Solidification effects on liquid diffusion measurements due to long capillary method -Experiments -

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ABSTRACT

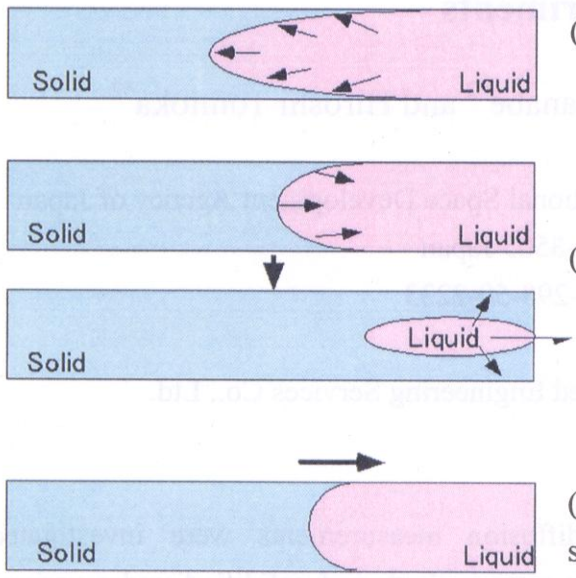
The solidification effects on liquid diffusion measurements were investigated experimentally. Diffusion couple samples were melted, and solidified under various cooling conditions. The concentration distributions were analyzed after solidification. It was found that the volume change effect can be avoided at low cooling rate and this condition is preferable for self- and impurity diffusion measurements, in which the segregation effect doesn't need to be considered. However, in order to avoid the segregation effect for mutual-diffusion measurements, diffusion measurements using the long capillary method should be conducted as follows: The diffusion sample must be cooled rapidly in order to avoid the segregation effect, and the concentration profile must be analyzed near the surface in order to avoid the volume change effect on solidification.

INTRODUCTION

The long capillary method is a simple method for diffusion measurements [1]. The samples of the diffusion couple are joined together from the start of the experiments to the end. The merit is its easy sample configuration, but the solidification effects on diffusion measurements must be investigated in detail. The concentration profile after the diffusion experiment may change because of the solidification effects. The reason can be considered as follows (Figure 1):

1. Solutal flow occurs because of the volume change ((a) and (b) in Figure 1).
2. The concentration changes because of the segregation ((c) in Figure 2).

Even for the self-diffusion measurements without the segregation, the solidification effects have to be taken into account because of the solutal flow by the volume change on solidification. The solidification experiments with various cooling conditions were performed in order to examine the solidification effects due to the volume change and to find the optimum cooling condition for long capillary diffusion experiments [2].



(a) Solutal flow occurred by shrinkage on solidification

(b) Solutal flow occurred by volume expansion on solidification

(c) Change of concentration profile due to segregation on directional solidification

Figure 1 Solidification effects on diffusion experiments due to change of the concentration profile

EXPERIMENTAL

A diffusion couple of Ag-$Ag_{0.95}Au_{0.05}$ was melted and kept at about 1250 K for a short period and solidified under various cooling conditions. Ag-Au system is completely miscible in both solid and liquid phases. In addition, the temperature width between the solidus and liquidus lines is narrow, as shown in Figure 2, and the dendritic solidification hardly occurs. This system is ideal for the solidification experiments to verify the solidification effects due to the volume change only. The EPMA analysis can be also applied with high resolution for Ag-Au system. The sample size was 1 mm diameter and 20 mm long as a diffusion couple (10 mm each). The melting points are 1234 K for Ag and 1243 K for Ag-$Ag_{0.95}Au_{0.05}$. The diffusion sample was kept just above the melting points for a short time to avoid the buoyancy

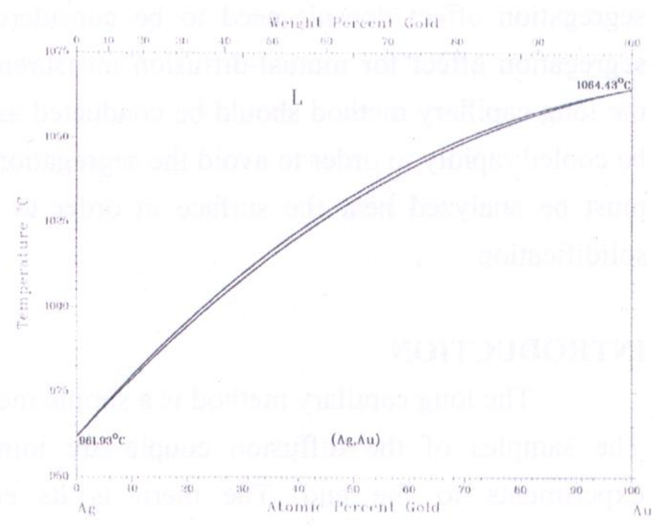


Figure 2 Phase diagram of the Ag-Au system [3]

convection. The sample was set in a graphite crucible, on which 9 thermocouples were put at the ends (top and bottom) and the center of the sample, as shown in Figure 3. Figure 4 shows the sample and the furnace configuration. The furnace moved down to heat the sample and moved up to cool it. This operation enabled us to keep the temperature of a sample to be lower at the bottom and higher at the top during the experiments in order to avoid the buoyancy convection. The cooling condition was varied depending on the height of the furnace. In cases that the furnace was completely removed from a sample, the top of the sample cooled rapidly and the temperature at the middle of the sample became the highest. Since the directional solidification from the bottom was planned to reduce the effect of convection, the top of the crucible was wrapped by glass wool for insulation, as shown in photograph 1.

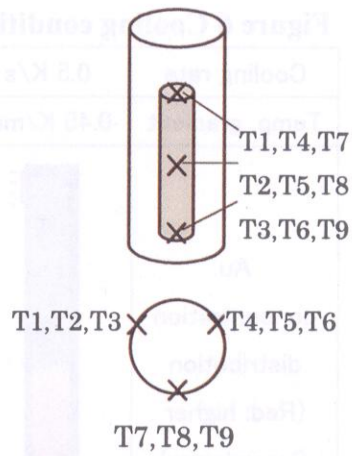


Figure 3 Position of the thermocouples put on a crucible

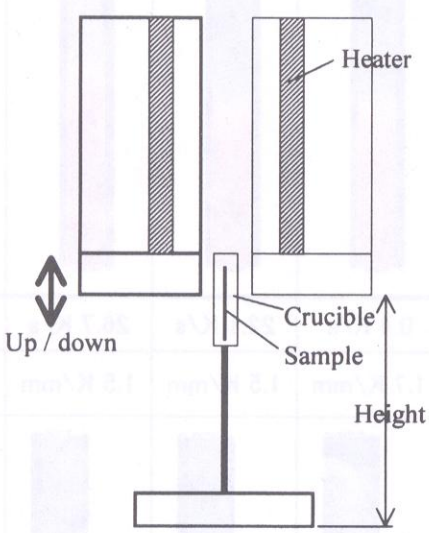
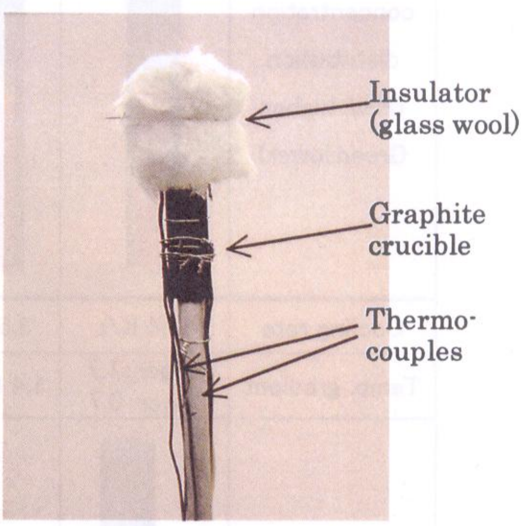


Figure 4 The configuration of sample and furnace



Photograph 1 Insulator to avoid solidifying from the top

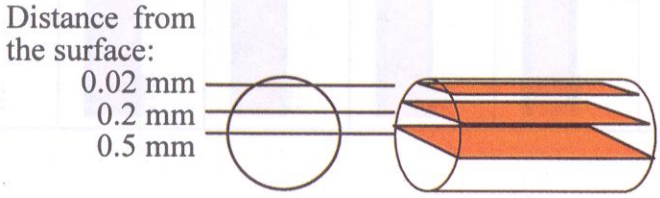
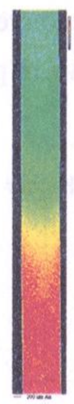


Figure 5 Analyzed planes for the EPMA in a solidification experiment sample

Figure 6 Cooling conditions and Au concentration profiles at the central plane

Cooling rate	0.5 K/s	4 K/s	12 K/s	18 K/s	20 K/s	5.7 K/s
Temp. gradient	0.45 K/mm	1.2 K/mm	2.0 K/mm	2.4 K/mm	4.2 K/mm	2.0 K/mm
Au concentration distribution (Red: higher Green:lower)						
Cooling rate	10.8 K/s	0.3 K/s	15.9 K/s	16.1 K/s	9.3 K/s	9.8 K/s
Temp. gradient	2.8 K/mm	0.2 K/mm	4.0 K/mm	4.0 K/mm	upper : 6.3 lower : 2.2	upper : 3.9 lower : 1.6
Au concentration distribution (Red: higher Green:lower)						
Cooling rate	13.4 K/s	3.5 K/s	0.4 K/s	22.1 K/s	26.7 K/s	26.6 K/s
Temp. gradient	upper : 1.7 lower : 0.7	1.4 K/mm	1.7 K/mm	1.5 K/mm	1.5 K/mm	1.9 K/mm
Au concentration distribution (Red: higher Green:lower)						

The sample was analyzed on three planes, about 0.02 mm, 0.2 mm and 0.5 mm from the surface by the EPMA (Electron Probe Microanalyzer), as shown in Figure 5.

RESULTS

Figure 6 shows the cooling conditions and the Au concentration distributions after the solidification experiments. The red and green part represents the higher and lower Au concentration, respectively. Even though $Ag_{0.95}Au_{0.05}$ is the concentration at which the solidus and the liquidus temperatures are almost the same in equilibrium state (the difference is 1 K), the dendritic structure was observed at higher Au concentration region. It can be considered that the temperature width between the solidus and liquidus lines may become larger in nonequilibrium state and the dendritic growth may occur.

In cases 106, 107 and 108, the temperature at the middle was higher than that at the top. In such cases, the concentration distributions didn't fit to Fick's second law, as shown in Fig.7. It may be caused by the convection or the solidification from both top and bottom sides (shrinkage to both sides).

From the observation of Fig.6, it was found that the isoconcentration line at the center was linear perpendicularly to the sample axis with a small cooling rate, and that it had a curvature with a larger cooling rate. Figure 8 shows a Au concentration region of about 280 +/- 10 counts, which represents the shape of the Au concentration distribution perpendicular to the sample axis. Figure 8(a) is the case of the sample No.103, which was solidified with low

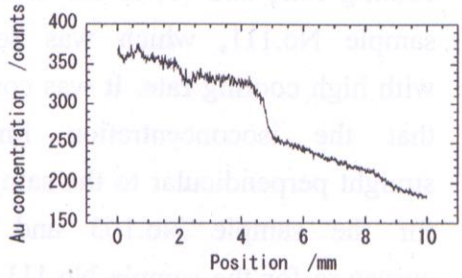
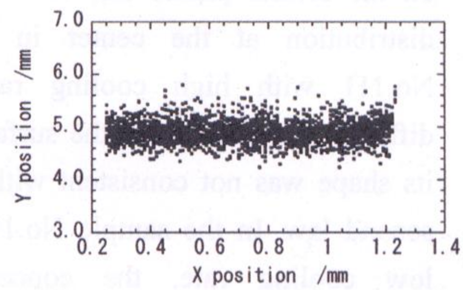
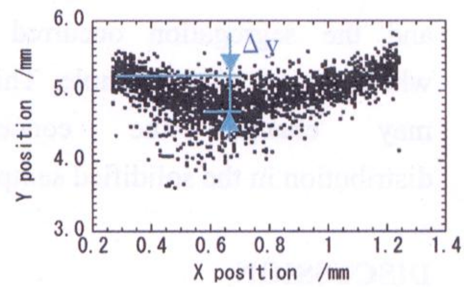


Figure 7 Au concentration distribution of the sample no.107



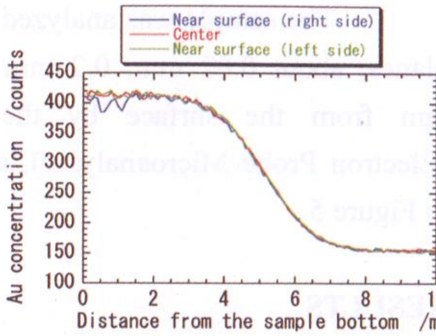
(a) Sample No.103 with low cooling rate and low temperature gradient (concentration of 282 +/- 10 counts)



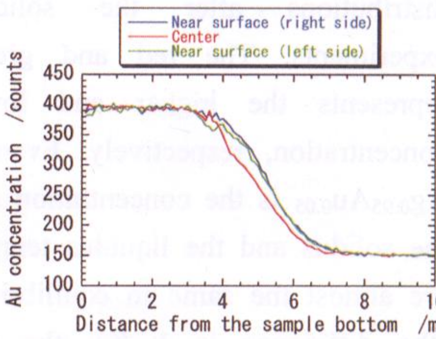
(b) Sample No.111 with high cooling rate (concentration of 272 +/- 10 counts)

Figure 8 Au concentration distribution shape around the central region (Y: parallel to the sample axis; X: perpendicular to it)

cooling rate, and (b) is the case of the sample No.111, which was solidified with high cooling rate. It was confirmed that the isoconcentration line was straight perpendicular to the sample axis for the sample No.103 and had a curvature for the sample No.111. Figure 9 shows the concentration distribution at the center and near the surface observed on the central plane. The concentration distribution at the center in sample No.111 with high cooling rate was different from that near the surface, and its shape was not consistent with Fick's second law. In the sample No.103 with low cooling rate, the concentration distribution at the center was almost the same as ones near the surface. However, in this case, the complete one directional solidification can be thought to occur, and the segregation occurred in the whole region of the sample. This effect may change the concentration distribution in the solidified sample from that in the melt.



(a) Sample No.103 with low cooling rate and low temperature gradient



(b) Sample No.111 with high cooling rate

Figure 9 Au concentration distributions at the center and near the surface observed on the central plane

DISCUSSION

Two kinds of factors on solidification can be considered as the influence upon the diffusion measurements. One is the segregation and the other is the volume change. Regarding to the segregation effect, the directional solidification should have the largest influence on diffusion measurements. In the Ag-Au system discussed in this paper, Au is ejected from the solid-liquid interface to the melt during solidification, and the concentration distribution may be changed from that in the melt. In this case, the Au concentration distribution is considered to be stretched and the diffusion coefficient obtained from this concentration distribution in the solidified sample may become larger than the real value, which should be calculated from the concentration distribution in the melt. The dendritic growth is preferable since the dendrites can preserve the Au segregation between the dendritic arms. But, in this case, the determination of the concentration should be carried out by averaging the concentrations in some wide area.

The effect of the volume change is closely related to the phenomena that the curved Au isoconcentration line appeared at the high cooling rate, as discussed above. The isoconcentration lines, for example shown in Fig.8, were evaluated from the y-position difference, Δy. Δy indicates the difference between the y position at the surface and that at the center, as shown in Fig. 8. Figure 10 shows the y-position difference, Δy, at various cooling conditions. For example, Δy was almost zero in the sample No.103 and about 0.6 mm in the sample No.111. It was confirmed that Δy was small at low cooling rate and large at high cooling rate. In the latter case, the concentration distribution at the central region may be compressed by the volume shrinkage and disturbed though it may be reliable near the surface. It was found that Δy was smaller at larger temperature gradient. This reason can be considered that the latent heat mainly transfers downward if the temperature gradient is large, and the isothermal line, which results in the isoconcentration line, becomes linear. On the other hand, if the temperature gradient is small, the latent heat transfers to the inside of the sample in addition to downward, and the temperature at the center becomes higher than that near the surface. Therefore, in this case, the isothermal line (the isoconcentration line) has a curvature.

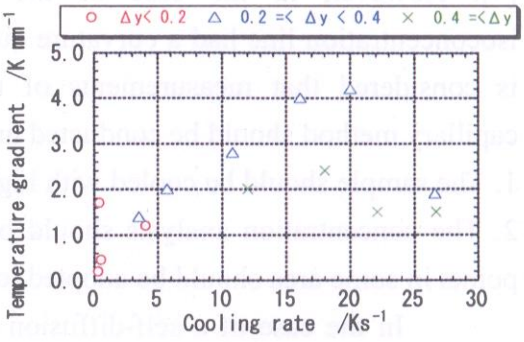


Figure 10 Shape of the Au concentration distribution at the central region related to the cooling

In this paper, the effects of solidification on liquid diffusion experiments were discussed through the solidification experiments with the volume shrinkage on solidifications. In the case of a self-diffusion experiment by using an isotope, the low cooling rate is preferable on solidification because the segregation doesn't appear. However, for the diffusion experiments with the volume expansion on solidification, the long capillary method should be avoided since too much serious volume effects exist even under slow cooling rate.

CONCLUSIONS

The solidification effects on diffusion measurements were examined by the solidification experiments with various cooling conditions. The concentration distributions after solidification were changed due to the segregation and the volume change. In order to avoid the segregation effect, a sample should solidify with a dendritic structure, which is realized with high cooling rate, but the averaging procedure was required for concentrations at many points measured in some local area [4]. However, in the case of the solidification with high cooling rate, the isoconcentration line had a curvature due to the effect of volume change. Therefore, it is considered that measurements of mutual diffusion coefficients using the long capillary method should be conducted under the following cooling conditions:

1. The sample should be cooled with high cooling rate;
2. The concentration analysis should be done near the surface, and many analytical points in some area should be adopted to cancel the interdendritic segregation.

In the case of a self-diffusion experiment by using an isotope, in which the segregation effects doesn't need to be considered, the low cooling rate is preferable on solidification.

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