Surface Properties of Liquid Alloys & Molten Slag

Toshihiro TANAKA

Div. Materials and Manufacturing Science, Osaka University, Suita, Osaka 565-0871, Japan

Abstract: Surface property of liquid alloys and molten ionic mixtures such as molten slag is one of the important physico-chemical properties directly related to various surface phenomena in metallurgical processing. Although there have been so far a lot of information on the surface properties of alloys and oxides *etc.*, a prediction of physico-chemical properties are quite important to design a new materials processing. The authors have tried to develop a system to predict various physico-chemical properties such as surface tension and viscosity on the basis of thermodynamic databases, which are usually used to calculate phase equilibria, chemical reactions and so on. The simultaneous evaluation of those various properties is quite significant to investigate complicated phenomena at high temperature material processing. We have already derived various models to predict surface properties of liquid alloys and molten ionic mixtures, such as surface tension of liquid metals and alloys, the effect of oxygen on surface tension of liquid metals, surface tension of molten ionic mixtures and interfacial tension between liquid steel and molten slag, the effect of particle size on nano-sized alloy phase diagrams. In the present paper, we summarize our trials to evaluate various surface properties of alloys and slag *etc.*, and mainly describe our recent models to predict the surface tension of molten slag.

Key words: surface tension, interfacial tension, thermodynamics, steel, molten slag

1. Introduction

Surface property of liquid alloys and molten slag is one of the important physico-chemical properties to investigate various surface phenomena in metallurgical processing, such as

- Wetting of liquid steel and molten slag with refractory and non-metallic inclusions

- Stability of interface between molten flux and liquid steel in CC mold

- Effect of oxygen adsorption on liquid steel surface causing Marangoni flow along the surface

Since those phenomena are related to surface properties, such as surface tension of melts, interfacial energy, wettability and contact angle, there have been accumulated a lot of experimental data and some estimation models have been reported on those properties so far. We have not, however, understood yet completely the followings :

Key factors determining

* change in surface tension of multi-component alloys by adsorption of oxygen

* wettability of liquid alloys with oxides, nitrides, sulphides *etc.*

* interfacial energy between solid/liquid phases in alloys

* dynamic change of interfacial energy between liquid steel and molten slag by chemical reactions *etc.*

If we could understand the phenomena listed above, it would give us big benefits to design an advanced metallurgical processing. The authors have tried to develop a system to predict various physico-chemical properties such as surface tension and viscosity on the basis of thermodynamic databases, which are usually used to calculate phase equilibria, chemical reactions and so on, as shown in Fig.1.
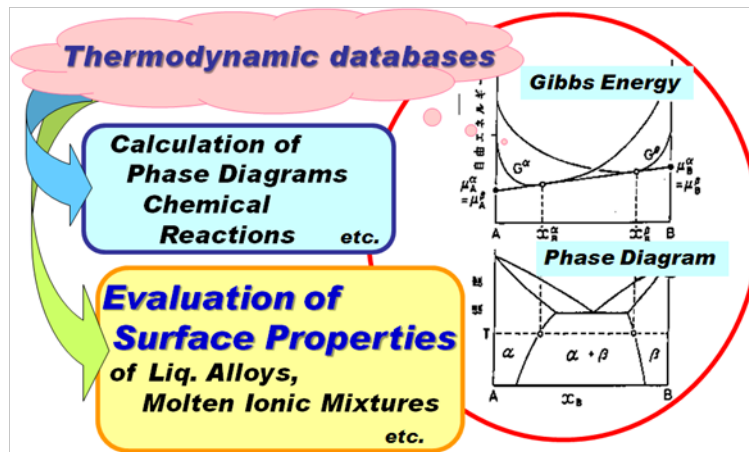

Figure 1   Concept of a prediction system using thermodynamic databases.

The simultaneous evaluation of those various properties is quite significant to investigate complicated phenomena at high temperature material processing[1-3]. In particular, we recently developed a new calculation procedure based on "Constrained Gibbs energy minimizer method" to evaluate the surface tension of multi-component alloy systems directly from thermodynamic databases with some additional physical properties[3]. As one of the examples on the combination of the surface properties prediction with phase equilibria calculation, we calculated phase diagrams in nano-sized alloys by considering the effect of the surface properties on phase equilibria[4-8]. Thus, although we can now evaluate some surface properties of liquid metals and alloys[1-3,9,10], we have still some difficulties to evaluate the surface properties of molten ionic mixtures and molten slag[11-13].   In addition to those problems, we have not understood completely yet what key factors determine an interfacial energy or interfacial tension among various materials at high temperature.   In particular, when we try to cope with the unsolved subjects listed above, we need to investigate deeply the interfacial free energy for solid-liquid interface in alloys and alloys-oxide interface *etc.* However, even if we focus on the interfacial tension between liquid steel and molten slag, it is difficult to predict precisely the surface tension of molten slag in multi-component systems, which is indispensable information to analyze the interfacial tension between liquid iron alloys and molten oxides.   From our investigations on these subjects for several years, we have found that we need additional information on ionic radii to evaluate the surface tension of molten ionic mixtures and molten slag[13]. In this paper, we summarize our trials to evaluate various surface properties of liquid alloys and molten slag, and mainly describe our recent models to predict the surface tension of molten slag.

2. Models for prediction of surface properties

The authors have derived various models for the prediction of surface properties of liquid metals / alloys and molten ionic mixtures so far.   Some examples are listed as follows :

* Surface tension of liquid metals and alloys : Refs.[1-3,9,10]

* Effect of oxygen on surface tension of liquid metals : Refs.[14]

* Surface tension of molten ionic mixtures and molten slag : Refs.[11-13,15-18]

* Interfacial tension between liquid steel and molten slag : Refs.[19]

* Effect of particle size on nano-sized alloy phase diagrams : Refs.[4-8]

As described in the references in the above list, we can now evaluate the surface tension of liquid metals and alloys, but it is still difficult to predict precisely the surface tension of liquid ionic mixtures and molten slag in multi-component systems. The authors have tried to make a model to predict the surface tension of molten silicate slag by thermodynamic models and neural network approach[18].   In the present paper, the outline of the thermodynamic models especially for liquid alloys and molten slag are summarized with some results in the following sections.

3. Evaluation of Surface Tension of Alloys

The surface tension σ of liquid A-B binary alloy is evaluated from the following equations (1)-(2) based on Butler's equation[20]:

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{N_A^S}{N_A^B} + \frac{1}{A_A} \left\{ G_A^{E,S}\left(T, N_B^S\right) - G_A^{E,B}\left(T, N_B^B\right) \right\} \tag{1}$$

$$\sigma = \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \left\{ G_B^{E,S}\left(T, N_B^S\right) - G_B^{E,B}\left(T, N_B^B\right) \right\} \tag{2}$$

where R : the gas constant, T: temperature, σ_X : surface tension of pure X (X=A or B), A_X=1.091$N_0^{1/3}V_X^{2/3}$: molar surface area in a monolayer of pure X (N_0 : Avogadro number, V_X : molar volume of pure liquid X.). N_X^S and N_X^B: mole fractions of a component X in a surface and a bulk, respectively. $G_X^{E,S}(T,N_X^S)$ and $G_X^{E,B}(T,N_X^B)$: partial excess Gibbs energies of X in the surface and the bulk as a function of T and N_X^S or N_X^B.

The partial excess Gibbs energies in the bulk can be obtained directly from thermodynamic databases.   The excess Gibbs energy in the surface is evaluated from the following equation (3) on the basis of the idea proposed by Speiser et al.[21,22]:

$$G_X^{E,S}\left(T, N_B^S\right) = \beta^{MIX} \cdot G_X^{E,B}\left(T, N_B^S\right) \qquad \text{where} \quad \beta^{MIX} = \frac{\left(Z^S\right)}{Z^B} = 0.83 \tag{3}$$

The procedure to obtain the surface tension σ of liquid alloys is described in detail in Refs.[1,9].   The calculated results of the surface tensions of liquid Fe-Si and Cu-Fe alloys are shown in Fig.2.   As can be seen in the figures, the calculated results of the surface tension in these alloys are in good agreement with the experimental values (See Refs.[10]).
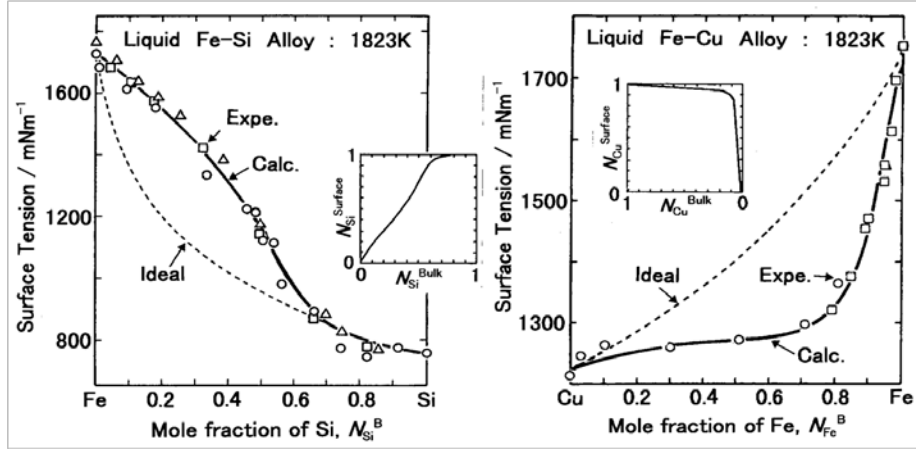
Figure 2　Surface tension of liquid Fe-Si and Cu-Fe alloys

4. Evaluation of Surface Tension of Molten Ionic Mixtures

At the present stage, we can evaluate the surface tension of alloys by using Butler's equation[20] with a procedure proposed by Speiser et al. [21,22].　On the other hand, we can not apply directly these procedures to evaluate the surface tension of molten ionic mixtures even in alkaline-halide binary systems, which are the simplest groups in molten ionic mixtures.

The authors have derived the equations (4) - (6) described below on the basis of the following assumptions: In ionic substances, it is well known that their ionic structures depend upon the ratio of the radius of cation to that of anion[13].　In order to evaluate ionic structure and physico-chemical properties of ionic materials, we should consider the ratio of the radius of cation to that of anion.　We use the ionic radius fraction considering the ratio of the radius of cation to that of anion instead of mole fractions.　Then, we have derived the following equations to evaluate the surface tension σ of molten ionic mixtures :

$$\sigma = \sigma_{AX}^{Pure} + \frac{RT}{A_{AX}} \ln \frac{M_{AX}^{Surf}}{M_{AX}^{Bulk}} \qquad (4)$$

$$\sigma = \sigma_{BY}^{Pure} + \frac{RT}{A_{BY}} \ln \frac{M_{BY}^{Surf}}{M_{BY}^{Bulk}} \qquad (5)$$

Here, $M_{AX}^{P} = \dfrac{(R_A / R_X) \cdot N_{AX}^{P}}{(R_A / R_X) \cdot N_{AX}^{P} + (R_B / R_Y) \cdot N_{BY}^{P}}$ and $M_{BY}^{P} = \dfrac{(R_B / R_Y) \cdot N_{BY}^{P}}{(R_A / R_X) \cdot N_{AX}^{P} + (R_B / R_Y) \cdot N_{BY}^{P}}$ (6)

In the above equations, subscripts A and B are cations, and X and Y are anions.　Superscripts *Surf* or *Bulk* indicate the surface and the bulk.　R_A and R_B are the radius of cations, and R_X and R_Y are the radius of anions.　The information on the radius of ions can be obtained from the compilation by Shannon [23,24].　$A_i = N_0^{1/3} V_i^{2/3}$ (N_0 : Avogadro's number, V_i : molar volume of pure component i) is the molar surface area of pure component i.

The calculated results of the surface tension in some alkaline-halide ionic mixtures obtained from Eqs. (4) - (6) are shown in Fig.3 with the previous calculated results[5-7]. As shown in Fig.3, the calculated results (solid curves) agree well with the experimental values (■)[25]. The previous calculated results were obtained by applying Eqs.(1)-(3) with $\beta^{MIX} = 0.94$ to molten ionic mixtures. In addition, the model reproduces the characteristics of the composition dependence quite well in common ionic mixtures. That is to say, their composition dependence of the experimental surface tension shows almost linear change in common cation systems. On the other hand, common anion systems have concave feature in the composition dependence.
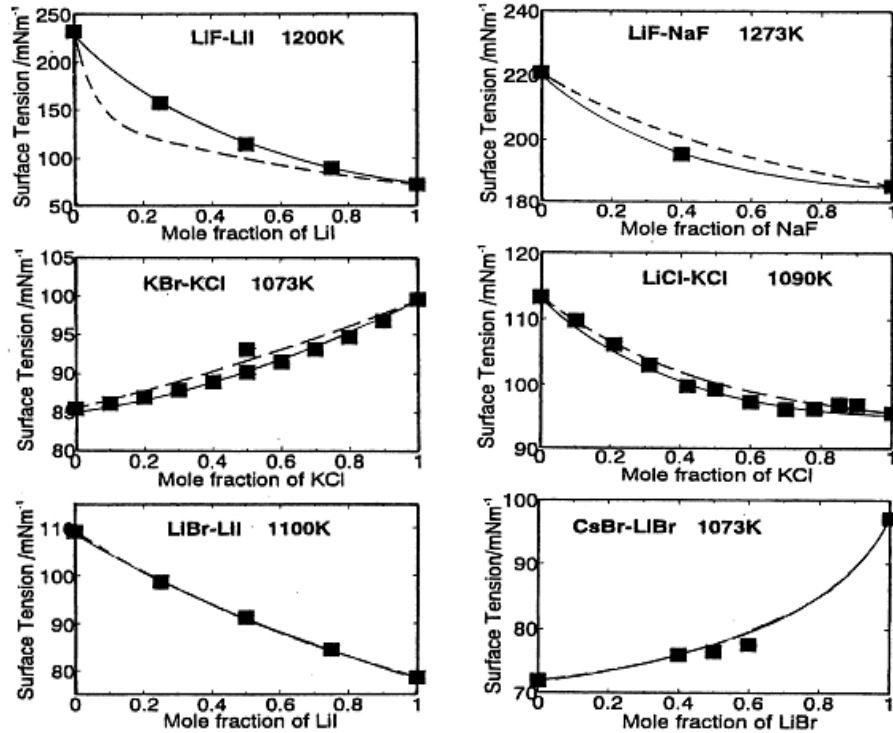
Figure 3   Surface tension of molten alkaline-halide systems.
(Solid curves: Present Calc.; Dashed Curves : Previous Calc.[11]; :Expe.[25])

5.   **Evaluation of Surface Tension of Molten SiO$_2$ based Slag**

In this section, we have extended the above model derived for molten ionic mixtures to molten SiO$_2$ based slags. Since the complex ion SiO$_4^{4-}$ exits in molten SiO$_2$ systems, we assumed that Si^{4+} is cation, and SiO$_4^{4-}$ is anion unit to evaluate the ratio $R = (R_{Anion} / R_{Cation})$ for SiO$_2$.   However, we do not know the value of the ratio of the radius of Si^{4+} ion to that of SiO$_4^{4-}$ ion, which is therefore treated as a parameter.   In addition, when we apply the above equations (4) - (6) to molten slag, we need the information on the surface tension of pure molten oxides, for example, pure liquid CaO at around 1873K because pure CaO exists as solid state at the temperature.   Therefore, it is necessary to treat the surface tension of pure oxide components as another parameter at around 1873K.

We calculated the surface tension of molten SiO$_2$ based slags from Eqs.(4)-(6) with the following assumptions:

1) We assume that the ratio of ionic radius of cation to that of anion for SiO_2 is regarded as the ratio of the radius of Si^{4+} to that of SiO_4^{4-} ($R_{Si^{4+}}/R_{SiO_4^{4-}}$) which was determined to be 0.5 to fit calculated results with experimental values.

2) We determine the surface tension of pure components with high melting point, e.g. CaO by parameter-fitting procedure to reproduce experimental values of the surface tension of molten slag.

Tables 1-3 shows data on radii of cationic and anionic ions, molar volume of pure components and temperature dependences of surface tension for pure oxides[15,16].

Table 1 Radii of cationic and anionic ions (Å).

Si^{4+}	0.42
B^{3+}	0.23
Ca^{2+}	0.99
Na^+	0.97
F^-	1.33
O^{2-}	1.44

Table 2 Molar volume of pure component (m^3/mol).

Oxide	Temperature (K) depedence of molar volume (m^3/mol)
SiO_2	$27.516 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} 10^{-6}$
B_2O_3	$45.8 \{ 1 + 1 \cdot 10^{-4} (T - 723) \} 10^{-6}$
CaF_2	$31.3 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} 10^{-6}$
CaO	$20.7 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} 10^{-6}$
Na_2O	$33.0 \{ 1 + 1 \cdot 10^{-4} (T - 1773) \} 10^{-6}$

Table 3 Temperature dependences of surface tension for pure oxides : [*] NIST[31), [**] Ref.[15], [***] Ref.[16]

Oxide	Temperature dependence (K) of surface tension (mN / m)	
SiO_2[*]	$243.2 + 0.031T$	1773-2073 K
B_2O_3[*]	$37.9 + 0.0354T$	973-1673 K
CaF_2[*]	$1604.6 - 0.72 T$	1670-1880 K
CaO[**]	$791 - 0.0935 T$	1573 - 1873 K
Na_2O[***]	$438 - 0.116 T$	873 - 1863 K

The calculated results of molten SiO_2 based slag[15] is shown in Fig.4 with the experimental values (see Ref.[15]).
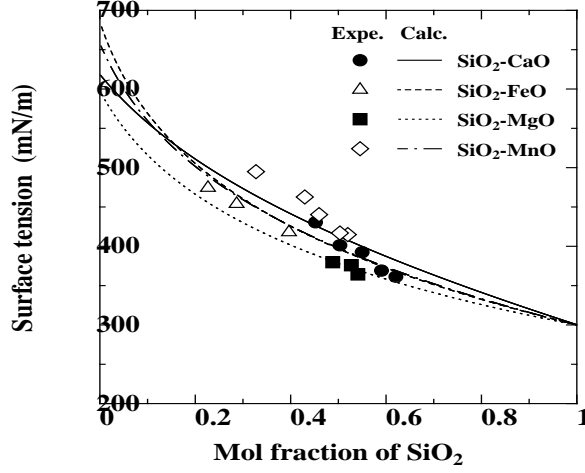

Figure 4   Surface tension of molten SiO_2 based binary slag.

Expe. : see Ref.[15]

As shown in Fig.4, we found that we can evaluate the surface tension of various molten SiO_2 based slag from Eqs. (4) - (6) although we need to select the values of $R = (R_{Anion}/R_{Cation})$ for SiO_2 and the surface tension of pure molten oxides. The above equations (4) - (6) can be easily extended to ternary or multi-component systems as follows:

$$\sigma = \sigma_{AX}^{Pure} + \frac{RT}{A_{AX}} \ln \frac{M_{AX}^{Surf}}{M_{AX}^{Bulk}} \qquad (7)$$

$$\sigma = \sigma_{BY}^{Pure} + \frac{RT}{A_{BY}} \ln \frac{M_{BY}^{Surf}}{M_{BY}^{Bulk}} \qquad (8)$$

$$\sigma = \sigma_{CY}^{Pure} + \frac{RT}{A_{CY}} \ln \frac{M_{CY}^{Surf}}{M_{CY}^{Bulk}} \qquad (9)$$

Here $\quad M_{AX}^{P} = \dfrac{(R_A/R_X) \cdot N_{AX}^{P}}{(R_A/R_X) \cdot N_{AX}^{P} + (R_B/R_Y) \cdot N_{BY}^{P} + (R_C/R_Z) \cdot N_{CZ}^{P}} \qquad (8)$

$$M_{BY}^{P} = \frac{(R_B/R_Y) \cdot N_{BY}^{P}}{(R_A/R_X) \cdot N_{AX}^{P} + (R_B/R_Y) \cdot N_{BY}^{P} + (R_C/R_Z) \cdot N_{CZ}^{P}} \qquad (9)$$

$$M_{CZ}^{P} = \frac{(R_C/R_Z) \cdot N_{CZ}^{P}}{(R_A/R_X) \cdot N_{AX}^{P} + (R_B/R_Y) \cdot N_{BY}^{P} + (R_C/R_Z) \cdot N_{CZ}^{P}} \qquad (10)$$

Some calculated results on the surface tension of molten ternary slag systems are shown in Figs.5-10[15,16].
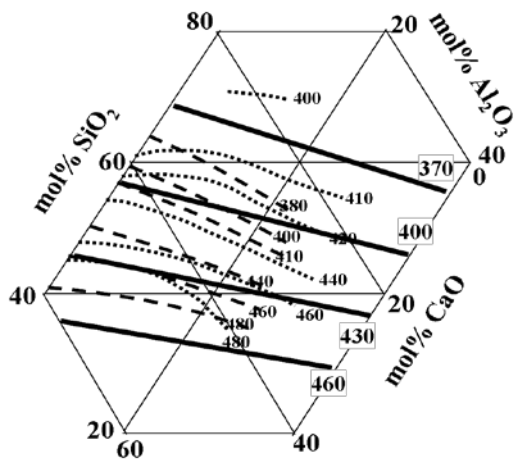
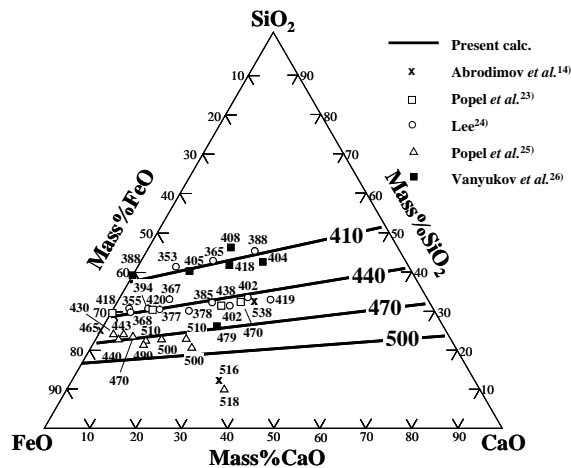Figure 5   Surface tension (mN/m) of molten SiO₂-CaO-Al₂O₃ system at 1673 K.

Figure 6   Surface tension (mN/m) of molten SiO₂-CaO-FeO system at 1673 K. Expe.: Ref.[15]

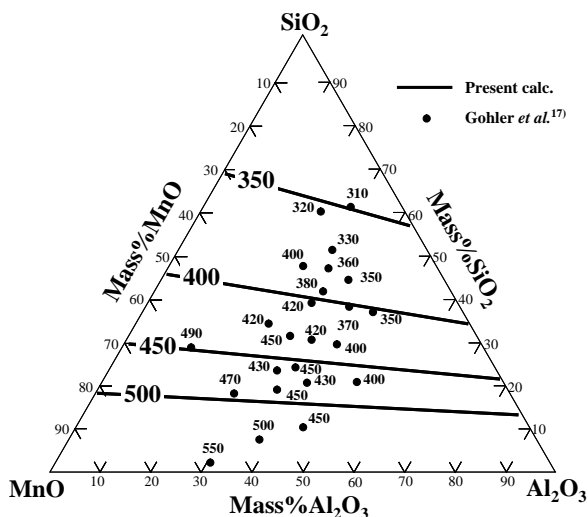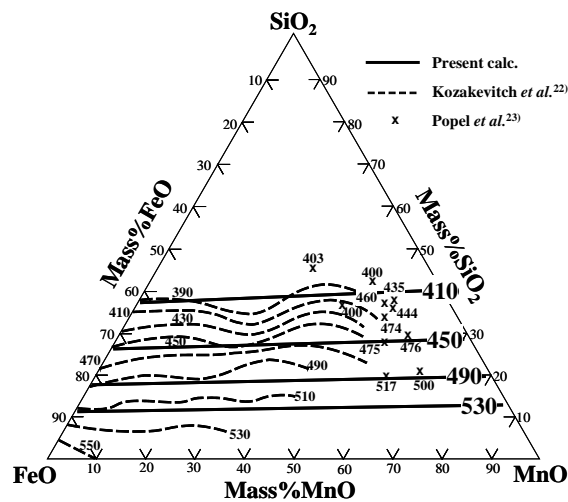Figure 7   Surface tension (mN/m) of molten SiO₂-Al₂O₃-MnO system at 1873 K. Expe. : Ref.[15]

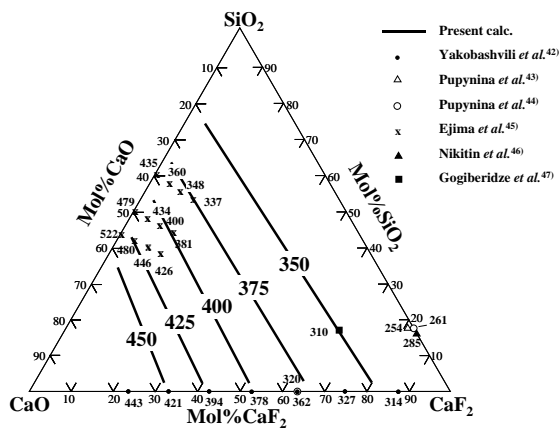Figure 8   Surface tension (mN/m) of molten SiO₂-FeO-MnO system at 1873 K. Expe. : Ref.[15]

Figure 9   Surface tension of molten SiO₂-CaO-CaF₂ system at 1773 K. Expe.:   Ref.[16]
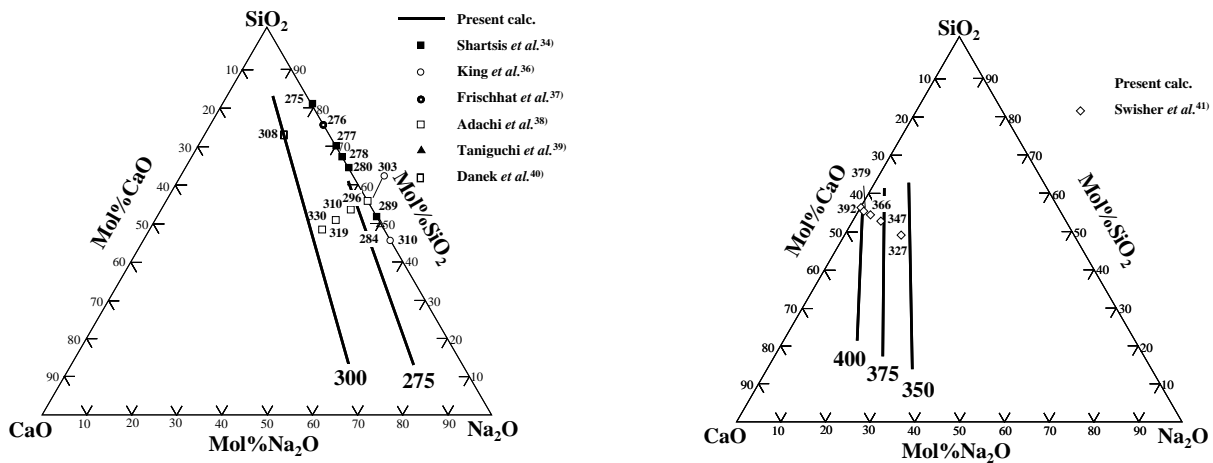
Figure 10   Surface tension of molten SiO$_2$-CaO-Na$_2$O system at (a) 1473 and (b) 1863 K.
Expe. : Ref.[16]

In Figs.4-10, the detail information on the experimental data can be obtained from the references in Refs.[15 & 16]. As shown in Fig.5-10, the calculated results of σ agree with the experimental values although the present model has very simple formula.   However, the present calculated results indicate almost linear dependence of σ on compositions. Therefore, more intensive attention should be paid to revise the model reproducing more clearly composition dependence of the surface tension in multi-component molten slag systems in the future.

6. Concluding Remarks

Some examples have been described on the evaluation of the surface tension of liquid alloys and molten slag. Based on those evaluations, we are now deriving some models to predict interfacial free energy or interfacial tension between solid and liquid phases in alloys as well as between liquid steel and molten slag.   Furthermore, we will extend those approaches to evaluate wettability of liquid alloys with solid compounds such as oxides, nitrides. We are now aiming to apply those evaluations with thermodynamic databases as well as kinetic approach to understand various phenomena related to interfacial reactions among different phases coexisted in metallurgical complex systems.

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