Oxygen Adsorption Behavior on the Surface of Liquid Cu-Ag Alloys

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The behavior of oxygen adsorption on the surface of liquid Cu-Ag alloys was investigated by measuring their surface tension (\(\sigma\)) with the sessile drop method in the oxygen partial pressures (\(p_{O_2}\)) between \(2.5 \times 10^{-11}\) and \(2.5 \times 10^{-3}\) Pa. The oxygen adsorption (the surface excess concentration of oxygen) was calculated from the slope of \(dr/d\ln p_{O_2}\) by applying Gibbs adsorption isotherm, for liquid Cu, Cu-5 at%Ag, Cu-10 at%Ag, Cu-20 at%Ag and Ag. It was found that the oxygen adsorption increased with the oxygen partial pressure, up to saturation on the surface. The oxygen adsorption on the surface of liquid Cu-20 at%Ag alloys exhibited almost the same behavior as that of pure liquid Ag, because surface saturation was not achieved for the Cu-20 at%Ag alloys, even at high oxygen partial pressures. Thermodynamic calculations using Butler’s model indicated that the mole fraction of Ag in the surface of liquid Cu-Ag alloys drastically increases to 0.81 when the mole fraction of Ag in the bulk is only 0.2. Thus, it is considered that the outermost surface of liquid Cu-20 at%Ag alloys contains an enhanced level of Ag, which determines the oxygen adsorption behavior on liquid Cu-20 at%Ag alloys.

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1. Introduction

Merely a small amount of oxygen in atmosphere may preferentially adsorb onto the surface of the liquid metals and alloys, considerably decreasing the surface tension. There have been a number of studies on the effect of the oxygen on the surface tension of pure liquid metals (Ag, Cu, Al, Fe, Ni, Pb, Si and Sn), whereas only few studies address liquid alloys (Ag-Au, Au-Cu and Ag-Sn). The key parameter determining the oxygen adsorption behavior on the surface of liquid alloys is the nature of the surface layer such as the variation in composition with respect to the bulk. Recently, the authors have demonstrated that the dependence of the surface tension of liquid Ag-Sn alloys, subsequent to oxygen adsorption, was much closer to pure liquid Sn than pure liquid Ag, even with low concentrations of Sn in the alloys. Thermodynamic calculations suggest that this was due to the preferential surface segregation of Sn. In the previous work, however, as it was noted that SnO\(_2\) was easily formed (Sn has very little oxygen solubility), the surface tension of liquid Ag-Sn alloys was evaluated only at extremely restricted oxygen partial pressure less than \(10^{-12}\) Pa. In the present study, in order to clarify the effect of the surface layers of liquid alloys on the oxygen adsorption behavior, Cu-Ag alloys were selected, as they require a much higher oxygen partial pressure to form oxides in the bulk. The effect of oxygen adsorption on the surface tension was investigated at oxygen partial pressures between \(2.5 \times 10^{-11}\) and \(2.5 \times 10^{-3}\) Pa at 1373 K. Experimental results were compared with the surface concentrations predicted from thermodynamic calculations.

2. Experimental Procedure

The experimental apparatus used for the present measurements consisted of an image capturing system and a horizontal furnace with a SiC heating element. A schematic diagram of the experimental setup is shown in Fig. 1. A piece of sample alloy (higher than 99.995% purity) on an alumina substrate (22 mm dia.) was placed in the uniform-temperature area (about 30 mm) of an alumina reaction tube, and accurately leveled by adjusting the four furnace supports. The sample size was determined, by simulation, to have a maximum diameter of about 7 mm at the experimental temperature, using reported data. The temperature was measured with a Pt/Pt-13%Rh thermocouple set directly under the substrate. Once the sample assembly was placed in the furnace, the reaction tube was sealed and evacuated to 1.33 Pa and filled with purified Ar-10%H\(_2\) gas mixture. During experiments, the oxygen partial pressure was controlled by a suitable mixture of purified Ar-10%H\(_2\) and CO\(_2\) gases. In order to confirm the oxygen partial pressure in the gas, a zirconia oxygen sensor, equipped with reference electrodes (Fe/FeO couple), was placed under the substrate. In case the effect of the electronic conduction is negligible, the oxygen partial pressure in the atmosphere (\(p_{O_2}\)) can be computed from the electromotive force (\(E\)) expressed by eq. (1).

\[
E = \frac{RT}{4F} \ln \left( \frac{p_{O_2}}{p_{ref}^{O_2}} \right)
\]

where \(F\): Faraday’s constant, \(p_{ref}^{O_2}\): the oxygen partial pressure in the reference electrode. Here, the oxygen partial pressure...
in the reference electrodes was determined using reported values below.\(^{27}\) \(p_{\text{ref}}^O = \exp(\Delta G^\circ/RT)\)
\[
\text{Fe} + 1/2\text{O}_2 = \text{FeO} \quad \Delta G^\circ = -263.4 + 64.81T \quad (\text{kJ}) \quad (2)
\]

The image capturing system comprised of a He-Ne laser (\(\lambda = 632.8 \text{ nm}\)) and a CCD camera (512 \(\times\) 512 pixels) fitted with an optical zoom lens and filters. A clear threshold shape of a drop could be obtained by using image analysis software. This drop profile was then used to determine the surface tension using a computer program developed by Krylov et al.\(^{28}\)

### 3. Results and Discussion

In Fig. 2, the experimental results of the surface tension of liquid Cu are plotted as a function of oxygen partial pressure on a logarithmic scale. The surface tension was almost constant when \(p_{\text{O}_2}\) is less than \(10^{-6}\) Pa, but then gradually decreases with increasing oxygen partial pressure. In Fig. 2, reported values obtained by previous investigators\(^{4,8-11}\) are shown for comparison. Reported values show large scatter. However, the present results appear to be very close to the data of Mehrrota et al.,\(^{4}\) O’Brien et al.,\(^{8}\) Gallios et al.,\(^{10}\) and Ghetta et al.,\(^{11}\) in the low oxygen partial pressure region, but close to those of Morita et al.\(^{9}\) in the high oxygen partial pressure region. Oxygen partial pressure in the previous studies was controlled by the reaction of \(\text{CO}_2\)-\(\text{H}_2\) or \(\text{CO}_2\)-\(\text{CO}\) mixtures. Sasaki et al.\(^{26}\) pointed out that the rate of the homogeneous reaction (without catalyst) of those gas mixtures is very slow, thus the oxygen partial pressure will be at a steady-state value if the gas flow rate is too high as the gas mixture is not equilibrated. (In the present work, a Pt catalyst was placed close to the sample in the furnace to obtain the target oxygen partial pressure at equilibrium, as confirmed with the zirconia oxygen sensor placed under the substrate.) Thus, it is likely that the large scatter in the measurements is due to the failure in obtaining the target oxygen partial pressure at equilibrium. It is also likely that the scatter in data could be caused by inaccuracy in the surface tension measurements. Nevertheless, the present results show good agreement overall with the previous data, particularly if the wide oxygen partial pressure range is taken into account.

In Fig. 3, the experimental results of the surface tension of liquid Ag are plotted, together with reported values,\(^{1-5,25}\) as a function of the oxygen partial pressure on a logarithmic scale. The present results (1373 K) show good agreement with those of Sangiorgi et al.\(^{21}\) (1373 K), but are slightly lower than those of Mehrrota et al.\(^{27}\) (1273 K) and Lee et al.\(^{25}\) (1253 K). This result is acceptable, because the surface tension of pure liquid metal typically decreases with increasing temperature.\(^{26}\)

In Fig. 4, the surface tension data for the liquid Cu-Ag alloys in the present study are shown as a function of the oxygen partial pressure on a logarithmic scale. The surface tension of each sample decreases with increasing oxygen partial pressure in atmosphere, but the slope of the surface tension change was different from sample to sample. Thus, with \(p_{\text{O}_2} = 2.5 \times 10^{-11}\) Pa, the surface tension of liquid alloys decreased with increasing Ag content, whereas with \(p_{\text{O}_2} = 2.5 \times 10^{-3}\) Pa, the surface tension of liquid Cu-20 at%Ag alloy exhibited a maximum value.

\[
\sigma(\text{Cu}) > \sigma(\text{Cu-5 at\%Ag}) > \sigma(\text{Cu-10 at\%Ag}) > \sigma(\text{Cu-20 at\%Ag}) > \sigma(\text{Ag})
\]

This complex change in the surface tension may be related to the oxygen adsorption (the interactions between oxygen and surface atoms).

Owing to the surface-active nature of oxygen in metal and alloys, the oxygen adsorption behavior on the surface of liquid metals and alloys can be simply obtained from information of the surface tension dependence on the oxygen partial pressure according to Gibbs adsorption isotherm (1).\(^{30}\)

\[
\Gamma_O = -\frac{1}{RT} \frac{d\sigma}{d\ln a_O} = -\frac{4.6}{RT} \frac{d\sigma}{d\log p_{\text{O}_2}}
\]

(3)
Fig. 4 Effect of oxygen partial pressure on the surface tension of liquid Cu-Ag alloys at 1373 K.

Fig. 5 Adsorption of oxygen on the surface of liquid Cu-Ag alloys at 1373 K.

where \( R \): gas constant, \( T \): temperature, \( \sigma \): surface tension of liquid metal or alloy, \( a_O \): oxygen activity in the metal or alloy and \( p_{O_2} \): oxygen partial pressure. The oxygen adsorption on the surface was computed from the slope of the surface tension variations with respect to \( \log p_{O_2} \) in Fig. 4. The calculated results of the oxygen adsorption are plotted in Fig. 5. From this figure, it is found that the oxygen partial pressure to reach saturation (\( \approx 5 \times 10^{-6} \) mol m\(^{-2} \)) increases with Ag concentration. At \( p_{O_2} \approx 10^{-5} \text{ to } 10^{-3} \text{ Pa} \), accordingly, the oxygen adsorption on the surface of liquid Cu, Cu-5 at%Ag and Cu-10 at%Ag alloys have a constant value at saturation, while that of liquid Cu-20 at%Ag is close to pure liquid Ag. Thus, it is likely that the surface of liquid Cu-20 at%Ag alloy contains an enhanced level of Ag, and the drastic change in the oxygen adsorption behavior when the Ag concentration increases from 10 at% to 20 at% is caused by a considerable change in the surface concentration.

The surface concentration of binary liquid alloys can be calculated from Butler’s model.\(^{31} \) Butler determined the surface tension and the outermost monolayer concentrations of liquid alloys by assuming that the difference in the surface tension between a pure component metal and the alloy is equal to the difference in the chemical potential for unit area between the pure component metal and that in the alloy. Based on this model, thermodynamic equilibrium between surface and bulk for liquid Cu-Ag alloys can be expressed as eq. (4).

\[
\sigma = \sigma_{Cu} + \frac{RT}{S_{Cu}} \ln \left( \frac{N^S_{Ag}}{N^B_{Ag}} \right) + \frac{1}{S_{Cu}} \left( \frac{G_{ex,Cu}^{ex,S}(T, N^S_{Cu}) - G_{ex,B}(T, N^B_{Cu})}{N^B_{Cu}} \right) + \frac{1}{S_{Ag}} \left( \frac{G_{ex,Ag}^{ex,S}(T, N^S_{Ag}) - G_{ex,B}(T, N^B_{Ag})}{N^B_{Ag}} \right)
\]

(4)

where \( \sigma_{Cu}, S_{Cu}, N^S_{Cu}, N^B_{Cu}, G_{ex,Cu}^{ex,S}(T, N^S_{Cu}) \) and \( G_{ex,B}(T, N^B_{Cu}) \) (= \( RT \ln \gamma_{ij}, \gamma_{i} \): the activity coefficient of \( i \)) are, respectively, surface tension, molar surface area of pure liquid \( i \) (\( S_{i} = 1.091 \cdot (6.02 \cdot 10^{23})^{1/3} \cdot V_i^{3/2} \)) \(^{32,33} \)) where \( V_i \) is molar volume of pure liquid \( i \), mole fraction of \( i \) in the surface and in the bulk, and partial excess Gibbs energy of \( i \) in the surface and in the bulk. Here, \( G_{ex,B}(T, N^B_{Cu}) \) can be obtained directly from a thermodynamic database, and \( G_{ex,Cu}^{ex,S}(T, N^S_{Cu}) \) is obtained using eq. (5) assuming that the partial excess Gibbs energies in the bulk and the surface have the same concentration dependence.\(^{33} \)

\[
G_{ex,S}(T, N^S_{i}) = \beta \cdot G_{ex,B}(T, N^B_{i})
\]

(5)

where \( \beta \) was determined as the sum of the coordination number ratio of a single component atom between surface and bulk, and the surface relaxation energy. For liquid alloys, \( \beta \) is usually assumed to be 0.83.\(^{33} \) The surface tension and molar volume data for pure liquid Ag and Cu are derived from ref. 26, and the partial excess Gibbs energy in the bulk was calculated with the reported values at 1243 K\(^{34} \) with a regular solution model.

In Fig. 6, the surface concentration has been plotted as a function of the bulk concentration. From this figure, we can find that Ag is preferentially segregated in the surface of the liquid Cu-Ag alloys. For example, when the mole fraction of Ag in the bulk is only 0.2, the calculated mole fraction of Ag in the surface rises as high as 0.81. Bearing in mind that the oxygen in atmosphere adsorbs onto the outermost surface layer, the adsorption behavior may be determined by the nature of the surface layer. Thus, when the surface is enriched with Ag atoms, the oxygen adsorption behavior may follow that of pure Ag, which is in reasonable agreement with experimental results in Fig. 5. Accordingly, it may be concluded that it is the nature of surface enhancement of Ag in liquid Cu-Ag alloys that yields the dramatic change in the oxygen adsorption behavior.
4. Conclusions

In the oxygen partial pressure between $2.5 \times 10^{-11}$ and $2.5 \times 10^{-3}$ Pa, the oxygen adsorption behavior on the surface of liquid Cu-Ag alloys was investigated by measuring its surface tension using the sessile drop method. The oxygen adsorption behavior on the surface of liquid Cu-Ag alloys approached to that of pure liquid Ag with increasing Ag content, even at low Ag concentrations. Thus, these experiments indicated that the oxygen adsorption behavior on the liquid Cu-20 at%Ag alloys is almost the same as that on liquid Ag. From thermodynamic calculations, it was proposed that the surface of liquid Cu-20 at%Ag alloys contained an enhanced level of Ag (81 at%).

REFERENCES