The reference experiment for the IAO plan

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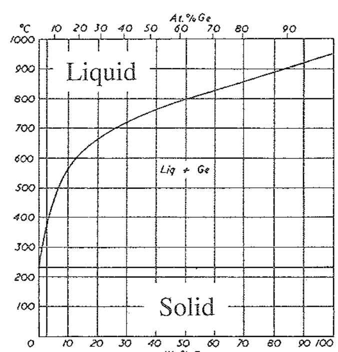
Abstract: We are studying the shear cell method for the diffusion experiment on the ground to establish the reliable experimental process of diffusion in liquids even on the ground and to present the reference data for experiment under microgravity. The adopted systems are liquid Ge-Sn and Ge-Si systems. It is not always easy to measure diffusion coefficients in these systems, because those solid-liquid coexisting regions are wide. The wide solid-liquid coexisting region causes the segregation problems on the sample preparation, and the analysis of concentration profile.

We investigated the methods for obtaining homogeneous pieces of diffusion couple sample and for analyzing accurately a concentration profile after the diffusion experiment. We performed shear cell experiments of Ge-Sn system in the temperature range, 750-1300K, as a prototype experiment. Moreover, we studied the method of the concentration analysis of the Ge-Si sample.

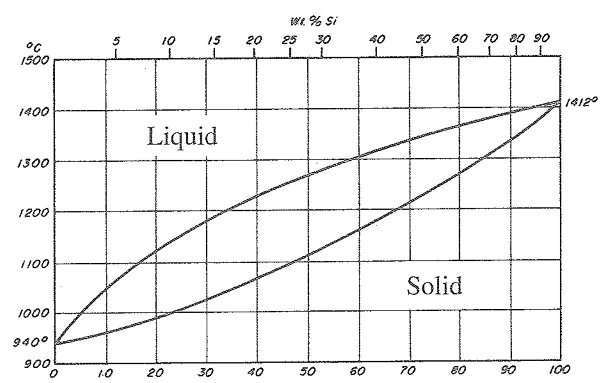
1. Introduction

We have established an experimental technique for the diffusion in liquid alloys based on the shear cell method. For this process, we adopted Au-Ag alloy as a model system [1] because of its rather complete mixing in a whole concentration range. Because Ge-Sn and Ge-Si systems have a wide solid-liquid coexisting region in their phase diagrams (Fig.1), the effect of solidification seems to be larger for these systems than for Au-Ag system on the convectional long-capillary diffusion experiments. We have a plan to perform a shear cell diffusion experiment under microgravity for liquid Ge and liquid Ge alloys containing Sn and Si.

Already, on the ground, we started the reference experiment for the microgravity one. Our purpose is to measure the impurity diffusion coefficients in a wide temperature range. Therefore, we measured the diffusion coefficient of Ge-Sn system using the shear cell method.



Ge-Sn



Ge-Si

Fig.1 Phase diagram of Ge alloys.

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In this report, we describe two parts of our experimental activity for the accomplishment of this microgravity diffusion experiment. One is the development of the preparation method of homogeneous samples for the diffusion couple of system with large segregation tendency. The other is the development of the analyzing method of the concentration of sample pieces, which were obtained by shearing, with large segregation in spite of small size.

2. Diffusion experiment for liquid Ge-Sn system

2.1 Sample preparation

We used a casting method to prepare $Ge_{0.05}Sn$ sample (ϕ1mm-rod) as a piece of a diffusion couple. Fig.2 shows the casting system. The component materials, Sn and Ge, were put in the upper part of graphite mold in a quartz tube. After the evacuation followed by the introduction of He gas, the quartz tube was heated in a ceramic furnace. At the planned experimental temperature, the alloy was cast into the graphite mold by pushing the quartz rod in the quartz tube. Then, the quartz tube was taken out from the furnace, and was immersed in water or was cooled in air as soon as possible. We changed the cooling rate after casting in order to find the condition under which Ge grains in Sn may be as small as possible and may be distributed homogeneously. For the combination of He atmosphere of 10^5 Pa and cooling in air, we got a sample, in which the small Ge particles are homogeneously distributed in Sn (Fig.3). Finally, we cut the sample into pieces of 22mm in length, and then we polished the end face of each piece.

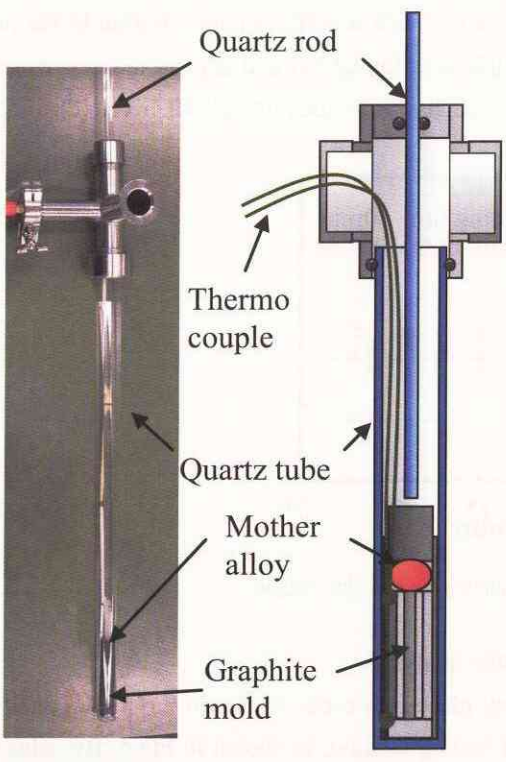


Fig.2 Casting system

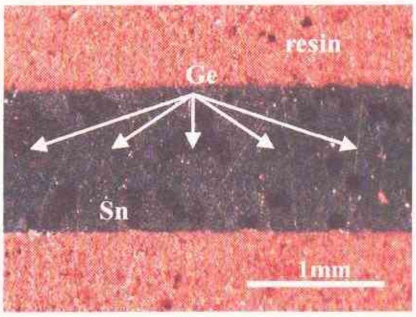
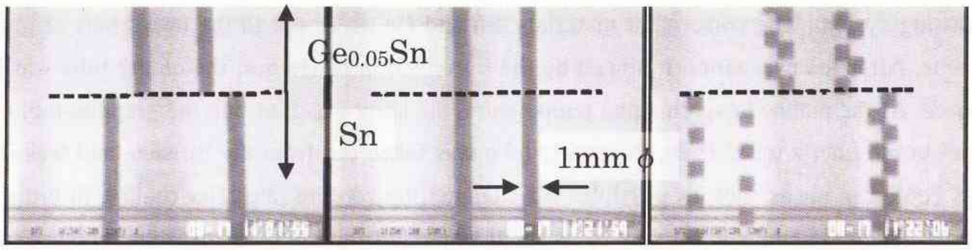


Fig.3 Section of sample (cooling rate: 9.7 K/sec.)

2.2 Shear cell experiment

Shear cell method is known as an advanced technique to measure a liquid diffusion coefficient accurately. This method is favorable for such systems as Ge-Sn system that has a serious effect of segregation on solidification. A diffusion couple is only joined at the planned experimental temperature to avoid the diffusion during heating and cooling periods, and to remove the effects of segregation on solidification by dividing the liquid diffusion column into pieces. The shear cell consists of 30-40 disks with holes, a rotation shaft, a key bar and a cartridge. To join or to divide a diffusion sample, a stepping motor rotates the rotation shaft, and the key bar controls the rotating angle. Fig.4 shows the X-ray image of the diffusion couple.



(a) Before joining (b) after joining (c) after dividing

Fig.4 X-ray images of the shear cell operation

At first, the diffusion couple was set separately in the shear cell (a). The sample was heated up to the experimental temperature, and was hold during 60-120 minutes to obtain a uniform concentration in the piece of diffusion couple samples (Fig.5). Then, the diffusion couple was joined (b) and kept at the experimental temperature during the diffusion time, and finally, the diffusion couple was divided into 30-40 pieces (c).

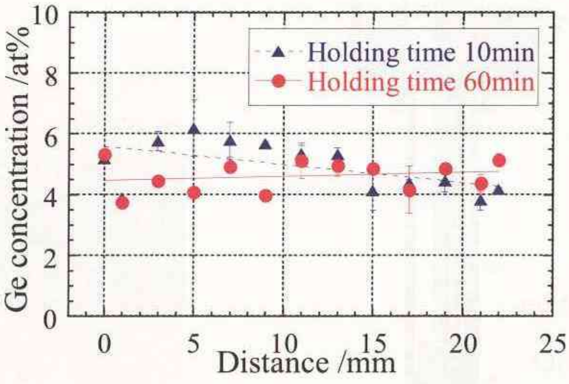


Fig 5 Ge concentration profile before joining the diffusion couple

3. Concentration profile analysis

After the experiment, the samples are divided into many pieces. In order to obtain the homogeneity of the concentration in each piece, we adopted the pressing and folding method, as shown in Fig.6. By using this method, the quick and reliable method of concentration analysis was realized by the fluorescence X-ray analysis.

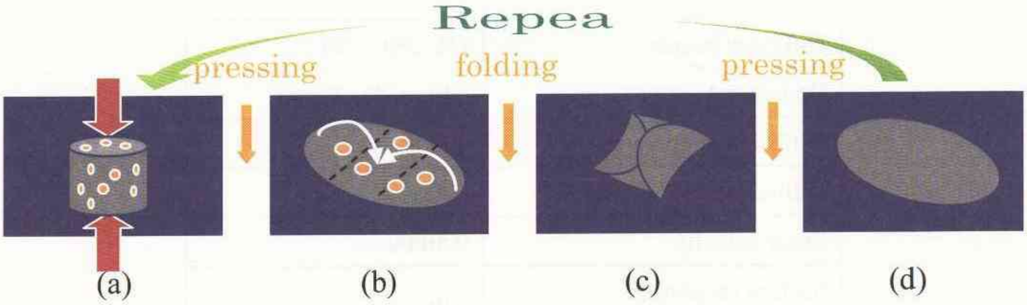


Fig.6 Pressing and folding method for the concentration analysis

The effect of the number of the pressing and folding, ΔN, is shown in Fig.7. We studied the difference of the concentration between the front face and the back face of the pressed-folded plate as a function of ΔN. It can be seen in this figure that the concentration difference becomes small for ΔN≧10. Therefore, the analysis of Ge concentration was performed after 10 times of pressing and folding.

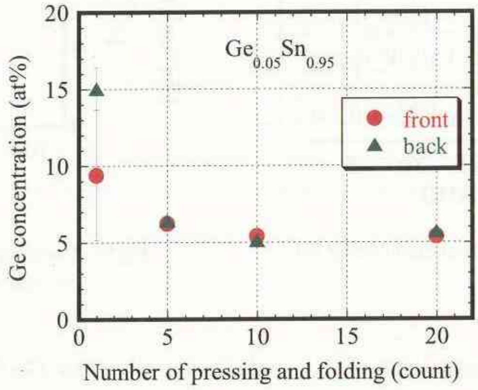


Fig.7 The dependence of Ge concentration on the number of pressing and folding.

We adopted a fluorescence X-ray analysis for the concentration analysis of divided pieces of sample. The analysis was performed 2 times both for the front face and for the back one. The advantage of this method is to measure the concentration of the sample as a whole accurately. In addition, by this method, we could analyze the concentration of many pieces of the shear cell method in our laboratory by ourselves.

4. Result of diffusion experiment of Ge in liquid Sn by the shear cell method

The experimental condition is shown in Table 1. The concentration distribution of Ge in Sn after the diffusion experiment is shown in Fig.8. This concentration distribution was in accordance with that given by Fick's second law. The diffusion coefficient was calculated to be $1.47\times10^{-8}\ m^2s^{-1}$ at 1300K for the 600-second diffusion time. The temperature dependence of the diffusion coefficient is shown in Fig.9. The diffusion coefficients become larger with the increase of the temperature. The error bar of diffusion coefficient at each temperature was estimated to be about ±10%.

Table.1 Experimental condition

Diffusion couple	$Ge_{0.05}Sn_{0.95}$-Sn
Diameter, Length	φ1mm, 22+22mm
Diffusion temperature	1300K
Diffusion time	600sec
Shear velocity	0.5mm/sec
Surface roughness of the disk (Ra)	0.9μm

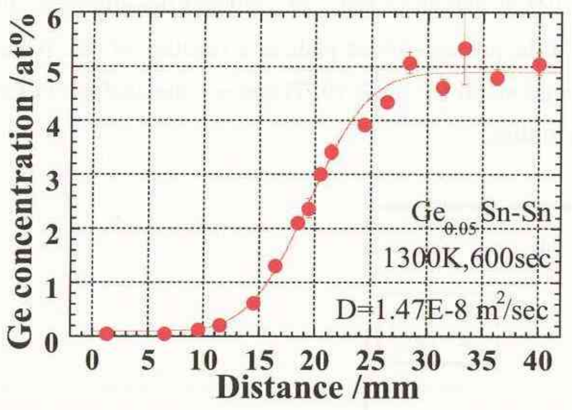


Fig.8 The concentration distribution of Ge in liquid Sn

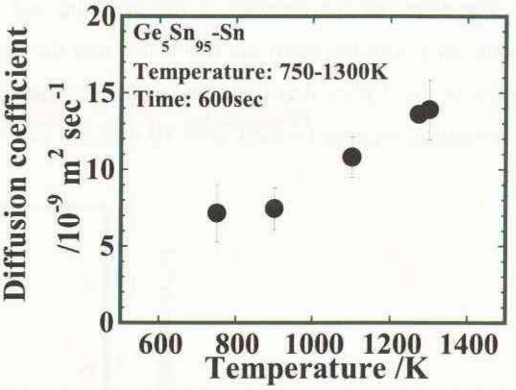
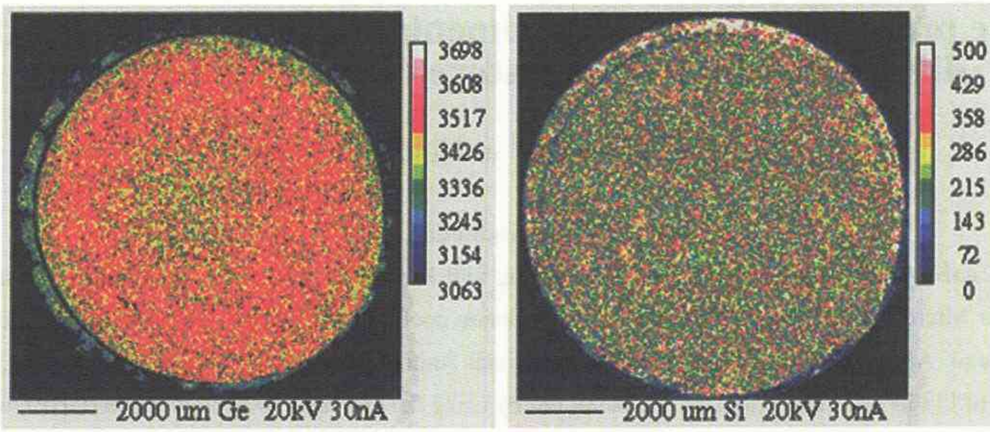


Fig.9 The temperature dependence of the diffusion coefficient

5. Investigation of the analytical method for Ge-Si alloy

We studied the method for the concentration analysis for Ge-Si alloy. It is difficult to analysis the Si concentration by using the EPMA because Ge-Si system has a wide solid-liquid coexisting region, as shown in Fig.1. In addition, the pressing and folding method cannot be used for this system because of its inherent brittleness. Prior to the concentration analysis of Ge-Si diffusion sample, we studied the method of the concentration analysis for Ge-Si system.

The analytical method considered was the fluorescence X-ray analysis, which was adopted also for the Ge-Sn sample. Therefore, as a first stage, it was examined whether the method of the preparation of homogeneous sample is present or not. The powdered sample was made with the pestle and mortar. It was formed into the pellet sample(φ10×3mm) by pressing in the mold. The concentration and it was analyzed with the use of EPMA. Fig.10 shows the obtained mapping image of distribution of Ge and Si. Fig.11 shows the Si distribution in the pellet sample. Thus, it can be concluded that it is possible to obtain the sample with almost homogeneous concentration distribution. Based on this method, the standard sample for the concentration analysis will be prepared in future.



(a) Ge (b) Si

Fig.10 The obtained mapping image of EPMA for Ge and Si

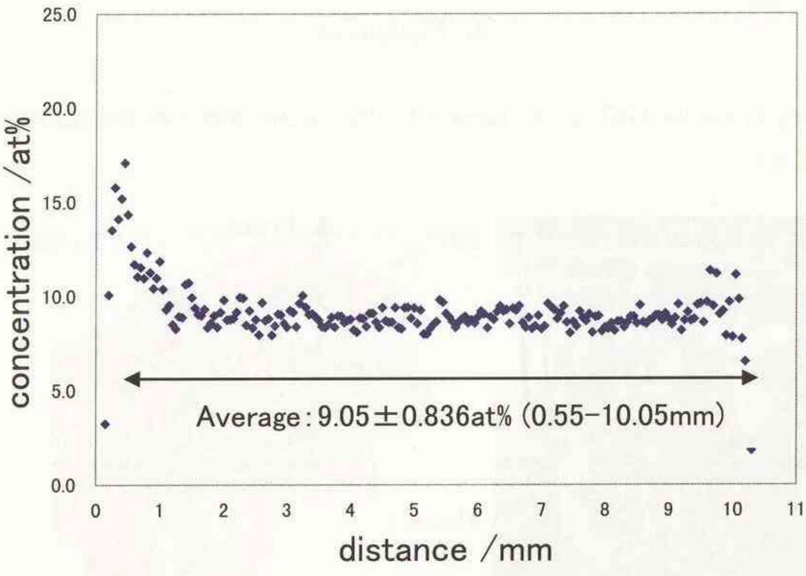


Fig.11 Si concentration in the pellet sample as a function of the distance from the surface along the diameter

6. Conclusions

Detailed investigations were performed for the condition of the diffusion experiments for liquid Sn containing Ge. We investigated the methods of the preparation and the concentration analysis for diffusion couple samples with a large segregation tendency. In addition, we performed shear cell experiments for liquid $Ge_{0.05}Sn$-Sn diffusion couple, and could measure the liquid diffusion coefficient of Ge in liquid Sn.

We studied the methods of the preparation of the homogeneous sample also for Ge-Si alloy. Moreover, we obtained the promising method for making the standard sample for the concentration analysis.

References

1. M.Uchida, Y.Watanabe, "Diffusion measurements of Au in liquid Ag using high-precision shear cell method with *in-situ* X-ray observation system", Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity Annual Report 2001, pp.119-122