The solidification effects on diffusion experiments –Experimental examination –

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Abstract

In order to evaluate the solidification effects on diffusion experiments by the long capillary method, solidification experiments were carried out. Diffusion couples were melted, solidified with various cooling conditions, and analyzed the concentration distribution after solidification. It was found that the solidification effect was smaller if the temperature gradient at cooling was smaller, and that the smaller temperature gradient was preferred for diffusion experiments.

Introduction

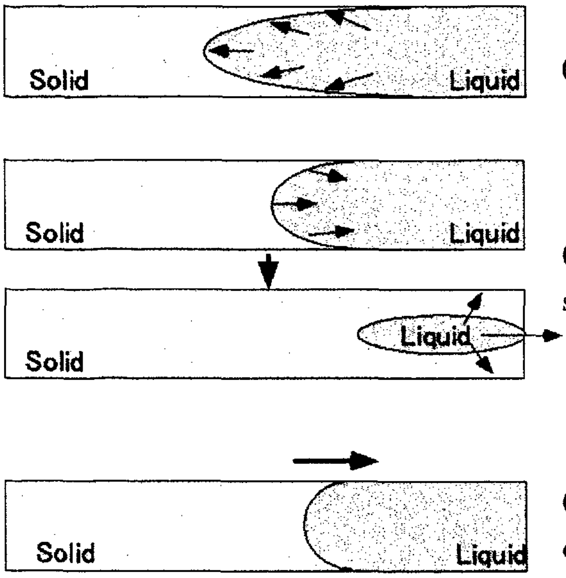
The long capillary method is a simple method for diffusion measurements. The diffusion couples are joined together throughout the course of the experiments (heating,, keeping at the diffusion temperature, cooling and solidifying process). The merit is its easy sample configuration, but the solidification effects on diffusion measurements have to be considered. The concentration profile after a diffusion experiment may be changed because of the solidification. 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 is changed 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. The solidification experiments with various cooling conditions were performed in order to examine the solidification effects by the volume change and to find the optimum cooling condition for long capillary diffusion experiments.

Expereimental

A diffusion couple of $Ag\text{-}Ag_{0.95}Au_{0.05}$ was melted and kept at about 1250 K for a short period and solidified with various cooling conditions. Ag-Au system is the complete solid solution system with a narrow band between the solidus and liquidus lines (see Figure 1 in 4.3.1.4), and the dendritic solidification hardly occurs. This system is convenient to investigate the effect of the volume change on solidification. In addition, the EPMA (Electron Probe



(a) Flow derived from shrinkage on solidification

(b) Flow derived from the volume expansion on solidification

(c) Concentration change by the segregation due to directional solidification

Figure 1 Schematic figures of solidification effects on diffusion experiments

Microanalyzer) analysis can be applied with high resolution for Ag-Au system. The sample size was 1 mm diameter and 20 mm length in total (10 mm each). The melting points are 1234 K for Ag and 1243 K for $Ag_{0.95}Au_{0.05}$. The diffusion sample was kept just above the melting points for a short period in order to avoid the buoyancy convection. The sample was set in a graphite crucible, on which 9 thermocouples were put at the ends (top and bottom) and the middle of the sample, as shown in Figure 2. Figure 3 shows the sample and the furnace configuration. The furnace can be moved downward to heat the sample and upward to cool the sample. The cooling condition was varied by the height of the furnace and 5 experiments were carried out as shown in Table 1. When the sample was completely taken out from the furnace, the temperature at the top became lower than that at the bottom and the sample was solidified from the top. Since the direction of the solidification was needed to be similarly to the other experiments (from the bottom to the top), the top of the crucible was wrapped by glass wool for insulation, as shown in Photograph 1.

The sample was analyzed on three plains, about 0.02 mm, 0.1 mm and 0.5 mm from the surface by the EPMA as shown in Figure 4. The diffusion coefficients were calculated on each plain. The diffusion coefficients were evaluated by the ratio of the diffusion coefficient at the center of the sample to that near the surface (0.02 mm plane in Figure 4), since the diffusion temperature was kept only for a short time to avoid the buoyancy convection, and the diffusion didn't proceed at

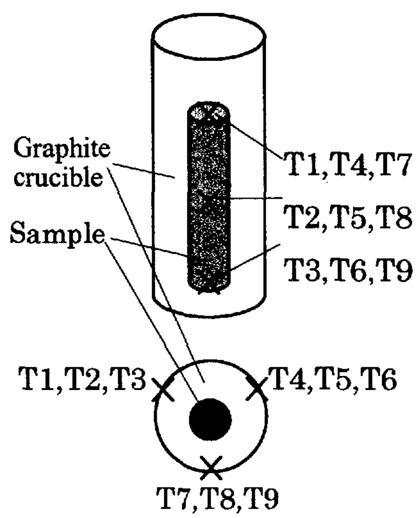


Figure2 Position of the thermo-couples put on a crucible

steady state.

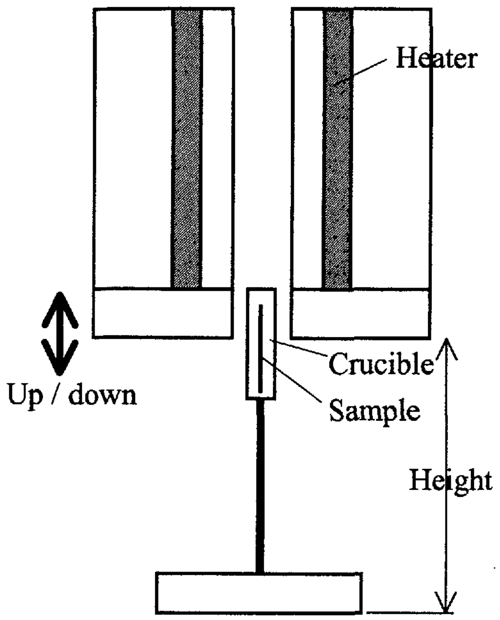
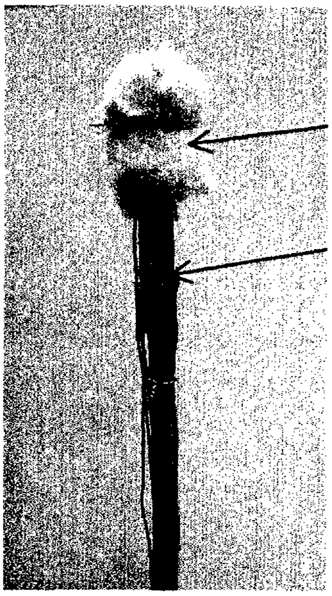


Figure 3 Configuratioin of the sample and the furnace



Photograph 1 Insulator to avoid the solidification from the top

Table 1 Cooling condition of the experiments

	Height of the furnace (in Figure 3)	Sample and furnace configuration
(1)	0 mm	Sample was in the furnace.
(2)	110 mm	Part of sample was in the furnace.
(3)	187 mm	Part of sample was in the furnace.
(4)	206 mm	Sample was out of the furnace
(5)	265 mm	Sample was out of the furnace

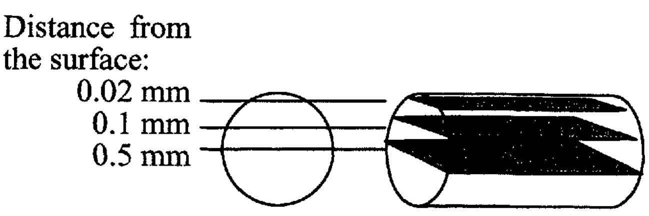


Figure 4 Analyzed plains in a solidification experiment sample

Results and discussion

Table 2 shows the cooling conditions and the concentration distributions after the solidification experiments. The concentration profile at the center was flat perpendicular to the sample axis with a low temperature gradient and with a small cooling rate, and was concave shape with a higher temperature gradient and with a larger cooling rate. Especially the concentration profile of the sample "height of furnace 187 mm" shows a remarkable concave shape and dendrites were observed. Although the $Ag_{0.95}Au_{0.05}$ is the concentration, at which the solidus and the liquidus temperatures are almost the same in equilibrium state, a dendritic growth may occur under some conditions in nonequilibrium state. The concentration profile of the sample "height of furnace 187 mm" was considered to be influenced by the directional solidification. Figure 5 and 6 shows the normalized diffusion coefficient (diffusion coefficient at the center divided by one at the surface) versus temperature gradient and cooling rate, respectively. The concentration profile near the surface was considered to contain the minimum solidification effects, and the diffusion coefficient obtained near the surface may be that without solidification effects. Therefore, the normalized diffusion coefficient should be 1.0 if the concentration profile isn't affected by the solidification. The normalized diffusion coefficient became larger if the temperature gradient and the cooling rate became larger. However, the normalized diffusion coefficient of the sample "height of 206 mm" was near 1.0 even though the cooling rate was large. In addition, even though the cooling rates of the sample "height of 206 mm" and "height of 265 mm" were almost the same, the normalized diffusion coefficient was much larger than 1.0 only in the latter sample. The difference of the experimental conditions between them was the larger temperature gradient in the case of the latter sample. Therefore it can be considered that the temperature gradient is more influential factor on the concentration profile after solidification. The cooling rate and the temperature gradient weren't controlled separately in these experiments, and more experiments with various cooling conditions are needed to confirm the effects of solidification on diffusion experiments.

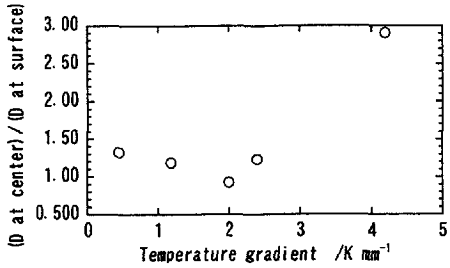


Figure 5 Normalized diffusion coefficient vs. temperature gradient

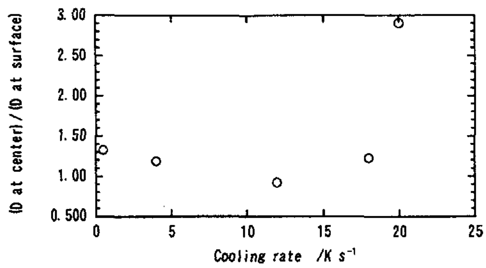


Figure 6 Normalized diffusion coefficients vs. cooling rate

Conclusions

The effect of volume change on the long capillary diffusion experiments was investigated. The small temperature gradient was found to be decisive to obtain the flat concentration profile in the solidified sample and it was preferred for diffusion experiments with smaller solidification effect.

Table 2 Cooling conditions and concentration distributions after the solidification experiments

Height of furnace	0 mm	110 mm	187 mm	206 mm	265 mm
Cooling rate	0.5 K/s	4 K/s	12 K/s	18 K/s	20 K/s
Temperature gradient	0.45 K/mm	1.2 K/mm	2.0 K/mm	2.4 K/mm	4.2 K/mm
Concentration distribution near the surface (0.02 mm from the surface)					
Concentration at the center (0.5 mm fro the surface)