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**Modeling and Precise Experiments of Diffusion
Phenomena in Melts Under Microgravity**

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1. Overview

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1.1 Background and Objectives of the Research

The diffusion in liquids with high melting temperatures is the most important and fundamental phenomena for the industrial applications¹⁾. In the refining processes of steel and metal in terms of reaction between their liquid states and the reagent for removing oxygen, sulfur, phosphorus, carbon, nitrogen etc., the diffusion in liquids determines their processes. Particularly the diffusion in liquids has been noted in the semiconductor industries. For example, the diffusion coefficients in semiconductor melts are fundamental and important quantities for the optimum operation of growth processes of semiconductor single crystals. In spite of such an importance, up to date, there have been no reliable data of diffusion coefficient for such melts. One reason is the highly reactive chemical properties of such melts. It is not always easy to find good containers for experiments. However, recently, advanced materials can be available for such experiments.

Nevertheless, there exist essential difficult problems in the diffusion experiments of such melts in laboratories on the ground. It is well known that even the extremely small temperature difference in liquid samples causes the convection in liquid samples under gravity. Thus, such convection is inevitable for diffusion experiments on the ground. The existence of such convection has spoiled the diffusion experiments on the ground. The absence of reliable data for diffusion coefficients has prevented us from understanding the mechanism of diffusion in liquids. Nothing to say, the mechanism and the model of diffusion in liquids should be discussed based on the reliable diffusion coefficients.

As is known from the random walk problem, the mechanism of diffusion is an attractive stochastic problem in the mathematical physics. In particular, in the case of study of diffusion in liquids, the disorder in liquid structures brings us not only the complexity and the difficulty but also the interest, which deserves challenging. The mechanism of diffusion in liquids has been a very fascinating and fundamental target in many body problems of statistical physics in addition to in the technical importance.

The break through for the study of diffusion in liquids is the utilization of microgravity circumstance for diffusion experiments of liquids with high melting points. Frohberg et al.²⁾ revealed, for the first time, the validity of microgravity circumstance for diffusion experiments. They showed that the self-diffusion of liquid Sn under microgravity can be measured to be far smaller than the previous data on the ground. The width of data scattering under microgravity was extremely narrow. These indicate that the microgravity circumstance is a very effective tool for the measurements of diffusion in liquids. In addition, the self-diffusion coefficients under microgravity for some liquid metals were shown to be proportional to the square of the absolute temperature, T . It is a fact that further studies must be performed for more various kinds of liquids to obtain the confirmation of existence of the universal(or common) diffusion law in liquid metals. However, this fact implies that only the microgravity diffusion experiment makes possible to discuss the mechanism of diffusion in liquids with high melting point.

Since 1993 the close relation was started between Hokkaido University and NASDA to develop the diffusion study under microgravity. One is the study of self-diffusion coefficient of liquid Sn in the extremely wide temperature range, which was performed under the microgravity of space shuttle "Columbia"^{3,4)}. The other was the self-diffusion of liquid Ge, which was performed under the microgravity of TR-IA No.5 rocket belonging to NASDA^{5,6)}. In these space shuttle and rocket experiments Hokkaido University employed the conventional long capillary method in the wide temperature range. NASDA tested the shear cell technique in these experimental chances. In 1996 the detailed investigation was performed whether the project study about the diffusion in melts with high melting points should be carried out or not. Finally, in 1997, we started the project study of diffusion

“Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity” by joining both extensive experiences.

The purposes of this project are as follows:

- 1) The establishment of model of diffusion in melts
- 2) The establishment of precise measurement technique of diffusion coefficient in melts on the ground with acceptable accuracy
- 3) The establishment of data base of diffusion in melts and related physico-chemical properties

It is desired to provide reliable diffusion data to many fields in which the data of diffusion plays an important role. One method is to give such information based on the experimental data.

However, such diffusion data are needed frequently for some melts for which reliable diffusion experiment is difficult because of high temperature and high reactivity. In such cases, we can provide reliable predicted values of diffusion if we have a reliable diffusion model. For this reason, purpose 1) is important. In addition to the requirement from the fundamental science, nothing to say, the understanding of diffusion in liquids is a difficult but a challenging and an interesting problem in many body physics. The establishment of diffusion in melts is desired also from the fundamental science. As is well known, the microgravity circumstance is an ideal one for the experimental study of diffusion of melts with high melting point. However, up to the international space station(ISS) age, we have not so many experimental chances for microgravity experiments. Therefore, it is very important to develop the technique of diffusion in melts with high melting point even on the ground with acceptable accuracy. This is the motivation of purpose 2). Finally, the reliable data of fundamental physical quantities, such as diffusion coefficient of melts, should be referred without the time loss for the data survey. Therefore, it is very convenient and important to store the reliable data in one place. Those should be utilized as the data base. The diffusion project prepares the data base of diffusion coefficients of melts with high melting point and related physical quantities. For a while this data base is open only to members of the present diffusion project and in future this data base is to be open to the scientists out of this project.

After three years activity from 1997~1999, in March in 1999, this diffusion project was reviewed by five international specialized scientists in the “Science Review”. The activity of diffusion project has been recognized to be advancing in a correct manner with some recommendations.

References

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1.2 Experimental Facilities related to the Diffusion Research

In this diffusion project, one important purpose is the improvement of technique for the measurements on the ground of diffusion of melts with high melting temperature. Therefore, efforts have been made to complete the experimental facilities for diffusion experiments on the ground. The large isothermal furnace(LIF) and the furnace with X-ray radiography(AFEX) are employed for the diffusion experiments on ground. In order to make the sample preparation freely from oxidation, the large glove box system(DRY-LAB) with atmosphere, O₂, N₂ and H₂O<1 ppm, was installed. In this project, the model of diffusion is studied with the relation to the structure of liquids. Therefore, the system for the study of liquid structures has been established. That is, for neutron scattering experiments, the cooperative study with Japan Atomic Energy Research Institute have been developed. Furthermore, the introduction was performed for the specialized high temperature furnace for the neutron diffraction analysis and the small angle X-ray scattering apparatus. For the diffusion experiments, the quick analysis of concentration profile is important. An x-ray fluorescent analysis system(OURSTEX) was installed for the establishment of the desktop analyzing system. In addition to these, many tools are available for sample preparation, sample analysis, measurements of physicochemical properties.

List of experimental facilities

<Furnaces for diffusion measurement>

- Isothermal Furnace : LIF [Large Isothermal Furnace]
- Furnace with X-ray observation system :
AFEX [Advanced Furnace for microgravity Experiment with X-ray radiography]

<Furnace for neutron diffraction>

- High temperature Furnace : I.L.L. 1800C Furnace (A S Scientific products)

<X-ray diffraction facilities>

- Paraforcasting X-ray diffractometer : M18XCE (MAC Science)
- Small angle X-ray diffractometer : RINT2000-SWXD(RIGAKU)

<Sample handling environment and tool>

- High purity Ar grove box : DRY-LAB (VAC)
- Glass fiber polisher : SRL-100E (SAN-EI Electric)

<Apparatuses for the measurements of thermo-physical properties>

- Viscosity : Rotation Viscometer (SINKU-RIKO)
- Thermal conductivity : LASER flash TC-7000H/MELT (SINKU-RICO)
- Thermal analysis : DTA/TGA7 (Perkin-Elmer)
- Thermal expansion : Push rod expansion meter (SINKU-RIKO)
- Surface tension : Sessile drop observation chamber (SINKU-RIKO)
- Calorimeter : multi HTC(SETARAM)

<Instruments for the sample assay>

- EPMA : SX-100 (CAMECA)
- X-ray fluorescent analysis : OURSTEX 120II (OURSTEX)

2. Brief Summary in 2003

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The year 2003 corresponds to the third year of the third stage in our diffusion research project. In the first stage (1997~1998) our attentions had been concentrated on simple liquid metals. In this stage, it has been clarified that the hard sphere model is appropriate for the description of the physico-chemical properties, such as thermodynamic properties and the atomic transport properties, of simple liquid metals. In March in 1999, this diffusion project was reviewed by five international specialized scientists in the "Science Review". The activity of diffusion project had been recognized to be advancing in a correct manner with some recommendations.

Since the second stage(1999~2000), our attentions have been concentrated on the diffusion and the related physico-chemical properties of group IVB liquids. Based on the activities for the study of group IVB liquids in 1999 and 2000, in January in 2001, a proposal of the experimental plan was presented to the first International Announcement of Opportunity(IAO), which is the first international competition of the experimental plan in the International Space Station(ISS). The title of our proposal is

"Roles of the short range order on the self- and impurity diffusion of liquid group 14(IVB) elements with a different degree of complexity".

In this proposal the self-diffusion and the impurity(Sn and Si) diffusion in liquid Ge are to be studied in order to confirm the theoretical predictions of diffusion; this predictions are closely related to the interplay between the atomic transport and the structure or the complexity of liquids. Fortunately this proposal was accepted as the candidate of the first IAO in February in 2002.

Prior to the formal announcement of this acceptance of our proposal, since April in 2001, the definition phase of this first IAO had started as the third stage of our diffusion research project because of the accordance between the original purpose of the diffusion project and the purpose of the IAO. The experimental and theoretical studies have started to establish the realization of the space experimental plan of IAO in the ISS.

This year corresponds to the third year of the definition phase of the first IAO(the third stage of the diffusion research project). Relating to this proposal, we have performed many theoretical and experimental studies. The particular feature of the group IVB liquids is the systematic variation of liquid structures if we note the shoulder in the high Q side just beyond the first peak position of $S(Q)$. With the decrease of atomic mass the shoulder in the high Q side increases; in the case of liquid Pb the liquid structure is hard sphere like with no shoulders; only a small shoulder is present for liquid Sn; large shoulders can be seen in liquid Ge and liquid Si. The mechanism of diffusion in group IVB liquids may be deeply related to these particular features of liquids. For the ISS proposal we planed to perform the impurity(Sn and Si) diffusion in liquid Ge in addition to the self-diffusion in liquid Ge. Rather a segregation tendency can be seen for liquid Ge-Sn system and an ideal solution tendency for liquid Ge-Si system. Therefore, it is also interesting to study the role of such tendencies on the diffusion mechanism. For this purpose, it is important to clarify the particular feature of the structures of liquid Ge-Sn and liquid Si-Ge systems.

The structure of liquids Ge-Sn alloys was studied by the neutron scattering analysis. The structure does not change on the addition of Ge into liquid Sn. However, the structure changes significantly with the addition of Sn into liquid Ge. The shoulder just after the first peak position was observed similarly to the case of pure liquid Ge for liquid alloys containing more than 40 at.%Ge. In addition, the slight enhancement was observed in the lower wave number side than the first peak position. This enhancement may indicate the tendency of two liquid phase separation.

The preliminary study of the first principle molecular dynamics simulation was performed for liquid Ge-Si alloys. The temperature adopted was 2773K. In spite of such high temperature, the shoulder of the structure factor over the first peak position does not disappear. The self-diffusion coefficient was estimated in this first principle molecular dynamics simulation.

As described, the first principle molecular dynamics is a powerful tool for the study of physical properties and the structure of complex liquids. However, it is desired to perform the computer simulation more simply without the neglect of particular feature of liquids. The classical molecular dynamics simulation was developed for liquid Ge by using the empirical many body potential.

To clarify the mechanism of atomic motions in liquids, it is important to obtain the information of inelastic scattering of liquids. To obtain the information of incoherent law of liquid Sn, the inelastic neutron scattering experiment was performed for the stable isotope ^{119}Sn in the liquid state by using the INC spectrometer and the neutron source of KENS. The obtained Q - ω spectrum depends on the static structure $S(Q)$. The diffusion coefficient obtained from the quasi-elastic scattering is smaller than the bulk liquid diffusion coefficient.

The structure of liquids at extremely high temperatures is important for the study of the present project. The containerless technique, which is advantageous for experiments of high temperature liquids, has been applied to the structure analysis of high temperature liquids with the cooperation with the electrostatic levitation team in JAXA. The specially designed levitator was prepared and the preliminary structure data of liquid Zr was obtained.

The liquid structure analysis requires the exact data of density up to a high temperature range. Unfortunately, at present, such data are absent or unreliable. The technique of the density measurements has been developed based on the transparency method of γ rays. The density of liquid Ge-Sn alloys was determined. The isotherm of the molar volume shows a very small positive deviation from the linear law. The preliminary result was reported for the density of liquid Si-Ge alloys.

The isothermal compressibility is an important quantity for obtaining the information of the attractive part of interatomic potential in liquids. In addition, this quantity is also important on the liquid structure analysis because of the relation between this quantity and the long wave length limit of the structure factor, $S(0)$, which is not always easy to obtain experimentally from the structure analysis of liquids. The velocity of sound was measured for liquid Sn containing Pb (up to 10 at.%) and Ge (up to 40 at.%) respectively. With the addition of Pb, the velocity of sound decreases slightly and as a result the isothermal compressibility increases slightly. On the contrary, with the addition of Ge, the velocity of sound increases and the isothermal compressibility decreases.

At present we consider that the shear cell technique is the best method for the measurement of the diffusion coefficient in liquids. In the shear cell technique, the sample container is a pile of many disks with holes, into which samples are contained. Before the start of diffusion time, the constituent pieces in the diffusion couple are kept to be separated each other. Liquid diffusion column is created at an experimental diffusion temperature by a coaxial rotation just at the start of diffusion time. At the end of diffusion time, also by a coaxial rotation a liquid diffusion column is divided into many pieces for the concentration analysis in the solidified state. By this method, the diffusion time can be determined strictly and the effect of segregation on solidification can be kept to be small. Although this technique is most reliable, the structure of the shear cell is very complicated. Therefore, detailed considerations are required for the design of the shear cell experiments particularly for melts with high melting temperatures and high reactivity. The targets for the first IAO plan are such materials. It is also important to obtain diffusion coefficients in liquids in laboratories on the ground with an acceptable accuracy. Furthermore,

we need the reference data on the ground of microgravity diffusion experiments. The experimental technique of shear cell must be polished up also on the ground.

At first, to grasp the effect of liquid flow induced on joining the diffusion sample, the diffusion time dependence was measured for the diffusion coefficient of Au in liquid Ag. The diffusion coefficient becomes constant with the increase of the diffusion time. It is also very important to study the shear cell method for liquid alloys with very high vapor pressure. The sealing method of shear cell was investigated for liquid InGaAs. It is crucial to have a reliable analytical method for the concentration profile to obtain the success of shear cell diffusion experiments. Therefore, detailed study was performed to obtain the good standard sample of the fluorescence X-ray analysis by using the portable fluorescence X-ray analyzer. In addition, it is very important to decrease the cost of shear cell experiment. The design and the preparation method were proposed for the laboratory-made shear cell.

3. The Experimental Plan for the First IAO (International Announcement of Opportunity) in the ISS (International Space Station)

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1. The first part of the document is a list of the names of the members of the committee who were appointed to study the problem of the development of the space program in the United States. The names are listed in alphabetical order and include the names of the following individuals: [illegible names]

Outline of proposal

Based on the activities in 1999 and 2000, a proposal of the experimental plan for the first international competition in the international space station was performed in January in 2001. The title of the proposal is

“Roles of the short range order on the self- and impurity diffusion of liquid group 14(IVB) elements with a different degree of complexity”.

In this proposal a microgravity experiment for the self- and impurity diffusion coefficients in liquid germanium is proposed. Based on the analysis of the hard sphere model, group IVB liquids are classified into two groups; one is the densely packed liquids of heavier elements, Sn and Pb; the other is the loosely packed liquids of lighter elements, Si and Ge, which are semiconductors in the solid state and whose structures of liquids are known to be “complex”. As for the self-diffusion in liquid germanium, the hard sphere model predicts rather an universal diffusion law among group IVB liquids in spite of the presence of the difference in the packing. On the other hand, molecular dynamics simulations predict different diffusion laws each other among group IVB liquids. The first purpose of the present proposal is to conclude which is correct between these two predictions. Together with the self-diffusion coefficient, the impurity diffusion coefficients for Si and Sn impurities respectively are also measured under microgravity. The Sn impurity tends to be excluded from the host Ge circumstance due to the intrinsic phase separation tendency. On the other hand, the Si impurity tends to be incorporated in the host Ge circumstance. We can investigate the possibility of the existence of covalent bond in liquid Ge by performing the comparison of impurity diffusion coefficients between Si impurity and the Sn impurity. The microgravity experiments from the melting temperature up to 1800K are to be performed based on the shear cell technique, in which the alignment of liquid column of diffusion sample is in-situ confirmed by the X-ray observation system installed in the Advanced Furnace for Microgravity Experiments with X-ray Radiography(AFEX).

The self- and impurity diffusion coefficients obtained in the present proposal provides the exact and important information for the advance of atomic transport theory of liquids, for which up to date we have obtained no rigorous standard theories due to the absence of reliable experimental data. In addition, they are to be utilized for the estimation of diffusion coefficient in melts of semiconductor materials; such information is required for the optimum control of crystal growth processes of semiconductors. The detailed description of the proposal is described in the next part.

A. OBJECTIVES

The main objectives of our “diffusion project” are to clarify the diffusion mechanism and to establish a diffusion model for simple molten metals and complex semiconductor melts such as Si and GaAs by means of highly precise diffusion measurements. Through this “diffusion project” we plan to investigate the relationship between the liquid diffusion and the microscopic liquid structure. We hope to answer which particular features of liquid structures crucially influences the diffusion mechanism in complex liquids. The research activities contained in this proposal consist of the diffusion measurements supported by the numerical simulations of fluid dynamics, the theoretical analysis using the hard sphere model, the classical and *ab initio* molecular dynamics and mode coupling theory, and liquid structure measurements by X-ray scattering and neutron scattering. Especially we have been fascinated with the relationship between the diffusion in liquids and the structure of liquids.

Our target in this proposal is to study the diffusion mechanism in liquid Ge in the systematic trend of the IVB group (Si, Ge, Sn, and Pb). Solid state Si and Ge with lighter atomic masses have the diamond type covalent bonds and show the semiconductive character. On the other hand Pb element with heavier atomic mass has the metallic character. The solid state Sn is intermediate between the metallic and the semiconductive character. It is metallic at the high temperatures while it is semiconducting with a diamond structure at the low temperatures. The structure of liquid group IVB elements reflects this systematic variation of the chemical bond in the solid states. Figure 1 shows the systematic trends of static structure factors, $S(Q)$'s, in the liquid state [1]. In the case of liquid Si, a distinct shoulder is present in the high Q side of the first peak of $S(Q)$. This trend is clear also for liquid Ge. In the case of liquid Sn, this shoulder is small but still present. On the other hand no such a shoulder can be seen in the typical metallic liquid Pb. Therefore, systematic investigation of diffusion in liquid group IVB elements corresponds to the study of diffusion with systematic variation of complexity.

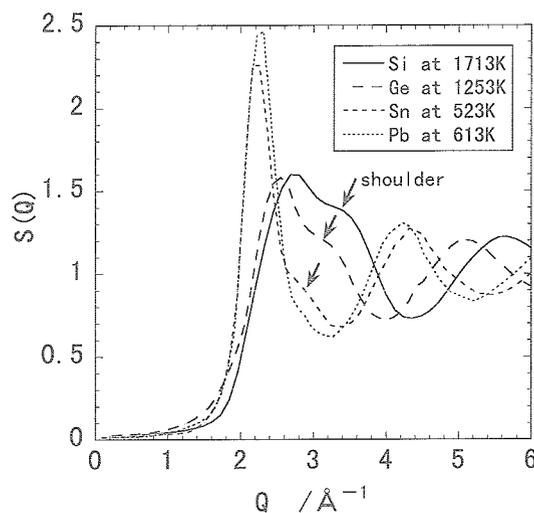


Figure 1. Structure factor of liquid IVB elements near the melting point.

Several excellent self-diffusion experiments have been performed under microgravity in rather simple liquids, the liquid Pb [2] and the liquid Sn [3,4,5]. Present proposal will start with the study of self-diffusion and the impurity diffusion in liquid Ge, and it will be expanded to include more complex liquids such as the liquid Si and the melts of compound semiconductor GaAs.

B. SPECIFIC AIMS

In order to clarify the role played by the complexity in the liquid structure on the diffusion in liquid Ge, the following two specific aims are presented.

- (1) Two hypotheses can be derived from the hard sphere model and the molecular dynamics study to find out whether the complexity in the liquid structure, such as the shoulder of the first peak in the static structure factors, $S(Q)$, will have any effects on the diffusion phenomena. The hard sphere model, which stresses the importance of packing of atoms but doesn't reproduce the shoulder in $S(Q)$, predicts the existence of a common law among the temperature dependence of self-diffusion coefficients of the group IVB elements (Hypothesis A). On the other hand, the molecular dynamics study predicts that the diffusion phenomena

in liquid Ge are different from those in liquid Sn due to the different degree of the complexity or due to the different degree of the existence of the shoulders (Hypothesis B). The first aim is to identify the correct prediction between these two predictions, and to clarify the role played by the particular feature in the short range order in Ge on the diffusion phenomena.

(2) In order to investigate the effect of the variation of the degree on the complexity in liquids, impurity diffusion measurements in liquid Ge will be conducted with the impurity of Si, which should make covalent bond with Ge, and Sn with no covalent bond with Ge, respectively. The second aim is to verify whether chemical bonds will play a role on the diffusion mechanism. Based on the deviation of observed impurity diffusion coefficients from values predicted by the hard sphere model (Hypothesis C), we can know whether the effect of chemical bonds is present or not on the diffusion mechanism in liquid Ge.

C. HYPOTHESES

C.1 Hypothesis A

Hypothesis A, derived from the hard sphere model, states that there exists a common temperature dependence among the diffusion coefficients of liquid group IVB elements in spite of the difference in their liquid structures (see Figure 2).

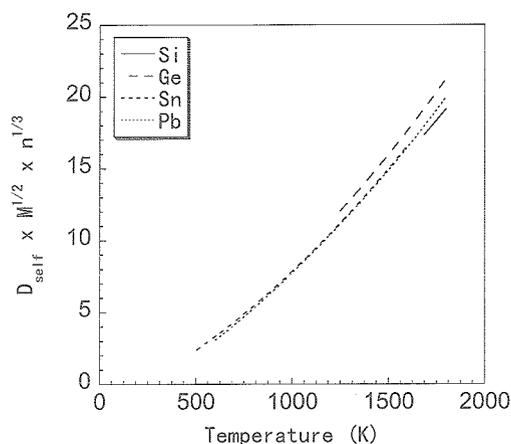


Figure 2. Temperature dependence of $D_{\text{self}} \times M^{1/2} \times n^{1/3}$ based on the hard sphere model (D_{self} : self diffusion coefficient; M : atomic mass; n : number density of atoms)

Melts of group IVB elements can be classified into two kinds of liquids, the densely packed liquids and the loosely packed liquids. Liquid Pb and liquid Sn belong to the former group while liquid Ge and liquid Si belong to the latter group. In spite of such a difference, there exists a common temperature dependence (diffusion law) among the self-diffusion coefficients of liquid group IVB elements.

According to the hard sphere model [6], the self-diffusion coefficient, $D_{\text{self}}^{\text{HS}}$, can be expressed by

$$D_{\text{self}}^{\text{HS}} = C_{\text{BS}} D_{\text{ENS}}. \quad (1)$$

In this equation, D_{ENS} is so called the Enskog formula, which represents the self-diffusion coefficient of dense gases. The explicit form of D_{ENS} is given by

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

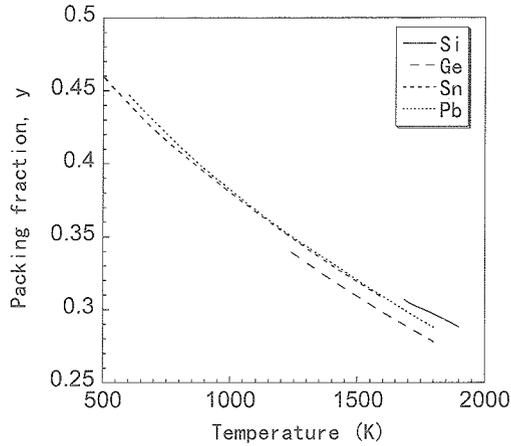


Figure 3. Temperature dependence of packing fraction of liquid IVB elements calculated from the entropy

In this equation, k_B , T and M are respectively the Boltzmann constant, the absolute temperature and the atomic mass. The parameters, y and σ , are respectively the packing fraction and the hard sphere diameter. These two parameters are related each other by the relation, $y = \frac{1}{6} \pi n \sigma^3$, where n is the number density. The symbol $g_{HS}(\sigma)$ designates the radial distribution function at the hard sphere contact. The particular feature of the hard sphere model is that the liquid structure can be expressed only by the packing fraction y (or σ). In liquids, the movement of a tagged particle is hindered by surrounding atoms due to the high liquid density. This cage effect is taken into account by the back scattering factor, C_{BS} . C_{BS} depends only on the packing fraction if one assumes the hard sphere pair interactions. Therefore, from a viewpoint of the hard sphere model, the (normalized) self-diffusion coefficient, D_{self} divided by the factor $(\sqrt{Mn}^{1/3})^{-1}$, is only a function of T and y (Note the relation, $\sigma = \left(\frac{6y}{\pi n}\right)^{1/3}$).

The packing fraction, y , can be determined by fitting the calculated values of entropy, S , to the experimental data [7,8]. The entropy is one of structure sensitive physical quantities. The explicit expression of the entropy on the hard sphere model is given as Eq. (3). (Note that Eq. (3) corresponds to the excess entropy, namely, the entropy of liquids minus that of ideal gas [9].)

$$\Delta S_{HS} = N k_B \frac{y(3y-4)}{(1-y)^3}. \quad (3)$$

Packing fraction of liquid group IVB elements calculated from the entropy is shown in Figure 3 as a function of temperature. From this figure we conclude that there is an almost unique y vs. T relationship in the liquid group IVB elements. In the case of the loosely packed liquids (Si and Ge), the values of packing fraction near the melting point are lower, 0.3~0.35. On the other hand, they are larger, ~0.45, for the densely packed liquids (Sn and Pb). It is well known that y is nearly 0.45 at the melting point for simple metals [10]. The loosely packed structure of liquid Si and liquid Ge may be closely related to the loosely packed structure of diamond lattice in the solid state.

In spite of such a difference, the calculated result of the (normalized) self-diffusion coefficient, $D_{self} \sqrt{Mn}^{1/3}$, shown in Figure 2, indicates that there exists a common temperature dependence in the self-diffusion coefficients

of the liquid group IVB elements. This temperature dependence can be represented by the power law, $D_{self} = AT^n$ (A : constant) with the power index (n), 1.5 ~ 1.7 for all liquid IVB elements. In order to verify the ‘‘Hypothesis A’’, whether the power index is in 1.5 ~ 1.7 or not, the experimental error must be lower than 5 %.

C.2 Hypothesis B

Hypothesis B, derived from the molecular dynamics study, states that the temperature dependence of the self-diffusion coefficient in liquid Ge is different from that of liquid Sn due to the difference of the degree of the complexity, or due to the different degree of the existence of the shoulder as shown in Figure 4.

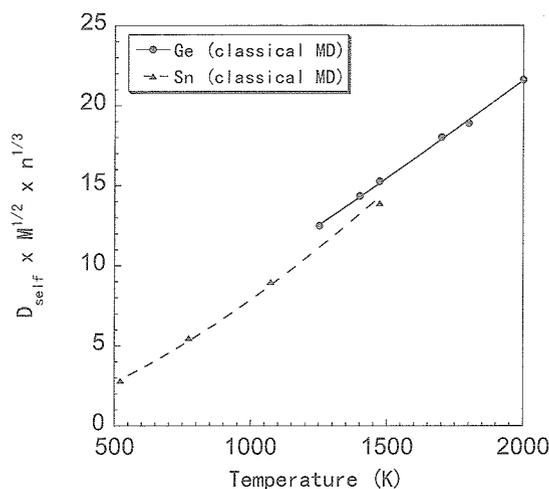


Figure 4. Temperature dependence of $D_{self} \times M^{1/2} \times n^{1/3}$ due to the classical molecular dynamics simulations

At present, we have some results for liquid Sn and liquid Ge obtained through the classical molecular dynamics. The interatomic potential of liquid Sn was obtained from the experimental $S(Q)$ [1] based on the inverse problem method developed by Munejiri and Hoshino [11,12]. Interatomic potential of liquid Ge was obtained from the pseudopotential theory of cohesive energy in liquid metals [10, 13]. We could successfully reproduce the experimental static structure factor, $S(Q)$, by these classical molecular dynamics.

Figure 5 shows the velocity autocorrelation function (VAF) of liquid Ge and liquid Sn calculated by the classical molecular dynamics. The calculated VAF of liquid Sn damps with oscillation around zero; the negative value of VAF implies a high probability of large-angle deflection of atom in its motion. Since a tagged atom is enclosed in a cage formed by its neighboring atoms, the atom cannot diffuse easily but vibrates in the cage for a relatively long time. On the other hand, VAF of liquid Ge does not oscillate but decays monotonously without taking negative values. This means that the cage effect does not exist so much and atoms can propagate over larger distances without any collision.

Obtained temperature dependence of self-diffusion coefficient in liquid Ge can be represented by the power law with the power index of 1.2, which is smaller than that of liquid Sn, 1.7, as shown in Figure 4. In order to verify the difference of the power index, the experimental accuracy of 5% is required.

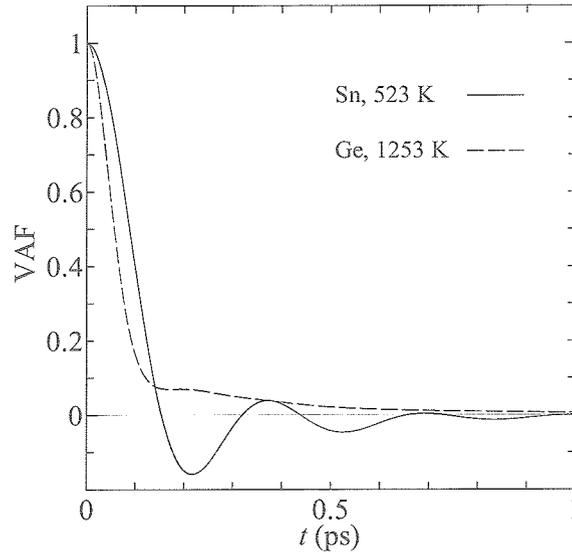


Figure 5. Velocity autocorrelation function of liquid Sn and liquid Ge calculated by the classical molecular dynamics

C.3 Hypothesis C

Hypothesis C states that the impurity diffusion in liquids can be predicted by the hard sphere model. If the observed impurity diffusion coefficient deviates from this prediction, we can tell the effect of the chemical bonds on the diffusion mechanism in liquids.

The impurity diffusion coefficient, $D_{impurity}$, can be written as Eq. (4) on the hard sphere model [10] in the form of the ratio to the self-diffusion coefficient, D_{self} , i.e.

$$\frac{D_{impurity}}{D_{self}} = \frac{\sigma_{\alpha\alpha}^2 g_0(\sigma_{\alpha\alpha})}{\sigma_{\alpha\beta}^2 g_{0\alpha\beta}(\sigma_{\alpha\beta})} \left(\frac{M_\alpha}{M_{\alpha\beta}} \right)^{1/2} = \frac{\sigma_{\alpha\alpha}^2 g_0(\sigma_{\alpha\alpha})}{\sigma_{\alpha\beta}^2 g_{0\alpha\beta}(\sigma_{\alpha\beta})} \left\{ \frac{1}{2} \left(1 + \frac{M_\alpha}{M_\beta} \right) \right\}^{1/2}. \quad (4)$$

In this equation, $\sigma_{\alpha\beta}$ is the average of hard sphere diameters of the species α and β . The symbol $g_0(\sigma_{\alpha\alpha})$ is the radial distribution function of pure liquids at the distance $\sigma_{\alpha\alpha}$. The symbol $g_{0\alpha\beta}(\sigma_{\alpha\beta})$ is the radial distribution function of liquid mixtures at the distance $\sigma_{\alpha\beta}$. $M_{\alpha\beta}$ is the reduced mass between atomic mass M_α of the species

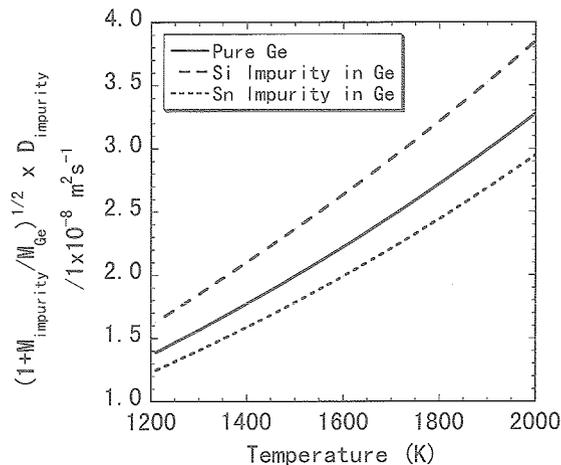


Figure 6. Temperature dependence of $(1 + M_{impurity}/M_{Ge})^{1/2} \times D_{impurity}$ of IVB elements in liquid Ge ($D_{impurity}$: impurity diffusion coefficient; $M_{impurity}$: atomic mass of impurity)

α and M_β of species β . If experimental impurity diffusion coefficients deviate from the predicted values from the hard sphere model, the effect of chemical bond must be present on the diffusion in liquids. In this case, the liquid diffusion model must take account of the effects of chemical bonds. If the agreement between experimental values and the predicted values is satisfactory, the effect of chemical bond may be small. In this study we select Si atom and Sn atom as an impurity in liquid Ge. It is well known that the phase diagram of Ge-Si system shows the complete mutual solubility each other both in the solid and liquid states. That is, Ge atoms tend to mix with the impurity Si atoms randomly. On the other hand, the phase diagram of Ge-Sn system is eutectic type, whose eutectic composition is in the extremely Sn rich side, 0.3%Ge. This indicates that the tendency of agglomeration of Ge atoms prevails compared with the tendency of mutual random mixing. Therefore, the effect of covalent bond, if present, may be expected not for Sn impurity but for Si impurity. The effect of chemical bonds may be investigated by the impurity diffusion of Si and Sn in liquid Ge.

The predicted values of the hard sphere model itself are shown in figure 6 for the impurity diffusion coefficient of Si and Sn together with the self-diffusion coefficient in liquid Ge. In this figure the explicit dependence on atomic mass is excluded by multiplying the factor, $(1 + M_{\text{impurity}} / M_{\text{Ge}})^{1/2}$, and D_{impurity} . The impurity diffusion coefficients of Sn in Ge are predicted to be 10 % lower than the self-diffusion coefficients of Ge, and those of Si are predicted to be 17 % higher than the self-diffusion of Ge. Since the self-diffusion of Ge will be measured with less than 5 % error, the impurity diffusion experiments must be performed with the accuracy of less than 4% to detect the effect of liquid structure on D_{impurity} on the hard sphere model.

D. BACKGROUND AND SIGNIFICANCE

Clarification of the roles played by the short range order on the physico-chemical properties in metallic and semiconductor melts belongs to the most advanced fields in the today's condensed matter science. We plan to give a clear answer to this problem through the proposed diffusion studies in liquid group IVB elements. These elements show a systematic trend in their liquid structure ranging from Si, that shows the distinct shoulder in the structure factor, to Pb that shows a typical liquid metal type of structure with no shoulders (see Figure 1).

The self-diffusion coefficients of Sn were measured by Froberg et al. during the D1 mission [3] and by Yoda et al. [4] and Itami et al. [5] during the MSL-1 mission. Froberg et al. also measured the self-diffusion coefficients of Pb during the D2 mission [2]. A good agreement was obtained between the hard sphere model and the self-diffusion coefficients of the liquid Pb and Sn. Structure of liquid Pb is typically liquid metal like, and liquid Sn shows a small shoulder in the first peak of the structure factor, $S(Q)$. The structure of liquid Ge is more complex and shows a distinct shoulder in its structure factor. It is very interesting to investigate the temperature dependence of self-diffusion coefficient of liquid Ge. Up to now, self-diffusion coefficient of liquid Ge has been measured by Itami et al. [14] and also by Yoda et al. [15] under the microgravity condition provided by the TR-1A 5 rocket flight. Itami et al. used the long capillary method while Yoda et al. adopted the shear cell technique. The shear cell technique gave an excellent concentration profile, that could be well fitted to the solution of Fick's second law. However, its measurement was made at only one temperature, the microgravity time was a little too short as will be discussed later. Thus, this shear cell data for liquid Ge cannot be considered more than a preliminary data. In the case of long capillary method, the diffusion experiment suffered from the volume dilation of solidifying Ge. It was concluded through this experience that the shear cell should be adopted in the diffusion experiments for liquids which show volume dilation on solidification. Also, it is important to allocate a long microgravity period for the diffusion experiments in liquid Ge.

If the effects of the short range order on the diffusion in liquid group IVB elements are clarified from the systematic study, the diffusion of Si, which has the lighter atomic mass in group IVB, can be evaluated. Si is the most important material for the semiconductor industry, but it is also the most difficult material for diffusion measurements because of its high reactivity. This will set the stage for the study of more complex melts, such as melts of III-V semiconductors.

Our project is organized involving various scientists for diffusion experiments, liquid structure measurements and liquid theories. The diffusion experiment group includes the development of the shear cell techniques and the numerical analysis of the fluid dynamics. Many of our members also have experiences of conducting diffusion experiments in microgravity as shown in Table 1. Especially their experiences were with the shear cell technique. We have succeeded in shearing and dividing the samples in all previous experiments.

The liquid structure measurement group employs the small angle X-ray scattering and the neutron elastic [16,17] and inelastic scattering [18] to obtain the microscopic information of static and dynamic structure of liquids. The neutron scattering experiments are conducted in cooperation with Japan Atomic Energy Research Institute.

The liquid theory group will clarify the diffusion mechanism and will produce a diffusion model. They use the hard sphere model, the classical molecular dynamics [19], the *ab initio* molecular dynamics [17] and the mode coupling theory [20]. The *ab initio* molecular dynamics, being free from the assumption on interatomic interactions, may in principle be the most accurate tool for the study of atomic motion. However, the *ab initio* molecular dynamics needs to confirm the system size dependence of simulations, that may exceed the capacity of even the present supercomputers. On the other hand, although the classical molecular dynamics is free from such a problem, it requires suitable interatomic potentials for simulations, which is not always available for complex liquids. The essential feature of hard sphere model is in its “simplicity”, and the “analytical expressions” for many physical quantities. The features in liquid structures essentially depend on a single parameter, the packing fraction η which is the ratio between the fractions of the repulsive region per atom to the whole region per atom. The hard sphere model has an additional advantage of grasping the global feature of liquids. Our theoretical and experimental expertise in combination with all the tools available in our disposal will enable us to establish a new diffusion model for the complex materials.

Table 1. The microgravity experimental experiences of the project members

Experiments (Method)	Mission (year)	Reference
Interdiffusion of lead-tin-telluride (Long capillary)	TEXUS ^{*1} ('88, '90, '92), TR-1A4 ^{*2} ('95), MSL-1 ^{*3} ('97)	[21,22]
Self-diffusion of Ge (Long capillary)	TR-1A 5 ^{*2} ('96)	[14]
Self-diffusion of Ge (Shear cell)	TR-1A 5 ^{*2} ('96)	[15]
Self-diffusion of Li (Long capillary)	TR-1A6 ^{*2} ('97)	[23]
Self-diffusion of Sn (Long capillary)	MSL-1 ^{*3} ('97)	[5]
Self-diffusion of Sn (Shear cell)	MSL-1 ^{*3} ('97)	[4]
Interdiffusion of Ag-Cu (Shear cell)	TR-1A 7 ^{*2} ('98)	[24]

*1 TEXUS : German sounding rockets

*2 TR-1A : Japanese sounding rockets

*3 MSL-1 : The First Microgravity Science Lab, a space shuttle mission

E. MICROGRAVITY ENVIRONMENT

E.1 Necessity of Long Microgravity Period

In spite of the efforts to suppress convection flows in melts, measuring accurate diffusion coefficient by the ground experiments has not been as successful as the microgravity experiments. Self-diffusion or impurity diffusion measurements should be performed under isothermal condition on the ground, however it is difficult to achieve such condition in practice especially at temperatures as high as 1300 K. Numerical simulations show that material transport is surely enhanced by convection. According to a numerical analysis even a temperature difference of less than 0.5 K across the sample at the vertical capillary configuration can cause flows in liquid samples even though calculated concentration profiles show good fits for the Fick's second law with apparent diffusion coefficient [25]. The measurement error is still higher than 10-20% on the ground due to convection. Recently, there have been attempts to measure diffusion coefficients under application of strong magnetic fields to reduce convection on the ground. Mathiak and Froberg [26] performed the experiments concerning the strong magnetic fields on interdiffusion. They compared their results with microgravity measurements. The mean diffusion coefficient in magnetic field was 6.4% higher than that in microgravity even at the relatively low diffusion temperature, 523 K. The experimental errors in diffusion coefficients should increase with temperature increase because of the lower viscosity and higher temperature inhomogeneity, and the error won't be low enough to verify our hypothesis.

In order to develop and verify our liquid diffusion model, we are aiming for the accuracy of measured diffusion coefficients within 4%. This requirement of accuracy comes from the necessity to verify our Hypotheses A, B and C. Our previous microgravity experience assures us that the necessary experimental accuracy can be readily obtained by our refined experimental method if the diffusion coefficients are measured in the space microgravity environment.

The shear cell method will be employed to prevent the concentration profile in liquids from the flow caused by the volume dilation on solidification, as described above. The demerit of the shear cell method is in the flow that is generated in the sample during the "shearing" procedures (joining and dividing of a sample). A long diffusion period is needed to make this error as small as possible in order to precisely measure the diffusion coefficients. It was reported that the length of the disturbance by shearing was about as long as sample radius [27]. We assumed that the disturbance occurred about ± 2 mm at the beginning of the experiments with 2 mm diameter sample. Therefore, the error due to the division of a liquid sample at the end of a experiment is negligibly small if the shear cell thickness is larger than the sample diameter. However, we need to clarify the initial disturbance from joining of the sample. We calculated the error from this disturbance with various diffusion times. Table 2 shows the calculated errors in the diffusion coefficients due to the initial disturbance of joining. It was found that 7000 seconds (117 minutes) is needed to make the error under 1 %. In order to satisfy the total error under 4 %, more than 2-hour microgravity period is needed.

Table 2. The errors in the diffusion coefficients due to the initial disturbance of joining

Diffusion time	2000 s (33.3min)	4000 s (66.7min)	6000 s (100.0min)	7000 s (116.7min)	8000 s (133.3min)
The error in the diffusion coefficient	2.9 %	1.7 %	1.1 %	0.9 %	0.8 %

E.2 Gravitational Disturbance in ISS

Our experiment will be designed to minimize the effects of convection flows which might affect the diffusion measurements. Concentration profiles will be readily disturbed by the flows which might be induced by the residual gravity and the g-jitters existing in the ISS environment. The experimental condition has to be optimized to carry out highly precise diffusion experiment in microgravity. Therefore, a numerical analysis of the effects of convection on diffusion measurements has been performed to estimate the experimental error and to optimize experimental conditions. A three-dimensional model with a container was employed for this analysis. The convection was induced by both temperature and concentration gradients. The diameter of a specimen was varied from 0.5 mm to 2.0 mm. The magnitude of residual gravity and g-jitter used in the analysis was chosen based on the data estimated by NASA for the ISS. The residual gravity was $2 \mu\text{g}$ and its direction was inclined 45 degrees against the specimen axis. The g-jitters used in the numerical analysis, which was artificially produced by summing sinusoidal vibrations ranging from 0.01 to 100 Hz, were added in random direction simulating the ISS g-environment. The result predicted a significant effect of the convection flows to the diffusion measurements. In the case of specimen 2 mm in diameter, the maximum flow velocity was $25 \mu\text{m/s}$ and the apparent diffusion coefficient became 3.6% higher than the pure diffusion, leading us to the conclusion that the experimental results might be spoiled by the convection. In the case of the 1mm diameter specimen, the error in diffusion coefficient was less than 1%. Hence, specimens with diameter less than 1 mm should be selected in order to avoid the effect of gravitational disturbances in the diffusion experiments conducted in the ISS environment.

One concern that is associated with the use of small specimen might be the wall effect. The wall effect can be considered as the Marangoni convection due to the roughness of crucible walls and as the rapid surface diffusion. The rapid surface diffusion is discussed frequently for the solid surface at rather low temperatures, where the difference of chemical potential between bulk and surface is important. It hasn't been found for liquids at high temperatures and can't be thought to affect the diffusion experiments in liquids because it occurs, if present, only in one atomic layer near the surface. The Marangoni convection at the crucible wall can be suppressed by reducing the free surface area, which can be achieved by using springs to push the samples during melting and also by reducing the crucible roughness to less than $50 \mu\text{m}$.

The experimental error due to the gravitational disturbance can be suppressed less than 1 % by using a 1 mm diameter sample, a spring and a crucible with less than $50 \mu\text{m}$ roughness even under the residual gravity and g-jitter in ISS.

F. EXPERIMENTAL DESIGN AND METHODS

To limit the experimental error to less than 4 % as required by our specific aims, the experiment is designed as follows:

F.1 Shear Cell Method

Diffusion measurements will be carried out with a diffusion couple method, in which a diffusion couple of two samples having two different concentrations will be melted. The concentration profile after a diffusion experiment will be analyzed. There are two ways in the diffusion couple method. One is the long capillary method in which a diffusion couple is kept even during heating and cooling periods. The other one is the shear cell method. In this method, each part of the diffusion couple is separated during heating process. Then a liquid column of diffusion is formed at the start of the diffusion, and it is divided into many segments at the final period

of diffusion. Finally, the small segments are cooled and solidified. These processes are described in Figure 7. The merit of shear cell method is that the diffusion time is precisely defined, and the effect of solidification, namely, the segregation and the flows caused by the volume change on solidification can be completely removed.

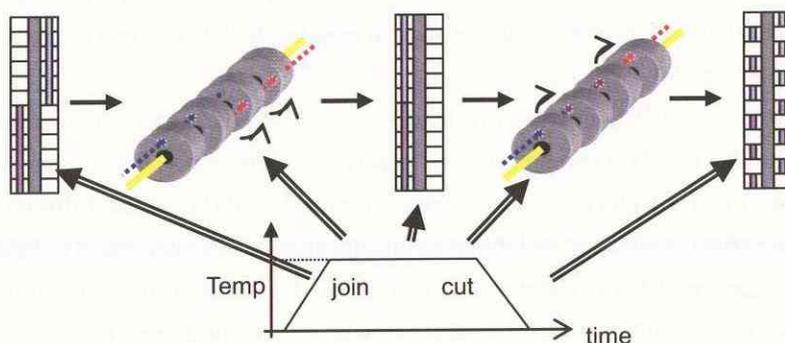


Figure 7. Concept of the shear cell method

For the material showing volume dilation on solidification, the shear cell method should be employed as described above. The demerit of the shear cell method is the disturbance on the concentration profile due to the flow on joining and dividing. A long diffusion time can make the error of this disturbance due to the flow on forming a liquid column less than 1%. The effects of the shearing on dividing sample into many segments can be neglected if the length of divided samples is longer than the sample radius as reported in Ref.27. At present, several experiments and simulations are in progress to clarify the effects of shearing and to optimize parameters that are needed for the shear cell operation and cell design. An additional demerit of the shear cell is the fact that the number of analytical points is limited by the number of segments which is not so large in practice. The number of analytical points also determines the error of the diffusion coefficients. According to the error theory the number of segments should be more than 10.

F.2 Sample Configuration

The sample cell consists of diffusion samples, springs for compensation of change of the sample volume, cell segments, a shaft to rotate the cell segments, a spring to keep the cell segments in tact, and thermocouples, as shown in Figure 8. The concept of each part design is described below.

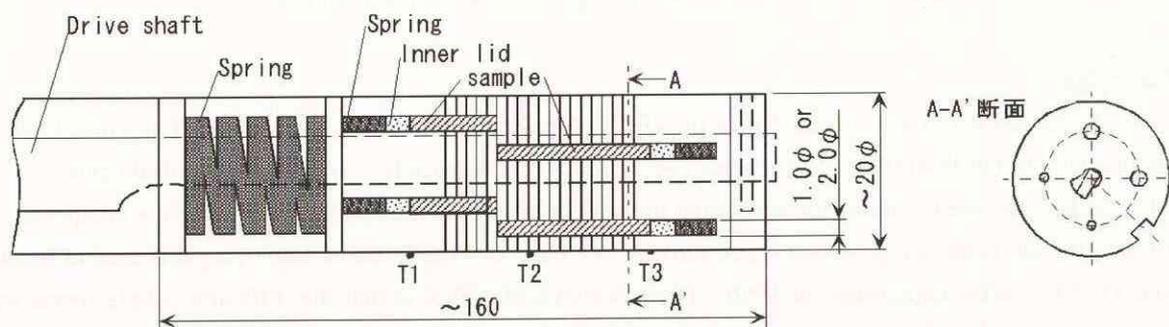


Figure 8. Shear cell sample configuration (unit: mm)

1) Sample

A self-diffusion sample consists of a natural Ge and a Ge enriched by stable isotopes. The sample is designed to minimize the sample weight difference, as shown in Table 3. It is possible to study the isotope effect on the diffusion in this sample design. Impurity diffusion samples consist of a pure Ge and a Ge doped by specific impurities. The impurity level of the initial sample may be about 0.1 % that is imposed by the detection limit of the analysis (SIMS and ICP-Mass).

The sample radius is selected to be 1 mm (g-jitter insensitive) and 2 mm (g-jitter sensitive). The sample length should be 50 mm for the 7000 second diffusion experiment. The experimental error from the flow due to g-jitter can be less than 1% if a 1 mm diameter sample is used. Also, 7000 second diffusion experiment is long enough to eliminate the effect of shearing and the experimental error can be suppressed to below 1 %.

Since the vapor pressure of Ge is about 4.8 Pa at 1800 K, it is needed to fill argon or helium gas in the cartridge. If necessary, it is possible to adopt the shear cell with sealing machinery [28].

Table 3. Concentration of sample for self-diffusion experiment

Atomic mass	70	72	73	74	76	Total atomic mass
Ratio in natural Ge (%)	20.5	27.4	7.8	36.5	7.8	72.71
Ratio of enriched Ge (%)	32.5	0	0	67.5	0	72.70

2) Shear cell

The cell material should have low wettability to the sample from the viewpoint of spring mechanism and should not react chemically with the sample liquid. We measured contact angles of boron nitride, pyrolytic boron nitride, glassy carbon and graphite to liquid Ge. The contact angles were around 160 degrees for all materials even after heating at 1773 K for 1 hour. We will do the same test for liquid Ge containing Si or Sn as impurity.

The dimensional tolerance of the cell alignment should be less than 50 micrometer for the 1 mm diameter sample. This estimation was derived from a calculated result that less than 5 % of misalignment has to be maintained to keep the error less than 1 %.

Graphite springs will be used after testing the changes in length and in spring constant at high temperatures. A shaft which rotates the cell segments will be made of mullite, a compound material of Al_2O_3 and SiO_2 which has low thermal conductivity and high strength even at high temperature, about 1800K.

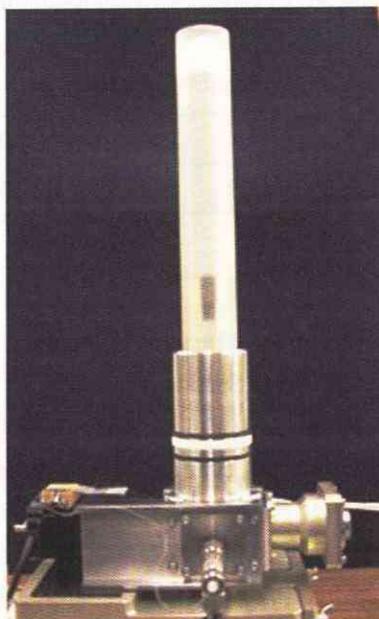
3) Cartridge

We are preparing our experimental plan by AFEX (Advanced Furnace for microgravity Experiments with X-ray radiography) or DMI (Diffusion Module Insert) in Material Science Research Rack described below.

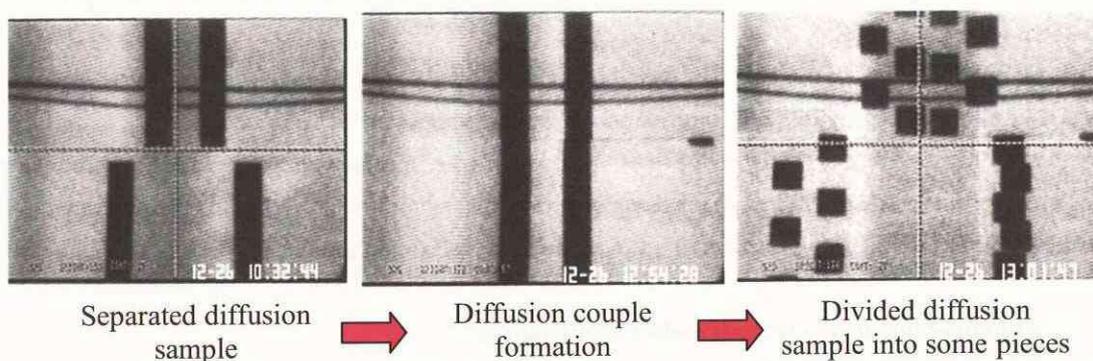
For AFEX, we need a heater for isothermal heating. We will use a ceramic heater, which is composed of pyrolytic graphite heater on pyrolytic boron nitride. We have an experience of employing this type of heater on the TR-IA5 rocket experiment in 1996. The advantage of AFEX is that the diffusion couple formation and separation can be observed during experiments by X-ray. We will seal the cell and heater in a sapphire or a glassy carbon cartridge, which has high transmissivity for X-ray and the ability to maintain the vacuum. Photograph 1 shows a shear cell cartridge for ground experiments using AFEX BBM (Bread Board Model). Photograph 2 shows the X-ray image of AFEX during a diffusion experiment using the shear cell technique. This

is the first direct observation of the shear cell operations, formation of the liquid diffusion column and division into small pieces.

For DMI, we will use a tantalum cartridge which was tested up to 1773 K through the MSL-1 mission in 1997.



Photograph 1. The shear cell cartridge for AFEX BBM



Photograph 2. X-ray image of a diffusion sample during a shear cell experiment

4) Safety

Most of the materials including the samples, Ge, Sn, and Si, in our proposal have already been used in the previous space shuttle experiments. The total sample weight in one shear cell is about 2 g. The sample will be sealed in a cartridge as described above, and the cartridge will be decompressed during the experiments. The decompression has an advantage for the safety requirement.

F.3 Experimental Condition

- 1) Atmosphere : argon gas
- 2) Temperature homogeneity : +/- 10 K for 50 mm length at 1773 K (1800 K if possible)
- 3) Experimental condition : 5 temperatures (1250 ~1773 K (1800 K if possible)) as shown in Table 4
- 4) Number of cartridges : 15 (5temperatures x (1self-diffusion+2impuritydiffusion samples))

Table 4. Experimental conditions

Temperature (K)	1250	1400	1550	1700	1773 (1800 if possible)
Diffusion time (s)	7000	5580	4550	3780	3400

G. DATA ANALYSIS

G.1 Concentration Analysis and Calculation of Diffusion Coefficients

ICP-MASS (Inductive Coupled Plasma Mass Spectroscopy) will be used for the isotope analysis of self-diffusion samples and for Sn impurity diffusion sample analysis. ICP-MASS can't be used for Si impurity diffusion sample analysis because the mass of Si is near to that of nitrogen or nitrogen compounds. Therefore, SIMS (Secondary Ion Mass Spectroscopy) will be used for Si impurity sample analysis.

Fick's second law is used to calculate diffusion coefficients. If the diffusion coefficient, D , doesn't depend on the concentration as in self- and impurity diffusion, the following equation will apply:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \quad (5)$$

The numerical or the analytical solutions will be used to reproduce the concentration distribution of experiments.

G.2 Analysis

We will organize various microscopic information of atomic structures and atomic dynamics as described below. As the results of this project, we will present a new diffusion mechanism along with a new model for the atomic dynamics and diffusion in liquids of complex structures taking into account those factors such as the covalency, the dynamics of local environment (life time), the multi-relaxation time.

1) *Ab initio* and many-body force classical molecular dynamics

Based on the *ab initio* molecular dynamics, we will analyze the atomic motion, which is strongly related to the diffusion mechanism, as follows:

- i) The electron density distribution function for the verification of covalent bonds.
- ii) Analysis of local configuration around a moving particle (angle distribution of three body distribution function).
- iii) Analysis of residence time distribution function around local configuration. Also, the role of the many body force of atomic interaction will be examined for liquids with the effect of covalent bonds by using the many-body force classical molecular dynamics.

2) Neutron elastic and inelastic scattering experiments in cooperation with Japan Atomic Energy Research Institute (JAERI)

The particular feature in the structure factor, $S(Q)$, of liquid group IVB elements is the existence of shoulders in the high Q side of the first peaks. We will use the neutron facility at JAERI and analyze the existence of shoulders as a function of temperature up to 1800K-2000K by the neutron elastic scattering. The experimental results will be analyzed to clarify the short range order in liquid Sn and liquid Ge.

We will also perform the neutron inelastic scattering and quasi-elastic scattering experiments for liquid Sn and liquid Ge to obtain the information about van Hove space-time correlation functions, which is the direct experimental information of microscopic atomic dynamics.

3) Small angle X-ray scattering experiments

The clusters in liquids, if present, can be detected experimentally by the small angle scattering either of X rays or neutrons by the liquids. Small angle X-ray diffraction apparatus was installed in NASDA. Using this apparatus we will analyze the structures of clusters in liquid Sn and Ge as a function of temperature.

4) Mode coupling theory coupled with large scale molecular dynamics and neutron inelastic scattering experiments

Mode coupling theory is a prevailing theory for the studies of dynamic atomic properties in liquids, glass forming liquids and liquid metals. In the present study, we will analyze the velocity auto-correlation function and the space-time correlation function given by the large-scale molecular dynamics along with the neutron inelastic scattering experiments. We will also clarify the role played by the correlation between density and current of atoms.

H. EXPECTED RESULTS AND POTENTIAL TO THE FUTURE

At first we will obtain the temperature dependence of the self-diffusion coefficient in liquid Ge and of the impurity diffusion coefficients of Si and Sn respectively in liquid Ge. These data can be employed as reliable reference data. It can help us to improve the ground diffusion measurement technique, for example, in magnetic field application, and thus it may help us to measure diffusion coefficients with low experimental errors enough for industrial application.

The next activities will be concentrated on the data analysis for theoretical modeling. We are deeply interested to find out whether or not the chemical bonds will affect the diffusion mechanism. If “Hypothesis A” and “Hypothesis C” from the hard sphere model is found to be right, the chemical bonds doesn't affect the diffusion mechanism, and there will be some cancellation effects between the complexity of liquids and loosely packed structures. This point offers an interesting viewpoint that will constitutes a subject of the fundamental science. For the applied science, self-diffusion and impurity diffusion coefficients in liquid group IVB elements can be estimated from “Hypothesis A” and “Hypothesis C”, respectively. It means the possibility that even the self- and impurity diffusion in liquid Si may be estimated from these hypotheses. As is well known, Si is the most important material for the semiconductor industry but, because of its high reactivity, it is the most difficult material to measure its diffusion coefficient. This will provide the starting point for the study of more complex melts, such as melts of III-V semiconductors (GaAs etc.).

If the “Hypothesis B” is found to be right, the microscopic details of liquid structures must be taken into

account for the diffusion model in such melts. Up to now the effect of short range order has been discussed only on the static liquid structures. Therefore, if correct, the “Hypothesis B” also provides a new branch of the fundamental science that concerns with the effect of short-range order on the atomic dynamics in liquids. The new model is required to explain the diffusion in liquid group IVB elements having different degrees of complexity.

The final goal of our proposal is to clarify the roles played by the loosely packed structures of liquids and the covalent bonds, and to reflect these in the diffusion model of complex liquids such as melts of Ge, Si and GaAs. We are confident that the results that will be born out of the presently proposed research project will be much appreciated by the semiconductor industry as much as by the many-body physicists in the fundamental science.

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4. Main Results

Part A. Approach to the Model Establishment of the Diffusion in Melts

Molecular dynamics simulations of liquid IV-IV alloys

by

Tadahiko Masaki¹ and Toshio Itami¹

Abstract: The partial structure factors of liquid Ge-Sn and Ge-Si are important for the modeling of diffusion phenomena in these liquid alloys. These partial structure factors were calculated by using two kinds of molecular dynamic simulations, *ab initio* molecular dynamics simulation and classical molecular dynamics simulation with the Stelling-Weber interatomic potential. Total structure factors obtained from these molecular dynamics simulations and neutron scattering experiments are in good agreement with each other.

1. Introduction

The atomic configuration of liquid alloys is one of the important subjects for the condensed matter physics. However, three kinds of partial structure factor (PSF) are required for the complete understanding of one alloy. It is almost impossible to obtain these PSF's experimentally. Computer simulation, such as a molecular dynamics simulation, provides us the information of atomic configuration of each atom in liquids and in principle, the PSF's can be obtained from this technique. Nevertheless, the classical molecular dynamics simulations have a problem on the application to liquid alloys because of the ambiguity of interatomic potential.

In the case of liquid IVB metals, Stelling and Weber developed a interatomic potential (SW potential) which includes many body interaction of silicon. This interatomic potential is rather simple but the classical molecular dynamics simulation with this potential well reproduces the structure and properties of liquid silicon and germanium. SW potential has been developed mainly for the simulation of pure liquid Si and Ge. However, it can be applicable for liquid alloys if the interatomic potential between different kind of atoms is assumed in some way.

On the other hand, the *ab initio* molecular dynamics simulation overcomes the problem of classical molecular dynamic simulation, in which the force of atoms can be directly evaluated from the atomic configuration and corresponding electron density in liquid metals without any empirical parameters. In spite of its advantage, however, it is rather not easy to perform this method because of the complexity of program. Therefore, in this research project, we calculate the liquid structures of Ge-Sn and Ge-Si based on *ab initio* molecular dynamic simulations in collaboration with Prof. Hoshino in Hiroshima Univ.

In this year, these two kinds of molecular dynamic simulations were performed for liquid Ge-Si alloys to obtain liquid structures and properties. In this report, the comparison of obtained results between these simulations is introduced briefly together with the results of neutron scattering experiments.

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2. Molecular dynamics simulations

2.1 Classical molecular dynamics simulation of liquid Ge-Si alloys

It is well known that the structure of liquid IVB metals shows a characteristic feature, namely the shoulder shape was observed at the high Q side of first peak of S(Q). The origin of this feature has not been clarified. As one of possibilities, the residue of crystal structure, such as a diamond structure, in the liquid is assumed. The interatomic potential which includes the many body interaction must be used for the simulation of such crystalline structure in liquids. The Stellingwerf-Weber interatomic potential is one of the many body interatomic potentials. In this potential the potential energy depending on distances and angles between three atoms are considered, as follows:

$$u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i < j} \phi_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} \phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots + \phi_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

$$\phi_2 = \epsilon f_2(r_{ij}/\sigma), \quad \phi_3 = \epsilon f_3(\mathbf{r}_i/\sigma, \mathbf{r}_j/\sigma, \mathbf{r}_k/\sigma)$$

$$f_2(r) = A(Br^{-p} - r^{-q}) \exp[(r-a)^{-1}], \quad r < a$$

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}] \left(\cos \theta_{jik} + \frac{1}{3} \right)^2, \quad r_{ij} < a, r_{ik} < a$$

Parameters of this potential are decided based on the properties of crystal at melting point. These parameters for Ge and Si have been presented by several researchers and the molecular dynamics simulations of pure Ge, pure Si and Ge-Si alloys have been studied. In this research, parameters presented by Yu et al.[1] were used for the simulation of partial structures of liquid Ge-50 atomic%Si. In this simulation, the unit cell contained 1728 atoms composed of Ge atoms and Si atoms. The periodic boundary condition was applied. The diamond structure of Ge was constructed as an initial configuration of simulation and a half of atoms are randomly replaced by Si atoms. The time developments of displacement of atoms were calculated due to the Verlet's velocity algorithm. The temperature of simulation was 2000 K. The time step was 0.5 fs and the total time of simulation was 20 ps.

2.2 *Ab initio* molecular dynamics simulation of liquid Ge-Sn and liquid Ge-Si alloys

Ab initio molecular dynamics simulation is one of the most up-to-date methods to obtain the structures and electronic states in liquids theoretically. In the present research, the *ab initio* molecular dynamics simulation is based on the density functional theory in which the generalized gradient approximation is used for the exchange-correlation energy. For the electron-ion interaction, the norm conserving pseudopotentials were used for Ge, Sn and Si. Details of the simulation were described in the previous report of this research project [2].

In this simulation, the super cell contained 64 atoms composed of Ge atoms and Sn or Si atoms, and the periodic boundary was applied for the model of these liquid alloys. The diamond structure of Ge was taken as an initial configuration and some atoms were replaced by Sn or Si atoms whose numbers corresponded to the concentration of alloys. The temperature of simulating system was controlled by the Nose-Hoover method. The initial temperature was kept at higher temperature than the melting temperature for the achievement of liquid state. After that, the temperature was gradually decreased to the target temperature. The simulation was carried out during 9.68 ps with a time step of 0.968 fs for Si-Ge alloys and during 86-102 ps with a time step of 2.7-3.2 fs for Ge-Sn alloys. The temperature of the simulations was 1593K for Si-Ge and 1273K, 1523K and 1773K for Ge-Sn respectively.

3. Results and Discussions

The space and time correlation of atoms in liquids is one of the essential factors to understand the static and dynamic properties of liquid alloys. Especially, correlations between same and different kinds of atoms, such as partial radial distribution function, are important to know the interaction of atoms. A molecular dynamic simulation can be employed as a powerful tool for this subject because these correlation functions are directly calculated from the mean of atomic configuration of each time step.

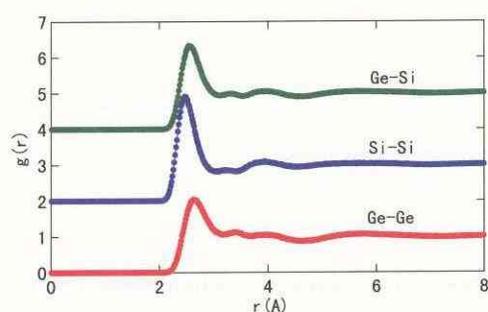


Figure 1 Partial radial distribution function of liquid Ge-50 atomic%Si by classical molecular dynamics simulation with SW potential

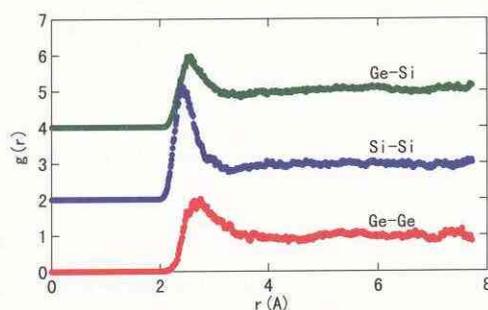


Figure 2 Partial radial distribution function of liquid Ge-50 atomic%Si by *ab initio* molecular dynamics simulation

In the activity of the diffusion project in this year, the static structure of liquid Si-Ge was calculated based on two different kinds of molecular dynamics (MD) simulations, *ab initio* method and the classical method.

The partial radial distribution functions of liquid Ge-Si are shown in figure 1 and figure 2. It can be seen in both cases that the height of the first peak of $g_{\text{Si-Si}}(r)$ was larger than that of $g_{\text{Ge-Ge}}(r)$ and $g_{\text{Ge-Si}}(r)$. Other characteristic features were slightly different. In the results of classical molecular dynamics simulation, the small peaks of $g(r)$ can be seen between the first peak and second one. This additional peak may be derived from the asymmetric term of SW potential. However, in the results of *ab initio* molecular dynamics simulation, such small peaks cannot be observed.

The partial structure factors are obtained from the Fourier transform of these radial distribution functions. The total structure factor is obtained from the sum of these partial structure factors by taking into account both atomic scattering factors and concentration of alloys.

In the case of Ge-50 atomic%Si, the static structure factor was measured by the use of neutron scattering in this project. This was described in our previous report. The static structure factors obtained from the *ab initio* MD and the classical MD can be compared with the experimental result. As shown in figure 3, results of these simulations are in good agreement with that of neutron scattering experiments.

It can be regarded from these results that the classical molecular dynamic simulation with SW potential is one of easily feasible methods to calculate the characteristic feature of total structure factor of liquid Si-Ge alloys. However, it should be carefully applied to the analysis of partial structure factors because details of partial radial distribution functions are different between the classical MD and the *ab initio* MD.

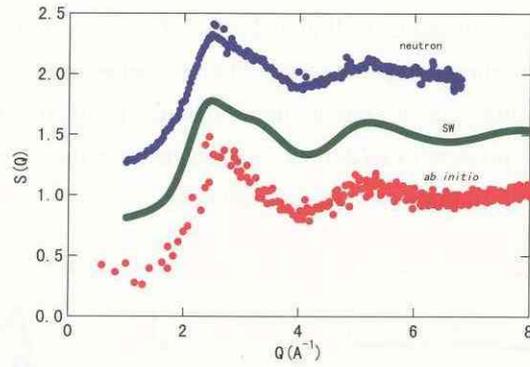


Figure 3 Total scattering factor of liquid Ge-50 atomic%Si

4. Summary

The molecular dynamics simulation is a powerful tool for the analysis structure of liquid metals. The total structure factors of liquid Ge-Si alloy were obtained and those are in good agreement with results of neutron scattering experiments.

Reference

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- [2] "Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity" Annual Reports 2002, NASDA-TMR-030005E.

Static structure of liquid germanium alloys

by

Tadahiko Masaki¹ and Toshio Itami¹

Abstract: Static structure of liquid germanium and alloys was measured by using the neutron scattering technique. The latest data of liquid structures measured by our research project are shown in this section.

1. Introduction

The liquid state can be regarded as a dense and disordered state. An atom migrates in the liquid with interaction to other atoms in the liquid. Therefore, for the understanding of the tracer atom of diffusion in liquids, it is important to know the configuration of its surrounding neighboring atoms in detail. The diffusion in liquid germanium is one of the main targets in this research project. The diffusion model of liquid germanium is being developed based on the hard sphere model coupled with actual liquid structures and molecular dynamics simulations. It is well known that the liquid germanium and liquid silicon show the characteristic liquid structures, in which a clear shoulders are observed at just beyond the first peak of Q (wave number) for the static structure factor, $S(Q)$. The origin of these shoulders has been studied from the theoretical and experimental points of view. However, it has not been identified clearly. In this research project, the structure of liquid germanium alloys was measured carefully with the use of neutron scattering techniques. The obtained data are important references for molecular dynamics simulations and model construction. In this section, the experimental method and data obtained are described briefly.

2. Crucible for the neutron scattering experiments in the high temperature

The neutron scattering technique is useful for the measurement of structure of liquid metals because of high transparency of neutron beam for the most of materials. This merit provides us that the wide variety of materials can be applied as the crucible material for the neutron scattering experiment of high temperature melts. In the case of liquid germanium alloys, the liquidus temperatures are higher than 1200K. Therefore, the crucible materials must be selected carefully and a few kinds of ceramic materials have been used for the neutron scattering experiments. In this project, the grassy carbon which has been used for shear cell in our project was for the first time applied to the crucible material for the neutron scattering experiments. The grassy carbon is a hard material and resists the corrosion by high temperature metallic melts. We made the cylindrical shape of crucible, whose diameter was 10 mm and wall thickness was 0.5 mm by using the glassy carbon. The diffraction pattern of glassy carbon is observed as amorphous-like halo pattern. Therefore, the neutron diffraction of sample can be obtained without obstacle Bragg peak of crucible material, as can be seen in figure 1. This is the great merit for the observation of characteristic liquid structure of germanium alloys because the Bragg peaks of the most of crucible materials are positioned near the first peak of Q for the $S(Q)$ of liquid matters.

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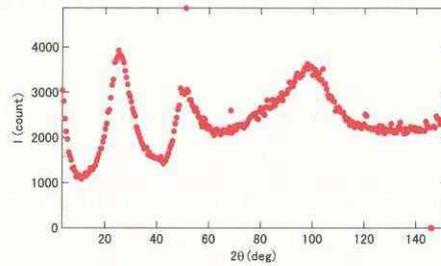


Figure 1 Diffraction pattern of glassy carbon crucible

3. Brief summary of experimental results

The neutron scattering experiments of liquid Ge-Sn and liquid Ge-Si alloys were performed at the Japanese Research Reactor 3 (JRR3) in Japan Atomic Energy Research Institute (JAERI) with the use of glassy carbon crucible. In this research project, members used two kinds of different diffractometers, HERMES for Ge-Sn and HRPD for Ge-Si. The crucibles containing samples were installed in a radiation heating furnace with Nb foil heater and were heated under a high vacuum condition. The details of experiments and correction procedures (absorption, normalization, etc.) were described in the previous report of our research project [1].

3.1 Static structure of liquid germanium-tin alloys

The $S(Q)$'s of liquid Ge-20 atomic%Sn were measured by using the neutron scattering technique at the temperatures of 1273K, 1523K and 1773K. The obtained $S(Q)$'s were shown in figure 2 together with those of liquid Ge and liquid Sn. The characteristic feature of $S(Q)$ of liquid Ge remains to be present in the $S(Q)$ of liquid Ge-Sn alloy, in which the shoulder shape was observed at the high Q side of the first peak of $S(Q)$. The temperature dependence of $S(Q)$ of Ge-Sn is not so large. However, the height of first peak decreases slightly with increasing the temperature.

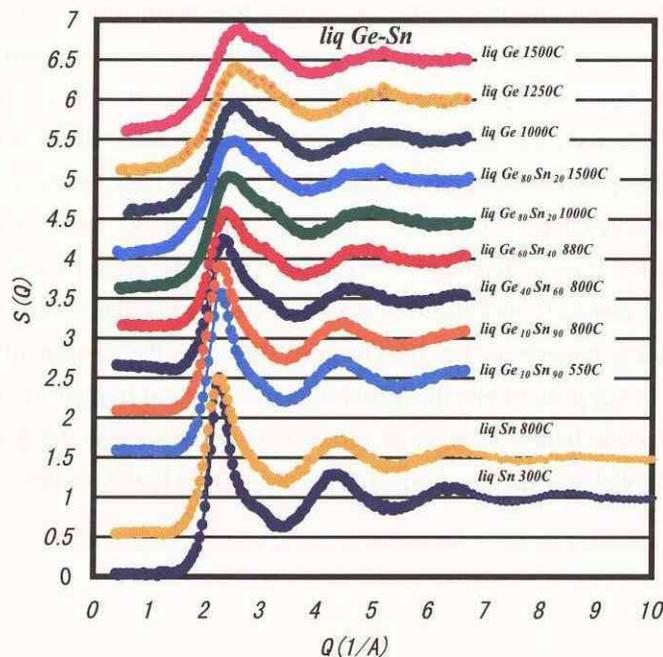


Figure 2 Static structure factor of liquid Ge-Sn alloys

3.2 Static structure of liquid germanium-silicon alloys

The $S(Q)$ of liquid Ge-50 atmic%Si was measured by using the neutron scattering technique at the temperature of 1583 K. The obtained $S(Q)$ was shown in figure 3. The shoulder of $S(Q)$ was clearly observed for the liquid Ge-Si alloy. This particular feature of $S(Q)$ for liquid Ge-Si alloy is same as that of liquid Ge.

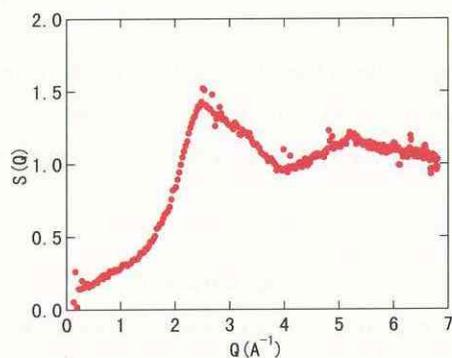


Figure 3 Static structure factor of liquid Ge-50 atmic% Si

4. Summary

The liquid structures of Ge-Sn alloys and Ge-Si alloy were measured by using the neutron scattering technique. The glassy carbon can be applicable for the crucible materials for neutron scattering experiments of reactive materials at high temperature. The shoulder of the first peak of $S(Q)$ was able to be observed in both liquid Ge-Sn alloys and liquid Ge-Si ones.

Reference

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Development of levitation technique for the liquid structure analysis

by

Tadahiko Masaki¹, Takehiko Ishikawa¹, Paul-Francois Paradis¹ and Toshio Itami¹

Abstract: The containerless technique is one of the latest methods for the handling of matters at high temperature and in undercooled liquid states. In this research project, the electrostatic levitation technique has been applied to the structural analysis of liquids by using the neutron and X-ray scattering techniques. The current status of this subject is described briefly.

1. Background

Nowadays, many attentions have been focused on the containerless techniques for the experimental research of high temperature melts or deeply undercooling liquids, especially for the structure analysis by neutron or X-ray scattering method. Recently, JAXA has been developing a droplet levitation technique due to the electrostatic force either for the microgravity experiments in the international space station or for the normal gravity experiments in a laboratory on the ground. Since this technique has merits for neutron scattering experiments, JAXA and Japan Atomic Energy Research Institute, JAERI, are developing the electro-static levitation furnace (ESL) for neutron scattering experiments of extremely high temperature melts and deeply undercooled liquids. In the last year, the basic model of ESL was developed and its applicability was verified through the neutron scattering measurements for sintered alumina levitated at room temperature. The levitation of sample was able to be kept for 11 hours. In this “cold” experiment, the diffraction peak of alumina was clearly observed without any other diffraction peak in the background [1].

2. Research activity in 2003

In this year, the actual performance of ESL for high temperature melts was verified as “hot” experiment. The facility configuration was same as that of “cold” experiment except for the sample heating system. In order to heat the levitated sample the CO₂ laser was installed in the facility. The heating laser, which was irradiated to the sample through the ZnSe optical window, was placed on the top of vacuum chamber. Zirconium was selected



Figure 1 Liquid zirconium at the temperature of 2500 K.

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as a test material of levitation system for the “hot” experiment because zirconium is one of the most suitable materials for keeping the levitation in long duration. The “hot” experiment was succeeded in keeping the levitated molten zirconium for 11 hours. Figure 1 shows the levitated liquid zirconium at 2500K. It can be seen that the levitation method provides the nearly spherical sample for which the data correction, for example the correction of absorption, can be easily performed on the diffraction data analysis. Since the sample size of 2 mm diameter was rather small, the counted scattering intensity from levitated sample was not sufficient within the duration of levitation in this experiment. As the next step, the experiments of much longer duration of levitation will be tried in order to obtain the scattering data.

3. Analysis of correction factors of spherical samples for scattering experiments

3.1 Correction factor of absorption

The correction of absorption is one of the most important factors to obtain the $S(Q)$ from the intensities of scattered neutron. The exact value of correction factors can be evaluated for the spherical shape such as the a sample of electro-static levitation. The correction factor is written in the following equation.

$$A = \frac{1}{V} \int \exp(-\mu T) dV, \quad (1)$$

where V is a volume of sample, μ is a absorption coefficient of sample and T is the optical pass of X-ray or neutron.

Fortunately, the correction factor of spherical sample is tabulated in “International tables for crystallography Volume C” [2] because the spherical sample is usually used for the structural analysis of single crystal. The values of data correction can be evaluated from the interpolation of this table values as a function of the product of mass absorption coefficient, μ , (or scattering cross section) and radius of spherical sample, R . However, in this research project, the correction factors were numerically evaluated directory from equation (1) because this calculation scheme can be applied also to the evaluation of correction factors of multiple scattering, which is described in the next subsection. Figure 2 shows the obtained correction factor corresponding to $\mu R=1.0$ together with the data of Ref.2. These are in good agreement with each other. The difference between them is less than 1%. Unfortunately, the table provides the correction factors whose parameter, μR , is less than 3.0. With the use of the present evaluation scheme, the correction factors corresponding to the μR greater than 3.0 can be obtained if necessary in a further research.

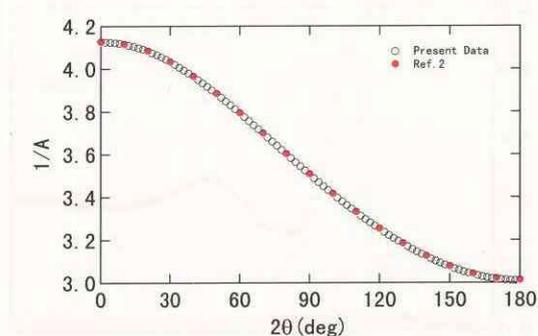


Figure 2 Correction factor of absorption for the spherical sample ($\mu R=1.0$)

3.2 Correction factor of multiple-scattering

In the case of neutron scattering experiments, the intensity of multiple scattering is not negligibly small though it is not so large. Some of previous researchers have published the correction factor of multiple scattering. However, those were the correction factors corresponding to a cylindrical or slab shape sample, which is popular for the conventional scattering experiment of liquid matters.

In this research project, the correction factors of spherical samples were evaluated for the preparation of further research. As the first step, the numerical simulation was performed based on the model liquid whose structure factor, $S(Q)$, was assumed to be hard sphere one.

The scattering intensity, dI , of volume element, dv , in a spherical sample is described as follows:

$$dI = s(2\theta) a dv, \quad (2)$$

where $s(2\theta)$ is scattering factor of 2θ and a is the atomic scattering factor.

The intensity of singlet scattering, I_{single} , can be obtained from the sum of dI with the factor of sample absorption, $\exp(-\mu l)$, along the path of beam, l , as follows:

$$I_{\text{single}} = \int s(2\theta) a \exp(-\mu l) dv. \quad (3)$$

In the case of doublet scattering, the intensity can be obtained from the sum of the twice of singlet scattering at the different volume element. The absorption by sample should be also taken into account similarly to the calculation of singlet scattering, as follows:

$$I_{\text{double}} = \iint s_1(2\theta) s_2(2\theta) a^2 \exp(-\mu l) dv_1 dv_2. \quad (4)$$

In this model calculation, the atomic scattering factor was assumed to be same as that of zirconium and the structure factor assumed was the analytical solution of hard sphere fluid derived from Percus-Yevick model. Figure 3 shows the scattering intensity of singlet and doublet scattering obtained from this numerical analysis. The intensity of doublet scattering is small. Therefore, the scale of doublet scattering is multiplied by 100 in this figure. The angular dependence of doublet scattering is almost constant. The intensity of doublet scattering is less than 1% of coherent scattering intensity at high Q region.

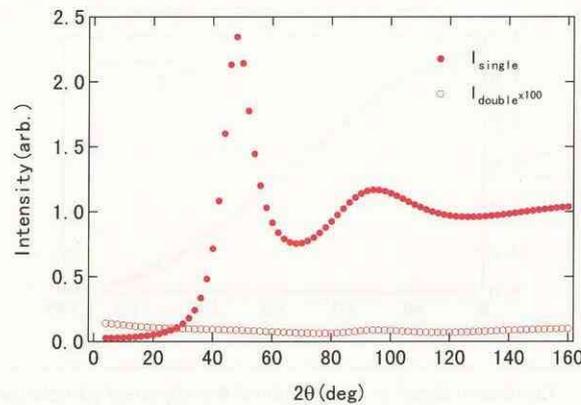


Figure 3 Intensity of singlet and doublet scattering

4. Summary

The neutron scattering experiment of liquid Zr was performed with the use of the electrostatic levitation method. The levitation of liquid Zr continued for 11 hours. However, the obtained scattering intensity was not sufficiently strong because of the small sample size. The correction factors due to respectively the absorption and multiple scattering of model fluid were evaluated in numerical way for the preparation of future further researches.

Reference

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- [2] "International Tables for Crystallography" Volume C, Kluwer Academic Pub. (1999).

Thermophysical properties of germanium and its alloys in liquid states related to the modeling of diffusion phenomena

by

Tadahiko Masaki¹ and Toshio Itami¹

Abstract: Thermophysical properties of liquid metals, such as the density, the viscosity and the compressibility, are necessary for the modeling of diffusion phenomena in liquid germanium alloys. These properties were investigated by several kinds of experimental method and have been accumulated as the database of thermophysical properties.

1. Introduction

Thermophysical properties give us important clues and essential information for the modeling of diffusion in liquid metals. Especially, the density, viscosity and compressibility are necessary to consider the relation between diffusion phenomena and liquid structures. In this project, these properties have been investigated in experimental studies by ourselves and obtained data have been distributed to the part of theoretical analysis of diffusion phenomena in our project. In this section, the latest data of these properties are shown briefly. The details of each measurement technique can be referred to the previous report of our research project [1].

2. Thermophysical properties of liquid germanium alloys

2.1 Density

Density is one of the most fundamental properties of matter. However, in the case of high temperature melts, it is difficult to measure the density with high accuracy because of the high chemical reactivity of high temperature melts to crucible materials and the limitation of observation ways. A gamma ray attenuation technique is one of the best ways for the measurement of density of metallic melts if the good crucible materials can be selected. The fused silica has been used for a crucible material of gamma ray attenuation techniques at the temperature less than 1500K. The glassy carbon was applied as a crucible material to several kinds of experiments and it is a good candidate of crucible material for the gamma ray attenuation method. In this project, the understanding of diffusion coefficient in the wide temperature range is a most important subject. Therefore, JAXA collaborated on the measurements of the density of liquid germanium alloys at the temperature higher than 1500K with Prof. Tsuchiya (Niigata University) who is the specialist of density measurements with the use of gamma ray attenuation method. Up to now, the new furnace for the high temperature experiments has been constructed and test run is in progress. Prior to the experiment at the temperature higher than 1500K, densities of Ge-Sn and Ge-Si alloys at the temperature lower than 1500K have been measured with the use of fused silica crucible. The results are shown in figure 1 and figure 2. The data reflect to the theoretical analysis and computer simulations those are described in previously.

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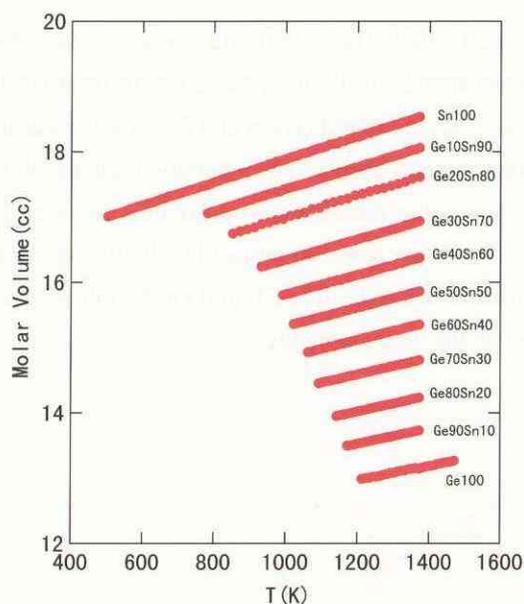


Figure 1 Molar volume of liquid Ge-Sn alloy

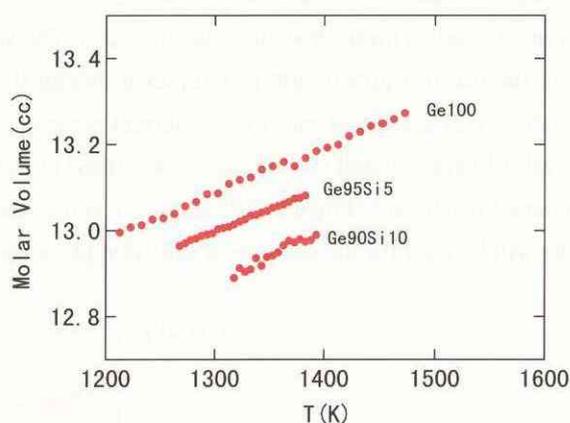


Figure 2 Molar volume of liquid Ge-Si alloy

2.2 Viscosity

Viscosity of liquid matter is derived from the momentum transport of atoms. It is well known that the viscosity coefficient can be related to the diffusion coefficient through the Stokes-Einstein equation. In this project, the viscosity coefficient of liquid germanium and its alloys were measured with the use of oscillating cup method. The details of this method have been described already in previous reports of our research project [1]. Therefore, the current results are shown in this report. Figure 3 shows the viscosity coefficient of Ge-3 atomic%Si and Ge-3 atomic%Sn. On the addition of Sn or Ge, the viscosity coefficients are increased compared to the case of the pure germanium.

Currently, the concentration dependence of viscosity coefficients of liquid Ge-Sn and liquid Ge-Si has been tried to be measured. In the near future, the detailed analysis will be performed about the relation between the viscosity coefficients and diffusion coefficients.

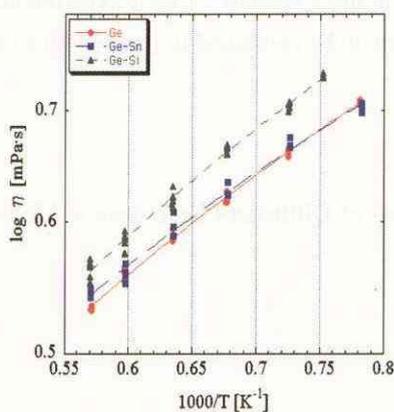


Figure 3 Viscosity of molten Ge and Ge alloys

2.3 Compressibility

The isothermal compressibility is important for theoretical calculations of liquid properties based on the liquid structure because the isothermal compressibility corresponds to the long wave length limit (or the thermodynamics limit) of static structure factor. The velocities of sound in liquid Ge-Sn and Ge-Si was measured with the use of transmission techniques to obtain the adiabatic compressibility. The adiabatic compressibility obtained was converted into the isothermal compressibility by using the standard thermodynamic relation. The details of experimental facilities were described in previous reports of our research project [1]. In this report, the obtained results are shown briefly. Figure 4 shows the isothermal compressibility of liquid Ge-Sn alloys. These data will be used for the analysis of diffusion phenomena based on the liquid structures.

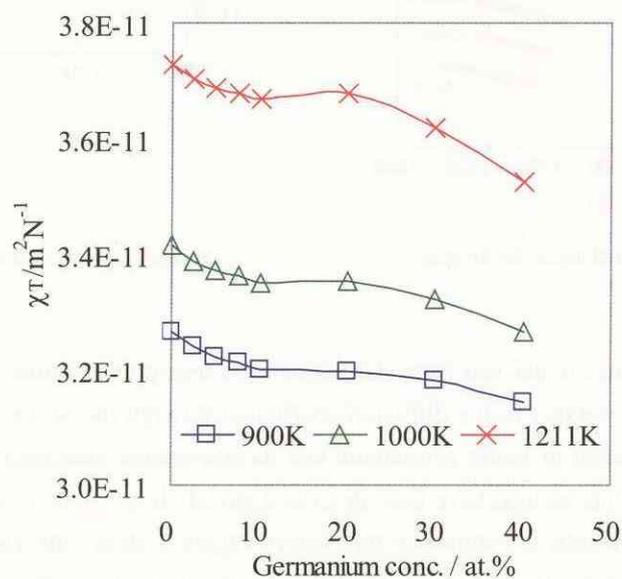


Figure 4 Isothermal compressibility of liquid Ge-Sn alloys

3. Summary

The thermophysical properties of liquid metals with high accuracy are important for the theoretical researches. However, it is hard to obtain these because of their experimental difficulty. In this project, efforts for the measurements of these properties are to be continued in future with a close relation to the theoretical research of diffusion phenomena.

Reference

- [1] "Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity" Annual Reports 2002, NASDA-TMR-030005E.

Part B. Approach to Accurate Measurements of
Diffusion Coefficients in Melts

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

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and Toshio ITAMI¹

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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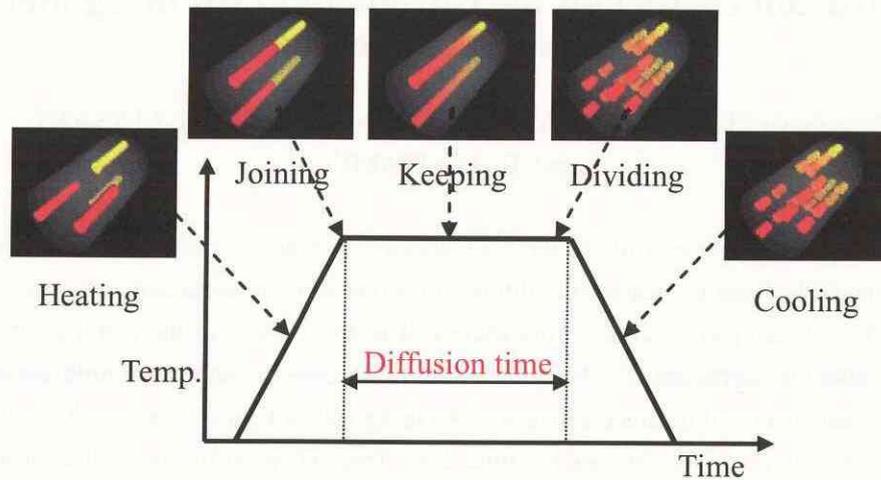


Fig.1 Shear cell method

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 $50\mu\text{m}$. 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 an 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.

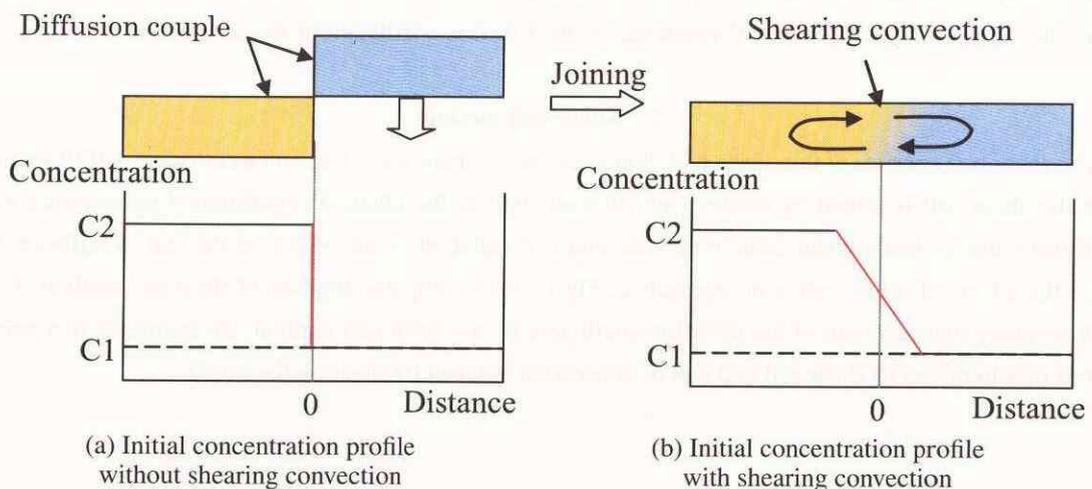


Fig.2 Initial concentration profile of diffusion couple

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 $3.14 \times 10^{-9} \text{ m}^2/\text{sec}$.

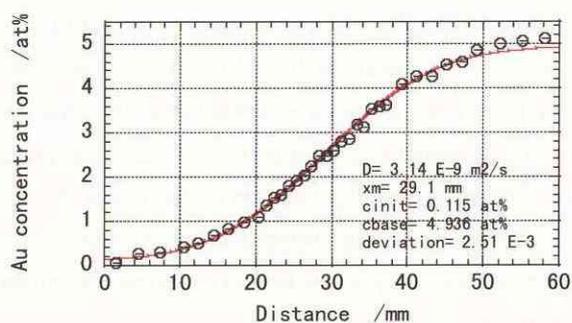
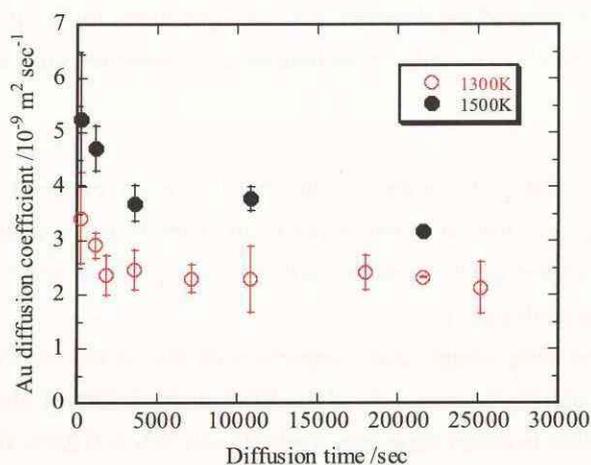
**Fig.3** Concentration profile of Au in Ag melt

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 $2.24 \pm 0.23 \times 10^{-9} \text{ m}^2/\text{sec}$ at 1300K and $3.37 \pm 0.36 \times 10^{-9} \text{ m}^2/\text{sec}$ 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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The reference experiment for the IAO plan

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and Toshio Itami²

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.

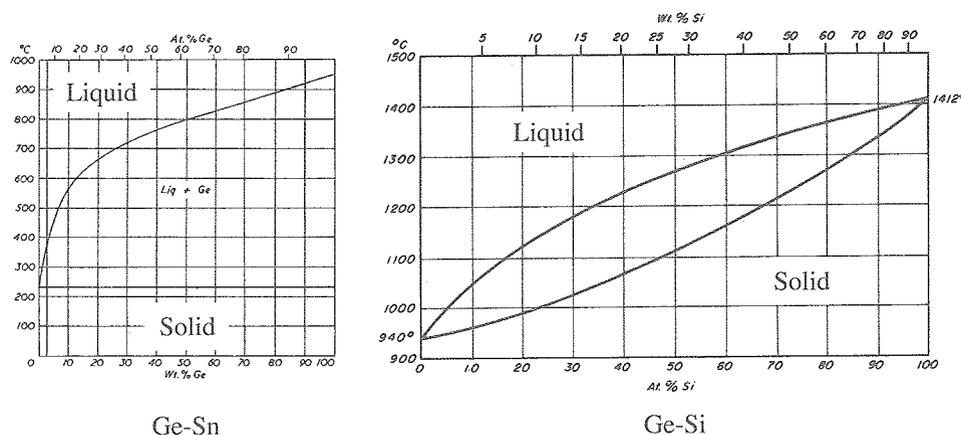


Fig.1 Phase diagram of Ge alloys.

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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 $\text{Ge}_{0.05}\text{Sn}$ sample ($\phi 1\text{mm}$ -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.

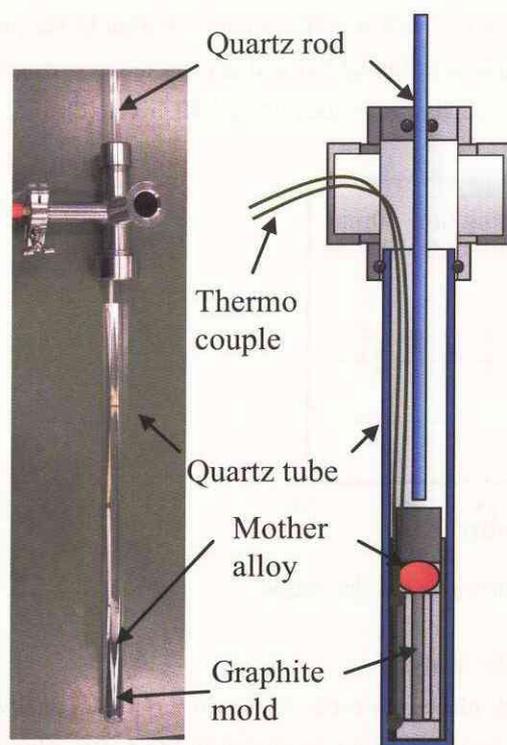


Fig.2 Casting system

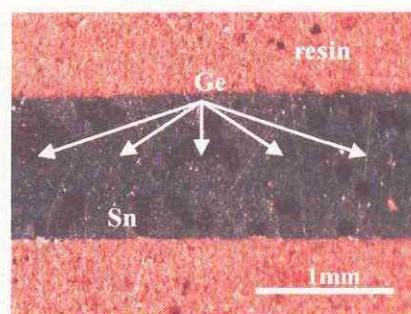


Fig.3 Section of sample
(cooling rate: 9.7 K/sec.)

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.

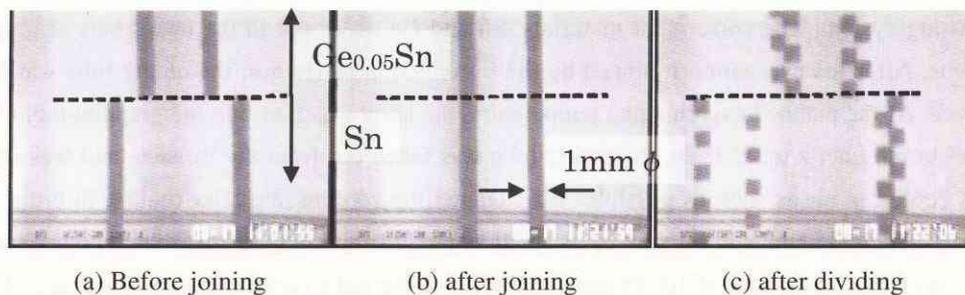


Fig.4 X-ray images of the shear cell operation

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).

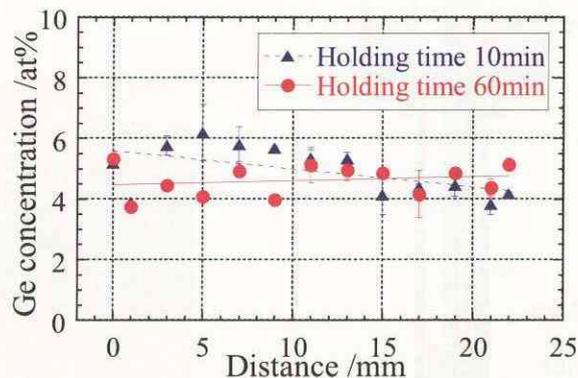


Fig 5 Ge concentration profile before joining the diffusion couple

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.

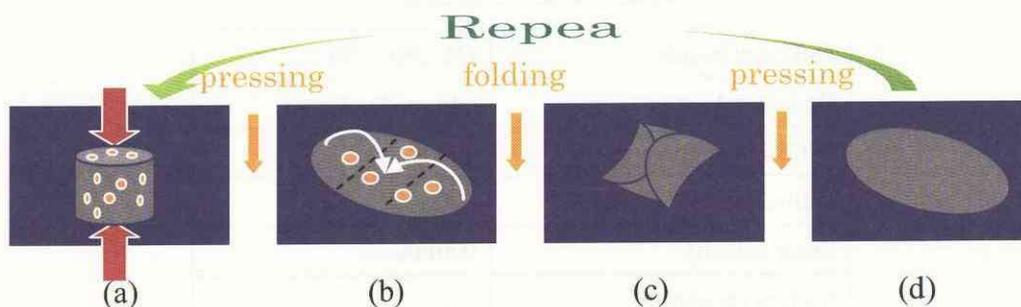


Fig.6 Pressing and folding method for the concentration analysis

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 $\Delta N \geq 10$. Therefore, the analysis of Ge concentration was performed after 10 times of pressing and folding.

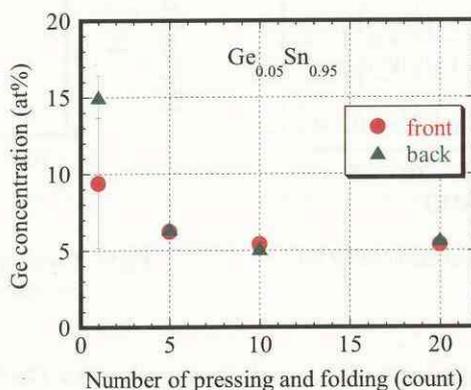


Fig.7 The dependence of Ge concentration on the number of pressing and folding.

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 $1.47 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ 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 $\pm 10\%$.

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

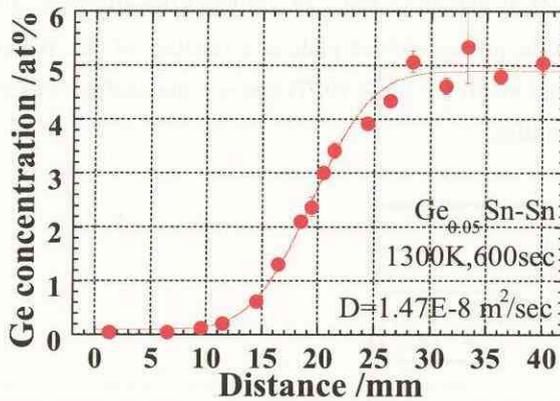


Fig.8 The concentration distribution of Ge in liquid Sn

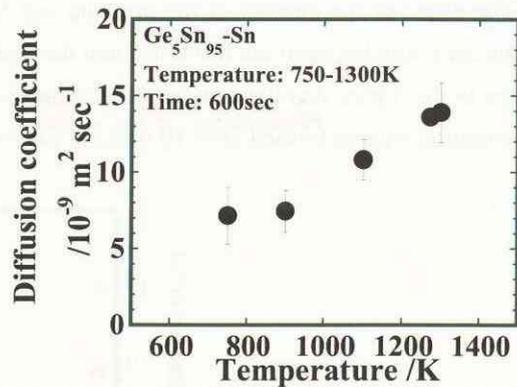


Fig.9 The temperature dependence of the diffusion coefficient

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.

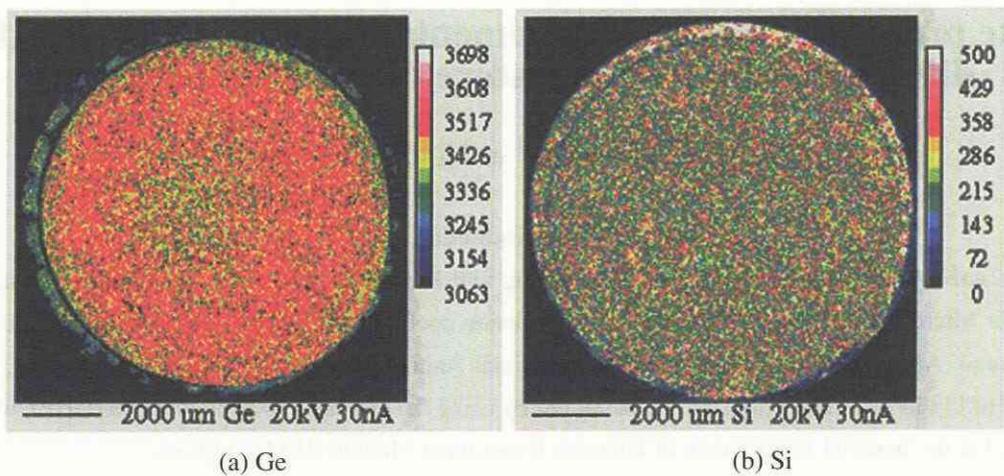


Fig.10 The obtained mapping image of EPMA for Ge and Si

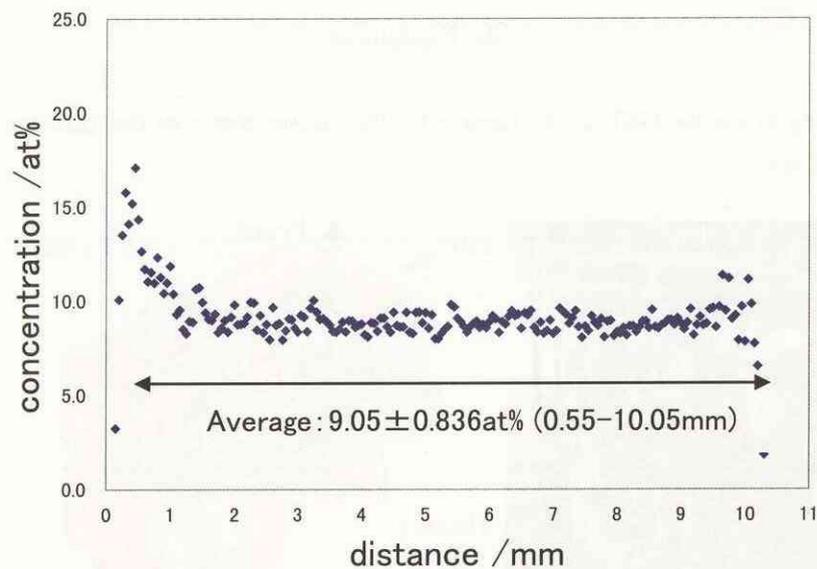


Fig.11 Si concentration in the pellet sample as a function of the distance from the surface along the diameter

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 $\text{Ge}_{0.05}\text{Sn}$ -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.

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The preparation of the experimental GHF cartridge for the diffusion in high temperature melts as an IAO plan

Tomoharu Fukazawa¹ and Tadahiko Masaki¹

1. Introduction

As an activity of the project of JAXA, “Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity”, we are measuring the diffusion coefficient of liquid alloys by the shear cell method on the ground. At present, as the first IAO (International Announcement of the Opportunity) plan, diffusion coefficient of liquid metals is planned to be measured by using the Gradient Heating Furnace (GHF), which is to be equipped in the material science rack of Japanese Experiment Module (JEM) in future.

We are advancing the trial preparation of the shear cell cartridge adapted to the GHF for the microgravity experiment in JEM.

2. Equipment

2.1 GHF-MP

We are planning to use the GHF as the furnace for the measurements of the diffusion coefficient under microgravity in ISS age.

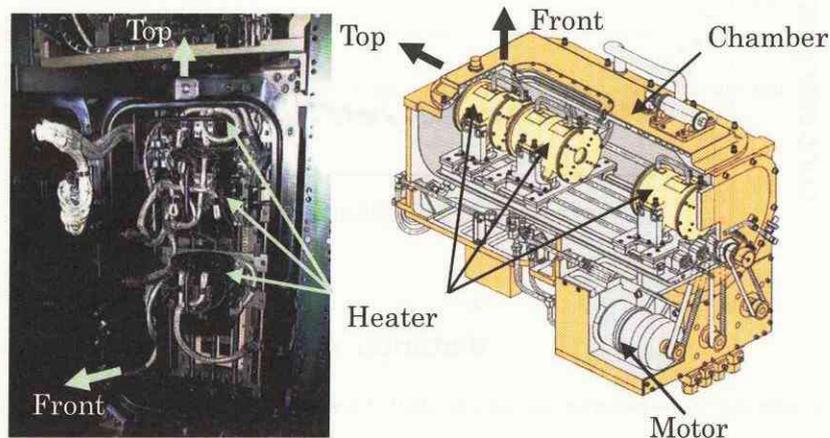


Fig.1 GHF-MP configuration

Fig.1 shows the schematic figure of GHF-MP, which is the experimental system for Material Processing by using the GHF. This system is composed of a 3-zone furnace and was originally planned to be used for the experiment under temperature gradient, such as crystal growth. Therefore, the experiment, which requires an isothermal condition like a diffusion experiment, has been out of targets. However, we investigated the relation between furnace configurations and a temperature distribution using the GHF (prototype model) currently installed in JAXA. As a result, it was concluded that an isothermal domain of $\pm 1.5^{\circ}\text{C}$ could be obtained in the range of sample length (60mm) at the temperature up to 1250°C .

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2.2 SCAM

In the JEM, the exchange of the sample cartridge for the experiment is to be performed automatically. Fig.2 shows the photograph and the schematic figure of SCAM, the system for Sample Cartridge Automatic exchange Mechanism, which is composed of magazine, robot arm, and cramp.

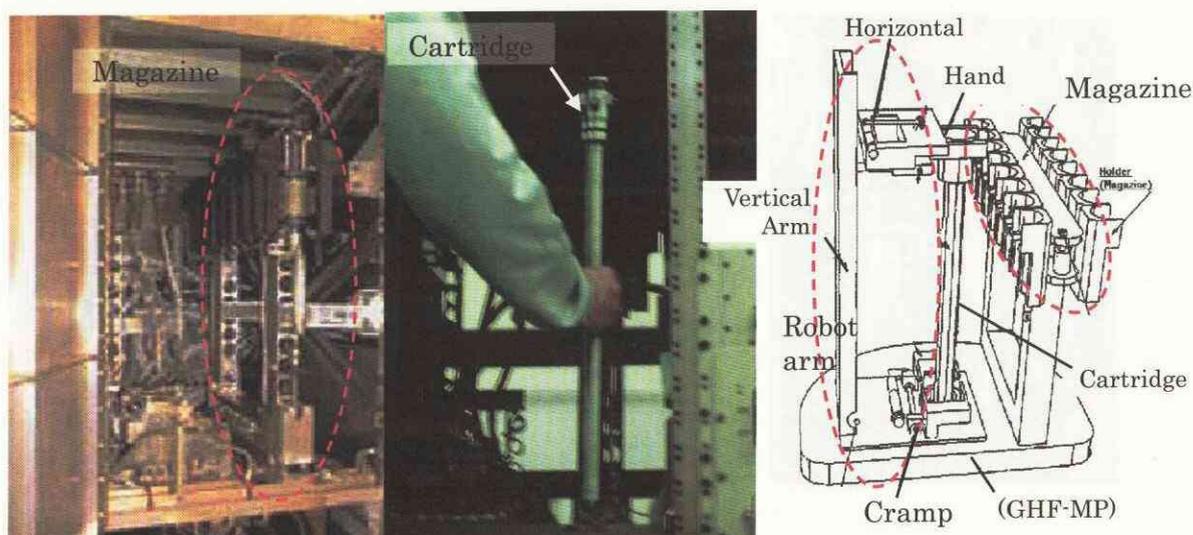


Fig.2 Photograph and schematic figure of SCAM

The magazine can store 15 sample cartridges (at the maximum). The arm is composed of vertical arm, horizontal arm and hand. They automatically exchange cartridges with the variation of experimental condition. Moreover, the cramp fixes the sample cartridge and seal off the GHF-MP.

3. Cartridge conditions for the GHF-MP

3.1 Sample configuration

The configuration of diffusion sample, for example that of the shearcell, is determined depending on the experimental condition of the cartridge configuration. The inside of the GHF-MP must keep vacuum to prevent the oxidation of heating elements. While, in the inside of the sample cartridge, it is necessary to keep at least one atmospheric pressure of inert gas to prevent the evaporation of sample. Therefore, the cartridge is constantly exposed to a pressure of more than one atmosphere. Thus, the minimum wall thickness of cartridge is determined by the condition that it may not be destroyed under such a pressure even at the maximum temperature of the GHF-MP.

3.2 Cartridge configuration

All cartridges used in the GHF-MP is handled by the SCAM. Therefore, the special cartridge for the shearcell should follow the cartridge condition for the SCAM. Moreover, it is necessary that the boss part of the cartridge must keep vacuum, because it is a sealing part of vacuum atmosphere of GHF-MP.

If the sample cartridge is incorporated with a new device, for example, “motor drive system” and/or “atmosphere control”, it is necessary for this special cartridge to be accommodated in the SCAM. Therefore, we examined in the SCAM the user area that should not interfere with the magazine and the arm movement of

SCAM. Fig.4 shows the photograph of the inside of the SCAM. The left side is robot arm to carry the sample cartridge and the other side is the magazine to store the sample cartridge. As a result, the left space becomes the area of the experiment sample. As can be seen in these photographs, the available area for users is the center part of the SCAM. The size of the user area is H:200mm×W:60mm×D:300mm.

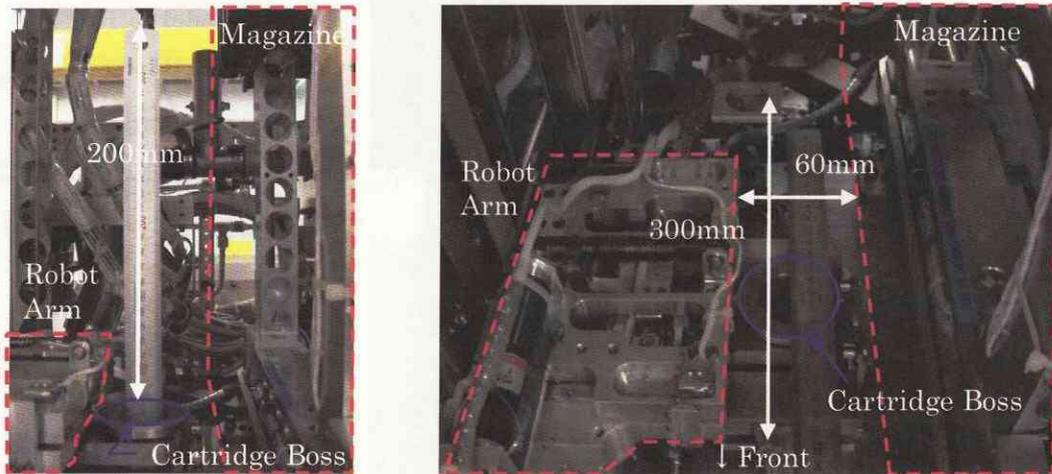


Fig.4 The inside of SCAM

4. Development of shearcell cartridge for GHF-MP

The measurement of diffusion coefficient is performed by the shearcell method. The shear cell method is known as one of most advanced techniques to measure a liquid diffusion coefficient accurately. This method is favorable for such Ge-Si and Ge-Sn systems which have a serious effect of solidification. A diffusion couple is only joined at the planned experimental temperature to avoid diffusion during heating and cooling, and is divided into many pieces to remove the effects of solidification. The shear cell consists of 60 disks with a hole, a rotation shaft, a key bar and a cartridge. To join or to divide a diffusion sample, a stepping motor rotates the rotation

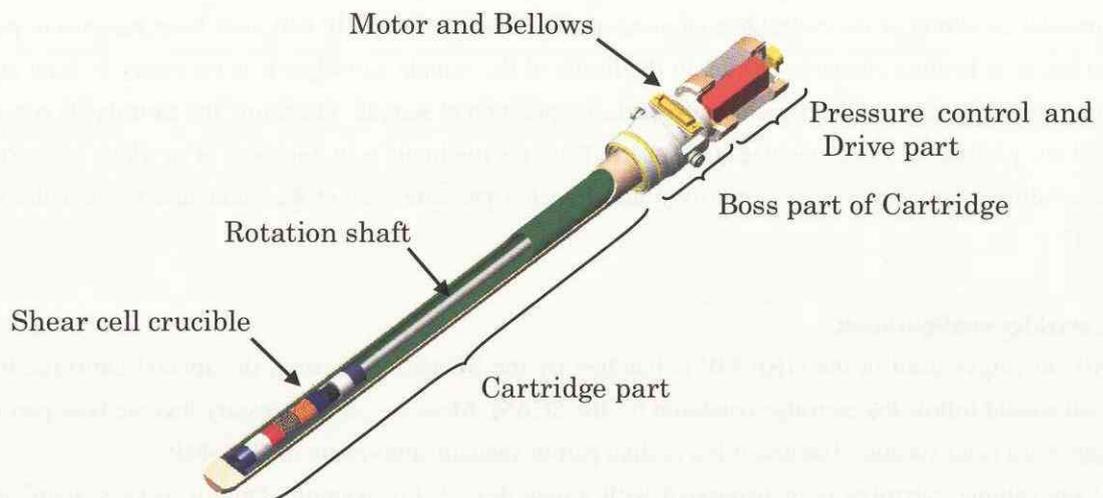


Fig.5 Shear cell cartridge for the GHF-MP

shaft, and the key bar controls the rotating angle of each disk. Therefore, the sample cartridge for the shear cell technique requires the rotation mechanism of the shear cell crucible, because the join and the cut of a liquid sample must be carried out at the experimental temperature. Moreover, the pressure inside the cartridge must be kept to be one atom.

Fig.5 shows the conceptual design of the shear cell cartridge for the GHF-MP. The sample cartridge of shear cell consists of cartridge part, boss part and pressure control part and drive part. The metal bellows was adopted on one end of the sample cartridge to control the atmosphere in the cartridge to be at one atom. Moreover, the drive part is included in the bellows. A small stepping motor, that can rotate the shear cell crucible, is selected (Fig.6).

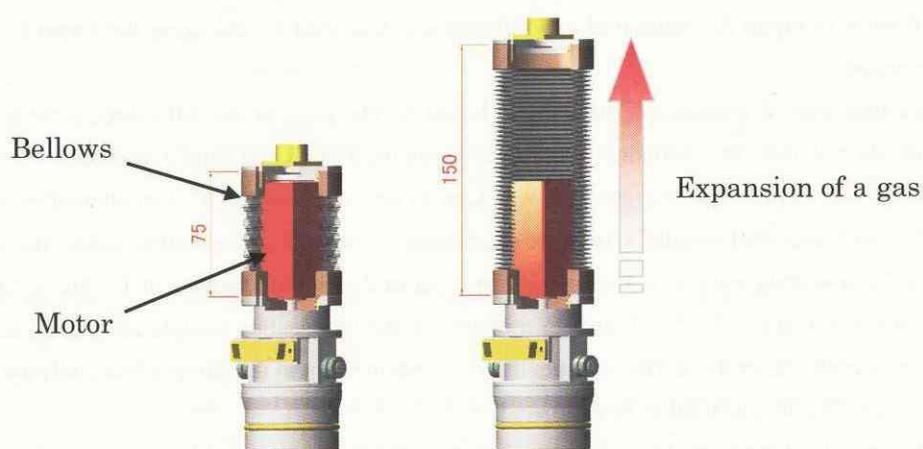


Fig.6 Pressure control and drive part

At present, we are advancing the trial preparation of the sample cartridge for the shear cell. In addition, we will perform the data acquisition on the ground by using the cartridge and GHF-MP described here for the coming ISS age.

Measurements of the impurity diffusion coefficient in liquid Si

by

Tadahiko Masaki¹ and Toshio Itami¹

It is very important for the control of the single crystal growth process to grasp the exact knowledge of the oxygen diffusion coefficient in liquid Si. The author has tried the experiments to obtain it. However, up to date, it has been very difficult to perform the exact experiments for the oxygen diffusion in liquid Si. With the collaboration with Prof. Terashima in Shonan Institute of Technology, JAXA has studying the experimental method of oxygen diffusion in liquid Si. In this report, to confirm the experimental method for the measurements of impurity diffusion in liquid Si, some trial experiments are described by changing the impurity species from oxygen to germanium.

For the measurements of germanium diffusion in liquid Si, two pairs of the diffusion couple were contained in the boron nitride crucible; the diffusion couple was composed of Si rod doped with Ge and that with low oxygen content. In one experiment, the crucible was kept to be vacuum ($\sim 2 \times 10^{-4}$ Torr) (hereafter, the sample in this case is called as "evacuated sample"). In other experiment, it was not sealed off (hereafter, the sample in this case is called as "non-sealing sample"). The crucible was set in the electric furnace at 1703K in Ar atmosphere. The diffusion time was taken to be 5, 15, and 45 minutes for the non-sealing sample and 5, 10, and 20 minutes for the evacuated sample. After the diffusion time, the Ge concentration in the sample was analyzed by the SIMS and the diffusion coefficient was tried to be estimated.

Among the non-sealing samples, only the sample of 15 minutes holding time looked sound. The concentration analysis of other samples was impossible because of the non-contact (5 minutes holding time) and the leakage of liquid sample (45 minutes holding time). Among the evacuated samples, only the sample of 5 minutes holding time looked sound. As for other samples (10 and 15 minutes holding time), it was impossible to determine the diffusion coefficient because of the homogeneity of concentration in the samples.

The diffusion coefficient of Ge in liquid Si may be estimated. However, at present there remain many problems in experiments of the impurity diffusion in liquid Si. Further improvements should be performed for the experimental condition.

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5. Appendix

Abstract

Publication List

Papers

1. T.Itami, S.Munejiri, T.Masaki, H.Aoki, Y.Ishii, T.Kamiyama, Y.Senda, F.Shimojo. and K.Hoshino: "Structure of liquid Sn over a wide temperature range from neutron scattering experiments and first-principles molecular dynamics simulation : A comparison to liquid Pb", *Phy. Rev.* **B67**(2003), 064201-11.
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