Solute Distribution in front of an Ice/Water Interface during Directional Growth of Ice Crystals and Its Relationship to Interfacial Patterns

Kazushige Nagashima[†] and Yoshinori Furukawa*

Institute of Low Temperature Science, Hokkaido University, Sapporo 060, Japan

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Directional growth experiments in a water−KCl solution were carried out using a new experimental apparatus combined with an optical system of a Mach−Zehnder interferometer, and the solute distribution in the solution in front of the ice/water interface, as well as the interfacial patterns, was observed *in situ*. This is the first study in which the solute diffusion field was obtained by analyzing the interference fringes. It was found that the solute distribution is strongly affected by the pattern of interface (*i.e.*, the diffusion field of solute varies greatly with the development of interfacial patterns). On the other hand, observations of interference fringes inside the ice crystal showed that the crystal shape develops in three dimensions even in a thin growth cell. Interaction between the diffusion field and the interfacial pattern is closely related to the three-dimensional structure of the ice/water interface.

1. Introduction

Directional growth experiments on crystal from its melt including impurities (solutes) are very useful for discussion of pattern formation under nonlinear and nonequilibrium conditions and have been carried out for many kinds of materials.[1−8] It is well-known that, as the interface advances, the interfacial patterns sequentially change in the following way: a planar interface advances in the initial stage, then perturbation is initiated on the planar interface and develops to form a cellular pattern, and finally a marginally stable cellular pattern is achieved. Morphological instability during directional growth originates from coupling between the local shape of the interface and the diffusion process of impurities rejected by the crystal growth at the interface. Recently, the authors[8] carried out a directional growth experiment on water−KCl solution and showed that sequential change in the interfacial pattern is the same as that of other materials. Even though many experimental and theoretical studies have been carried out to clarify the pattern-formation mechanism during directional growth, there are many ambiguities and disagreements between theoretical and experimental results. One of the reasons for this is thought to be the lack of information on the diffusion field of solutes in front of the solid/liquid interface.[9]

In this study, we observed the directional growth of ice crystals in a water−KCl solution system. The development of interfacial patterns and distribution of the KCl concentration in front of the ice/water interface were observed *in situ* using an optical system of a Mach−Zehender interferometer. The KCl diffusion field in front of the interface was quantitatively obtained by analyzing the interference fringes observed in the vicinity of interface, and the relationship between diffusion field and interfacial pattern was investigated.

2. Experimental Procedure

Since the experimental apparatus and procedure for the directional growth system are described in detail in the previous paper,[8] we explain them here very briefly. In this system, a very thin growth cell is forced to move transversally at an arbitrary constant velocity in a fixed temperature gradient, which is applied along the direction of growth cell movement (Z-axis in Figure 1). In the present experiment, an optical system of a Mach−Zehnder interferometer was combined with the directional growth system for observing the solute concentration in a solution in front of an advancing ice/water interface. The growth cell used was composed of two $20 \times 2 \times 20$ mm³ optical glasses, which were glued together with a gap of 200 μm between them. Thus, the inside dimensions of the growth cell were $1.6 \times 0.2 \times 20$ mm³. A water−KCl 3 wt % solution was used as the mother material and was poured into the growth cell. The physicochemical properties of the solution are given in the previous paper.[8] It should be noted that, according to the measurement by Gross *et al.*,[10] the segregation coefficient k of KCl for an ice crystal is nearly equal to zero ($k = 2.7 \times 10^{-3}$).

An ice crystal growing from the water−KCl 3 wt % solution in the temperature gradient $G = 4.0$ K/mm was observed at the velocity of growth cell $V = 10$ μm/s, using the Mach−Zehnder interferometer. Results of *in situ* observations were recorded by a time-lapse video recorder system. Figure 1 shows the time-sequence pictures of the interfacial patterns and the interference fringes. In this experiment, the orientations of the ice crystal against the growth cell were fixed (*i.e.*, the directions of the *c*- and *a*-axes of the crystal coincided with the directions of the *Y*- and *Z*-axes, respectively). The effects of ice crystal orientations on the interfacial patterns were discussed in the previous paper.[8] The time evolution of morphological instability at the interface and the subsequent development of a cellular pattern were first observed, and then the KCl concentrations in the solution in the vicinity of interface were analyzed from the interference fringes.

3. Results

3.1. Development of the Interfacial Pattern and the Solute Distribution in front of the Interface. At the initial condition of $V = 0$ (time $t = 0$ s), the ice/water interface is completely flat and perpendicular to the direction of G (Z-axis direction). The initial position of the interface coincides with the position of $T = T_{eq}$ in the temperature gradient, and the solute is uniformly distributed in the solution in front of the interface. When movement of the growth cell starts at $V = 10$ μm/s, the

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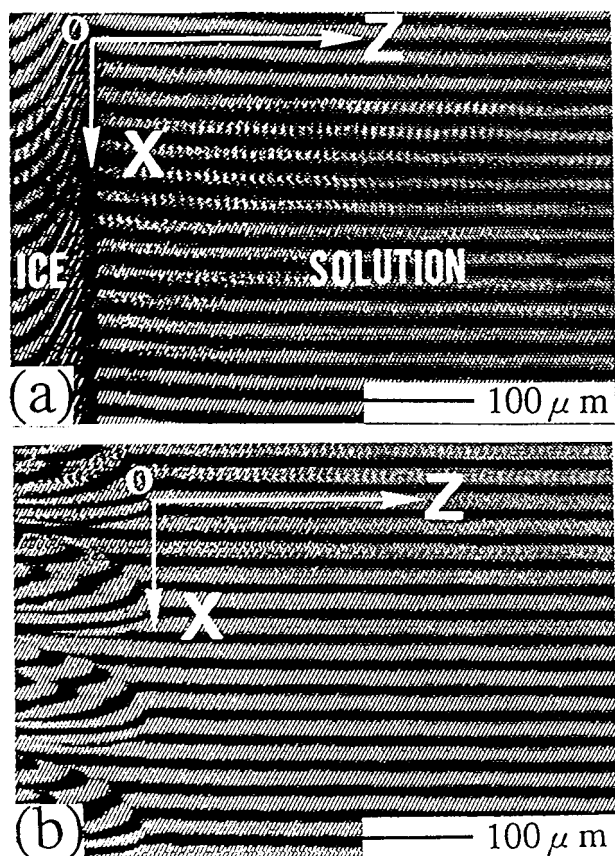
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Figure 1. Ice crystals growing at $V = 10$ μm/s and $G = 40$ K/cm during directional growth from the 3 wt % KCl solution observed by a Mach−Zehnder interferometer. (a) planar interface and (b) cellular interface. Times after the beginning of crystallization are (a) 90 s and (b) 610 s. Crystals on the left edge of the picture grow in the Z-axis direction.

ice/water interface also starts to grow. Since $k \approx 0$ in this case, there is little incorporation of the KCl solute into the ice crystal lattices.[10] As a result, the concentration of KCl in the vicinity of the interface gradually increases and the diffusion field of the solute is constructed in front of the interface. Since the refractive index of the solution depends on the concentration, a shift in the interference fringes is observed. Figure 1a shows a picture of the planar interface just before the beginning of instability and the interference fringes depending on the solute concentration in front of the interface at $t = 90$ s. When the concentration at the interface reaches a critical value, morphological instability starts to develop on the planar interface, and finally a finger-like cellular structure is formed as shown in Figure 1b. By analyzing the interference fringes, we can quantitatively obtain the solute diffusion field in the solution in the vicinity of interface.

3.2. KCl Diffusion Field in the Solution in front of the Advancing Interface. In Figure 1a, although the interference fringes are observed as parallel lines almost along the Z-axis, they are curved upward in the solution region near the interface. Then, the solute concentration $C(X,Z)$ in the solution is given by the equation

$$\frac{C - C_0}{C} = \frac{\lambda \delta X}{(n(C) - n_0)hw} \tag{1}$$

where C_0 is the initial solute concentration in the solution, δX is the shift in the interference fringe from the initial position, λ is the wavelength of the laser used ($= 632.82$ nm), h is the sample thickness ($= 200$ μm), and w is the fringe width ($= 23$

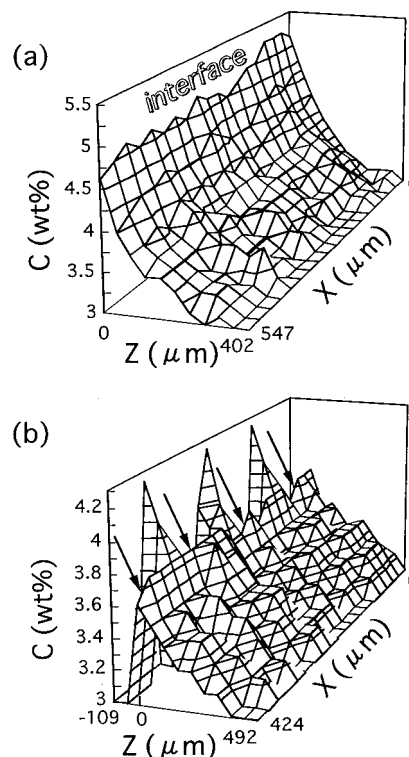**Figure 2.** Solute diffusion field in the solution in front of (a) the planar interface and (b) the cellular interface. $V = 10$ μm/s, $G = 40$ K/cm, and $C_0 = 3$ wt %. The positions of cellular branches are indicated by arrows in (b).

μm). Furthermore, the index of refraction $n(C)$ for a solution with a concentration C is given by the relation $n(C) = n_0 + bC$. Here n_0 is the index of refraction for pure water (1.3327 at 0 °C) and the coefficient b is 1.20×10^{-4} L/g in the case of a KCl solution.

Figure 2 shows three-dimensional illustrations of the distributions of solute concentration obtained from analysis of the pictures shown in Figure 1. In Figure 2a, we can clearly see that the concentration is a maximum at the interface ($Z = 0$) and exponentially decreases along the Z-axis. It should be noted that the contour lines of equiconcentration in the solution are nearly parallel to the planar interface. In contrast, periodic variations in equiconcentration lines, which are dependent on the cellular structure of the interface in Figure 2b, can be clearly seen. Furthermore, the concentration in the grooves between the neighboring cellular branches ($Z < 0$) is much higher than that at the tips of cellular branches ($Z = 0$), as indicated by arrows in the Figure 2b. Thus, these results strongly indicate that the coupling effects between the cellular interface structure and the diffusion field are very important for understanding the pattern formation of directional growth.

4. Discussion

4.1. Diffusion Length of KCl in the Solution. The diffusion length l_S of the solute, which is defined as the distance where $(C(l_S) - C_0)/(C_{int} - C_0) = 1/e$, may possibly be obtained from the solute distribution. In this experiment, l_S was found to be about 160 μm and independent of growth time. On the other hand, l_S is also estimated to be $l_S = D/V$ by two-dimensional theory, where D is the diffusion coefficient of the solute in the solution and V is the movement velocity of the interface. Since $D = 1.70 \times 10^{-9}$ m^2/s and $V = 10$ μm/s in the present case, $l_S = 170$ μm, which is consistent with the actual value obtained by the experimental result. It should be
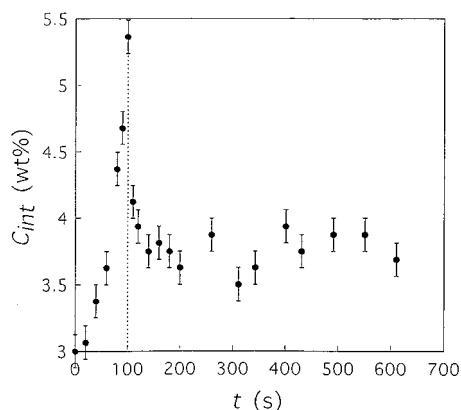
Figure 3. Changes in the solute concentration C_{int} at the interface in the solution as a function of growth time t. $V = 10 \; \mu\text{m/s}$, $G = 40$ K/cm and $C_0 = 3$ wt %. After interface instability developed, C_{int} was measured at the tips of cellular branches (*i.e.*, at $Z = 0$). Morphological instability was initiated at the time indicated by the dotted line ($t = 100$ s).

emphasized that l_S is much longer than the average cell spacing ($\approx 100 \; \mu\text{m}$). This result indicates that spacial fluctuation in the solute distribution was caused by the mutual interaction among growing cellular branches through the diffusion field around each branch.

4.2. Relationship between the Interfacial Pattern and the Solute Concentration at the Interface. Now, let us examine the variations in the diffusion field that occur due to the development of the interfacial pattern. Figure 3 shows variations in the solute concentration C_{int} ($=C(X,0)$) at the flat interface or at the tip of cellular branches as a function of growth time. At the initial stage of the flat interface ($0 < t < 100$ s), C_{int} increased from 3 to 5.4 wt % with the growth time. As soon as morphological instability occurred on the planar interface at t 100 s, C_{int} suddenly decreased to 3.7 wt %. After the cellular structure developed, a stable diffusion field was maintained during growth ($t > 200$ s).

Attention should also be given to the three-dimensional shape of the ice/water interface. We also observed curved interference fringes inside the crystal as shown in Figure 1. This means that the actual shape of the interface in Figure 1a is wedged and the shapes of cellular branches in Figure 1b are actually three-dimensional. Other recent theoretical and experimental studies[8,11−12] have also indicated that consideration of the morphological instability at the interface in three dimensions is essential for gaining an understanding of pattern formation.

The intrinsic behavior of the solute concentration in the interfacial region is also related to the development of the three-dimensional structure at the interface (*i.e.*, the sudden decrease in the solute concentration at the moment when morphological instability occurred at $t = 100$ s was caused by preferential capturing of the solute in the grooves between neighboring cellular branches and in the space between the crystal and the inner surface of the glass cell).

Furthermore, the theory[13] concerning cellular growth in two dimensions does not except steady state growth in the case of $k = 0$ such as the water−KCl system. However, we observed a quasi-steady state of the solute diffusion field during cellular growth. This result may be explained by the fact that the actual interface shapes are not two-dimensional but three-dimensional. Recently, we carried out simultaneous observations of the three-dimensional crystal shape and the diffusion field during directional growth. The results of these observations will be reported in a separate paper.

5. Conclusions

Directional growth experiments in a water−KCl solution were carried out to observe *in situ* the solute distribution in the solution in front of an advancing interface, using a Mach−Zehnder interferometer. As a result, the solute diffusion field was analyzed quantitatively for the first time.

It was found that the diffusion field fluctuates according to the pattern of the interface. This means that the interactions among cellular branches through the diffusion field must be taken into account to elucidate the mechanism of cellular pattern formation. In addition, the value of C_{int} rapidly decreases with growth time as soon as morphological instability begins to develop on the planar interface and is subsequently maintained at a constant level during cellular growth. On the other hand, it was found that the interference fringes are also curved inside the crystal. It was concluded that these results are strongly related to the three-dimensional pattern formation of the crystal shape at the ice/water interface.

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