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ISS搭載ELFによる高温融体界面張力計測（Interfacial Energy プロジェクト）の進捗報告

Current States of Interfacial-Energy Project using Electrostatic Levitation Furnace (ELF) in ISS

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1. Introduction

Interfacial tension measurements are required in steel industries, which include smelting, continuous casting, and welding. In the continuous casting process, mold flux made of molten oxides covers steel melt in the casting pool. Here, the interfacial tension prevents the oxide from being pulled down into the steel melt. In the welding process, the welding flux, made of an oxide, encloses the steel melt in order to prevent the melt from oxidizing and to control the shape of the welded part. For this control, the interfacial tension between the welding flux and the steel melt plays an important role. The interfacial tension in these processes is changed empirically by changes in the oxide composition. Therefore, in order to systematically be able to control the interfacial tension between molten oxide and the steel melt, we need to obtain the values of this tension for many kinds of these media 1). However, oxide compositions were limited by the temperature in previous measurements using a sessile drop with an X-ray radiograph 2) due to the difficulty in raising the temperature above the melting point of iron with conventional methods using a container. Therefore, a container-less technique must be used to measure the temperature dependence of interfacial tension between molten oxides and steel melts. As such, we planned to measure this interfacial tension using core-shell droplets with an oscillating drop technique in microgravity 3). Under microgravity conditions, two immiscible liquids form a core-shell droplet which is dominated by the surface and interfacial free energies. Then the interfacial tension, which is the interfacial free energy per unit area, can be found. The surface tension is measured using the drop oscillating technique from the eigenfrequencies of the surface oscillation of levitated liquid droplets. To perform the measurement of interfacial tension between molten oxide and steel melts forming a core-shell droplet, we selected the electrostatic levitation method to achieve the requirements needed for the measurement. We were able to use the electrostatic levitation furnace (ELF) 4) installed in the KIBO module of the International Space Station (ISS). In this report, we review the current status of our research using the ELF for finding the interfacial tension between molten oxides and liquid Fe.

2. Surface oscillation of core-shell droplet

The surface oscillation of core-shell droplets was analytically investigated by Sufferen et al. 4) as follows from the incompressible fluid motions using velocity potential $\vec{v} = -\nabla\varphi$. The pressure difference is supported by the boundary stress and P denotes the pressure in the fluid of density ρ. The pressure difference across a spherical boundary of radius R and interfacial tension σ is described by the Young-Laplace formula as $\Delta P = -(2\sigma)/R$. On the assumption of small deviations of a boundary from the original sphere as $r = R_0 + R(\theta,\phi)$ in the polar coordinate, we delivered from the Young-Laplace formula to the following equation,

$$\rho\frac{\partial^2\varphi}{\partial t^2} - \frac{\sigma}{R_0^2}\left[2\frac{\partial\varphi}{\partial r} + \frac{\partial}{\partial r}\left(\nabla_s^2\varphi\right)\right] = 0 \quad \text{at } r = R_0, \tag{1}$$

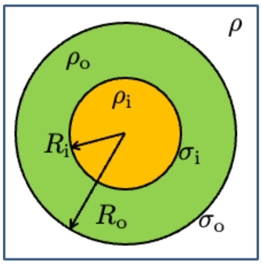

Figure 1. Three liquid systems for normal mode analysis of core-shell droplet.

where, ∇_s^2 is the surface Laplacian. For core-shell droplets, from the existing two boundary conditions the solutions of the eq.(1) for φ are in the three regions for shell, core and host(atomospher) as:

$$\varphi(r,t) = \sum_{l,m}\left[A(l,m;t)r^l + B(l,m;t)r^{-(l-1)}\right]Y_{lm}(\theta,\phi), \tag{2}$$

$$\varphi_i(r,t) = \sum_{l,m} A_i(l,m;t)r^l Y_{lm}(\theta,\phi), \tag{3}$$

$$\varphi_o(r,t) = \sum_{l,m} A_o(l,m;t)r^{-(l+1)}Y_{lm}(\theta,\phi). \tag{4}$$

where A and B are constant values, $Y_{lm}(\theta,\phi)$ is a spherical harmonic function with the normal mode index integer l and m. If the condition that the normal component of velocity across each boundary is continuous is imposed, we obtain $A_i = A - [(l+1)/l]BR_i^{-(2l+1)}$ and $B_o = B - [l/(l+1)]R_i^{(2l+1)}$. The conditions for existing these velocity potentials simultaneously are obtained from the eigenvalue equation, and then we obtain eigenfrequencies of the normal mode of surface oscillation of core-shell droplet as,

$$\omega_\pm^2 = \omega_0^2 K_\pm \frac{\tau^8}{\sigma}\frac{1}{(1+\Delta\rho_i)\tau^{10} - 2/3\Delta\rho_i}, \tag{5}$$

$$K_\pm = \frac{1}{2}\left(\frac{\sigma m_i}{\tau^3} + \frac{m_o\tau^3}{\sigma}\right) \pm \sqrt{\frac{1}{4}\left(\frac{\sigma m_i}{\tau^3} - \frac{m_o\tau^3}{\sigma}\right) + 1}. \tag{6}$$

In eqs.(5) and (6), symbols are shown in **Fig. 1** and follows,

$$\sigma = \sqrt{\sigma_o/\sigma_i}, \quad \tau = \sqrt{R_o/R_i}, \quad \Delta\rho_i = \frac{(l+1)(\rho_i - \rho_o)}{(2l+1)\rho_o}, \quad \Delta\rho_o = \frac{l(\rho_a - \rho_o)}{(2l+1)\rho_o},$$
$$m_i = (1+\Delta\rho_i)\tau^{(2l+1)} - \Delta\rho_i\tau^{-(2l+1)}, \quad m_o = (1+\Delta\rho_o)\tau^{(2l+1)} - \Delta\rho_o\tau^{-(2l+1)}.$$

If the eigenfrequencies ω_+ and ω_- can be obtained from measurements, the interfacial tension σ_i can be obtained by transforming eq. (1) with $l = 2$ for the fundamental mode as follows

$$\sigma_i = \omega_-^2\omega_+^2 \frac{J^2}{m_i m_o - 1}\frac{R_i^3 R_o^3}{\sigma_o}\left(\frac{5\rho_o}{24}\right)^2, \tag{7}$$
$$J = \frac{3}{5}(1+\Delta\rho_i)\tau^5 - \frac{2}{5}\Delta\rho_i\tau^{-5}.$$

From eq.(7), it can be seen that to obtain the interfacial tension value σ_i from the eigenfrequencies of the core-shell droplet by two immiscible liquids, the density of core liquid ρ_i, the density of shell liquid ρ_o, and the surface tension of shell liquid σ_o are required. For our target research to obtain the interfacial tension, the core liquid is liquid Fe and the shell liquid is molten oxides. Since the density of liquid Fe was reported much number in previously, we can obtain it easily. On the other hand, for molten oxide, we can obtain its density by ELF and also use the literature value but it is difficult to find the surface tension from literature at the same compositions for the target oxides. Therefore, we have measured the molten oxide surface tension using the oscillating drop technique by ELF. However, it is difficult to obtain accurate surface tension of multi-component molten oxides containing Fe even in ELF due to their electrification behavior. For this reason, we try to make a new equation to obtain the interfacial tension σ_i without the surface tension of molten oxide σ_o with an approximation of eqs. (5) and (6). Details of the equation are described and discussed in late section 4.

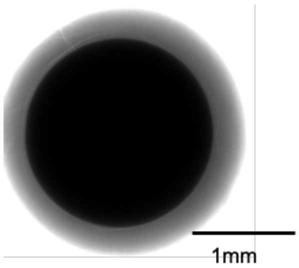

Figure 2. X-ray radiograph image of a core-shell sample by oxide (shell) and Fe (core), which is installed in ISS.

3. Preparation of core-shell sample by Fe and oxides

Core-shell samples made by liquid Fe and molten oxides for oscillating drop experiments in ELF were prepared as follows. First, the oxide sample powder was dried and weighed after removing water, and then provisionally sintered by a CO_2 laser. The sample was melted by a CO_2 laser on a water-cooled copper plate with a conical hole, and during the cooling process, spherical iron was dropped into the oxide and completely solidified in the spherical oxide. The solidified samples were checked by X-ray radiography for the presence of air bubbles, and those without bubbles were selected for installation on the ISS. From numerical simulations 6), surface oscillations can be clearly observed when the radius ratio of core to shell is 1.3. We made core-shell samples by adjusting the radius ratio of 1.3 by the volume estimating from their masses. An X-ray radiograph image of a core-shell sample prior to the ISS installation is shown in **Fig. 2**. For the first tried observation of surface oscillation observation of core-shell droplets by molten oxide and Fe melt, we used oxide compositions as SiO_2:CaO:Mn_3O_4:TiO_2:Fe_2O_3=25:7:20:18:30 mass%, which is the flux material model composition used in the welding process (named as Flux9). In this sample, the core is aligned with the center of the shell, but in some cases, the centers of the core and shell were not aligned.

4. Oscillating drop experiments using ELF in ISS

Using the ELF 4) (**Fig. 3**) installed in the ISS, core-shell droplets were formed by heating and melting a core-shell sample made of a flux material model composition (Flux9) oxide in the welding process using a semiconductor laser with a wavelength of 980 nm. After the core-shell droplet formation, an alternating electric field was applied between the electrodes to excite the surface oscillation of the droplet and the time variation of the droplet shape was measured by the shadow sensing method 7) and the time variation of the surface oscillation amplitude was obtained.

The density of the oxide melt was obtained by levitating a single oxide melt at ELF and measuring the droplet shape using backlight optics to obtain the volume, then calculating the temperature variation of the density from the mass of the returned sample on the ground to obtain the density at the temperature when the surface vibration of the core-shell droplet was measured. The sample temperature was determined as the apparent temperature using a single-color pyrometer with a wavelength of 1.6 μm by emissivity set to 1. Since the surface of the core-shell droplet is covered with molten oxide, we need the emissivity of the molten oxide in the shell phase to measure the droplet temperature using a pyrometer. The normal spectral emissivity of the molten oxides (Flux9) used in the present experiment was then obtained by the following procedure 8) and used to determine the core-shell droplet temperature in the present drop oscillating experiments.

First, the normal spectral emissivity of the molten Flux9 was determined in a simultaneous levitation experiment of Fe and Flux9 using the electromagnetic levitation method 8). Since the Fe melting point (T_m = 1535 °C 9)) and the normal spectral emissivity of liquid Fe ($\varepsilon_{Fe} = 0.327$ 10,11)) are known, the radiance at the Fe melting point R_{Fe} was determined to match that of the black body R_b. Since the normal spectral emissivity of Fe is known, a correction constant C_s is calculated so that the radiance R_{Fe} at the Fe melting point is equal to the blackbody radiance R_b, and the temperature of molten Fe is determined from the emissivity at the wavelength of 1.6 μm.

$$C_s R_{Fe}(T_m) = \varepsilon_{Fe} R_b(T_m) = \varepsilon_{Fe} \frac{C_1}{\lambda_0^5} \frac{1}{\exp\left(\frac{C_2}{\lambda_0 T_m}\right) - 1}. \tag{8}$$

where $C_1 = 2\pi hc^2$ the first constant of radiation, $C_2 = hc = k_B$ the second constant of radiation, where h: Planck constant, c: the speed of light, k_B: Boltzmann constant.

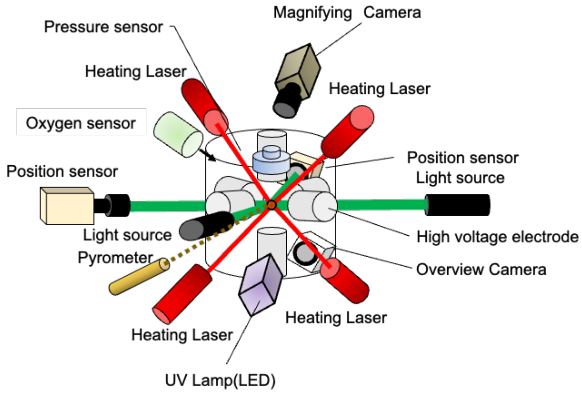

Figure 3. Schematic diagram of ELF installed in ISS.

The normal spectral emissivity of Flux9 was determined to be $\varepsilon_{ox} = 0.76 \pm 0.01$ 12) from the ratio $\varepsilon_{ox} = \varepsilon_{Fe}(R_{ox}/R_{Fe})$ to the emissivity of the molten oxide at the same temperature, $R_{ox}(T)$, which was determined from the temperature of the molten Fe part using the correction constants. Using this ε_{ox} and the radiance R_{ox} converted from the measured temperature as the ELF instrumental constant C_s^{EL} and emissivity of 1, the following eq.(9) was used to determine the temperature T_{EL} for the surface oscillation of the core-shell droplet at the ELF.

$$T_{EL} = \frac{C_2}{\lambda_0} \frac{1}{\ln\left(\frac{C_1}{\lambda_0^5} \frac{\varepsilon_{ox}}{C_s^{EL} R_{ox}} + 1\right)}. \tag{9}$$

5. Surface oscillation analysis of core-shell droplet by liquid Fe and molten oxides

Surface oscillation of core-shell droplets was measured by applying an alternating electric field to core-shell droplets levitated in the ELF with applying frequencies from 130Hz to 145Hz. During the measurements, the droplet temperature was 1920K which was corrected using the Flux9 emissivity of 0.76 ± 0.01. The amplitude of the surface oscillation increased near the resonance frequency of the eigenfrequency of the surface oscillation.The Fourier transform of the time variation of the surface oscillation amplitude in the free oscillation region after the AC electric field reduced is shown in **Fig. 4** that the amplitude increased at two frequencies (ω_- = 76Hz, ω_+ = 153Hz). This is consistent with the analytical results that the surface oscillation of core-shell droplets oscillates at two frequencies, and is the first demonstration that the surface of core-shell drop oscillates at two frequencies in core-shell droplets by immiscible liquids with very different densities. Using these two frequencies, we can obtain the interfacial tension from eq.(7). However, we did not obtain the surface tension of molten oxides of Flux9. Therefore, we make an approximation for $K_\pm$ in eq.(6) with the assumption that the surface tension of molten oxide σ_o is larger than the interfacial tension between liquid Fe and molten oxide σ_i. This assumption is caused by the core-shell drop formation by these two liquids. For the assumption, we find $\sigma m_i/\tau^3 > m_o\tau^3/\sigma$ and also that $K_\pm$ is simplified **?**). On the assumtion, ω_+ and ω_- are described as follows;

$$\omega_+^2 = \omega_o\left(1 - \frac{5}{3}\Delta\rho_i\tau^{-10}\right), \ \omega_- = \omega_o\frac{3}{5}\frac{\tau^6}{\sigma^2}\left(1 - \tau^{-10}\right), \tag{10}$$

where, ω_o is $\omega_o^2 = 8\sigma_o^2/(\rho_o R_o^3)$which corresponds to the Rayleigh frequency of eigenfrequency of the normal mode of single-liquid surface oscillation by molten oxides. On the basis of the features of eigenfrequencies of surface oscillation of core-shell droplet, thus ω_- only includes σ, and then we find that the interfacial tension σ_i is described only by ω_- as following;

$$\sigma_i = \omega_- \frac{5\rho_o R_o}{24} \frac{1}{\tau^6(1 - \tau^{-10})}. \tag{11}$$

To obtain σ_i using eq.(11), we need ρ_o of molten oxide density,R_o of radius of molten oxide and τ including R_i of liquid Fe radius. We can obtain these values from the inside observation of the core-shell droplet by for instance an X-ray radiograph technique.

We perform only on the ground the X-ray radiograph observation for the solidified sample processed by ELF in ISS, therefore we must estimate the radius of core and shell parts during levitation in ELF. During core-shell droplet levitation using ELF, we obtained the shadow image of the molten core-shell droplet and its temperature.

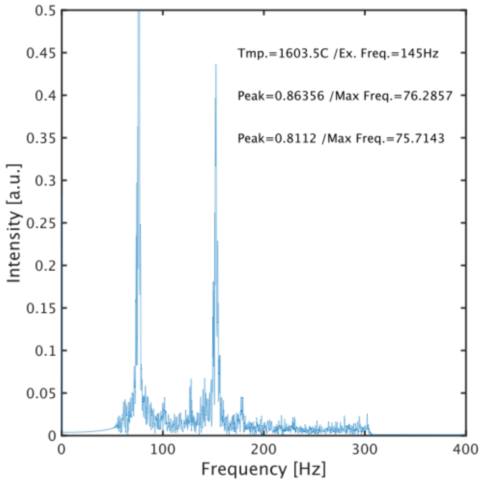

Figure 4. Power spectral density of surface oscillation frequencies of core-shell droplet obtained by FFT analysis of the surface oscillation data by ELF.

The mass of core-shell dorp processed by ELF can be known when the solidified sample returns to the ground as M^{s}_{to}. From these results, we can estimate ρ_o, R_o and R_i because the density of Fe is known well in solid and liquid states with temperature dependence. If we are able to perform the inside observation of the solidified sample processed by ELF and to obtain both radius core and shell R^s_i and R^s_o. Using M^s_{to}, R^s_i and R^s_o, we can obtain the density of molten oxide ρ_o during levitated by ELF as,

$$\rho_o = \frac{M^s_{to} - \rho^s_{Fe} V^s_{Fe}}{(4\pi/3)R^3_o - \rho^s_{Fe}\,\rho^L_{Fe}\,V^s_{Fe}}, \quad V^s_{Fe} = \frac{4\pi}{3} R^{s\,3}_{Fe}. \tag{12}$$

From these procedures, we can calculate the interfacial tension from eq.(12) without new measurements of molten oxide surface tension and density. In the presentation, experimental results will be applied to the procedure and the obtained interfacial tension value will be discussed with the previous literature values.

6. Conculsion

Using the ELF on the ISS, we successfully measured the surface oscillation of core-shell droplets of liquid Fe and molten oxide using the drop oscillating technique. On the ground, it is difficult to form core-shell droplets due to the large density difference between liquid Fe and molten oxide, but core-shell droplets were successfully formed in a microgravity environment without the density difference. The surface oscillation of the core-shell droplet was excited, and it was found that the surface oscillation occurred at two different frequencies even in liquids with large density differences. The interfacial tension will be calculated using the two surface oscillation frequencies with a new equation of the interfacial tension with approximations. The new equation of the interfacial tension does not include molten oxide surface tension and density, therefore, we do not need the measurement of the thermophysical properties of molten oxide. In the presentation, we discussed about details of the procedure for obtaining the interfacial tension values from the data of experiments by ELF. In the future, we will conduct measurements using oxide melts with systematically varied compositions to develop a model for the interfacial tension between oxide melts and molten iron.

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