Surface Tension Measurements of 430 Stainless Steel

Joongkil CHOE,1) Han Gyeol KIM,1) Youngjin JEON,1) Hyeok Jun PARK,1) Youngjo KANG,2) Shumpei OZAWA3) and Joonho LEE1)*


(Received on January 17, 2014; accepted on June 9, 2014)

The surface tension of 430 stainless steel was measured using an electromagnetic levitation (EML) method at temperatures of 1707–2000 K, under a 5 vol% H2–He atmosphere. For comparison, the surface tension was also measured using a constrained drop method; specifically the advanced sessile drop method. At 1823 K, the surface tension of the 430 stainless steel was estimated from the electromagnetic levitation and the constrained drop methods to be 1.802 and 1.614 N/m, respectively. A subsequent analysis of oxygen content showed that the former contained ~7 ppm oxygen, whereas the latter had 60 ppm. It was therefore considered that the observed difference in measurements was the result of a contamination by oxygen. Furthermore, the EML experimental results were found to be close to the theoretically calculated values for the Fe–Cr–Si system. Consequently, for complex multi-component commercial steels such as the 430 stainless steel, the levitation method is recommended for the measurement of surface tension.

KEY WORDS: contamination; electromagnetic levitation; oxygen; surface tension; undercooling.

1. Introduction

Compared to 304 stainless steel, 430 stainless steel (SUS430) exhibits similar mechanical properties, albeit with a slightly degraded corrosion resistance.1) More importantly however, SUS430 does not contain nickel, and is therefore considered a cost-effective anti-corrosion material for general use. Although the mechanical properties of SUS430 are already well-known, its thermo-physical properties in a molten state have not yet been studied well.2)

Surface tension is one of the most important thermo-physical properties of liquid steel, specific data on this being essential to understanding the various phenomena associated with refining, casting, and welding processes; including the separation of inclusions from steel to slag, spreading of inclusions in slag, nucleation of bubbles and inclusions, growth of bubbles and inclusions, floating by Stokes law, inclusion absorption time, and shaping of the weld pool.3–5)

There are presently several very different surface tension measurements techniques, including the sessile drop, maximum bubble pressure, pendent drop, detachment, liquid surface contour, capillary rise, and levitation methods.6) Most of these utilize a contact between the sample and a crucible or refractory ceramic material; however, the levitation method is non-contact. When a contacting method is used at high temperatures, contamination of the liquid steel by the ceramic material may happen. Consequently, a non-contacting method is preferred to ensure reliable surface tension data is obtained.

For high temperatures, three types of non-contacting method can be considered: (1) electromagnetic levitation, (2) electrostatic levitation, and (3) aerodynamic levitation. Among these, the electromagnetic levitation is the only method that can be applied under different oxygen partial pressures by controlling the gas mixture.7–10) Since the levitation method prevents heterogeneous nucleation, it can be also used to investigate the surface tension of the undercooled liquid.11)

In the present study, the surface tension of SUS430 was investigated by means of the electromagnetic levitation (EML) method12) in order to prevent any possible contamination from a refractory ceramic material. For comparison, the surface tension was also measured using a contacting method; specifically the constrained drop method (CDM), which represents an advanced sessile drop method.13) The experimental results obtained were subsequently compared with theoretically and empirically calculated values14) to validate a suitable experimental technique to measure the surface tension of SUS430.

2. Experimental

2.1. Electromagnetic Levitation Method

Figure 1 shows a schematic illustration of the EML facility used in the present study, capable of producing a maximum power and frequency of 12 kW and 210 kHz, respectively. The chemical composition of the SUS430 sample is present-
ed in Table 1. A 0.7–1.0 g cube sample was placed in a glass sample holder, which was then positioned between the upper and lower coils. After sealing the quartz reaction tube (inner diameter: 18 mm, length: 300 mm), it was evacuated using an oil-sealed rotary pump (KODIVAC, GHP-240K) to $1.0 \times 10^{-2}$ Pa, and then filled with a high-purity He gas (99.999%). The sample was then heated under a flow of a 5 vol% H$_2$–He gas mixture, which was introduced at a rate of 1 dm$^3$/min at STP. Once the cubic sample was levitated, the glass sample holder was lowered and the sample was heated continuously. A typical melting sequence of the levitated sample is shown in Fig. 2.

Figure 3 shows a typical example of the heating and cooling curve obtained. The temperature of the sample was measured using a pyrometer (Metis MS09, SensorTherm, 80 points/s), calibrated against the melting point of the sample (1 774 K). The initial heating rate was ~20 K/s. Once it reached to the melting point, a plateau was observed; this temperature was the same as that observed at recalescence during cooling. Once the temperature was stabilized at the target temperature (1 915 K in the figure), the surface oscillation was recorded using a high speed camera (FASTEC IMAGING, HiSpec1L, 250 fps) and the sample was quenched by blowing He gas at a flow rate of 25 dm$^3$/min at STP. In order to suppress the weight change of the sample due to evaporation, all experiments were completed within 300 s. The weight change observed in most of the samples following experimentation was 0.2–0.6%, which is considered unlikely to significantly affect the surface tension measurements. Selected samples were also subjected to chemical analysis using ICP-AES and an oxygen analyzer (ELTRA GmbH, ONH-2000).

Values for the center of gravity of a two-dimensional image from the top-side, and the radius from the center of the gravity to the $x$ and $y$ directions ($R_x$, $R_y$) were determined by the image processing program developed with MATLAB (Fig. 4). The frequencies of the surface oscillations of $m = 0, \pm 1, \pm 2$ for the $l = 2$ mode were then analyzed through fast Fourier transformation from the $(R_x+R_y)$, $(R_x-R_y)$, and surface area; taking into account the influence of the droplet’s rotation.12,15 The surface tension of the liquid steel was calculated from the surface oscillation frequencies, following the modified Rayleigh equation16 of Cummings and Blackburn.17

$$
\sigma (N/m) = \frac{3}{8} \pi M \left[ \frac{1}{5} \sum_{n=2}^{2} v_n^2 - v_0^2 \right] \left( 1.905 + 1.200 \left( \frac{\zeta_0}{a} \right)^2 \right) \\
\zeta_0 = \frac{g}{8 \rho^2 v_l^2} \\
a = \sqrt{\frac{3M}{4 \rho \pi}}
$$

**Table 1.** Chemical composition of the 430 stainless steel used in the present study.

<table>
<thead>
<tr>
<th>Chemical composition (mass%)</th>
<th>Cr</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>S</th>
<th>O</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.00</td>
<td>0.30</td>
<td>0.55</td>
<td>0.003</td>
<td>0.003</td>
<td>0.008</td>
<td>0.04</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** Schematic illustration of the EML facility. (Online version in color.)

**Fig. 2.** Typical melting sequence of a levitated droplet. (Online version in color.)

**Fig. 3.** Typical example of the heating and cooling curve. (Online version in color.)

**Fig. 4.** Typical example of the heating and cooling curve. (Online version in color.)
where \( M \) is the sample mass, \( \nu_{2,m} \) is the surface oscillation frequency for the \( l = 2 \) mode, \( \nu_t \) is the translational frequency, \( g \) is the gravitational acceleration, and \( \rho \) is the sample density.

### 2.2. Constrained Drop Method

Figure 5 shows a schematic illustration depicting the constrained drop facility used in the present study, in which the horizontal reaction furnace is heated by MoSi\(_2\) heating elements to a maximum temperature of 1 973 K. An alumina tube (inner diameter: 72 mm, length: 1 000 mm) was used as a reaction tube, into which a cylindrical sample (~8.3 g) in a special alumina crucible was placed in the center. After sealing the reaction tube, it was evacuated using a rotary pump (ULVAC, G-100D) to \( 6.7 \times 10^{-2} \) Pa. Once filled with a high-purity He gas (99.9999%), a purified 5 vol% H\(_2\)-He gas mixture was introduced at a flow rate of 0.3 dm\(^3\)/min at STP. The furnace was then heated to 1 073 K, at which point the heating rate was reduced to 6 K/min. After reaching 1 843 K, the furnace was held at that temperature for 20 min and images of the liquid metal were captured using a high-resolution digital camera (4 288 \( \times \) 2 848 pixels). The temperature was constantly monitored using a Pt-30%Rh/Pt-6%Rh thermocouple placed just below the sample, and a He–Ne laser (\( \lambda = 632.8 \) nm) provided a back light for imaging. After reducing the temperature by 10 K to 1 783 K, the imaging procedure was repeated; with all images captured being used to calculate the density and surface tension of the sample. Further details pertaining to this constrained drop method have been previously reported.\(^{13,18}\) Following experimentation, the sample was subjected to chemical analysis using an ICP-AES and an oxygen analyzer. In addition, the interface between the sample and the alumina crucible was investigated using a Scanning Electron Microscope (SEM, Hitachi, S-4300) and an Energy Dispersive X-ray Spectroscope (EDX, Horiba, EX-200).

### 3. Results

The density of the liquid SUS430 was determined from the constrained drop method as shown in Fig. 6, and the temperature dependence of the density is given by Eq. (4). This demonstrates that the density of liquid SUS430 lies somewhere between that of pure Fe and pure Cr,\(^{19,20}\) the present result being used in the surface tension measurements described hereafter:

\[
\rho(\text{kg m}^{-3}) = 7.064 - 1.13 \left( T - 1774 \right) \quad \text{(4)}
\]

For comparison, density data reported by Kobatake and Brillo Fe-19wt%Cr alloy are shown together.\(^{21}\) The present results are close to but slightly higher than the data reported by Kobatake and Brillo. It is considered that the difference
was caused by the composition difference. Figure 7 shows the surface tension values measured by EML at temperatures of 1707–2000 K, along with those obtained by the CDM at temperatures of 1783–1873 K. The experimental scatter with the EML was ±6%, whereas that with the CDM was ±2%. The temperature dependence of the surface tension for each case is given by Eqs. (5) and (6), respectively.

\[
\sigma(N/m) = 1.8225 - 0.4226 \times 10^{-3} \times (T - 1774) \quad \cdots (5)
\]

\[
\sigma(N/m) = 1.6243 - 0.1982 \times 10^{-3} \times (T - 1774) \quad \cdots (6)
\]

It is therefore found that the surface tension measurements by EML are higher than those obtained by the CDM. For example, the surface tension at 1823 K was estimated to be 1.802 N/m from EML measurements, but just 1.614 N/m by the CDM. In addition, the temperature dependence of the former measurement is slightly higher than in the case of the latter.

4. Discussion

The oxygen content analysis showed that the EML sample contained 4–9 ppm of oxygen, whereas the CDM sample contained 60 ppm. It was therefore considered that the difference in surface tension observed reflects the contamination of the sample by the alumina crucible used in the CDM. From ICP analysis, the aluminum content in the sample after experimentation was determined to be 81.6 ppm, which is slightly higher than the initial value of 30 ppm. It therefore stands to reason that some quantity of Al2O3 was dissociated from the crucible during experimentation. Figure 8 shows the interface between the metal sample and the alumina crucible after the experiment, in which solid-solution Al2O3–Cr2O3 can be seen to be partially formed. It can therefore be concluded that some dissociated oxygen must be consumed to form Cr2O3 at the interface. This is supported by Lee et al., who found that a thermodynamic equilibrium was achieved between solutes of metals (Cr and O) and Cr2O3 in solid solution.14)

Theoretically, the surface tension of a ternary alloy (\(\sigma\)) can be calculated using Butler’s equation.22)

\[
\sigma = \sigma_A + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}} = \sigma_B + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}} = \sigma_C + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}}
\]

\[
\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)
\]

where \(\sigma, \sigma_i, a_{i}^{\text{Surf}}, a_{i}^{\text{Bulk}}, R, \) and \(T\) are the surface tension of \(i\), the molar surface area of \(i\) (\(A_i = 1.091 N_{A} V_i^{1/3}\)), \(N_{A}\) is Avogadro’s number, \(V_i\) is the molar volume of \(i\), the activity of \(i\) in the surface, the activity of \(i\) in the bulk, the gas constant, and the temperature, respectively. (i = A, B, or C) If we consider SUS430 to be a ternary alloy composed of Fe, Cr, and Si, then the surface tension can be calculated using Eq. (7). Table 2 provides a summary of the thermodynamic and thermo-physical data used in the calculations.19,20,23–26)

In Fig. 7, the calculated values are plotted together for comparison. The theoretically calculated surface tension can be expressed by the following equation.

\[
\sigma(N/m) = 1.8847 - 0.4268 \times 10^{-3} \times (T - 1774) \quad \cdots (8)
\]

It has been well recognized that the surface tension calculated using Butler’s equation generally show good agreements with the experimental data.27–34) From Eq. (8), the surface tension at 1823 K is evaluated to be 1.864 N/m, which is slightly higher than that obtained from EML measurement.

Lee et al. suggested an empirical equation for the surface tension of a ternary alloy.22)

\[
\sigma = \sigma_A + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}} = \sigma_B + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}} = \sigma_C + \frac{RT}{A_i} \ln \frac{a_{i}^{\text{Surf}}}{a_{i}^{\text{Bulk}}}
\]

\[
\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)
\]

where \(\sigma, \sigma_i, a_{i}^{\text{Surf}}, a_{i}^{\text{Bulk}}, R, \) and \(T\) are the surface tension of \(i\), the molar surface area of \(i\) (\(A_i = 1.091 N_{A} V_i^{1/3}\)), \(N_{A}\) is Avogadro’s number, \(V_i\) is the molar volume of \(i\), the activity of \(i\) in the surface, the activity of \(i\) in the bulk, the gas constant, and the temperature, respectively. (i = A, B, or C) If we consider SUS430 to be a ternary alloy composed of Fe, Cr, and Si, then the surface tension can be calculated using Eq. (7). Table 2 provides a summary of the thermodynamic and thermo-physical data used in the calculations.19,20,23–26)

In Fig. 7, the calculated values are plotted together for comparison. The theoretically calculated surface tension can be expressed by the following equation.

\[
\sigma(N/m) = 1.8847 - 0.4268 \times 10^{-3} \times (T - 1774) \quad \cdots (8)
\]

It has been well recognized that the surface tension calculated using Butler’s equation generally show good agreements with the experimental data.27–34) From Eq. (8), the surface tension at 1823 K is evaluated to be 1.864 N/m, which is slightly higher than that obtained from EML measurement.

Lee et al. suggested an empirical equation for the surface tension of a ternary alloy.22)
than those obtained with EML. This difference in the measured surface tension was also measured separately using the levitation technique. The levitation technique is therefore recommended for the measurements of surface tension with complex multi-component commercial steels, such as SUS340.

5. Conclusions

Using EML, the surface tension of SUS340 was successfully investigated and found to have a temperature dependence of \( \sigma(N/m) = 1.8225 - 0.4226 \times 10^{-3} \times (T - 1774) \). The surface tension was also measured separately using the CDM for comparison, producing results which are lower than those obtained with EML. This difference in the measured surface tension was found to be attributable to the contamination by oxygen. When the measurements were compared with theoretically or empirically calculated values, it was concluded that the theoretical values are close to the EML measurements obtained. The levitation technique is therefore recommended for the measurements of surface tension with complex multi-component commercial steels, such as SUS340.

Acknowledgments

This research was supported by the Space Core Technology Development Program (2012MA3A3A02033446) and the Converging Research Center Program (2013K000309) through the Ministry of Science, ICT & Future Planning. The authors would like to thank Professor Masahito Watanabe (Gakushuin University, Japan) and Dr. Juergen Brillo (DLR, Germany) for their helpful discussion. One of the authors (SO) also acknowledges the support provided by JSPS Kakenhi (Grant Number 24760617).

REFERENCES