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電磁浮遊法で測定した銅融体の表面張力に対する不純物元素の影響

Influence of adsorption of minor impurities on the surface tension of liquid copper measured by oscillating droplet method using the electromagnetic levitation technique

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1. Introduction

Numerical calculations have been widely employed in concert with an experiment to deeply understand and optimize various high temperature melt processes such as welding and casting. An accurate value of surface tension is indispensable for considering a free surface shape of melt and a heat/mass transport induced by the Marangoni convection in the calculation. Since surface tension of liquid metals is extremely decreased by even a small amount of adsorption of surfactant [1-7], it is crucial to know the influence of minor impurities on the surface tension. However, it has not been systematically investigated the influence of the minor impurities for the surface tension of liquid copper even though it is one of the most important industrial materials.

The purpose of this study was to investigate the influence of adsorption of oxygen and phosphorus on the surface tension of liquid copper by oscillating droplet method using the electromagnetic levitation technique. It is well known that oxygen is one of the strongest surfactants for metallic melt, which can exist in an atmosphere as gas phase. Since a small amount of phosphorus decreases the surface tension of liquid iron [8], it may also act as surfactant in liquid copper [9]. Phosphorus-copper is used as a deoxidant, alloying agent, and wetting agent for the copper industry, and as a nucleant for the aluminum industry.

2. Experimental

Copper and its phosphorus alloy sample was electromagnetically levitated and then melted under flow condition (2 L/min) of Ar-He-5% H_2 mixture gas. Furthermore, mixture gas of Ar-He-H_2-CO_2 was also used as an atmospheric gas to control the P_{O_2} through gas phase equilibrium between H_2 and CO_2. The P_{O_2} of the gas was confirmed by zirconia oxygen sensors operated at 1008 K calibrated by in-situ observation of oxidation and reduction reactions of metals such as iron and nickel [10]. The oscillation behavior and the temperature of the levitated droplet were monitored from above simultaneously by a high-speed video camera and a monocolor pyrometer, through a dichroic mirror. The frequencies of the surface oscillation and translational oscillation of the droplet were analyzed from the high-speed video images in consideration of the influence of droplet rotation and the apparent droplet rotation [11-13]. Surface tension of the liquid sample was calculated from these frequencies using the Rayleigh equation calibrated by Cummings and Blackburn [14, 15].

3. Results and discussion

Figure 1 shows the surface tension of liquid copper as functions of temperature and oxygen partial pressure of atmospheric gas (P_{O_2}). The surface tension is linearly decreased with elevating temperature under the flow condition of Ar-He-5%H_2 atmosphere, at which the P_{O_2} varies from 10^{-22} atm for1365 K to 10^{-16} atm for 1840 K due to the temperature dependence of equilibrium constant of the reaction for forming H_2O. When the P_{O_2} of the atmospheric gas is controlled at

a constant value from 10^{-13} atm to 10^{-11} atm regardless of sample temperature through gas phase equilibrium between H_2 and CO_2, boomerang shape temperature dependence of surface tension is observed; the surface tension increases as the sample temperature, and then it decreases. The boomerang shape temperature dependence of surface tension is caused from the fact that oxygen is desorbed from the melt surface with increasing temperature even if oxygen adsorption decreases surface tension at low temperature.

It is converged the measurement results under the P_{O_2} of 10^{-13} atm to 10^{-11} atm at high temperature, which becomes almost the same as the surface tension measured under Ar-He-5% H_2 atmosphere. Therefore, surface tension of pure state value can be deduced from the measurement result under Ar-He-5% H_2 atmosphere and the plots under the P_{O_2} of 10^{-13} atm to 10^{-11} atm at high temperature using least squares as follows,

$\sigma = 1335\text{-}0.1800(T\text{-}1356)$ [10^{-3}N・m^{-1}].

As mentioned above, it is found that the surface tension of liquid copper is not influenced by oxygen adsorption under Ar-He-5% H_2 atmosphere. It was investigated the influence of phosphorus content on the surface tension of liquid copper free of oxygen adsorption under Ar-He-5% H_2 atmosphere. The result is shown in Fig. 2. The surface tension of molten Cu-0.1mass%P sample shows almost the same surface tension of liquid copper. However, the surface tension decreases when phosphorus content is increased more than 0.6 mass%, indicates that phosphorus acts as surfactant in liquid copper.

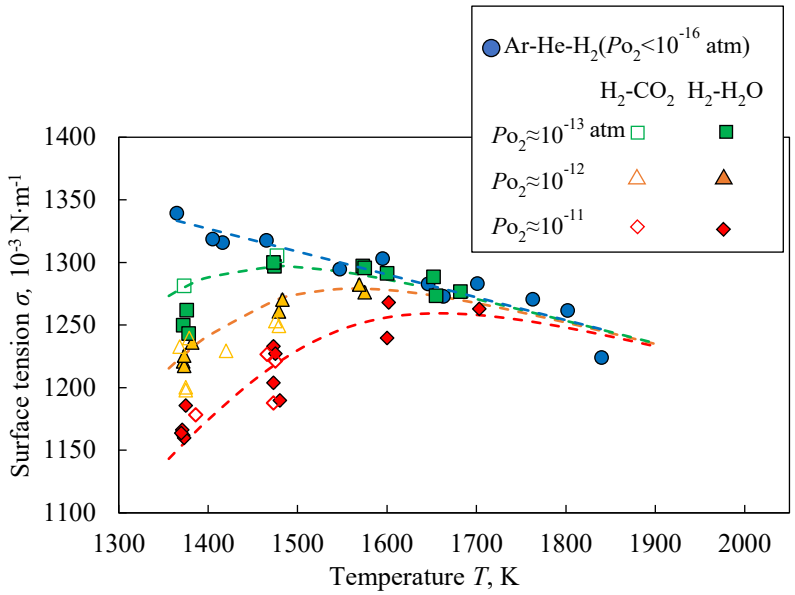

Figure 1 Surface tension of molten copper

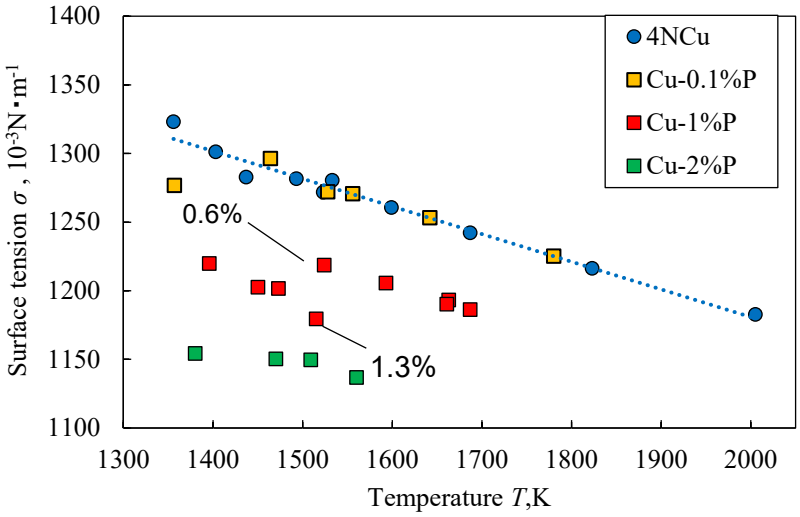

Figure 2 Surface tension of molten Cu-P alloy

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