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Oxygen partial pressure dependence of surface tension and its temperature coefficient for metallic melts: a discussion from the viewpoint of solubility and adsorption of oxygen

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Abstract Surface tension of molten Si, Ag, and Fe–18Cr–8Ni alloy (Type-304 stainless steel) were measured as a function of the temperature and oxygen partial pressure of an ambient atmosphere by an oscillating drop method using electromagnetic levitation, which assures measurement over a wide range of temperatures below and above the melting point and of oxygen partial pressure. For molten silicon, the lower limit of measured temperature was determined by equilibrium oxygen partial pressure for SiO_2 formation; as oxygen partial pressure increases, undercooled conditions necessary for taking measurements become smaller. This is attributed to the low solubility of oxygen in molten silicon. For Ag, however, surface tension can be measured in a wide range of temperature and oxygen partial pressures due to the high solubility of oxygen. A boomerang-shaped behavior of surface tension was observed for Ag in an atmosphere with high oxygen partial pressure; surface tension has a maximum value when plotted against temperature. This boomerang-shaped behavior is attributed to desorption of oxygen at high temperature; surface tension increases with increasing temperature. The boomerang-shaped behavior was also observed for Fe–18Cr–8Ni alloy.

Introduction

To improve the quality of products and reduce the turn-around-time for process improvement in high-temperature melt processes for manufacturing highly value-added products, such as fine casting for jet-engine turbine blades, welding for nuclear reactor containers, and crystal growth of semiconductors, numerical modeling for heat and mass transport is required; this will contribute to cost reduction. Accurate values of surface tension and its temperature coefficient are required for the numerical modeling of these industrial processes, because, for the system with a free surface, flow is dominated by the Marangoni effect, which depends on surface tension-temperature coefficient.

In particular, the Marangoni effect is essential for welding process, because the ratio of surface to pool volume is relatively large, compared with other cases, such as the Czochralski melt for Si crystal growth or casting. Depending on the sign of temperature coefficient, i.e., positive or negative, the flow direction and depth in the weld pool are determined and consequently controlling weldability [1]. The sign of a temperature coefficient has been reported to be affected by a surfactant such as adsorption of sulfur [2–7] or oxygen. Ogino et al. [8] reviewed a history of the study on the effect of oxygen on surface tension of molten iron. Besides molten Fe, the effects of oxygen on surface tension were studied, for example, for molten Ag [9–13], Cu [14, 15], Co [16], Ni [17], Pb [18], Sn [19], and Al [19]. The effect of oxygen on surface tension was studied theoretically [20] and experimentally for not only molten single component metals but also for alloys, such as Ag–Sn [21] and Cu–Ag [22].

Although surface tension is expected to be a function of not only the temperature but also the amount of surfactants adsorbed, such as oxygen and/or sulfur, studies on the

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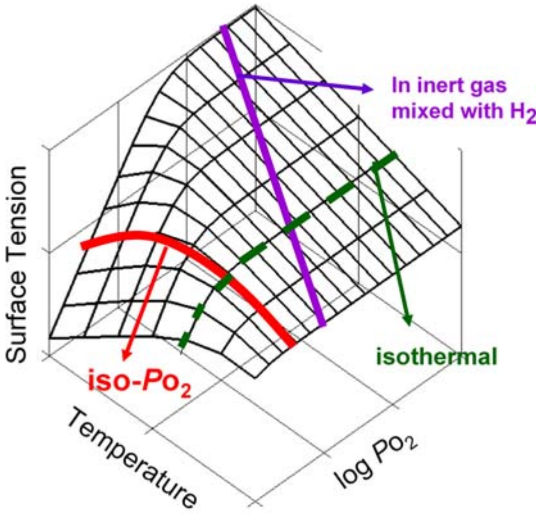

Fig. 1 Three categories of surface tension measurement modes

effect of oxygen on surface tension have been carried out for various oxygen partial pressures, mainly at constant temperatures. Theoretically surface tension measurement methods are classified into three categories, as shown in Fig. 1. They are (i) measurement at iso-P_{O_2} with variable temperature, (ii) isothermal measurement with variable P_{O_2}, and (iii) measurement both with variable P_{O_2} and temperature. Iso-P_{O_2} conditions can be obtained by a mixture of inert gas (Ar or He) with a small amount of oxygen for the high P_{O_2} case and by an oxygen pump for the wide range of P_{O_2} case. Measurement using a mixture of Ar with H_2 or He with H_2 corresponds to category (iii), because constant oxygen partial pressure cannot be sustained. As long as Ar or He gas mixed with H_2 is used, residual H_2O causes temperature dependence of oxygen partial pressure, because of the temperature dependence of equilibrium constant for the following dissociation: $H_2O = 1/2O_2 + H_2$. The higher the temperature is raised, the higher the P_{O_2} becomes. Furthermore, it is usually difficult to estimate P_{O_2} in this case, due to a lack of information on residual amount of water vapor. When CO_2 gas is used, oxygen partial pressure also shows temperature dependence due to a similar mechanism: $CO_2 = 1/2O_2 + CO$. Iteration of iso-P_{O_2} measurements with various P_{O_2} is an elegant way to measure surface tension as a function both of temperature and oxygen partial pressure, whereas iso-P_{O_2} conditions cannot be assured as long as a mixture of Ar with or He with H_2 is employed.

For the case of molten semiconductor silicon, there were many data measured without accounting for oxygen; see review by Keene [23]. Although some data are accompanied by a single point of P_{O_2} [24, 25], these kinds of measurements result in confusion [26]. Thus, measurements in the wide and controlled temperature and P_{O_2} range are required to improve reliability [27, 28]. Difficulties in measurement of surface tension of molten silicon as a function of oxygen partial pressure are due to (i) formation of a thin oxide film on the melt surface and (ii) determination of P_{O_2} at the melt surface. As reported by Mukai et al. [28], surface tension like data, in other words surface stress, can be obtained for a droplet coated with a thin oxide film. The droplet behaves as a liquid from a mechanical viewpoint, but its surface is solid from a chemical–thermodynamical viewpoint.

Oxygen partial pressure at the melt surface must be estimated from its measurement at a point far from the melt surface since measuring P_{O_2} at the melt surface experimentally is almost impossible. For the case of molten silicon, P_{O_2} shows a large difference between that in a bulk gas phase and that at the melt surface; this is due to evaporation of SiO through reaction between molten Si and O_2 from the gas phase. Thus, P_{O_2} at the melt surface is estimated using the Ratto–Ricci–Arato model either from the inlet or outlet gas flow [29]; this model was validated experimentally by Azami and Hibiya [30].

For molten Ag and Cu, above the critical value of P_{O_2}, surface tension shows an almost constant value; this suggests that the melt surface is pure and free from oxygen adsorption. However, below the critical value of P_{O_2}, surface tension shows P_{O_2} dependence; i.e., surface tension decreases with increasing P_{O_2} [9–13, 21, 22]. The critical P_{O_2} is reported to be 1 and 10^{-8} Pa for molten Ag and Cu, respectively. Molten Si also shows similar behavior. When the surface tension shows P_{O_2} dependence, oxygen adsorbs with decreasing temperature (surface tension decreases) and desorbs with increasing temperature (surface tension increases). This suggests that in certain high P_{O_2} conditions, surface tension increases with increasing temperature and that it shows a maximum value at certain temperature; i.e., a boomerang-shaped behavior. Above this temperature, there is no oxygen adsorption and surface tension is supposed to decrease again due to the entropy effect. However, this kind of boomerang-shaped behavior has been less observed experimentally for high-temperature melts.

When melt surface is free from adsorption, the temperature dependence of surface tension shows the same behavior (same temperature coefficient), regardless of the method for P_{O_2} control; i.e., under iso-P_{O_2} conditions or a mixture of inert gas with H_2. This means that surface tension projected into the surface tension-temperature plane shows the same value; see Fig. 1. However, in the region of P_{O_2} and temperature where boomerang behavior is observed, the value of surface tension is different between that obtained under iso-P_{O_2} conditions and in an inert gas atmosphere with H_2, because P_{O_2} prepared by inert gas with H_2 does not display a constant value in the temperature range of surface tension measurement.

In order to discuss the effect of oxygen partial pressure on surface tension universally, surface tension must be measured as a function of both temperature and oxygen partial pressure, which are controlled independently. Combination of an oscillating drop method by a containerless technique and use of an atmosphere with controlled oxygen partial pressure can meet this requirement. As this technique does not use a container, which could be a source of contamination and a nucleation center, surface tension can be obtained in the wide temperature range of over 2,000 K, which is sufficiently below and above the melting point. An increase in the measurement temperature range not only contributes to reduced uncertainty, particularly for the temperature coefficient, but also assures the opportunity to experimentally confirm the boomerang behavior of surface tension under higher P_{O_2} conditions.

This article reports the effect of oxygen partial pressure on surface tension of molten Si, Ag, and Fe–18Cr–8Ni alloy (Type 304 stainless steel).

Experimental

Surface tension measurements were carried out by an oscillating drop method using electromagnetic levitation, as shown in Fig. 2. Surface oscillations were observed by a high-speed video camera with frame rate of 500 fps. Resolution is 512 × 512. Recording time was 16 s. The $m = 0$, ± 1, and ± 2 frequencies for the $l = 2$ mode were analyzed by the Cummins and Blackburn equation [31], as shown in Eqs. 1–3, as the frequency of the $l = 2$ mode is split into five frequencies due to gravitational and magnetic forces:

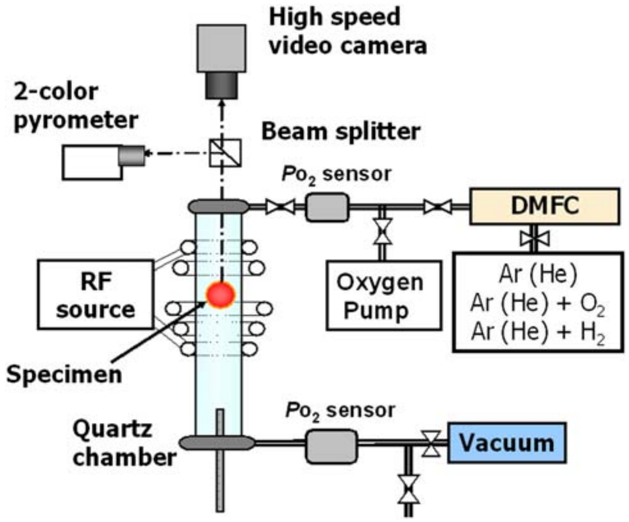

Fig. 2 Electromagnetic levitation facility equipped with oxygen control system. DMFC stands for Digital Mass Flow Controller

$$\sigma = \frac{3}{8}\pi M\left[\frac{1}{5}\sum_{m=-2}^{2}\nu_{2,m}^{2} - \nu_{t}^{2}\left\{1.9 - 1.2\left(\frac{z_0}{a}\right)^{2}\right\}\right], \tag{1}$$

$$z_0 = \frac{g}{8\pi^2\nu_t^2}, \tag{2}$$

$$a = \sqrt[3]{\frac{3M}{4\rho\pi}}. \tag{3}$$

Here σ is the surface tension, ν_m the surface oscillation, ν_t the oscillation of center of gravity position, M the sample mass, ρ the density, and g the gravitational acceleration. Mass losses during measurements were, e.g., 0.3 and 1.5% for Ag and Fe–18Cr–8Ni alloy, respectively. Mass of specimens was measured before and after levitation and average value was used for surface tension calculation. Estimated uncertainty was 2–3%.

Oxygen partial pressure was controlled by the following three methods; (a) flow rate control of an Ar (He) and Ar (He) mixture with 3 or 5% O_2 for rather high oxygen partial pressures such as $P_{O_2} = 10^{-2}$–10^{2} Pa, (b) a mixture of Ar (He) with H_2; residual H_2O gas creates a P_{O_2} of lower than 10^{-12} Pa depending on temperature, and (c) use of an oxygen pump (Canon Machinery ROX-500), which assures P_{O_2} control (independent of temperature) and covers a wide P_{O_2} range from 10^{-25} to 10^{5} Pa using a solid-state electrolyte. Oxygen partial pressure was measured using a zirconia oxygen sensor manufactured by Daiichi Nekken Co., Ltd., which were installed in the inlet position of the system after a digital mass flow controller for P_{O_2} control and in the outlet position of the gas flow system (see Fig. 2).

Surface tension for molten Si, Ag, and Fe–18Cr–8Ni alloy (Type 304 stainless steel)

In this section, we report the results of our recent measurement of oxygen partial pressure dependence of surface tension of molten Si, Ag, and Fe–18Cr–8Ni alloy (Type 304 stainless steel).

Silicon

Figure 3 shows surface tension of molten silicon as a function of temperature measured by electromagnetic levitation in an atmosphere with various oxygen partial pressures, P_{O_2}, from 5.43×10^{-24} to 1.00×10^{-14} Pa [32]. In this measurement, P_{O_2} shows the melt surface value calculated from the inlet P_{O_2} value of the system using Ratto's model [29]. The surface tension of molten silicon with a pure surface at the melting point was determined to be $\sigma = 830 - 0.75 \quad (T - T_{\mathrm{m}}) \quad [10^{-3}\ \mathrm{N/m}]$. Przyborowski

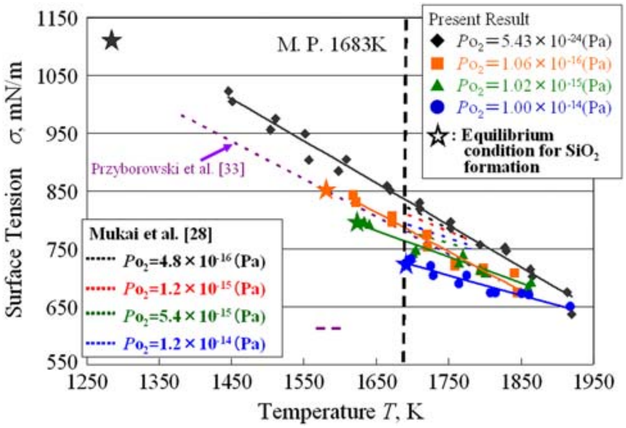

Fig. 3 Surface tension of molten silicon measured by levitation technique [32]. Surface tension measured by Mukai et al. [28] and Przyborowski et al. [33] are also shown

et al. [33] were the first to measure surface tension by an electromagnetic levitation technique: $\sigma = 783.5 - 0.65 (T - T_m)$ [10^{-3} N/m].

The present surface tension showed a similar tendency to that reported by Mukai et al. [28] who used a sessile drop method. A slight difference between the present data and that of Mukai et al. would be attributed to a systematic error depending on a working equation for measurement. When calculating a temperature coefficient, they both show good agreement with each other. The surface tension measurement was assured across a wider temperature range by the levitation technique than by a conventional sessile drop technique. A star symbol shows the maximum undercooled condition; in other words, the lowest possible measurable temperature. This is an equilibrium condition for SiO_2 formation, which was confirmed theoretically [34] and experimentally [35]. Below this temperature at a given P_{O_2}, neither surface tension nor temperature coefficient could be measured by levitation because of oxidation of the droplet. Mukai et al. reported the existence of a kink at the equilibrium condition for SiO_2 formation, when surface tension measured isothermally was plotted against P_{O_2}; the behavior of surface tension of molten silicon is quite different, between below and above the equilibrium oxygen partial pressure.

For molten silicon, many surface tensions, which have been previously reported, showed lower values such as 700 [10^{-3} N/m] [23]; these lower values are attributed to the fact that they were measured without considering the effect of P_{O_2}. Note that surface tension-like data could be obtained even over the equilibrium P_{O_2} for SiO_2 formation, as reported by Mukai et al. Under such conditions, a droplet does not show a free surface anymore, but is coated with a thin oxide film; the surface is thermodynamically solid. However, as long as the droplet sustains an appropriate shape, surface tension-like data can be obtained. For the temperature coefficient, values of −0.10 to −0.05 [10^{-3} N/m K] have been reported previously [23]. However, the absolute value of the temperature coefficient is larger than |−0.30| [10^{-3} N/m K] at P_{O_2} lower than the equilibrium condition for SiO_2 formation. These surface tension-like values and their temperature coefficients have no physical meaning for explaining the Marangoni effect for molten silicon. Crystal growth experiment in such conditions show that the solidified crystal is not a single crystal any more but poly-crystalline; this is due to multiple nucleation at the interface between the SiO_2 thin film and the Si melt [36]. For the molten silicon case, no inversion of the temperature coefficient was observed from negative to positive with increase in oxygen partial pressure.

Silver

For molten silver, surface tension was measured at three inlet P_{O_2} levels; i.e., $P_{O_2} = 10^{-21}$ Pa prepared by an oxygen pump, $P_{O_2} < 10^{-12}$ Pa by Ar—5% H_2, and $P_{O_2} = 10^2$ Pa by an oxygen pump. For the molten silver case, there is no metastable volatile oxide; the P_{O_2} value at the inlet must be the same as that at the melt surface. Figure 4 shows surface tension of molten silver measured under the above-mentioned conditions. Surface tension measured at $P_{O_2} < 10^{-12}$ Pa showed almost the same value as that measured at $P_{O_2} = 10^{-21}$ Pa. This suggests that the surface tension of molten silver obtained at $P_{O_2} < 10^{-12}$ Pa corresponds to that for a pure surface, i.e., $\sigma = 966 - 0.245 (T - 1{,}234)$ [10^{-3} Nm^{-1}], although P_{O_2} varies with temperature under this measurement condition from 10^{-20} to 10^{-12} Pa. The surface tension at the melting point of 966 [10^{-3} Nm^{-1}] is rather higher than

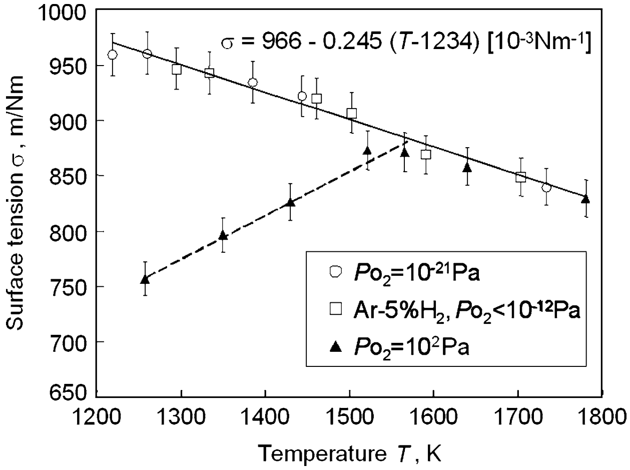

Fig. 4 Surface tension of molten silver as a function of temperature for various oxygen partial pressures

conventionally reported values [9–13, 21, 22]. This is attributed to the fact that the present measurement was carried out under the contamination-free condition using levitation, since impurity, which affects surface tension was not detected [37]. For $P_{O_2} = 10^2$ Pa, the surface tension showed a maximum value at 1,570 K.

According to Lee et al. [22], who summarized surface tension of molten Ag with reference to oxygen, silver shows a constant value of surface tension below at 1 Pa in the temperature range between 1,253 and 1,373 K; i.e., the surface tension of a pure surface [9–13, 21]. The surface tension shows P_{O_2} dependence between 1 and 10^5 Pa, above which the surface is supposed to be coated with oxide. As their measurements were carried out within a very small temperature range, the surface tension temperature dependence is not clearly observed in this P_{O_2} region; see Fig. 3 of reference [22]. As shown in Fig. 4, the surface tension of molten silver showed a maximum value around at 1,570 K, when measured in a wide temperature range from 1,250 to 1,780 K. A positive temperature coefficient of surface tension observed between 1,250 and 1,570 K suggests desorption of oxygen with increasing temperature. A negative temperature coefficient above 1,570 K suggests that there is no oxygen adsorption above this temperature and that the surface is pure. Although surface tension appears to show a linear relationship against temperatures below 1,570 K (see Fig. 4), the curve would be continuous above and below 1,570 K and surface tension would show a "boomerang shape". The effect of oxygen partial pressure on surface tension was discussed by Syzkowski [38] for the first time for organic liquids by combining the Langmuir and Gibbs adsorption isotherms. Later, this idea was extended to metallic melt by Belton [39]. The dependence of surface tension on oxygen partial pressure for molten silver is now being analyzed precisely by Ozawa et al. [37], taking accounting of the adsorption of oxygen at the melt surface.

Fe–18Cr–8Ni alloy (Type 304 stainless steel)

Figure 5 shows surface tension of molten Fe–18Cr–8Ni alloy (Type 304 stainless steel) measured by the oscillating droplet method using electromagnetic levitation in a wide temperature range of 700 K including undercooled and superheated conditions [40]. Chemical analysis showed no concentration change for sulfur before and after measurement: less than 10 ppm. In an atmosphere with a P_{O_2} of 10^{-15}–10^{-9} Pa, the surface tension is described as $\sigma = 1676 - 0.3063\ (T - T_m)\ [10^{-3}\ \text{N/m}]$. In this measurement Ar—5% H_2 and He—5% H_2 were used to obtain low oxygen partial pressure. He gas was used to lower the sample temperature. As the equilibrium constant shows temperature dependence for the reaction of $H_2O = 1/2O_2 + H_2$, oxygen partial pressure is not constant for this measurement. However, melt surface is assumed to be sufficiently pure. In an atmosphere with a rather high oxygen partial pressure of $P_{O_2} = 10^{-2}$ Pa, surface tension is described in the temperature range between 1,620 and 2,070 K as follows: $\sigma = 1423 + 0.3896\ (T - T_m)\ [10^{-3}\ \text{N/m}]$. The temperature coefficient changes from positive to negative at 2,070 K, above which the temperature coefficient looks similar to that observed in the low P_{O_2} case.

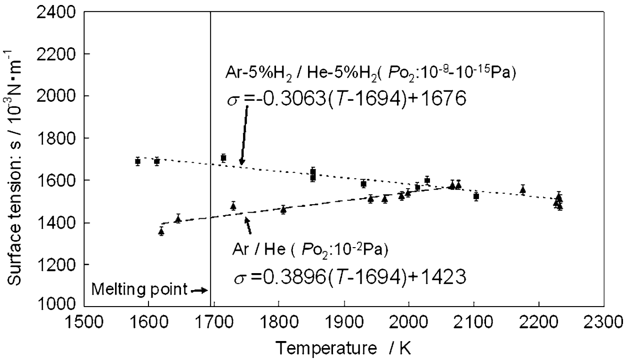

Fig. 5 Surface tension of molten Fe–18Cr–8Ni alloy (Type-304 stainless steel) [40]

Surface tension and temperature coefficient of molten iron and several kinds of stainless steel have been reported to be sensitive both to oxygen and sulfur to a great extent. Takiuchi et al. [41] reported that the sign of the temperature coefficient changed from negative to positive with increasing oxygen concentration after measurement within a small temperature range such as from 1,820 to 2,020 K. This is also the case for combinations of stainless steel and sulfur [4–7]. Although, generally speaking, the constituents affect surface tension and temperature coefficient for alloy cases, it was reported by Su et al. [5] that differences in the concentrations of elements in various steels are unlikely to have a large effect on the surface tension of the clean metal. If the measurements had been carried out in a wider temperature range, the existence of a boomerang effect would have been experimentally confirmed, regardless of chemical species of surfactant, such as oxygen and sulfur, through measurements reported in references [4–7] and [41].

Discussion

The surface tension of molten metals is affected by an ambient atmosphere through an adsorption mechanism. This is explained by the Gibbs adsorption isotherm, as follows:

$$\Gamma_O = -2(1/RT)(\partial\sigma/\partial \ln Po_2). \qquad (4)$$

Table 1 The effect of chemical species on oxygen adsorption

	Equilibrium oxygen partial pressure $P_{O_2}^{Sat}$ (Pa)	Oxygen solubility c_s (ppm)	Excess Amount of oxygen adsorbed at surface Γo (mol/m^2)
Si (at 1,683 K)	10^{-14}	18	2.1×10^{-6} [28]
Fe (at 1,808 K)	10^1	3,500	20×10^{-6} [41]
Ag (at 1,234 K)	10^7	20,000	4.81×10^{-6} [9]

Here, Γ_O is the excess amount of adsorbed oxygen. R and T are the gas constant and temperature, respectively. σ and P_{O_2} are the surface tension and oxygen partial pressure, respectively. Let us discuss the effect of melt chemical species on oxygen adsorption, surface tension, and its temperature coefficient. Table 1 shows equilibrium oxygen partial pressure, oxygen solubility, and the excess amount of oxygen adsorbed at the melt surface. For molten silicon, the equilibrium oxygen partial pressure is as low as $P_{O_2}^{Sat} = 10^{-14}$ Pa. This corresponds to low oxygen solubility of 18 ppm (ca. 0.001 mass%). For molten silver, $P_{O_2}^{Sat}$ is 10^7 Pa and solubility is as large as 20,000 ppm (ca. 0.3 mass%). Molten iron shows medium values of $P_{O_2}^{Sat}$ and solubility between that for molten silicon and silver; i.e., 3,500 ppm (ca. order of 0.1 mass%). Nevertheless, the excess amount of oxygen adsorbed at the melt surface shows almost the same order of 10^{-6} mol/m^2, regardless of melt chemical species.

As reported in the previous section, molten Ag and Fe–18Cr–8Ni alloy (Type-304 stainless steel) show a positive temperature coefficient in an atmosphere with high P_{O_2}, whereas molten silicon shows only a negative temperature coefficient. The change of sign from negative to positive appears to be related to the solubility of oxygen. For molten silicon, the melt surface is coated with an oxide layer, i.e., oxidation, even if the temperature coefficient shows a strong negative value, such as -0.30×10^{-3} N/m K. For molten Ag and Fe, temperature coefficient inversion takes place with an increase in oxygen concentration; molten Ag shows a very large positive temperature coefficient of $+0.38 \times 10^{-3}$ N/m K; see Fig. 4. This inversion changes flow direction of the Marangoni effect, such as that observed at the weld pool surface.

Summary

The surface tension of molten Si, Ag, and Fe–18Cr–8Ni alloy (Type-304 stainless steel) were measured as a function of temperature and oxygen partial pressure of an ambient atmosphere by an oscillating drop method using electromagnetic levitation, which assures measurements in a wide range of temperature above and below the melting point and of oxygen partial pressure. The boomerang-shaped behavior of surface tension was experimentally confirmed for molten Ag and Fe–18Cr–8Ni alloy (Type-304 stainless steel). Employing an oxygen pump, surface tension is assured to be measured as a function of both temperature and oxygen partial pressure, which are controlled independently. A data base of surface tension for molten metals and alloys would be constructed using the techniques discussed in the present report, so that numerical modeling for high-temperature melt processes, such as welding, fine casting, and crystal growth can be improved to a great extent.

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