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シアーセル法による蛍光 X 線分析用 Al-Cu 合金の標準試料作製

Standard Samples of Al-Cu Alloy for X-ray Fluorescence Analysis Obtained by Shear Cell Technique

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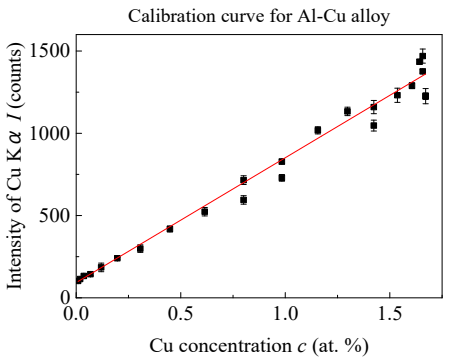
Abstract: The objective of this study is to evaluate error sources on Al-Cu standard samples. Shear cell technique was used to obtain standard samples with different Cu concentration. 20 Al-Cu standard samples were analyzed by X-ray fluorescence analysis (XRF) and inductively coupled plasma optical emission spectrometer (ICP-OES). Linear fitting was processed for obtained calibration curve. Concentration profile of shear cell diffusion analyzed by ICP-OES was coincident with error function. Thus, errors on the obtained calibration curve has come from XRF analysis. The main source is thought to be due to taking out and inserting the same standard sample.



Keywords: Impurity diffusion coefficient, Calibration curve, X-ray fluorescence analysis, Shear cell technique, Al-Cu alloy

1. Introduction

Diffusion coefficient of liquid metal is important for understanding material processing. To measure diffusion coefficient accurately, natural convection should be suppressed. Experiments in space were performed previously. Stable density layering[1)] enabled to measure the diffusion coefficient precisely on the ground. Recently, in-situ measurement of impurity diffusion coefficient by XRF analysis was proposed[2)]. However, obtaining precise concentration standard samples for calibration curve is difficult because melting alloy one by one has large concentration error and takes much time. By using shear cell technique[2)], accurate and various concentration standard samples can be obtained in one diffusion process.

Prediction formula for impurity diffusion coefficient was proposed[3)], but in some Al solvent alloys, impurity diffusion coefficient was measured lower than the prediction[4)]. There are few reliable experimental data of impurity diffusion coefficient in Al solvent. Therefore, reliable method to measure accurate impurity diffusion coefficient in Al solvent is necessary. This study aims to evaluate the source of errors in analyzing standard samples.

2. Experimental Procedures

Shear cell technique[1)] was used to obtain standard samples. Diffusion samples of Al-1.7 at.%Cu alloy and pure Al were prepared and set into the cells. A capillary is 60 mm in length and consists of 20 cells with 3 mm

thickness. Further details of the design and diffusion procedure can be referred to the previous experiment.[3] Pure Al was set into upper 27 mm area and intermediate cell. Al-Cu alloy was set into lower 30 mm. Diffusion was processed at 973 K, under 6.8×10^{-2} Pa, for 9000 s. Diffusion started when intermediate cell was inserted. After the diffusion, the capillary was separated into 20 cells and solidified.

XRF analysis was performed to measure the Cu Kα intensity. Before the analysis, the standard samples were formed from ϕ 1.50 mm cylinder to 1.50×1.50 mm² column to obtain flat irradiated surface in order to increase the intensity counts. Two adjacent standard samples were inserted in the Boron Nitride crucible which has 1.50×1.50×63 mm³ capillary and analyzed at the same time. The apparatus of the XRF analysis can be referred to the previous experiment[2]. The fluorescence X-ray was detected from the solid sample with an integration time of 60 s. The experiment for each pair was performed four times, and averaged intensity was used for calibration curve.

After the XRF analysis, Cu concentration of each standard sample was analyzed by ICP-OES. In this analysis, each standard sample was dissolved by nitric acid and hydrochloric acid.

3. Results

Figure 1 shows the obtained standard sample (from x=0.021 to 0.024 m). **Figure 1(a)** is before the forming process, and **Fig. 1(b)** is after the forming process. This reaction was also reported in the Al-Sn diffusion of shear cell technique[5]. Black area on **Fig. 1** is graphite reacted area and silver area was Al-Cu alloy area.

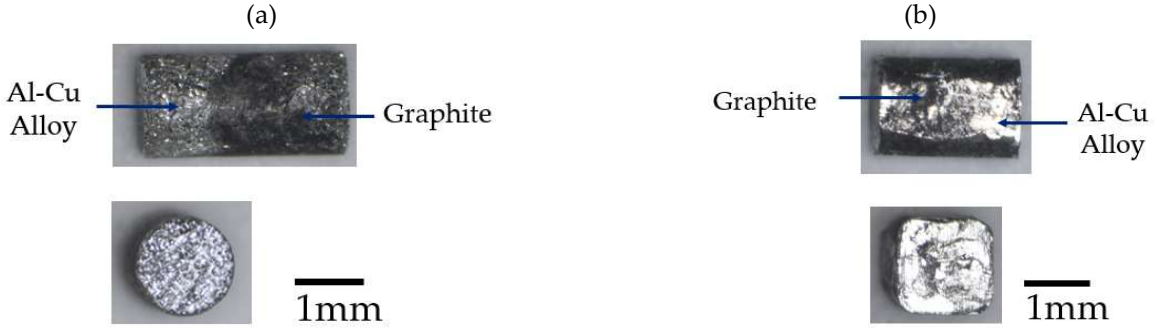


Figure 1. (a) Standard sample before forming (cylinder), (b) standard samples after forming (square column). Graphite reaction and surface unflattens can be seen.

Figure 2 shows the results of XRF analysis. Since the intensity was measured for two standard samples at once, the position was calculated as the center of two cells position. Intensity distribution was similar shape to concentration distribution on shear cell diffusion.

Figure 3 presents the intensity and concentration of standard samples. Error bars show the standard deviation of averaged intensity. Each Cu concentration was the average of two standard samples where XRF analysis was performed at the same time. To evaluate the error on taking out and inserting the same samples, additional measurements were performed for some standard samples. The error was larger than the error bar.

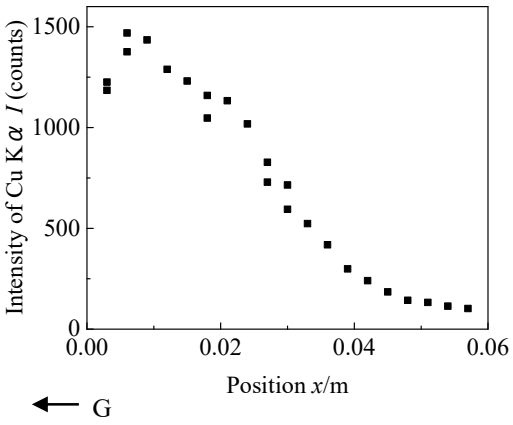


Figure 2. Intensity profile of Cu in obtained standard samples by using shear cell technique. "←G" indicates the direction of gravity.

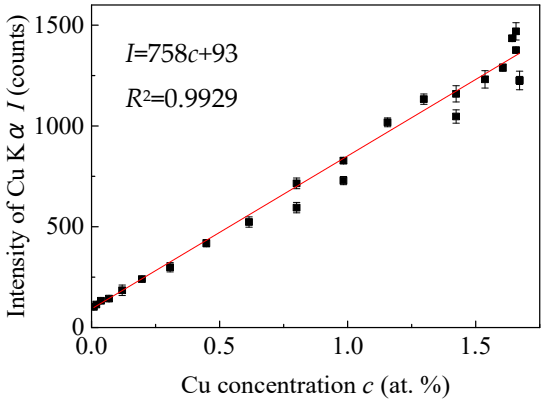


Figure 3. Intensity of Kα at each concentration. Red line presents linear fitting results of calibration curve.

4. Discussions

The results of ICP-OES analysis were highly reliable since it was mostly match with concentration profile expected from the initial condition using shear cell technique. Reaction between graphite and Al-Cu alloy can be neglected. Thus, the source of error in **Fig. 3** was on XRF analysis. For example, taking out and inserting of standard samples and surface roughness can be considered.

On **Fig. 3**, linear fitting was processed. **Eq. (1)** is the result of the fitting. Obtained linear calibration curve has R^2 value more than 0.99. The highest residual was 27.2% at x=0.030 m.

$$I = 758c + 93 \tag{1}$$

5. Conclusions

By using shar cell technique, reliable standard samples can be prepared. Intensity error sources on XRF analysis have been discussed. The main source thought to have come from taking out and inserting the same standard samples.

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Conflicts of Interest

The authors declare no conflict of interest.

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