

Solidification effects on diffusion experiments due to long capillary method – Numerical simulation –

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Abstract

In order to evaluate the solidification effects on diffusion experiments due to the long capillary method, numerical simulations have been carried out. The simulation program to calculate the heat conduction, the flow due to solidification shrinkage and the concentration distribution under equilibrium solidification has been developed based on a two dimensional model with axial symmetry using a finite difference method. The initial concentration distribution and the heat flux by fluid flow was included in the program this year. The calculated results corresponded satisfactorily to the experimental results.

The program was extended to the case of non-equilibrium solidification. It was confirmed that the effect of non-equilibrium solidification on the concentration distribution was small.

Introduction

As for the diffusion experiments due to long capillary method, the effects of solidification on diffusion measurements should be investigated in detail. Solidification experiments corresponding to this long capillary diffusion experiments were performed previously with various cooling rate and temperature gradient by one of the authors^[1]. The effect of these solidification conditions on these previous experiments was analyzed by numerical simulation in this study.

The concept of this analysis was as follows: the temperature distribution change was calculated including the phase transition (solidification); then, the flow due to the solidification shrinkage, the movement of the concentration profile and the solid-liquid interface were computed; finally, the concentration profile after solidification was obtained from the flow pattern.

Analytical system

The calculation was performed for a diffusion couple of Ag-Ag_{0.95}Au_{0.05} based on the two

dimensional model with axial symmetry, as shown in Figure 1. The size of sample was 1 mm diameter and 20 mm length (10 mm each), and it was put in a graphite crucible. The temperatures at positions 1, 2, and 3 in Figure 1, which were measured in the previous experiments^[1], were inserted as input data of the numerical simulation. The change of the temperature profile on the crucible surface was calculated based on these input experimental data. The upper and the lower ends of crucible were considered to be adiabatic.

The heat flux in the diffusion couple and the graphite crucible was modeled basically as a heat conduction problem. Heat transfer was considered at the interface between them. Also, the convective heat flux due to the melt flow was taken into account for the diffusion couple. The governing equation is as follows:

$$\frac{\partial T}{\partial t} + \frac{1}{r} U_r T + U_r \frac{\partial T}{\partial r} + U_z \frac{\partial T}{\partial Z} = a \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) \quad (1)$$

T : temperature; t : time; r,z : coordinate;

$a = \lambda / (\rho C_p)$; λ : heat conductance; ρ : density;
 C_p : specific heat; U_r, U_z : velocity of fluid flow in the direction of r and z respectively.

As shown in Figure 1, pure Ag was in contact with $Ag_{0.95}Au_{0.05}$ in the initial state. In the experiment, the concentration distribution was considered to be diffused in stead of a step function profile at the beginning of solidification. The initial concentration distribution was evaluated by the following error-function equation with diffusion coefficient of 0.01 mm²/s and diffusion time of 60 s.

$$c(y) = 2.5 [1 - \text{erf}\{0.65 (y - y_m)\}] \quad (2)$$

$c(y)$: Au concentration (at%); y : distance from the bottom of diffusion couple (mm); y_m : initial interface position (mm).

The concentration distribution for radial direction was considered to be constant.

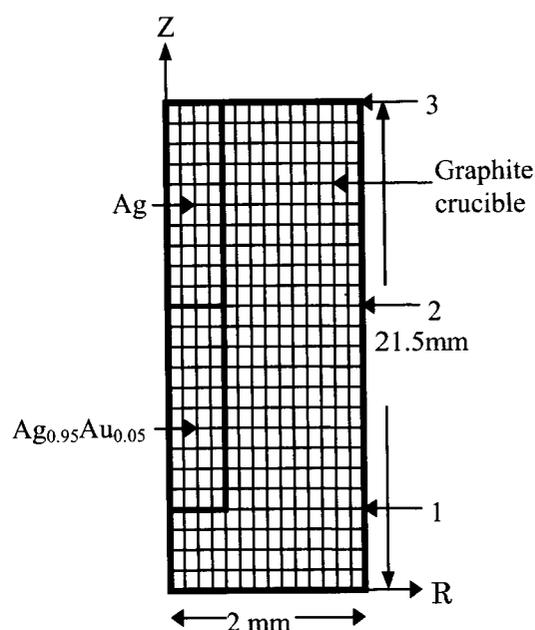


Figure 1 System analyzed

The equilibrium phase diagram is realized on the assumption that the solid diffusion was fast enough in the solidified part. If the cooling rate is high and the solid diffusion is slow, the solidification should be considered under the non-equilibrium state. In non-equilibrium solidification, it is considered that the solidus temperature is lower and this brings some effect on the solid-liquid interface and the movement of the concentration profile during solidification.

When the solute concentration is low in the initially solidified part and high in the finally solidified part, this inhomogeneity is called as microsegregation. Several equations about the concentration in the solidifying region have been proposed depending on the limited diffusion in the solidified part.

The microsegregation was generated between the dendrites. Supposing the simplified volume element shown in Figure 2, the solute allocation was analyzed. Brody and Flemings presented the following equation, considering that the solidification proceeds according to a square root law in the volume element^[2].

$$C_s = k_0 C_0 \left[1 - (1 - 2\alpha k_0) f_s \right]^{\frac{k_0 - 1}{1 - 2\alpha k_0}} \quad (3)$$

C_s : concentration in solid phase; k_0 : equilibrium distribution coefficient; C_0 : initial concentration of alloy; f_s : solid fraction; $\alpha = 4D_s t_f / l^2$ (D_s : diffusion coefficient in the solidified part; t_f : local solidification time; l : dendrite secondary arm spacing).

The value of α was limited between 0 and 0.5. In case of $\alpha = 0$, equation (3) expresses a perfectly non-equilibrium solidification. In case of $\alpha = 0.5$, it expresses a equilibrium solidification. The simulation program was extended to the case of non-equilibrium solidification based on equation (3).

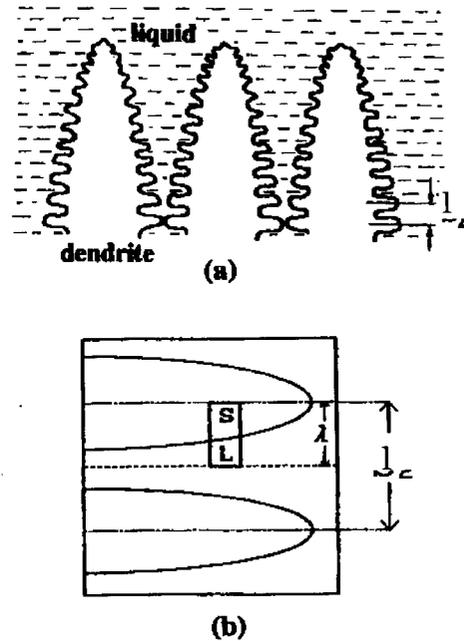


Figure 2 Volume element in dendrite

Calculated results

The temperature change on the outer surface of the crucible was calculated from the actual experimental data. The calculation was performed under equilibrium solidification condition for two experimental cases, of which cooling rate and temperature gradient are shown in Table 1.

Table 1 Calculation cases

Case	1	2
Cooling rate K/s	0.3	16.1
Temperature gradient K/mm	0.2	4.0

The calculated concentration profile after solidification was shown in Figure 3. In case 1, AgAu (lower) part solidified earlier than Ag (upper) part because of very slow cooling rate. Therefore, case 1 shows a directional solidification on cooling and the concentration distribution was same between the center and the surface of the diffusion couple (Figure 4). On the other hand, in case 2, Ag part began to solidify earlier than the complete solidification of AgAu part because of faster cooling rate. Therefore, the concentration profile differed between the surface and the center, as shown in Figure 4. These results corresponded satisfactorily to the experimental results^[1].

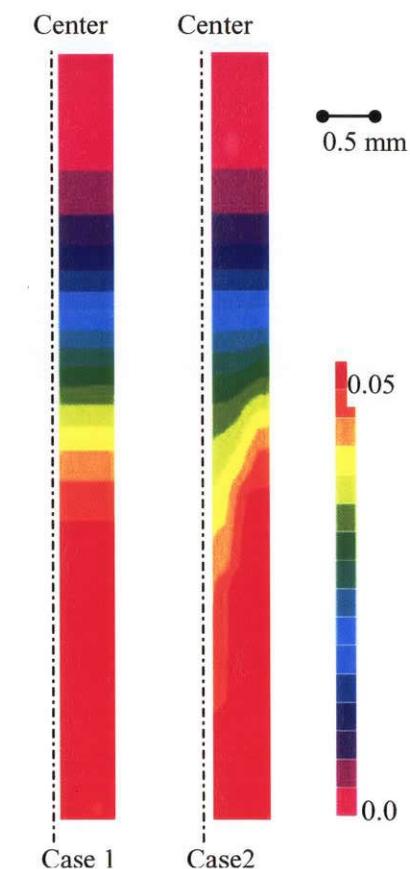


Figure 3 Calculated Au concentration profiles

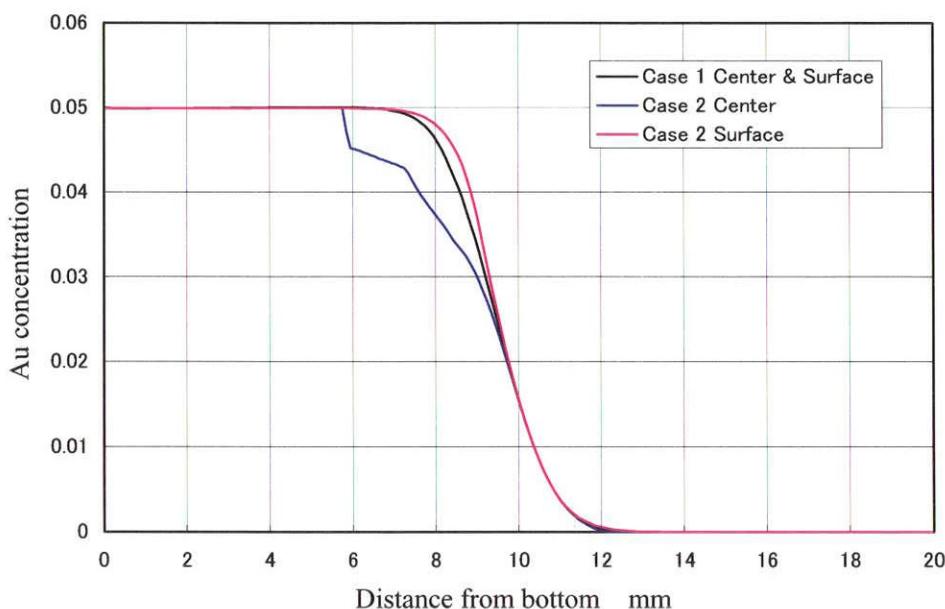


Figure 4 Concentration distribution

In order to evaluate the effect of non-equilibrium solidification, the calculation was performed for equilibrium and non-equilibrium solidification under the same cooling rate. The cooling rate was 6.2 K/s at the bottom (position 1 in Figure 1), 4.5 K/s at the center (position 2 in Figure 1) and 3.0 K/s at the top (position 3 in Figure 1). The initial temperature was 975 °C. The concentration distributions after solidification were shown in Figure 5 and 6.

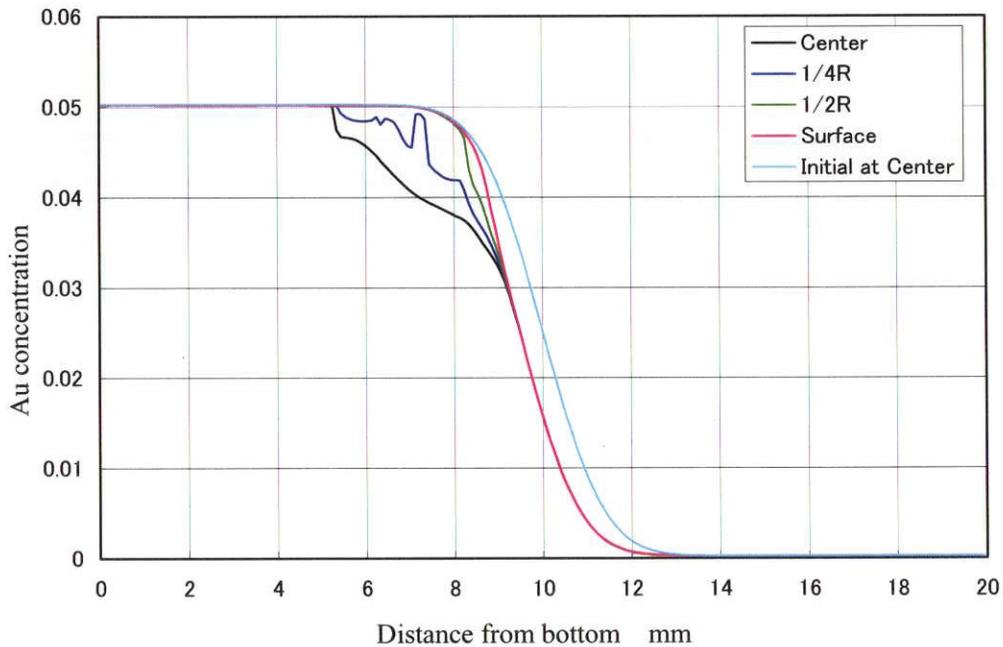


Figure 5 Concentration distribution for the equilibrium solidification

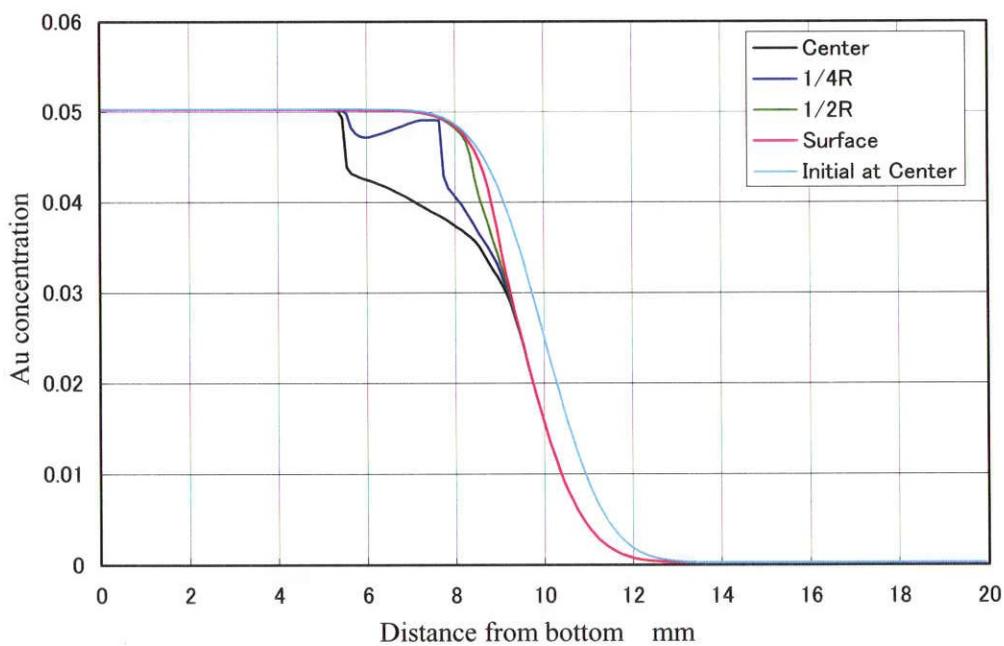


Figure 6 Concentration distribution for the non-equilibrium solidification

In the case of the non-equilibrium solidification, the change of the distribution at the center was bigger than that in the case of the equilibrium solidification. This may be derived from the fact that it takes longer time to complete the solidification because of the wider solidification range under the non-equilibrium solidification, and the flow due to shrinkage occurs during this longer time. But the difference between the equilibrium and the non-equilibrium solidification was small compared to the effect of the cooling rate. Therefore, the effect of the non-equilibrium solidification on the concentration distribution is not significant in this case.

Concluding remarks

Based on a two dimensional model with axial symmetry, a simulation program was developed to evaluate the effects of solidification for the long capillary diffusion experiments. This program, which includes the initial concentration distribution and the heat flux by fluid flow, enables us to calculate the heat conduction, the flow due to the solidification shrinkage and the concentration profile. The calculation was performed by adopting the measured temperature change as a boundary condition. The concentration profile after solidification, calculated from the flow due to solidification shrinkage, corresponded satisfactorily to the experimental results. The program was extended to the case of non-equilibrium solidification. It was confirmed that the effect of non-equilibrium solidification on the concentration distribution was small.