Pattern Formation of Ice Crystals during Free Growth in Supercooled Water

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In-situ observations of ice crystals grown in supercooled bulk water were carried out using an interferometric optical system. Three-dimensional patterns of ice crystals were analyzed using the interference fringes. It was found that the growth of circular disk crystals can be categorized into two types, depending on whether screw dislocations are included in the disk crystal. It was also found that morphological instability on the circular disk of the ice crystals starts to develop at the moment that its *thickness* reaches a critical value and that the instability is independent of the radius of the disk crystal. The study also showed that the growth of an ice dendrite is not consistent with the universal law for dendritic growth.

1. Introduction

Study of the growth of ice crystals is of great importance for clarifying the melt growth mechanism, morphological stability, dendrite pattern formation, etc. The growth form of an ice crystal that is freely growing in supercooled bulk water changes from a circular disk to a perturbed disk and finally to a well-developed dendrite with hexagonal symmetry. Many theoretical and experimental studies[1−4] about the ice crystal growth have been carried out in connection with the general theory of dendritic growth.[5] However, many points remain unsolved and a full understanding of the growth forms of ice crystals has not yet been reached, probably because most past investigations have only examined the pattern formation of ice dendrites in two dimensions.

Recently, the authors[6] carried out *in-situ* observations of ice crystals grown in supercooled water using a Mach−Zehnder interferometer and analyzed the three-dimensional patterns of ice dendrites for the first time. It was found that the three-dimensional forms of ice crystals consists of a combination of flat basal interfaces and rounded interfaces and that the patterns of dendrite tips are not symmetrical about the basal plane. The results revealed that the pattern formation of ice dendrites in three dimensions is not consistent with the universal law for dendritic growth originally proposed by Langer and Müller-Krumbhaar.[5]

In addition to knowledge of the dendritic pattern development, knowledge of the morphological stability of circular disk crystals is also of importance for understanding the mechanism of pattern formation during the growth of ice crystals. Fujioka and Sekerka[7] theoretically analyzed the morphological stability at the periphery of a circular disk with a constant thickness on the basis of Mullins−Sekerka's instability theory.[8] However, there has been never any systematic investigation of the growth process of a circular disk because three-dimensional observations of thin disk crystals are difficult by conventional observation systems.

The purpose of this study was to carry out *in-situ* observations of ice crystals in three dimensions. Based on the results, the morphological stability of a circular disk and the pattern formation of an ice dendrite are discussed in this paper, in conjunction with theoretical considerations concerning morphological stability.

2. Experimental Procedure

An experimental apparatus was designed for the purpose of observing ice crystals growing in supercooled water. A cylindrical growth cell (50 mm in diameter and 40 mm in length) made from optically flat glasses was immersed in a cubic water container with glass windows. An ice crystal, which had been seeded inside a glass capillary tube inserted downward into the center of the growth cell, began to grow freely in supercooled bulk water. The water used in this experiment was purified by deionization, distillation, and filtration. The temperature of the water was monitored by a thin thermocouple inserted into the growth cell within an absolute accuracy of 0.01 K.

The growing ice crystal was observed through a Mach−Zehnder interferometer. Interference fringes observed in this experiment were dependent on the ice crystal thickness. The shift of interference fringes originating from the thermal diffusion field around an ice crystal is negligibly small compared to its sensitivity. Consequently, the thickness interval of each interference fringe corresponds to a difference of 25.4 μm for the He−Ne laser light (wavelength = 632.8 nm). The results of *in-situ* observations were recorded by a video system and analyzed to obtain three-dimensional forms of ice crystals.

3. Results

3.1. Morphological Instability Occurring on a Circular Disk Crystal. Figure 1 shows time-sequence pictures (on the left side) of an ice crystal growing in supercooled water at ΔT = 0.23 K and the three-dimensional patterns (on the right side) analyzed from the interference fringes. Here, it should be noted that the morphology of an ice dendrite is completely different from not only that of a body of revolution but also from that of a symmetric paraboloid, which are usually proposed in theoretical considerations for dendritic growth. Furthermore, this asymmetric pattern is observed immediately after morphological instability occurs at the periphery of the circular disk.

In order to clarify the morphological stability occurring on a circular disk crystal, we measured the radius r and thickness h of circular disk at the same time, using the interference fringes. Figure 2 shows changes in both r and h for several disks grown under a fixed supercooling condition of $\Delta T = 0.09$ K. The growth of the disk crystals was stable up until the time indicated by open squares and perturbation began to develop along the

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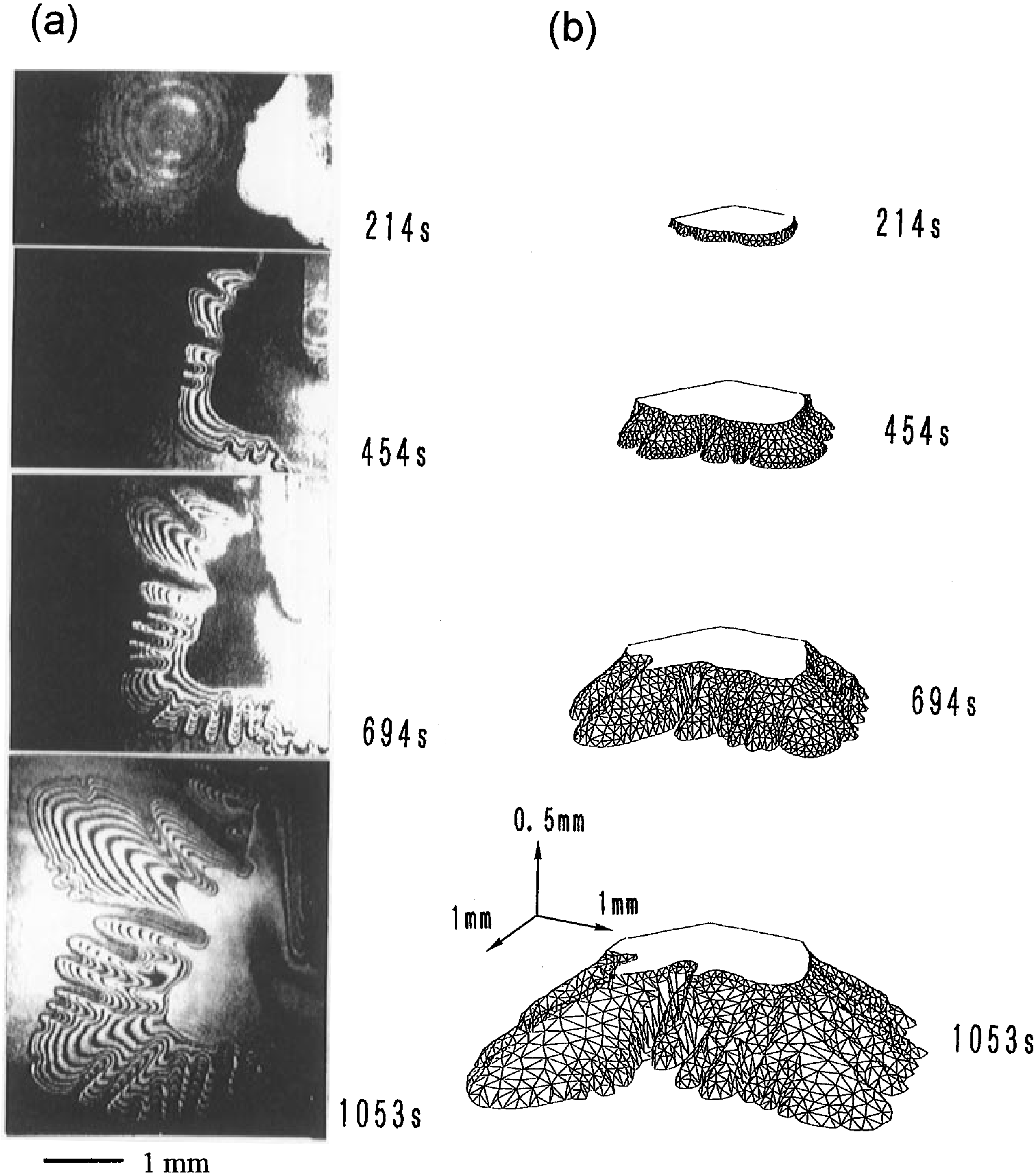

Figure 1. Time evolution of the growth of an ice crystal. Asymmetric patterns in three dimensions are clearly shown: $\Delta T = 0.23$ K.

periphery of the disk crystals at the moment indicated by open squares. Even though all the crystals in Figure 2 grew at the same supercooling conditions, two growth modes were apparent: type I (crystals A, B, and C) and type II (crystals D and E). Type I crystals grew by almost constant velocities in both the radial and the *c*-axis (thickness) directions of the circular disk, while type II crystals grew preferentially in the radial direction at the initial state and then began to grow in both directions. It should be emphasized that the boundary between stable growth and unstable growth is concentrated in a very narrow range of thickness between 180 and 230 μm regardless of growth-mode types.

3.2. Dendritic Growth. Perturbations initiated at the periphery of a circular disk crystal gradually develop and finally a dendritic crystal with a hexagonal symmetry is formed as a marginally stable structure. In the present experiment, three basic parameters (growth velocity and two distinct principle radii at a dendrite tip), which characterize the dendritic patterns, can be measured at the same time. From the measurement of these parameters as a function of supercooling, we can discuss the relationship between the growth state of ice dendrite and the universal law for dendritic growth. Since the results of the above have already been published,[6] we summarize the points to be emphasized as follows. Namely, the supercooling dependencies of growth velocities at the dendrite tips completely coincide with theoretical predictions determined by the universal law[5] on the assumption that the shape of a dendrite tip approximates a paraboloid of revolution. On the other hand,

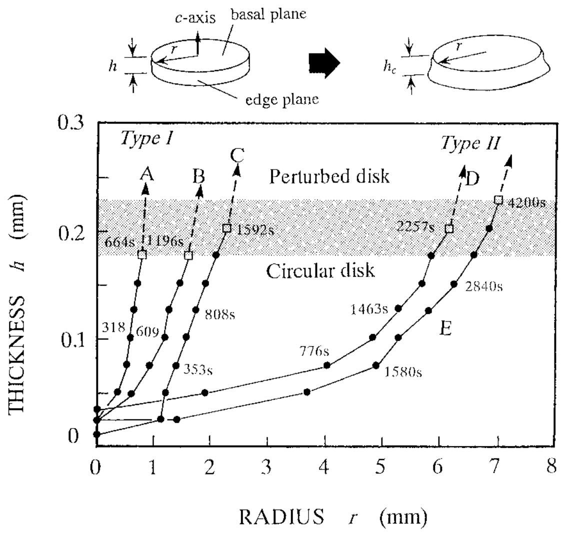

Figure 2. Variations in thickness and radius of a circular disk crystal. Crystals A, B, and C are type I and crystals D and E are type II. All crystals were grown under the same supercooling conditions of 0.09 K. Open squares indicate the limits of stable growth of circular disks. (Note that the scales of thickness and radius are different.)

the stability criteria estimated for both distinct tip radii are inconsistent with theoretical assumptions in the universal law. This discrepancy observed on the shape of dendrite tips is thought to be closely related not only to the anisotropy of interfacial free energy but also to the anisotropy of growth kinetics.

4. Discussion

Transition from stable to unstable growth observed on the circular disk crystal occurred when the *disk thickness* reached at a critical value as shown in Figure 2. This indicates that the critical factor for morphological instability is not the crystal radius but the crystal thickness. Fujioka and Sekerka[7] theoretically analyzed the morphological instability of circular disk crystals with a constant thickness and showed that morphological instability occurs when the *disk radius* exceeds a critical value. This result contradicts with the present experimental result. Consequently, a new theoretical approach is needed to consider the effect of growth in the *c*-axis direction.

Next, let us consider the reason why two growth types of circular disks were observed. It is known that only the {0001}-faces are always observed as flat faces on a crystal and that step migrations are sometimes observed on basal planes.[9] However, Nada and Furukawa[10,11] recently carried out molecular dynamics simulation of the interface between ice and water under nonequilibrium conditions, and their results showed that the growth of {0001}-faces is dominated by a layer-by-layer mechanism, while the growth of $\{10\bar{1}0\}$-faces is dominated by a mechanism of collective incorporation of water molecules. Thus, we can conclude that type I crystals included screw dislocations even at the initial state of disk growth, while type II crystals did not include any screw dislocations at the initial state. In the situation of type II crystals, the disk crystal can grow preferentially in the direction of the radius, because the growth is basically dominated by the transport efficiency of latent heat released by solidification at the periphery of the disk crystal. This means that, the smaller the thickness of the disk crystal is, the higher the lateral growth rate of disk crystal will be.

The growth of an ice dendrite also is influenced by the kinetic effect mentioned in the previous paragraph. The discrepancy between the actual ice dendrite and the pattern assumed by universal law may be due to this kinetic effect. A recent study of one-directional growth of an ice crystal by Nagashima and Furukawa[12] clearly indicated the anisotropy of interfacial kinetics for melt growth in planes parallel to the *c*-axis (*i.e.*, in the prismatic planes). That is, the kinetic effect was the largest in the direction of the $\langle 10\bar{1}0\rangle$-axes (*i.e.*, on the $\{10\bar{1}0\}$-faces) and the smallest in the direction of the $\langle 11\bar{2}0\rangle$-axes (*i.e.*, on the $\{11\bar{2}0\}$-faces). This result also supports the notion that the pattern formation of ice crystals is strongly dominated not by the anisotropy of interfacial free energy but by the anisotropy of interfacial kinetics.

5. Conclusions

Growth processes of ice crystals in supercooled water were observed *in-situ* using a Mach−Zehnder interferometer. From analysis of interference fringes that originated from the ice crystal thickness, three-dimensional patterns of ice crystals were obtained. Morphological instability of the circular disk crystal began to develop when the disk thickness exceeded a critical value and was independent of the circular disk radius. Dendritic ice crystals were also analyzed in three dimensions, and it was found that the pattern formation of an ice dendrite can not explained by the universal law of dendritic growth. The pattern formation of ice crystals in supercooled water is thought to be strongly dominated by the effects of anisotropic interface kinetics.

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