Measurement of diffusion coefficient of Au in liquid Ag due to the shear cell technique

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Abstract: Diffusion coefficients of Au in liquid Ag were measured carefully due to the diffusion couple method combined with the shear cell technique at the temperature of 1300 K and 1500 K. The shear cell was so-called modified long capillary crucible and is known to be the best method for the measurement of diffusion coefficient of liquids. The major cause of experimental error was derived from the liquid motion by the connection of liquid sample at the start of diffusion. In the present study, by changing the diffusion time from 300 seconds to seven hours, the time dependence of measured diffusion coefficient was clarified. The effects of the initial disturbance were sufficiently small in the case that the diffusion time was longer than 2 hours, for which the diffusion coefficient became independent on the diffusion time. The diffusion coefficient was compared with the theoretical value which was evaluated from the hard sphere mixture model.

Keywords: Shear Cell, Diffusion, Alloy, Hard sphere model

1. INTRODUCTION

Atomic transport properties are essential and significant to understand disordered condensed matters. Especially, diffusion phenomena play an important role of the reaction and the phase transition process relating to liquid materials. Therefore, the exact value is necessary not only for the understanding of condensed matter physics but also for the improvement of material processing due to numerical simulations, by which the optimization of condition can be obtained, for example, for the process of single crystal growth or the control of microscopic structure of casting. Many efforts have been devoted in order to obtain exactly the diffusion coefficient of liquids [1].

The diffusion couple method is one of the most popular methods for the measurement of diffusion coefficient, in which two pieces of different concentration are contacted as the diffusion sample. Each concentration in both pieces of the diffusion couple develops due to the diffusion, which should obey the Fick's diffusion equation. In the case of liquid sample, the concentration profile due to the diffusion is easily spoiled by the convection in the liquid sample. Therefore, the diffusion sample is contained in a narrow capillary in order to suppress it. This method is called as the long capillary method. Because of its simplicity and easiness for the experiments and for the numerical treatment of data analysis, this method is widely applied to the measurement of diffusion coefficients of liquids. Nevertheless, this long capillary method has some inherent defects for the measurement of diffusion coefficient with high precision. The worst point is excess diffusion; if the experimental temperature is much higher than the melting temperature of sample, the diffusion progresses during the heating and cooling stages. The second one is the bad effect of volume change on melting and solidifying sample. Most of materials change its volume on melting. Therefore, the concentration profile in liquid diffusion sample is spoiled by the fluid motion induced by the volume change. The third one is the segregation on the solidification of diffusion sample. This problem is restricted to alloy samples. Many kinds of alloys show the segregation on solidification. It makes difficult to obtain the concentration profiles of diffusion couple in the liquid state.

The shear cell method was innovated in order to remove these problems. If the two liquid columns can be joined into one liquid diffusion couple and be separated into many pieces at the experimental liquid temperature, it is not necessary to be bothered about these problems. Nachtrieb *et al.* [2] developed for the first time the shear cell for the measurement of self-diffusion coefficient of liquid mercury and

gallium. The shear cell was composed of thin stainless steel disks which can rotate co-axially. Around the center axis the disk possesses a few holes, into which the solid sample was contained. At the experimental temperature, with the rotation of each disk, the liquid sample can be joined into the diffusion couple at the start and separated into many pieces at the end. Barras *et al*. [3] measured the self-diffusion coefficient of liquid thallium. Bruson *et al*. [4, 5] measured the self- and impurity-diffusion of liquid tin in the wide temperature range. Yoda *et al*. [6] measured the self-diffusion coefficient of liquid tin by the refined shear cell method under the microgravity condition. Recently, shear cell method has been applied to molten semiconducting materials and liquid alloys, for example, molten GaSb [7] and aluminum impurity diffusion in liquid gallium and indium [8].

The sample diameters of previous shear cell experiments were typically 1.5 millimeter because of the feasible joining of liquid sample. It was somewhat large to prevent the convection under the normal gravity. Recently, many kinds of novel crucible materials have been developed. The precision of finishing of crucibles can be extremely improved enough to make the refined shear cell whose sample diameter can be less than 1 millimeter. The considerably precise measurement of diffusion coefficient can be performed even on the ground. In this paper, the feature of our shear cell is briefly introduced and the experimental results of the diffusion of Au in liquid Ag are described.

2. MEASUREMENT OF DIFFUSION COEFFICIENT OF AU-AG LIQUID ALLOY DUE TO THE SHEAR CELL METHOD

2.1 Shear cell assembly

In the shear cell, the liquid sample is contained in the long and narrow space in the same manner as the long capillary method. However, this space is composed of the pile of thin disk crucible with small sample holes, which are placed around the center of disk. In the shear cell assembly of the present study, the thickness of disk crucible and the diameter of sample hole were one millimeter respectively. The disk crucible was made of glassy carbon for which the fine machine work can be applied. The end crucibles, spacer and springs were made of sintered carbon. The center rod was made of mullite because of its low thermal conductivity. The diffusion sample, which was cast into the rod shape beforehand, were installed in the shear cell together with small carbon springs and carbon rods as can be seen in figure 1. Each sample of diffusion couple was placed on the separated position before the heating of sample. Liquid diffusion couple was formed and was divided by the rotation of center rod at the experimental temperature. All the shear cell assembly, a ceramic heater and three thermocouples, were covered by the sintered ceramic tube and were fixed on the fitting parts of the observation chamber which was equipped with a two directional X-ray radiography. The inside of observation chamber and that of ceramic tube were evacuated and were filled with high purity argon gas in order to prevent the oxidation of sample and crucible. The feasible joining and dividing of diffusion sample was confirmed by the use of X-ray radiography [9]. Figure 2 shows the X-ray image of diffusion sample in the shear cell. The misalignment of diffusion sample was regarded to be less than 0.1 millimeter which is smaller than the resolution of this X-ray radiography. The temperature of sample was measured by the use of three thermocouples which were installed beside the disk crucible. The temperature of upper part of diffusion couple was 5 K higher than that of lower part due to the optimization of the design of ceramic heater, the amount of thermal insulator and radiation foil around the shear cell assembly.

2.2 Measurement of diffusion coefficient of Au in liquid Ag

For the measurement of diffusion of Au in liquid Ag, the diffusion couple was prepared between pure Ag and $Au_{0.05}Ag_{0.95}$. Each material was cased into the graphite crucible and was formed into a narrow rod shape which was one millimeter diameter and 30 millimeter length. Both end faces of diffusion samples were finished with the use of optical fiber polisher. The samples were installed into the shear cell which was described in the sub-section 2.2.

The diffusion coefficients were measured at 1300K, which was 56 K higher than the liquidus temperature, and 1500K. The diffusion time, i.e. from the time of joining into the diffusion couple to that of dividing it, was varied from 300 seconds to 25200 seconds (seven hours) in order to clarify the influence of liquid joining at the start of diffusion. After the diffusion experiments, the shape of each divided sample was changed into thin plate of about 8mm diameter by the repetition of pressing and folding for the measurement of average concentration of overall piece by the X-ray fluorescence analysis.
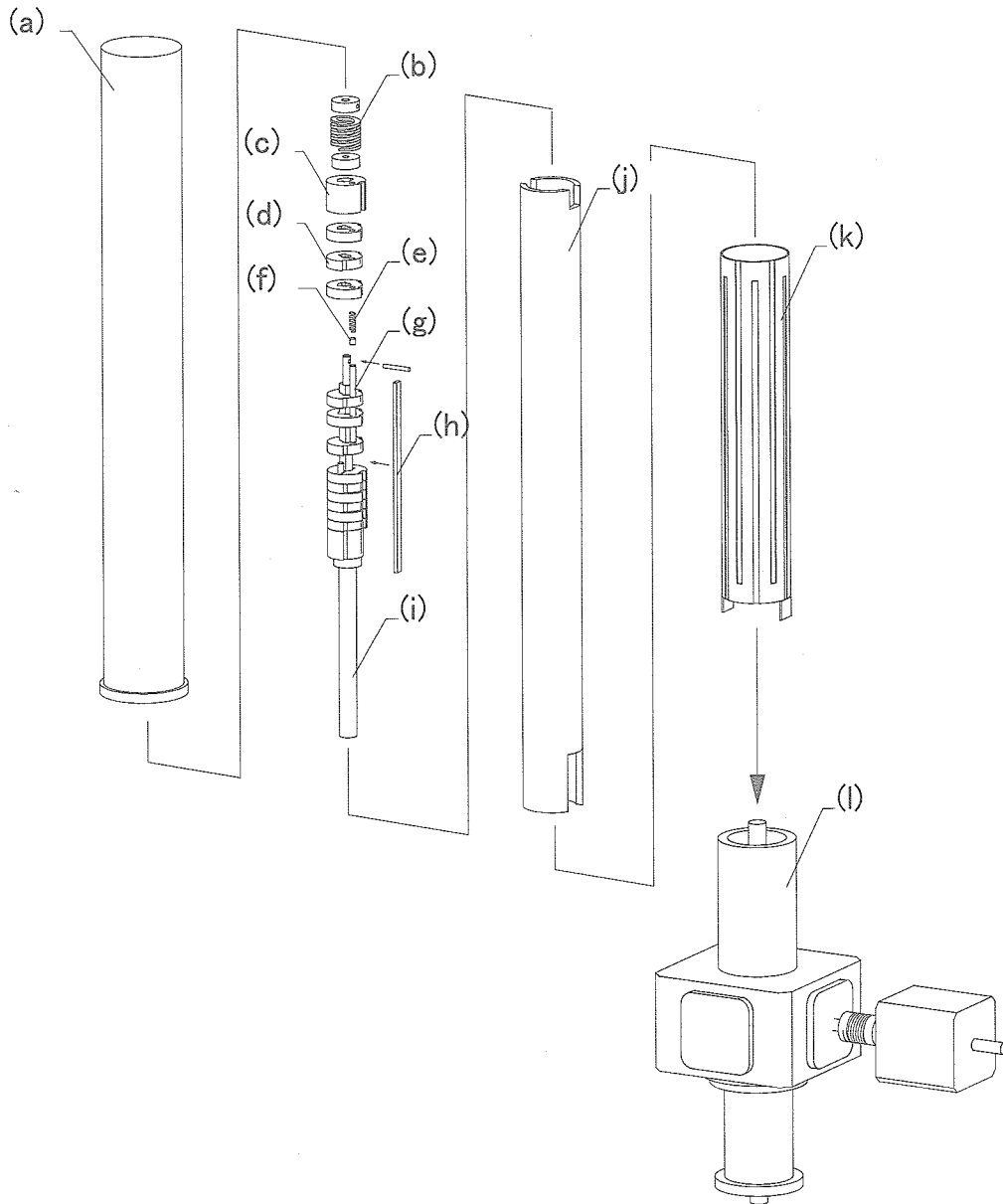
Fig. 1 Shear cell assembly.
(a) ceramic tube; (b)graphite spring; (c)end part; (d)disk crucible; (e) graphite spring; (f) graphite rod; (g) diffusion sample; (h) stop bar; (i) center rod; (j) spacer; (k) ceramic heater; (l) fitting part of observation chamber
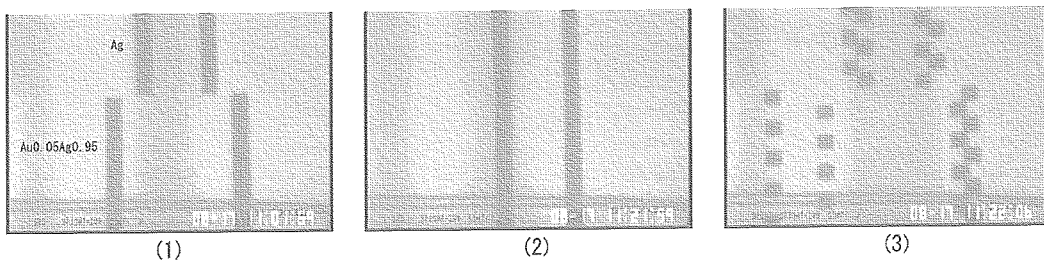

Fig. 2 X-ray image of diffusion sample.
(1): Before joining; (2): Connected; (3): Divided.

3. THE DATA ANALYSIS AND THE EXPERIMENTAL RESULTS

The concentration profile of Au in the sample should obey the error function, which is the analytical solution of the diffusion equation for the present diffusion couple and is given as follows:

$$\frac{2(c\,(x,t) - c_1}{c_2 - c_1} = 1 - Erf\,(Y).\tag{1}$$

In this equation, c_1 and c_2 are the concentrations of each piece of the diffusion couple at the start of diffusion. The error function, Erf, is defined as follows:

$$Erf\,(Y) = \frac{2}{\sqrt{\pi}} \int_0^Y \exp\,(-y^2)dy \tag{2}$$

The concentration profiles obtained from experiments were in good agreement with equation (2). The typical experimental result is shown in figure 3. The diffusion coefficient of Au in liquid Ag was evaluated by the least square fitting of experimental data to this analytical solution (equation (1)). The diffusion coefficients obtained were strongly depended on the duration of diffusion, as can be seen in figure 4. The observed diffusion coefficient decreased with increasing the duration of diffusion at both 1300 K and 1500K. From the in situ observation of fluid flow in the model experiment by the use of transparent materials [10], the small amount of liquid is found to be exchanged at the interface of the diffusion couple due to the liquid joining at the start of diffusion. However, the disturbance by the liquid joining becomes negligibly small if the duration of diffusion is sufficiently long, as can be seen figure 3. In the present experiment, the diffusion coefficients were adopted from the diffusion experiments whose durations of diffusion were 21600 second. The diffusion coefficients of Au in liquid Ag are obtained as $2.30 \times 10^{-5}\,cm/s^2$ at 1300K and $3.16 \times 10^{-5}\,cm/s^2$ at 1500K.
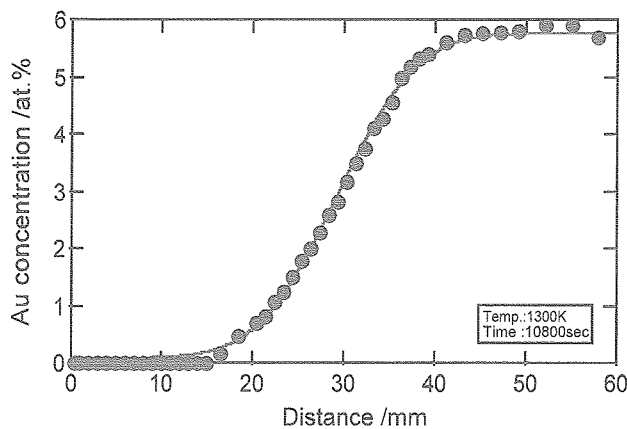

Fig. 3   Diffusion profile of Ag- $Au_{0.05}Ag_{0.95}$ diffusion couple.
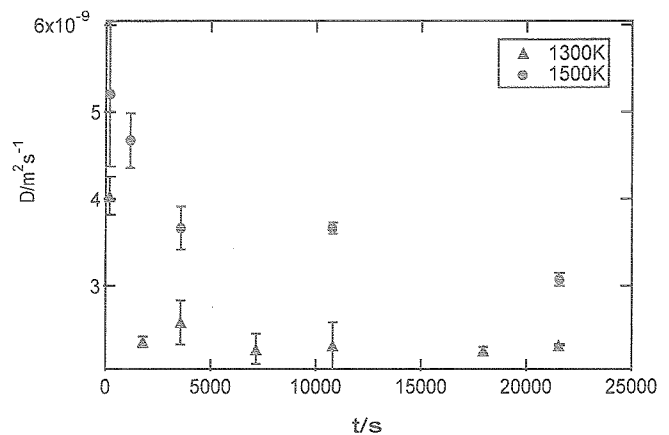

Fig. 4   The diffusion time dependence of diffusion coefficient measured by using the shear cell method.

4. DISCUSSION

The Ag, Au and these alloys are familiar materials for the experiments of liquid metals. However, the self and mutual diffusion coefficient of these systems have not always been measured frequently. In the case of Ag-Au liquid alloys, Gupta [11] published the diffusion coefficients at the temperatures between 1253 K and 1533K. The diffusion coefficients of present work are slightly lower than Gupta's data. The cause of experimental errors in the previous long capillary method, i.e. the undesirable diffusion on heating and cooling process and the segregation on solidification, may tend to increase the measured diffusion coefficient. The shear cell method adopted here is advantageous for the removal of these errors. In the present experimental configuration, the density of liquid silver in the upper position is lighter than that of Ag-Au alloy in the lower one. Additionally, the temperature of upper part was kept to be about five degrees higher than that of

lower part in order to prevent the convention. The present configuration can suppress the occurrence of the convection in the liquid sample.

The diffusion coefficient of Au in liquid Ag was estimated based on the hard sphere model coupled with the back scattering factor, C_{BS}, given by Protopapas and Parlee [12] and compared with the present experimental results. The diffusion coefficient of a dense binary fluid, D_{HS}, is given as follows;

$$D_{HS} = C_{BS}D_{ENS}.$$ (3)

The back scattering factor, C_{BS}, represents the many body effect of dense fluid. In this equation, D_{ENS} is described by the following equation.

$$D_{ENS} = D_{12,g} / g_{12}(\sigma_{12}),$$ (4)

where $D_{12,g}$ is the diffusion coefficient of dilute state of mixture whose components are solute 1 and solvent 2. In the case of hard sphere interatomic potential, $D_{12,g}$ is written as follows;

$$D_{12,g} = \frac{3}{8n\sigma_{12}^2} \left\{ \frac{k_B T(m_1 + m_2)}{2\pi m_1 m_2} \right\},$$ (5)

where n is the total number density of mixture; σ_{12} is the mean hard sphere diameter of two components; mi is the atomic mass of component i, kB is Boltzman constant; T is the temperature of system. The notation, $g_{12}(\sigma_{12})$, in the equation (4) is the radial distribution function at the contact of different hard spheres. C_{BS} is evaluated from the ratio of the diffusion coefficients obtained from molecular dynamics simulations of hard sphere mixture, D_{HSMD}, to the D_{ENS}, as follows;

$$C_{BS} = D_{HSMD} / D_{ENS}.$$ (6)

Protopapas and Parlee [12] provided the numerical table of C_{BS} of hard sphere mixture, which can be available with the knowledge of the ratio of atomic mass and hard sphere diameter. In this calculation, values of C_{BS} for Ag-Au mixtures are evaluated by the interpolation of the table.

The temperature dependence of hard sphere diameter of pure metal is evaluated from following equation [12].

$$\sigma = 1.228M / d \{1 - 0.112) T / T_m)^{1/2}\},$$ (7)

where, M is the mass and d is the mass density at the melting point, T_m. For the calculation of diffusion coefficient of Ag-Au mixtures, it was assumed that the hard sphere diameters of Ag and Au in alloys were equal to those of the pure state respectively. The pure Au becomes solid at 1300K. Therefore, the values of density, d, and hard sphere diameter, σ, are estimated from the extrapolation of the respective temperature dependence at higher temperature than its melting point. The numerical values for this calculation and the diffusion coefficient obtained, D_{HS}, are shown in table 1. The hard sphere model is one of the simplest models for the treatment of liquid properties. Nevertheless, the D_{HS} are in good agreement with present experimental results. Pure Ag and pure Au in liquid state can be regarded as the simple hard sphere fluid based on the liquid structure analysis by Waseda [13]. Ag and Au belong to the same column of periodic table and

Table 1   The comparison of diffusion coefficient of Au in liquid Ag between calculations based on the hard sphere model and experiments.

T (K)	σ_{Ag} (cm)	σ_{Au} (cm)	C_{BS}	D_{HS} (cm²/s)	D_{exp} (cm²/s)
1300	2.579×10^{-8}	2.579×10^{-8}	0.6564	2.25×10^{-5}	2.30×10^{-5}
1500	2.556×10^{-8}	2.555×10^{-8}	0.7191	3.07×10^{-5}	3.16×10^{-5}

the charge transfer between Ag and Au in liquids might be small. As the zeroth approximation, the atomic transport properties of Au in liquid Ag can be regarded as the simple hard sphere mixtures. It is possible that this hard sphere model can be improved by taking account of the charge transfer effect and its concentration dependencies on the evaluation of C_{BS}. Such studies must be studied in future.

5. CONCLUSION

The diffusion coefficients of Au liquid in Ag were measured with the use of shear cell method at both 1300K and 1500K. The diffusion coefficient corresponding to the present experimental conditions were calculated by using the hard sphere mixture model. Diffusion coefficients of hard sphere model are in good agreement with the experimental data.

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