

The Study of Diffusion in Complex Metallic Liquids With High Melting Points —The Study of Self-Diffusion and Mutual-Diffusion of Liquid Cu–Ag Alloys—

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Abstract

The experiments of self and mutual diffusion coefficient measurements for liquid Cu–Ag alloys were performed under the microgravity of TR–IA–7 rocket with the use of diffusion couple method and shear cell technique. Measured temperatures were 1433, 1483 and 1533 K. The shear cell containing ten diffusion couples was developed. It worked successfully to create the liquid columns of all 30 diffusion couples and cutting of these liquid columns into divided pieces without any troubles. The obtained self diffusion coefficients for pure Cu and pure Ag were slightly spoiled by the effect of fluid motion. These data were compared with theoretically calculated values based on the hard sphere model, in which the hard sphere diameters are calculated from the thermodynamic variational theory. The present mutual diffusion data in liquid Cu–Ag alloys were also spoiled by the effect of fluid motion. Discussion is given to the cause of this fluid motion and it is concluded that careful attentions must be paid for the perfect performance of microgravity diffusion experiments particularly in the case of liquid mixtures.

1. Introduction

Still now the understanding of liquid states has not so advanced compared with gas and solid states. Atoms or molecules are moving almost independently in gases except for the moment of collision between them. Therefore, their physicochemical phenomena are explained essentially by rather simple probability theories. On the other hand, atoms in solids interact strongly each other. As a result, they move cooperatively and their arrangement is periodic on lattices. The physicochemical phenomena are explained

rigorously based on this periodic atomic configurations. Liquid states are intermediate between solid and gas states. As for density, liquids are rather similar to solids and in fact the volume change on melting is only a few at.%. However, on melting the fluidity increases drastically and rather akin to gases. Atoms or molecules in liquids move continuously in space with strong inter-atomic (or -molecular) interactions and no more are situated on the periodic lattice. The position of atom is only represented by the probability of finding them in the volume element around position r . Therefore, physicochemical properties should be represent-

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ed by the complex probability theories with strong correlations. This point makes the understanding of physicochemical properties of liquids very difficult particularly in the case of dynamic properties such as diffusion, viscosity, etc. In addition to this theoretical challenging difficulty, the study of diffusion of liquids with high melting points contains experimental difficulty. In the measurements of diffusion coefficient in liquids with high melting points on the ground, the thermal convection is included inevitably in the course of the measurement particularly due to heating and cooling processes in addition to holding period. Microgravity, under which no convection is present in liquids, is considered to be an ideal circumstance for the measurements of diffusion coefficients. It has been well recognized that the exact knowledge of diffusion in the melt is essential to establish the optimum production processes of many important materials from the melts, such as crystal growth processes. In addition, liquids in many such processes are multi-component liquids with complex structures. Therefore it is very interesting to study the diffusion of liquids with complex structures with the use of microgravity circumstances.

The purpose of this paper is to report the outline of TR-IA No. 7 rocket experiment for the measurements of the self and mutual diffusion coefficients of liquid binary alloy, liquid Cu-Ag alloys, with the use of shear cell technique.

2. Experimental

The self and mutual diffusion coefficients for liquid Cu-Ag alloys were measured by the diffusion couple method with the combination of shear cell technique. The shear cell adopted in this experiment is shown in Fig. 1. In the case of self diffusion experiment the sample piece in one side of couple was made of stable isotopes, ^{65}Cu and ^{107}Ag . The sample piece in the other side was made of natural metals, Cu and Ag. In the case of mutual diffusion experiment in liquid alloys, the diffusion couple was constructed in the combination of two pieces of alloy sample, between which the concentration difference was taken to be 10 at.%. In addition to this configuration, the diffusion couple was made between pure Cu and pure Ag. Figure 2 shows the combination of sample pieces in the diffu-

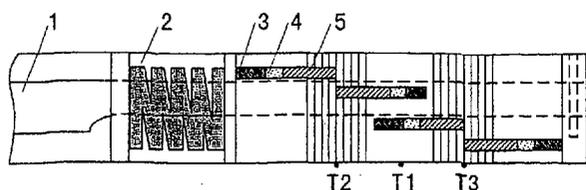


Fig. 1 Schematic drawing of the shear cell; 1: rotary axis; 2: carbon spring; 3: W spring; 4: lid; 5: sample for diffusion couple; T1: thermocouple (temperature control point); T2 and T3: thermocouples.

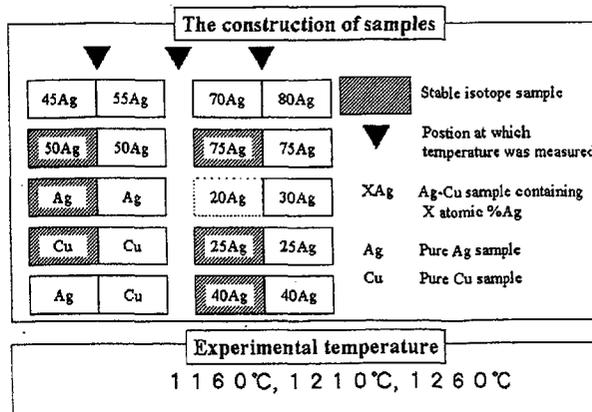


Fig. 2 Combination of samples for diffusion couples.

sion couples adopted in this experiment.

The samples of diffusion couples for self diffusion measurements were made by casting the melts of weighed amount of ^{65}Cu and ^{107}Ag into the graphite mold. Similarly the samples for the mutual diffusion coefficients were made from natural Cu and Ag. The dimension of each sample piece was adjusted to be 10 mm length and 1.5 mm diameter. The centerless grinder was employed for the polish of side faces and both end surfaces were polished by the grinder for optical fibers. Liquid samples were pressed by the W spring in order to avoid the Marangoni convection, which was induced by the formation of free surface or void formation due to the volume change throughout the course of experiments.

Shear cell adopted in this experiment was made by piling up 19 boron nitride (BN) discs with five holes. In this shear cell ten diffusion couples were contained, that is, a bundle of 5 diffusion couples were placed in one side of crucible and another bundle of 5 diffusion couples were in the other side in a series arrangement, as shown in Figs. 1 and 2. At first respective sample pieces in each diffusion couple were positioned separately and after the establishment of microgravity at the experimental temperature they were joined each other to create a diffusion couple in the liquid state. At the end of diffusion period liquid columns of diffusion couple were divided into 10 small pieces by the rotation procedure.

In this experiment three shear cells were employed to perform diffusion experiments at three different temperatures. These shear cells were contained under He gas atmosphere in the Ta cell cartridges, which were contained respectively in three independent small furnaces in the multi purpose furnace (MPS) respectively. These three furnaces were kept at temperatures, 1433, 1483 and 1533 K.

The shear cell employed in this experiment is shown in Photo 1. The concentration of profile of isotope was analyzed by the Induction Coupled Plasma-Mass

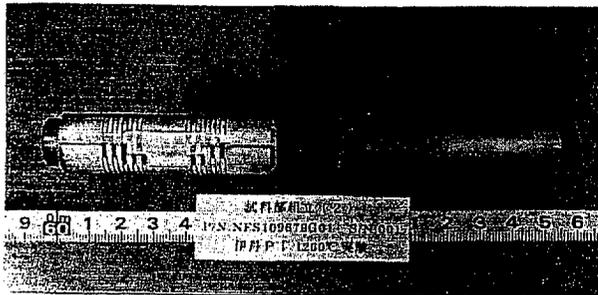


Photo. 1 Outlook of the shear cell before 1533 K experiment.

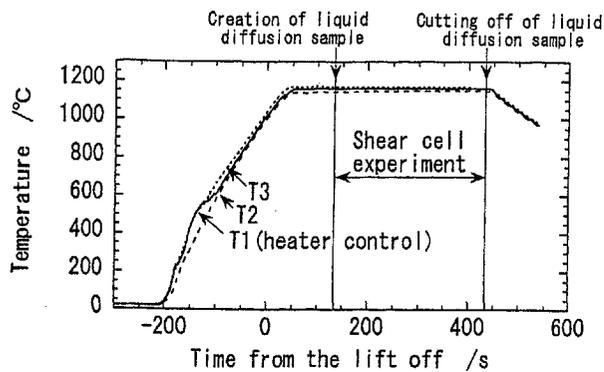


Fig. 3 Example of the temperature variation of sample.

Spectroscopy (ICP-MS) and that of alloys was analyzed by the Induction Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

3. Results

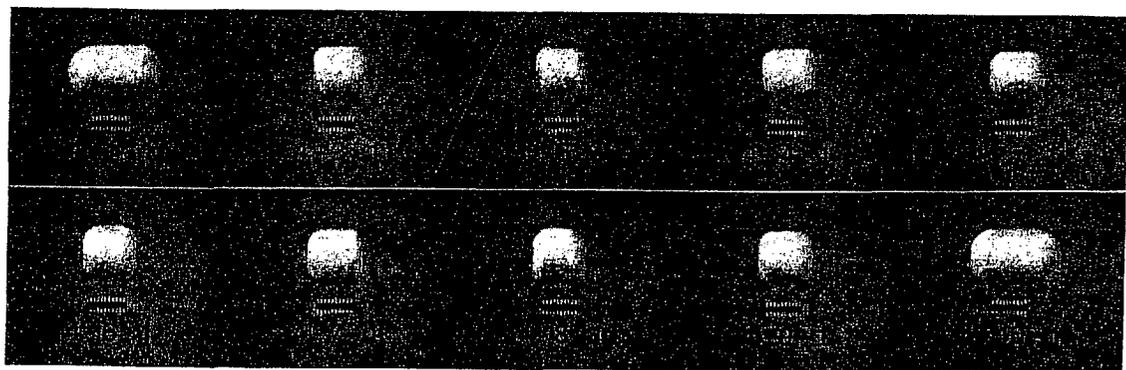
The temperature change during the course of rocket experiment is shown in Fig. 3. As shown in this figure, during the microgravity period, liquid diffusion couples were created successfully. At the end of diffusion period under microgravity the liquid samples were divided also successfully into 10 small pieces. Photo. 2 shows the outlook of divided samples.

Typical examples of concentration profiles are shown in Figs. 4 and 5.

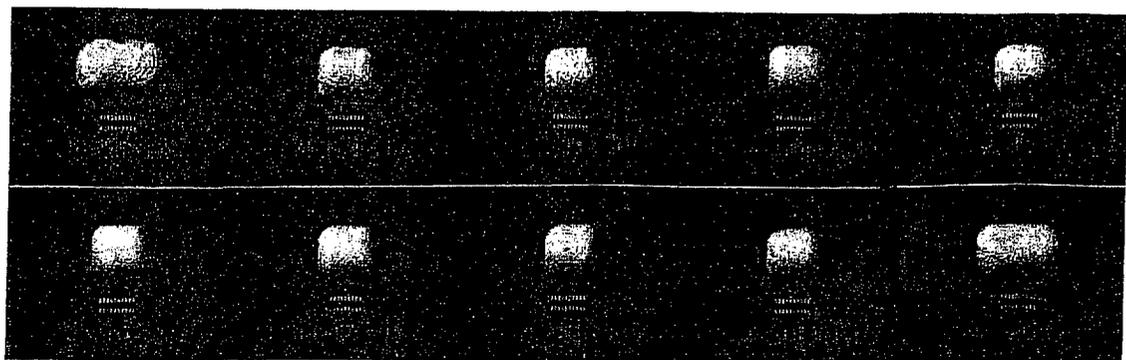
4. Discussion and Conclusion

4.1 Determination of Experimental Condition

As described above, the mechanism of W spring was adopted to press the samples throughout the course of experiments. For this purpose it is necessary to select cell materials with less wettability with liquid samples. Therefore the contact angle was measured between liquid Cu-Ag alloys and BN. As a typical example, the result of contact angle measurement is shown in Fig. 6 for a liquid of 50 at.%Cu-50 at.%Ag alloy. As can be seen in Fig. 6, the contact angle is kept to be over 158 degrees even at 1350 K. It is concluded that BN is a good material for cell materials with less

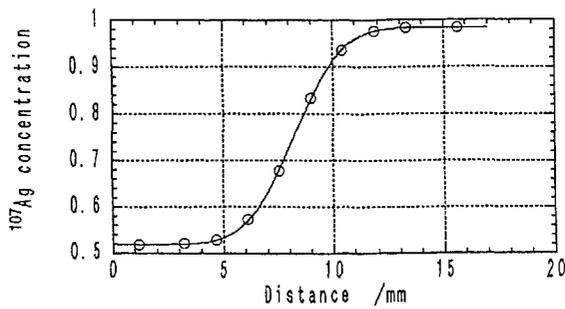


1-1~1-10

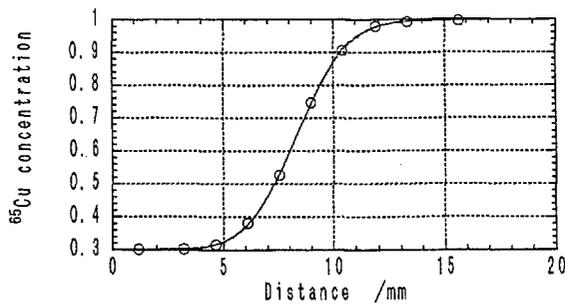


1-11~1-20

Photo. 2 Examples of divided samples.



(a) ¹⁰⁷Ag



(b) ⁶⁵Cu

Fig. 4 Concentration profiles of ¹⁰⁷Ag (a) and ⁶⁵Cu (b) in pure Ag and pure Cu respectively.

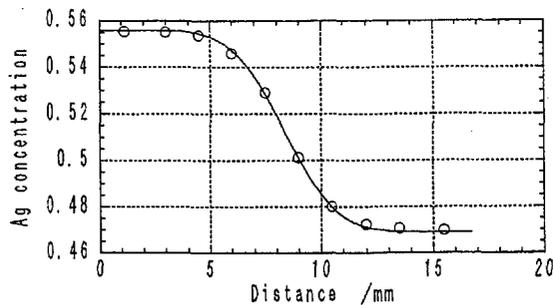


Fig. 5 Concentration profile of Ag after the diffusion couple experiment at 1433 K of 55 at.%Cu-45 at.%Ag-45 at.%Cu-55 at.%Ag.

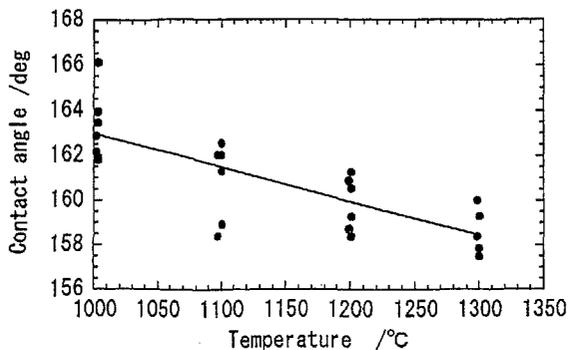


Fig. 6 Example of the measured contact angle between liquid 50 at.%Cu-50 at.%Ag alloy and boron nitride (BN).

wettability with liquid Cu-Ag alloys. In this experiment the upper temperature range was limited to be 1533 K because of the evaporation loss of silver. This situation can be clearly shown from the experimental result of TG-DTA, shown in Fig. 7.

4.2 Determination of Diffusion Coefficients

The solution of Fick's second law¹⁾ for the diffusion couple method is written as follows:

$$C(x, t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2} \operatorname{erf} \left[\frac{x-h}{2\sqrt{D^*t}} \right] \quad (1)$$

In this equation $C(x, t)$ is the concentration at position x and time t and $\operatorname{erf}[u]$ is the error function, defined as follows:

$$\operatorname{erf}[u] = \frac{2}{\sqrt{\pi}} \int_0^u \exp(-z^2) dz \quad (2)$$

The self and mutual diffusion coefficients were obtained by fitting the analytical solution, Eqn. (1), to observed concentration profiles.

4.3 Discussion for the results of self diffusion coefficients of pure liquid Cu and pure liquid Ag

Obtained self diffusion coefficients for liquid Cu and Ag are shown in Fig. 8. In the case of liquid Cu, the temperature dependence of self diffusion coefficient is larger compared with the experimental data on the ground²⁾. On the other hand, the self diffusion coefficient of liquid Ag is larger than the ground literature data^{3,4)} in the temperature range studied here. In the previous microgravity experiment, for example in the MSL-1 project⁵⁾, the self diffusion coefficient and its temperature coefficient of liquid Sn under microgravity are smaller than the ground data. Therefore, unfortunately there is a possibility that the present experimental data were slightly spoiled by the fluid motion. There are two special situations for the present experimental conditions. One is the inhomogeneous temperature distribution of furnace and the other is the rather weak strength of W spring. The former situation was derived from the fact that too

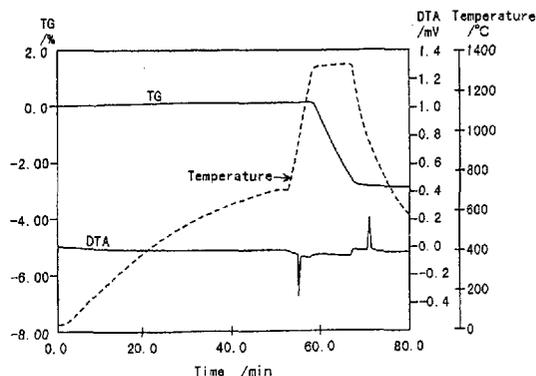


Fig. 7 TG-DTA chart for pure Ag.

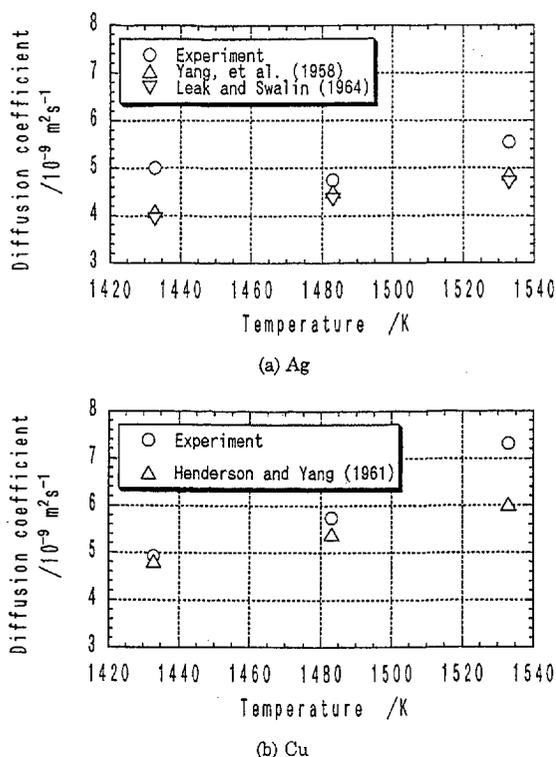


Fig. 8 Temperature dependence of measured self diffusion coefficients for pure liquid Ag and pure liquid Cu.

many samples were installed to accomplish the purpose of the experiment in small furnaces in the MPF of TR-IA, that is 2 bundles with five cells respectively in a series connection, as shown in Fig. 2. Therefore, samples were situated out of homogeneous temperature range. The temperature difference along one sample was 20~40 K. The other situation was derived from the limitation of small diameter of crucible (1.5 mm), into which the W spring with rather weak strength is forced to be selected during the limited period of experimental preparation. The criterion of the range of force applied by spring was already given elsewhere⁶⁾. The length of shrinkage of spring was set to be 4~5 mm. The spring constant adopted in this experiment was 0.85~1.3 g/mm. Three times of these values for spring constants at experimental temperatures are found to be required to avoid completely the free surface of liquid samples. The appropriate choice of spring is very important for the diffusion experiments under microgravity. Fundamentally these problems described above can be removed in future space experiments. In future these points must be taken care of.

4.4 Hard Sphere Model

The self diffusion coefficient was theoretically calculated based on the hard sphere model⁷⁾. Based on this theory the diffusion coefficient is given as follows:

$$D_S^{\text{HS}} = C_{\text{BS}} D_{\text{ENS}} \quad (3)$$

In this equation D_{ENS} is the Enskog formula for the self-diffusion of dense gas, which includes the contribution of binary collisions. C_{BS} represents the effect of cage effects of surrounding atoms in dense liquids against the diffusing particle. Explicit formulae are written as follows:

$$D_{\text{ENS}} = \frac{3}{8} \sigma \left(\frac{k_B T}{\pi M} \right)^{1/2} \left(\frac{6y g_{\text{HS}}(\sigma)}{\pi} \right)^{-1} \quad (4)$$

$$C_{\text{BS}} = \frac{(1-y/2)}{(1-y)^3} \left(1 - \frac{6y}{1.09\pi} \right) \times \left[1 + \left(\frac{6y}{\pi} \right)^2 \left\{ 0.4 - 0.83 \left(\frac{6y}{\pi} \right)^2 \right\} \right] \quad (5)$$

In these equations M is the atomic mass; k_B is the Boltzmann constant; $g_{\text{HS}}(\sigma)$ is the radial distribution function at the hard sphere contact; y is the packing fraction.

4.5 Thermodynamic Variational Method

In this paper the hard sphere diameter, σ , was determined from a purely theoretical point of view by using the thermodynamic variational method⁸⁾ based on the Gibbs-Bogoliubov inequality for the Helmholtz free energy.

$$F \leq F^V = \frac{3}{2} k_B T - T S_{\text{HS}} + N u_g - T S_{el} + \frac{1}{2} n N \int g_{\text{HS}}(r; \sigma) \phi(r; \sigma) d^3 r \quad (6)$$

In this equation S_{HS} is the entropy of the hard sphere system; u_g is the energy of electron gas, S_{el} is the entropy of electron gas, $\phi(r; \sigma)$ is the interionic potential; $g_{\text{HS}}(r; \sigma)$ is the radial distribution function of the hard sphere system. According to this inequality, σ can be determined so that the right hand side of Eqn. (6) may be as small as possible.

Interionic potential was calculated by the adoption of empty core approximation. Adopted core diameters are 0.099 nm for Ag and 0.093 nm for Cu⁹⁾. The determined σ from the purely theoretical point of view is 0.223 nm for Ag and 0.250 nm for Cu. Up to date, the applications of thermodynamic variational method have been only limited to the prediction of thermodynamic properties of liquid metals and there are almost no applications to atomic transport properties. In this situation present calculated self diffusion coefficients from purely theoretical point of view described above are rather close to the present experimental values, as shown in Fig. 9. This indicates that the hard sphere model with the proper choice of hard sphere diameters may be fundamentally a good starting point for complex liquids and liquid alloys.

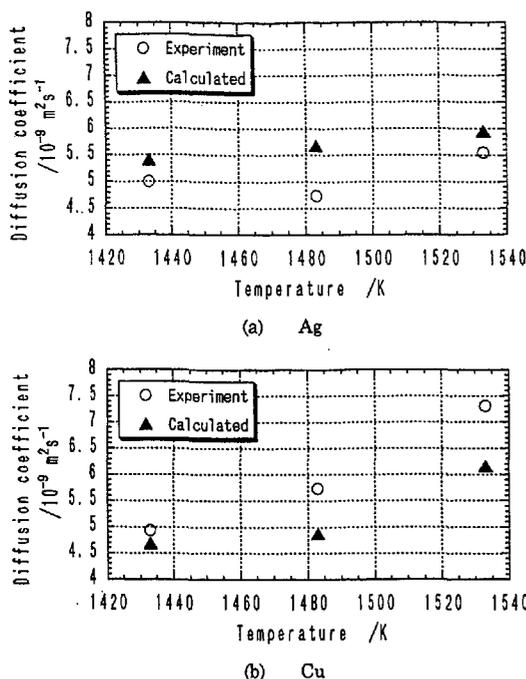


Fig. 9 Comparison of self diffusion coefficient between experimental values and calculated values for pure liquid Ag and pure liquid Cu.

4.6 Discussion for the Cause of Fluid Motion for Liquid Alloys

Experiments for mutual diffusion coefficients of liquid Cu–Ag alloys were also spoiled by the fluid motion. This tendency was particularly large for the diffusion couple composed of pure Ag and pure Cu. This situation may be also caused by the larger temperature inhomogeneity along samples and the weak strength of W spring adopted, as described above. In addition to these, there is a possibility that the fluid motion might be induced by the concentration difference. In fact, as described above, the concentration profile of diffusion couple between pure Cu and pure Ag was considerably different from concentration profile given in Eqn. (1). This anomalous concentration profile was qualitatively reproduced in the fluid dynamical simulation by the assumption of existence of free

surface on the side wall of the liquid sample. In the case of liquid Cu–Ag alloys, the concentration dependence and the temperature dependence of surface tension are small around 50 at%Cu–50 at%Ag^{10,11}) and a mutual diffusion coefficient obtained for this concentration is smaller compared with those of other compositions. Still now we are now analyzing the experimental data for self and mutual diffusion coefficients of liquid Cu–Ag alloys. These points will be discussed in detail elsewhere. It is found in this study that the attentions to many factors, such as the temperature homogeneity, strength of the spring, optimized concentration difference for diffusion couples, etc., should be paid for the perfect performance of microgravity diffusion experiments. It is fundamentally possible to resolve all these points and microgravity itself is surely an ideal circumstance for measurements of diffusion for melts with high melting point.

Acknowledgement

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