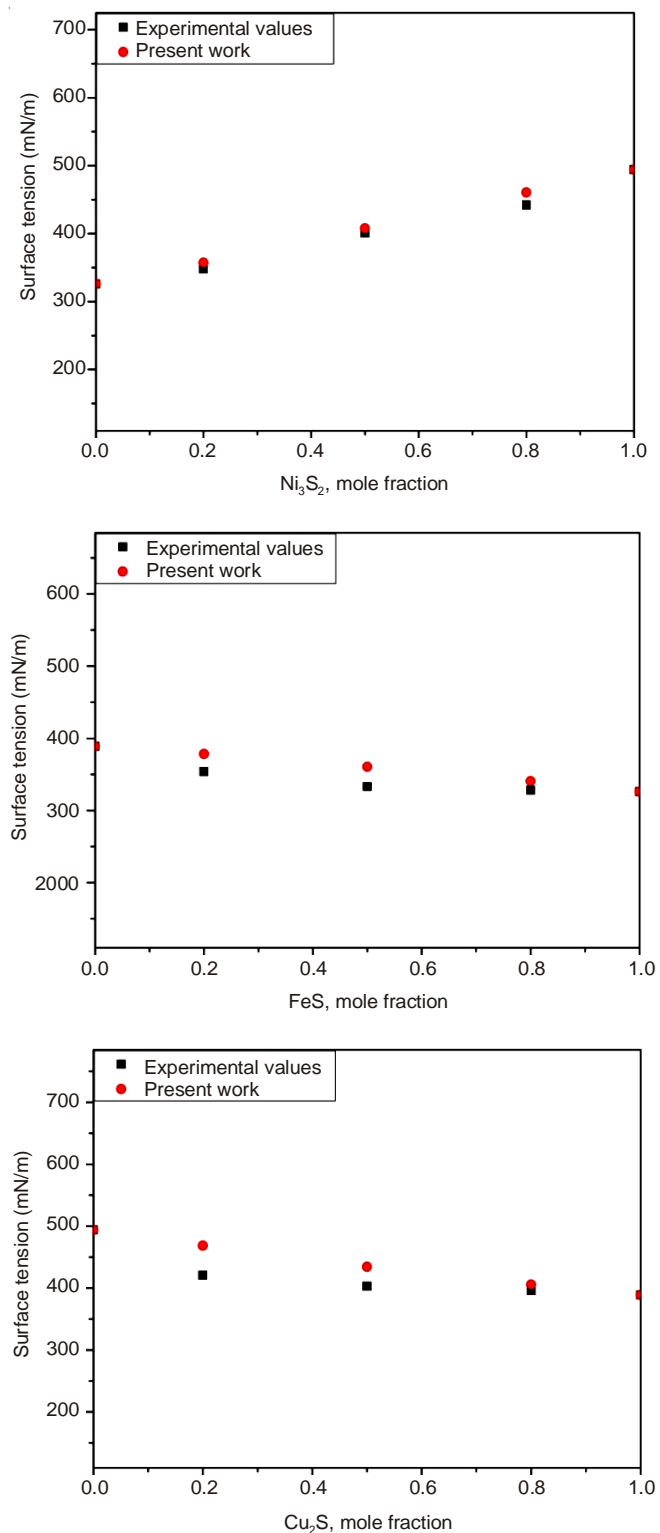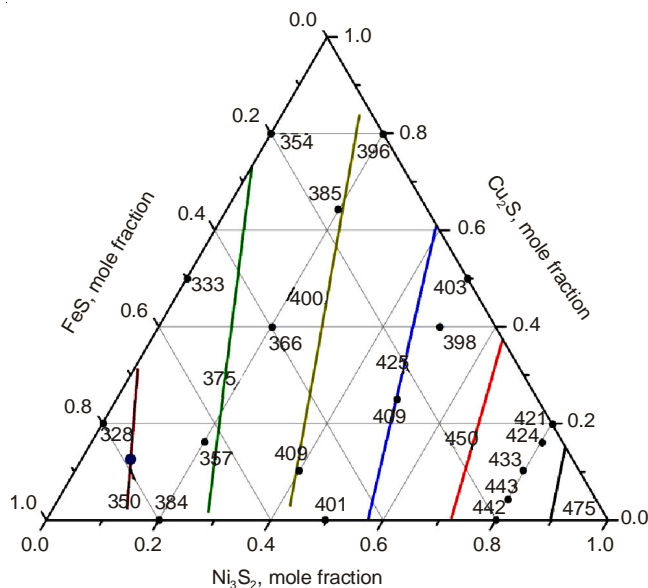

Fig. 2.   Calculated iso-surface tension curves of Ni_3S_2-FeS-Cu_2S ternary system at 1473 K

Reproducibility: The deviation between the evaluated results and surface tension data in literatures for the Ni_3S_2-FeS-Cu_2S molten matte systems has been studied. Here, the literature data are the same as those in Figs. 1 and 2. The reproducibility is evaluated as the error and the average error defined as eqns. 8 and 9.

$$\text{Error} = \frac{\sigma_{Calc} - \sigma_{Expe}}{\sigma_{Expe}} \times 100\,\% \qquad (6)$$

$$\text{Average error} = \frac{1}{N} \sum_{1}^{N} \left| \frac{\sigma_{Calc} - \sigma_{Expe}}{\sigma_{Expe}} \right| \times 100\% \qquad (7)$$

where the σ_{Expe} and σ_{Calc} values correspond to the experimental surface tension values in the literature and the calculated surface tension, respectively and N corresponds to the number of the literature data.

The maximum errors for binary systems and ternary system between the calculated values and the experimental data are 11.28 % (Fig. 3) and 10.11 % (Fig. 4), respectively.

Fig. 1.   Comparison between calculated results and experimental data of binary systems at 1473 K
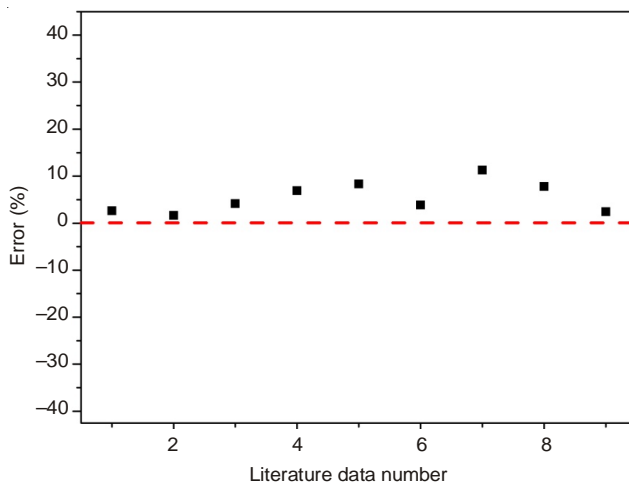

Fig. 3.   Errors between the calculated results and experimental values for binary systems at 1473 K
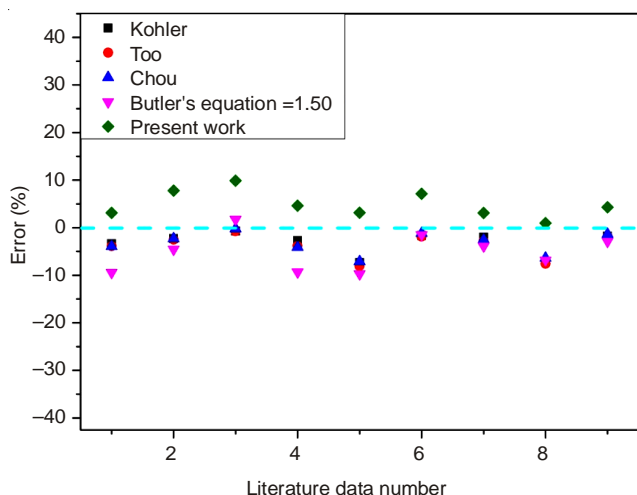
Fig. 4. Errors between calculated results and experimental values for ternary systems at 1473 K

The average errors of the present model for binary and ternary systems are 5.44 and 5.02 %, respectively, showing that the evaluated surface tensions based on the present model are in good agreement with the experimental values.

The comparison of the various prediction models for the Ni_3S_2-FeS-Cu_2S ternary system has been investigated, as shown in Fig. 4. As mentioned above, the predicted values based on the present model are positive deviation because that the contribution from excess Gibbs energy terms is neglected. However, the calculated results of Kohler, Toop, Chou geometric models[5] and the Butler's equation (β = 1.50) are all smaller than the experimental values and the reason maybe result from the error of the evaluation model for the excess Gibbs free energy. The average error of each model is listed in Table-4. Taking account of experimental accuracy ± 2.5 %, the calculated results agree with the experimental data and there is no obvious difference among the used models.

TABLE-4
AVERAGE ERROR OF EACH MODEL
FOR TERNARY SYSTEM AT 1673 K (%)

Model	Kohler	Toop	Chou	Butler's equation (β = 1.50)	Present work
Average error	3.21	3.67	3.22	5.54	5.02

However, the Kohler, Toop, Chou and Butler's equation cannot be used in the case of the absence of the excess Gibbs free energy. But the present model get rid of the limitation of the excess Gibbs free energy and its influencing factors are the variations of molar volumes and surface tensions for pure oxides with temperature (Table-5). The temperature dependence of molar volumes are calculated according to the linear relation of the density and the temperature dependence of surface tensions are calculated by the linear regression (Fig. 5) according to the least square method.

A thermodynamic model for determining the surface tension by considering the surface tension and molar volume of the pure oxide components and their ionic radii was extended to the molten mattes bearing Ni_3S_2, FeS, Cu_2S. The iso-surface tension curves of the Ni_3S_2-FeS-Cu_2S ternary molten matte system has been calculated based on the present model. The

TABLE-5
TEMPERATURE DEPENDENCE OF MOLAR
VOLUMES AND SURFACE TENSIONS OF THE PURE SULFIDES

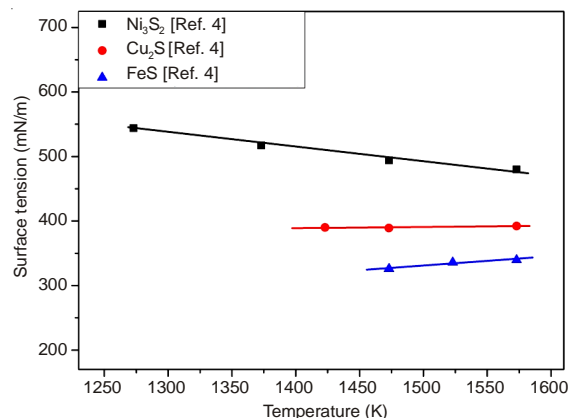| Sulfide	Density (g/cm^3)	Molar volume (cm^3/mol)	Surface tension (mN/m)
FeS	$5.435-1.1T(K)\times10^{-3}$	$88/(5.435-1.1T(K)\times10^{-3})$	$127+0.136T(K)$
Ni_3S_2	$6.144-5.4T(K)\times10^{-4}$	$241/(6.144-5.4T(K)\times10^{-4})$	$815-0.215T(K)$
Cu_2S	$6.075-6.6T(K)\times10^{-4}$	$160/(6.075-6.6T(K)\times10^{-4})$	$367+0.0157T(K)$

Fig. 5. Surface tensions for pure sulfides

average errors of the present model for binary and ternary systems are 5.44 and 5.02 %, respectively, showing that the evaluated surface tensions based on the present model are in good agreement with the experimental values.

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