Temperature Dependence of Surface Tension of Molten Iron under Reducing Gas Atmosphere

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Abstract. Surface tension of molten iron was measured under Ar-He-5vol.\%H\(_2\) gas by oscillating droplet method using electromagnetic levitation furnace in consideration of the temperature dependence of oxygen partial pressure, \(P_{O_2}\), of the gas. For comparison, the measurement was carried under Ar-He atmosphere to fix the \(P_{O_2}\) of the inlet gas at \(10^{-2}\)Pa. The surface tension was successfully measured over a wide temperature range of about 780K including undercooling condition. When \(P_{O_2}\) is fixed at \(10^{-2}\) Pa, the surface tension increased and then decreased with increasing temperature like a boomerang shape. When the measurement was carried out under the H\(_2\)-containing gas atmosphere, the temperature dependence of the surface tension shows unique kink at around 1810K instead of linear relationship due to competition between the temperature dependence of the \(P_{O_2}\) and that of the equilibrium constant of oxygen adsorption reaction. The relationship between the calculated \(\ln K_{ad}\) with respect to inverse temperature using Szyszkowski model was different between the atmospheric gases.

1. Introduction

An accurate surface tension and its temperature dependence are strongly required to improve and optimize various high temperature melt processes involving a free surface such as welding and casting through a numerical calculation because the surface tension difference is a driving force of the Marangoni convection [1]. The Marangoni convection is characterized by the following dimensionless number,

\[
Ma = \frac{\partial \sigma}{\partial T} \cdot \frac{\Delta TL}{\mu \alpha}
\]  

(1)

where \(\sigma\) is the surface tension, \(T\) is the temperature, \(L\) is the characteristic length, \(\mu\) is the viscosity, and \(\alpha\) is the thermal diffusivity.

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The surface tension of molten metals has often been measured under a reducing atmosphere such as H\textsubscript{2} containing gas to suppress oxidation of the melt surface [2-5], in which the P\textsubscript{O2} of the ambient atmosphere becomes lower by condensing the H\textsubscript{2}O formed from the following reaction,

\begin{equation}
H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O
\end{equation}

The P\textsubscript{O2} varies depending on the sample temperature due to the temperature reliance of the equilibrium constant of $K_{H_2O}$ in the reaction (2). However the influence of the temperature dependence of the P\textsubscript{O2} on surface tension of molten metal has not been considered carefully in many cases though surface tension is strongly affected by the P\textsubscript{O2}.

In this article, we would like to report the surface tension of molten iron measured by oscillating droplet method using electromagnetic levitation (EML). This paper is intended as an investigation of the effect of the P\textsubscript{O2} and atmospheric gas on surface tension measurement of molten metal.

2. Experimental Procedure

The experimental facility is exhibited elsewhere [5]. The high purity of electrolytic iron placed onto a quartz sample holder was positioned in the center of levitation coil. The chemical composition of the iron is depicted in table 1. The sample was electromagnetically levitated and then melted under flow condition (2 L/min) of the Ar-He-5vol.%H\textsubscript{2} mixed gas with a moisture content of 2.66 ppm to lower the P\textsubscript{O2}. For comparison, the sample was also melted under flow condition of a mixed gas of high purity commercial argon and helium to fix the P\textsubscript{O2} of 10\textsuperscript{-2}Pa regardless of temperature. The P\textsubscript{O2} of the inlet gas was confirmed by zirconia oxygen sensors operated at 1008K.

| Mn | Ni | Cr | Si | Mo | P |
|----|----|----|----|----|---|
| <0.0001 | <0.0001 | <0.0001 | <0.002 | <0.0001 | <0.001 |
| Cu | Al | C | O | S | Fe |
| 0.0001 | <0.0001 | <0.0004 | 0.0013 | 0.001 | Bal. |

The oscillation behavior and the temperature of the droplet were monitored from above using a high speed video camera and a single color pyrometer using a half mirror. The temperature of the droplet was controlled by changing the flow rate of atmospheric gas.

The frequencies of the surface oscillation of the $m = 0, \pm 1, \pm 2$ for the $l = 2$ mode and motion of the center of gravity of two dimensional image were analyzed through fast Fourier transformation (FFT) and maximum entropy method (MEM) from the time-sequential data of the observed images in consideration of the influence of two types of droplet rotations, i.e. real rotation and apparent rotation [6]. The surface tension of the molten iron was calculated from these frequencies by the following equations in which the Rayleigh equation [7] is calibrated by Cummings and Blackburn [8],

\begin{equation}
\sigma = \frac{3}{8} \pi M \left[ \frac{1}{5} \sum_{m=-2}^{2} v_{2,m}^2 - v_{i}^2 \left( 1.9 - 1.2 \left( \frac{z_0}{a} \right)^2 \right) \right], \quad (3)
\end{equation}

\begin{equation}
z_0 = \frac{g}{8\pi^2 v_i^2}, \quad (4)
\end{equation}

\begin{equation}
a = \sqrt{\frac{3M}{4\rho \pi}}, \quad (5)
\end{equation}
where \( v_m \) is the surface oscillation, \( M \) is the sample mass, \( \rho \) is the density, and \( g \) is the gravitational acceleration. The density of the molten iron was determined from data reported by Beutel et al. [9].

3. Results and discussions
When the Ar-He-5vol.%H\(_2\) gas was used for the surface tension measurement, it is important to consider that the \( P_{O_2} \) varies depending on temperature because the following equilibrium constant of reaction (2) shows temperature dependence.

\[
K_{H_2O} = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}} \quad (6)
\]

The \( P_{O_2} \) of the Ar-He-5vol.%H\(_2\) gas was evaluated as a function of temperature using the following standard Gibbs energy of formation of H\(_2\)O and the \( P_{O_2} \) of 2.0×10\(^{-23}\)Pa of the inlet gas measured by the oxygen sensor maintained at 1008K,

\[
\Delta G^\circ = -246535 + 54.94T \quad [\text{J} \cdot \text{mol}^{-1}] \quad (3)
\]

The result is exhibited in figure 1. This confirms that \( P_{O_2} \) of the Ar-He-5 vol.%H\(_2\) gas increases with rising temperature.

\[\text{Figure 1. Temperature dependence of oxygen partial pressure (} P_{O_2} \text{) of Ar-He-5vol.%H}_2 \text{ gas evaluated through the standard Gibbs energy of formation of H}_2\text{O}\]

Figure 2 depicts the surface tension of molten iron measured by oscillating droplet method using EML under the flow condition of mixed gases of Ar-He-5vol.%H\(_2\) (□) and Ar-He (◆). Uncertainty for the measurement plot was evaluated based on the GUM (ISO Guide to the Expression of Uncertainty in Measurement) [10] using the coverage factor of \( K_p = 2 \). The qualitative magnitude of the equilibrium constant of oxygen adsorption reaction, \( K_{ad} \), is expressed by a color gradient of the background in this figure. Surface tension of molten iron was successfully measured over a wide temperature range of 780K including undercooling state regardless of the atmosphere gas.

When \( P_{O_2} \) is controlled at 10\(^{-5}\) Pa, the FeO is formed in solid state below 1650K and in liquid state above this temperature from simple thermodynamic calculations using the Gibbs energy of FeO formation [11]. However, no appreciable FeO was detected in the droplet images and temperature profile by high speed camera and pyrometer. If FeO is formed on the droplet, the droplet image becomes bright due to its higher emissivity, and it can be detected in the time sequential data of droplet image and emissivity. Since Fe-O system has a miscibility gap in the liquid state between Fe and FeO, the liquid FeO may be mixed as an immiscible state inside the droplet. The strong
Electromagnetic stirring would promote the mixing of the electromagnetically levitated droplet. Even in this case, apparent emissivity of the droplet becomes higher than that of the liquid iron. Furthermore, the apparent emissivity of the droplet image should be enhanced because the volume fraction of liquid FeO increases in the droplet with time.

Since the small amount of evaporation for the iron droplet was observed during the containerless levitation of the droplet, a metallic iron vapor would work as an oxygen getter pump in the vicinity of the melt surface as is the case for molten tin [12, 13].

When the $P_{O_2}$ of the measurement atmosphere is fixed at $10^{-2}$Pa regardless of sample temperature using high purity Ar-He gas, boomerang shape temperature dependence of surface tension is observed; the surface tension increases as the sample temperature rises up to about 2150K, and then it decreases above this temperature. When $P_{O_2}$ is high during surface tension measurement, oxygen adsorption induces a significant decrease of the surface tension. However it is desorbed from the melt surface as the sample temperature rises because the equilibrium constant of oxygen adsorption reaction becomes small. As a result surface tension temperature coefficient becomes positive value. When the Po2 becomes less effective at about 2150K, the surface tension temperature coefficient is changed from a positive value to a negative value.

![Figure 2](image.png)

**Figure 2.** The surface tension of molten iron measured by oscillating droplet method using EML under the Ar-He-5vol.%H2 and Ar-He gases.

When the measurement is carried out under the Ar-He-5vol.%H2 gas atmosphere, the temperature dependence of the surface tension shows a peculiar kink at around 1810K; the surface tension decreases and then increases once when the sample temperature rises up to 1950K. When the sample temperature exceeds about 1950K, the surface tension decreases with increasing temperature again. Since the variation of the surface tension at this kink is beyond the uncertainty of the measurement, it is not the scattering of the measurement originating from the measurement accuracy. This unique kink in the temperature dependence of the surface tension can be explained when the temperature dependence of the $P_{O_2}$ under the Ar-He-5vol.%H2 gas is considered [5]. The $P_{O_2}$ increases from $3.6 \times 10^{-14}$Pa to $4.1 \times 10^{-12}$Pa as the sample temperature rises from 1580K to 1810K (see figure 1). Higher $P_{O_2}$ usually induce a lower surface tension of molten metal due to oxygen adsorption as observed at the region I.
Note that equilibrium constant of oxygen adsorption reaction becomes small due to the temperature elevation simultaneously. Therefore there is competition between the temperature dependence of $P_{O_2}$ and that of equilibrium constant of oxygen adsorption reaction to decide the amount of the oxygen adsorption. If the amount of oxygen adsorption becomes small due to the temperature elevation even at high $P_{O_2}$, the surface tension of molten iron would increase to approach the surface tension at pure state as observed at region II. Eventually pure surface tension is observed at high temperature as exhibited at region III because the $P_{O_2}$ becomes less effective.

von Szyszkowski empirically derived the following equation about the influence of the surfactant on surface tension of a dilute solution [14],

$$
\sigma = \sigma^p - RT \Gamma^0 \ln(1 + K_{ad} a_O) \quad (7)
$$

where $\sigma^p$ is the pure surface tension without any contamination [N·m$^{-1}$], $\sigma$ is the surface tension contaminated by surfactant, $R$ is the gas constant [J·K$^{-1}$·mol$^{-1}$], $T$ is the temperature [K], $\Gamma^0$ is the full-coverage oxygen adsorption at the liquid surface [mol·m$^{-2}$], and $a_O$ is the activity of oxygen in the liquid. This equation is theoretically formulated by March and Tosi from the combination of Langmuir and Gibbs adsorption isotherms [15]. Belton also derived this equation for the surface tension of liquid Fe-S system theoretically [16]. Our group successfully expressed the surface tension of molten silver as functions of both $P_{O_2}$ and temperature using this model. When the experimental results are applied to this model, the ln$K_{ad}$ can be calculated as a function of inverse temperature. The validity of the measurement result was confirmed by the second-law method using the equation (7). The enthalpy of the oxygen adsorption reaction on the melt surface is considered as constant within the short temperature range, which can be calculated from the slope of the ln$K_{ad}$ and inverse temperature (van’t Hoff plot). If a good linearity of the ln$K_{ad}$ with respect to the 1/$T$ is confirmed, the validity of the measurement result is confirmed. The result is shown in figure 3. Although a good linearity of the ln$K_{ad}$ with respect to the 1/$T$ is confirmed, the absolute values of the ln$K_{ad}$ deviate between the atmospheric gases used in the measurement. As mentioned in the previous section, metallic iron vapor would act as an oxygen getter pump in the vicinity of the melt surface as is the case for molten tin [12, 13]. In this case, the calculated ln$K_{ad}$ would exhibit the discrepancy between the atmospheric gases because the $P_{O_2}$ in the vicinity of the melt surface becomes lower than that of the bulk gas used in the calculation of ln$K_{ad}$. Furthermore, another possibility of the discrepancy in the calculated ln$K_{ad}$ is oxygen adsorption reaction under $H_2$-containing gas is different from that under Ar-He gas. A continuous investigation of the influence of oxygen partial pressure of atmospheric gas on surface tension of molten metals would clarify the discrepancy of the calculated $K_{ad}$ between the atmospheric gases.

![Figure 3. Relationship between calculated ln$K_{ad}$ and temperature](image-url)
4. Conclusion
The surface tension of molten iron was measured over a very wide temperature range of over 780K under Ar-He and Ae-He-5vol.%H$_2$ gas atmosphere by an oscillating droplet method using EML. When the $P_{O_2}$ is fixed at $10^{-2}$Pa using high purity Ar-He gas, the boomerang shape temperature dependence of surface tension was observed. When the measurement was carried out under Ae-He-5vol.%H$_2$ gas atmosphere, the temperature dependence of surface tension exhibited a peculiar kink at around 1810K instead of a usual liner relationship due to the competition between the temperature dependence of $P_{O_2}$ and that of equilibrium constant of oxygen adsorption reaction. Although the ln$K_{ad}$ showed a good liner relationship against 1/$T$, the absolute values of it was different between the atmospheric gases.

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