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蛍光 X 線分析を用いた液体金属の拡散係数に対する *in-situ* 測定と時系列解析

In-situ Measurement and Time Series Analysis of Diffusion Coefficient in Liquid Metals using X-ray Fluorescence Analysis

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1. Introduction

In-situ measurements with X-ray fluorescence analysis (XRF) were shown to be effective as the diffusion coefficient can be directly obtained by fitting the change of the measured intensity with error function formula [1,2]. However, the obtained value apparently fluctuates over diffusion time due to experimental measurement error. The objective is to establish an analytical method to obtain a reasonable diffusion coefficient by applying time series analysis to the obtained value. In order to obtain the diffusion coefficient, the unit root test[3] applied to the data published in the previous conference[2].

2. Experimental Procedure

Fig.1 shows the experimental apparatus to obtain the data[2]. The sample of Sn-Bi was heated to and kept at 555 K and held for about 3×10^4 s. During that time, X-ray was radiated at a fixed point, and the fluorescent X-ray of Bi causing impurity diffusion in Sn was detected.

The measured intensity was obtained by calculating the area of Bi-Lβ peak. The fitting value D_{fit} was obtained by fitting the temporal change of detected intensity with the theoretical intensity formula[2]. D_{fit} at each diffusion time t_D was calculated by setting each t_D as the end of the time range for fitting.

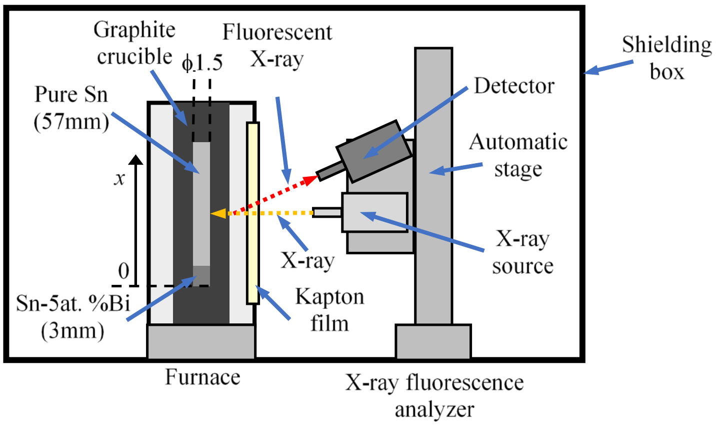

Fig. 1　Schematic illustration of XRF experimental apparatus for measurements of diffusion coefficient

3. Results

Fig. 2(a) shows D_{fit} according to t_D over 10000 s, the standard error of which is less than 5%. At a small t_D, since the number of the measured values is small, the standard error of D_{fit} was large. In this reason, D_{fit} with a standard error of 5% or more were rejected. D_{fit} fluctuated due to experimental measurement error, especially at near t_D = 20000 s.

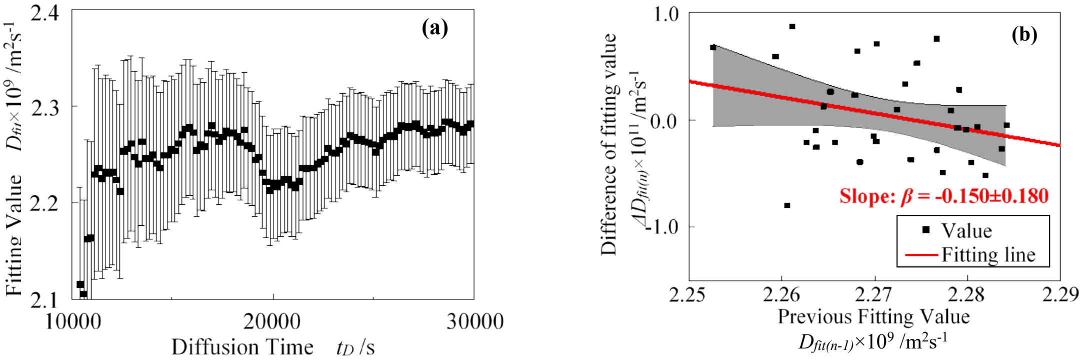

Fig.2 Measured and analyzed data about diffusion coefficient: (a) Fitting values, (b) the result of the unit root test at t_D = 23658~29277 s, gray area is 95% confidence interval (95%CI) of β

4. Discussion

To detect the confidence range in **Fig. 2(a)**, the unit root test was applied to the results. The unit root test[3] is a statistical test that determines whether the time series data is a random walk. A random walk is expressed by

$$D_{fit(n)} = D_{fit(n-1)} + u_n \tag{1}$$

where $D_{fit(n)}$ is D_{fit} of n-th plot and u_n is a random number. In the test, the correlation between $\Delta D_{fit(n)}$ (= $D_{fit(n)}$-$D_{fit(n-1)}$) and the previous value $D_{fit(n-1)}$ was evaluated with β, which is the value in

$$\Delta D_{fit(n)} = \beta D_{fit(n-1)} + u_n \tag{2}$$

If the time range is a randam walk, β is equal to 0 since the difference is a random number. So, distribution of $\Delta D_{fit(n)}$ to $D_{fit(n-1)}$ in the applied range was fitted with **Eq. 2**, and if 95%CI of β in fitting line contained 0, the applied range was determined as a random walk. **Fig. 2(b)** shows the result of the unit root test in t_D = 23658~29277 s, where t_D is largest in two of the time ranges accepted by the test. This range was regarded as the confidence range, and the average value of D_{fit} in the confidence range was determined as the diffusion coefficient, which was 2.27×10^{-9} m²/s. This value was contained by 95%CI of the temperature dependence fitting this value and the reference data.

5. Conclusion

An analysis method that adapts the unit root test to time-fluctuating value was demonstrated to be effective to eliminate significant measurement errors in measurements of diffusion coefficient using XRF and obtain a reasonable diffusion coefficient in good agreement with the reference data.

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