Evaluation of Surface Tension and Adsorption for Liquid Fe–S Alloys

Joonho LEE and Kazuki MORITA

Graduate Student, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan. E-mail: juno@wood2.mm.t.u-tokyo.ac.jp
1) Department of Metallurgy, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan.

(Received on December 11, 2001; accepted in final form on February 16, 2002)

Surface tension of liquid iron is strongly influenced by the adsorption of sulfur. In this study, surface tensions of liquid Fe–S alloys at 1 823 K were measured by the sessile drop technique in a purified argon atmosphere. Experimental results were compared with the model based on Butler’s equations considering the effect of size and interactions of the adsorbed elements assuming that the system was composed of Fe–“FeS” binary. The model could evaluate the surface tension and the adsorption of sulfur more reasonably rather than a simple ideal adsorption model. In the calculations, excess free energy expanded by Margules’ series over the entire composition range of Fe–FeS system was used.

KEY WORDS: surface tension; adsorption of sulfur; Butler’s equation; Margules’ series; sessile drop technique.

1. Introduction

Surface tension of liquid iron is considerably decreased by the adsorption of the surface active elements which are known to be present in large concentrations at a surface. Thus, preferential adsorption of surface active elements at a surface can be predicted by accurate surface tension values. Among the surface active elements, sulfur is one of the most important elements in steelmaking processes. Therefore, it is essential that the surface tension of liquid iron containing sulfur should be evaluated properly.

Usually, the surface tension of liquid iron containing sulfur, \( \sigma \), has been given by the simple ideal adsorption model (so-called Szyszkowski equation) proposed by Belton.\(^1\)

\[ \sigma = \sigma_{Fe} - RT \Gamma^0 S \ln(1 + K_S a_S) \]  

where \( \sigma_{Fe} \), \( \Gamma^0 S \), \( K_S \) and \( a_S \) are surface tension of pure iron, surface adsorption of sulfur at saturation, adsorption coefficient and activity of sulfur with respect to 1 mass% as standard state, respectively. Most of the experimental results of surface tension of liquid iron containing sulfur were expressed as an ideal adsorption isotherm of Eq. (1).\(^2-4\)

However, the derived value of \( K_S \) varies from 185 to 365. Chung and Cramb\(^5\) asserted that surface tension curves may not be very sensitive to values of the adsorption coefficient. Meanwhile, Lupis\(^6\) found that the adsorption of surface active elements such as sulfur in an ideal adsorption model disagrees with the experimental observations which yield a much steeper rise of the adsorption curve. Therefore, it is believed that Eq. (1) is not proper to evaluate the sulfur adsorption on liquid iron.

Recently, attention has been paid to the development of a more general relationship between surface tension and adsorption for liquid iron containing surface active elements. Bernard and Lupis\(^7\) indicated that differences in size of the adsorbed elements and interactions between them cause deviations of experimental results from an ideal adsorption behavior, and Eq. (1) is only valid near the saturation stage, since adsorbed elements may exclude adjacent sites from occupancy. Belton\(^8\) developed a two-step isotherm model, which considers repulsive interactions between surface active elements on liquid iron. However, the surface tension values obtained by the two-step model are indistinguishable from those by the ideal adsorption model,\(^1\) because he used reported values scattered by more than 0.2 N/m. By some other groups, there have been several attempts to explain the surface tension of liquid iron containing surface active elements based on Butler’s equations, considering the equilibrium between a bulk phase and a monolayer at the surface. Tanaka and Hara\(^9\) calculated the surface tension of liquid Fe–O alloys with a regular solution model. In their calculations, the alloy was regarded as a Fe–“FeO” system. Likewise, Hajra\(^9\) et al. calculated the surface tension of molten Fe–S alloy regarding the alloy as a Fe–“FeS” system. They assumed that the system follows a sub-regular model. These previous models\(^8,9\) agreed with the experimental results within \( \pm 0.2 \) N/m. They, however, ignored interactions or extrapolated thermodynamic data of interactions for dilute solutions to high content regions, although the surface may be highly occupied by sulfur and oxygen.

Recently, Hajra and Divakar\(^10\) have explained the surface tension of the liquid Fe–S–O system based on the modified Butler’s equations. However, this model still uses the first order interaction coefficients of dilute solutions. Accordingly, in order to evaluate surface tension and adsorption of sulfur for Fe–S alloys more accurately, it is necessary to de-
termine a moderate excess free energy equation across the composition range.

In this paper, surface tensions of Fe–S alloys were measured using the sessile drop technique. At the same time, a thermodynamic model calculation of surface tensions for Fe–S alloys based on Butler’s equations was presented. By comparing the model calculation with the experimental results, the surface adsorption of sulfur on liquid iron could be deduced.

2. Theory

2.1. Butler’s Equation

Butler’s equations for A–B binary system can be expressed as

\[ \sigma = \sigma_A^p + \frac{RT}{S_A} \ln \left( \frac{1 - X_B^i}{1 - X_B} \right) \]

\[ + \frac{1}{S_A} \left( G_A^{\text{ex}}(T, X_B^i) - G_A^{\text{ex}}(T, X_B) \right) \]

\[ = \sigma_B^p + \frac{RT}{S_B} \ln \left( \frac{X_B^i}{X_B} \right) \]

\[ + \frac{1}{S_B} \left( G_B^{\text{ex}}(T, X_B^i) - G_B^{\text{ex}}(T, X_B) \right) \]............(2)

where \( R, T, \sigma, S_B \) are the gas constant, the absolute temperature, the surface tension and molar surface area of the pure element \( i \), respectively. \( G_A^{\text{ex}}(T, X_B^i) \) is the partial excess free energy of \( i \) in the surface as a function of \( T \) and \( X_B^i \) (the mole fraction of \( i \) in the surface). \( G_B^{\text{ex}}(T, X_B^i) \) is the partial excess free energy of \( i \) in the bulk as a function of \( T \) and \( X_B^i \) (the mole fraction of \( i \) in the bulk). \( S_A \) is calculated from the molar volume \( V \) on the assumption that the elements occupy a close-packed configuration in a monolayer.\(^5\) \((i = A \text{ or } B)\)

\[ S_A = 1.091 \cdot N_A^{\frac{1}{3}} V_i^{\frac{2}{3}} \].................(3)

where \( N_A \) is Avogadro’s number. Thus, in calculations based on Butler’s equations, it is necessary to know the surface tension and density of each component element of pure state and the excess free energy between the component elements. However, if B is a surface active element such as sulfur, it is impossible to determine physical properties such as surface tension and density of the component B at such high temperatures. Hence, such system can be regarded as A–AB pseudo binary one.\(^8\)\(^9\)

3. Experimental

The sessile-drop method was employed in the present investigation. This technique proved to be one of the most popular techniques to determine surface tension of molten metals after Bashforth and Adams empirical equation.\(^12\) Recently, Jimbo et al.\(^13\) have developed more accurate way of non-subjective and numerical determination of surface tension.

The experimental apparatus is shown in Fig. 1. A SiC heating element furnace was used in this study. The alloy samples on a high purity (99.95 mass%) alumina boat with an alumina cover were placed at the center of a mullite reaction tube. (I.D.: 0.040 m, O.D.: 0.050 m) The samples were prepared with high purity electrolytic iron (see Table 1) and FeS (99.9 mass%), and concentrations of oxygen and sulfur in the samples were analyzed by LECO analyzers after experiments. The temperature was well adjusted by PID controller with a Pt–30%Rh/Pt–6%Rh thermocouple located by the heating element, which was preliminarily calibrated by the temperature of the exact position where a liquid droplet was settled.

The experimental procedure was as follows. Cubes of alloy samples weighing about 1–2 g were ground on edges and corners and polished on faces with a grinder, then washed in acetone by a ultrasonic cleaner and dried before being placed on ceramic substrates. Al₂O₃ (or graphite for FeS) was used as a substrate in order to prevent the reaction of the molten alloy with the substrate. Contamination from substrates was negligible in this study. After the specimen assembly was settled at the center of the furnace, the reaction chamber was sealed and evacuated, and then purified Ar gas was introduced at a flow rate of 0.3 l/min STP. Then, the system was heated to the experimental temperature (1823 K). Once the sample was melted, measurements of surface tensions were started.

The shape of the sessile drop of the liquid alloy on the ceramic substrate was monitored by a digital video camera for 30–60 min. Several selected still images then could be directly converted into image files. The digitized dots were used to calculate the surface tension with a computer program that has been developed by Jimbo et al.\(^13\)

4. Results and Discussion

4.1. Surface Tension of Fe–S

The experimental results of the surface tension for Fe–S alloy were the same or slightly higher than the reported values measured by the sessile drop technique. In Fig. 2, the experimental and reported results were shown as a function of sulfur content for comparison. Data after Kozakevitch\(^14\)
and Dyson \textit{et al.}\textsuperscript{15}) showed relatively lower values even for pure iron as 1.788 and 1.754 N/m, respectively. Samples of Halden \textit{et al.}\textsuperscript{17}) contained oxygen from 0.0006 to 0.3 mass\%. Among the reported values, those of Keene \textit{et al.}\textsuperscript{18}) are noticeable. They measured the surface tension of Fe–S alloys using a levitation technique at 1 923 K, which eliminated the possibility of contamination by substrates. In Fig. 2, only selected data of Keene \textit{et al.} containing less than 0.005 mass\% of oxygen were presented. It is expected that in a lower sulfur content region the surface tension at 1 923 K is lower than that of 1 823 K, whereas in a higher sulfur content region that of 1 923 K is higher, because temperature coefficient of surface tension (d\(\sigma\)/dT) changes from negative to positive by increasing sulfur content.\textsuperscript{19)} However, even in a lower sulfur content region, the surface tension values of Keene \textit{et al.} showed higher values than other experimental data. In the present investigation, oxygen remained constant at 60 ppm. Therefore, it is considered that the reported values using the sessile drop technique may contain more than 60 ppm of oxygen.

Effect of oxygen on the surface tension of Fe–S alloys can be considered, if we assume the effects of both sulfur and oxygen on the surface tension in the manner of Ogino \textit{et al.}\textsuperscript{20}) Ogino suggested the following equation for the surface tension of Fe–O–S alloys.

\begin{equation}
\sigma=\sigma_0 - R T \Gamma_0^O \ln(1+K_O a_O) - R T \Gamma_0^S \ln(1+K_S a_S) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
4.2. Thermodynamic Model Calculation

In order to evaluate the sulfur adsorption on liquid iron, a proper thermodynamic model that reasonably describes the resulting surface tension for the Fe–S system is required. In the model calculation of the present study, Fe–S system was regarded as Fe–"FeS" system based on Butler’s equations. Each parameter was introduced as follows.

4.2.1. Physical Properties of Pure Elements

The accurate values of density and surface tension for Fe and FeS are assessed as follows. There are a number of studies on the surface tension of pure iron. In order to avoid oxygen contamination by ceramic substrates, some investigators have used the levitation technique. Using this technique, Kasama et al.21), Lee et al.23) and Brooks24) have reported the surface tension of pure iron at 1 823 K as 1.913, 1.919 and 1.884 N/m, respectively. In the calculation of this paper, the value of 1.913 N/m was used as the surface tension of pure iron, while the value of 7.10103 kg/m3 at 1 723 K and Elliot 30) found very similar tension range using Margules series.

The density and surface tension of FeS were measured simultaneously in this work using the sessile drop technique. Figure 4 shows the density of FeS as a function of temperature. The density of FeS slightly increases with increasing temperature, which is unusual. Kawai et al.26) Henderson,27) and Schenk et al.28) found very similar temperature dependence of the density of FeO that increases with elevating temperature. In this study, the partial pressure of sulfur was not controlled, and the reason of the increase in the density of FeS with increasing temperature is unclear at present. Nevertheless, the reported values of Kozakevitch29) (4.10103 kg/m3 at 1 723 K) and Elliot30) (3.88103 kg/m3 at 1 473 K) are very close to the present results. Assuming that density data is represented by a linear function of temperature, the density of FeS can be expressed by the following regression equation.

\[ \rho_{\text{FeS}} = 2.26 \times 10^3 + 1.21 T \]  

The results of surface tension of FeS are shown as a function of temperature in Fig. 5.

\[ \sigma_{\text{FeS}} = 0.650 - 0.155 \times 10^{-3} T \]  

The data of this study is slightly higher than that of other researchers.31–33) Considering that the surface tension of pure materials generally decreases by increasing temperature, the negative temperature dependence of the present results seems to be reasonable.

4.2.2. Excess Free Energy

Chipman34) calculated the excess free energies of the Fe–"FeS" system from the phase diagram of the Fe–S system. He had taken the data of \( \gamma_{\text{Fe}} \) from the phase diagram (pure liquid iron was taken as the standard state) and calculated \( \gamma_{\text{FeS}} \) by Gibbs–Duhem equation. In the present work, through a similar but more general way, the values of \( \gamma_{\text{Fe}} \) and \( \gamma_{\text{FeS}} \) could be calculated at 1 823 K across the composition range using Margules series.

\[ \ln \gamma_{\text{Fe}} = \alpha_{1}X_{\text{Fe}} + \frac{1}{2}\alpha_{2}X_{\text{Fe}}^{2} + \frac{1}{3}\alpha_{3}X_{\text{Fe}}^{3} + \frac{1}{4}\alpha_{4}X_{\text{Fe}}^{4} + \cdots \]  

\[ \ln \gamma_{\text{FeS}} = \beta_{1}X_{\text{Fe}} + \frac{1}{2}\beta_{2}X_{\text{Fe}}^{2} + \frac{1}{3}\beta_{3}X_{\text{Fe}}^{3} + \frac{1}{4}\beta_{4}X_{\text{Fe}}^{4} + \cdots \]  

Applying Gibbs–Duhem equation with ignoring coefficients \( \alpha_{i}'s \) and \( \beta_{i}'s \) higher than \( i=4 \), one can obtain \( \alpha_{1} \) and \( \beta_{1} \) as zero, and Eqs. (8) and (9) can be rewritten by Eqs. (8-1) and (9-1).

\[ \frac{\ln \gamma_{\text{FeS}}}{(1-X_{\text{Fe}})^2} = \frac{1}{2}\alpha_{2} + \frac{1}{3}\alpha_{3}X_{\text{Fe}} + \frac{1}{4}\alpha_{4}X_{\text{Fe}}^{2} \cdots \]  

\[ \frac{\ln \gamma_{\text{FeS}}}{(1-X_{\text{Fe}})^2} = \frac{1}{2}\beta_{2} + \frac{1}{3}\beta_{3}X_{\text{Fe}} + \frac{1}{4}\beta_{4}X_{\text{Fe}}^{2} \cdots \]  

In this study, data of \( \gamma_{\text{Fe}} \) were taken from the phase diagram35) with the same manner as Chipman34) (Table 2). Then, In \( \gamma_{\text{Fe}}/(1-X_{\text{Fe}})^2 \) can be plotted as a function of \( X_{\text{Fe}} \) at 1 823 K as shown in Fig. 6. These values could be expressed by a second order equation graphically, yielding

![Fig. 4. Effect of temperature on the density of FeS.](image1)

![Fig. 5. Variation of the surface tension of FeS with temperature.](image2)
The error of this fitting is within \( 0.2\% \) across almost the entire concentration region. Then we can decide the each value of \( a_2 \), \( a_3 \) and \( a_4 \). From Eq. (10), the following equation is obtained by Gibbs–Duhem equation.

\[
\frac{\ln \gamma_{Fe}}{(1 - X_{Fe})^2} = 3.79 - 5.19 X_{FeS} + 2.53 X_{FeS}^2 \quad \cdots \cdots \cdots \cdots (10)
\]

The error of this fitting is within \( \pm 0.2\% \) across almost the entire concentration region. Then we can decide the each value of \( \alpha_{Fe}, \alpha_{s} \) and \( \alpha_{t} \). From Eq. (10), the following equation is obtained by Gibbs–Duhem equation.

\[
\frac{\ln \gamma_{FeS}}{(1 - X_{FeS})^2} = 1.07 - 1.56 X_{Fe} + 2.53 X_{Fe}^2 \quad \cdots \cdots \cdots \cdots (11)
\]

From Eq. (11), we could obtain the \( \gamma_{FeS}^{eq} \) by inserting \( X_{Fe} \rightarrow 0 \). Then the value of \( \gamma_{FeS}^{eq} \) was obtained as \( 2.04 \) at 1823 K. Chipman \(^{34}\) has obtained the value of \( \gamma_{FeS}^{eq} \) as 1.95 and 2.14 at 1873 K and 1773 K respectively by both experiments and calculations, with which our value was in reasonable accord. Then, we can also deduce the excess free energy as Eq. (12) based on the three parameters equation suggested by Lupis. \(^{5}\)

\[
G_{FeS}^{ex} = X_{Fe} X_{FeS} (31X_{Fe} - 17 X_{FeS} - 13 X_{FeS} X_{FeS}) \quad (kJ/mol)
\]

It is likely that elements having mutual interactions in a bulk phase also show interactions with each other at a surface. Assuming that the coordination number of each element (Fe or FeS) has the same value, and the net bonding energies in the surface have the same concentration dependence as those in the bulk phase, the partial excess free energy ratio between the surface and the bulk phase is determined only by the coordination number ratio \( \beta = Z_s/Z_b \) as Eq. (13).

\[
\bar{G}_{i}^{ex}(T, X_i) = \beta \cdot \bar{G}_{i}^{ex}(T, X_i) \quad \cdots \cdots \cdots \cdots (13)
\]

Note that for \( \beta = 0 \) Eq. (13) yields an ideal adsorption model. For \( \beta = 1 \), interactions between adsorbed elements are equal to those in the bulk phase. In calculations for a non-ideal adsorption model, the value of \( \beta \) was suggested as 1/2–1 by many researchers. \(^{5,11,36,37}\) Figure 7 shows the effect of the value of \( \beta \) on the surface tension of liquid Fe–S alloy at 1823 K.

![Figure 7. Effect of the value of \( \beta \) on the surface tension of liquid Fe–S alloy at 1823K.](image)

<table>
<thead>
<tr>
<th>Components</th>
<th>( \sigma ) (N/m)</th>
<th>( S ) ( 10^{-3} ) (m(^2)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1913</td>
<td>3.64</td>
</tr>
<tr>
<td>FeS</td>
<td>367</td>
<td>6.98</td>
</tr>
</tbody>
</table>

Fig. 6. Plot of ln \( \gamma_{i}/(1-X_i)^2 \) as a function of \( X_i \) for the graphical determination of polynomials across the composition range at 1823 K.

Fig. 7. Effect of the value of \( \beta \) on the surface tension of liquid Fe–S alloy at 1823K.
excluding the effect of oxygen. The non-ideal adsorption model is in reasonable accordance with the experimental results. It is believed that the slight difference between the non-ideal model and experimental results may be caused by the simple assumption of Ogino et al.\textsuperscript{20} The non-ideal adsorption curve shows higher values than the ideal adsorption curve especially in the low sulfur concentration region. The difference between these two models appears to be maximum when the sulfur content in the bulk phase is about 0.005 mass%. Similar behaviors were found in the study on Cu–O system by Sasaki\textsuperscript{38} using data of Gallios\textsuperscript{39}

It is noticeable that most of the previous results could be expressed by Szyszkowski equation, which assumed that the molar surface area is constant and atoms adsorbed on the surface have no interactions. Figure 8 shows the difference of the surface tension values between the non-ideal adsorption model ($\beta = 0.83$) and the ideal adsorption models assuming $S = S_0$ or $S = S_{\text{FeS}}$. The surface tension values of the ideal adsorption model assuming $S = S_0$ deviate from the non-ideal adsorption model by 0.466 N/m at most, whereas those assuming $S = S_{\text{FeS}}$ are very close to the non-ideal adsorption model. In the latter case, the surface tension deviates from the non-ideal model less than 0.040 N/m. It is considered that the effect of the change in the molar surface area could be compensated for the change in interactions between the adsorbed elements at the liquid iron surface when $S = S_{\text{FeS}}$. Therefore, it is considered that, assuming that the molar surface area is equal to the surface adsorption of sulfur at saturation, the surface tension can be expressed as a form of Szyszkowski equation. Graphically, we may determine the ideal adsorption coefficient of sulfur in Eq. (1) as 123 at 1823 K by plotting $\exp[\frac{\sigma_{\text{FeS}} - \sigma}{RT_{\text{FeS}}}] - 1$ as a function of sulfur activity with respect to 1 mass% as standard state (Fig. 9). It is shown that the slope of regression line in Fig. 9 may vary from 113 to 158 depending on the regression range, which explains why the adsorption coefficients for the ideal adsorption model differed with investigators.\textsuperscript{2–4} Consequently, as a form of Szyszkowski equation, the surface tension of Fe–S alloy at 1823 K may be given by Eq. (14).

$$\sigma = 1.913 - 0.217 \ln(1 + 123a_S) \quad \text{(14)}$$

It can be concluded that the surface tension of Fe–S alloy without oxygen can be estimated reasonably by the model calculation of the non-ideal adsorption, whereas it can be also expressed as a form of the ideal adsorption style equation (Eq. (14)) within errors of 0.040 N/m.

4.2.4. Surface Adsorption of Sulfur

Surface adsorption of sulfur on liquid iron can be obtained by Eq. (15).

$$\Gamma_S = \Gamma_{\text{FeS}} = \frac{X_{\text{FeS}}}{S_{\text{Fe}}X_{\text{Fe}} + S_{\text{FeS}}X_{\text{FeS}}} \quad \text{(15)}$$

The sulfur adsorption variations against the sulfur content are shown in Fig. 10. Those for the non-ideal adsorption...
model show more rapid increase than the ideal adsorption model at about 0.005 mass% of sulfur. Thus, it may be concluded that an ideal adsorption model is not proper to evaluate sulfur adsorption on the liquid iron. In the non-ideal adsorption model, it is considered that the sudden decrease in surface tension at around 0.005 mass% is caused by the fast increase in sulfur adsorption in this concentration region. Moreover, the adsorption of sulfur on the surface of liquid iron increases very rapidly up to about 0.1 mass% of sulfur, then approached to almost constant value of \(1.42 \times 10^{-3}\) mol/m². In the kinetic studies of nitrogen adsorption, residual reactions at ambient sulfur have been investigated on liquid iron containing more than 0.1–0.2 mass% sulfur by numerous researchers.\(^{40–44}\) These results are in good accordance with the present work. In this stage, the mole fraction of sulfur at surface is close to 0.5, which indicates that the surface ratio between Fe and S is almost 1:1. Consequently, we may consider the surface composition is close to FeS at the sulfur saturation.

5. Conclusions

The followings are the major conclusions of this work.

1. The surface tensions and the adsorption for liquid Fe–S alloys were well estimated by the Butler’s equation involving effects of size and interactions of adsorbed elements.

2. The surface tension for Fe–S alloys containing 60 ppm oxygen showed lower values than the model calculations for Fe–S alloys without oxygen by about 0.150 N/m.

3. In an ideal model assuming that \(S = S_{\text{s}}\), the effect of the change in molar surface area may compensate for the change in interactions between the adsorbed elements on the liquid iron surface. Hence, assuming that \(S = S_{\text{s}}\), a simple Szyszkowski equation for the surface tension of Fe–S alloys could be suggested.

4. The adsorption of sulfur on the surface of liquid iron increased very rapidly up to about 0.1 mass% sulfur, then approached to almost constant value of \(1.42 \times 10^{-3}\) mol/m².

Acknowledgements

The authors express their gratitude to Professor I. Jimbo and Dr. Y. Chung for discussion and helpful advices on the surface tension measurements.

REFERENCES