

Surface Tension of Molten Silver in Consideration of Oxygen Adsorption Measured by Electromagnetic Levitation

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Abstract

The surface tension of molten silver was measured as a function of temperature and oxygen activity, a_{O_2} , by the oscillating droplet method using electromagnetic levitation. The surface tension of molten silver was successfully measured over the very wide temperature range of 515 K. The pure state value of the surface tension was measured when a_{O_2} is lower than 5.3×10^{-19} . The surface tension shows a boomerang shape temperature dependence at a_{O_2} of 3.2×10^{-5} to 2.0×10^{-3} . The excess amount of oxygen adsorption on the molten silver was deduced from the Gibbs adsorption isotherm. The equilibrium constant, standard enthalpy, and standard entropy for the oxygen adsorption reaction on molten silver was revised, using the measurement result based on the Szyszkowski model. Furthermore, the relationship between the surface tension, temperature, and a_{O_2} was also updated.

Keyword(s): Surface tension, Oxygen adsorption, Electromagnetic levitation, Molten silver, Oscillating droplet method

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1. Introduction

In order to respond to difficult demands for the improvement of quality of products and their manufacturing, various high-value-added high-temperature melt processes such as blazing of high performance automobile radiators and precision casting of turbine blades for jet airplanes have been growing in complexity. Therefore, numerical calculations employed together with experiments have begun to play an increasingly important role. This will also contribute to cost reduction, shorter development periods, and energy saving. For simulating a free surface shape of melt and a heat/mass transport induced by the Marangoni convection¹⁾, an accurate surface tension and its temperature coefficient is strongly required.

Surface tension of liquid metals is strongly influenced by even a small amount of contamination of the sample. In particular, oxygen is well known as one of the strongest surface active elements for liquid metals²⁻⁹⁾. One must note that oxygen can exit in the measurement atmosphere as a gas phase, even at room temperature.

One of the authors, Ozawa, measured the surface tension of molten silver by the oscillating droplet method using electromagnetic levitation, to investigate the influence of oxygen activity and temperature on surface tension of liquid metals as a model⁷⁾. Electromagnetic levitation (EML) is one of the best tools for accurate surface tension measurement of a molten metallic sample, in which surface tension can be calculated from the surface oscillations of the levitated droplet^{10,11)}. The major

advantages of this technique are that it assures measurements (a) free of contaminants from the container, (b) at high temperatures that are sufficiently above the melting point, and (c) under deeply undercooled conditions. This is attributed to the sample not being in contact with the container, which is chemically reactive with the sample at high temperatures, and plays a role in the nucleation center below the melting point. This technique also assures (d) atmosphere control during the measurement. As a result, the surface tension of molten silver was measured over a very wide temperature range of about 515 K under conditions free of contamination from the container, in consideration of the influence of oxygen adsorption from atmospheric gas. Furthermore, the influence of oxygen activity (a_{O_2}) on surface tension of molten silver, σ , was described from the measurement result using the following Szyszkowski model¹²⁾,

$$\sigma^P - \sigma = RT\Gamma_0^{\text{sat}} \ln(1 + K_{\text{ad}} \sqrt{a_{O_2}}) \quad (1)$$

where σ^P is the pure state value of surface tension, R is the gas constant, T is the temperature, Γ_0^{sat} is the excess amount of oxygen adsorption, K_{ad} is the equilibrium constant for the following oxygen adsorption reaction at the melt surface, and a_{O_2} is defined as oxygen partial pressure of atmospheric gas (P_{O_2}) relative to 1 atm.



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However the influence of sample purity on surface tension was not taken into account in that study. Furthermore, Γ_0^{sat} was not evaluated experimentally, because the effect of oxygen adsorption on the surface tension was investigated only under the $a_{\text{O}_2}=10^{-3}$, though it can be estimated from the relationship between surface tension and a_{O_2} using the following Gibbs adsorption isotherm.

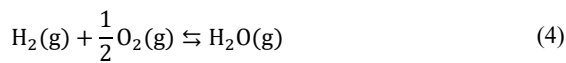
$$\Gamma_0^{\text{sat}} = -\frac{2 \log e}{RT} \cdot \frac{d\sigma}{d \log a_{\text{O}_2}} \quad (3)$$

Instead, the mean of the reported value of the Γ_0^{sat} measured by a conventional container technique such as the sessile drop method was used reluctantly.

In this study, the surface tension of molten silver was measured by the oscillating droplet method using EML under various a_{O_2} conditions, to evaluate the Γ_0^{sat} under conditions free of contamination from the container. The influence of sample purity on the surface tension was also investigated. Furthermore, the relationship between the surface tension of molten silver, temperature, and a_{O_2} was revised from the experimental results.

2. Experimental Procedure

Three types of silver samples with nominal purities of 99.9+% (3N+), 99.998 % (4N8), and 99.9999 % (6N) were used in this study. The chemical composition of the 4N8 and 6N samples are shown in **Table 1**. Although the material supply company informed us that the 3N+ sample contains at least Au, Cu, Fe, Pb, and Bi as impurities, the details of the chemical composition of the sample were not obtained. The experimental facility is depicted elsewhere⁷. About 400 mg of the silver sample was electromagnetically levitated and then melted under the flow condition (2 L/min) of Ar-He-10 vol. % H₂ mixed gas with moisture content of about 2.66 vol. ppm to lower the a_{O_2} , by forming the H₂O formed from the following reaction:



Furthermore, high purity commercial Ar and He gases, the oxygen contents of which are less than 0.1 vol. ppm, were introduced into the chamber together with Ar-1 vol. % O₂ and Ar-0.01 vol. % O₂ gases, by using a precision digital gas mass flow meter to control the a_{O_2} to 10⁻⁵ to 10⁻³. The a_{O_2} of the inlet gas was confirmed by a zirconia oxygen sensor operated at 1008 K. The zirconia oxygen sensor was calibrated by using oxidation and reduction reactions of metals such as nickel and iron¹³.

The oscillation behavior and the temperature of the levitated droplet were monitored from above, using a high-speed video camera (500 FPS, 16 sec) and a monochlor pyrometer. The temperature of the droplet was controlled by changing the flow ratio of argon and helium gases.

Table 1 Main impurities in the silver sample (mass ppm)

	P	Si	Cu	Fe
4N8	<0.1	<0.1	15.2	<0.1
	Pb	Bi	Pd	Cd
	2.7	0.3	2.5	<0.1
6N	P	Si	Cu	Fe
	<0.01	0.03	<0.01	<0.01
	Pb	Bi	Pd	Cd
	<0.05	<0.01	<0.05	<0.01

The frequencies of the surface oscillations of the $m = 0, \pm 1$, and ± 2 for the $l = 2$ mode, and motion of the center of gravity of two-dimensional-image, were analyzed from time-sequential data of the observed images through fast Fourier transformation (FFT) and the maximum entropy method (MEM). The influence of two types of droplet rotations of real rotation and apparent rotation^{10, 14} was taken into account in the analysis. The surface tension of molten silver was calculated from these frequencies by using the Rayleigh equation¹⁵, and the Cummings and Blackburn calibration¹⁶. The density of the molten silver used in the calculation was determined from the following equation, reported by Kirshenbaum *et al.*¹⁷.

$$\rho = 9346 - 0.9067(T-1234) \text{ [kg}\cdot\text{m}^{-3}] \quad (5)$$

3. Results

When the Ar-He-10 vol. % H₂ mixed gas is used, the a_{O_2} shows temperature dependence due to a dissociation equilibrium of H₂O described in the reaction (4). The a_{O_2} of the Ar-He-10 vol. % H₂ gas was evaluated as a function of temperature, using the standard Gibbs energy for formation of H₂O¹⁸ and the a_{O_2} of the inlet gas measured at 1008 K. From this result, the temperature dependence of a_{O_2} is calculated as shown by the solid line of **Fig. 1**, while assuming that the ratio of activities of H₂O and H₂ ($a_{\text{H}_2\text{O}}/a_{\text{H}_2}$) is constant independent of temperature. This result agrees well with the a_{O_2} calculated from the nominal values of the contents of hydrogen (10 vol. %) and that of moisture (2.66 vol. ppm) in the Ar-He-H₂ gas (dashed line).

Figure 2 shows the temperature dependence of surface tension for molten silver under the flow condition of Ar-He-10 vol. % H₂ gas as a function of sample purity, together with the literature data^{3,4,6,7,19-23}. The maximum value of uncertainties for the measurement plots was calculated as $\pm 9.8 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$ based on the GUM (ISO Guide to the Expression of Uncertainty in Measurement)²⁴, in which the coverage factor of $k_p = 2$ was selected. The surface tension of molten silver is measured in the wide temperature range of over 515 K in this study.

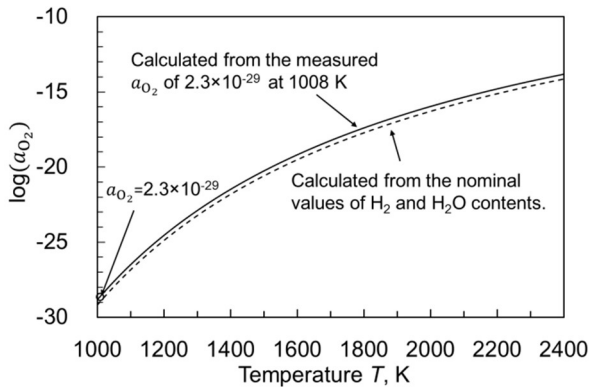


Fig. 1 Temperature dependence of Ar-He-10 vol. % H₂ gas used in this study. The solid line corresponds to that calculated from the a_{O_2} of 2.3×10^{-29} measured by a zirconia oxygen sensor operated at 1008 K. The dashed line corresponds to that calculated from the nominal values of H₂ and H₂O contained in the gas.

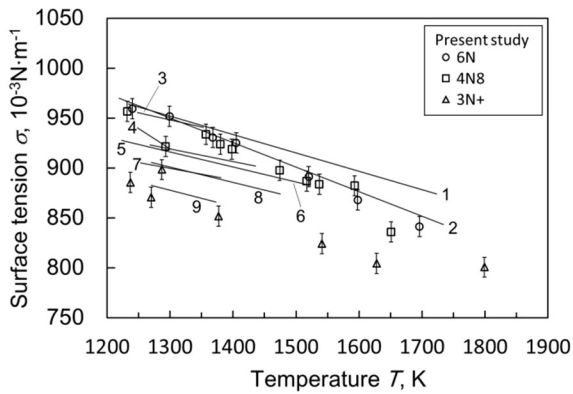


Fig. 2 Surface tension of molten silver with purity of 6N, 4N8, and 3N+, together with literature values. (1: Kasama⁶), 2: Ozawa⁷, 3: Rhee¹⁹), 4: Kingery²⁰), 5: Brunet²¹), 6: Krause²²), 7: Bernard and Lupis³), 8: Lee²³), 9: Sangiorgi⁴).

The surface tension of molten silver with 4N8 purity is almost the same as that with 6N purity. However, decreases in the surface tension are observed when the sample purity becomes low down to 3N+. These results confirm that the sample purity influences the surface tension. A high purity sample of more than 4N8 should be used to measure the accurate surface tension of molten silver.

Figure 3 shows the temperature dependence of surface tension for molten silver with 6N purity at the constant a_{O_2} conditions of 3.2×10^{-5} (\square), 2.5×10^{-4} (Δ) and 2.0×10^{-3} (\diamond) under Ar-He-O₂ gas. The measurement results for 6N and 4N8 purities samples at the $a_{O_2} < 5.3 \times 10^{-19}$ ($T < 1700$ K) under the Ar-He-10 vol. % H₂ condition (\circ and \bullet) are also exhibited, which corresponds to **Fig. 2**. For comparison, the reported value for 4N purity silver measured by one of the authors, Ozawa⁷, at the $a_{O_2} < 10^{-17}$ (\bullet) under the Ar-He-5 vol. % H₂ and $a_{O_2} = 10^{-3}$ (\blacklozenge)⁷ are also

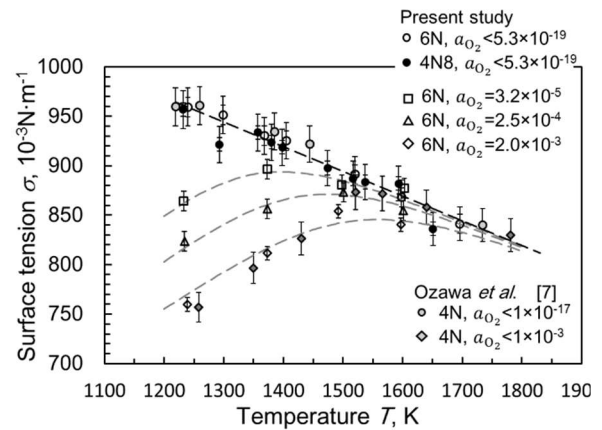


Fig. 3 Surface tension of molten silver measured under Ar-He mixture gas with a_{O_2} of 3.2×10^{-5} , 2.5×10^{-4} , and 2.0×10^{-3} , together with that measured under Ar-He-10 vol. % H₂ gas ($a_{O_2} < 5.3 \times 10^{-19}$). Also shown are the surface tension measured under $a_{O_2} < 1 \times 10^{-17}$ and $a_{O_2} = 1 \times 10^{-5}$ reported by Ozawa *et al.*⁷.

depicted. When the a_{O_2} is controlled at 3.2×10^{-5} , 2.5×10^{-4} and 2.0×10^{-3} , the surface tension of molten silver increases and then decreases as the sample temperature rises. This boomerang shape temperature dependence of surface tension is explained by the temperature reliance of the equilibrium constant for oxygen adsorption reaction⁷); higher a_{O_2} usually induces lower surface tension of molten metal, owing to surface-active effects by oxygen adsorption at comparatively low temperature. However, oxygen is desorbed from the melt surface with increasing temperature, because of a decrease in the equilibrium constant of oxygen adsorption reaction (K_{ad}). That is, oxygen adsorption is an exothermal reaction. As a result, the surface tension of molten silver increases to approach to the surface tension of a pure state free from oxygen adsorption, σ^P , at high temperature.

Since the surface tension measured at the a_{O_2} of 3.2×10^{-5} to 2.0×10^{-3} is converged into the measurement result under the Ar-He-10 vol. % H₂ gas atmosphere at high temperature, it is reasonable that the measurement result corresponds to σ^P . The temperature dependence of σ^P can be described as follows,

$$\sigma^P = 961 - 0.25(T - 1234) [10^{-3} \text{N} \cdot \text{m}^{-1}] \quad (6)$$

the intercept of which ($961 \times 10^{-3} \text{N} \cdot \text{m}^{-1}$) corresponds to the surface tension at the melting temperature of silver (1234 K).

Figure 4 shows the surface tension of molten silver with 6 N purity, as a function of a_{O_2} at 1373 K. When a_{O_2} becomes higher than 3.2×10^{-5} , it is confirmed that the surface tension is decreased dramatically due to oxygen adsorption, which agrees well with the literature data by Sangiorgi *et al.*⁴) and Bernard and Lupis³). The excess amount of oxygen adsorption at the surface of molten

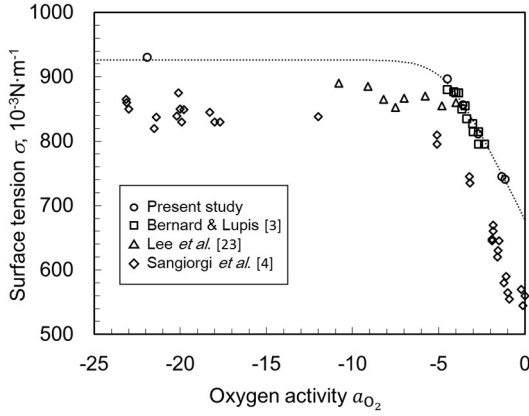


Fig. 4 Surface tension of molten silver with purity of 6N as a function of oxygen activity, together with the literature data reported by Bernard and Lupis, Lee *et al.*, and Sangiorgi *et al.*

silver can be evaluated to be $\Gamma_0^{\text{sat}} = 4.06 \times 10^{-6} [\text{mol} \cdot \text{m}^{-2}]$ from the slope of the fitting line of the measurement plots at $a_{\text{O}_2} > 10^{-5}$, shown by the dotted line, using the Gibbs adsorption isotherm (see Eq. 3).

4. Discussion

As mentioned in the previous section, the excess amount of oxygen adsorption at the surface of molten silver, Γ_0^{sat} , was experimentally deduced. It will be validated by using the Kozakevitch model²⁵⁾, assuming a monolayer adsorption. This model also assumes that only oxygen ions are located at the first layer of melt surface, where an electrical double layer is formed by ionizations of adsorbed oxygen and molten metal. Furthermore, the structure of melt surface with oxygen adsorption is hypothesized to be similar to that of its suboxide or lower oxide. These assumptions are satisfied at the (100) plane of Ag_2O structure shown in **Fig. 5**, in which the amount of oxygen ions with respect to the area that corresponds to the Γ_0^{sat} is calculated at $7.42 \times 10^{-6} [\text{mol} \cdot \text{m}^{-2}]$ from the following equation,

$$\Gamma = \frac{n_{\text{O}^{2-}}}{A \cdot N_A} \quad (7)$$

where $n_{\text{O}^{2-}}$ is the number of oxygen ions, A is the area of lattice plane, and N_A is the Avogadro number. Almost the same Γ_0^{sat} value is obtained from both our experiment and the calculation result of the Kozakevitch model²⁵⁾. These values are also in good agreement with the reported values^{2,3,26)}. Thus, the Γ_0^{sat} value deduced from our measurement is thought to be reasonable.

Since the σ^P and Γ_0^{sat} for molten silver were obtained, the equilibrium constant of oxygen adsorption reaction, K_{ad} , was evaluated from the measurement result at a_{O_2} of 3.2×10^{-5} , 2.5×10^{-4} , and 2.0×10^{-3} , by using the following equation deformed

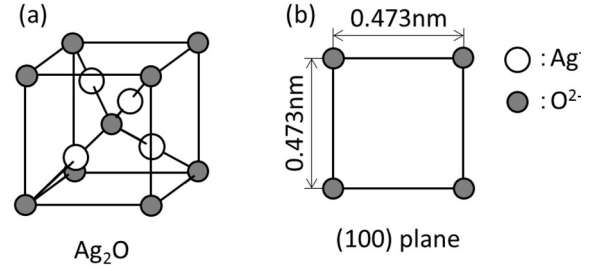


Fig. 5 Structure of Ag_2O (a) and its (100) plane (b)

from the Szyszkowski equation¹²⁾ (see. eq. 1),

$$K_{\text{ad}} = \frac{\exp\left(\frac{\sigma^P - \sigma}{RT\Gamma_0^{\text{sat}}}\right) - 1}{\sqrt{a_{\text{O}_2}}} \quad (8)$$

The reported K_{ad} in the previous study of our group⁷⁾ was also revised using the σ^P and Γ_0^{sat} obtained in this study. The result is shown in **Fig. 6**. A good linearity of the $\ln K_{\text{ad}}$ with respect to $1/T$ implies the validity of our surface tension measurement. The temperature dependence of K_{ad} is expressed as follows,

$$\ln K_{\text{ad}} = 27075T^{-1} - 14.391 \quad (9)$$

According to the following van't Hoff equation, the slope of the good linearity of $\ln K_{\text{ad}}$ with respect to $1/T$ within the measurement temperature range corresponds to the standard enthalpy for the oxygen adsorption reaction, ΔH° ,

$$\frac{\Delta H^\circ}{-R} = \frac{d(\ln K_{\text{ad}})}{d(1/T)} \quad (10)$$

The reported ΔH° for the oxygen adsorption reaction of molten silver in the previous study of our group is revised to be $\Delta H^\circ = -225.1 \text{ kJ} \cdot \text{mol}^{-1}$ ($1230 \text{ K} < T < 1610 \text{ K}$) in this study.

The temperature reliance of the standard Gibbs energy for the oxygen adsorption reaction, ΔG° , can be described as shown in **Fig. 7** from the result of **Fig. 6** by using the following relationship with K_{ad} ,

$$\Delta G^\circ = -RT \ln K_{\text{ad}} \quad (11)$$

ΔG° shows good linearity increasing within the measurement temperature range. The standard entropy, ΔS° , is also updated to be $\Delta S^\circ = -103.4 \text{ J} \cdot \text{K}^{-1}$ from the slope of the line using the following equation,

$$\Delta S^\circ = -\frac{d\Delta G_{\text{ad}}^\circ}{dT} \quad (12)$$

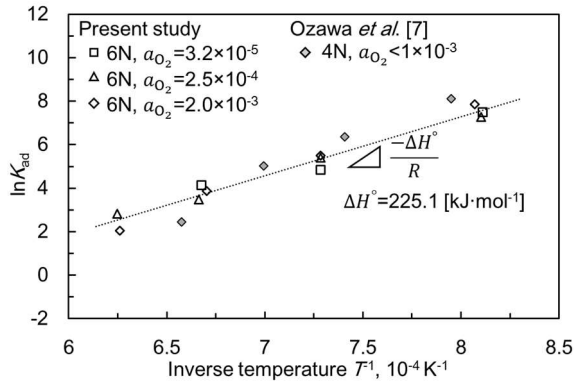


Fig. 6 van't Hoff plot of the equilibrium constant of oxygen adsorption reaction for molten silver. The standard enthalpy for oxygen adsorption reaction is calculated at $\Delta H^\circ = -225.1 \text{ kJ} \cdot \text{mol}^{-1}$ from the slope of the line determined by a least-square approach for the plots.

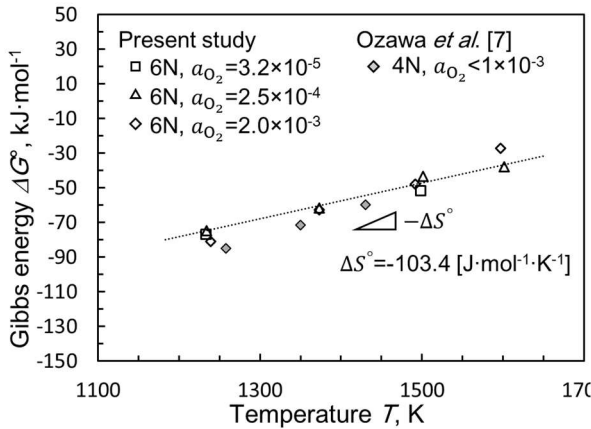


Fig. 7 Temperature dependence of the standard Gibbs energy for oxygen adsorption reaction for molten silver. The standard entropy is calculated at $\Delta S^\circ = -103.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ from the slope of the line determined by a least-square approach for plots.

Having deduced the σ^P , Γ_0^{sat} , and K_{ad} for molten silver as mentioned above, the surface tension of molten silver can be described as functions of temperature and oxygen activity, using the Szyszkowski equation¹²⁾ as follows,

$$\sigma_{\text{Ag}} = 961 - 0.25(T - 1234) - 4.06 \times 10^{-6}RT \quad (13)$$

$$\times \ln \left(1 + \exp \left(\frac{27075}{T} - 14.39 \right) \times \sqrt{a_{\text{O}_2}} \right) [10^{-3} \text{N} \cdot \text{m}^{-1}]$$

The relationship between the surface tension, temperature, and oxygen activity for molten silver is depicted as a 3D graph using this equation as shown in **Fig. 8**, in which the boomerang shape temperature dependence of surface tension is represented pertinently.

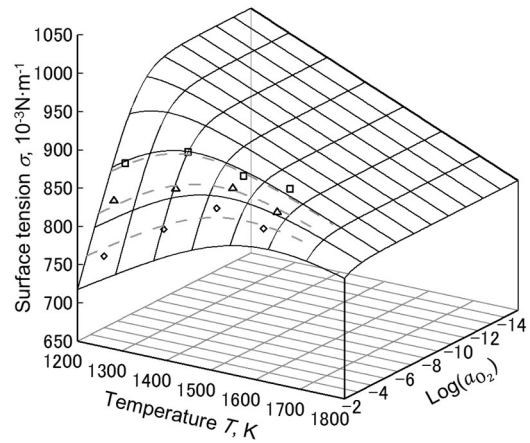


Fig. 8 Relationship between surface tension, temperature, and a_{O_2} for molten silver described from experimental results using the Szyszkowski model¹²⁾.

4. Summary

The surface tension of molten silver was measured over a wide temperature range of about 515 K under various a_{O_2} conditions, by oscillating droplet method using electromagnetic levitation. The boomerang shape temperature dependence of surface tension was observed when a_{O_2} is controlled at 3.2×10^{-5} , 2.5×10^{-4} , and 2.0×10^{-3} . The Γ_0^{sat} was determined by using the Gibbs adsorption isotherm. Based on the Szyszkowski model¹²⁾, the temperature dependence of K_{ad} and the relationship between the surface tension, temperature, and a_{O_2} were updated from the reported data of the previous study of our group. Furthermore, the standard enthalpy and entropy for oxygen adsorption reaction of molten silver were also revised.

Acknowledgments

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