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Technical Note

Layer merging during solidification of supereutectic $NH_4Cl–H_2O$ system

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Nomenclature

C	concentration
C_e	concentration at the eutectic point
C_i	initial concentration
C_1	concentration in the lower layer
C_2	concentration in the upper layer
H	height of test cell
L	length of test cell
l	horizontal length of the diffusive interface
N	buoyancy ration defined by eqn (1)
Ra	thermal Rayleigh number defined by eqn (2)
T	temperature
T_c	temperature at the cold wall
T_h	temperature at the hot wall
T_i	initial temperature ($= T_h$)
T^*	liquidus temperature
T_m	temperature at the mushy front
t	time
x	vertical coordinate
y	horizontal coordinate.

Greek symbols

α	thermal diffusivity
β_c	volumetric coefficient with concentration
β_T	volumetric coefficient with temperature
γ	kinematic viscosity.

1. Introduction

In recent years, experimental and numerical treatments of solidification of a binary system have been stimulated by material processing problems such as semiconductor crystal growth and casting of metallic alloys [1–6]. Most of them focus on double-diffusive convection which is naturally present in the melt of a binary system. In particular, multiple double-diffusive layer formation has been well known in the horizontal directional solidification [3–6]. Nishimura et al. [6] studied experimentally the occurrence and development of multiple layer for a supereutectic $NH_4Cl–H_2O$ system and found that the criteria for successive layer formation are determined by the buoyancy ratio and the Rayleigh number based on thermal buoyancy force in the diffusive interface separating two layers.

However, depending on the thermal conditions imposed on the solidification process, flow patterns in the melt are quite different. For example, when solidification is induced at one of the vertical walls of the enclosure and the opposite wall is maintained at the initial (superheated) temperature of the solution, the break-up and merging processes of the layers occur. The layer merging has an impact on the solidification process because the concentration field in the melt suddenly changes [1, 2]. However, the initial temperature and concentration effects on the onset of layer merging have not been known and the mechanism has not been understood fully, which motivates the present investigation. In this communication, we examine the criteria for layer merging during solidification of a supereutectic $NH_4Cl–H_2O$ system.

2. Experimental apparatus and procedure

Solidification experiments were conducted in a rectangular test cell with inner dimensions 50 mm in height, 37 mm in width and 30 mm in depth. The two vertical walls consisted of two copper heat exchangers that fitted

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snugly into the test cell. Copper–constantan thermocouples placed at the center of the heat exchangers monitored their temperatures continuously. The test cell was covered on all sides with 60 mm thick Styrofoam insulation to minimize heat losses.

Experiments were performed with NH_4Cl–H_2O solutions of different concentrations in the range of 22–28 wt%. The initial temperature of the fluid is uniform and is identical to the hot wall temperature which is variable. The cold wall temperature is fixed at $-14.4^\circ C$ above the eutectic temperature and thus the solidification is characterized by a mushy zone composed of dendritic crystals of NH_4Cl and interdendritic melt. Although the flow and temperature fields in the melt have been previously examined by a shadowgraph technique and thermocouples [1, 2], we visualized the flow and temperature fields using encapsulated liquid crystals suspended in the solutions. The change in time of the concentration in the melt was measured by the sample extraction method using microsyringes. These procedures are described in references [4, 6].

3. Results and discussion

We observed the time history of the diffusive interface which exists between the dilute fluid layer as a result of dendritic crystal growth and the initially homogeneous dense fluid layer for 40 parameter combinations. Out of these, in the present experiment we varied the initial superheat $T_i - T^*$ and concentration C_i and we identified three types, as shown in Fig. 1: Type I; no diffusive interface, Type II; fade-out of the diffusive interface and Type III; break-up of the diffusive interface. Type I occurs when the initial concentration is close to the eutectic one, i.e. $C_e = 19.7$ wt%, and the formation of dendritic crystals at the cold wall is minute. Type II is observed at a high initial superheat, where thermal convection is dominant. The diffusive interface is initiated at the top of the test cell and then moves downwards with progression of solidification. However, the diffusive interface eventually returns to the top of the test cell to finally fade. Type III indicates the layer merging, and it is found that the layer merging occurs even for a larger initial superheat as the initial concentration increases. This suggests a thermo-solutal interaction. We further focus on the transport processes in Type III.

Figure 2 shows representative photographs of solidification morphology and temperature field in the melt, revealed by a narrow band liquid crystal for $C_i = 25$ wt%, $T_i = 12.5^\circ C$ and $T_c = -14.4^\circ C$. This liquid crystal has a working range of -3–$-1^\circ C$, and the green color indicates approximately the $-2^\circ C$ isotherm. The magnified photographs demonstrate that the liquid crystal can be used not only to indicate temperature but also to trace fluid motion. Schematic flow patterns as observed by liquid crystal particles are shown in Fig. 3.

In the supercooling process not shown here, heat transfer is the only transport process and a large clockwise rotating circulation is observed due to thermal convection. At the beginning of the crystal growth process, crystallization occurs at the several positions along the cold wall. A water-rich fluid is released and therefore rises along the crystal front, in spite of the fact that the fluid is cooled down. This is solutal convection. It should be noted that some dendritic crystals detach from the cold wall and accumulate at the bottom of the test cell.

As the cooling progresses, a cold water-rich fluid rises up through the mushy zone and accumulates at the top of the test cell, thus causing thermally unstable and solutally stable conditions. Therefore, there is a sharp diffusive interface between the dilute fluid layer and the initially homogeneous dense fluid layer, that marks the beginning of the filling-box process with double-diffusive effects, i.e. compositional stratification (see Figs 2(a) and 3(a)). The fluid below the diffusive interface is dominated by thermal convection, which is, however, damped by the compositional stratification in the fluid above the diffusive interface. The upper layer above the diffusive interface eventually reaches a certain thickness, and a clockwise circulation is formed inside the layer in the presence of a horizontal temperature difference between the left hot wall and the mushy front (see Figs 2(b) and 3(b)).

Under these experimental conditions, the temperatures near the diffusive interface are within the working range of the isotherms indicated by liquid crystal. The behavior of isotherms, as indicated by liquid crystal corresponds to that of the diffusive interface. As solidification progresses, the position of the diffusive interface moves downwards and the circulation in the upper layer becomes stronger (see Figs 2(c) and (d) or Figs 3(c) and (d)). Although the temperature field at the diffusive interface indicates an unstable stratification, stable stratification is observed in the core region of the upper and lower layers. It should be also noted that the thermal condition of the hot wall imposed on the solidification process generates only one layer within the region of dilute fluid rejected from dendritic crystals, in contrast to multiple layers observed for the insulated wall (see Nishimura et al. [6]). With a further elapse of time, however, the movement of the diffusive interface becomes slow and finally its position is fixed. This feature means that progression of solidification is suppressed. After that, the diffusive interface is increasingly tilted and has a wavy appearance (see Figs 2(e) and (f) or Figs 3(e) and (f)). Then, within the next 7 min, the diffusive interface breaks up due to the penetration of the hot wall boundary layer fluid in the lower layer into the upper layer and violent mixing characterized by salt fingers occurs (see Figs 2(g)–(i) or Figs 3(g)–(i)).

Solidification morphology depends on the flow patterns in the melt. Before the layer merging, the remelting

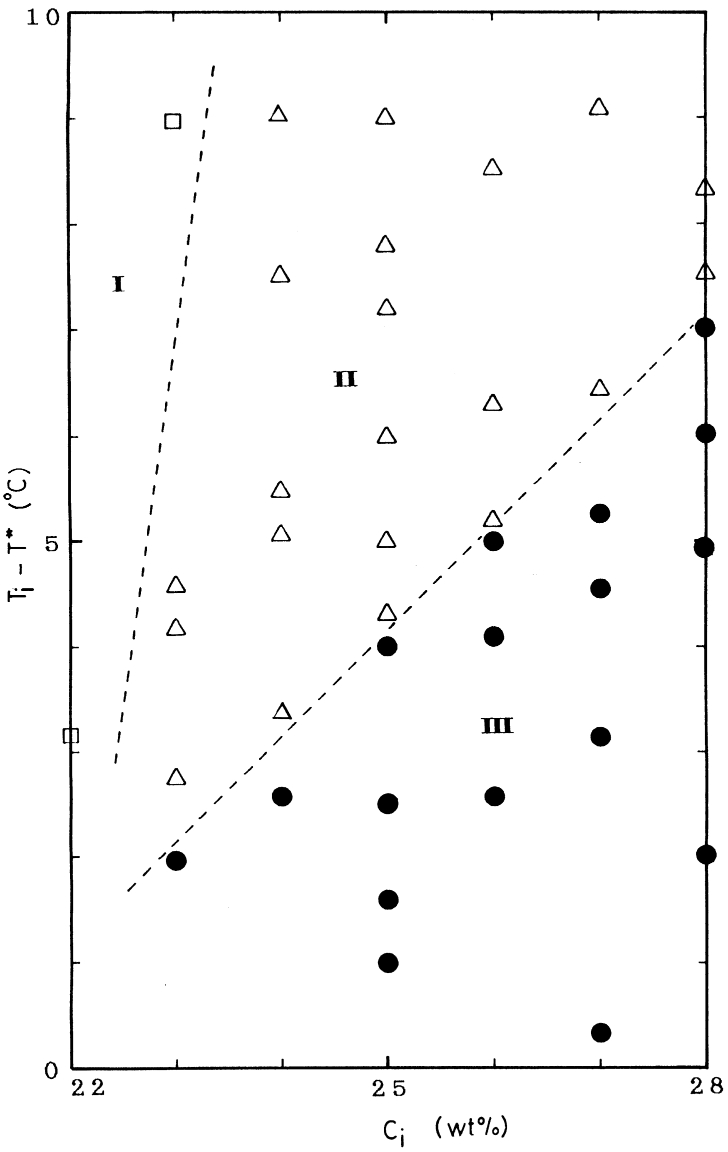
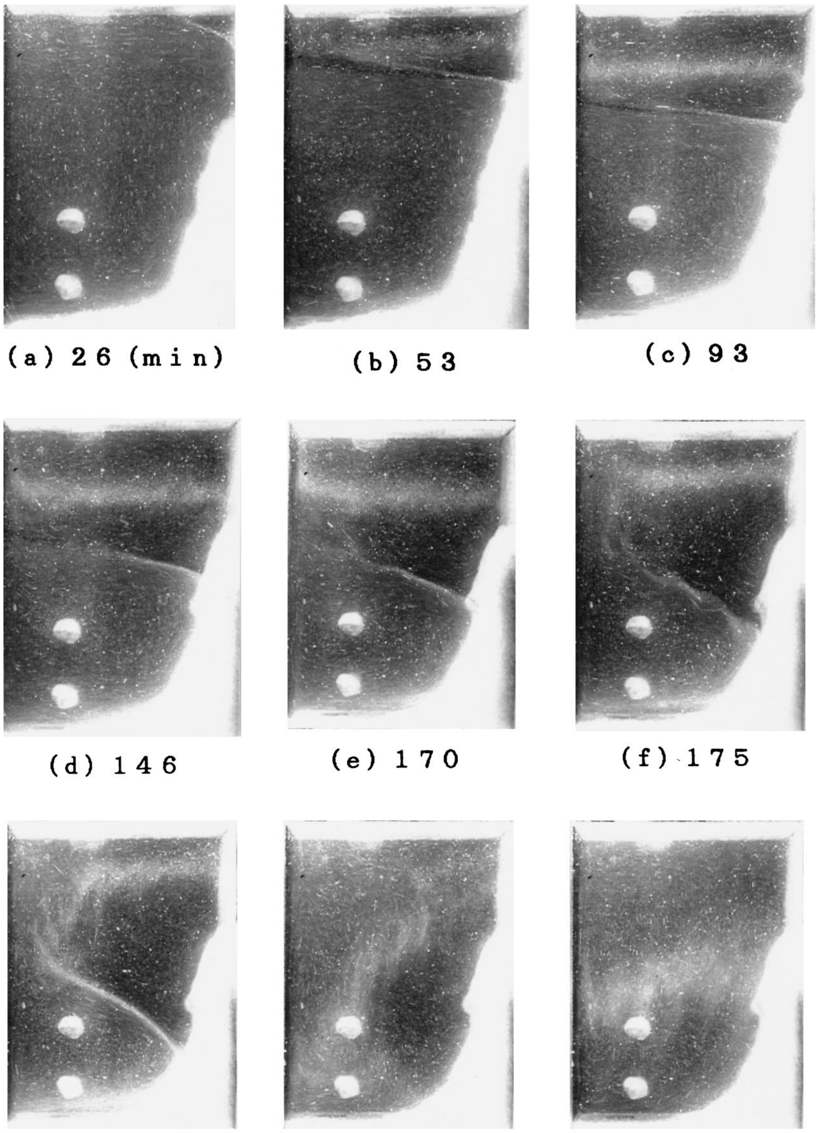


Fig. 1. Schematic diagrams representing the behavior of the diffusive interface during solidification for various experiments.

of the mushy front occurs in the upper portion of the cold wall, but after that the remelting is observed even in the lower part of the test cell.

The break-up of the diffusive interface is related to the concentration difference between the upper and lower layers separated by the diffusive interface. Figure 4 shows the change of concentration in time at two positions A and B, as an example, because the concentration in each layer is almost uniform. In the initial stages of solidification, concentrations are equal at the two positions. However, after the diffusive interface passes the measuring point A, the concentration rapidly decreases and then becomes constant, whereas, at the measuring point B, the concentration gradually decreases because this position is located only in the lower layer. Thus a concentration difference exists between the upper and lower layers and mass transfer occurs across the diffusive interface. However, the change in time of the concentration difference is small unexpectedly, which means that the diffusion process is dominant at the diffusive interface, rather than the convection effect. Thus, the layer merging is found to occur in the presence of a finite concentration difference. This trend is also observed under other experimental conditions. Since the solutal



(a) 26 (min) (b) 53 (c) 93

(d) 146 (e) 170 (f) 175

(g) 176 (h) 179 (i) 182

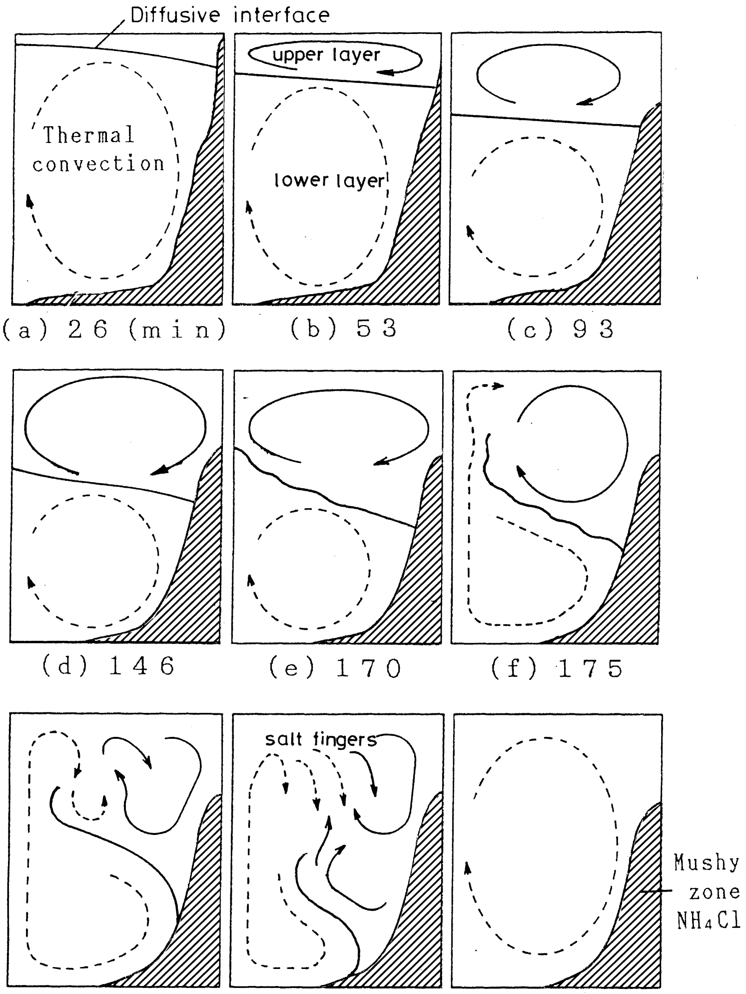
Fig. 2. Solidification morphology and temperature field in the melt at selected times ($C_i = 25$ wt%, $T_i = 12.5°\mathrm{C}$, $T_c = -14.4°\mathrm{C}$).

and thermal buoyancy forces are competingly stabilizing and destabilizing at the diffusive interface separating the two layers, we estimate the buoyancy ratio and thermal Rayleigh number at the onset of the break-up of the diffusive interface under several experimental conditions. The buoyancy ratio and thermal Rayleigh number are defined as follows:

$$N = \beta_c(C_1 - C_2)/\beta_T(T_h - T_m) \quad (1)$$

$$Ra = g\beta_T(T_h - T_m)l^3/\gamma\alpha \quad (2)$$

where C_2 and C_1 are the concentrations in the upper and lower layers, T_h and T_m are temperatures at the hot wall and the front of the mushy zone and l is the horizontal length of the diffusive interface. Under the experimental conditions of Figs 2 and 3, N and Ra are 0.634 and 6.6×10^6, respectively. In the experimental range of type III shown in Fig. 1, the buoyancy ratio covers from 0.33 to 0.63 and the Rayleigh number is the order of 10^6. Thus at $N < 1$, the diffusive interface is kinematically unstable. This conclusion is analogous to the result for double-diffusion between impermeable boundaries without phase change (Bergman und Ungan [7] and Hyun and Bergman [8]). The details of the mechanism of mass transport across the diffusive interface is the object of a future work.



(a) 26 (min) (b) 53 (c) 93

(d) 146 (e) 170 (f) 175

(g) 176 (h) 179 (i) 182

Fig. 3. Solidification morphology and flow patterns in the melt at selected times ($C_i = 25$ wt%, $T_i = 12.5°C$, $T_c = -14.4°C$).

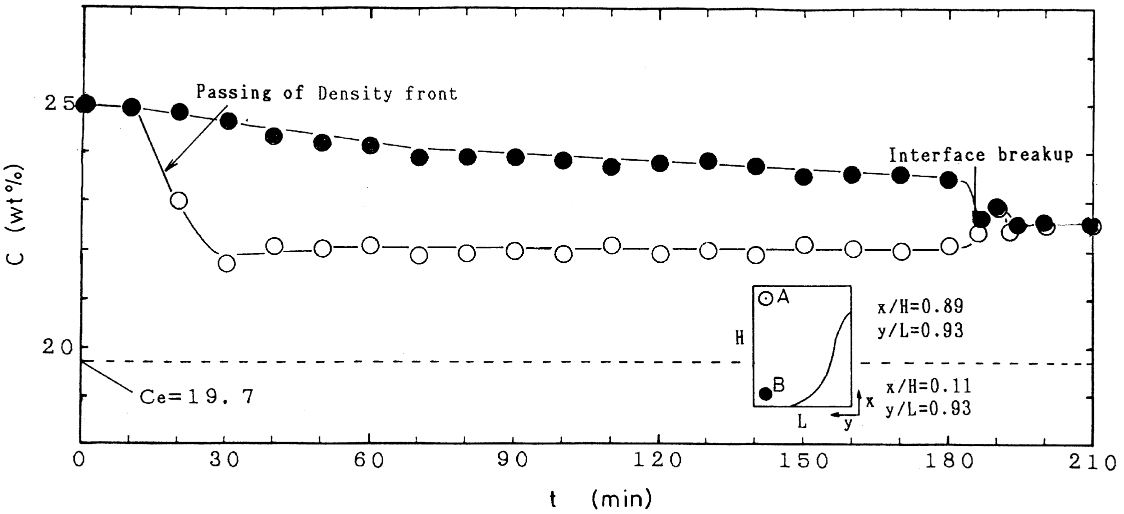


Fig. 4. Concentration histories at two positions in the melt ($C_i = 25$ wt%, $T_i = 12.5°C$, $T_c = -14.4°C$).

4. Concluding remarks

We studied experimentally the layer merging during solidification of a NH_4Cl–H_2O system. The following remarks have been drawn:

(1)We present the diagram representing the behavior of the diffusive interface during solidification for various parameters. The layer merging occurs for a larger initial superheat as the initial concentration increases.

(2)The criteria for layer merging appear to be primarily determined by the buoyancy ratio and thermal Rayleigh number at the diffusive interface. In particular, at buoyancy ratios less than unity, the diffusive interface is kinematically unstable.

References

[1] Beckermann C, Viskanta R. Double-diffusive convection during dendritic solidification of a binary miture. Physico Chemical Hydrodynamics 1989; 10:195–213.

[2] Christenson MS, Incropera FP. Solidification of an aqueous ammonium chloride solution in a rectangular cavity—I Experimental study. Int. J. Heat Mass Transfer 1989;32:47–68.

[3] Thompson ME, Szekely J. Mathematical and physical modeling of double-diffusive convection of aqueous solutions crystallizing at a vertical wall. J. Fluid Mech. 1989;186:409–33.

[4] Nishimura T, Fujiwara M, Miyashita H. Visualization of temperature fields and double-diffusive convection using liquid crystals in an aqueous solution crystallizing along a vertical wall. Exp. Fluids 1992;12:245–50.

[5] Nishimura T, Fujiwara M, Miyashita H. Double-diffusive convection during solidification of a binary system. Heat Transfer Jpn. Res. 1992;21:586–600.

[6] Nishimura T, Imoto T, Miyashita H. Occurrence and development of double-diffusive convection during solidification of a binary system. Int. J. Heat Mass Transfer 1994;37:1455–64.

[7] Bergman TL, Ungan A. A note of lateral heating in a double-diffusive system. J. Fluid Mech. 1988;194:175–86.

[9] Hyun MT, Bergman TL. Direct simulation of double-diffusive layered convection. Trans ASME, J. Heat Transfer 1995;117:334–9.