The Microgravity Diffusion Experiment for Highly Reactive Liquid Metals

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Abstract

The space experiments are generally performed under extremely restricted conditions and have been done for chemically rather mild materials. Therefore, it is important to develop experimental techniques for highly reactive but important materials. In this study the experimental technique was developed for the diffusion of highly reactive liquid lithium under microgravity by the combination of the glove box system and the stainless steel ampoule system. This technique was successfully applied to the experimental chance of TR-IA No.6 rocket in Sept. in 1997. Good concentration profiles were obtained for the recovered lithium samples without being suffered from the contamination due to oxygen, nitrogen and water. Obtained diffusion coefficient of ^{6}Li in liquid ^{7}Li is larger than that of ^{7}Li in liquid ^{6}Li though experimental improvements are required for the further rigid conclusion. Therefore, the isotope effects in liquids is still now desired to be studied experimentally and theoretically.

1. Introduction

The microgravity has very fascinating characters for the fundamental science, for examples, no gravity, no convection in liquids, large scale vacuum, etc[1]. It is very promising to employ it as an experimental circumstance for experiments which tend to be suffered from the convection on the ground. The experiment of diffusion in liquids is one of such experiments. The diffuison experiments on the ground have been spoiled by the convection due to the temperature gradient and the concentration gradient in liquids, which are present inevitably and are applied on purpose respectively. The validity of microgravity circumstance with no convection for diffusion experiments in liquids was clarified by the pioneering experimental study by Frohberg et al[2]. They demonstrated many important aspects; the obtained diffusion coefficient is smaller than the literature data on the ground particularly at higher temperatures than the melting temperature, obtained self-diffusion coefficient obeys a T^2 law, even the isotope effect can be detected for liquid Sn, etc. Some of present authors also demonstrated the validity of microgravity for diffusion in the high temperature melts by performing the measurements of self-diffusion coefficient of liquid Sn in the extremely wide temperature range[3]. Up to date the diffusion experiments under microgravity have been performed only for liquids with mild chemical properties. Main reason for it is that usually the space experiment is performed after long time since the sample is delivered to the space organization. In addition the complete safety must be kept for the space circumstances in which the acticity of human being are performed. Chemically stable materials have been more preferred to than chemically reactive materials. However, there are many important materials with a strong chemical reactivity, such as alkali metals. Therefore it is very important to develop the techniques by which we can perform safely the microgravity experiments for very reactive materials. As an example of the performance of the diffusion experiment under microgravity for such reactive materials, the self-diffusion experiment under microgravity was performed for liquid Li, which is chemically reactive and for which the isotope effect can be expected because of relatively light atomic mass. The purpose of this paper is to report the outline of microgravity experiment for the diffusion of liquid lithium due to TR-IA No.6 rocket particularly on the emphasis on the sample treatment and the construction of sample containers.

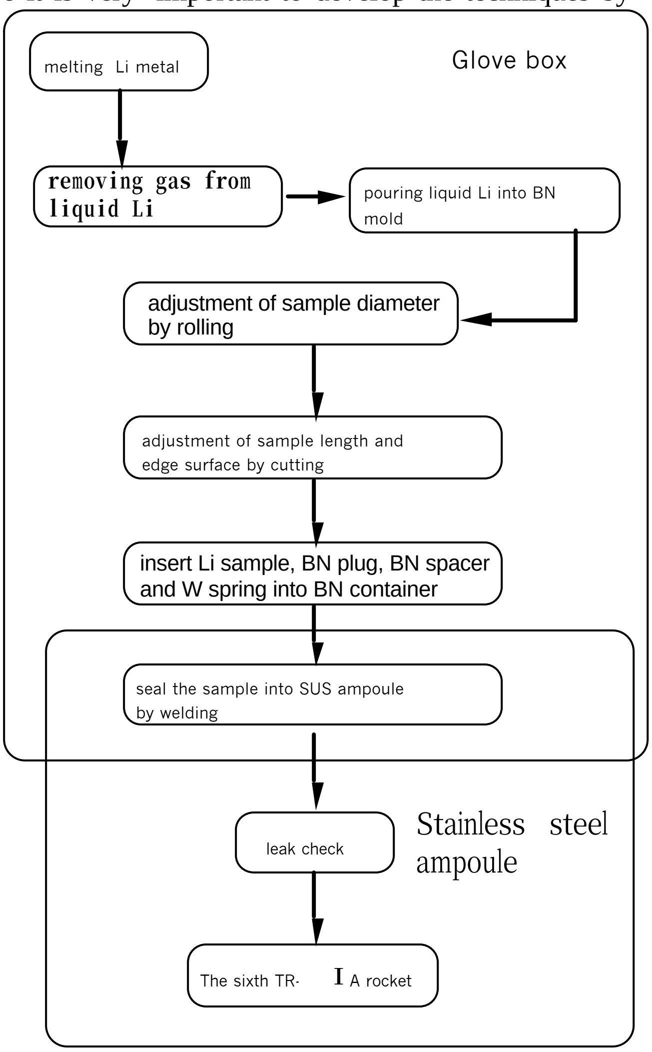

Fig.1. The flow chart of preparation of the samples for the sixth TR-IA rocket experiment.

2.Experimental

The flow chart of sample preparation is shown in Figure 1. As is well known, lithium metal is very reactive to oxygen, nitrogen and water. Therefore, Li samples must be kept under a completely inert atmosphere from the stage of sample preparation to that of microgravity experiment. For the realization of this, the system composed of glove box and stainless steel ampoule was adopted. The sample preparation was performed in a glove box (VAC Co. Ltd), in which oxygen and water contents in atmosphere were kept to be below 1 ppm. Nitrogen was removed by a home made N-getter. The lithium metal was melted, dissolved gases in liquid lithium were removed under vacuo, melted lithium metals were solidified into the rod shape in a BN mold, the sample shape was adjusted to be desired shape and size and shape. The reactive Li sample was contained in a BN container together with the BN plug(separator lid) and stainless steel spring, by which a slight pressure was applied to the liquid sample during the course of experiment in order to prevent the void or free surface formation in the liquid sample. The construction of cell assembly is shown in Figure 2. As shown in this figure three samples were inserted into one BN container to increase the experimental chances. This BN container was contained in the stainless steel ampoule under Ar atmosphere. Finally, this

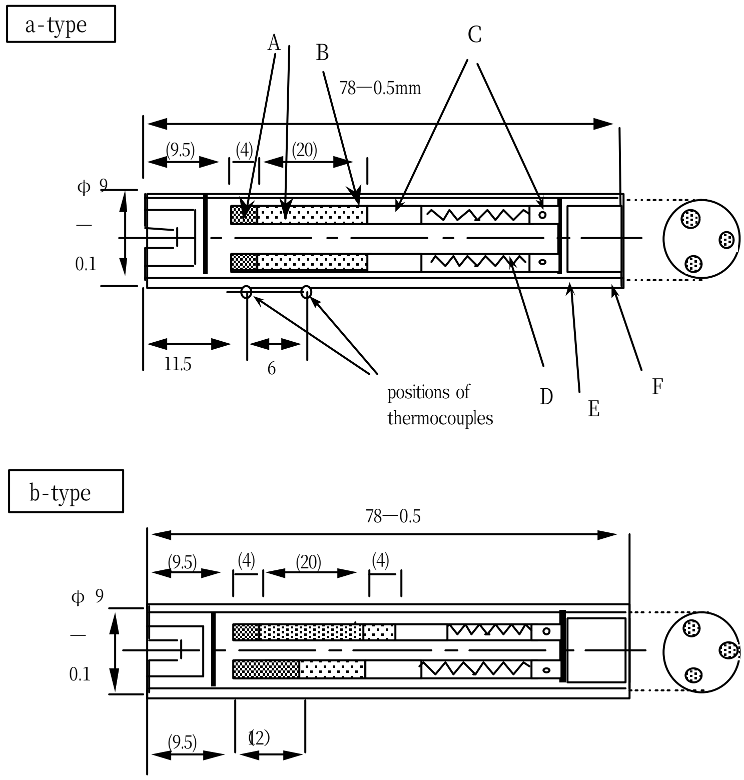

Fig.2. Cell configurations; A:Sample ; B:BN container ; C:BN plug D:W spring E:Cushion material F:SUS ampoule.

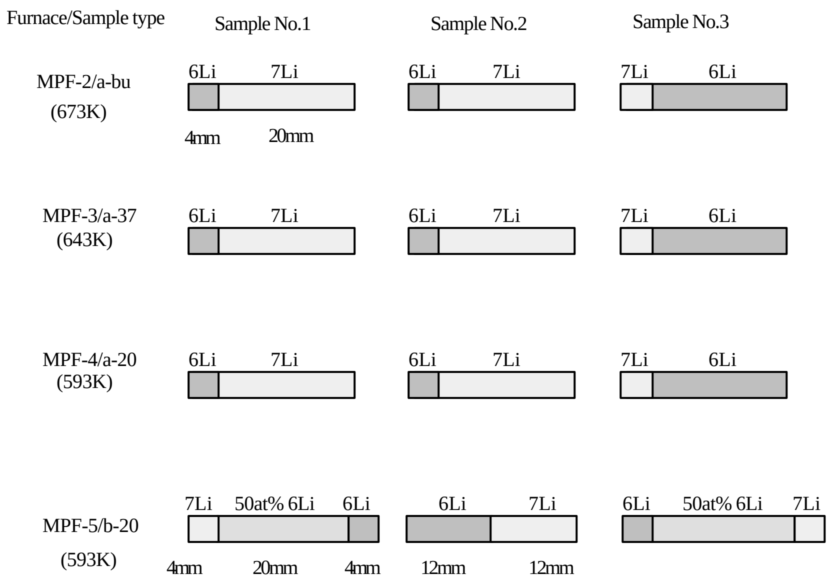

Fig.3. The configuration of the samples for the sixth of TR-IA rocket experiment.

stainless steel ampoule was closed by welding in the glove box to prevent samples from the contamination due to oxygen, nitrogen and water until the performance of microgravity experiment.

Microgravity experiment was performed in the chance of TR-IA No.6(Sept. in 1997). The experiment of long capillary method(Type a in Figure 2) was performed at three temperatures, 593K, 643K and 673K. The diffusion couple experiment(Type b in Figure 2) was performed at 593K. These experiments were performed by using four independent furnaces in the Multi-purpose Furnace(MPF) of TR-IA rocket. The construction of diffusion sample is schematically shown in Figure 3. The lithium sample employed is shown in Table 1. The concentration profile of isotope was analyzed by the SIMS analysis.

3. Results and Discussion

Table 1. The isotopic abundance of Li

	^{7}Li	^{6}Li
Natural Li	92.5 atom%	7.5 atom%
^{7}Li	99.0 atom%	1.0 atom%
^{6}Li	4.38 atom%	95.62 atom%

As is well known, in the case of liquid diffusion experiment under microgravity, the occurrence of Marangoni convection must be avoided completely. Therefore in this experiment a slight pressure was applied to the liquid sample throughout the course of experiment in terms of tungsten spring. Otherwise the volume change on melting, solidification, thermal expansion and thermal shrinkage in the experimental course results in the formation of void or free surface formation, which inevitably causes the Marangoni convection. If the strength of spring is too strong, the liquid sample leaks out from the gap between the inner wall of BN container and BN-plug(see Figure 2). If it is too weak, it is difficult to contain the sample in the BN container without any void, for example, in the corner part of bottom. To find the optimum strength of spring[4], it is easy in the case of container materials with poor wettability to liquid samples. Therefore, the measurements of contact angle were performed between many(13) refractory materials and liquid lithium. Unfortunately liquid lithium has large wettability to most of refractory materials. In most cases measured contact angles were below 90 degrees. Only candidate was boron nitride(BN). Measured contact

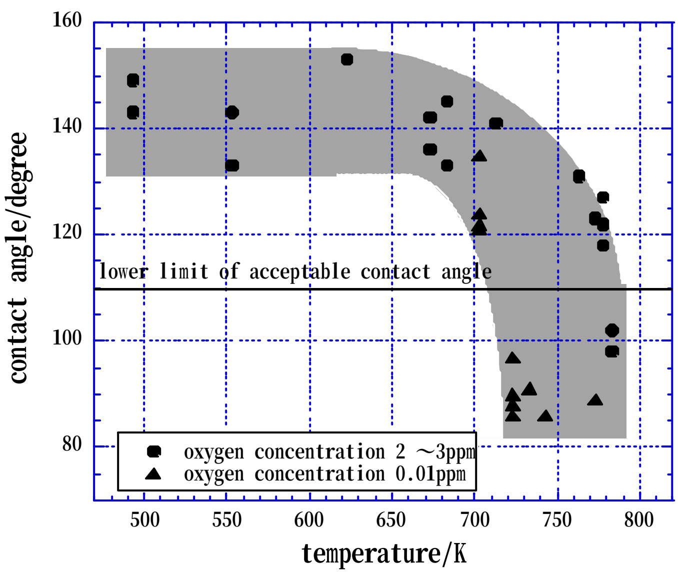

Fig 4. The contact angle of liquid lithium against boron nitride.

angle of liquid Li on the BN plate is shown in Figure 4. The contact angle was kept to be over 130 degrees up to 690K. Over this temperature it decreases rapidly. Therefore, BN was adopted as the container material and experimental temperatures were determined by considering this result.

The microgravity experiment was successfully performed; the stability of temperature is ±3K; the holding times are 170~224 s. All samples showed a metallic color on the inspection after the microgravity experiment. The typical examples of profile of ^{6}Li and ^{7}Li are shown in Figure 5.

From these concentration profiles, the diffusion coefficient was calculated based on the flow chart, shown in Figure 6. In this analysis the contribution of heating and cooling processes to the diffusion was taken into account on the assumption that the concentration profile changes only at temperature over the melting temperature. The diffusion coefficient was calculated self-consistently[3] between two equations, the solution $n(x,t_{eff})$ of Fick's second law for the long capillary with a finite tracer depth[4] and the effective time, t_{eff} . It is to be noted that it is necessary for the calculation of t_{eff} to know the diffusion coefficient to be determined. The explicit forms for these are given in Figure 6.

The obtained diffusion coefficients of ^{6}Li in liquid ^{7}Li and ^{7}Li in liquid ^{6}Li are shown in figure 7. The lighter ^{6}Li diffuses faster than the heavier ^{7}Li. This ratio is 1.3 at the largest in the present experiment. However, further improvements should be added for experimental conditions, such as the longer holding time for diffusion, the structure of containers, etc.

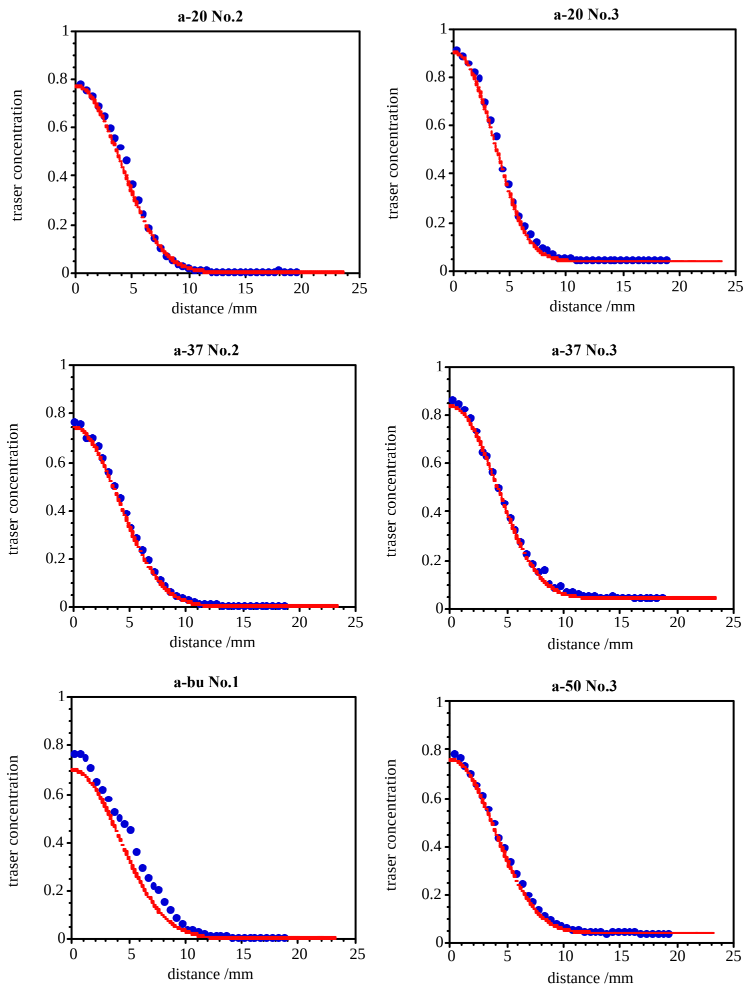

Fig.5 The examples of concentration profiles for the sixth TR-IA rocket experiment

Finally the theoretical analysis of self-diffusion coefficient of liquid Li was performed based on the hard sphere model of liquids[5], in which only the hard sphere diameter, σ, represents the role of inter-atomic potentials. For the calculation of the hard sphere diameter, at first, an empirical analysis was tried. In the empirical calculations, the packing fraction, $y(=\pi/(6n\sigma^3)$; n: number density), is given as 0.472 at the melting temperature and the empirical temperature dependence was assumed. Calculations give a fair agreement with experiment though the temperature dependence becomes a little smaller compared with experiment. Then more rigorous analyses were tried. That is, two thermodynamic liquid theories[6] were applied, one is the thermodynamic variational theory due to the Gibbs-Bogoliubov(GB) inequality and the other is the thermodynamic perturbation theory developed by Weeks, Chandler and Anderson(WCA). In these treatments interionic potentials are calculated from the point of view of electron theory of metals[7]. Calculated results are also in fair agreement particularly in the case of WCA. However, the temperature coefficient was not reproduced. In addition, from these analyses, only the square root of the ratio, 7/6(=1.17), which can be predicted from only the contribution of kinetic energy in the kinetic theory of gases and liquids[7], were obtained for the isotope effect for self-diffusion coefficient. Still now further studies must be performed for the isotope effects in liquids experimentally and theoretically.

4. Conclusion

In this article, the technique for performing the microgravity diffusion experiment for very reactive materials were described. The

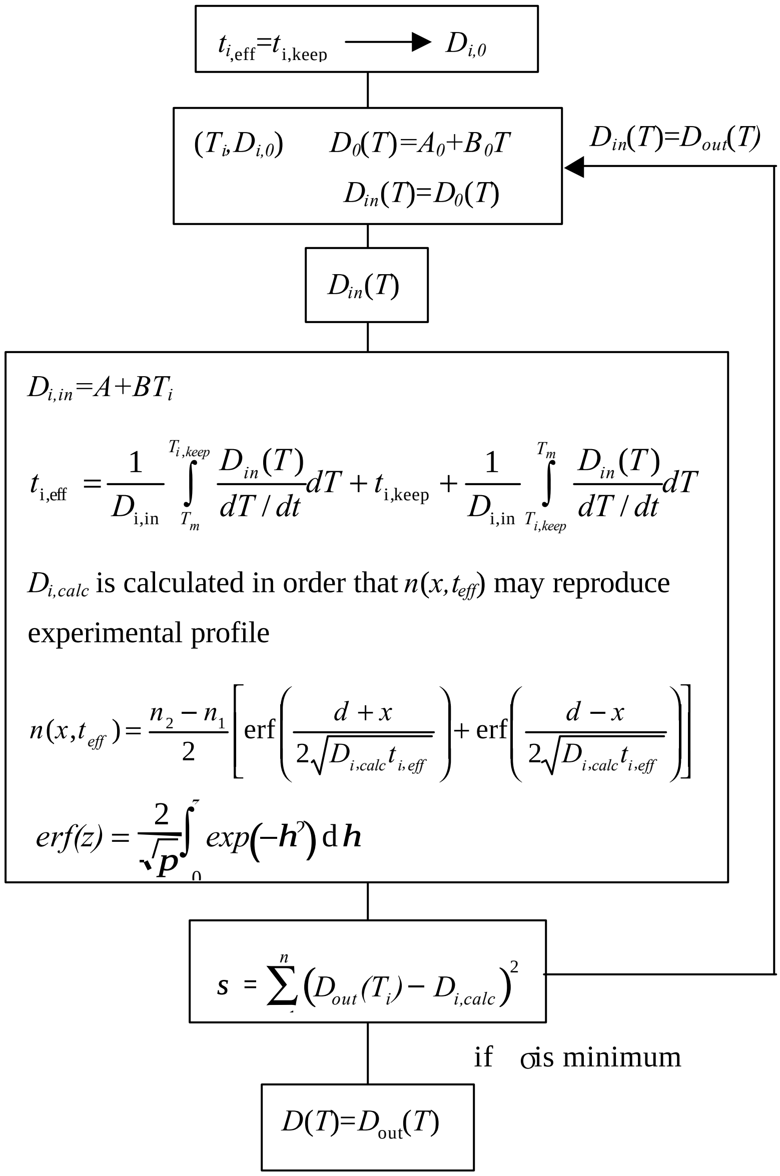

Fig.6 The flowchart of the iteration procedure for the determination of the temperature dependence of diffusion coefficient

combination of the glove box system and the stainless steel ampoule system with welding sealing enabled us to perform microgravity experiments completely in an inert atmosphere from the sample preparation to the performance of microgravity experiment. This technique was applied successfully to the measurement of diffusion coefficient of liquid lithium on the experimental chance of TR-IA No.6 rocket.

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