Effects of Carbon and Oxygen on Fe–C–O Melt Surface Tension

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For this study, we measured surface tension of Fe–C and Fe–C–O melts accurately under controlled carbon and oxygen activities using an oscillating droplet method with an electromagnetic levitator (EML). The results are summarized as follows. The carbon activity has no influence on the surface tension of Fe–C melt at temperatures of 1823–2023 K under oxygen partial pressure of 10^{-10} Pa. For Fe–C–O melts, the carbon activity has no influence on the surface tension at a constant oxygen partial pressure of 10^{-7} Pa and temperatures of 1873–1973 K. It is noteworthy that oxygen activity is reduced by carbon in the melt because of the negative interaction between oxygen and carbon. Considering the interaction, the surface tension of the Fe–C–O melts was formulated as a function of carbon and oxygen concentrations and temperature.

KEY WORDS: surface tension; Fe–C–O melts; carbon activity; oxygen activity; oscillating droplet method; electromagnetic levitation; gas–liquid equilibrium.

1. Introduction

Recently, numerical simulations have been used widely to optimize steel processes such as refining, casting, and welding. Therefore, accurate thermophysical properties of molten steel are required for simulations. The surface tension of Fe–C–O melts is necessary to simulate Marangoni flow in molten steel. We previously measured the surface tension of Fe–O melts under various oxygen activities and temperatures.¹⁾ Results show that an oxygen atom acts as a strong surface-active element, and that the surface tension of Fe–O melts is reduced significantly by oxygen adsorption. We developed the surface tension of Fe–O melt as a function of oxygen activity and temperature based on the Szyszkowski model.²⁾

The next step is to clarify the effect of carbon on the surface tension of Fe–C melts. Many data have been reported in relation to the surface tension of Fe–C melts as Keene reviewed in 1988.³⁾ However, the effects of carbon on the surface tension have not been viewed with consensus yet among the investigators. Kawai *et al.*⁴⁾ reported that carbon acted as a surface-active element. Halden and Kingery,⁵⁾ and Monma and Sudo⁶⁾ reported that carbon has no influence on the surface tension. In contrast, Jimbo and Cramb⁷⁾ reported the positive dependence of carbon on surface tension.

Considering that oxygen is a strong surface-active element, we believe that oxygen obscures the true behavior of surface tension of Fe–C melt. Therefore, controlling the oxygen activity is a key issue in solving the discrepancy among these investigators previous reports for the Fe–C system.

We found that oxygen partial pressure should be less than

10^{-10} Pa to remove its influence on the surface tension.¹⁾ In this study, we first examined the effect of carbon on the surface tension of Fe–C melts under oxygen partial pressures below 10^{-10} Pa. Subsequently, the surface tension of Fe–C–O melts was studied at a constant oxygen partial pressure. An oscillating droplet method was used to measure the surface tension with an electromagnetic levitator (EML). The carbon and oxygen activities were controlled using a CO/CO₂ gas–liquid equilibrium method. The Fe–C samples were also prepared using an iron/graphite pre-melting method. Based on the results, we formulated the surface tension of the Fe–C–O melts.

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.

Oxygen and carbon activities are controlled according to the following equilibrium relations:

$$\log a_{\text{O}_2} = 2 \log \frac{a_{\text{CO}_2}}{a_{\text{CO}}} - \log K_{(1)} \quad \dots\dots\dots (3)$$

$$\log a_{\text{C}} = \log \frac{a_{\text{CO}}^2}{a_{\text{CO}_2}} - \log K_{(2)} \quad \dots\dots\dots (4)$$

where a_{O_2} , a_{CO} and a_{CO_2} respectively represent the activities of O₂, CO and CO₂ relative to 10⁵ Pa. Furthermore, a_{C} is a carbon activity relative to pure graphite at 10⁵ Pa. $K_{(i)}$ is the

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equilibrium constant of reaction (i), and the values of $K_{(1)}$ and $K_{(2)}$ were determined using thermochemical data.⁸⁾ Flow rates of Ar, He, CO, and CO₂ gases were adjusted to obtain the intended a_{O_2} and a_C . The calculated a_{O_2} and a_C were confirmed by quantitative chemical analysis of oxygen and carbon dissolved in the iron sample after quenching.

2.2. Experimental Procedure

Figure 1 shows an experimental setup of the EML facility used to measure the surface tension of Fe–C–O melts. The maximum power and frequency of the radio frequency generator of the EML were, respectively, 15 kW and 200 kHz. High-purity (99.9972 mass%) iron was prepared using the purification process containing anion exchange separation and Ar–H₂ arc plasma melting.⁹⁾ High-purity iron was used as a sample to prevent any effect of minor elements. The chemical composition of the high-purity iron is presented in **Table 1**.

The sample of about 1.0 g was placed on a quartz sample holder and positioned in a levitation coil. The quartz tube was evacuated to the order of 10^{-2} Pa using a diaphragm pump and turbo molecular pump, and was filled with high-purity Ar gas (99.9999 vol.%). The iron sample was initially levitated in an Ar gas atmosphere using the EML facility, and an Ar–He–CO–CO₂ gas mixture was alternatively introduced into the quartz tube to control oxygen and carbon activities. The Fe–C samples were also prepared by melting iron with graphite under an Ar–5 vol.% H₂ gas atmosphere in a BN crucible before surface tension measurements. For pre-melted Fe–C samples, an Ar–He–5 vol.% H₂ gas was used for surface tension measurements. Here, these gases were purified using an Mg-deoxidizer kept at 873 K before introduction into the quartz tube.

The sample temperature was measured using a mono-color pyrometer (wavelength, 0.9 μ m; temperature resolution, 1 K; sampling rate, 2 Hz). The pyrometer was calibrated at the

melting temperature of iron (1 808 K). The sample temperature was controlled by changing the He gas flow rate in the gas mixture. The images of the oscillating droplet were recorded using a high-speed camera with resolution of 512 $\times$ 512 pixels at a frame rate of 250 fps for 16 s from the sample top.

The gas–liquid equilibrium was confirmed by monitoring the surface tension variation with time. After recording the images, some samples were quenched, and were subjected to quantitative chemical analysis of oxygen and carbon in the sample to assure the gas–liquid equilibrium. Carbon and oxygen 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 Fe–C–O melts was calculated from the following modified Rayleigh equation proposed by Cummings and Blackburn.^{10,11)}

$$\sigma = \frac{3\pi M}{8} \left[\frac{1}{5} \sum_{m=-2}^2 v_m^2 - v_t^2 \left\{ 1.9 - 1.2 \left(\frac{g}{8\pi^2 v_t^2 R_0} \right)^2 \right\} \right] \dots (5)$$

Therein, σ [N·m⁻¹] denotes the surface tension, M [kg] represents the sample mass, v_m [Hz] is the surface oscillation frequency for $m = 0, \pm 1$ and ± 2 for the $l = 2$ mode, v_t [Hz] stands for the translation frequency of center of gravity, g [m·s⁻²] is the gravitational acceleration, and R_0 [m] is the sample radius. The values of v_m and v_t were determined through fast Fourier transformation (FFT) using the time-sequential images of the oscillating droplet. The details of frequency analysis were explained with consideration of sample rotation in previous papers.^{1,12,13)} The value of R_0 was calculated using the density for the Fe–C melt reported by Jimbo and Cramb,¹⁴⁾ which is given as

$$\rho / \text{kg} \cdot \text{m}^{-3} = 7100 - 73.2w_C - (0.828 - 0.0874w_C) \times (T - 1823), \dots (6)$$

where ρ stands for the density, T denotes the absolute temperature, and w_C signifies the carbon concentration in mass% in the Fe–C alloy.

3. Results

3.1. Surface Tension of Fe–C Melts

Figure 2 shows the surface tension of Fe–C melts as a function of carbon concentration at 1 873 K together with the previously reported values.^{4–7)} **Figure 3** shows the surface tension as a function of a_C . **Table 2** shows details of data presented in Figs. 2 and 3. Here, the activity coefficient of carbon at 1 873 K was evaluated from that at 1 823 K¹⁵⁾ assuming a regular solution model, and was used for the activity-concentration conversion. In this study, all data were measured under a_{O_2} below 10^{-15} because the surface tension of liquid iron is sensitive to a_{O_2} . It is necessary to control a_{O_2} below 10^{-15} to remove its effect.¹⁾ The present result demonstrates that the surface tension of Fe–C melts is independent of the carbon activity (carbon content). This is because that considering the positive deviation of a_C from Raoult's law,¹⁵⁾ carbon does not behave as a surface-active element for liquid iron.

Fig. 1. Schematic diagram of an electromagnetic levitator to measure the surface tension of Fe–C–O melt with control of oxygen and carbon activities.

Table 1. Chemical composition of the high-purity iron (mass ppm).

Al	Si	P	S	Ti	Cr	Mn	Co
0.19	0.17	0.20	0.15	0.59	0.011	0.049	1.6
Ni	Cu	Se	Sr	Nb	Mo	Ag	Cd
0.092	22	0.52	0.13	0.23	0.37	0.10	0.20

Fig. 2. Carbon concentration dependence of surface tension of Fe-C melt at 1873 K.

Fig. 3. Carbon activity dependence of surface tension of Fe-C melt at 1873 K. Symbols used in the figure are the same as those used in Fig. 2.

Table 2. Details of data presented in Figs. 2 and 3.

Symbol	Investigators	Temp./K	Method and Sample preparation	Ref.
□	Morohoshi <i>et al.</i>	1873	OD in Ar-He-H ₂ , pure iron	[1]
◆	Present study	1873	OD in Ar-He-CO-CO ₂ , gas-liquid equilibrium	
●	Present study	1873	OD in Ar-He-H ₂ , iron/graphite pre-melting	
(1)	Jimbo and Cramb	1823	SD in CO, iron/graphite pre-melting	[7]
(2)	Kawai <i>et al.</i>	1823	SD in Ar, iron/graphite pre-melting	[4]
(3)	Monma and Sudo	1873	SD in H ₂ , iron/graphite pre-melting	[6]
(4)	Halden and Kingery	1843	SD in He, iron/graphite pre-melting	[5]

OD, Oscillating droplet method; SD, Sessile drop method.

Jimbo and Cramb reported the positive dependence of carbon on the surface tension of Fe-C melts as shown in Figs. 2 and 3.⁷⁾ They used a constant density data of liquid iron for surface tension calculation without considering effect of carbon on the density. Recalculation using Eq. (6) for the Fe-C density reduced the carbon dependence, which agrees with the present data within their experimental uncertainty of ± 50 mN·m⁻¹. On the other hand, Kawai *et al.*²⁾

Fig. 4. Temperature dependence of surface tension of pure Fe and Fe-C melts.

Fig. 5. Carbon activity dependence of surface tension of Fe-O-C melt at $a_{O_2} = 10^{-12}$ and 1873 K.

reported the negative carbon-dependent value, and other previous data shows lower and carbon-independent values.^{3,4)} The reason for the different behaviors among the previous studies is not clearly understood yet. However, Jimbo and Cramb pointed out the effect of sulfur associated with carbon addition.⁷⁾ Sulfur is a strong surface-active element, and trace amounts of sulfur would cause the decrease in the surface tension.

Figure 4 shows the temperature dependence of surface tension of Fe-C melts at high carbon concentration varying from 1.94 to 4.71 mass% together with that of pure liquid iron.¹⁾ All the data present identical temperature dependence within experimental uncertainty.

3.2. Surface Tension of Fe-C-O Melts

Figure 5 presents the surface tension of Fe-C-O melts as a function of a_C at 1873 K at a constant a_{O_2} of 10^{-12} corresponding to an oxygen partial pressure of 10^{-7} Pa. The surface tension was constant with a_C . **Figure 6** shows the temperature dependence of surface tension of Fe-C-O melts for two carbon activities 10^{-2} and 10^{-3} at $a_{O_2} = 10^{-12}$. The surface tension at $a_{O_2} = 10^{-12}$ was less than that of pure iron because of oxygen adsorption. However, it is readily apparent that solid squares ($a_C = 10^{-3}$) and open diamonds ($a_C = 10^{-2}$) are located along the identical curve: the difference in carbon activity causes no difference in surface tension, even

Fig. 6. Temperature dependence of surface tension of Fe–C–O melt measured under various carbon activities at $a_{O_2} = 10^{-12}$ compared to that of pure iron.

Table 3. Oxygen and carbon concentrations, 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 concentrations.

Experimental condition	Calculated values using a_{CO} and a_{CO_2}	Results of chemical analysis	Calculated values using w_O and w_C
Temp./K	a_{CO} a_{CO_2}	$\log a_{O_2}$ $\log a_C$	w_O , [mass%] w_C , [mass%] $\log a_{O_2}$ $\log a_C$
1873	2.5×10^{-1} 5.5×10^{-6}	–16.0 –0.3	0.0011 4.4 –16.6 –0.2
1923	4.9×10^{-1} 1.1×10^{-3}	–12.0 –2.0	0.0022 0.26 –12.3 –2.0
1973	3.4×10^{-1} 3.0×10^{-4}	–12.0 –2.0	0.0017 0.23 –12.3 –2.1

at $a_{O_2} = 10^{-12}$.

Table 3 shows the oxygen and carbon concentrations, w_O and w_C (by mass%) in the Fe–C–O samples obtained through the chemical analysis after the experiments conducted for different conditions. The values of a_{O_2} and a_C calculated from w_O and w_C agree with the values calculated from CO–CO₂ gas compositions used in the experiments, which means that the a_{O_2} and a_C were well controlled using the gas–liquid equilibrium method.

4. Discussion

4.1. Modeling Surface Tension of Fe–C–O Melts

This study revealed that carbon activity has no influence on the surface tension of Fe–C–O melts. Therefore, the effect of oxygen activity should be considered simply for estimation of the surface tension. We previously proposed the following expression to deduce the surface tension of Fe–O melts.¹⁾

$$\begin{aligned} \sigma / \text{mN} \cdot \text{m}^{-1} &= (1925 \pm 65) - (0.455 \pm 0.034) \times (T - 1808) \\ &- 0.155T \ln \left(1 + \exp \left(\frac{(4.27 \pm 0.04) \times 10^4}{T} - (10.1 \pm 0.3) \right) a_{O_2}^{1/2} \right) \end{aligned} \quad (7)$$

Using Eq. (7), the surface tension of Fe–C–O melts at 1873 K is evaluated as a function of oxygen and carbon activities

Fig. 7. Surface tension of Fe–C–O melts presented in the σ – a_C – a_{O_2} 3D diagram at 1873 K. The gray area shows where oxygen and carbon concentrations are controlled using the gas–liquid equilibrium method.

as portrayed in **Fig. 7**. The surface tension for each carbon activity is presented with identical parallel curves because the carbon effect was negligible. The gray area in the figure represents conditions under which oxygen and carbon activities are controlled using the gas–liquid equilibrium method.

4.2. Modeling Surface Tension of Fe–C–O Melts as a Function of Oxygen and Carbon Concentrations

To express Eq. (7) as a function of oxygen and carbon concentrations, the interaction between carbon and oxygen in molten iron should be regarded as follows. The dissolution reaction of oxygen in liquid iron is expressed as

where $\underline{O}$ represents an oxygen atom dissolved in liquid iron. The equilibrium constant of Eq. (8) $K_{(8)}$ is presented as

$$K_{(8)} = \frac{h_O}{a_{O_2}^{1/2}} = \exp \left(\frac{1.34 \times 10^4}{T} + 0.8 \right) \quad (9)$$

where h_O is the oxygen activity relative to 1 mass% of oxygen in liquid iron based on Henry's law. The value of $K_{(8)}$ was determined using the standard Gibbs energy of the reaction: $\underline{O} + H_2 = H_2O^{16)}$ and the standard Gibbs energy of formation of $H_2O(g)$.⁸⁾ The value of h_O is defined using the activity coefficient f_O and oxygen concentration in mass% w_O .

$$h_O = f_O w_O \quad (10)$$

The f_O is expressed using interaction parameters as

$$\log f_O = e_O^O w_O + e_O^C w_C \quad (11)$$

where e_i^j is an interaction parameter of j for i . The following interaction parameters were used for this study.¹⁶⁾

$$e_O^O = -0.17 \quad (12)$$

$$e_O^C = -0.427 \quad (13)$$

These interaction parameters are applicable in the condition: $T = 1823\text{--}1873$ K, $w_C \leq 1$ mass% and $w_O \leq 0.21$ mass%. Substituting the equilibrium relation and interaction parameters Eqs. (9)–(13) into Eq. (7) produces Eq. (14) shown

Fig. 8. Surface tension of Fe–C–O melts presented in the σ - w_C - w_O 3D diagram at 1 873 K. The gray area shows where oxygen and carbon concentrations are controlled using the gas–liquid equilibrium method.

below.

$$\begin{aligned} \sigma / \text{mN} \cdot \text{m}^{-1} &= (1925 \pm 65) - (0.455 \pm 0.034) \times (T - 1808) \\ &\quad - 0.155T \ln \left(1 + 10^{-0.17w_O - 0.427w_C} w_O \exp \left(\frac{2.93 \times 10^4}{T} - 10.9 \right) \right) \end{aligned} \quad (14)$$

Using Eq. (14), the surface tension of Fe–C–O melts at 1 873 K can be shown in the σ - w_O - w_C 3D diagram as presented in **Fig. 8**. Comparing Figs. 8 to 7, carbon reduces oxygen activity in the melt, which eventually engenders increased surface tension. This is because of the negative interaction parameter between oxygen and carbon as presented in Eq. (13).

5. Summary

The surface tension of Fe–C and Fe–C–O melts were measured using the oscillating droplet method with EML. The surface tension of Fe–C melt is constant with carbon

activities from $a_C = 0.1$ – 0.73 at temperatures of 1 823–2 023 K below $a_{O_2} = 10^{-15}$. The surface tension of Fe–C–O melts is also constant with carbon activities from 10^{-3} to 10^{-2} at $a_{O_2} = 10^{-12}$ at temperatures of 1 873–1 973 K. The surface tension was formulated as a function of carbon and oxygen concentration and temperature considering the interaction between oxygen and carbon in the melts. Carbon itself has no influence on the surface tension. However, carbon reduces oxygen activity in the melt, which engenders an increase in the surface tension.

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