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# 微小重力環境における Fe–Cu 合金融体の表面張力測定結果を利用した Butler モデルの評価

# Evaluation of the Butler Equation Using Surface Tension of Fe-Cu Alloys Measured under Microgravity Conditions

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## 1. Introduction

Space provides an ideal environment for measuring the thermophysical properties of high-temperature melts. In this unique environment, the absence of containers eliminates any risk of sample contamination from the container, even at elevated temperatures. In addition, the measurements are conducted free from the effects of natural convection and hydrostatic pressure, which often degrade the accuracy and precision of measurements on Earth. As a result, several space missions have been conducted on the International Space Station (ISS) to measure the thermophysical properties of various high-temperature melts using the Electrostatic Levitation Furnace aboard the KIBO (ELF-ISS) and European Space Agency Materials Science Laboratory Electromagnetic Levitator (MSL-EML). These missions aim to optimize materials processes and enhance our understanding of phenomena. However, it would be short-sighted to use these results solely for their initial intended purposes. These measurements can also serve as benchmark data to validate and improve terrestrial methods and predictive models for measuring thermophysical properties.

This study utilizes space-based measurements of the surface tension of molten Fe-Cu binary alloys from the "Thermal Storage" mission to validate the effectiveness of terrestrial electromagnetic levitation (EML) for surface tension measurements and the Butler model 1) for predictions. Based on these results, we have extended the Butler model to the ternary Fe-Si-Cu alloy system and evaluated its effectiveness.

## 2. Experimental procedure

### 2.1. Measurement of Surface tension using EML

A piece of Fe-Si master alloy was placed on a quartz holder within the EML coil, alongside a high-purity iron ingot. The alloy was electromagnetically levitated with a piece of the iron ingot and then melted uniformly under a high-purity mixture of argon and helium gas flowing at 2 L/min. The sample temperature was controlled by adjusting the partial pressures of argon and helium gases, which have different thermal conductivities, using a two-color pyrometer. After the droplet temperature stabilized, the oscillation behavior of the droplet was monitored from above at 500 fps for 16 sec using a high- speed camera. The frequencies of the surface oscillations of $m = 0, \pm 1$, and $\pm 2$ for the $l = 2$ mode, and those of the center of gravity were analyzed from time-sequential data of the HSV images. The surface tension of the droplet was calculated from the frequencies using the Rayleigh equation 2) and the Cummings and Blackburn calibration 3).

### 2.2. Butler model

Butler derived an equation to calculate the surface tension of a liquid solution by considering the activities at the surface and in the bulk phase, assuming equilibrium between a bulk phase and a hypothetical surface phase. The equation is given by:

$$\sigma = \sigma_i^{\mathrm{Pure}} + \frac{RT}{A_i}\ln\frac{n_i^{\mathrm{S}}}{n_i^{\mathrm{B}}} + \frac{G_i^{\mathrm{E.S}} - G_i^{\mathrm{E.B}}}{A_i} \tag{1}$$

where $\sigma_i^{\mathrm{Pure}}$ is the surface tension of the liquid alloying element, $R$ is the gas constant, and $T$ is the temperature. $A$ is the molar surface area of the molten alloy calculated from the molar volume $V$ as $A_i = 1.091 N_0^{1/3} V_i^{2/3}$. $n_i^{\mathrm{S}}$ and $n_i^{\mathrm{B}}$ are the molar fractions of the alloying element at the surface and in the bulk, respectively. $G_i^{\mathrm{E.S}}$ and $G_i^{\mathrm{E.B}}$ are the partial excess Gibbs free energies at the surface and in bulk, respectively. Following the approach by Speiser et al., if we assume the dependence of temperature and alloy composition on $G_i^{\mathrm{E.S}}$ is identical to that on $G_i^{\mathrm{E.B}}$, it can be expressed as follows,

$$G_i^{\mathrm{E.S}} = \beta G_i^{\mathrm{E.B}} \tag{2}$$

where $\beta$ is the ratio of coordination number on the surface to those in the bulk for pure substances, reflecting surface relaxation. In this study, we adopted $\beta = 0.83$, as proposed by Tanaka et al.[4)], which was derived from the relationship between surface tension of liquid metals and binding energy at the surface.

For a ternary alloy consisting of components labeled as 1, 2 and 3, $G_i^{\mathrm{E.B}}$ can be expressed using the Redlich-Kister polynomial:

$$G_i^{\mathrm{E.B}} = \sum_{i=1}^{3}\sum_{j>i}^{3}\sum_{m=0}^{M} L_{ij}^{m} n_i n_j (n_i - n_j)^m + n_1 n_2 n_3 \sum_{i=1}^{3}\sum_{k=0}^{K} L_{123}^{k} n_i \tag{3}$$

where L is the interaction parameter, subscript $i$ and $j$ attached to the symbol denote alloy components, superscripts m and k represent the numbers of interaction parameters determined by the combination of alloy elements. Due to the nonlinear nature of these equations, solutions were computed using the Newton-Raphson method.

## 3. Results and Discussion

Figure 1 shows the surface tension of molten Fe-Cu alloys at 1800 K, measured on Earth using EML and calculated using the Butler equation. The figure also includes results from the "Thermal Storage" mission using ELF-ISS and comparative literature data. As the Cu composition increases to 20at%, the measured surface tension of molten Fe-Cu decreases dramatically and approaches that of molten copper, indicating surface segregation of the copper atoms. The results calculated using the Butler equation closely align with these measurements. Additionally, the data obtained with ELF-ISS are consistent, supporting the validity of the Cumming and Blackburn approach for calibrating droplet deformation by gravitational acceleration and electromagnetic force to droplet oscillation in terrestrial experiment. Furthermore, these findings support the assumption in the Butler model that the bulk phase is thermodynamically equivalent to a hypothetical surface phase, at least within the context of the Fe-Cu alloy system.

Figure 2 displays the surface tension of molten Fe-Si-Cu ternary alloys at 2100 K, as measured using EML and calculated with the Butler equation. Although the measurements exhibit some scatter, they consistently show a gradual decrease in surface tension with increasing Cu composition. The results calculated with the Butler equation are in comparative agreement with the experimental data, demonstrating that the Butler model is effectively practical for estimating surface tension amidst observed scatter. The observed scatter may be attributed to a strong phase separation tendency affecting surface segregation of atoms. To further validate the Butler equation for these ternary alloys, a more detailed study at higher temperatures, which promoted atomic mixing, will be necessary.

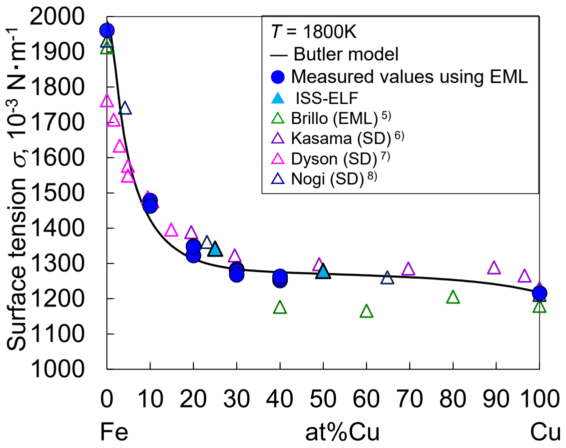

**Figure 1**. Surface tension of molten Fe-Cu alloy estimated with the extended Butler equation and measurement plots obtained using EML.

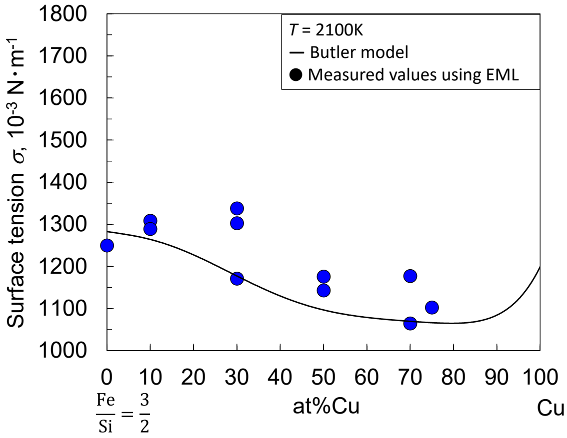

**Figure 2**. Surface tension of molten Fe-Si-Cu alloy estimated with the extended Butler equation and measurement plots obtained using EML.

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