Diffusion coefficient measurement of Au in Ag melt by shear cell method

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Abstract: Shear cell method is one of the most advanced experimental techniques to measure diffusion coefficients in liquids. In order to measure the diffusion coefficient more accurately, we studied error factors of this method. The shearing convection in the shear cell method is one of the major error factors of the measurement of diffusion coefficient. To clarify the effect of shearing convection on diffusion coefficient, we carried out the measurement of diffusion coefficient of Au in Ag melt at temperatures of 1300K and 1500K with the variation of diffusion time. We obtained the time dependence of Au diffusion coefficient in Ag melt and clarified the feature of experimental error arising from the shearing convection.

1. Introduction

We are studying the diffusion phenomena and the experimental method of diffusion for liquid metals and semiconductors in Japan Aerospace Exploration Agency (JAXA). In addition, in future, we will perform the measurement of diffusion coefficient under microgravity by using the shear cell method.

The shear cell method is favorable for alloy samples which have a serious effect of solidification or segregation. A diffusion couple is separated during heating, joined at the planned experimental temperature, and divided into small pieces before cooling. Thus, this method is able to avoid the diffusion during heating and cooling, and to remove the effects of solidification.

On the ground, we performed the diffusion experiments by using the shear cell method for Au-Ag alloys to clarify the cause of the experimental errors in the experimental process. The Au-Ag alloy is suited for the evaluation of this cause of errors, because it has a narrow solid-liquid coexisting region and has only a small effect of segregation on solidification.

In this report, we describe improved points of the shear cell method for the high accuracy measurement, and as a result, we report the temperature dependence of the diffusion coefficient of Au in Ag melt.

2. Shear cell method

The shear cell consists of thin disks with holes, a rotation shaft, a key bar, and a cartridge. A diffusion couple inside the shear cell is joined by rotating the rotation shaft at the planned experimental temperature to avoid the diffusion during heating and cooling periods, and is divided into many pieces at the end of diffusion time to remove the effects of solidification or segregation. Fig.1 shows computer graphics of shear cell method. To aim at a high accuracy measurement of the diffusion coefficient by the shear cell method, we examined two points, the effect of misalignment of shear cell and that of convection induced by shearing the liquid.

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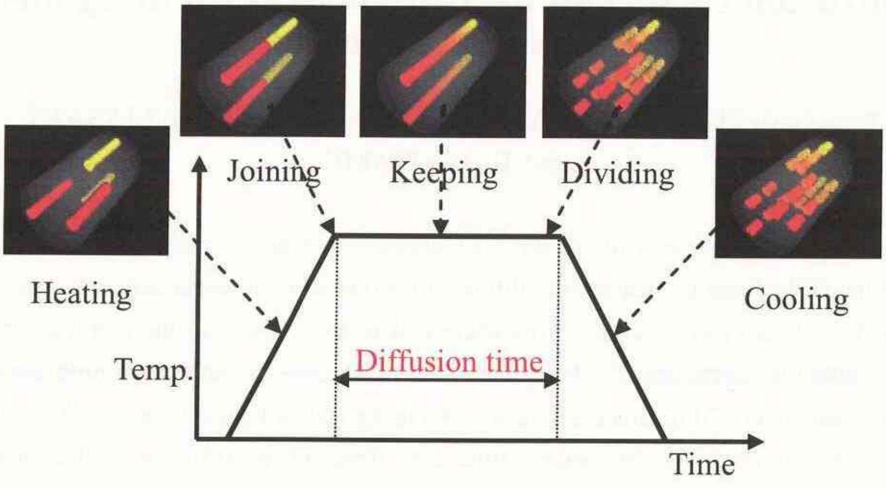

Fig.1 Shear cell method

To avoid the experimental errors due to the misalignment on joining a diffusion couple, we developed the in-situ observation system of diffusion couple by X-ray image [1]. It was possible to observe the diffusion couple by selecting the material of the crucible, the heater and the cartridge used for the shear cell experiment. The glassy carbon as the crucible material contributed to the improvement of the accuracy of machine work and the misalignment was kept to be less than 50μm. We investigated the influence of shearing convection on joining a diffusion couple.

Fig.2 shows a schematic figure of the concentration profile of shear cell method. The concentration profile at the interface of diffusion couple at diffusion time t=0, shown in Fig.2(b), may differ from the step function (Fig.2(a)), due to the convection induced by the shearing. In other words, when the diffusion couple is joined, the sample mixing has already occurred by the convection over some distance around the interface. It can be thought that the experiment begins from a advanced state of diffusion. Thus, the observed diffusion coefficient may be larger than the true diffusion coefficient due to the influence of convection induced by the shearing of liquid.

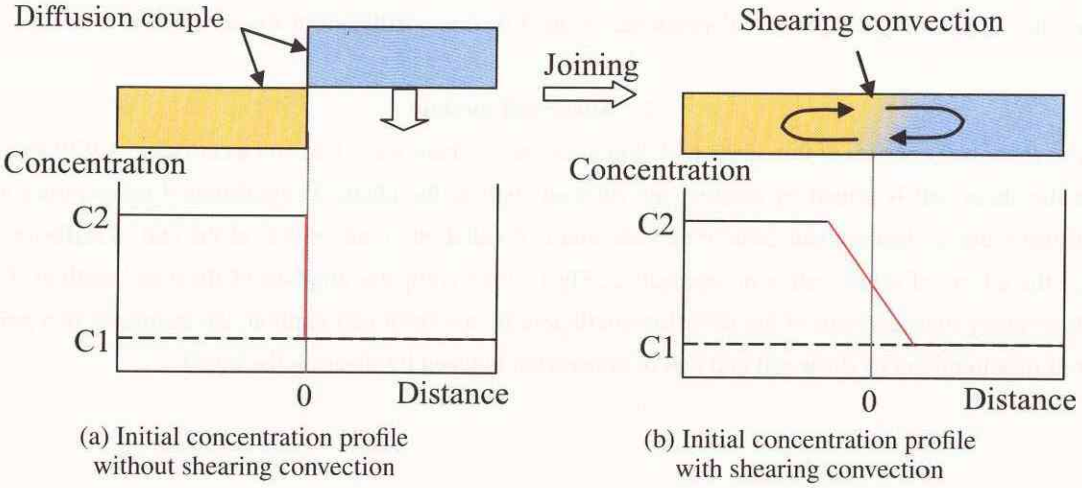

Fig.2 Initial concentration profile of diffusion couple

To perform the measurement of the diffusion coefficient by the shear cell method, we found the optimum condition about the surface roughness of the shear cell disks and the shearing velocity [2]. Moreover, these results qualitatively correspond to the fluid simulation which visualized the convection on shearing [3].

In this report, we intended to clarify the influence of the convection on shearing on the measured diffusion coefficients by changing the diffusion time.

3. Experiment

3.1 Preparation of sample for diffusion experiment

The influence of convection on shearing occurs at the beginning of the experiment. It seems to be possible to reduce it by extending the diffusion time t as long as possible. Hence, the length of diffusion sample was taken to be 60mm (30mm+30mm). This length enables us to take the diffusion time long enough.

The diffusion sample of 1mm diameter and 30mm length for the Ag -$Ag_{0.95}Au_{0.05}$ diffusion couple was made by a casting method. By adopting this length, it was possible to perform an experiment with seven hours of diffusion time. The diffusion sample was made of the alloy. At first, the alloy was put on the upper part of graphite mold with a capillary of 1mm inner diameter and 50mm length, which was put in a quartz tube. After, the quartz tube was evacuated and was heated in a ceramic furnace up to the planned experimental temperature, the alloy was cast into graphite capillary by pushing the plug on the top of the alloy. As soon as the quartz tube was taken out from the furnace, it was immersed into water to obtain a homogeneous sample. In addition, prior to the every start of diffusion experiment, the sample was heated up to the experimental temperature, and was hold during 60 minits to obtain a homogeneous sample.

3.2 Experimental condition

The diffusion experiment was performed at 1300K and 1500K. To prevent the buoyancy convection, the temperature of the top of sample was kept to be 20K higher than that of the bottom side. The temperature was observed at three points of sample along the shear cell crucible by using thermocouples.

It can be thought that the influence of convection on shearing may become small with the increase of diffusion time t. Therefore, we adopted the diffusion time as a parameter for the present experiment, and it was changed from 240 to 25200 seconds to investigate the influence of convection on shearing.

3.3 Concentration analysis

After the experiment, the diffusion couple was divided into many pieces. It is necessary to analyze the concentration of about 120 pieces for every one experiment. Therefore, we adopted the fluorescence X-ray analysis (EDX) to analyze samples quickly together with 'the compression and folding method' to obtain the homogeneity of sample for the analysis [4].

The result of EDX for the same sample was compared with that of the Inductively-Coupled Plasma Mass Spectroscopy (ICP-MS) to confirm the accuracy of the EDX method. Table1 shows these comparisons. The difference of the analyzed value between these two methods was below 0.2at% for the $Ag_{0.95}Au_{0.05}$ sample. It became to be possible to analyze two diffusion couple in about six hours by the introduction of the EDX.

Table 1 Difference of concentration between EDX and ICP methods

Sample	EDX (at%)	ICP (at%)	Δ (at%)
A	3.01	2.98	0.03
B	5.35	5.56	-0.21

4. Experimental results

Fig.3 shows the result of concentration distribution of Au in Ag melt. This result was obtained at 1500K for the diffusion time of 21600 seconds. The circle indicates the experimental value and the full line indicates the analytical solution which was given by the Fick's second law. The experimental value is in good agreement with the analytical solution. The diffusion coefficient was calculated to be 3.14×10^{-9} m^2/sec.

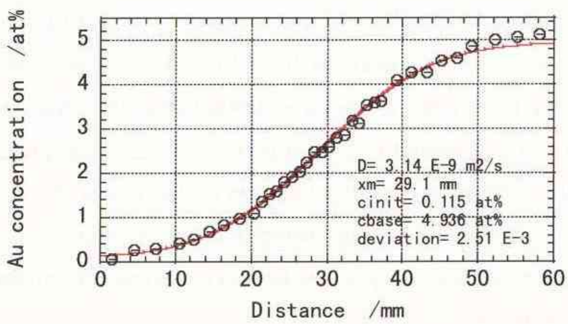

Fig.3 Concentration profile of Au in Ag melt

Fig.4 shows the time dependence of the diffusion coefficient. The observed diffusion coefficient became small and constant when the diffusion time was taken to be longer than 10800 seconds both at 1300K and 1500K. Thus, it is clearly seen that the influence of the turbulence can be removed by taking the diffusion time as long as possible.

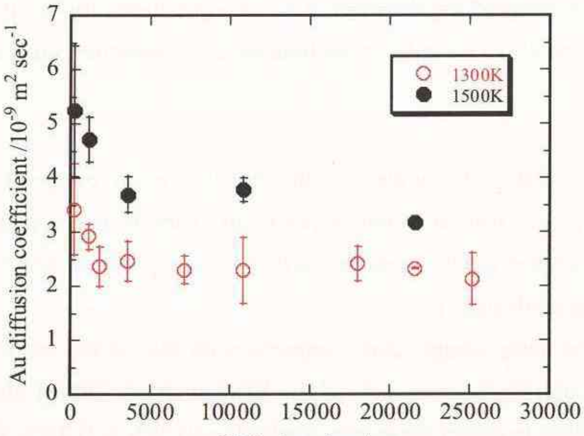

Fig.4 Time dependence of diffusion coefficient of Au in Ag melt

5. Conclusion

Based on the shear cell method, we obtained the time dependence of diffusion coefficient of Au in Ag melt at 1300K and 1500K by using Au-$Ag_{0.95}Au_{0.05}$ diffusion couple. The diffusion coefficient was $2.24 \pm 0.23 \times 10^{-9}$ m^2/sec at 1300K and $3.37 \pm 0.36 \times 10^{-9}$ m^2/sec at 1500K. The present experiment for a long time diffusion enabled us to measure the diffusion coefficient under the condition of very small influence of the convection on shearing. Thus, if once it is possible to clarify the relationship between the diffusion experiment under microgravity and that on ground, it can be thought that it is possible to obtain an almost true diffusion coefficient only by performing the diffusion experiment on the ground. In future, it will be able to perform diffusion experiments at higher temperature by improving the heater of the shear cell cartridge. In addition, we have a plan to obtain the temperature dependence and the composition dependence of the diffusion coefficient systematically.

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