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電磁浮遊法で測定した金属融体の酸素分圧依存性に対する緩衝ガスの影響

Influence of buffer gas on the oxygen partial pressure dependence of molten metal measured by electromagnetic levitation

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1. Introduction

Surface tension plays a key role in various high temperature processes involving a free surface of the melt including, for example, welding, casting, and crystal growth. It is indispensable for an accurate surface tension of high temperature liquid metal to suppress a contamination of sample from measurement device because of an extreme sensitivity of surface tension to impurities. In addition, it is crucial to consider the influence of oxygen partial pressure of the atmospheric gas (P_{O_2}) in the measurement because oxygen is one of the strongest surfactants for liquid metals. From this viewpoint, our group employed an oscillating droplet method using the electromagnetic levitation technique to measure the surface tension of liquid iron precisely. As a result, it was experimentally confirmed the boomerang shape temperature dependence of the surface tension, for the first time for high melting point metals, when the P_{O_2} is controlled at 10^{-7} atm under high purity inert gas [1)]. Furthermore, it was reported the unique kink in the temperature dependence of the surface tension under hydrogen mixture gas as reducing agent, for the first time in the world [2)].

Morohoshi and co-workers also observed a similar boomerang shape temperature dependence in the surface tension of liquid iron by using EML as we employed, when the P_{O_2} was controlled by gas phase equilibrium between CO and CO_2. However, the surface tension reported by Moroboshi et al. appears to be grater affected by the P_{O_2} compared to that of our previous study. Furthermore, Morohoshi et al [3)] do not detect the kink in the temperature dependence of the surface tension even though the measurement was carried out almost the same experimental condition.

In this study, surface tension of liquid iron and nickel was measured as functions of temperature and the P_{O_2} by using oscillating droplet method using EML. The P_{O_2} of atmospheric gas was controlled by a simple gas mixture of oxygen and inert gases and gas phase equilibrium of H_2 and CO_2. The purpose of this investigation was to clarify the reason for the contradictions of the measurement results of the surface tension of liquid iron between our previous result and that by Morohoshi and co-workers.

2. Experimental procedure

Table 1 shows a chemical composition of iron and nickel samples used in this study. The sample cut into a cubic shape was chemically cleaned in nitric acid solution using ultrasonic cleaner followed by an acetone cleaning. The sample was electromagnetically levitated and then melted under the flow condition of atmospheric gas. The P_{O_2} of the atmospheric gas was confirmed by a stabilized zirconia oxygen sensor operated at 1008 K. The stabilized zirconia oxygen sensor was calibrated by in-situ observation of oxidation and reduction reactions at the solid surface of metals such as nickel and iron[3)]. Furthermore, it was superimposed irradiation of semiconductor laser to the levitated sample to assist the heating for the measurement was carried out at very high temperature

The surface oscillations and translational oscillation of the levitated droplet were observed from the above using a high-speed video camera (500 FPS, 16 sec). Furthermore, temperature of the droplet was measured by a monocolor pyrometer. The frequencies of the surface oscillation and translational oscillation of the droplet were analyzed by the fast Fourier transformation and maximum entropy method from the time sequential data of high speed camera images, at which the influences of droplet rotation and the apparent droplet rotation were considered. Surface tension of the liquid sample was calculated from the frequencies using the Rayleigh equation [4)] calibrated by Cummings and Blackburn [5)].

Table 1 chemical composition of iron and nickel samples used in this study

Composition of composition of iron sample (mass ppm)							
C	Si	Mn	P	S	Cu	As	Sn
9	<5	1	1	1	1	1	1
B	N	O	H	Al	Bi	Cd	Co
1	5	10	1	1	1	1	1
Cr	Ni	Pb	Sb	Zn	Fe		
1	1	1	1	1	Bal.		
Composition of composition of nickel sample (mass ppm)							
C	N	H	O	Na	Mg	Al	Cr
40.0	0.5	0.3	5.3	<0.1	<0.1	0.1	<0.1
Fe	Mn	Co	Cu	Zn	As	Si	P
2.8	<0.1	1.3	0.3	<0.1	<0.1	01	<0.1
S	Cl	K	Ca	Ti	Se	Ru	Ag
0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.2	<0.1
Cd	Sn	Sb	Pb	Ni			
<0.1	0.2	<0.1	<0.1	Bal.			

3. Results and discussion

3.1. Influence of oxygen adsorption on surface tension under simple oxygen gas mixture and buffer gas mixtures

Figure 1 shows the surface tension of liquid iron as functions of temperature and P_{O_2} measured by the EML technique, together with the literature data [1) 2)]. When the surface tension of liquid iron was measured under mixture gas of Ar-He with the P_{O_2} of 10^{-7}atm (▲), it shows the boomerang shape temperature dependence as almost the same as that in our previous study (…) [1)]. Although it is also measured the boomerang shape temperature dependence of surface tension under at the P_{O_2} of 10^{-12} to 10^{-10} atm (■), under gas phase equilibrium H_2 and CO_2, the influence of P_{O_2} on the surface tension becomes a large as similar to the report of Morohoshi et al (----) [3)]. Because the $P_{O_2}$of 10^{-7} atm in the simple oxygen mixture gas is already very low value, it is reasonable to suppose that the P_{O_2} is extremely decreased at the vicinity of melt surface due to even a slight consumption of oxygen such as adsorption and chemical reaction with sample vapor. Since almost the same surface tension was measured at 10^{-7} atm of Ar-He gas and at 10^{-12} atm prepared by using gas phase equilibrium reactions of CO/CO_2 and H_2/CO_2, the P_{O_2} would be decreased down to around 10^{-12} atm at the vicinity of melt surface under the Ar-He mixture gas.

Since a change in the temperate coefficient from a positive value to a negative value at high temperature indicates the oxygen desorption from the melt surface. it can be deduced the pure state value of surface tension free of oxygen from the measurement plots at high temperature including the measurement results of our previous study and Morohoshi et al, as follows,

$$\sigma = 1962.6 - 0.4689(T - 1808) \quad (10^{-3}\ \mathrm{N \cdot m^{-1}}).$$

It was also detected the decrease of P_{O_2} in the vicinity of melt surface in the surface tension measurement for liquid nickel. The surface tension shows the boomerang temperature dependence of surface tension when the P_{O_2} is controlled at 10^{-11} to 10^{-7} atm by using gas phase equilibrium of H_2/H_2O and H_2/CO_2, as depicted in Figure 2. Whereas, even when the measurement is carried out under simple gas mixture of Ar-He-O_2 with comparatively high P_{O_2} of 10^{-7} atm, the surface tension shows a pure state value free of oxygen adsorption

3.2. Kink in the temperature dependence of surface tension

In order to confirm the existence or nonexistence of the kink in the temperature dependence of surface tension under reducing gas atmosphere where the P_{O_2} shows the temperature dependence, the measurement was carried out under Ar-He-5%H_2 gas atmosphere, as same as our previous study [1) 2)] and the report by Morohoshi et al [3)]. The measurement plots at high temperature well agrees with the pure state value of the surface tension. Furthermore, the measurement plots at comparatively low temperature become lower than the pure state value of surface tension as we reported in the previous study. This confirms the kink in the temperature dependence of surface tension, which is revised as shown by a red dashed line when it is considered all the measurement plots including our previous result and that of Morohoshi et al.

The maximum temperature is only around 2070 K in the measurement at the Po_2 of 10^{-12} – 10^{-10} atm by Morohosi et al, which is not high enough to deduce the pure state value of the surface tension, because the measurement plots have not been converged to the same value. Surface tension should be the same value even at the different Po_2 condition when oxygen is desorbed from the melt surface at high temperature because of decrease in the equilibrium constant of oxygen adsorption reaction. Moreover, they estimate the pure state value by using the least squares method from the measurement plots under Ar-He-5%H_2 gas mixture without deep thinking even though only the plot at 2140K, corresponding to their maximum measurement temperature, shows the pure state value of the surface tension. Thus, it may be overlooked the kink in the temperature dependence of surface tension in their study.

The kink is clearly detected in the temperature dependence of surface tension of liquid nickel under Ar-He-5%H_2 mixture gas as shown by dotted line (…) in Figure 2.

4. Summary

(1) The boomerang shape temperature dependence is observed in the surface tension of liquid iron and nickel when the Po_2 is controlled at comparatively high values.

(2) Although gas phase equilibrium between H_2/H_2O and H_2/CO_2 can control the Po_2 during the surface tension measurement of liquid iron and nickel, the Po_2 becomes lower at the vicinity of melt surface due to a consumption of oxygen such as adsorption and chemical reaction with the sample vapor when using a simple gas mixture of oxygen and inert gas is used to control the Po_2 at very low value.

(3) It is clearly detected the kink in the tempera dependence of surface tension under constant concentration of reducing gas atmosphere such as Ar-He-5%H_2.

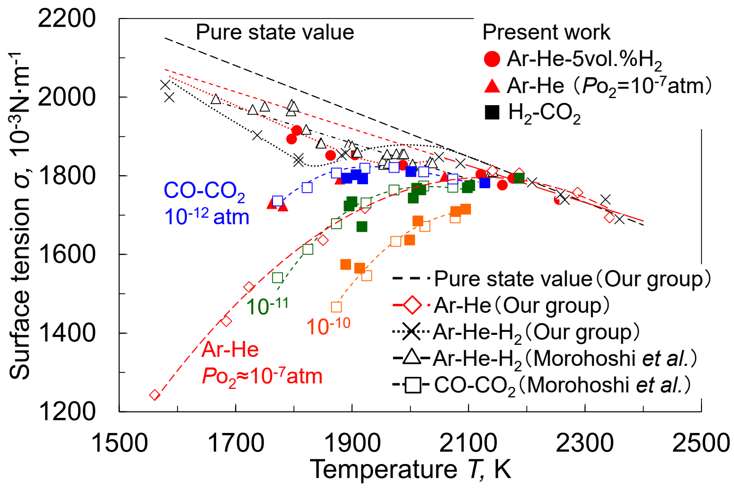

Figure 1 Temperature dependence of surface tension of molten iron

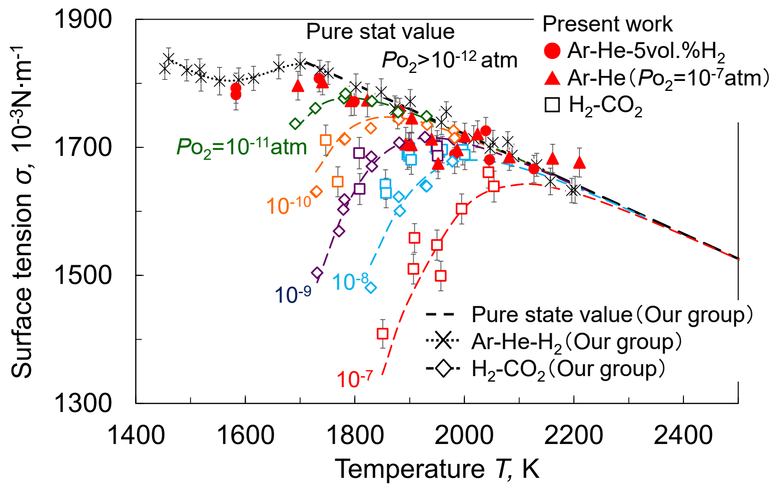

Figure 2 Temperature dependence of surface tension of molten nickel

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