OS2-2

微小重力環境での溶融鉄と酸化物融体によるコア・シェル液滴体積変化

Volume change of core-shell droplets of liquid iron and molten oxide under microgravity conditions

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1. Introduction

Under microgravity conditions, two immiscible liquids form a core-shell droplet dominated by surface and interfacial free energies. Liquid iron and molten oxides are immiscible, and their immiscibility is utilized in the steel industries, including smelting, continuous casting, and welding. Therefore, controlling the interfacial tension between liquid iron and molten oxide is crucial in the steel process [1]). We succeeded in forming the core-shell droplet with liquid iron and molten oxide using the electrostatic levitation furnace (ELF) [2]) installed in the KIBO module of the International Space Station (ISS). We performed the core-shell droplet oscillating drop experiments under constant temperature conditions and found a volume increase during the experiments. The volume increase is attributed to the dissolution of Fe from core-liquid iron to shell-molten oxide. In this report, we focus on the volume change of core-shell droplets by liquid iron and molten oxide under constant temperature and discuss the volume increase from the viewpoint of oxidation of core-liquid iron.

2. Core-shell droplet forming using ELF in ISS

The samples for processing by ELF in ISS were prepared on the ground using the aerodynamic levitation technique with two steps. We made each spherical sample of iron and oxides in the first step. In the second step, a CO_2 laser melted an oxide sample, and then a spherical iron sample was dropped into the melted oxide. The interfacial tension incorporated a spherical iron sample into melted oxide samples, and after rapid cooling, we obtained a solid compound drop. Using the ELF [2,3]) installed in the ISS, the solid compound drop was heating up and the melted forming a core-shell droplet using a semiconductor laser with a wavelength of $980\,nm$. The oxide sample composition was the flux material model composition ($SiO_2:CaO:Mn_3O_4:TiO_2:Fe_2O_3 = 25:7:20:18:30\ mass\%$, named Flux-9) oxide in the welding process.

After the core-shell droplet formation, it was kept at a constant temperature at the center of the ELF electrode to perform the oscillating drop experiments. During the experiments, the total volume of the core-shell droplet was simultaneously obtained from its shape using backlight optics. The sample temperature was determined as the apparent temperature using a single-color pyrometer with a wavelength of $1.45 - 1.8\,\mu m$ by emissivity set to 1.0. The apparent temperature was corrected using sample emissivity and system constant as reported in [4]). The emissivity of Flux-9 oxide is 0.76, which was obtained by our original method using liquid iron melting temperature and its emissivity [5]).

3. Volume change core-shell droplet by liquid Fe and molten oxides

The volume of core-shell droplets by liquid iron and molten oxide under constant temperature increased linearly with time shown in **Fig. 1**. Before and after onboard experiments, we observed solidified samples of

the core-shell drop using X-ray radiography. From the X-ray radiograph images shown in **Fig. 2**, it was found that the radius of the core iron changed from 0.76 mm before the experiment (**Fig. 2**(a)) to 0.67 mm after the experiment (**Fig. 2**(b)). We found that the core iron size was reduced, but the sample mass of the core-shell droplet remained unchanged. These results showed that the volume increase of core-shall droplets by liquid iron and molten oxide was attributed to the dissolution of Fe from core iron to shell oxides. The shell oxides incorporated Fe volume would increase with Fe amount. From the assumptions, we can estimate the volume increase of shell oxide using the density of molten oxide incorporated Fe. Therefore, we investigated the density change of Flux-9 oxides with the change in the Fe amount using the aerodynamic levitation on the ground [6].

Since the volume after solidification changes from its molten state, the volume at the molten state must be determined from the density and mass of the molten sample. The mass of reduced Fe δm_{Fe} is known from the x-ray radiography results. Moreover, since the mass of the entire sample m_{ox}, m_{fe} is unchanged, it can be assumed that all the reduced Fe is dissolved into the shell oxide. Therefore, the volume of the shell oxide in a molten state V_{shell} can be determined from the following equation if the density of the molten oxide in which Fe is dissolved ρ_{ox+Fe} is known.

$$V_{shell} = \frac{(m_{ox} + \delta m_{Fe})}{\rho_{ox+Fe}} \tag{1}$$

The density of Flux-9 oxide alone obtained by the aerodynamic levitation method on the ground is $3.24 \times 10^3 \, kg/m^3$, which is consistent with the value obtained by Thermo-calc simulation and ELF measurements under microgravity. Therefore, the density measurement by the aerodynamic levitation method is accurate, and it is possible to estimate the change in shell oxide volume from the result of density measurement by the aerodynamic levitation method. The density of the oxide melt was $3.85 \times 10^3 \, kg/m^3$ based on the volume of the core-shell droplet after 20 min of melting, using the reduced mass of Fe δm_{Fe} to calculate the shell oxide volume.
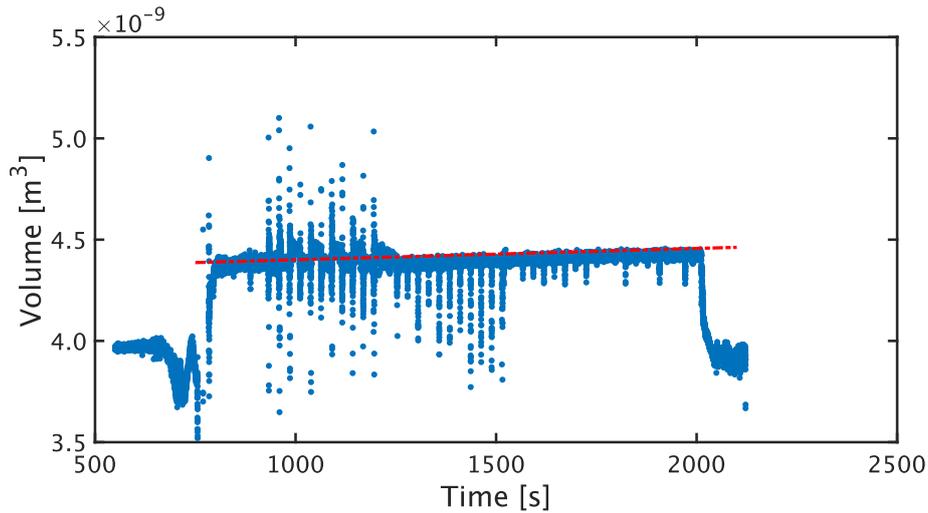
Figure 1. Volume change of core-shell droplet with time at 1605°C. The large deviation was sample position change by applying an electrical field to excite the drop oscillations.
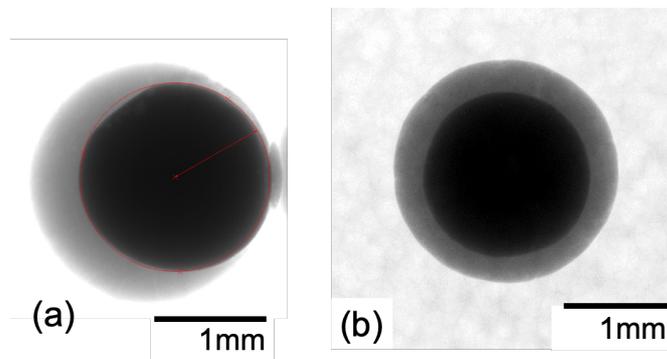
Figure 2. X-ray radiograph images of solidified core-shell drop samples: (a) before and (b) after being processed by ELF in the ISS.

4. Dissolution of Fe into shell oxide from core iron

From the above, Fe dissolves from core iron to shell oxide in the core-shell droplet, and the density of shell oxide increases from $3.24 \times 10^3\,\mathrm{kg/m^3}$ to $3.85 \times 10^3\,\mathrm{kg/m^3}$. ThermoCalc simulations show that the density of Flux-9 oxide at equilibrium with liquid iron is $3.4 \times 10^3\,\mathrm{kg/m^3}$ at $1605\,^\circ\mathrm{C}$. The dissolution of Fe into shell oxide is larger than the thermal equilibrium. The dissolution of Fe for this density increase is thought to be due to oxidation of liquid iron. Since the sample's mass did not change before and after melting, it is unlikely that the oxygen used for oxidation was supplied from the outside. The oxygen source for the oxidation of liquid iron at the interface is attributed to the oxygen included in core iron [7] and/or to the oxygen from the reaction in the molten oxide in which Fe_2O_3 decomposed to Fe_3O_4 and O_2 ($6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$)[8]. Decomposed oxygen from Fe_2O_3 near the interface is considered to be adsorbed on liquid iron and diffused as FeO into the shell oxide, where it decomposes into Fe and O. The Fe decomposed from FeO diffused into the shell oxide expands in volume because the Fe in the oxide breaks the oxide network structure. Moreover, we should consider the effect of an electrical double layer [9] at the interface between liquid iron and molten oxide because the core-shell droplet stays in the electrical field to maintain its position in the electrode of ELF. Because of the electrical charge at the interface would affect the change of interfacial properties. This phenomenon of dissolution and diffusion of Fe from liquid iron into the oxide and the increase in the volume of the molten oxide is difficult to observe on the ground, and we believe that it was first extracted in the levitation experiment in a microgravity environment.

The change in the core-shell radius ratio and the density of the shell oxide affect the initial purpose of the interfacial tension measurement. However, since the density of the oxide melt change was obtained from this measurement, these two can also be inferred if the change in the core-shell droplet volume is known. Therefore, it is possible to measure the interfacial tension even when Fe is dissolved. Furthermore, the value of the interfacial tension decreases if there is oxygen adsorption on liquid iron, necessitating the assumption that the interfacial tension is lower than in the equilibrium state during the measurement. In the future, we will elucidate the source of oxygen causing the oxidation of liquid iron and explore the behavior of liquid iron and molten oxide at the core-shell droplets' interface.

5. conclusion

Core-shell droplets of liquid iron and molten oxide were successfully formed using the ELF on board the ISS. The volume of the core-shell droplet sample was observed while it was held at a constant temperature at $1605\,^\circ\mathrm{C}$ for oscillating drop experiments, and it was found that the volume increased with time. This is thought to be due to the diffusion of Fe atoms into the shell oxide by oxidation of liquid iron; the dissolution of Fe atoms disrupts the network structure of the molten oxide, causing the volume to increase. This phenomenon was picked up by observation in microgravity conditions. In the future, the oxidation phenomenon of liquid iron will be clarified, and the interface phenomenon between liquid iron and molten oxide will be clarified in conjunction with oscillating drop experiments of core-shell droplets.

References

1) K. Ogino: Interfacial Tension between Molten Iron Alloys and Molten Slags (*in Japanease*), Tetsu-to-Hagane, **61** (1975) 2118, DOI: https://doi.org/10.2355/tetsutohagane1955.61.8_2118.

2) H. Tamaru, T. Ishikawa, J. Okada, Y. Nakamura, Y. Ohkuma, S. Yukizono, Y. Sakai and T. Takada: Overview of the Electrostatic Levitation Furnace (ELF) for the International Space Station (ISS), Int. J. Microgravity Sci. Appl., **32** (2015) 320104, DOI: https://doi.org/10.15011/jasma.32.1.320104.

3) T. Ishikawa, C. Koyama, H. Oda, H. Saruwatari and P. .-F. Paradis: Status of the Electrostatic Levitation Furnace in the ISS -Surface Tension and Viscosity Measurements, Int. J. Microgravity Sci. Appl., **39** (2022) 390101, DOI: https://doi.org/10.15011/jasma.39.390101.

4) S. Taguchi, H. Hasome, S. Shimizu, R. Ishiwata, R. Inoue, M. Yamada, M. Watanabe, T. Matsushita, T. Ishikawa, H. Oda, C. Koyama and T. Ito: Proposal of Temperature Correction of Molten Oxide Based on Its Emissivity for Measurement of Temperature Dependence of Its Density Using ELF in ISS, Int. J. Microgravity Sci. Appl., **40** (2023) 400101, DOI: https://doi.org/10.15011/jasma.40.400101.

5) R. Sato, R. Ishiwata, S. Taguchi, and M. Watanabe: Measurement of the Normal Spectral Emissivity of Molten Oxide Using an Electromagnetically Levitated Complex Droplet of Molten Oxide and Liquid Fe, High Temp. High Press., **52** (2023) 249, DOI: https://doi.org/10.32908/hthp.v52.1433.

6) A. Nakamura, S. Hakamada, A. Mizuno and M. Watanabe: Measurement of the Normal Spectral Emissivity of Molten Oxide Using an Electromagnetically Levitated Complex Droplet of Molten Oxide and Liquid Fe, Int. J. Microgravity Sci. Appl., **34** (2017) 340404, DOI: https://doi.org/10.15011/ijmsa.34.4_340404.

7) K. Ogino, S. Hara, T. Miwa and S. Kimoto: The Effect of Oxygen Content in Molten Steel on the Interfacial Tension between Molten Steel and Slag(*in Japanease*), Tetsu-to-Hagane, **65** (1979) 2012
, DOI: https://doi.org/10.2355/tetsutohagane1955.65.14_2012.

8) J. Wiencke, H. Lavelaine, P. .-J. Panteix, C. Petitjean and C. Rapin: Electrolysis of iron in a molten oxide electrolyte, J. Appl. Electrochem., **48** (2018) 115, DOI: https://doi.org/10.1007/s10800-017-1143-5.

9) E. Karimi-Sibaki, A. Kharicha, M. Wu, A. Ludwig and J. Bohacek: Modeling electrochemical transport of ions in the molten CaF_2-FeO slag operating under a DC voltage, Appl. Math. Comput., **357** (2019) 357, DOI: https://doi.org/10.1016/j.amc.2018.01.008.