

OR1-3

蛍光 X 線分析を用いた液体金属の *in-situ* 拡散係数測定
の誤差要因解析

Analysis for the Error Factor in the *in-situ* Diffusion Measurement through X-ray Fluorescence Analysis in Liquid Metals

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1. Introduction

Diffusion coefficients in liquid metals are important for understanding the solidification process in metallic materials and the atomic transport in liquid metals. Recently, the combination of *in-situ* X-ray fluorescence analysis and a long capillary technique has been proposed as the diffusion measurements in liquid metals¹. The apparent diffusion coefficient obtained in the *in-situ* diffusion measurement fluctuated at the initial diffusion states. The initial fluctuation has the potential to induce a systematic error in the measured diffusion coefficient. The objective of this study is to reduce the initial fluctuation in the results of the previous diffusion measurement²) by eliminating or evaluating the error factors, such as averaging effect³), and matrix effect⁴).

2. Experimental procedure

In the experiment, the intensity distribution in the detection range and the calibration curve between the X-ray intensity and the concentration were prepared to evaluate averaging effect and matrix effect. The experimental apparatus was the same as that in the reference¹). In the experiment for the intensity distribution, the Bi rod was casted into 1.5×1.5×10 mm³ and contained in the capillary, the size of which is 1.5×1.5×63 mm³. The fluorescent X-ray was detected with an integration time of 60 s while changing the point where the X-ray is emitted on the sample at each measurement. In the experiment for the calibration curve, the Sn-Bi rods were weighed and casted into ten of 1.5×1.5×6 mm³ and contained in the capillary. Bi concentrations of the Sn-Bi rods were set as 0, 0.5 1.0 1.5, and 2.0 at.%. The fluorescent X-ray was detected from the melted sample at 573 K with an integration time of 6000 s. The experiment for one sample was performed four times.

3. Results

By scanning the sample in the capillary, the intensities at each measurement point were obtained. The shape of the distribution between the intensity and the measurement point resembled an error function. **Figure 1**

shows the calibration curve between the fluorescent X-ray intensity and the Bi concentration.

4. Discussion

The apparent diffusion coefficients were calculated from the results of the previous diffusion measurement by fitting the analytical solution for the diffusion to the measured concentration distribution. Averaging effect was eliminated by performing the convolution of the analytical solution with the intensity distribution. The intensity distribution in the detection range was prepared by fitting the error function to the intensities at each measurement point. The initial fluctuation was suppressed and the systematic error of 7% was eliminated by the convolution, according to **Fig. 2**. The linear and quadratic functions were successfully fitted to the detected intensities, according to **Fig. 1**. The coefficients of determination (R^2) of both functions were larger than 0.999. This indicates the prepared calibration curve could be considered linear and matrix effect caused no significant error in the concentration range of 0~2 at.%, where the previous diffusion measurement was performed.

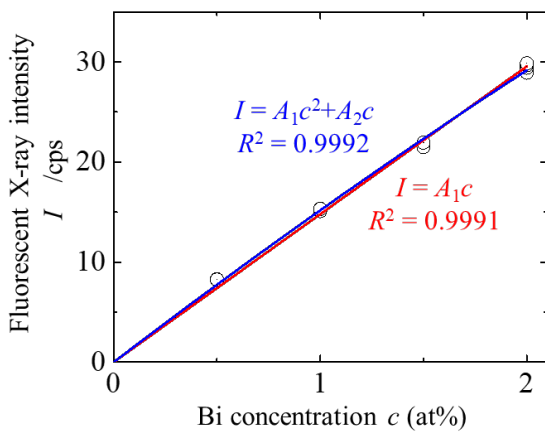


Figure 1. Prepared calibration curve between the fluorescent X-ray intensity and Bi concentration

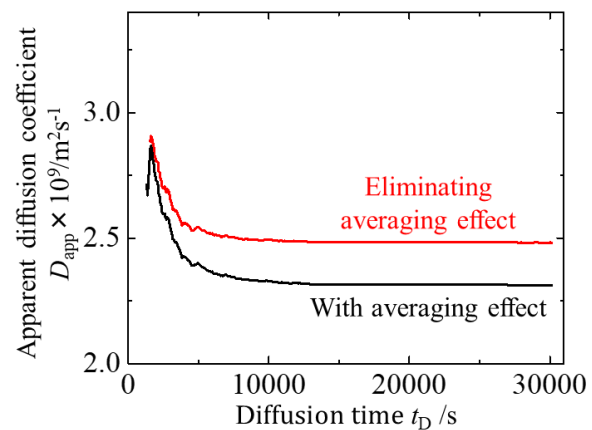


Figure 2. Apparent diffusion coefficients obtained by eliminating averaging effect or not

5. Conclusion

By eliminating averaging effect through the convolution, the systematic error in the measured diffusion coefficient of 7% was eliminated. Matrix effect caused no significant error in the diffusion measurement.

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