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IIIII In-situ Observation of Crystal Growth IIIII
(Review)

Crystal Growth Experiments of Ice in Kibo of ISS

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Abstract

Microgravity experiments for ice crystal growth were conducted twice in the Japan Experiment Module "Kibo" of the International Space Station. Experimental cartridges newly developed for each experiment were transported to the space station and installed in the SCOF facility. All of the experiments were possibly could be performed by using a tele-control system on the ground. Crystal patterns during free growth of ice crystals in supercooled water were observed by using specially designed interference microscopes. Experiments were carried out for ice crystal growth in supercooled pure water (D_2O) and in a supercooled solution (H_2O) of antifreeze glycoprotein. Based on analysis of moving images, the pattern formation mechanism of ice dendrites in pure water and the fluctuation mechanism of growth rates in protein solution are discussed.

Keyword(s): Kibo, Ice crystal, Melt growth, Pattern formation, Antifreeze glycoprotein

1. Introduction

Shapes of growing crystals are determined by the interplay of complex processes that include transport of energy and matter through bulk phases, capillarity-related processes that determine local equilibrium conditions at the crystal-nutrient interface, and non-equilibrium kinetic processes that take place locally at that interface. By treating the above three processes in pairs, Sekerka[1)] showed that the interplay of transport and interface kinetics controls the development of facet instability, that the interplay of diffusive transport and capillarity leads to morphological instability, and that the interplay of capillarity and interface kinetics controls the development of corner instability.

Ice crystals, the most ubiquitous crystalline materials in our daily life, grown in supercooled pure water, show the most beautiful patterns of all kinds of crystals in nature. It is well known that the ice crystals grown in supercooled water under atmospheric pressure show two-dimensionally developed hexagonal dendrites as do snow crystals grown from water vapor. Actually, an ice crystal has a three-dimensional pattern consisting of a combination of two flat basal faces and a rounded face during its growth, and the tip pattern of an ice dendrite is not symmetric with respect to the basal plane[2-5)] that is, the interface joining basal faces is not parallel to the c-axes. This indicates that the determination of shapes of ice crystals growing in supercooled water must be controlled by all of those factors described in the previous paragraph, different from the simple cases described in the paper of Sekerka[1)], because the basal faces related to facet instability and the rounded side face related to morphological instability exist together in an ice crystal shape[6-7)]. Consequently, the role of the interaction between the flat basal faces and rounded face in pattern formation of an ice crystal is a very interesting subject.

On the other hand, patterns of ice crystals grown in supercooled water containing a small amount of a special protein called antifreeze glycoprotein (AFGP) show a hexagonal plate or the hexagonal dendrite surrounded by faceted interfaces depending on the growth conditions[8-10)]. This means that the growth kinetics of ice crystals are modified by the effect of AFGP and that the mechanisms of morphological instability and pattern formation are completely different from those for the ice dendrite in pure water.

Thus, crystal growth and pattern formation of ice crystals in supercooled water include many kinds of basic subjects related to the fundamentals of crystal growth. Various studies have been carried out to understand the mechanisms of morphological instability and pattern formation of ice dendrites. Nonetheless, their details are still surrounded by many controversial points, even though the growth rates at dendrite tips have been repeatedly measured under a gravity condition by many researchers[3,4,11,12)]. Consequently, it is important to carry out experiments on ice crystal growth with no convection effect. We have conducted space experiments twice using the Japan

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Experiment Module (generally called "Kibo") of the International Space Station (ISS) in periods from 2008 to 2009 and from 2013 to 2014. We have measured growth velocities both at the dendrite tip and at the basal plane simultaneously as a function of the supercooling state and we have discussed the growth and pattern formation mechanisms and also the effects of biomolecular additives on ice crystal growth. In this review, we describe the procedures and the results of the space experiments.

2. Experiments on Free Growth of an Ice Crystal in Pure Supercooled Water (Ice Crystal)

2.1 Experimental Procedures

An experiment on free growth of an ice crystal in pure supercooled water ("Ice Crystal" experiment) was carried out in the period from December 2008 to February 2009. **Figure 1(a)** shows a picture of a cartridge that was newly developed for this experiment called an Ice Crystal Cell (ICC)[13]. The picture was taken in "Kibo" during the handling process by an astronaut. This cartridge consisted of two main parts: an apparatus for the growth of an ice crystal and a Mach-Zehnder interference microscope. **Figure 1(b)** shows an inside structure of the ICC. After being transported by a space shuttle, it was loaded on the stage of the Solution Crystallization Observation Facility (SCOF), which had been set up in Kibo of the ISS and equipped with a Mach-Zehnder interference microscope employing two-wavelength light sources. Consequently, it was possible to observe ice crystal growth by two interference microscopes installed in both the ICC and SCOF, which have optical axes at right angles to each other. The SCOF also supports "tele-science" operations for extemporarily monitoring crystal growth.

Figure 2 shows a schematic diagram of the growth apparatus in the ICC, which is composed of two parts: a cylindrical growth cell (26 mm in diameter and 24 mm in length) and a disk-shaped nucleation cell (6 mm in diameter and 1.2 mm length). The two cells are connected by a thin glass capillary (40 mm in length and 1 mm in outside diameter). The growth apparatus was completely filled with pure water degassed by vacuum evacuation. The temperature of each cell could be independently controlled within an accuracy of ±0.05℃ by Peltier cooling elements combined with the PID controllers. In this experiment, heavy water (D_2O) was used as the water sample instead of H_2O, because the higher melting point of D_2O than that of H_2O could compensate the limited power supply to the apparatus from the SCOF.

The growth and melting processes of an ice crystal could only be controlled by setting the temperature remotely from the ground. Video images and temperature data were downloaded from the ISS to the ground with a time lag of several seconds. The experimental procedure started from making a homogeneous supercooling state of the D_2O sample in the growth cell. After complete establishment of supercooling, the nucleation cell was rapidly cooled to initiate ice nucleation.

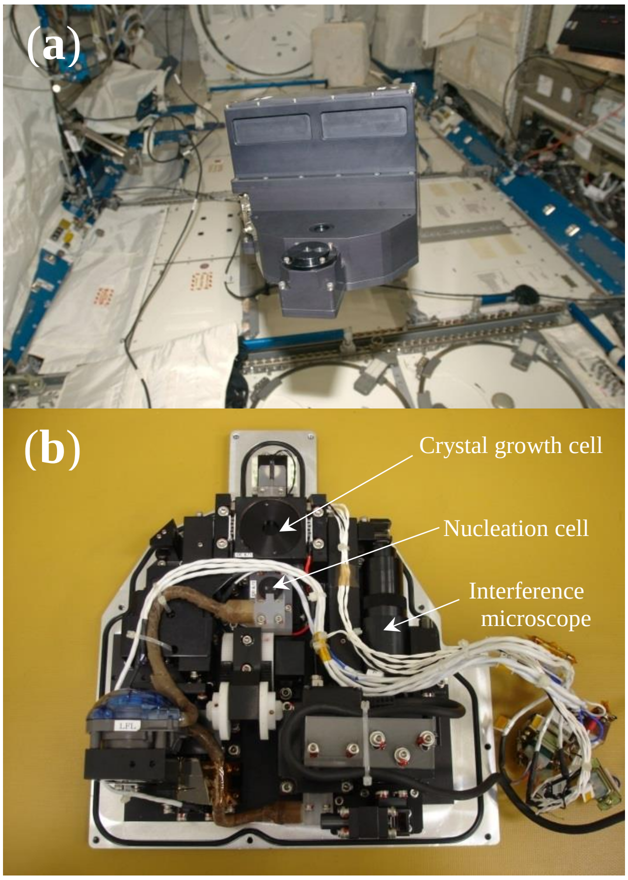

Fig. 1 Pictures of (a) the Ice Crystal Cell (ICC) floating inside the Kibo and (b) inside of the ICC.

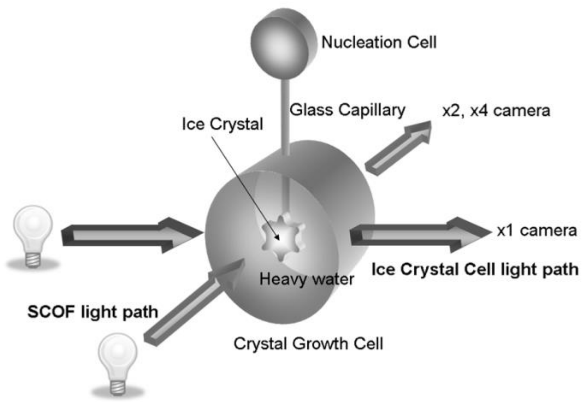

Fig. 2 Schematic diagram of the ice growth apparatus.

Then nucleated ice particles continued to grow inside the capillary and compete against each other, and only one crystal could finally survive inside the capillary. An ice crystal with its c-axis perpendicular to the capillary axis positively started to grow from the end of the capillary into the supercooled D_2O. In order to prevent excessive pressure inside the growth cell by cubical expansion during the ice crystal growth, the ice crystal was melted at an appropriate time by terminating the temperature control. All of the ice crystals in the growth apparatus were completely melted and then the growth apparatus was reset to the initial state.

A total of 134 experiments were successfully carried out using a single growth apparatus in the supercooling range from 0.03 to 2 K.

2.2 Experimental Results

2.2.1 Growth Rates along c- and a-axes

As a typical example of ice crystal growth obtained in space, time-sequence images of an ice crystal grown under the condition of supercooling of 0.4 K, which were imported from the moving image file, are shown in **Fig. 3**. The ice crystal shape observed in space was symmetric with regard to the central axes of the branches, unlike the shape of an ice crystal observed on the ground, as shown in **Fig. 4**. These movie images were analyzed using a two-dimensional spatiotemporal image produced from the recorded data of both an interferogram and normal optical image sequences[13-15]. **Figure 5** shows the growth rates v_{tip} along the c-axis, $\langle 0001\rangle$ and v_{basal} along the a-axis, $\langle 11\bar{2}0\rangle$ as a function of temperature. **Figure 5(a)** shows the dimensionless tip growth velocity V as a function of dimensionless supercooling Δ, which is defined by the equation

$$\Delta = \frac{\Delta T c_p}{L} \quad , \tag{1}$$

where ΔT ($= T_m - T_\infty$, where T_m is the melting temperature and T_∞ is the temperature far from the crystal interface) is the supercoiling temperature, L is the latent heat released per unit volume of D_2O ice, and c_p is the specific heat. The tip growth velocity v_{tip} is also scaled by the ratio of capillary length d_0 to thermal diffusivity κ_T of D_2O water, which is indicated as the equation

$$V = \frac{d_0 v_{tip}}{\kappa_T} \quad , \tag{2}$$

where $d_0 = \frac{\gamma c_p T_m}{L^2}$ including the isotropic surface tension γ. **Figure 5(b)** shows the rate increase in thickness between both-sided basal faces, $\frac{dh}{dt}$ ($\approx 2v_{basal}$), as a function of supercooling ΔT.

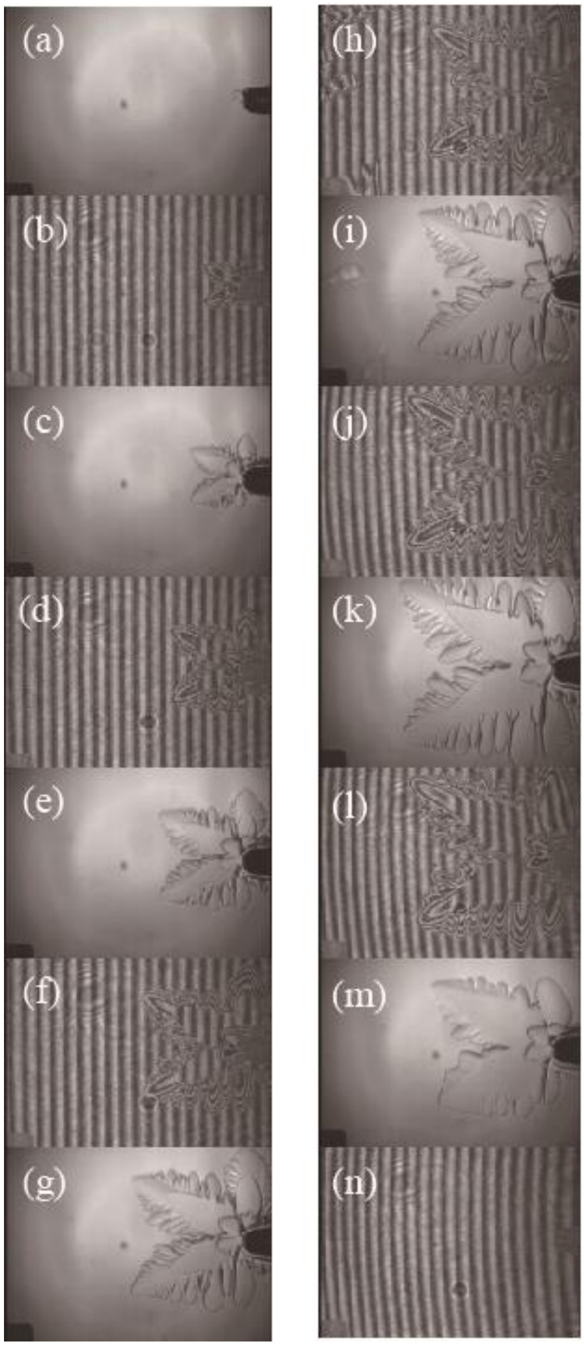

Fig. 3 Time-sequence normal optical and interferogram images of an ice crystal grown in space from supercooled heavy water with ΔT=0.4 K using the ICC. The time intervals are about 30 s. Each image size is 6.4 mm in width and 4.8 mm in height. The growth process is shown from (a) to (h), and the melting process is shown from (i) to (n). The observation windows are covered with ice in (h) and (i).

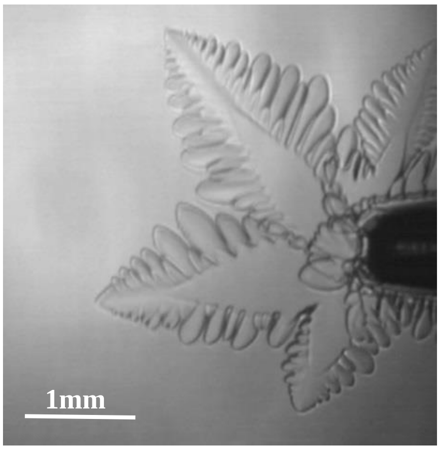

Fig. 4 Picture of an ice crystal grown on the ground. The pattern is not symmetric due to the effect of thermal convection around the crystal. Initial supercooling was 1 K.

The values of V plotted as both open and solid circles in **Fig. 5(a)** indicate the situations of no growth on the basal faces for Δ smaller than the critical value of 0.002 (=0.16K) and growing basal faces with Δ larger than this value, respectively. The corresponding patterns of ice crystals during the situation of no growth of basal faces were a disk shape for $\Delta<0.0007$, a disk with a perturbed periphery for $\Delta \sim 0.0007$ and a perturbed disk having broad and short primary stalks for $0.0008<\Delta<0.002$. Compared with this, we found that well-developed dendrites including secondary branches appeared with the growth of basal faces. The solid curve in this figure shows the theoretical prediction obtained from the universal law for dendrite tip growth proposed by Langer and Müller-Krumbhaar (LMK) with the assumption that γ is isotropic in three dimensions and the nose shape of a dendrite is the paraboloid of revolution[16,17].

Even though there is no growth for basal faces at very low supercooling of less than 0.1 K, they start to grow with increase in supercooling as shown in **Fig 5(b)**. The growth rates change as a function of supercooling with a power law with an

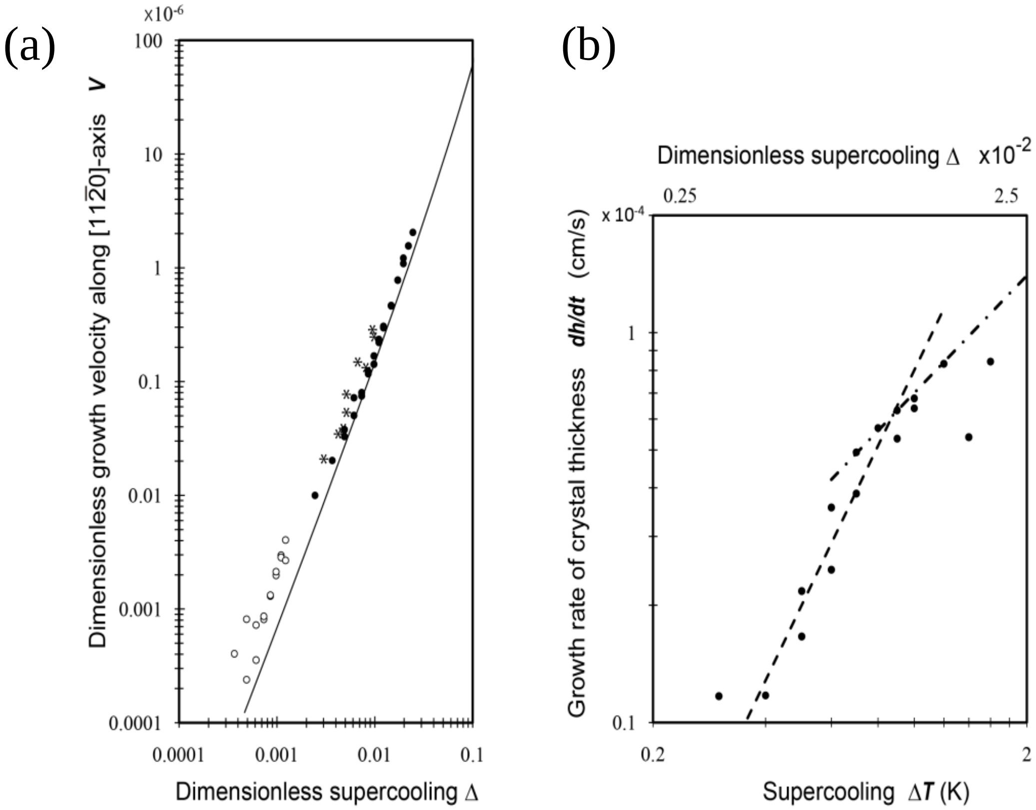

Fig. 5 Growth rates of ice crystals measured in space[15]. (a) Dimensionless tip growth velocity V as a function of dimensionless supercooling Δ. The solid curve was obtained from the universal law proposed by LMK theory[16,17]. The open circles indicate no growth on the basal faces and the solid circles indicate the situation of growing basal faces. The star marks were obtained by ground experiments under 1 G[3] (b) Rate of increase in thickness $\frac{dh}{dt}(=2v_{basal})$ as a function of supercooling ΔT.

exponent of about 2 from 0.2 to 0.5 K and with an exponent approaching 1 as supercooling increases to above 0.5 K. It should be noted that the temperature dependence of tip growth velocity appears to be linked to the growth of basal faces. Namely, the tip velocities agree with the LMK theoretical curve

in the region of supercooling for $\Delta > 0.002$ (=0.16 K), when the growth on the basal faces is not zero, but shift from the theoretical prediction at smaller supercooling. We concluded that the basal face kinetics significantly affects the tip growth velocity rather than the asymmetric shape with respect to the basal plane.

2.2.2 Tip Radii of Dendrites

We also measured the tip radii of dendrites using the results of space experiments and estimated the stability criterion, σ, which is defined by the equation

$$\sigma = \frac{2\alpha d_0}{v_{tip}R^2} \quad , \tag{3}$$

where R is the tip radius of a dendrite. The LMK model indicates that this value is a constant estimated to be roughly σ^*=0.025 in the limit of a small Peclet number ($P_e = \frac{v_{tip}R}{2\alpha}$). The three-dimensional shapes of dendrite tips of ice crystals were obtained by image analysis for ice dendrites observed in space[13]. **Figure 6** shows the estimated values of σ^*as a function of supercooling temperature for ice and succinonitrile (SCN) crystals[18]. It should be noted that the values estimated from the radii in the basal planes, R_1, were constant around 0.007 against supercooling. This value is about 30-times less than the theoretical prediction, while the values measured under a microgravity condition for SCN was very close to the prediction. This tendency has already been pointed out on the basis of ground-based experiments conducted by Furukawa and Shimada[3] and is qualitatively supported by the results obtained in microgravity.

This discrepancy between the measured values of σ^* and the theoretical prediction was due to the fact that the tip shape of the ice dendrite deviated from the paraboloid of revolution. As reported by Furukawa and Shimada[3], the tip of an ice dendrite has two radii, R_1 and R_2, which are tip radii in the basal plane and in the direction perpendicular to the basal plane, respectively. Though R_1 equals R_2 in the case of SCN, R_1 and R_2 for ice are two orders of magnitude different from each other. Consequently, R_1 or R_2 cannot be used for the calculation of σ^* for ice dendrites. The calculated values of σ^* with the geometric mean radius R_{mean} defined as $\sqrt{R_1 \cdot R_2}$ are also plotted in **Fig. 6**, with values of R_2 having been estimated using the empirical relation of $\frac{R_2}{d_0} = 425 \times \Delta^{-0.58}$ deduced by the ground experiments[3]. The value of σ^* calculated by using

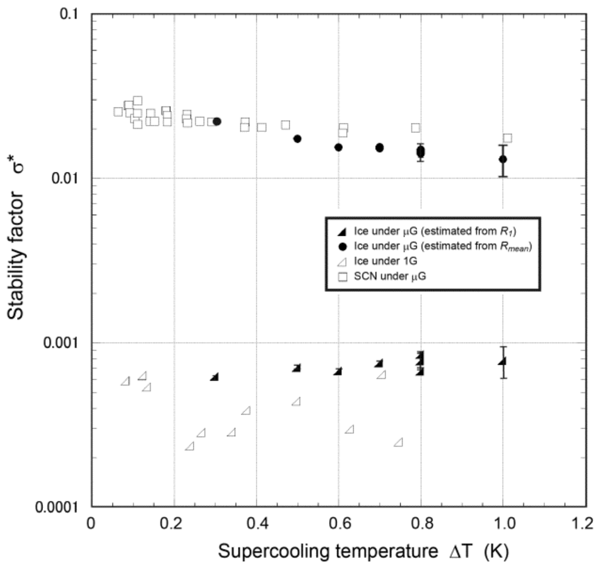

Fig. 6 Relation between stability factor σ^* and supercooling[13]. The solid circles and triangles are results in microgravity using R_{mean} and using R_1, respectively. The open triangles indicate ground-based results for ice dendrites obtained from the reference[3], and the open squares indicate the results SCN in microgravity[18].

R_{mean} became about 0.03, which was nearer to the theoretically predicted value, even though tip shapes of ice dendrites were far from the paraboloid of revolution. Alternatively, the most apical part of the dendrite tip may have a shape with rotational symmetry around the central axis of the dendrite.

3. Ice Crystal Growth in Supercooled Water Containing a Protein (Ice Crystal 2)

3.1 Ice Crystal Growth Affected by Biological Macromolecules

It is well known that many kinds of fish make their habitats even in the subzero environment of seawater underneath the sea surface covered by ice in polar or sub-polar regions. In order to head off a crisis of freezing death in a supercooled state, they rely on a kinetic mechanism for ice crystal growth controlled by functional proteins with an antifreeze effect[19]. One of the most popular proteins with this function is called antifreeze glycoprotein (AFGP), and its effect on ice crystal growth has been studied. Recently, Zepeda et al.[10,20,21] conducted experiments on free growth of an ice crystal in supercooled water containing a small amount of AFGP and they obtained direct evidence for a relationship between adsorption of AFGP molecules and ice growth prohibition. Furthermore, they proposed a two-step reversible adsorption model for AFGP molecules on the ice/water interface and showed that growth rates may depend on the amount of adsorbed protein molecules. Consequently, it is important to clarify the mechanism by which ice crystal growth is inhibited. Microgravity experiments for ice crystal growth in a supercooled protein solution will provide important information for a basic understanding of the mechanism. Thus, from 2008, we began planning the second experiment for ice crystal growth (“Ice Crystal 2” experiment). The experiment was actually started in Kibo of the ISS in November 2013 and is still proceeding at the time of writing this review. Consequently, only a brief introduction of this experiment is given.

The purpose of this experiment is to observe the fluctuation of growth velocities under a condition without any influence of convection. The convective flow of the solution covers over the self-organizing fluctuation of growth, which is strongly expected on the basis on the kinetic effect of adsorbed proteins on the interface.

3.2 Experimental Procedure

The experimental cartridge, which was newly developed for this experiment, was composed of two parts, as was the cartridge used for first space experiment, but the two parts were extensively modified for the second experiment. For the growth apparatus of an ice crystal, a spherical growth cell (40 mm in diameter) was made and it was equipped with the rotating mechanism of a glass capillary around its axis. As the optical system to observe ice crystal growth, a Michelson-type interference microscope combined with a phase contrast microscope was installed in the cartridge. These systems allow observation of step migrations on the growing basal plane and measurement of growth velocity of the basal plane at the same time.

The cartridge was transported to the ISS in August 2013 and the first experiments were started at the end of this month. However, our experiment fell into difficulties in the power supply system immediately after starting experiments. Fortunately, experiments could be started again after troubleshooting, and before now more than 50 growth experiments have been carried out in space under various supercooling conditions in the range between 0.2 and 0.4 K. Ice crystal growth was observed in almost every experiment, and interference fringes on the basal faces were successfully observed in more than 20% of the experiments.

3.3 Prospective Results

Time fluctuation of growth rate for the prism face of an ice crystal in the AFGP solution was first observed in one-directional growth experiments conducted in a thin growth cell with no convection in the cell[22]. Zepeda et al.[10,21] directly observed that the prism faces for which growth had been stopped by adsorption of AFGP molecules started to grow again along with desorption of AFGP molecules from the interface. These observations indicate that the growth velocities of prism faces should not be constant but fluctuate with growth time. This kind of fluctuation may give suggestions for the self-oscillatory growth of a prism face.

In the present space experiments, we measured the growth rates of basal faces using an interference microscope. **Figure 7** shows a picture of an ice crystal grown by the cartridge as ground reference experiment before launching. Clear interference fringes are observed on the basal face. Similar ice crystals and fringes have already been obtained in space, and fluctuations of fringe migrations have been observed. Detailed analysis is continuing.

The mechanism for the self-oscillations of growth rates should be explained in relation to the adsorption-desorption processes of AFGP molecules on the growing interfaces. Consequently, the experimental data obtained in space will provide direct information about why adsorption and desorption can occur periodically on both prism and basal interfaces of an ice crystal. Such information is expected to contribute to elucidation of the mechanism of the antifreeze effect.

Oscillations of growth rates are strongly related to various phenomena generally occurring with crystal growth. For example, striped patterns, which are usually regarded as “striation”, are commonly observed inside mineral crystals or semiconductor crystals. It is considered that the formation of striation is strongly related to the oscillation of growth rate originating from the interaction between impurity diffusion and released latent heat at the growing interface. However, direct evidence for oscillatory growth has not been provided as far as

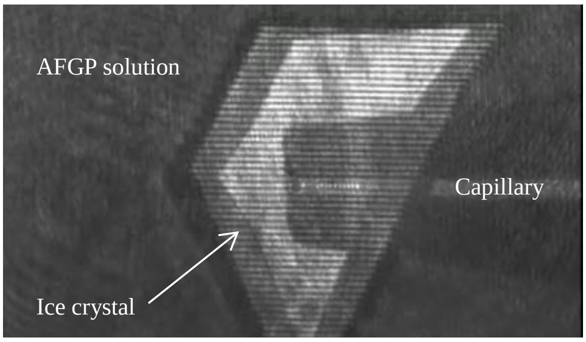

Fig. 7 An ice crystal grown in supercooled water containing small amount antifreeze glycoprotein (0.07 mg/mL) on the ground. Fringes inside the crystal obtained by the Michelson interference microscope are clearly observed. Similar images have been obtained by the space experiments.

we know. We single out the effect of convection that may drastically change the growth rate as the main reason. Recently, Miura and Tsukamoto[23] proposed a model to explain the oscillatory growth of a crystal based on the effect of impurity adsorption for the growing interface. Our experimental data may provide the possibility for validating the theoretical consideration.

4. Summary

Free growth experiments of ice crystals, which were planned on our own accord, have been carried out twice using the facility equipped in the Japan Experiment Module "Kibo" of the ISS. The apparatuses newly developed for the space experiments showed superlative performance, and ice crystal growth was successfully observed in both series of experiments. The unexemplified benefit of our apparatus is that growth experiments can be easily repeated many times. As a result, we could obtain an enormous quantity of motion image data for ice crystal growth under various growth conditions. Interference fringes obtained by optical systems specialized for growth rate measurements of ice crystals enabled quantitative analysis of their time fluctuation. By analyzing these data, precise growth rates without any effect of disturbance such as convection were obtained.

We confirmed that the pattern formation of an ice dendrite in pure water occurs in conjunction with the growth of basal faces. This is the first confirmation for pattern formation that is simultaneously controlled by rough and flat interfaces.

The second series of space experiments for ice growth affected by antifreeze glycoprotein have been successfully conducted and are continuing at the present time. We expect that direct evidence for self-oscillatory growth will be obtained for the first time.

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