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Reduction of Convection in Diffusion Measurement using the Shear Cell by Stabilization of Density Layering on the Ground

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Abstract

An inter-diffusion experiment between a ternary alloy of SnBiIn and pure Sn was performed using the shear cell technique on the ground. The capillary was set vertically and the SnBiIn sample was set in the lower side of the capillary. The obtained concentration profiles were smooth and were able to be fitted by theoretical functions. The diffusion coefficients of In and Bi obtained by fitting and corrections for the shear convection and the averaging effect agreed well with those obtained in a microgravity experiment performed in Foton-M2. Under assumption of the power law, the obtained data were lying on the same curves of temperature dependence as other available reference data of inter-diffusion of SnIn-Sn and SnBi-Sn. It was found that the addition of Bi to SnIn does not bother the diffusion of In and stabilizes the density layering to suppress convection in an experiment on the ground.

1. Introduction

Diffusion coefficients of liquid metals are very important data for understanding physics of condensed matter and development of material processing, such as casting, crystal growth and so on. However, the amount of reliable diffusion data is still not large enough for these purposes, since accurate diffusion measurements are difficult. If convective flow exists in liquid sample, it is difficult to distinguish the diffusive mass transport from the convective one.

Diffusion measurements might be disturbed by several kinds of convections, such as, buoyancy convection caused by the density difference on the ground, Marangoni convection caused by the difference in the surface tension of the free surfaces, shear-convection caused by the mechanical movement of the container of the liquid sample, and so on.

Therefore, measurement methods for diffusion in liquid metals have been developed aiming at suppressing convections. For example, diffusion experiments were performed under microgravity conditions in space environment¹⁻⁷⁾ and in strong magnetic field⁸⁻¹⁰⁾. These experiments demonstrated the effectiveness of suppression of convection with the following results. The measured values of the diffusion coefficients in these experiments were smaller than that obtained on the ground, where convection might exist; the measured values of the diffusion coefficients have a small standard deviation; and, the measured values agree with each other among these experiments.

Recently, this research group reported the development of a method of diffusion experiments using the shear cell, reservoir

technique and a stable density layering¹¹⁻¹⁶⁾. A shear cell^{17,18)} has a lot of thin disks with thin holes (cells). Since capillaries are formed by accumulation of the disks and connection of the holes, it is possible to form and disconnect the capillaries by rotation of the disks. This function is advantageous to form a capillary only during the diffusion time (**Fig.1**). Therefore, diffusion during the heating and cooling time of the sample, thermal expansion, and segregation during solidification can be eliminated from the concentration profile in the shear cell experiments. These are the main error sources of the conventional long capillary method. Furthermore, the shear cell in this study has reservoirs on the both ends of a capillary to provide pressure on the liquid sample so as to minimize free surfaces, which cause Marangoni convection¹⁹⁾.

Since the shear cell technique allows for a homogenization time before the diffusion time and eliminates the segregation effect, alloys can be used for diffusion experiments. Furthermore, some of diffusion pairs with a pure metal and its alloy allow for stable density gradient in the capillary axis. When the capillary axis is set vertically and the sample with a lower density is set in the upper side of the capillary, the density increases monotonously in the gravity direction. When the sufficient density gradient is kept during the whole diffusion time, the density layering is stable enough to suppress the convection. The effectiveness of this method to suppress convection has been confirmed in diffusion experiments with diffusion pairs of Sn-SnIn^{10, 11)}, In-InSn¹¹⁾, Sn-SnBi^{11, 12)}, Pb-PbAg¹³⁾, Pb-PbGa¹⁴⁾, and Al-AlNi¹⁵⁾.

However, a stable density layering has been confirmed only

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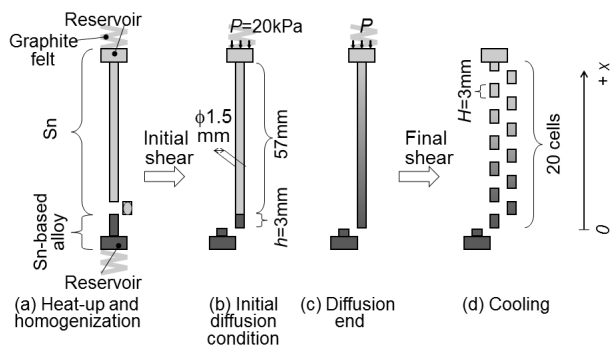


Fig. 1 Schematic illustration of the experimental procedure using the shear cell technique in this study.

with combinations of a pure metal and its binary alloy, as mentioned above. On the other hand, it is necessary to investigate the stability of the density layering and its improvement for combinations; a pure metal and its isotope; a pure metal and its ternary alloy; a pure metal and its binary alloy with weak stable density layering, and so on.

This study was aimed at enlargement of possible material combinations by improvement of stability of density layering by adding a third element. Bismuth was added to SnIn alloy sample to increase the stability of the density layering. Inter-diffusion experiments were performed with a sample setting of a thick layer of SnInBi to Sn using the shear cell on the ground. The obtained diffusion coefficients of Bi and In in Sn were compared with data obtained under microgravity in the Russian Foton-M2 satellite, and with other available reference data. From the reliability of the measured diffusion coefficient, the effect of the stability improvement by adding the third element was discussed.

2. Experimental

2.1 Structure and operation of shear cell

Figure 1 shows a schematic illustration of the experimental procedure using the shear cell technique. Although the shear cell used in this study is called Foton shear cell, because it was developed for the Foton missions¹¹⁾, it is applicable to experiments on the ground, also.

A shear cell unit has an outer cylinder, inner cylinder, and 20 graphite disks with holes (cells) with a diameter of 1.5 mm. The thickness H of a disk is 3 mm. By connecting these cells, a capillary with a length of 60 mm is formed. On the both ends of the capillary, reservoirs are equipped.

The experimental procedure is as follows. Two kinds of solid samples are set in the capillaries at room temperature. Here, only one cell (intermediate cell) is set away from the capillary (**Fig. 1 (a)**) to disconnect two kinds of samples. **Figure 1** shows the setting for diffusion from a thick layer to a semi-infinite space. The samples with the same composition as that in the

capillary are set in the both reservoirs with elastically compressed graphite felts. Then the shear cell is set in a furnace.

The furnace is fixed so that the diffusion axis is vertical. The top side of the furnace is determined by the density of the samples in the capillary.

After evacuation of the furnace, the shear cell unit and the samples are heated. After a homogenization time of about one hour at the diffusion temperature, the intermediate cell is moved between the two samples by initial shearing (**Fig. 1(b)**) and a capillary for a diffusion pair is formed. This is the start of diffusion. During the diffusion time (**Fig. 1(c)**), pressure of about 20 kPa is given by the graphite felts from the reservoir.

After the diffusion time, every second disks are rotated backwards by final shearing and the capillary is divided into small cells (**Fig. 1(d)**).

The shear cell is disassembled at room temperature and the concentration of the elements in the sample in each cell is analyzed. Concentration profiles are obtained by plotting the analyzed concentration of elements in the middle position of each cell. The position x is set along the capillary axis as the distance from the capillary end (**Fig. 1(d)**).

2.2 Ground (1g) experiment

An alloy sample SnInBi and a pure Sn were set in the capillaries and the reservoirs (**Fig. 1(a)**). The initial concentrations c_0 of In and Bi in the alloys sample were 7.8 and 3.4 at%, respectively.

The length h of the thick layer of the SnInBi alloy was 3 mm, which was the same as the thickness of a disk, and the length of the Sn sample was 57 mm. The SnInBi alloy sample was set in the bottom side of the capillary.

The diffusion experiment was performed by following the procedure in 2.1 on the ground. The diffusion temperature T and diffusion time t were 773 K and 21600 s, respectively. The vacuum pressure in the chamber was 0.8 Pa. The temperature gradient was about 100 K/m with a maximum temperature in the middle of the capillary. The linear speed of the cell by both initial and final shearing was 0.5 mm/min. The concentrations c of In and Bi in the sample in each cell were analyzed individually by atom absorption spectroscopy (AAS, Varian SpectraAA300).

2.3 Microgravity (μg) experiment in Foton-M2

An alloy sample SnInBi and a pure Sn were set in the capillaries and the reservoirs (**Fig. 1(a)**). The initial concentrations c_0 of In and Bi in the alloys sample were 4.5 and 4.7 at%, respectively. Although these initial concentrations were different from those for the ground experiment, the differences were considered to be too small to affect the diffusion coefficient.

The shear cell was set in the furnace, named AGAT, and was

set in the Foton-M2 satellite. The Foton-M2 was launched by Soyuz-U rocket on May 30, 2005 from Baikonur Cosmodrome. The μg -diffusion experiment was performed during a two-week flight in the low earth orbit. The dimension of the samples and the procedure of the diffusion experiment were the same as those of the 1g-experiments explained in 2.1. The diffusion temperature T and diffusion time t were 773 K and 18000 s, respectively. The vacuum pressure in the chamber was 0.8 Pa. The temperature gradient was about 100 K/m with a maximum temperature in the middle of the capillary. The steady g-level and its vibration level were smaller than some $10^{-5}G$.

3. Results and Discussion

3.1 Concentration Profiles and Diffusion Coefficients

The Bi and In concentration profiles obtained in 1g- and μg -experiments (Fig.2) can be fitted well with the theoretical function of diffusion from a thick layer to a semi-infinite space.

$$c(x,t) = \frac{c_0}{2} \left[\operatorname{erf} \left(\frac{H+x}{\sqrt{4D_{\text{eff}}t}} \right) + \operatorname{erf} \left(\frac{H-x}{\sqrt{4D_{\text{eff}}t}} \right) \right] \quad (1)$$

Since the diffusion coefficient in this equation is supposed to be larger than the real diffusion coefficient D as explained below, this is described as D_{eff} instead of D .

The linear plots of the Bi and In concentrations (Fig.3) can be well described by a thin layer profile of the Gaussian function;

$$c(x,t) = \frac{c_0 h}{\sqrt{\pi(D_{\text{eff}}t + h^2/6)}} \exp \left(\frac{-x^2}{4(D_{\text{eff}}t + h^2/6)} \right) \quad (2)$$

where $h^2/6$ the square diffusion depth caused by the step of the start profile.

The concentration profiles were fitted to the equations using the following mean square diffusion depth as a fitting parameter;

$$\langle x^2_{\text{meas}} \rangle = 2D_{\text{meas}}t \quad (3)$$

The obtained value of the mean square diffusion depth was supposed to be larger than that caused by the ideal pure diffusion, because of the averaging effect $\langle x^2_{\text{aver}} \rangle$ and the shear convection $\langle x^2_{\text{shear}} \rangle$

In a shear cell experiment, the average concentration value in a cell is plotted at the center of the cell. Therefore, the plotted value is different from the real concentration just after the completion of the diffusion process at each point. As a result, the obtained concentration profile seems as if the diffusion time were prolonged. This error source is known as ‘‘averaging effect’’. In the case of the Foton shear cell, the value of $\langle x^2_{\text{aver}} \rangle$ was calculated geometrically as $H^2/12$, which was $0.75 \times 10^{-6} \text{ m}^2$ with $H=3\text{mm}^{18)}$.

Although $\langle x^2_{\text{shear}} \rangle$ increases with an increase in temperature²⁰⁾, the constant value was used as shown above. As the

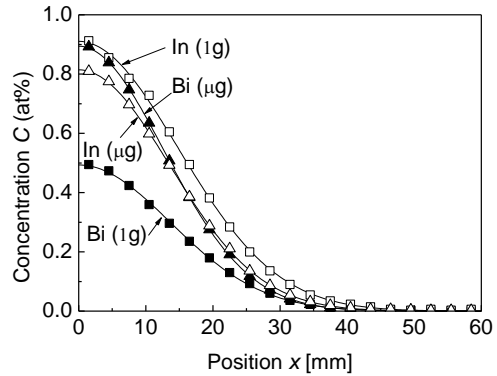


Fig. 2 Concentration profiles of Bi and In obtained in 1g- and μg - diffusion experiments with SnInBi-Sn in this study.

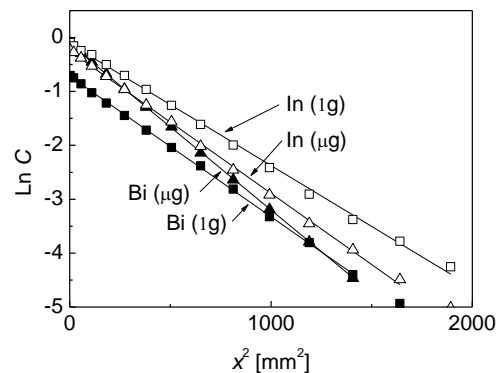


Fig. 3 Linear plots of the Bi and In concentrations (Fig.2) obtained in 1g- and μg -diffusion experiments with SnInBi-Sn in this study.

diffusion coefficients in the reference were calculated with the constant value of $\langle x^2_{\text{shear}} \rangle (=2 \times 10^{-7} \text{ m}^2)$, the diffusion coefficients in this study were calculated with the constant value, in order to compare the diffusion coefficient with them. The error caused by ignoring the temperature dependence of $\langle x^2_{\text{shear}} \rangle$ is not so significant in the temperature range in this study.

By subtraction of these errors as the following equation, the diffusion coefficient was obtained.

$$D = \frac{1}{2t} \left(\langle x^2_{\text{meas}} \rangle - \langle x^2_{\text{shear}} \rangle - \frac{H^2}{12} \right) \quad (4)$$

The obtained diffusion coefficients are shown in Table 1. The obtained values agree well each other within the measurement error range between 1g- and μg -data for each element.

There are discrepancies in the concentration profiles between the 1g and the μg experiments. The differences were caused by the differences in the initial concentration (In and Bi) and diffusion time. Therefore these discrepancies are supposed not to be significant enough to affect the diffusion coefficient due to the agreement of the diffusion coefficients. However, additional experiments are needed to discuss this point precisely.

Table 1 Experimental conditions and diffusion coefficients of this study and previous shear cell experiments

Sample	Gravity	T [K]	$D \times 10^9$ [m ² /s]	Plot (Fig.4)	Ref.
SnInBi-Sn	1g (SDL) ^{1]}	773	(In)4.99 (Bi)4.26	▽ ▼	This study
	μg (FotonM2)	773	(In)5.02 (Bi)4.37	△ ▲	This study
	μg (Foton12)	574	(In) 3.0 (Bi) 2.3	□ ■	6)
SnIn-Sn	1g (SDL)	548	2.44	x	10),11)
		673	3.73		
		873	5.82		
		1073	8.62		
	1g (MF) ^{2]}	548	2.6	○	8)
μg (FotonM2)	673	3.62	◇	18)	
SnBi-Sn	1g (SDL)	573	2.41	+	11,12)
		773	4.35		
		1073	7.62		
	1g (MF)	548	2.18	●	8)
	μg (FotonM2)	673	3.45	◆	18),20)
		773	4.36		

1] SDL:stable density layering

2] MF: strong magnetic field

3.2 Comparison with other experiments

The diffusion coefficients obtained in this study were plotted in **Fig.4** with the relating reference data obtained from previous shear cell experiments (**Table 1**). The experimental apparatus and procedure were almost the same for the 1g (SDL) and μg (Foton M2 and 12) as those in this study. The plots are overlapping for at 773 K for Bi in this study and in the μg experiment (SnBi-Sn).

All of the data in Table 1 were fitted by the power law of the temperature dependence $D=AT^n$ (**Fig.4**). The fitting parameters (A, n) were $(3.59 \times 10^{-14} \text{ m}^2/\text{sK}^n, 1.78)$ for In and $(2.61 \times 10^{-14} \text{ m}^2/\text{sK}^n, 1.81)$ for Bi.

Since the 1g-data in this study agree well with the μg-data and are lying on the same lines of the power law with other reference data, convection is considered to be suppressed in the 1g-experiment in this study by the stable density layering.

The density ρ of pure Sn and SnIn (In 20.5 at%) are 6804 and 6784 kg/m³ at 773K.²¹⁾ The density ρ of SnIn binary alloys at 773 K can be described as

$$\rho(c_{In}) = 6804 - 0.98 \cdot c_{In} \quad (5)$$

within the range of the In concentration c_{In} between 0 and 20 at% under assumption of a linear decrease of the density with increase in c_{In} . When the c_{In} profile in a SnIn binary sample has

the same as that of the 1g-experiment in this study (**Fig.2 In(1g)**), the density increases slightly in the x-direction as shown in **Fig.5 (SnIn)**. Therefore, the In rich side should be set in the upper side of the capillary to obtain stable density layering (**Fig.6 (a)**).

The density ρ of pure Bi is 9867 kg/m³ at 773K²¹⁾. The density ρ of SnBi binary alloys at 773 K can be described as

$$\rho(c_{Bi}) = 6804 + 30.6 \cdot c_{Bi} \quad (6)$$

within the range of the In concentration c_{In} between 0 and 100 at%. Predel *et al.*²²⁾ reported that the density of SnBi binary alloy increases almost linearly with increase in c_{Bi} . When the c_{Bi} profile in a SnBi binary sample has the same as that of the 1g-experiment in this study (**Fig.2 Bi(1g)**), the density decreases in the x-direction as shown in **Fig.5 (SnBi)**. Bi varies the density of Sn alloys in the opposite direction from In. Therefore, the Bi rich side should be set in the lower side of the capillary to obtain stable density layering (**Fig.6 (b)**).

Although the exact density data of SnInBi ternary alloy are not available, it is clear from **Fig.5** that In does not vary the density of SnInBi so significantly compared to Bi within the concentration range in this study. The density variation calculated by a simple pile of the contribution of In and Bi is the dotted line in **Fig.5**. This can be used as an approximation of the density profile at the end of the diffusion. A monotonous decrease in the density can be supposed in the x-direction during the whole diffusion time, also. Therefore, the sample setting with the SnInBi alloy in the lower side is stable (**Fig.6 (c)**).

These results demonstrate that an unstable density layering (**Fig.6 (d)**) can be changed to a stable one (**Fig.6(c)**) by adding third element.

Figure 4 shows that it does not affect the measured diffusion data whether Bi and In diffuse in Sn simultaneously or individually. Therefore Bi and In are considered not to disturb the diffusive motion each other in the concentration range in this

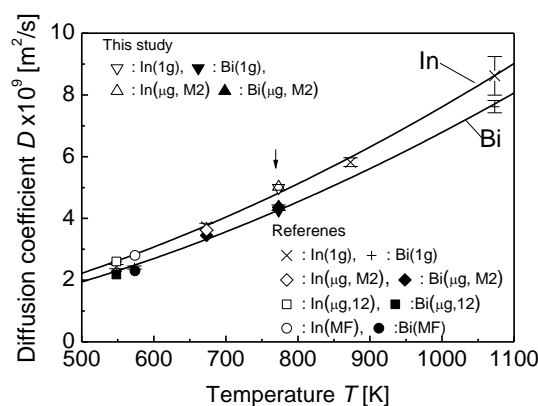


Fig. 4 Temperature dependence of the diffusion coefficient of Bi and In in Sn. The details of the reference data are shown in **Table 1**. The data in this study are shown by the arrow.

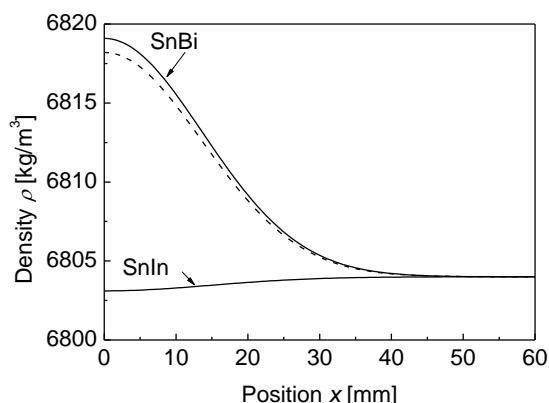


Fig. 5 Density distribution of SnIn and SnBi binary samples with the same concentrations as In(1g) and Bi(1g) in Fig.3, respectively.

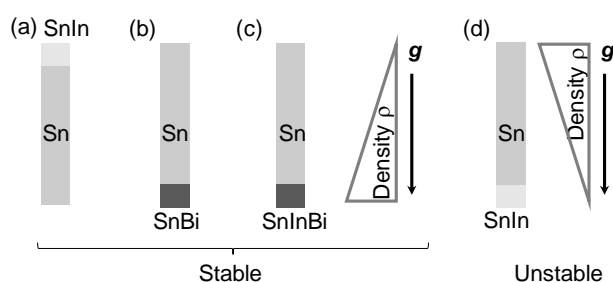


Fig. 6 Schematic illustration of the setting of the samples materials and its stability of density layering.

study. It is an essential requirement for the adding third element not to disturb the diffusion of the second element. For further research, a precise investigation of the interaction between In and Bi is required.

4. Conclusion

The diffusion coefficient of In and Bi in Sn obtained from the 1g-experiment of inter-diffusion between SnInBi and Sn agreed well with other reliable reference data. And it was confirmed that In and Bi do not disturb the diffusion of the other element each other.

Therefore, it is effective to stabilize the density layering by adding third element to the binary alloy in a diffusion couple of a pure metal and its alloy as long as the added element does not bother the diffusion of the other elements. This technique is helpful to enlarge the possible variation of diffusion sample for 1g-experiments.

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