Surface Tension of Liquid Iron as Functions of Oxygen Activity and Temperature

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Surface tension of liquid iron is an important property for process simulations evaluating Marangoni flow in the melt. In this study, we succeeded to measure accurate surface tension of liquid iron under various oxygen activities and temperatures with overcoming experimental difficulties through the following attempts: (1) To prevent chemical contamination of sample, an oscillating droplet method using an electromagnetic levitator was employed. Surface oscillation frequencies were determined with taking into account sample rotation. (2) To control the oxygen activity of liquid iron, a gas-liquid equilibrium method using CO/CO2 containing gas mixtures was employed. This method enables precise control of oxygen activity with keeping carbon activity low, and therefore, oxygen activity dependence of surface tension was clarified without carbon effect. (3) To measure the surface tension for higher oxygen activities up to the Fe/FeO equilibrium, high-purity iron (99.9972 mass%) was used. Otherwise, minor reactive impurities in the melt such as aluminum are oxidized, which affects the surface tension measurement. Based on the experimental data, the surface tension of liquid iron was expressed as functions of oxygen activity and temperature using the Szyszkowski model. In addition, thermodynamic properties on the oxygen adsorption reaction and structure of the adsorbed oxygen layer on the melt surface were also discussed.

KEY WORDS: surface tension; liquid iron; oxygen activity; oscillating droplet method; oxygen adsorption; electromagnetic levitation.

1. Introduction

Recently, numerical simulations have been widely used to optimize steel-related processes such as refining, casting and welding. Therefore, accurate thermophysical properties of molten steel are required for the simulations. The Fe–O–C system is the most basic system for steel-related processes, and its surface tension data is essential to simulate Marangoni flow in molten steel.

The surface tension of liquid iron depends on chemical potentials (activities) of oxygen and carbon. The surface tension of liquid iron is significantly scattered among the data previously reported,1,2) and its temperature dependence presents wide variation depending on the investigators. This disagreement is attributed to the experimental difficulties regarding surface tension measurement of high-temperature liquid metals. In this study, we propose here three attempts to measure accurate surface tension of liquid iron with overcoming experimental difficulties:

(1) To prevent chemical contamination of sample, an oscillating droplet method using an electromagnetic levitator (EML) was employed. This method is also contributed to assure measurements at higher temperatures that are sufficiently above the melting temperature and under deeply undercooled conditions.3–6) In addition, surface oscillation frequencies were determined with considering sample rotation, which contributes improvement of frequency identification.5,7)

(2) To control oxygen activity of liquid iron, a gas-liquid equilibrium method using Ar–He–CO–CO2 gas mixtures was employed. This method enables precise control of oxygen activity with keeping carbon activity low, and therefore, oxygen activity dependence of surface tension was clarified without carbon effect.

(3) To measure the surface tension under higher oxygen activities, high-purity iron8) (99.9972 mass%) was used. Otherwise, reactive impurities such as aluminum are oxidized, and an oxide film covers the melt surface under higher oxygen activities, which affects surface oscillation.

Applying the ingenious attempts described above, we measure the surface tension of liquid iron under various oxygen activities and temperatures. From the experimental data, the surface tension of liquid iron is determined as functions of oxygen activity and temperature.

2. Experimental

2.1. Gas-liquid Equilibrium Method

We controlled oxygen and carbon activities using Ar–He–CO–CO2 gas mixtures. The following equilibrium reactions exist in the gas mixtures:

\[
2\text{CO}(g) + \text{O}_2(g) = 2\text{CO}_2(g) \quad \text{(1)}
\]

\[
\text{C}(s) + \text{CO}_2(g) = 2\text{CO}(g) \quad \text{(2)}
\]
Oxygen and carbon activities are controlled by the following equilibrium relations:

\[
\log a_{O_2} = 2 \log \frac{a_{CO}}{a_{CO}} - \log K_{(1)} \quad \text{......... (4)}
\]

\[
\log a_{C} = \log \frac{a_{CO}^2}{a_{CO}} - \log K_{(2)} \quad \text{......... (5)}
\]

where \(a_{O_2}, a_{CO}\) and \(a_{CO}^2\) are activities of \(O_2, CO\) and \(CO_2\), respectively, relative to 1 bar \((10^5 \text{ Pa})\). \(a_{C}\) is a carbon activity relative to a pure graphite at 1 bar. \(K_{(i)}\) is the equilibrium constant of reaction \((i)\), and \(K_{(1)}\) and \(K_{(2)}\) are determined as follows using thermochemical data.

\[
K_{(1)} = \exp \left( \frac{6.77 \times 10^4}{T} - 20.6 \right) \quad \text{......... (6)}
\]

\[
K_{(2)} = \exp \left( -\frac{2.03 \times 10^4}{T} + 20.7 \right) \quad \text{......... (7)}
\]

We calculated \(a_{O_2}\) and \(a_{C}\) using Eqs. (4)–(7). Flow rates of \(Ar, He, CO\) and \(CO_2\) gases were adjusted based on the equations. The calculated \(a_{O_2}\) and \(a_{C}\) were confirmed by quantitative chemical analysis of oxygen and carbon dissolved in the sample after quenching.

### 2.2. Experimental Procedure

Figure 1 shows an experimental set up of the EML facility to measure the surface tension of liquid iron. The maximum power and frequency of the radio frequency generator of the EML were 15 kW and 200 kHz, respectively. High-purity \((99.9972 \text{ mass\%})\) iron prepared using an ion exchange method was used as a sample. The chemical composition of the high-purity iron is presented in Table 1. A cubic iron of about 0.6 g was placed on a quartz sample holder and positioned in a levitation coil. The quartz tube mounted in the levitation coil was initially evacuated to the order of \(10^{-2} \text{ Pa}\) using a diaphragm pump and turbo molecular pump. Subsequently, high-purity \(Ar\) gas \((99.9999 \text{ vol.\%})\) was filled in the quartz tube. The iron was initially levitated in an \(Ar\) gas atmosphere, and heated using the EML facility. Oxygen and carbon activities were controlled using \(Ar\)–\(He\)–\(CO\)–\(CO_2\) gas mixtures. \(Ar-5 \text{ vol.% H}_2\) and \(He-5 \text{ vol.% H}_2\) gases were used to measure the intrinsic surface tension of high-purity liquid iron. \(Ar, He, Ar-5 \text{ vol.% H}_2\) and \(He-5 \text{ vol.% H}_2\) gases were purified using an Mg-deoxidizer kept at 873 K before introducing into the quartz tube. The temperature of the sample was measured using a monochromator pyrometer (wavelength: 0.9 \(\mu\)m, temperature resolution: 1 K, sampling rate: 5 Hz). The pyrometer was calibrated at melting temperature of iron \((1808 \text{ K})\). The temperature of the sample was controlled by changing flow rates of \(Ar\) and \(He\) gases in the gas mixture. The images of the oscillating droplet were recorded by a high-speed camera with a resolution of \(512 \times 512\) pixels at a frame rate of 250 fps for 16 s from the sample top. After recording the images, some samples were quenched, and subject to quantitative chemical analysis of oxygen and carbon in the sample. Oxygen and carbon contents were analyzed using an infrared-absorption method with LECO TC-436 for oxygen analysis and LECO CS-444 LS for carbon analysis.

### 2.3. Determination of Surface Tension

The surface tension of the liquid iron was calculated from the following modified Rayleigh equation proposed by Cummings and Blackburn:

\[
\sigma = \frac{3\pi M}{8} \left[ \frac{1}{5} \sum_{m=2}^{\infty} \frac{\nu_m^2 - \nu_t^2}{1 - 1.2 \left( \frac{g}{8\pi^2 v_t^2 R_0} \right)^2} \right] \quad \text{......... (8)}
\]

Here, \(\sigma \text{ [N·m}^{-1}]\) is the surface tension, \(M \text{ [kg]}\) is the sample mass, \(\nu_0 \text{ [Hz]}\) is the surface oscillation frequency for \(m = 0, \pm 1\) and \(\pm 2\) for the \(l = 2\) mode, \(\nu_t \text{ [Hz]}\) is the translation frequency of center of gravity, \(g \text{ [m·s}^{-2}]\) is the gravitational acceleration and \(R_0 \text{ [m]}\) is the sample radius. The values of \(\nu_0\) were determined through fast Fourier transformation (FFT) using the time-sequential data of \(R^+ (=R_x + R_y)\) and \(R^- (=R_x - R_y)\), where \(R_x\) and \(R_y\) are radii along the \(x\) and \(y\) axes of the droplet, respectively. The value of \(\nu_t\) was determined through FFT using the time-sequential data of motion of the center of gravity of the droplet. These time-sequential data were obtained from the time-sequential data of recorded images. The droplet rotation around vertical axis makes the peaks of surface oscillation frequencies for \(m = \pm 1\) and \(\pm 2\) split into two

Figure 1. Schematic diagram of an electromagnetic levitator to measure the surface tension of liquid iron with controlling oxygen and carbon activities.

| Table 1. Chemical composition of the high-purity iron (by mass ppm). |
|------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|                  | Al   | Si   | P    | S    | Ti   | Cr   | Mn   | Co   | Ni   | Cu   | Se   | Sr   | Nb   | Mo   |
|                  | 0.19 | 0.17 | 0.20 | 0.15 | 0.59 | 0.011| 0.049| 1.6  | 0.092| 0.52 | 0.13 | 0.23 | 0.37 | 0.10 |
|                  | Ag   | Cd   |      |      |      |      |      |      |      |      |      |      |      |      |
|                  | 0.20 |      |      |      |      |      |      |      |      |      |      |      |      |      |

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apparent peaks.4,7) The true frequencies for \( m = \pm 1 \) and \( \pm 2 \) oscillations correspond to the center of the split peaks, which is demonstrated in section 3.1. The value of \( R_0 \) was calculated using the following equation;

\[
R_0 = \frac{3M}{4\rho \pi} \tag{9}
\]

where \( \rho \) [kg m\(^{-3}\)] is the density. The density data of the liquid iron reported by Nishizuka et al.12) was used in this study, which is given as,

\[
\rho = 7041.0 - 0.9316 \times (T - 1808) \tag{10}
\]

3. Result

3.1. Frequency Analysis

Figure 2 shows a typical result of FFT of surface oscillation frequencies of liquid iron. There are five large frequency peaks appeared in both \( R^+ \) and \( R^- \) results. The surface oscillation frequency was split into five peaks for \( m = 0, \pm 1 \) and \( \pm 2 \) appeared from lower frequency to higher frequency in order because of influences of the gravity and electromagnetic force. The peaks of surface oscillation frequencies for \( m = \pm 1 \) and \( \pm 2 \) are again split into two apparent peaks by rotation around \( z \) axis. The true frequencies of \( m = \pm 1 \) and \( \pm 2 \) oscillations correspond to the center of the split peaks as presented by black dashed lines in Fig. 2. In this study, the frequencies of \( m = \pm 1 \) and \( \pm 2 \) oscillations were identified by the method described above in consideration of the influence of the rotation. This significantly reduces experimental uncertainty in peak identification.

3.2. Surface Tension of Pure Liquid Iron

Figure 3 shows the surface tension of high-purity liquid iron measured under Ar-5 vol.% H\(_2\) gas atmosphere as a function of temperature together with the previously reported values.\(^{13-16}\) The surface tension obtained in this study is larger than the previous data at the melting point, and it has larger temperature dependence than others. We believe that the present results are more reliable than others from the following points: (1) High-purity iron (99.9972 mass%) was used as a sample, (2) Ar-5 vol.% H\(_2\) gas was purified using the Mg-deoxidizer, and (3) There was no contamination from contact materials to the sample. Thus, the surface tension of high-purity liquid iron, \( \sigma \) [mN m\(^{-1}\)], was determined as a function of temperature using a linear regression analysis as,

\[
\sigma/mN\cdot m^{-1} = (1925 \pm 65) - (0.455 \pm 0.034) \times (T - 1808) \tag{11}
\]

The experimental uncertainty associated with each plot presented in Fig. 3 was evaluated based on the GUM (Guide to the Expression of Uncertainty in Measurement).\(^{4,17}\) Table 2 presents an uncertainty evaluated for the surface tension obtained at the lowest temperature as an example, which has the maximum value of uncertainty (\( \sigma = 1995 \) mN m\(^{-1}\) at

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Component} & \text{Value} & \text{Standard uncertainty} & \text{Sensitivity coefficient} & \text{Contribution, mN m}^{-1} \\
\hline
\text{Mass, } M & 7.94 \times 10^{-4} \text{ kg} & 6.46 \times 10^{-6} \text{ kg} & \partial \sigma / \partial M = 2.58 \times 10^{-7} \text{ N m}^{-1} \text{ kg}^{-1} & 16.7 \\
\text{Density, } \rho & 7.17 \times 10^{3} \text{ kg m}^{-3} & 3.59 \times 10^{2} \text{ kg m}^{-3} & \partial \sigma / \partial \rho = -1.01 \times 10^{-5} \text{ N m}^{-2} \text{ kg}^{-1} & -2.06 \\
\text{Translation frequency, } \nu_t & 6.210 \text{ Hz} & 1.76 \times 10^{-2} \text{ Hz} & \partial \sigma / \partial \nu_t = -1.86 \times 10^{2} \text{ N m}^{-1} \text{ s} & -3.27 \\
\text{m}=0 \text{ oscillation frequency, } \nu_{m=0} & 36.011 \text{ Hz} & 1.76 \times 10^{-2} \text{ Hz} & \partial \sigma / \partial \nu_{m=0} = 1.35 \times 10^{-1} \text{ N m}^{-1} \text{ s} & 2.38 \\
\text{m}=\pm1 \text{ oscillation frequency, } \nu_{m=\pm1} & 45.716 \text{ Hz} & 1.76 \times 10^{-2} \text{ Hz} & \partial \sigma / \partial \nu_{m=\pm1} = 3.43 \times 10^{-1} \text{ N m}^{-1} \text{ s} & 6.03 \\
\text{m}=\pm2 \text{ oscillation frequency, } \nu_{m=\pm2} & 53.914 \text{ Hz} & 1.76 \times 10^{-2} \text{ Hz} & \partial \sigma / \partial \nu_{m=\pm2} = 7.12 \times 10^{-1} \text{ N m}^{-1} \text{ s} & 7.12 \\
\hline
\text{Combined standard uncertainty} & & & & 19.7 \\
\text{Extended uncertainty} & & & & 39.3 \\
\hline
\end{array}
\]
1666 K). The standard uncertainty in the sample mass resulted from evaporation during the measurement. The standard uncertainty in the density was evaluated as 5% from the original reported value. The standard uncertainties in the frequencies resulted from the frequency resolution of FFT. The table shows that the uncertainty in the sample mass is a major contribution. The combined standard uncertainty is evaluated as 19.7 mN·m⁻¹; therefore, the expanded uncertainty at the 95.45% level of confidence is 39.3 mN·m⁻¹.

3.3. Effect of Oxygen Activity on Surface Tension of Liquid Iron

Figure 4 shows the temperature dependence of surface tension of liquid iron for controlled \(a_{O_2}\) varying from \(10^{-12}\) to \(10^{-10}\). Here, the carbon activity was controlled to be as low as \(10^{-3}\). The surface tension decreases with increasing \(a_{O_2}\). The temperature coefficient of surface tension varies from a positive value to a negative one at constant \(a_{O_2}\) with increasing temperature. As presented in Fig. 4, the \(a_{O_2}\) dependences of surface tension were beautifully consistent with the results for pure iron, which support experimental justification.

Figure 5 shows the surface tension of liquid iron as a function of \(a_{O_2}\) at 1873 K together with the previously reported values. The decrease in surface tension with increasing \(a_{O_2}\) is caused by oxygen atoms adsorbed on the surface of liquid iron. The adsorbed oxygen atom acts as a surfactant.

In the present study, all the data were measured under the condition that \(a_C\) was controlled at \(10^{-3}\) or \(10^{-4}\). The surface tension of liquid iron is less sensitive to \(a_C\) as known from the previous data. The low \(a_C\) below \(10^{-3}\) has almost no influence on the surface tension. This is also supported by the result as presented in Fig. 5 showing no gap between the results obtained at \(a_C = 10^{-3}\) and \(10^{-4}\). The effect of \(a_C\) on the surface tension will be separately published by the present authors.

Table 3 shows the oxygen and carbon concentrations, \(w_O\) and \(w_C\) (by mass%) in the iron sample after the experiments conducted for different conditions, which were obtained from the chemical analysis. The values of \(a_{O_2}\) and \(a_C\) were calculated from \(w_O\) and \(w_C\) using the following equations and thermodynamic data:

\[
\frac{1}{2} O_2(g) = O \quad \ldots \ldots \ldots (12)
\]

\[
\text{C(graphite)} = \text{C} \quad \ldots \ldots \ldots (13)
\]

\[
\log a_{O_2} = 2(\log f_o + \log w_O - \log K_{(12)}) \quad \ldots \ldots (14)
\]

\[
\log a_C = \log f_c + \log w_C - \log K_{(13)} \quad \ldots \ldots (15)
\]

\[
K_{(12)} = \exp \left( \frac{1.34 \times 10^4}{T} + 0.8 \right) \quad \ldots \ldots (16)
\]

\[
K_{(13)} = \exp \left( \frac{3.24 \times 10^4}{T} + 5.5 \right) \quad \ldots \ldots (17)
\]

Table 3. Chemical contents of oxygen and carbon, \(w_O\) and \(w_C\), obtained from the chemical analysis. Comparison between \(a_{O_2}\) and \(a_C\) calculated from CO/CO₂ gas compositions and those calculated from the chemical contents.

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>(a_{CO})</th>
<th>(a_{CO_2})</th>
<th>(\log a_{O_2})</th>
<th>(\log a_C)</th>
<th>(w_O/\text{mass}%)</th>
<th>(w_C/\text{mass}%)</th>
<th>(\log a_{O_2})</th>
<th>(\log a_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp., T/K</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>0.011</td>
<td>0.023</td>
<td>–11.2</td>
<td>–3.2</td>
</tr>
<tr>
<td></td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>0.009</td>
<td>0.026</td>
<td>–11.2</td>
<td>–3.2</td>
</tr>
<tr>
<td></td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>0.028</td>
<td>0.006</td>
<td>–10.2</td>
<td>–3.9</td>
</tr>
<tr>
<td></td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>(10^{-1})</td>
<td>0.022</td>
<td>0.005</td>
<td>–10.2</td>
<td>–3.9</td>
</tr>
</tbody>
</table>

Fig. 4. Temperature dependence of surface tension for liquid iron measured under various \(a_{O_2}\). Curves for \(a_{O_2}\) from \(10^{-12}\) to \(10^{-10}\) were calculated using Eq. (28).

Fig. 5. \(a_{O_2}\) dependence of surface tension of liquid iron measured at 1873 K.
\[ \log f_0 = \epsilon_0^{a \text{O}_2} \omega_0 + \epsilon_0^{e \text{C}_2} \omega_e \] .......................... (18)
\[ \log f_e = \epsilon_0^{e \text{C}_2} \omega_0 + \epsilon_0^{a \text{O}_2} \omega_e \] .......................... (19)

where \( K_{(2)} \) was determined using the Gibbs energy of the reaction: \( \text{O} + \text{H}_2 = \text{H}_2\text{O} \) and the standard Gibbs energy of formation of \( \text{H}_2\text{O} \). \( \Omega \) and \( \bar{C} \) represent oxygen and carbon dissolved in liquid iron. \( f_0 \) and \( f_e \) are activity coefficients of oxygen and carbon, respectively, relative to 1 mass\% of oxygen and carbon in liquid iron. \( e \) is an interaction parameter of \( j \) for \( f_e \). The values of \( \alpha_0 \) and \( a_c \) calculated from \( \omega_0 \) and \( \omega_e \) agree with the values calculated from CO/CO\(_2\) gas compositions used in the experiments, which means that the \( \alpha_0 \) and \( a_c \) were well controlled using the gas-liquid equilibrium method.

4. Discussion

4.1. Oxygen Adsorption on Surface of Liquid Iron

The value of the surface excess of oxygen, \( \Gamma_0 \), is calculated using the Gibbs adsorption isotherm expressed by Eq. (20);

\[ \Gamma_0 = \frac{1}{R T} \frac{\partial \sigma}{\partial \ln a_o} = -\frac{2}{2.303 R T} \frac{\partial \sigma}{\partial \log a_o} \] .......................... (20)

where \( R \) is the gas constant. Figure 6 shows the relationship between \( a_o \) and \( a_0 \) at 1873 K using the relationship between \( \sigma \) and \( a_o \) described in Fig. 5. The value of the surface excess of oxygen at saturation, \( \Gamma_0^{\text{sat}} \), is the maximum value of \( \Gamma_0 \), and the value was obtained by extrapolating the \( \Gamma_0^{\text{ad}} \), relation to the \( a_0 \) at the Fe/FeO equilibrium as shown in Fig. 6. Thus, the value of \( \Gamma_0^{\text{sat}} \) is determined to be 18.6 \( \times \) 10\(^{-6}\) mol\( \cdot \)m\(^{-2}\). Table 4 shows the comparison of the present value of \( \Gamma_0^{\text{sat}} \) with those reported by several investigators.\(^{19-21,23-26}\) The value of \( \Gamma_0^{\text{sat}} \) obtained in this study is in good agreement with the data reported by Kasama et al.\(^{19}\) and Nakashima et al.\(^{20}\).

Assuming that the oxygen adsorption is a monolayer, the area, \( A_0 \), occupied by an adsorbed oxygen atom on the surface is expressed by the following equation:

\[ A_0 = \frac{1}{\Gamma_0^{\text{sat}} N_A} \] .......................... (21)

where \( N_A \) is Avogadro constant. Using \( \Gamma_0^{\text{sat}} \) obtained in this study, \( A_0 \) was calculated to be 8.9 \( \times \) 10\(^{-10}\) m\(^2\). The following discussion has been made on the adsorbed oxygen layer on the melt surface using this value. Ritter et al.\(^{25}\) studied the initial growth of FeO (111) thin films from submonolayer to 2.2 monolayers thickness grown on Pt (111) at temperatures between 870 and 1000 K using a scanning tunneling microscopy (STM) and high-resolution low-energy electron diffraction (LEED). They measured the oxygen-oxygen interatomic distance, which varied from 3.09 \( \times \) 10\(^{-10}\) to 3.15 \( \times \) 10\(^{-10}\) m depending on the film thickness. These values correspond to \( A_0 / m^2 = (8.3–8.6) \times 10^{-20} \) This value is close to the present value (8.9 \( \times \) 10\(^{-20}\) m\(^2\)) obtained from the surface tension measurements at 1 873 K. It is, therefore, concluded that the adsorbed oxygen layer on the melt surface at saturation is similar to that of oxygen-terminated FeO (111) bilayer. This is also supported by Kasama et al.\(^{19}\)

![Fig. 6. Relationship between surface excess of oxygen and \( a_0 \) at 1873 K.](image)

**Table 4.** The values of \( \Gamma_0^{\text{sat}} \) on liquid iron reported and obtained in this study.

<table>
<thead>
<tr>
<th>( \Gamma_0^{\text{sat}} ) (10(^{-6}) mol( \cdot )m(^{-2}))</th>
<th>Temperature, ( T )K</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.6</td>
<td>1873</td>
<td>Oscillation droplet</td>
<td>Present work</td>
</tr>
<tr>
<td>19.4</td>
<td>1873</td>
<td>Oscillation droplet</td>
<td>Kasama et al.(^{19})</td>
</tr>
<tr>
<td>18.5</td>
<td>1873</td>
<td>Sessile droplet</td>
<td>Nakashima et al.(^{20})</td>
</tr>
<tr>
<td>23.4</td>
<td>1823</td>
<td>Sessile droplet</td>
<td>Ogino et al.(^{21})</td>
</tr>
<tr>
<td>21.2</td>
<td>1823</td>
<td>Sessile droplet</td>
<td>Zhu and Mukai(^{22})</td>
</tr>
<tr>
<td>14.5</td>
<td>1833, 1918</td>
<td>Oscillation droplet</td>
<td>Murakwa et al.(^{20})</td>
</tr>
<tr>
<td>18.0</td>
<td>1823</td>
<td>Sessile droplet</td>
<td>Barnard and Lupia(^{23, 26})</td>
</tr>
</tbody>
</table>

using a lattice constant of bulk FeO having a NaCl-type structure.

4.2. Modeling Surface Tension of Liquid Iron as Functions of Oxygen Activity and Temperature

In the present study, the carbon activity was controlled to be as low as 10\(^{-3}\) or 10\(^{-4}\), and therefore, the effect of carbon on the surface tension can be ignored. The \( \alpha_3 \) dependence of the surface tension of liquid iron is discussed as follows. The following equation derived by Szyszkowski\(^{28}\) presents the influence of oxygen adsorption on the surface tension;

\[ \sigma = \sigma^0 - RT \Gamma_0^{\text{sat}} \ln \left( 1 + K_{\text{ad}} a_{\text{O}_2}^{1/2} \right) \] .......................... (22)

Here, \( K_{\text{ad}} \) is the equilibrium constant of oxygen adsorption reaction at surface of liquid iron. This reaction is expressed as;

\[ \frac{1}{2} \text{O}_2(g) = \text{O}_{\text{ad}} \] .......................... (23)

where \( \text{O}_{\text{ad}} \) represents adsorbed oxygen at surface of liquid iron. \( K_{\text{ad}} \) can be determined using \( \sigma^0, \sigma \) and \( \Gamma_0^{\text{sat}} \). The relationship between \( \ln K_{\text{ad}} \) and inverse temperature was presented in Fig. 7, and the following relation was obtained from a linear regression analysis as,

\[ \ln K_{\text{ad}} = \frac{4.27 \pm 0.04}{T} \times 10^4 - (10.1 \pm 0.3) \] \( (1 773–2 073 \text{ K}) \) .......................... (24)

The standard enthalpy of the oxygen adsorption reaction, \( \Delta H_{\text{ad}}^{\circ} \), can be calculated using the following van’t Hoff equation.
The standard enthalpy of the oxygen adsorption reaction was determined to be \( \Delta_{ad} H^\circ = -355 \pm 4 \text{ kJ·mol}^{-1} \) using Eq. (25).

Figure 8 shows temperature dependence of the standard Gibbs energy of the oxygen adsorption reaction, \( \Delta_{ad} G^\circ \), calculated using the following equation:

\[
\Delta_{ad} G^\circ = -RT \ln K_{ad} \quad \text{(26)}
\]

The Gibbs energy increases linearly with increasing temperature. The standard entropy of the oxygen adsorption reaction, \( \Delta_{ad} S^\circ \), was determined to be \( \Delta_{ad} S^\circ = -84.0 \pm 2.5 \text{ J·mol}^{-1}·\text{K}^{-1} \) using the following equation:

\[
\Delta_{ad} S^\circ = -\frac{\partial \Delta_{ad} G^\circ}{\partial T} \quad \text{(27)}
\]

Substituting the value of \( \Gamma_{Osat} \) and Eq. (24) into Eq. (22) gives Eq. (28).

The surface tension of liquid iron is expressed as functions of temperature and \( a_{O_2} \). The surface tension for \( a_{O_2} \) varying from \( 10^{-12} \) to \( 10^{-10} \) was calculated using Eq. (28), and presented as solid and dashed curves in Fig. 4. The behavior of the surface tension is well explained using the model proposed by Szyszkowski.\(^{28}\) The surface tension of liquid iron was presented in the \( \sigma-T-a_{O_2} \) 3D diagram using Eq. (28).

5. Summary

The surface tension of liquid iron was successfully measured for \( a_{O_2} \) varying from \( 10^{-10} \) to \( 10^{-12} \) under carbon activity below \( 10^{-3} \) at temperatures ranging from \( T = 1773 \) to \( 2073 \) K through the oscillation droplet method using the electromagnetic levitator. The temperature dependence of the surface tension under various \( a_{O_2} \) was well expressed using the model proposed by Szyszkowski. Based on the model, the equilibrium constant, standard enthalpy and entropy of oxygen adsorption reaction were determined. In addition, the surface excess of oxygen at saturation was determined using the Gibbs adsorption isotherm. From this value, it was concluded that the adsorbed oxygen layer on the melt surface at saturation is similar to that of oxygen-terminated FeO (111) bilayer.

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