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

Atsushi Hirata [*1], Kenichi Ohsasa[*2] and Misako Uchida [*3]

*1 Industrial Machine and Plant Development Center, Ishikawajima-Harima Heavy Industries Co., Ltd.

*2 Research Group of Interface Control Engineering, Hokkaido University

*3 Space Utilization Research Center, National Space Development Agency of Japan

Abstract

In order to evaluate the solidification effects on diffusion experiments due to the long capillary method, numerical simulations were carried out. The simulation program to calculate the heat conduction, the flow due to solidification shrinkage and the concentration distribution was developed based on two dimensional model with axial symmetry using finite difference method. The calculated result corresponded with actual concentration change.

Introduction

As mentioned in the former section, the effects of solidification on diffusion measurements should be examined. In this section, this effect is analyzed by numerical simulation. The concept of this analysis is to calculate the temperature variation during experiments and to compute the flow due to solidification shrinkage, the profile variation of concentration and the solid-liquid interface. The concentration profile after solidification was calculated from the flow pattern.

Analytical system

The calculation was performed for a diffusion couple of Ag-$Ag_{0.95}Au_{0.05}$, which is 1 mm diameter and 20 mm length (10 mm each) in a graphite crucible, based on the two dimensional model with axial symmetry, as shown in Figure 1. Positions 1, 2, and 3 were those of temperature measurement in experiments. The temperature profile change on the surface of crucible was calculated from the experimental data at positions 1, 2 and 3. The upper and the lower ends of crucible were considered as an adiabatic condition.

The heat conduction in the diffusion couple and graphite crucible is calculated, and the heat transfer between them is considered at the inner surface of the crucible. The governing equation of the heat conduction is as follows:

$$\frac{\partial T}{\partial t}=\alpha\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial z^2}\right). \qquad (1)$$

T : temperature, t : time, r,z : coordinate,
$\alpha=\lambda/(\rho C_p)$, λ : heat conductance,
ρ : density, C_p : specific heat.

The solidification effect on the heat conduction is considered by the apparent specific heat C_p', in which the contribution of latent heat on solidification is taken into account.

$$C_P^{'}=C_P+\frac{L}{\Delta T}. \qquad (2)$$

L : latent heat, ΔT : the temperature width of solid-liquid coexistence.

As shown in Figure 1, pure Ag is in contact with $Ag_{0.95}Au_{0.05}$ in the initial state and the solidification temperature is different at the interface. In addition, the solidification temperature changes during solidification process due to concentration change as shown in Figure 2. In this calculation, these phenomena are taken into account.

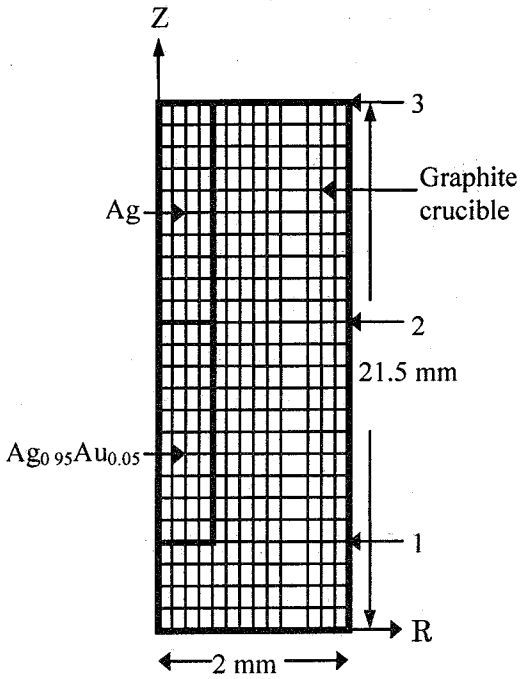


Figure 1 Analytical System

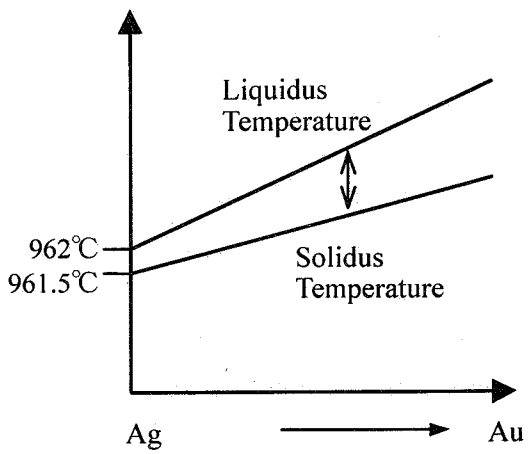


Figure 2 Ag-Au equilibrium phase diagram modified for present calculation

The mass conservation involving the solidification shrinkage is expressed for a finite difference mesh as follows:

$$\sum_n \rho_L f_L^n S_n U_n \Delta t=(\rho_S-\rho_L)V_{i,J}\Delta f_S^{i,J}. \qquad (3)$$

The left-hand side of Eq. (3) expresses the amount of mass flow into or out from the mesh(i,j) and the right-hand side of Eq.(3) expresses the solidification shrinkage in the mesh(i,j). Superscript or subscript "n" in Eq.(3) expresses the all neighboring meshes surrounding the mesh(i,j). ρ_L and ρ_S are densities (L : liquid ; S : solid), S_n and U_n are the sectional area and the flow velocity between the mesh(i,j) and mesh(n), $V_{i,j}$ is the volume of the mesh(i,j), f_L^n is the mean liquid fraction between the mesh(n) and mesh(i,j), $\Delta f_S^{i,j}$ is the change of solid fraction due to solidification in the mesh(i,j) and Δt is the time step used in the numerical calculation. The change of solid fraction ,

$\Delta f_S^{i,j}$, was calculated from the heat transfer analysis described above.

The velocity of interdendritic fluid flow U_n is expressed by using Darcy's law.

$$U_n = \frac{K}{\mu \cdot f_L^n}\left(\frac{P_n - P_{i,j}}{\Delta x}\right). \qquad (4)$$

where K is permeability in the solidifying alloy, μ is viscosity, P_n and $P_{i,j}$ are pressure in the mesh(n) and mesh (i,j), respectively, and $\triangle x$ is the distance between the meshes. The flow velocity U_n can be calculated by solving the simultaneous equations (3)$\sim$(4) for all meshes. Then the change in the concentration in the specimen can be calculated by considering the conservation of solute in each mesh.

$$V_{i,j}\overline{\rho} \cdot \Delta C_{i,j} = \rho_L \sum_n S_n \cdot U_n \cdot C_u \cdot \Delta t. \qquad (5)$$

In Eq.(5), $\overline{\rho} = \rho_S f_S + \rho_L f_L$, $\triangle C_{i,j}$ is change of the concentration in the mesh(i,j) at the time interval $\triangle t$. The concentration C_u, is taken to be $C_u = C_{i,j}$ when $U_n < 0$ and $C_u = C_n$ when $U_n > 0$ based on the upwind difference scheme.

Calculated results

The temperature change on the outer surface of the crucible was calculated as shown in Figure 3. The calculated temperature is in good agreement with measured one. This indicates that the present simulation scheme of solidification from the melt works well. The temperature of the sample decreases with the decrease of the temperature of crucible, as shown in Figure. 4(a). The temperatures at positions 1, 2, 4 and 5 stagnate at the liquidus temperatures due to the latent heat. But the temperature at position 3, near the interface of Ag and $Ag_{0.95}Au_{0.05}$, decreases fast below the liquidus temperature since the latent heat can be transported to Ag side, whose liquidus temperature is lower than that of $Ag_{0.95}Au_{0.05}$. Therefore the part of $Ag_{0.95}Au_{0.05}$ near the interface solidifies earlier than the bottom part, as shown in Figure.4 (b). The Au concentration near the interface becomes lower because of downward flow due to the solidification shrinkage. As the melt solidifies from outer surface,

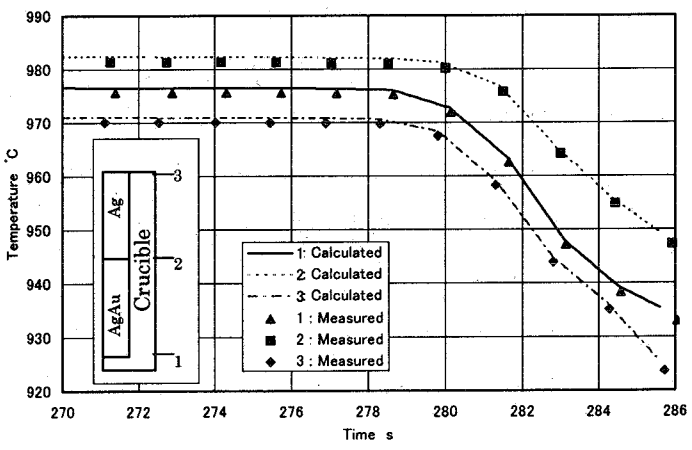
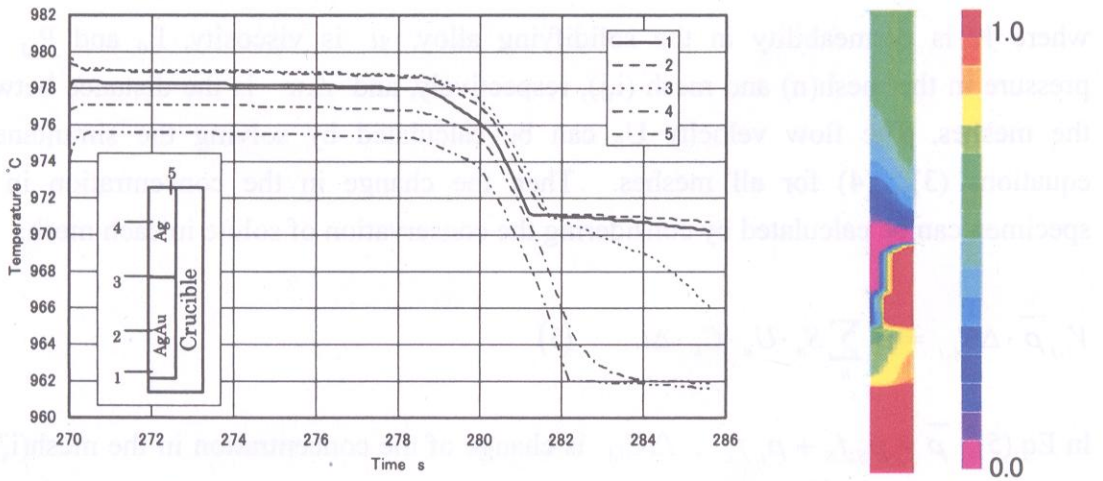


Figure 3 Temperature change of crucible

the melt flows faster in center part. So the concentration profile differs between the surface and the center. The concentration profile after solidification is shown in Figure 5. The results are considered to correspond with the actual concentration profile.



(a) Temperature change in sample (b) Solid fraction distribution

Figure 4 Temperature change in sample and solid fraction distribution

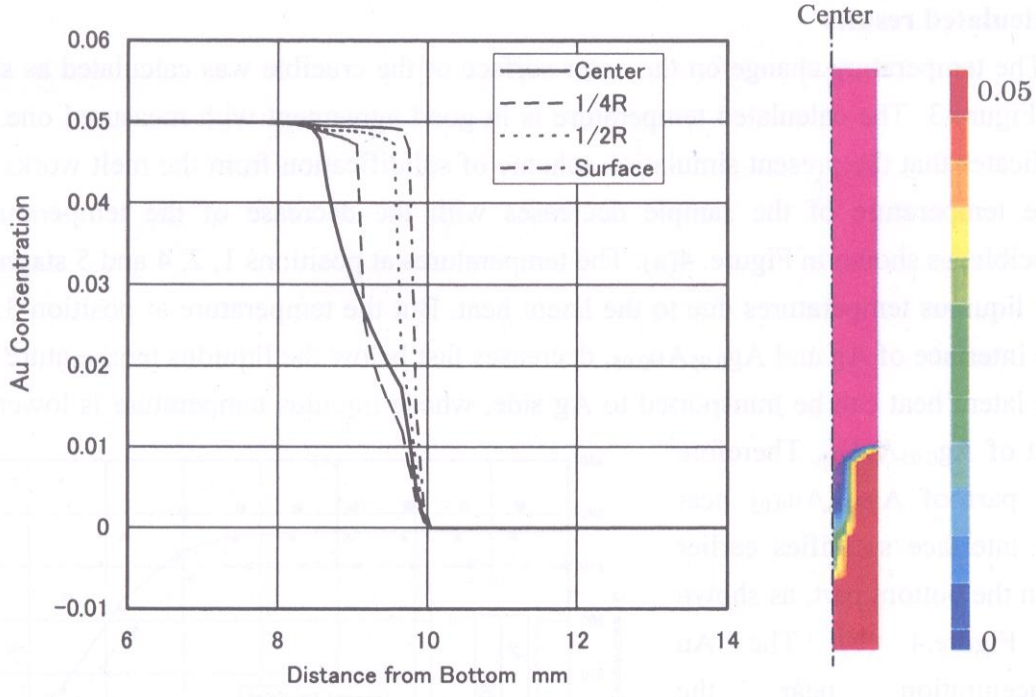


Figure 5 Au concentration profile in the solidified diffusion couple

Concluding remarks

The simulation program to calculate the heat conduction, the flow due to solidification shrinkage and the concentration distribution was developed for two dimensional model with axial symmetry. 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 with the actual concentration results.

But in this calculation, the part near the interface of the diffusion couple solidifies earlier than the bottom part in $Ag_{0.95}Au_{0.05}$ as mentioned above. However, in case of "hot" experiment, the bottom part solidifies earlier than the interface part, as described in the "Experiments" paper in this annual report. To remove the disagreement between the simulation and the experiment, following effects should be considered.

1) Initial concentration distribution : In this calculation, pure Ag is directly in contact with $Ag_{0.95}Au_{0.05}$ in the initial state. But in actual condition, concentration distribution exists in the initial state.

2) Heat flux by the flow due to solidification shrinkage : In this calculation, only the heat conduction is considered because of the high heat conductance of Ag. But the heat flux by the fluid flow must be considered in low heat conductance metals such as Ge.

3) Non-equilibrium solidification : In this calculation, the equilibrium solidification was supposed. But, when an alloy solidifies rapidly, its process isn't under equilibrium condition and the solidification temperature under non-equilibrium condition differs from that under the equilibrium condition.