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3 元系合金融体の表面張力の推算

Estimation of the Surface Tension for Molten Fe–Si–Cu Ternary System Alloys

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1. Introduction

Microgravity conditions at the International Space Station (ISS) offer an ideal environment for measuring the surface tension of high-temperature melts. This is because the measurement does not require a container that might chemically react with the sample at elevated temperatures. The measurements are free from any influences such as droplet deformation, gravitational convection, and hydrostatic pressure, which can compromise the accuracy and precision of ground-based measurements. However, the opportunities for measuring the surface tension at the ISS are still limited at present. To enhance the use of the measurement results of the surface tension at the ISS, it is important to develop an estimation model for the surface tension of high-temperature melts. The accurate and precise measurement results of surface tension for liquid pure metals at the ISS can serve as parameters for the model, while those for molten alloys can be used as benchmark data for the model.

In this study, the surface tension of molten binary Fe–Si and ternary Fe–Si–Cu alloys was calculated using the Butler model[1)], which often provides a comparatively accurate representation of the surface tension of molten binary alloys. The calculated results were then compared with the surface tension measured by oscillating droplet method using the electromagnetic levitation (EML)[2)]. The purpose of this research was to extend the Butler model for estimating the surface tension of molten ternary alloys and to evaluate the validity of this extended model.

2. Extension of the Butler equation for ternary system alloys

A list of nomenclatures used throughout this study is provided in **Table 1.** The surface tension of a molten multi-component alloy, σ, can be described by the Butler equation as follows,

$$\sigma = \sigma_i^{\mathrm{Pure}} + \frac{RT}{A_i}\ln\frac{n_i^S}{n_i^B} + \frac{G_i^{E.S} - G_i^{E.B}}{A_i} \quad (1)$$

Table 1. nomenclature lists.

Symbol	Definition	Unit
σ	Surface tension of molten multi-component alloys	N·m^{-1}
σ_i^{Pure}	Surface tension of liquid alloy element	N·m^{-1}
T	Temperature	K
R	Gas constant	mol^{-1}
A_i	Molar surface area of alloy element	m^2·mol^{-1}
n_i^S	Moler fraction of alloy element at melt surface	
n_i^B	Moler fraction of alloy element in bulk melt	
$G_i^{E.S}$	Partial excess Gibbs free energy of alloy element at melt surface	J·mol^{-1}
$G_i^{E.B}$	Partial excess Gibbs free energy of alloy element in bulk melt	J·mol^{-1}
V_i	Molar volume of alloy element	m^3·mol^{-1}
N_0	Avogadro number	J·K^{-1} mol^{-1}
β	Coordination numbers between surface and bulk	
L	Interaction parameters used to calculate $G_i^{E.B}$ for alloy	J·mol^{-1}

where the subscript i attached to the symbols represents the alloy element, while the superscripts S and B represent the surface and bulk, respectively. σ_i^{Pure} is the surface tension of liquid alloy element, R is the gas constant, T is the temperature, A_i is the molar surface area of the molten alloy, n_i is the molar fraction of the alloy element, and G^E is the partial excess Gibbs free energy. A_i was deduced from the following equation using the molar volume V_i and the Avogadro number N_0.

$$A_i = 1.091 N_0^{1/3} V_i^{2/3} \tag{2}$$

When assuming that the dependence of temperature and alloy composition on $G_i^{\mathrm{E.S}}$ is the same as that of $G_i^{\mathrm{E.B}}$, as proposed by Speiser et al.[3,4], it can be expressed as follows,

$$G_i^{\mathrm{E.S}} = \beta G_i^{\mathrm{E.B}} \tag{3}$$

where β represents the ratio of coordination number on the surface to that in the bulk for pure substances, taking into account the relaxation of the surface. In this study, we adopted $\beta = 0.83$, which was proposed by Tanaka et al.[5] from the relationship between surface tension of liquid metals and binding energy at the surface.

In a ternary alloy consisting with components labeled as 1, 2 and 3, $G_i^{E.B}$ can be expressed using the Redlich-Kister polynomial as follows,

$$G_i^{E.B} = \sum_{i=1}^{3}\sum_{j>i}^{3}\sum_{m=0}^{M} L_{ij}^m n_i n_j (n_i - n_j)^m + n_1 n_2 n_3 \sum_{i=1}^{3}\sum_{k=0}^{K} L_{123}^k n_i \tag{4}$$

where L is the interaction parameter, subscript j attached to the symbol denotes alloy components, just as i does, and superscripts m and k denote the numbers of interaction parameters determined by the combination of alloy elements. In this study, we used the values of L from Table 2 for the combinations of Fe, Si, and Cu[6-9].

Table 2. Interaction parameter L used in this study to calculate the partial excess Gibbs energy $G_i^{E.B}$ for molten ternary Fe–Cu–Si alloys.

Interaction parameter L [J·mol^{-1}]	Ref.
$L^0_{Fe,Si}$ = -164434.6 + 41.9773 T $L^1_{Fe,Si}$ = -21.523 T $L^2_{Fe,Si}$ = -18821.542 + 22.07 T $L^3_{Fe,Si}$ = 9695.8	6)
$L^0_{Si,Cu}$ = -36835 + 6.92 T $L^1_{Si,Cu}$ = -46727 + 19.94 T $L^2_{Si,Cu}$ = -37886 + 19.27 T	7)
$L^0_{Fe,Cu}$ = 35625.8 - 2.19045 T $L^1_{Fe,Cu}$ = 1529.8 - 1.15291 T $L^2_{Fe,Cu}$ = 12714.4 - 5.18624 T $L^3_{Fe,Cu}$ = -1177.1	8)
$L^0_{Fe,Si,Cu}$ = 19000 - 22.5 T $L^1_{Fe,Si,Cu}$ = 19000 - 22.5 T $L^2_{Fe,Si,Cu}$ = 19000 - 22.5 T	9)

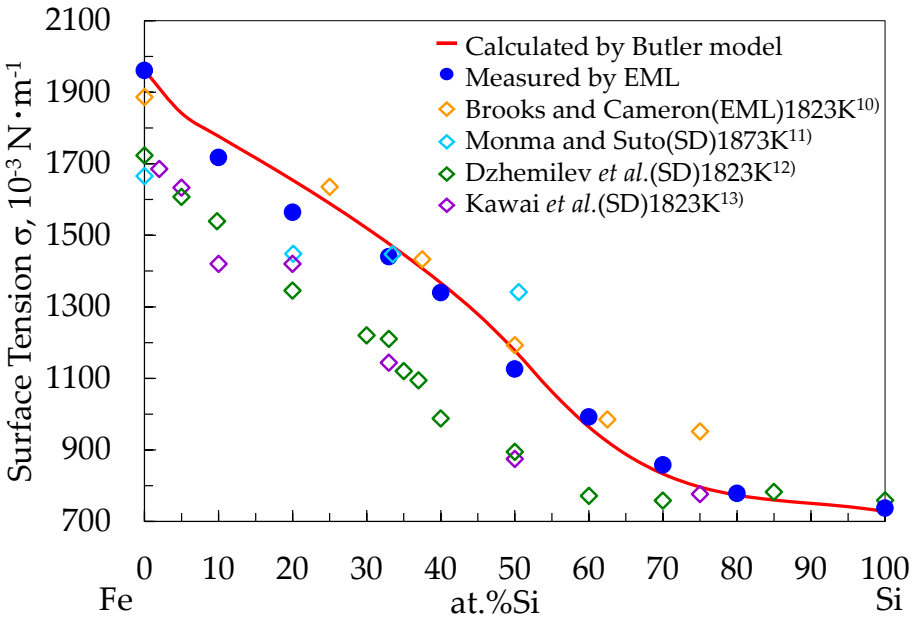

Figure 1. Surface tension of molten Fe–Si alloys at 1850 K calculated by the Butler equation, along with the results by EML. Literature data are also shown for comparison.

3. Results

Figure 1 shows the surface tension of the molten Fe-Si binary alloy at 1850 K as a function of sample composition calculated by the Butler equation, along with the results measured by EML. Literature data are also shown for comparison [10-13]. The calculated surface tension decreases as the silicon composition increases to about 70%, and then nearly plateaus, approaching the value for pure silicon. This behavior is in very good agreement with the experimental results, including our measurements with EML, which are shown as plots.

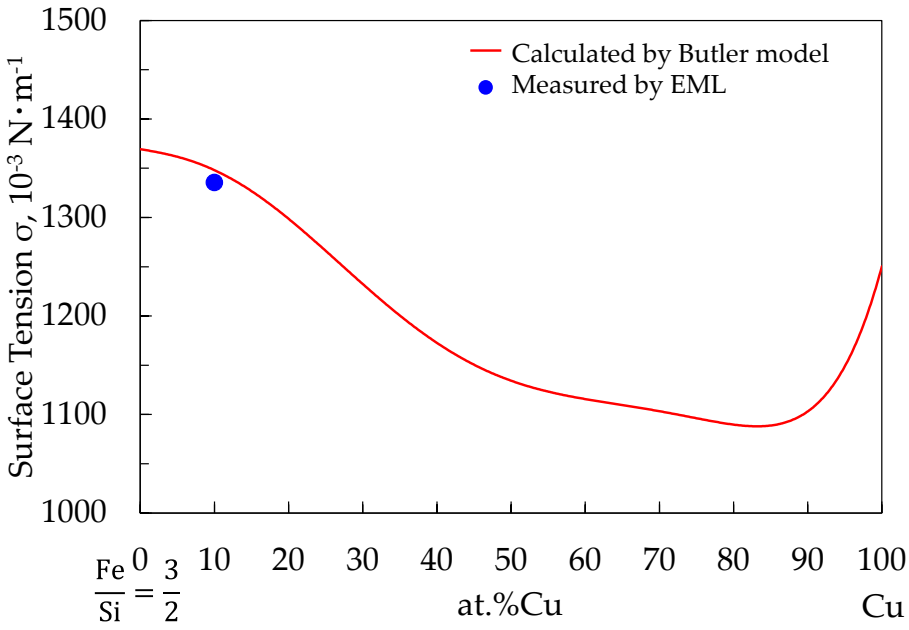

Figure 2. Surface tension of molten Fe-Si-Cu alloys at 1800 K, with a fixed molar ratio of Fe to Si of 3:2, calculated using the extended Butler equation. The measurement result of the alloy with a copper composition of 10at% is also shown.

Since it has been confirmed that the Butler equation expresses the surface tension of molten Fe–Si binary alloys well, we calculated the surface tension of molten Fe–Si–Cu ternary alloys using the extended Butler model. As an example, Fig. 2 displays the calculated result of the alloy at 1800 K in which the molar ratio of Fe to Si is fixed at 3:2. The calculated surface tension decreases as the Cu content is increased to 40at%, followed by a plateau up to about 80at% before a sudden increase. Although the measurement plot, we now have is only one for the alloy with a copper composition of 10at%, it agrees well with the calculated result. Further experimental measurements will confirm the validity of our extended Butler equation for ternary alloys.

4. Summary

Using the Butler equation, we calculated the surface tension of molten Fe–Si binary alloys. We then extended the Butler equation to calculate the surface tension for molten Fe–Si–Cu ternary alloys. The calculated results for these molten alloys align well with measurements obtained using EML.

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