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気液平衡を考慮した金属融体の正確な表面張力測定

Surface Tension Measurement of Molten Metals Considering Gas-Liquid Equilibrium of Oxygen Adsorption Reaction

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1. Introduction

When measuring the surface tension of liquid metallic melts, accurate evaluation of oxygen activity (a_{O}) is crucial due to the strong surfactant effect of oxygen¹⁻³. This is especially important for samples with high oxygen solubility, where equilibrium between the atmospheric oxygen partial pressure (P_{O_2}) and the oxygen concentration in the melt ($[\text{O}]$) may not be reached in a short time⁴⁻⁵. a_{O} can only be defined by the P_{O_2} when this equilibrium is reliably established. Moreover, when P_{O_2} is controlled through gas phase reactions, such as those between CO-CO₂ and H₂-CO₂, it is essential to maintain the equilibrium of these gases.

Alternatively, defining a_{O} by the $[\text{O}]$ in the sample requires maintaining a constant amount of dissolved oxygen throughout the measurement process, including during solidification and subsequent sampling. This is because the oxygen solubility in the molten sample decreases at lower temperatures.

Recent studies on surface tension measurements using containerless methods have assumed that the temperature of the atmospheric gas is the same as that of the sample. However, since the atmospheric gas is heated only by heat transfer and radiation from the small levitated sample, controlling P_{O_2} to target values using gas phase equilibrium may be inadequate due to insufficient heating of the gas. In addition, if the sample experiences a deep undercooling prior to solidification, not only is the oxygen solubility further reduced, but the duration of the liquid phase state until solidification begins is also prolonged. This may result in a lower $[\text{O}]$ after solidification compared to that during surface tension measurement.

In this study, we solidified iron sample using an electromagnetic levitation furnace, carefully considering the equilibrium between P_{O_2} and $[\text{O}]$ in the sample, as well as the equilibrium gas reaction between H₂ and CO₂. The purpose of this investigation was to demonstrate a reliable method for measuring surface tension using electromagnetic levitation while ensuring accurate accounting for oxygen activity.

2. Experimental product

Electrolytic iron with a mass purity of 99.99% was electromagnetically levitated and melted under the flow conditions (2 L·min⁻¹) of Ar-He-H₂-CO₂ mixed gas. The P_{O_2} of the atmospheric gas was controlled through the gas phase equilibrium between H₂ and CO₂ under the assumption that the gas temperature is the same as the sample temperature. The P_{O_2} of the atmospheric gas was monitored using a zirconia oxygen sensor, which operated at 1008 K, installed at the inlet and outlet of the chamber.

After the indicated values of the P_{O_2} of the sensors are stabilized, the oscillation behavior and the temperature of the levitated droplet were monitored from above using a high-speed video camera (500 FPS) and a monochromatic pyrometer. Subsequently, He gas was directed onto the sample, immediately solidifying the droplet in a containerless state. Furthermore, to minimize the liquid phase duration, the droplet was also dropped and solidified on a sample holder with directed He gas.

The frequencies of the surface oscillations and the motion of the center of gravity of the droplet were analyzed from the time-sequential data of the observed images. The surface tension of liquid iron was calculated from these frequencies by using the Rayleigh equation⁷⁾ and the Cummings and Blackburn calibration⁸⁾. The oxygen concentration in the solidified sample was analyzed using the inert gas fusion-infrared absorption method.

3. Results and Discussion

Figure 1 shows the analysis results of [O] in the solidified iron sample, maintained at 1900 K under various P_{O_2} conditions prior to solidification. The relationship between [O] and P_{O_2} for sample solidified on the sample holder (♦) shows a good agreement with one of the most reliable reported data by Sakao et al. This suggests that P_{O_2} of the atmospheric gas, flowing at 2 Lmin⁻¹ in the vicinity of the electromagnetically levitated droplet, was well controlled at the target values through the gas phase equilibrium between H₂ and CO₂: the droplet is heated to the same temperature as the droplet by heat transfer and radiation from the sample. Therefore, a_0 for the surface tension measurement can be defined using both P_{O_2} and [O] at least at temperatures above 1900 K.

On the other hand, [O] in the samples solidified under a containerless state (◇) are lower than these data, indicating that [O] decreases during the cooling stage before solidification due to the prolonged liquid state. In such cases, a_0 for the surface tension measurement should not be defined using [O]. These results confirm the essential need to ensure the equilibrium state of [O] and P_{O_2} to accurately define a_0 for surface tension measurement of molten metallic melts.

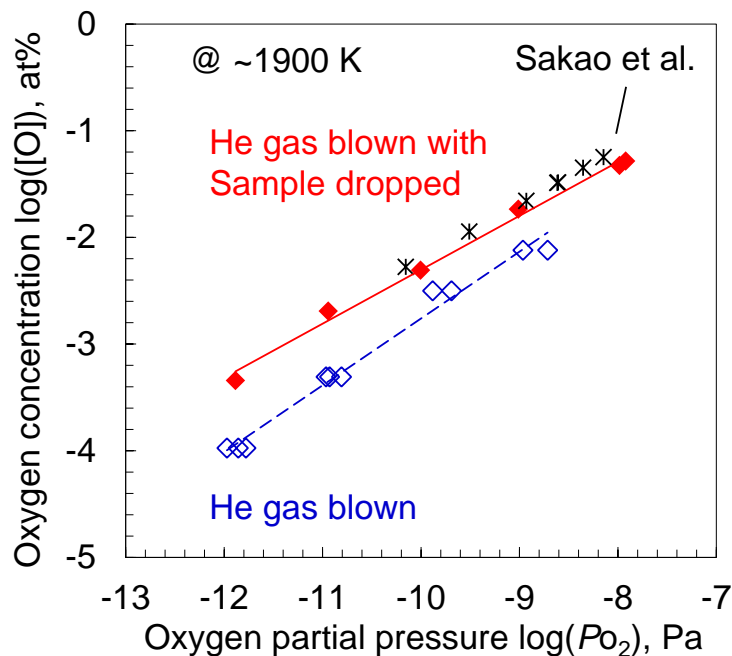


Figure 1. Relationship between P_{O_2} and [O] in molten iron solidified by He gas blown with sample dropped (♦) and by He gas blown (◇)

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