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Growth kinetics and pattern formation of ice dendrites at small subcoolings

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작은 과냉각 상태에서 ice dendrite의 결정 성장 특성

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Abstract An experimental study of the dendritic growth of ice crystals growing in quiescent pure subcooled water was made at small subcoolings of 0.035 $K < \triangle T < 1.000$ K. It was observed that the growth kinetics and morphology are functions of not only subcooling but also thermal convection. When the subcooling is less than 0.35 K, it was found that effect of thermal convection on growth kinetics of ice dendrites becomes important. Quantitative measurements of growth velocity, V_G, and tip radii of the edge and basal planes, R_1 and R_2, were made simultaneously as a function of subcooling.

요 약 과냉각도가 0.35 K보다 작은 영역에서 ice dendrite의 결정 성장 특성 및 morphology는 과냉각도 뿐만 아니라 자연대류의 함수임을 관찰하였다. 즉, 결정 성장에 대한 자연대류의 영향은 결정 성장 자체에 의한 moving boundary 효과보다 우세함을 알 수 있었다. 본 실험 범위에서 ice dendrite의 성장 속도 및 tip size(edge 및 basal plane)를 과냉각도의 함수로 정량화하였다.

1. Introduction

The growth of crystals from pure subcooled or constitutionally subcooled melts produces dendritic structures in which the leading tip of the main stem propagates in the preferred crystallographic direction. Traditionally, the understanding and control of this phenomenon is of great concern to materials scientists because the dendritic growth of materials during solidification processes leads to microsegrigation and this causes internal defects in final products [1, 2]. Also, physicists have devoted their attention to dendritic growth as an example of spontaneous pattern formation in nonequilibrium systems like snow flakes [3,4]. To understand the fundamental principles underlying such a system, the study of dendritic growth of ice crystal is valuable because the ice/water system is transparent and thus direct observation and recording of the solid - liquid interface is possible.

During the last two decades, many experimental studies have been done on the dendritic growth of ice crystals. The main goals of Kallungal [5], Kallungal and Barduhn [6] and Chang [7]'s experiments were to investigate the effect of forced convection on dendritic growth of ice. The purpose of Fujioka's study [8] was to model the growth mechanism of an ice disk and the objective of Tirmizi and Gill [9,10] was to consider the effect of thermal convection on an ice dendrites. All of these experiments showed that the shape of an ice dendritic tip is very close to an elliptical paraboloid and that thermal convection plays a significant role during dendritic growth.

However, there have been very few attempts to reconcile the experimental results for ice dendrites to the theories. Ananth and Gill [11 - 13] applied their theory, which was driven by using Oseen's viscous flow approximation, to dendritic growth of an ice crystal with forced convection. They showed that their results agree qualitatively with the experiments of Kallungal and Barduhn [6] and Chang [7]. However, these theories of dendritic growth have not been tested for the experimental results of ice in quiescent water, because of lack of experimental data available. The purpose of present work is to investigate pattern formation and obtain the simultaneous data of growth velocity and tip radii of both planes of ice dendrites growing in quiescent water at small subcoolings of $0.035\ K < \triangle T < 1.000\ K$.

2. Experimental apparatus and technique

This experimental study requires a direct, in situ observation of a crystals growing freely in the growth cell. For this purpose, the growth cell, thermistors for temperature measurement and control, a constant cooling and a heating unit, and stirrers are placed inside a thermostat. The thermostat is well insulated with 2 inch thick styrofoam sheets, and filled with an ethylene glycol solution as the thermostat fluid. Microscope - camera (or VCR) assembly and light source are installed in a line with the crystal growth cell. Detailed description of experimental set - up has been given elsewhere [14,15].

Growth cell : The cells are made of Pyrex glass and mainly consist of a nucleation chamber, a crystal growth chamber and a rotating and tilting system as shown in Fig. 1. Nucleation of the ice crystal is accomplished by using the latent heat of vaporization of liquid nitrogen. From the tip of the capillary, the ice crystal emerges and grows freely to form dendrites in the subcooled water. In order to ensure that the crystal growth is unencumbered by the chamber wall, a 6 cm diameter growth chamber was made.

In order to investigate the effect of dissolved air on dendritic growth, two cells with water of different levels of purity were used. One cell was operated in open air (open system). The other was filled with distilled air-free water using vacuum distillation (closed system). As can be seen from Fig. 1, the vacuum distillation column designed to get degassed pure water is made of Pyrex glass and consists of a 1 *l* round flask which is connected with a cylindrical reservoir and a growth cell. The cylindrical reservoir is used to trap the vacuum distilled water.

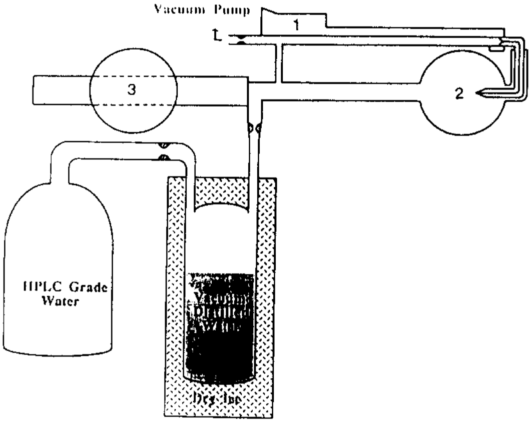


Fig. 1. Schematic diagram of growth cell with vacuum distillation column. 1. Nucleation chamber 2. Crystal growth chamber 3. Rotating and tilting system.

In order to evacuate the gas further before trapping the distilled water, the water in the bottom of the flask is partially solidified and melted because ice forms in a way that causes most of the dissolved air to be expelled. After this procedure is applied several times, the pure distilled water is collected in the cylindrical reservoir by cooling with dry ice. If enough water is collected, the sealing point between reservoir and flask is fused close under vacuum. Again the melting and solidification procedure is applied to all the distilled water of the reservoir several times under vacuum. Finally, the distilled water is transferred to the growth cell and the growth cell is hermetically sealed under vacuum.

Purity of water used : In this experiment, HPLC grade pure water (Fisher Scientific Co.) which is free from organic materials was used. By using a digital multimeter (Model 8012A, Fluke Co.) and a digital electrometer (Model 616, Keithley Co.) with an enclosed-type glass cell (platinum electrode, Fisher Scientific Co.), the electrical resistivity of HPLC grade water was measured and found to be 1.8 ~ 2.1 megohm-cm. Thus, by assuming that most of the impurity in this water is dissolved air, the purity level was calculated approximately using the solubility of air in water [16]. It was found to be about 99.99 %.

The purity level of the water in our closed cell can be obtained by measuring its triple-point. For this purpose, a triple-point cell was manufactured in this laboratory, and the purity level of the water was calculated by comparing its triple-point with that of a master triple-point of water cell manufactured by Jarrett Instrument Co. The vacuum distillation followed by several melting and freezing setps was used to fill the triple-point cell with pure water in the same way as for the growth cell. The triple-point condition has been made by using the inner sheath method [17,18]. The triple point temperatures of both our cell and the master cell were recorded in time. The difference of triple point of both cells is found to be reproducible within 0.5 mK. Thus the purity level can be calculated by using the equation [19] given by

$$\triangle T_f = T_f - T_e = K_f X = \frac{RT_f^2}{L} X,$$

where T_f is the triple point of the pure substance, T_e is the corresponding temperature for the actual sample with an infinitesimal amount of impurity, K_f is the cryoscopic constant, X is the mol fraction of the impurity, R and L are the gas constant and the molar latent heat of fusion, respectively. In this comparison of triple points, it was found that the purity level of the water purified in this laboratory by vacuum distillation with the melting and freezing process was above 99.999 %. For water triple point cells, the pressure head due to gravity will cause the equilibrium temperature to be slightly lower than that for zero head, because the Clausius-Clapeyron coefficient dP/dT in water is negative and has a magnitude on the order of 10^{-6} K/cm, hence, it is negligible [20].

Measurement of growth velocity : In order to get accurate data of growth velocity under the influence of thermal convection on dendritic growth of ice crystals, it is required that the ice dendrites grow parallel to the gravity vector, g. In addition, in order to photograph the edge and basal plane accurately, dendrites must lie in the plane of observation. For this alignment, the following steps are taken as dendrites emerge from the capillary tip. Firstly, a stop watch is started to record the elapsed time during the evolution of the ice crystal. Secondly, the growth cell is rotated and tilted to the desired direction for photography, and the microscope-camera assembly is also moved to the desired position. The rotating and tilting procedure must be done very slowly to prevent circular flow that may disturb thermal convection of subcooled water in the growth cell.

In order to calculate the ice growth velocity of the ice dendrite as a function of time, the distance traveled by the dendrite tip was measured by using a reticle inserted in the eye piece of the microscope. The time elapsed was measured with a stop watch. The capillary of the growth cell and a scientific scale (American Optics Co.) was used for calculating the magnification of the microscope.

Measurement of tip radii : Once the crystal emerges from the capillary tip, photographs of the dendrite are taken and the time elapsed is recorded. The negative films are then used to calculate the tip radii of the basal and edge planes as a function of time. Tip size measurements are carried out by using Microcalc-1 (Ram Optical Instrumemt Co.). The negative film is mounted on the transverse stage of Microcale-1, in which the magnified image of the dendrite is transmitted to the screen of the monitor via a microscope-CCD solid state camera system. The width w of crystal at a distance l from the tip of the crystal is measured by moving the transverse stage, whose resolution is 1 μm. Assuming the shape of the image of dendrites is parabolic, the tip radius can be calculated by the formula, $R = w^2/8\ l$.

Figure 2 and 3 which are typical data of R_1 and R_2 calculated by this formula, show that the parabolic approximation for the shape of the tip of the dendrite is reasonable. In the case of the basal plane, 15 ~ 20 points of w and l were measured in each negative film. From those data, points which are within 100 μm or points which are in a tip region not affected by a side branch are collected and then the average value of these points is taken for the analysis. In the case of the edge plane, data which are within 40 μm from the tip are taken because the tip radius of the edge plane decreases very slowly with distance from the tip, especially at low subcooling, as can be seen in Fig. 2.

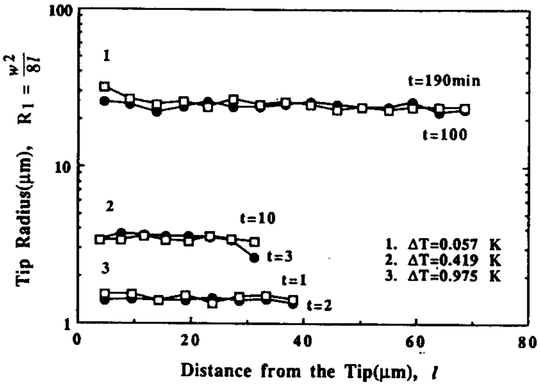


Fig. 2. Tip radius of the edge plane versus the distance measured from the tip.

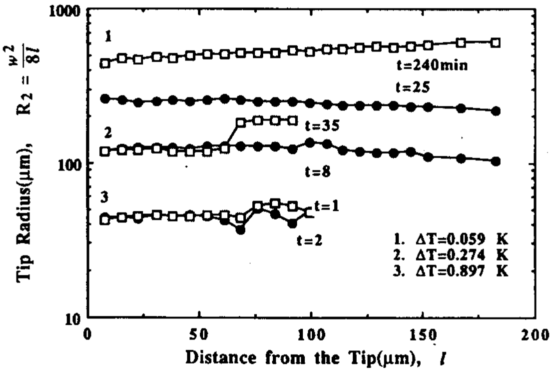


Fig. 3. Tip radius of the basal plane versus the distance measured from the tip.

3. Results and discussion

Pattern formation : Observations of pattern formation of growing ice crystals were made simultaneously with grow kinetics measurements, by taking microphotographs or taping the growing ice crystals with time for given subcoolings. Figure 4 illustrates the growth velocity of ice dendrites growing vertically upwards measured with time. Figure 4 (a) shows that, at $\triangle > 0.1$ K, a steady growth velocity developed as soon as the ice crystal emerged from the capillary tip. At $\triangle T < 0.1$ K, however, a steady state is reached after an initial transient state that lasts longer as the subcooling decreases. The transient state of growth velocity during dendritic growth is found to be in other

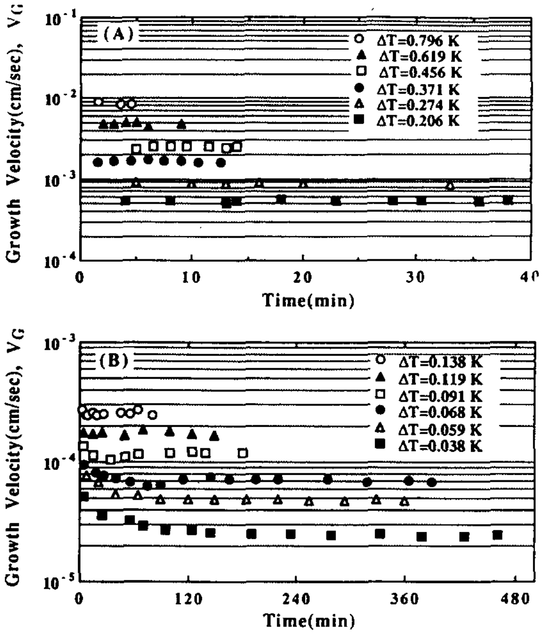
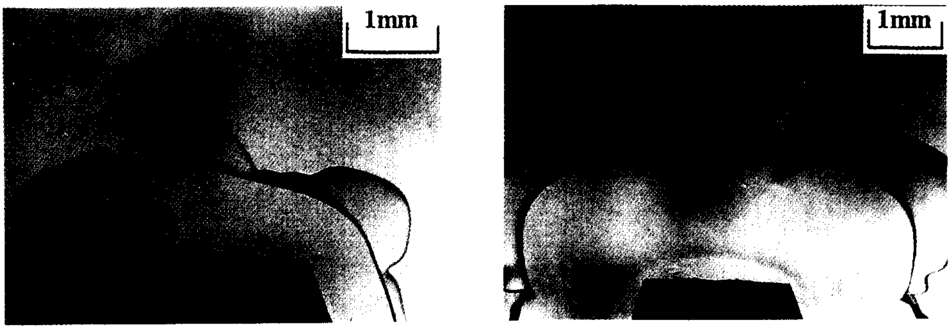
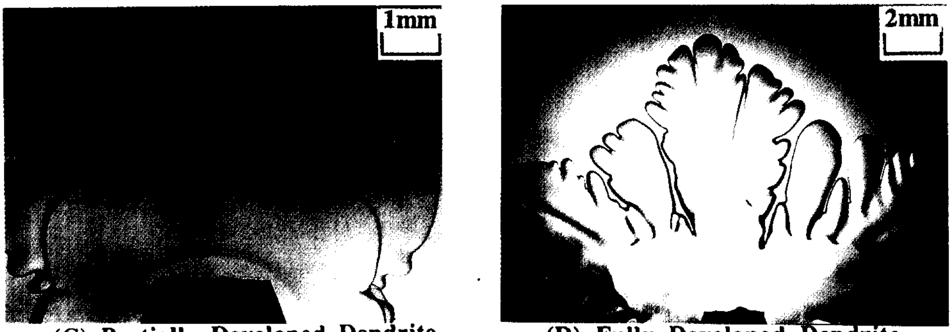


Fig. 4. Growth velocity of ice dendrites growing vertically upward with time.

materials such as krypton [21]. Unsteady nature of the growth velocity indicates that the growth pattern of an ice crystal evolves with time, namely, from smooth disk, to perturbed disk, to partially developed dendrite and to fully developed dendrite, as shown in Fig. 5. Figure 5 (A) is taken at 50 min after the crystal emerged from the capillary tip at △T = 0.062 K. During this period, the basal plane of ice crystal grows as a disk, following the preferred crystallographic direction. As the growth process continues, the disk morphology becomes unstable and perturbation of interface starts to take place as shown in Fig. 5 (B). And then number of perturbation increases and tip forms parabolic shape (Fig. 5 (C) ; partially developed dendrite). Finally, ice crystal grows as a fully developed dendrite with constant growth velocity (Fig. 5 (D)). The perturbations in ice disk or side branch formation of dendrite seems to occur by competition between destabilizing force, heat transfer at solid/liquid interface, and stabilizing capillary effect suggested by the morphological stability concept of Mullins and Sekerka [22]. Both the angles between the main growth directions and axile angles which are angles between a main branch and side branch are found to be 60° since ⟨1120⟩ direction is the preferred crystallographic direction of ice crystal which has a hexagonal closed packed structure. The transition of morphology with time seems to be accelerated as subcooling increases. Thus at subcooling greater than 0.1 K, one can observe only fully developed dendrites which grow steadily. Figure 6 are typical microphotographs of fully developed ice dendrites grown at △T = 0.542 K. Basically, the shape of dendrites at any subcooling is same. However, tip is sharper and more symmetric and side branch spacing is formed more regularly as subcooling increases. Tirmizi and Gill [7] has studied the pattern evolution of the ice dendrite intensively by using image analysis. They characterized each phase of pattern evolution by calculating complexity ratio ξ, which is ratio of total are length to square of total area of basal plane, as a function of time at given subcooling. They obtained that ξ remains constant during the initial stage (ice disc) and then ξ increases rapidly as interface of ice disc is perturbed and finally ξ increases



(A) Disk, t=50min **(B) Perturbed Disk, t=110min**



(C) Partially Developed Dendrite, t=130min **(D) Fully Developed Dendrite, t=285min**

Fig. 5. Pattern evolution of an ice crystal with time at $\triangle T = 0.062$ K.

Table 1

Growth kinetics, V_G, R_1 and R_2, reported by various investigators

Investigators	$\triangle T$ (K)	V_G (cm/sec)	R_1 (μm)	R_2 (μm)	A
Farrer & Hamilton (1965)*	0.03~1.02	$0.0096\triangle T^{2.04}$			
Pruppacher (1967) [23]	0.5 ~9.0	$0.035\triangle T^{2.22}$			
Fuige & Thijssen (1969)*	0.9 ~5.0	$0.03\triangle T^{2.22}$			
Simpson et al. (1974) [24]	0.4 ~1.0	$0.0182\triangle T^{3.0}$			
Kallungal (1977)	0.11~1.0	$0.0118\triangle T^{2.17}$	$\frac{0.6}{\triangle T}$	$\frac{43}{\triangle T^{1.24}}$	50~100
Fujioka (1978)	0.2 ~1.6	$0.0142\triangle T^{2.38}$			
Chang (1985)	0.2 ~1.0	$0.009\triangle T^{2.01}$		$\frac{39}{\triangle T^{1.1}}$	
Tirmizi (1985, 1987)	0.06~0.2	$0.00035\triangle T^{1.06}$			
	0.2 ~1.1	$0.0187\triangle T^{2.09}$	$\frac{0.88}{\triangle T}$		55~25
Present work	0.035~1.0	$0.011\triangle T^{1.94}$	$\frac{1.51}{\triangle T}$	$\frac{42.0}{\triangle T}$	28

* as cited by Kallungal [5].

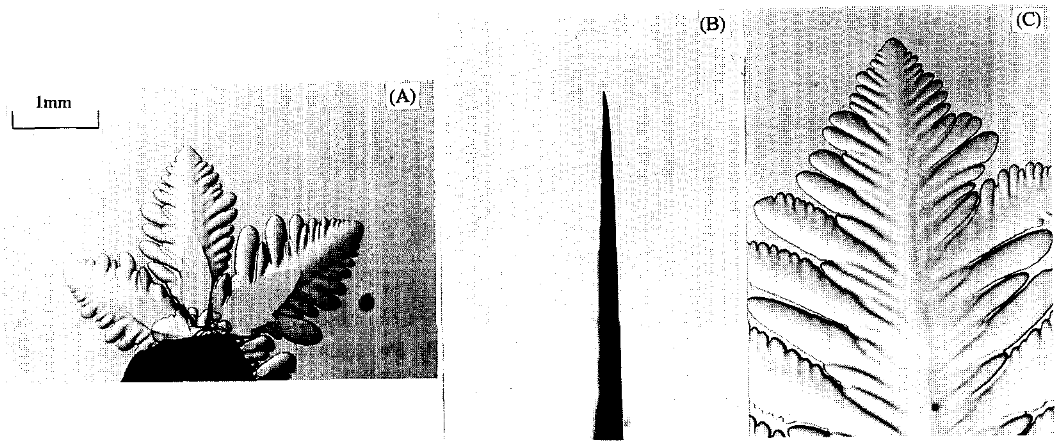


Fig. 6. Microphotogaphs of fully developed ice dendrites at $\triangle T = 0.542$ K. (A) Photograph taken at t = 1 min, (B) Edge plane growing verticlly upward (t = 5 min 30 sec) and (C) Basal plane growing verticlly upward (t = 6 min).

very slowly when the pattern has evolved into a fully developed dendrite. As can be seen from Fig. 5, it is natural that our observations are in agreement with their analysis qualitatively.

Growth kinetics : A review of dendritic growth of ice in quiescent water shows that the growth kinetics are not consistent among the investigators [5-8]. Present experimental data of V_G, R_1 and R_2 are correlated and tabulated with those published previously in Table 1. From Table 1, it can be seen that tip ratii of the edge and basal plane reported are very few to date. Furthermore, growth velocities very by as much as order of magnitude for the subcoolings of $0.1\ K < \triangle T < 1.0\ K$. Here it is interesting to consider why the experimental data are not consistent among the investigators, compared with present experiments.

Referring to Fig. 4, the transient time needed to reach steady state in growth velocity of ice dendrites was obtained. As shown in Fig. 7, the transient time increases rapidly due to lack of driving force as subcooling decreases. For quantitative analysis, data of growth velocities taken at steady state were averaged. These growth velocities are compared with the previous results of Kallungal [8], Fujioka [5] and Tirmizi [10]. Figure 8 shows that the growth velocity is not affected by dissolved air, and the present data are in good agreement with Kallungal and Fujioka's results at subcooling greater than 0.35 K. However, at $\triangle T < 0.35$ K, our experimental data show that the growth velocity is higher then the extrapolated lines of their results. This trend becomes stronger as the subcooling decreases, suggesting that the heat transport during solidification at the small subcoolings is strongly affected by the thermal convection.

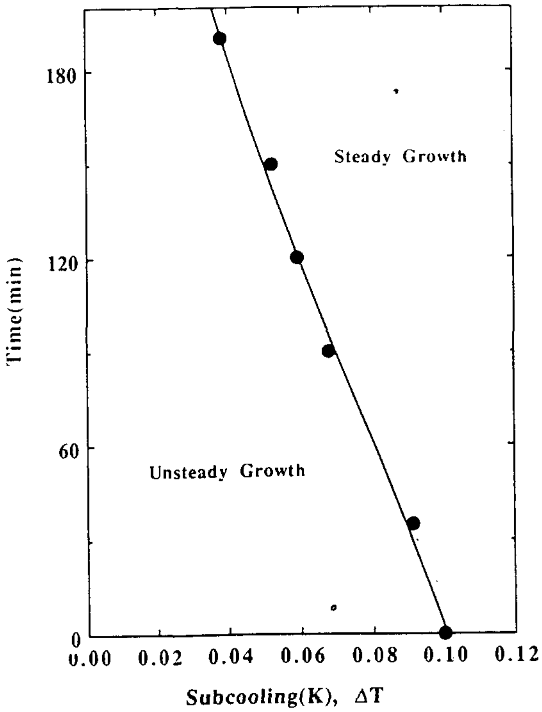


Fig. 7. Transitient time measured to reach steady state in growth velocity with subcooling.

This is in agreement with the theoretical prediction of Ananth and Gill [12].

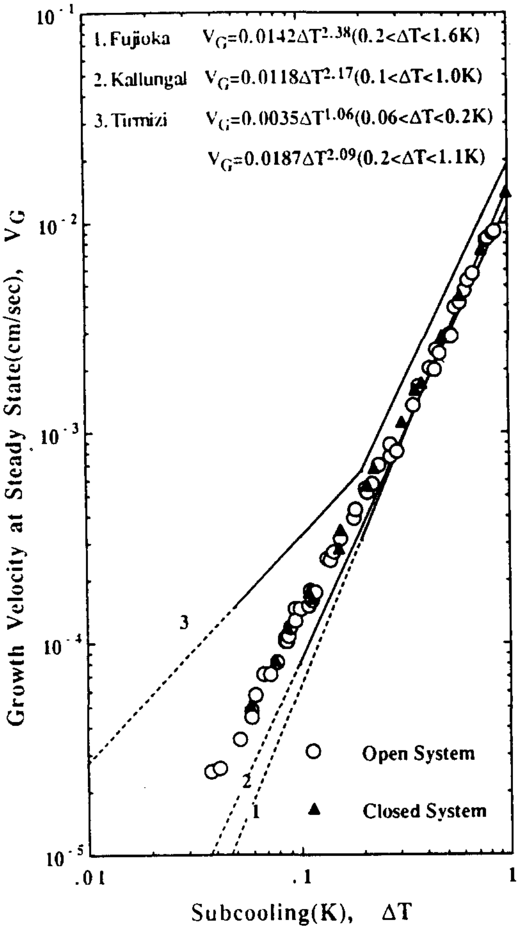


Fig. 8. Comparison of growth velocity with those of other investigators (…… : Extrapolation of experimental results).

Figure 8 illustrates that the experimental results of Tirmizi are higher than any other data in the entire range of the subcoolings. One possible reasoning of the discrepancy might be from error in his temperature measurement. If so, the experimental results of Tirmizi could be shifted in order to compare with our results at subcooling less than 0.2 K. The shifted velocities of Tirmizi are shown to be higher than the present work by a factor of 3 at △T = 0.06 K. This implies that the velocities measured by Tirmizi at the small subcoolings probably are transient state values, not steady state values, because our experiments show that it takes about 2 hrs at △T = 0.06 K, to reach steady growth velocity (See Fig. 7). Thus it is believed the effect of thermal convection on dendritic growth kinetics of an ice becomes strong as subcooling decreases, but the intensity is not as large as reported by Tirmizi. The effect of thermal convection on dendritic growth of ice crystals has been discussed quantitatively by Koo et al. [15].

The tip ratii of the edge plane R_1 were observed to be independent of time at $\triangle T > 0.1$ K. At $\triangle T < 0.1$ K, the time period of the initial transient state of R_1 was approximately coincident with that of the initial transient state of the growth velocity at a given subcooling. On the other hand, the dendritic tip of the basal plane seemed to grow with an invariant shape at $\triangle T > 0.35$ K. However, at $\triangle T < 0.35$ K, the tip radius of the basal plane R_2 dropped by a factor of about 2, which results from tip splitting [15].

Using our experimental data for R_1 and R_2, an aspect ratio A ($= R_2/R_1$) of the ice dendrite was calculated as a function of subcooling. For the calculation of the aspect ratio at $\triangle T < 0.35$ K, where the tip splitting occurs, maximum values of R_2 were selected because these values may be the maximum possible stable size of R_2 at a given subcooling. The average values of R_2 were used in the region where tip splitting does not occur and average values of R_1 obtained at steady state were used.

Figure 9 shows the plot of aspect ratio versus dimensionless subcooling, the Stefan number $St = \triangle T/(L/Cp)$, where L is the latent heat of solidification and Cp is the heat capacity, respectively. It shows that the aspect ratio of the ice is about 28 in the range of the present experiments. Thus approximation of elliptical paraboloid in shape of the tip of ice dendrites is reasonable. However, Kallungal [8] reported that the aspect ratio is in the range 50 to 100 at $0.1 \text{ K} < \triangle T < 1.0$ K. The deviation between our data and those of Kallungal's probably arises from the measurement of different parts of the edge plane. Figure 10 illustrates the tip ratius of edge plane R_1 is presented as a function of subcooling and compared with Kallungal's and Tirmizi's results. The R_1 data obtained by Kallungal are smaller than present data by a factor of 2. It is known that Kallungal also used the formula given in this article for the calculation of tip radii. Possible reason of the size difference in edge plane might be from microphotography. Contrast of solid/liquid interface in

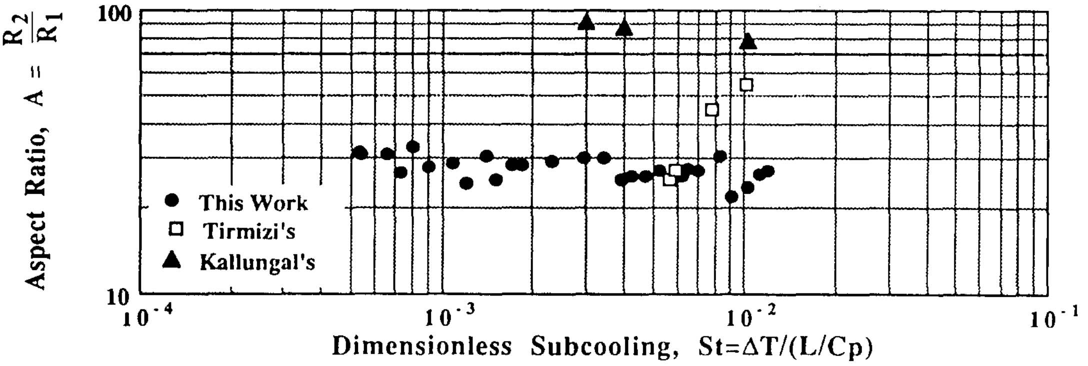


Fig. 9. Plot of aspect ratio versus dimensionless subcoolings.

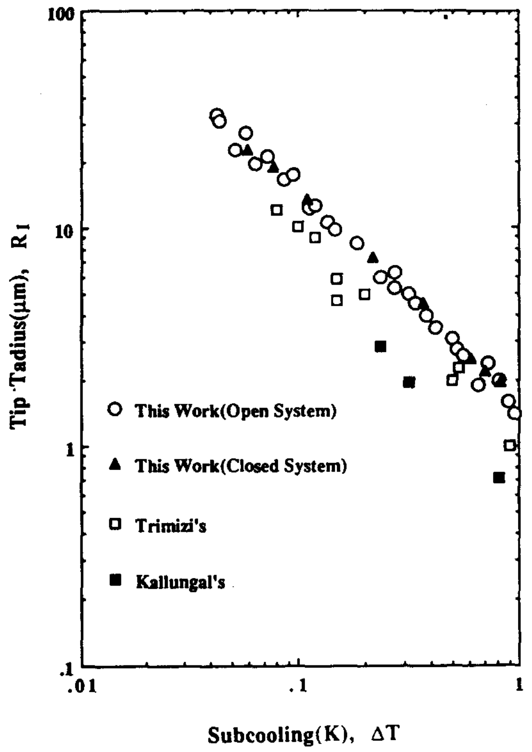


Fig. 10. Tip radius of the edge plane with subcooling.

their photographs is found to be much blurred than those taken by present photograph system. This effect may introduce a large error in size measurements of the tip radius of the edge plane, which is order of microns. The discrepancy between the present work and Tirmizi's data also might be attributed to same reason given to the comparison with Kallungal's result. In contrast to Kallungal's Tirmizi [10] reported that the aspect ratio decreases from 55 to 25 as subcooling decreases from 0.8 to 0.45 K as can be seen in Fig. 9. Combining the R_1 data and the aspect ratio given by Tirmizi [9], it can be deduced that R_2 decreases as the subcooling decreases. This trend is in contrast with the results of Kallungal [8], Chang [7] and present work. Clearly, Present experimental data which has been reported [15] are shown to be in good agreement with their results where the comparison is available. However, there is no report for the R_2 data of Tirmizi, which is contrary to the present experiments.

4. Conclusions

Growth kinetics of the ice dendrites growing vertically upwards were measured systematically as a function of time at the subcooling of $0.035\ K < \triangle T < 1.000\ K$. As subcooling decreases ($\triangle T < 0.35\ K$), it was observed that the flow induced by the thermal convection begins to contribute significantly to the dendritic growth kinetics of ice crystals. However, the effect of dissolved air on the dendritic growth kinetics of ice is negligible.

At $\triangle T < 0.1$ K, the growth pattern of an ice crystals was observed to evolve with time, namely, from smooth disk, to perturbed disk, to partially developed dendrite and to fully developed dendrite. However, at $\triangle T > 0.1$ K, a steady growth velocity developed as soon as the ice crystal emerged from the capillary tip. At steady state, the growth velocity, the tip radii of the curvature were correlated as a function of the subcoolings and their expressions are : V_G (cm/sec) $= 0.011\triangle T^{1.94}$, $R_1(\mu m) = 1.51/\triangle T$ and $R_2(\mu m) = 42.0/\triangle T$.

Acknowledgments

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