Measurement of Transient Double Diffusive Convection and Crystal Growth Using Real-Time Phase-Shifting Interferometer*

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In the process of growing crystals in solutions, double diffusive convection due to thermal and solutal gradients occurs. A measurement system comprising a rapid heat transfer control system and an accurate real-time phase-shifting interferometer has been developed to investigate the transient double diffusive convection. The heat-transfer control system has a small test-cell in which the liquid temperature is controlled by non-equilibrium thermoelectric devices. In-situ measurement of the transient double diffusive convection and crystal growth rates of NaClO_3 are carried out by using this system. Transient double diffusive fields are observed directly and clearly. The crystal growth rates in the present experiments show similar tendencies to the data of microgravity experiments.

Key Words: Crystal Growth, Double Diffusive Convection, Phase-Shifting Interferometer

1. Introduction

Investigation of the crystal growth in solutions is closely related to the effective and high quality production of medicine, food and new materials. During the process of crystal growth in the solutions, double diffusive convection occurs, driven by buoyancy forces due to thermal and solutal gradients, which has an effect on the mechanism of crystal growth. Therefore, it is important to investigate and understand the mechanism of double diffusive convection and its effect on crystal growth. Many previous studies have been carried out on double diffusive convection. Maruyama et al.⁽¹⁾ simulated the double diffusive convection in a cell when the direction of thermal and mass convection are the same or opposite, using thermal and solutal Rayleigh numbers as parameters.

Chang et al.⁽²⁾ performed an analysis to determine the influence of the ratio of thermal to solutal buoyancy on the transient double diffusive convection. They also investigated the flow mechanisms and behavior of unstable fluctuation.

In the present study, double diffusion fields and the crystal growth rates are examined under transient double diffusive convection. Transient concentration distribution and solutal gradients are determined from the double diffusion fields. The relation between the super-saturation ratio on the crystal surfaces and crystal growth rate is investigated from some transient experiments. In order to make an accurate measurement of the double diffusion fields, a real-time phase-shifting interferometer is adopted in which a phase dividing 3-CCD camera for the polarized beam is used. The test cell is made of the active thermal control units developed by Maruyama⁽³⁾ and solution around a seed crystal of NaClO_3 at the saturation temperature is rapidly cooled. The obtained growth rate result has been compared with the existing experimental data obtained in microgravity conditions.

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2. Experimental Apparatus

2.1 Measurement system

A schematic of the experimental apparatus is shown in Fig. 1. A specially designed real-time phase-shifting Mach-Zehnder interferometer⁽⁴⁾ is utilized to measure the thermal and mass diffusion fields. The interferometer can attain much higher measuring accuracy compared with the conventional ones by using the phase-shifting technique⁽⁵⁾. By using a polarizing beam splitter, the semiconductor laser beam (wavelength=680 nm) is separated into two beams, the reference beam and the measurement beam. The planes of vibration of these two beams are perpendicular to one another. After passing through the test-cell and a compensator, the beams are mixed by another beam splitter. Since the polarized planes are perpendicular to each other, the beams will not interfere just after mixing. The magnification of the objective lens can be changed as one, three, five, and ten times.

A quarter-wave plate is placed at an angle of $\pi/4$ to the two polarized beams. The two linearly polarized beams pass through the quarter-wave plate and become clockwise or counter clockwise polarized with respect to each other and interfere. The circularly polarized beams are delivered into a purpose built phase dividing 3-CCD camera, which includes a

Fig. 1 A schematic of the experimental apparatus

3-CCD prism, three CCD sensors and polarizers as shown in Fig. 1. The difference in polarizing angles between any two polarizers is $\pi/4$. The original phase-shifting interferometer constructed by Onuma et al.⁽⁶⁾ is composed of three independent TV cameras with polarizers, but it is difficult to adjust these cameras in the same optical condition. The present 3-CCD camera reduces this difficulty in optical arrangement, and reduces the size of the interferometer⁽⁴⁾. The interferograms obtained by the 3-CCD cameras are processed by a signal processor as described by Onuma et al.⁽⁶⁾ and Nakadate et al.⁽⁵⁾ The digital data of the interferograms are recorded by a video recorder in the gray scale.

2.2 Test cell

Figure 2 shows a schematic diagram of the test-cell. The test-cell is specially designed for the transient measurement of the thermal and diffusion fields. Saturated solution and a seed crystal are contained in the cell. Active thermal control units⁽³⁾ installed on the upper and lower sides of the walls accurately control the temperature in the test-cell. The active thermal control unit includes an aluminum base plate, Peltier elements and a heat sink. The four Peltier elements are independently operated by a computer to accurately control the temperature of the solution and seed crystal. The temperature in the cell can be controlled rapidly to within an accuracy of $\pm 0.1^\circ\text{C}$.

The size of the glass-cell is 12 mm square and approximately 1.6 mm in depth. The seed crystal is attached on the lower base plate. NaClO_3 crystal and its aqueous solution are used in the present experiments. The seed crystal has a solid rectangular shape. The saturation temperature of the solution was approximately 26°C . Before initiating a double diffusive convection experiment, a uniform temperature field in the cell is precisely maintained at the saturation value. As the experiment starts, the rapid

Fig. 2 A schematic diagram of the test-cell

Fig. 3 Various temperature sequences on the base plate

temperature control system is operated according to a programmed sequences. The operating time is 25 seconds. When the experiment finishes, the temperature in the cell is automatically set to the saturation temperature. Temperature profiles on the base plates are shown in Fig. 3. The temperatures are accurately maintained at steady values by the active thermal control unit and a digital computer controlled system. During the experiment, the double diffusive convection and generation of plumes were observed.

3. Results and Discussion

3.1 Relation between fringe shift and temperature or concentration

The interferogram contains the experimental data as a superimposition of temperature and concentration differences. In order to determine the temperature and concentration fields, the relation between fringe shift of the interferogram and temperature or concentration should be determined in advance. Hence, some preliminary experiments were carried out.

The relation between fringe shift and temperature can be obtained by using the test cell described above. At first, saturated solution is injected into the test cell, and the temperature of the solution is maintained at the saturation value. Then, the solution is cooled to the super-cooling temperature. By measuring the fringe shift, which moves across the measuring point in the bulk, we can obtain the relation between the fringe shift and the temperature. Here, the relationship between the obtained fringe numbers f_T and the temperature difference is determined from:

$$\Delta T = (T - T_0) = 0.220 \times f_T \quad (1)$$

Further, a specially designed test cell is set up to measure the relationship between the fringe shift and the concentration⁽⁷⁾. The relation between Δw and f_w was obtained by the following procedure. The solution is injected from the bottom of the test cell which

Fig. 4 Interferograms around the seed crystal

was filled with pure water. Then, the solution is injected uniformly through a membrane filter subjected to the flow resistance. The relation between the fringe shift and the concentration is obtained by measuring the fringe shift. The obtained fringe numbers f_w in an interferogram is related to the concentration difference by:

$$\Delta w = (w - w_0) = 0.0732 \times f_w \quad (2)$$

It is noted that the two relations given in Eqs. (1) and (2) are for the case of a 10 mm optical path in the test cell. These need to be corrected to match the length of the seed crystal.

3.2 Observation of plumes

Interferograms showing the seed crystal are presented in Fig. 4. To observe the transient double diffusive convection and plume development around the seed crystal clearly, in this case we used the one-time-magnification objective lens. The size of the seed crystal used in these experiments was 0.76 mm in height, 2.31 mm in width and 1.92 mm in length. Here, the photos shown in Fig. 4(a) correspond to Seq. A in Fig. 3 ($\Delta T_c = 2^\circ\text{C}$) and those in Fig. 4(b) are for Seq. C in Fig. 3 ($\Delta T_c = 5^\circ\text{C}$), respectively. The saturation temperature as noted previously is 26.0°C .

When the uniform temperature distribution in the test-cell is maintained at saturation temperature (i.e. $t=0$ s), natural convection does not occur in the small test-cell. As soon as a rapid temperature control sequence starts according to the programmed sequence in the computer, fringes appear on the interferograms (driven by temperature and concentration changes). In the case of $\Delta T_c = 5^\circ\text{C}$, plumes driven by the buoyancy force occurred. These plumes become larger as the solution is cooled and the seed crystal grows. On the other hand, in the case of $\Delta T_c = 2^\circ\text{C}$,

plumes were very weak and could hardly be observed. Therefore, for the case of $\Delta T_c = 2^\circ\text{C}$, there plume influence is almost negligible (compared with the case of $\Delta T_c = 5^\circ\text{C}$) and the observed field in this case is nearly the same as the genuine diffusion field.

To examine the condition at which plumes appear, the solutal Rayleigh number Ra_D needs to be evaluated. The solutal Rayleigh number is defined as:

$$Ra_D = g\beta_D \frac{(w - w_r)l^3}{D\nu} \quad (3)$$

where g is the gravitational acceleration [m^2/s], β_D is the volume coefficient of expansion [$1/\text{K}$], w is the local concentration at the measurement point [wt%], w_r is the bulk solution concentration, l is the height of the seed crystal [m], D is the solute diffusivity [m^2/s], and ν is the kinematic viscosity [m^2/s].

The volume coefficient of expansion (β_D) is determined from the relation between the concentration and density of NaClO_3 solution obtained from a preliminary experiment. β_D is defined as follows:

$$\beta_D = \frac{\rho - \rho_r}{\rho_r(w_r - w)} \quad (4)$$

where ρ is the local density of solution at the measuring point [kg/m^3], and ρ_r is the bulk solution density.

The value of viscosity η [$\text{Pa}\cdot\text{s}$] is calculated following the approximation suggested by Maruyama et al.⁽⁸⁾ for the case of NaClO_3 saturated solution at 20°C .

$$\eta = 2.67(T + 273.15)^{-7.26} \times 10^{16} \quad (5)$$

The solute diffusivity (D) is a function of temperature and for estimating its value the Stokes-Einstein⁽⁹⁾ equation is adopted. This equation can be used in conjunction with Eq.(5) to calculate the solute diffusivity value as a function of temperature as proposed by Maruyama et al.⁽⁸⁾:

$$D(T) = D_0 \left(\frac{T + 273.15}{T_0 + 273.15} \right)^{8.62} \quad (6)$$

where D_0 is the solute diffusivity at T_0 . The solute diffusivity of NaClO_3 solution at saturation temperature $T_s = 25^\circ\text{C}$ was measured by Maruyama et al.⁽¹⁰⁾.

Now, by using these quantities, the Rayleigh number Ra_D can be calculated. For instance, for the case of $\Delta T_c = 5^\circ\text{C}$ when the seed crystal height (i.e. the characteristic length l) is 0.76 mm, the Rayleigh number Ra_D is 2.67×10^4 at time $t = 24$ s. Similarly, for the case of $\Delta T_c = 2^\circ\text{C}$, Ra_D is 1.34×10^4 at 24 seconds. Therefore, at this point in time Ra_D for the case of $\Delta T_c = 5^\circ\text{C}$ is about twice as large as that of $\Delta T_c = 2^\circ\text{C}$.

3.3 Transient double diffusive fields

Figure 5 shows the transient double diffusion field in the vicinity of the crystal surface. In this figure, a comparison is made between $\Delta T_c = 3^\circ\text{C}$ (Seq. B in Fig. 3) and $\Delta T_c = 5^\circ\text{C}$ (Seq. C in Fig. 3). It is noted that these photos were taken by using the three-

Fig. 5 Interferograms of diffusion field in the vicinity of crystal surface

times-magnification objective lens. The transient double diffusive fields can be clearly seen in Fig. 5. As soon as the rapid temperature control unit starts, horizontal fringes due to thermal diffusion can be seen in the bulk solution region. At first, the fringe density is high, however when the temperature in the test cell reaches the super-cooling temperature, the fringe density reduces. On the other hand, in the vicinity of the crystal surface, fringes due to mass diffusion develop with time. Clearly, the interferograms are affected by the double diffusive convection.

3.4 Super-saturation of bulk solution and crystal surface

A schematic diagram showing the measurement points for temperature and surface concentration is shown in Fig. 6. It can be considered that the temperature in the vicinity of the crystal surface is nearly equal to that of the bulk, because the thermal diffusivity is two orders of magnitude larger than the solute diffusivity. Consequently, f_r can be obtained by measuring the fringe shift which moves across the Temperature point in Fig. 6. The variation of temperature with time at the measuring point is shown for different cases in Fig. 7. The data is extracted from the relationship between the fringe shift and temperature as given in Eq.(1). Sequences indicated in Fig. 7 correspond to the cases noted in Fig. 3. The measured temperature variations are somewhat different

Fig. 6 A schematic drawing showing the measurement points

Fig. 7 Variation of the measured bulk temperature for different super-cooling temperatures

compared to the base plate temperature variation because of the influence of heat conduction and mass diffusion.

The variations of super-saturation ratio σ_s as a function of time for three different cases are shown in Fig. 8. The super-saturation ratio is defined as:

$$\sigma_s = (w - w_{sat}) / w_{sat} \quad (7)$$

where w [wt%] is the concentration at the measuring point and w_{sat} is the saturation concentration at the cooling temperature. In Fig. 8 solid symbols represent bulk super-saturation ratio whereas the blank symbols are those at the surface of the seed crystal (as shown in Fig. 6). Because the measurement time is very short, i.e. 25 seconds, the concentration field in the cell is not affected by the plume. It is considered that the bulk solution temperature and that of the surface of the seed crystal are almost the same. The higher super-cooling temperature ΔT_c results a larger difference in super-saturation between the bulk and the surface. The bulk super-saturation ratio increases with time and gradually reaches a constant value. Super-saturation in the vicinity of the surface

Fig. 8 Variation of super-saturation ratio (σ_s) with time

also increases just after the start of experiment, but later it begins to decrease with time. This phenomenon is clearly noticeable in particular for the case of $\Delta T_c = 5^\circ\text{C}$. In the vicinity of the crystal surface, concentration decreases as crystal grows. Therefore, as time passes, the decrease of super-saturation ratio becomes more noticeable compared with the increase of super-saturation at bulk. Super-saturation ratio in the vicinity of the surface is less than that in the bulk, because solute is absorbed on the crystal surface.

3.5 Crystal growth rate measured from diffusion fields

Concentration profiles in the vicinity of the crystal surface obtained from fringe shifts in the interferograms are plotted in Fig. 9. This data is for the case of super-cooling temperature $\Delta T_c = 5^\circ\text{C}$. Using this data the solute gradients at the crystal surface (dw/dx) can be obtained. Here, the crystal growth rate is estimated by:

$$R = \frac{\rho_{sol}}{\rho_{cry}} D(T) \frac{dw}{dx} \quad (8)$$

where ρ_{sol} is the density of solution, ρ_{cry} is the density of crystal, D is the solute diffusivity, x is the distance from the side of crystal and dw/dx is the solute gradient at crystal surface. Solute gradient is measured from the concentration profile in the vicinity of the crystal surface (e.g. data shown in Fig. 9). The solute diffusivity for NaClO_3 solution at saturation temperature $T_s = 25^\circ\text{C}$ was measured by Maruyama et al.⁽¹⁰⁾ and $D = 0.7 \times 10^{-9} \text{ (m}^2/\text{s)}$ is used here.

Crystal growth rates of NaClO_3 (extracted from the experimental data reported here) at different times as a function of super-saturation ratio are shown in Fig. 10. For comparison purposes, crystal growth rates for several super-cooling temperatures obtained during the microgravity experiments of Maruyama et al.⁽¹¹⁾ are also plotted. The growth rates

Fig. 9 Measured Concentration in the vicinity of the crystal surface

Fig. 10 Crystal growth rates of NaClO₃

for small super-saturation ratios as reported by Bennema⁽¹²⁾ are also included in this figure. It is noted that the microgravity data was obtained under the microgravity environment generated during a parabolic flight of an airplane. The present data shows a similar tendency compared to that of the microgravity experiments. The growth rate increases with σ_s at small super-saturation ratios, then the growth rate increase becomes small at comparatively large σ_s . It is interesting to note that the data scatter of crystal growth rates obtained in the present experiments is less than that of the microgravity experiment. Effect of g-jitter induced by a parabolic flight of an airplane on the experiment deal with solution is significant. One of the reason for the data scatter in the microgravity experiments is considered to be due to the g-jitter. It is seen that the influence of the gravity is small under the condition of present experiments.

The present data trend compared to the Bennema's growth rates at small σ_s is substantially different with the present experimental growth rates being almost ten times larger. The difference is believed to be due to the roughness of the crystal

surface, which promotes the growth of crystal. In the present experiments, seed crystal grows by rapid cooling, which makes the surface rough and molecule transported to the vicinity of crystal is absorbed into the crystal. Hence, the growth rates become larger⁽¹³⁾. Further experiments and analyses are required to obtain a detailed and better understanding of this phenomenon.

4. Conclusions

Transient double diffusive convection and crystal growth rate in the process of crystal growth in solutions were observed and measured by employing a novel rapid temperature control system and a real-time phase-shifting interferometer. In the performed experiments, the transient double diffusive convection could be directly and clearly observed. The transient behavior of plumes could be observed in the short length of experimental time (about 25 seconds). The existence of plumes became clearly evident when the super-cooling temperature ΔT_c was about 5°C. However, in the case of $\Delta T_c = 2^\circ\text{C}$, plumes could not be observed. It is recommended that the relationship between occurrence of transient plumes and super-cooling temperature was investigated by further experiments and analysis.

The relationship between the super-saturation ratio on the surface of the seed crystal and the crystal growth rate was measured. Crystal growth rates obtained from the present data were compared with those of microgravity experiments as well as experiments at very low super-saturation. The present experimental data exhibit a similar tendency to the data of Maruyama et al.⁽¹¹⁾ obtained in microgravity experiments. However, the growth rate data scatter is less in the present experiments compared with the microgravity data. Further, the data is an order of magnitude larger than that of small super-saturation results of Bennema⁽¹²⁾. This is believed to be due to the rough crystal surface in the present experiments. Further experiments are required to allow a better understanding of this phenomenon.

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