Air Bubble Formation in Ice Crystals*

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Abstract

Formation of air bubbles in ice crystals was investigated to reveal the mechanisms of regular, sometimes periodic distributions of air bubbles in natural and artificial ice crystals. When an ice crystal grows in water, air bubbles develop between solid particles and the ice-water interface, which suggests that surfaces of solid particles provide the seats of air bubble nucleation. Most of the solid particles migrate with the advancing ice-water interface leaving rows of spherical or cylindrical air bubbles in the ice crystal.

The metamorphism of air bubbles trapped in ice crystals was observed under various conditions and discussed in reference to defects in ice crystals.

I. Introduction

Ice crystals grown from melt usually contain spherical or cylindrical air bubbles which are distributed in the freezing directions. These air bubbles may be considered as gas enclosures filled with air which was dissolved in water. The concentration of air in water may be increased at an ice-water interface as the freezing proceeds, because ice does not incorporate with the air in the crystal lattices. When the concentration of air reaches some supersaturation small air bubble may be formed at the ice-water interface and develop to visible size, then it is captured by the interface and becomes a gas enclosure.

The formation of gas enclosures or air bubbles during solidification from melt has been noted by many metallurgists and crystallographers, but so far few studies have been made for the air bubble formation in ice crystal. Carte (1961) carried out an experiment of unidirectional freezing of a film of water contained between two glass plates, and found that the number and the sizes of air bubbles trapped in ice were dependent upon the rate of freezing and the amount of air dissolved in water. Corte (1963) observed the migration of solid particles which had been placed on a growing ice-water interface, in order to investigate the mechanism of sorting of soil particles during freezing-thawing cycles in permafrost layers. He observed that unless the rate of freezing was high, almost all solid particles migrated with the interface, while the air bubbles were trapped as oriented in row in the ice crystal. His main attention was not directed to the interaction between particles and the ice-water interface or the formation and inclusion of air bubbles in ice. The phenomena, however, are very interesting and closely

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correlated with the mechanism of frost heaving.

When an ice crystal is subjected to various thermal or mechanical disturbances, the contained air bubbles may change their characters. The metamorphism of the air bubbles involves not only the change in shape or arrangement but also in size. If an ice crystal is kept for a long time near the melting point, air bubbles shrink in size, suggesting some kind of diffusion process of defects in ice crystal.

The main purpose of the study is to clarify the formation process of air bubbles at a growing ice-water interface with regard to their nucleation and growth, and interaction between solid particles and the interface, and to observe the metamorphism of air bubbles under various conditions.

II. Air Bubble Formation at an Ice-water Interface

Experimental apparatus. Figure 1 shows a simple apparatus to observe the formation of air bubbles when solid particles are placed at an ice-water interface. The water container, 8 cm×2 cm×8 cm, consists of glass walls (1 mm thick) and a brass bottom (2 cm thick), and its side walls are insulated thermally so that the water in the container begins to freeze from the bottom when the container is placed in a cold room. An electric heater suspended in the upper part of the container prevents freezing from the water surface and controls the rate of freezing. The rate of freezing was changed within a range of 0.4 to 15.0 μ/sec to maintain a smooth planar ice-water interface. Cellular or dendritic growth was observed for the rates of freezing higher than about 15 μ/sec. Temperature distribution in the water was recorded automatically by six copper-constantan thermocouples suspended in the container with intervals of about 5 mm. The record showed a gradual decrease of temperature from the bottom without changing the temperature gradient.

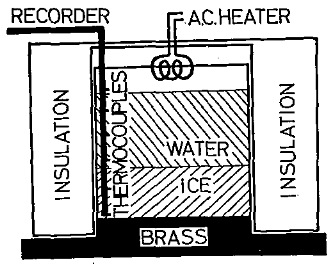

Fig. 1. Experimental apparatus

Concentration of oxygen dissolved in water was measured to estimate the total concentration of air in water. Winkler's method* was employed for the chemical analysis. The concentration of free oxygen was 65% for ordinary distilled water, 20% for distilled water boiled for 30 minutes, and 95% for distilled water mixed with air by shaking and stirring, where the normal solubility of oxygen in water is 10.29 cm^3/(1 liter of water) at 0°C and 1 atmospheric pressure. In this study most experiments were conducted with the distilled water saturated with air.

Formation and stability of air bubbles. When a solidification occurs slowly from melt or solution, the impurities are generally rejected in front of the advancing solid-liquid interface. The main impurity in the distilled water is considered to be air. The molecules of air must be rejected and accumulated ahead of the ice-water interface, since an ice crystal does not incorporate with them and their diffusion coefficient is very small

* This is an iodometry frequently adopted in the oceanographical observations. The procedure is given in a text book by Taylor (1949).

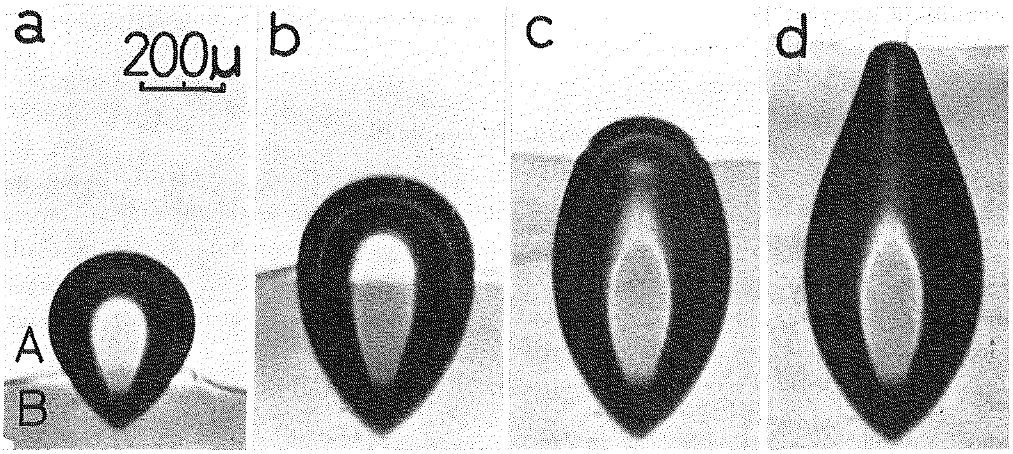

Fig. 2. An air bubble formed at an ice-water interface
A: Water, B: Ice. Time: a, 0 sec (5 sec after the formation); b, 90 sec; c, 180 sec; d, 270 sec

in water and is 1.1×10^{-5} cm^2/sec at 0°C and under 1 atmospheric pressure (Carte, 1961). In our experiment, the maximum density water existed at a higher level than the interface and caused a faint convection reducing the concentration of air at the interface. However, some degree of supersaturation of air may be always created at the developing interface because air-saturated water was used.

When a critical supersaturation is reached, an air bubble is nucleated and grown to a visible size at the ice-water interface. A formation of an air bubble and the process by which it is trapped in ice is shown in a series of photographs in Fig. 2, where A and B denote water and ice, respectively. Its nucleation and growth was almost instantaneous. The average rate of freezing was 3.3 μ/sec. The nucleus of the air bubble cannot be seen in the photographs, but the existence of some kind of foreign nucleus may not be doubtful.

According to our observation some of the nucleated air bubbles escaped away from the interface because of their bouyancy, but most of them were trapped at the interface soon after the formation. Careful observation of Fig. 2 shows that when an air bubble is captured by the interface, ice climbs up along the surface of an air bubble. If the bouyancy of the air bubble is large enough to overcome the adhesive force to the interface, it must rise up to the water surface. Figure 3 illustrates a schematic diagram of an air bubble trapped at an ice-water interface. In this case, the adhesive force between the air bubble and the interface may be caused by the surface tension, and it can be roughly estimated as $2\pi x \sigma_w \sin\theta$, where $2x$ is a diameter of the contact area between the bubble and the interface; σ_w and θ are the surface tension of water and the observed contact angle between the air bubble and the ice surface, respectively. If we denote the volume of the air bubble,

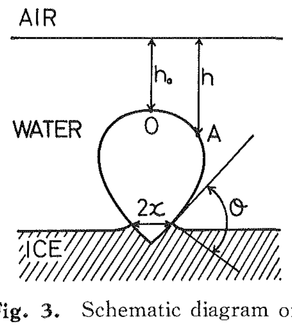

Fig. 3. Schematic diagram of an air bubble fixed at an ice-water interface

densities of water and air, and the acceleration of gravity by V, ρ_w, ρ_a, and g, respectively, the criterion, at which the bouyancy of the air bubble overcomes the adhesive force may be written as follows;

$$V(\rho_w-\rho_a)\,g>2\pi x\sigma_w \sin\theta\,. \tag{1}$$

If we take $\sigma_w=80$ dyne/cm and $\theta=75°$ (the angle dispersed among 60°–100°) and we consider a spherical air bubble having a radius of 100 μ, the diameter of the contact area, $2x$, is only 0.17 μ. This suggests that the nucleated air bubbles can be easily trapped by the ice-water interface. This estimation, however, is available only when no water film exists between the air bubble and the ice surface as shown in Figs. 2 and 3. The other case will be discussed in section V.

The shape of an air bubble in water may be determined by the following equation,

$$\frac{2\sigma_w}{R_0}=\rho_w(h-h_0)\,g+\sigma_w\left(\frac{1}{R_1}+\frac{1}{R_2}\right), \tag{2}$$

where R_0 is the radius of curvature at the top of the air bubble O, and R_1 and R_2 are those at an arbitrary point on the surface in contact with water A; $h-h_0$ is the difference of head in water.

Growth of air bubbles. Air bubbles nucleated at an ice-water interface grows as far as the surrounding water is supersaturated with air. The supersaturation of air is maintained by a continuous development of the ice-water interface. When an air supply to an air bubble is reduced or stopped, it may be enclosed in ice in the shape of an egg as shown in Fig. 2. When the air supply is continuous and constant the air bubble grows in the shape of a cylinder. Assuming that a cross section of air bubble is a circle, the volume of air bubble was estimated from the microphotographs and plotted against time in Fig. 4. The growth curves a, b and c are for the air bubbles of egg-type, and d and e for the long cylindrical air bubbles.

When the rate of growth of ice or advancement of ice-water interface changes periodically, a wavy change in diameter may be observed on cylindrical air bubbles. If the growth rate is intermittent, spherical or egg-shaped air bubbles may be distributed in line with definite intervals. A row of spherical air bubbles found in natural ice crystals can be also formed as a result of thermal metamorphism of a cylindrical air bubble. The phenomenon will be discussed later.

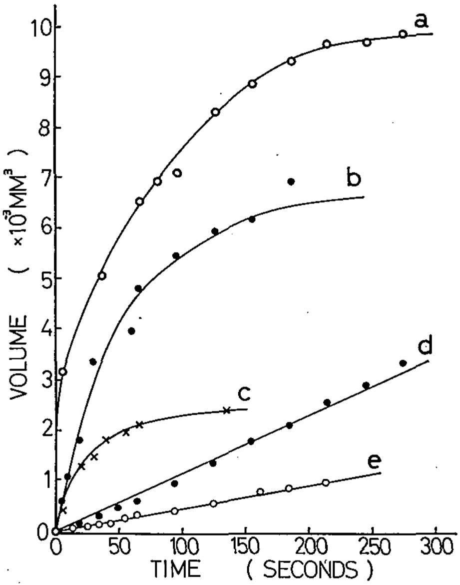

Fig. 4. Growth curves of air bubbles. Average rate of freezing (μ/sec): a, 3.3; b, 6.2; c, 2.7; d, 5.5; e, 3.3

Nucleus of air bubbles. As expected from the nucleation theory, some kind of nucleus must be necessary to form an air bubble. In our experiment the ice-water interface was kept so smooth that there were no irregularities

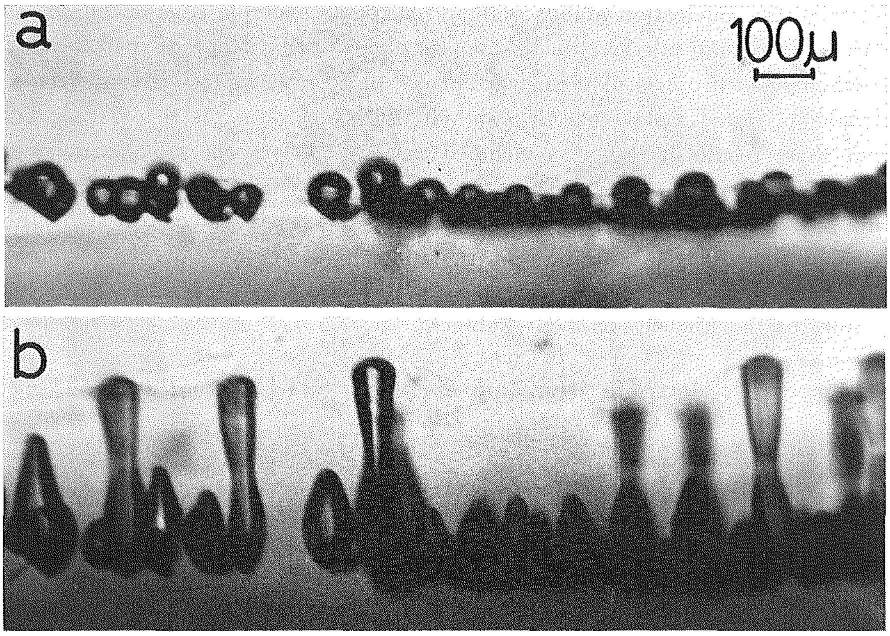

Fig. 5. Air bubble formation along a scratched line on ice surface.
a: 5 sec after nucleation, b: 20 sec after a

to act as the nucleation site for the air bubble formation, and grain boundaries did not act as the nucleus. It was often observed that no air bubbles were formed after the smooth interface grew substantially. However, when the ice surface was scratched with a fine glass rod, a number of tiny air bubbles were nucleated only along the scratched line (Fig. 5 a). This simple experiment proves that a supersaturation of air has been created at the growing ice-water interface, but no air bubbles were formed because there existed no nuclei. The growth of the air bubbles was not homogeneous as shown in Fig. 5 b. The air bubbles located apart from others grew continuously, while the air bubbles situated closely could not develop enough because of the poor supply of air.

In order to investigate what kind of materials act as the nucleus to form air bubbles and how they behave at an advancing ice-water interface, various kinds of particles, metallic, nonmetallic or liquid, have been placed at the interface. Carborundom particles were carefully washed and soaked in distilled water near 0°C and then transferred to a growing ice-water interface in such a way that their surfaces were not exposed to the air. Air bubbles were formed between the particles and the ice surface, suggesting that the surfaces of carborundom particles acted as the nucleation sites for bubble formation. After the particles were soaked in methanol or dilute hydrochloric acid, and rinsed in distilled water, they were placed again on the ice-water interface. In this case, no air bubbles were formed. Similarly, the particles boiled previously in distilled water for thirty minutes did not produce any air bubbles. The same tests were repeated with small lead and glass particles. The results indicated that untreated surfaces of these particles nucleated many air bubbles, but their nucleation abilities were lost after the treatments.

To study the nucleation ability of liquid surface, insoluble organic liquids such as chloroform, aniline and ethylene dichloride, were examined. None of them produced air bubbles when small droplets of them were placed on a growing ice-water interface. The small droplet of liquid metal, mercury, showed the same result as the organic liquid.

From these results it may be concluded that the surfaces of solid particles can act as the nucleation sites for air bubble formation unless they are treated chemically or physically. When the carborundom particles which had been boiled to destroy their nucleation abilities, were dried completely and tested again, they recovered the nucleation abilities. This experiment implies that the adsorbed air on solid surfaces play an important role for the nucleation of air bubbles.

III. Particle Migration and Air Bubble Formation

Corte (1963) observed that various particles which had been placed on an ice-water interface developing upward, migrated without being captured in ice. He found, however, many rows of air bubbles left in ice. Uhlmann *et al.* (1964) studied the critical velocities of solidification above which particles were trapped at a solid-liquid interface. The fact that particles are not trapped by a growing ice surface suggests that there was no direct contact between them, or that there existed a layer of water and that solidification must be continued at a speed sufficient for their migration with the ice surface (Taber, 1930; Corte, 1963). The continuous replenishment of water between them can be suggested by the fact that particles migrate with the ice-water interface leaving rows of air bubbles at definite intervals.

Figure 6 shows carborundom particles being pushed by an ice-water interface, and two air bubbles which were formed by them. The air bubble a was already enclosed in ice and b has just been formed between the particle and the ice surface. The particles were situated at a lower level with the ice surface when the air bubble a was formed. Such a process is shown schematically in Fig. 7. The shape and size of the air

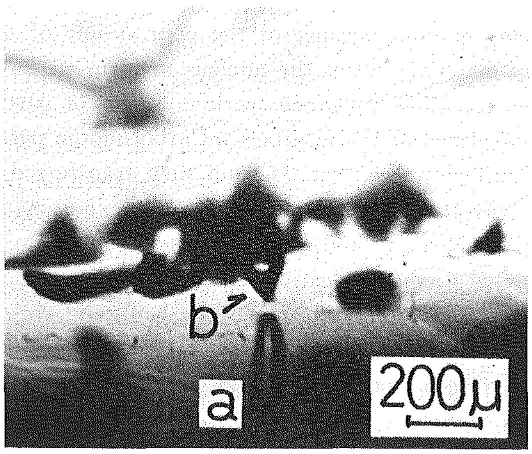

Fig. 6. Air bubbles formed between carborundom particles and ice surface, b, and enclosed in ice, a

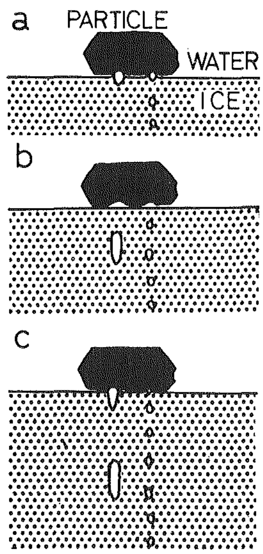

Fig. 7. Schematic process of the air bubble formation between a solid particle and an ice surface

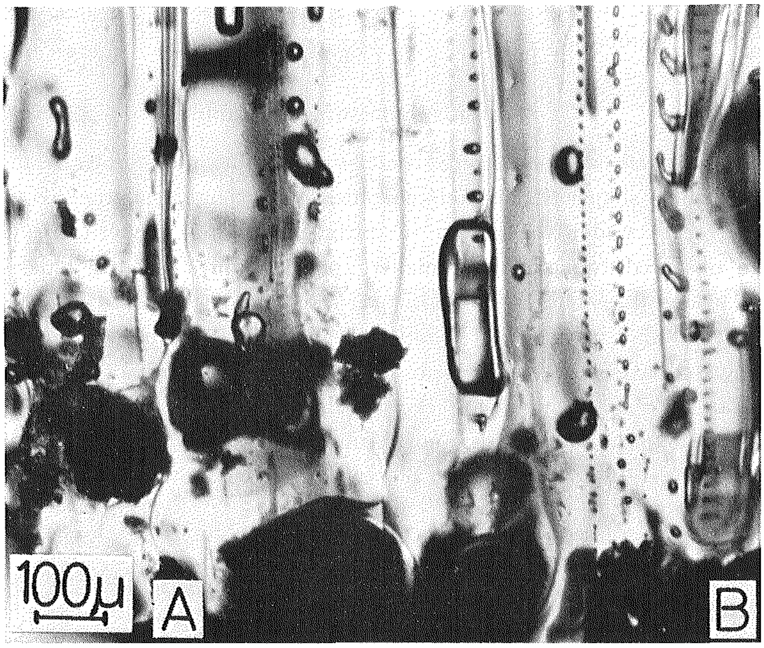

Fig. 8. A vertical thin section of a Shimobashira. A–B indicates solid particles on a ground surface

bubble seems to depend on the character of nucleation site on particles and the mode of diffusion of air in the layer of water.

Figure 8 shows a vertical section of a "Shimobashira"* which grew to about 3 cm from a ground surface into the air. A Shimobashira is usually composed of bunches of long needle ice crystals, and it stands erect from the soil surface. A–B indicates the boundary between the Shimobashira and the ground surface. Many small air bubbles are distributed along the growth direction as seen in the ice crystals grown from melt. This air bubble formation in a Shimobashira seems to be very important in understanding the growth mechanism of Shimobashira.

The formation of a Shimobashira has been considered to be a crystallization of water at a ground surface where the water is transported through the soil from underground. When a Shimobashira grows on a ground surface, the temperature of the surface is maintained at 0°C, but the air is colder than 0°C and the ground is warmer than 0°C. Therefore, the water-saturated soil particles on the ground surface make contact with the bottom of the Shimobashira, forming an ice-water interface. This situation is quite similar to that of our experiment except that the interface advances downward in this case. It may be concluded from our experimental results that the numerous air bubbles contained in the Shimobashira were formed in a layer of water between soil particles and the Shimobashira and captured in the ice. The average diameter of air bubbles in the Shimobashira suggests that a fairly thick layer of water

* Shimobashira is a Japanese name and it is most descriptively translated in English as "soil needle ice" (Takagi, 1965).

(at least 30 or 40 μ in thickness) should have existed between the soil particles and the ice to form the air bubbles.

IV. Metamorphism of Air Bubbles

Metamorphism under an isothermal condition. The air bubbles enclosed in ice tend to change their shapes. The metamorphism of air bubbles proceeds by reduction of the surface areas under the action of surface tension. Sometimes cylindrical air bubbles were observed to split into smaller spherical ones when a block of ice was kept slightly below the melting point of ice for a long time. In Fig. 9, a series of photographs shows the splitting of cylindrical air bubbles into rows of spheres. The block of ice was soaked in kerosene to keep it from sublimation. The splitting of a cylindrical air bubble occurred at several points where the diameters were already smaller than other parts. The metamorphism was often observed in cylindrical air bubbles whose diameters were less than 500 μ, but it was noted that larger air bubbles did not split easily.

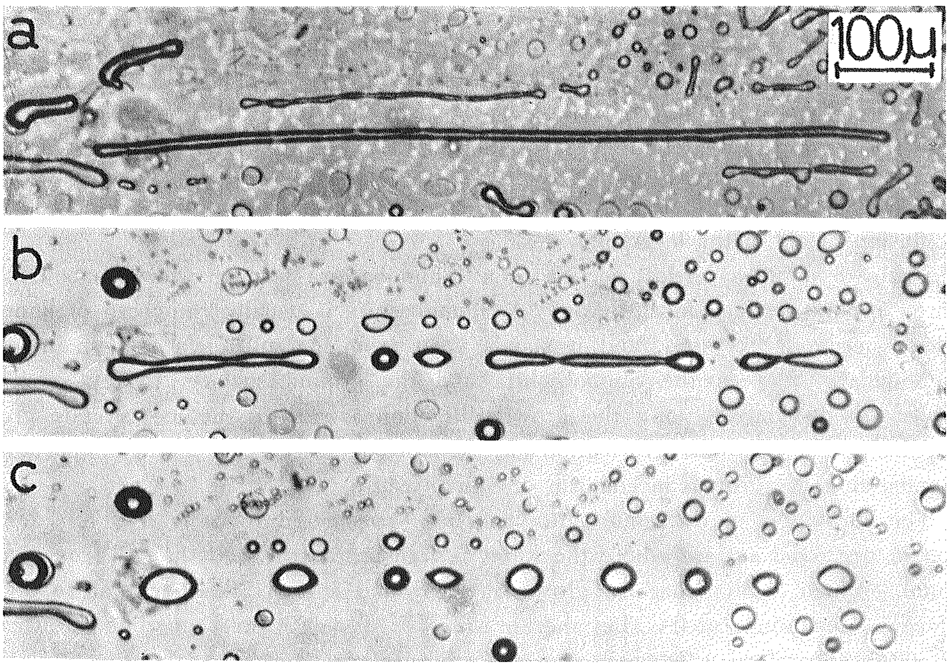

Fig. 9. Metamorphism of air bubbles under an isothermal condition (−10°C). Time: a, 0 hr; b, 20 hr; c, 120 hr

As seen in Fig. 9, shrinkage and disappearance of air bubbles were also observed when the ice was annealed in kerosene for a long time. This phenomenon may suggest a dissolution of molecules of air into ice, or a mass transportation through diffusion of some kind of defects in the ice crystal.

Metamorphism under a thermal gradient. Migration of vapor figures in a single ice crystal under a thermal gradient was extensively studied by Nakaya (1956). According

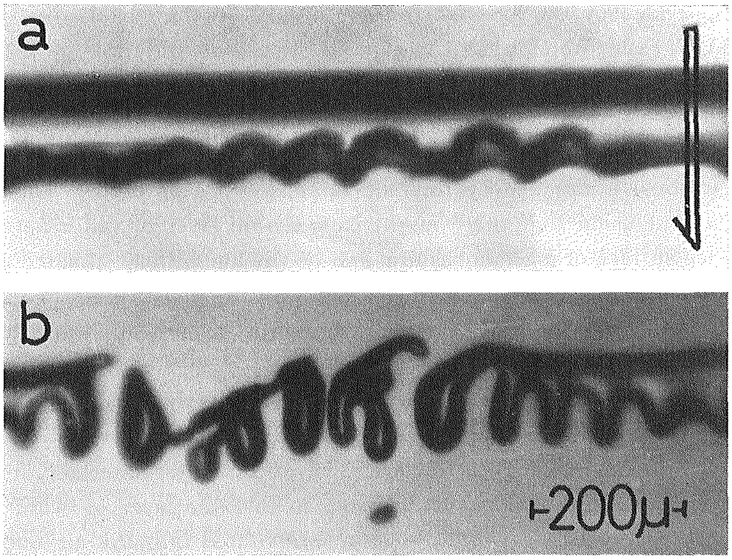

Fig. 10. Metamorphism of an air bubble under a faint thermal gradient indicated by an arrow. The photographs were taken three (a) and eight (b) days after applying the thermal gradient

to his observation the vapor figures migrated toward the warmer direction revealing the crystal faces only on their warmer sides, but when a slight amount of air was introduced in a vapor figure its migration was almost stopped and finally it was filled with numerous hoar crystals.

However, under a very faint thermal gradient air bubbles can undergo a metamorphism, forming solid ice crystals in them. Figure 10 shows the metamorphism of a cylindrical air bubble in ice across which a faint thermal gradient (smaller than a hundredth of one degree per centimeter) was applied in the direction of the arrow at $-15°C$. After three days ice crystals of solid-very-thick-plate-type grew with somewhat regular intervals of 100 μ on the colder side (Fig. 10 a). After eight days they reached the warmer side and resulted in a splitting of the air bubble (Fig. 10 b).

Metamorphism under a mechanical stress. An ice bar was cut from a block of single crystal ice and was bent. The direction of load was perpendicular to the bar and parallel to the *c*-axis. The bar was deformed by slip along the basal plane, and it was observed that the air bubbles contained shrank in the direction of the slip. Hitherto the deformation of air bubbles under stress or flow has been assumed to occur only following an increase of pressure inside them. However, the air would be able to diffuse into the surrounding ice crystal, since the spatious lattice of ice may be much distorted by the mechanical disturbances.

V. Discussion

When water freezes slowly a high supersaturation of dissolved air is created at an advancing ice-water interface, and air bubbles are formed as a result of heterogeneous nucleation. Air bubbles are formed on the surfaces of solid particles. The nucleation sites may be provided by the air adsorbed or trapped on the surfaces of solid particles, which is a similar result obtained in the experiment of bubble formation in boiling water (Dean, 1944).

Solid particles migrated upward with a developing ice-water interface, leaving rows of air bubbles in ice. In a crystal of a Shimobashira which was formed by suction of water through soils, a number of tiny air bubbles were observed. Our experimental result led to a conclusion that there might exist a thin layer of water between soil particles and the ice surface of a Shimobashira, and its thickness was estimated approximately as 30 or 40 μ because the thickness of water might be needed to form the air bubbles in it. For the particles to migrate and for a Shimobashira to grow, water must be transported between particles and ice surface.

Most of the air bubbles were trapped in ice immediately after the formation. This fact may imply that there no layer of water existed between the air bubble and the ice surface. When an air bubble was nucleated at an ice-water interface, it developed to about 50 μ in diameter almost instantaneously; so that the layer of water between the air bubble and the ice surface would be soon evaporated into the air bubble, allowing the appearance of a dried ice surface within the air bubble. The dried area makes the actual contact between the air bubble and the ice surface. In this case, the air bubble may be fixed on the ice surface by surface tension, and cannot rise unless the bouyancy of the air bubble overcomes the adhesive force as shown in the formula (1).

It is not always the truth that no layer of water between an air bubble and an ice surface exists. This can be shown by a simple experiment: an air bubble of 1.17 mm

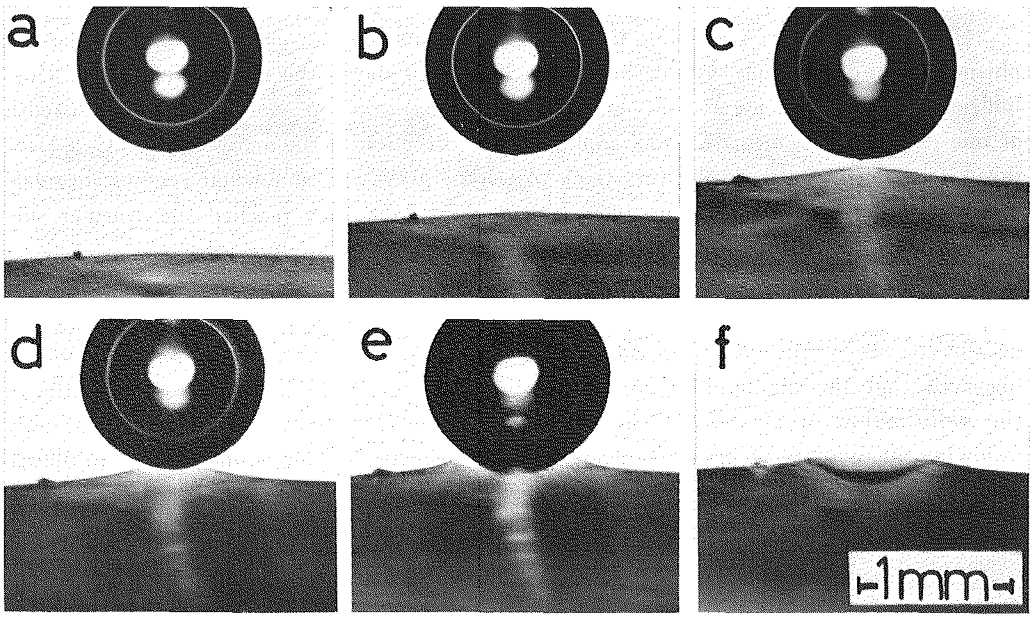

Fig. 11. A simple experiment to show an existence of a thin layer of water between a fixed air bubble and a growing ice surface. The air bubble escaped (f) just after the stage e, when the plate was inclined. Time: a, 0 min; b, 3 min; c, 5.5 min; d, 6 min; e, 7 min

diameter was fixed about 2 cm ahead of a developing ice-water interface, under a small plate suspended in water. As the surface of the plate was coated with a thin film of paraffin, the air bubble could escape if the plate was inclined slightly. Figure 11 a shows the air bubble and the advancing ice-water interface. As the interface approached to the air bubble, the ice surface just under it rose up as shown in Fig. 11 b and c. This phenomenon may be attributable to the thermal insulating effect of the air bubble; as the direction of heat flow is from above in the photographs, the water under the air bubble may be colder than other portion of water of the same level. When the interface reached the air bubble, ice growth just under the bubble almost terminated, but the overall advancement of the interface continued enclosing the air bubble (Fig. 11 d and e). After the stage of e, the plate was inclined gently to allow the rise of the air bubble. The air bubble rose up from the ice surface as shown in Fig. 11 f. It may be suggested that the air bubble was not in close contact with the ice surface, that is, there existed *a thin layer of water* between the air bubble and ice. If we assume no layer of water between them and take $\theta=87°$ in the formula (1), the diameter of contact area, $2x$, required for the air bubble to be fixed against its bouyancy, is calculated as 0.03 mm. The diameter of the apparent contact area in the photograph was 0.72 mm, but the air bubble floated up easily.

From this result, it may be concluded that when a developing ice-water interface touches an air bubble, a thin layer of water can exist between them just as in the case of solid and liquid particles (Corte, 1963; Uhlmann *et al.*, 1964). However, the continuous transportation of water through the layer does not seem probable, because the air bubble was trapped by the ice surface when it was brought into contact with the interface for a long time. If the layer of unfrozen water exists between the air bubble and ice surface for a long time, the air bubble may be compressed and deformed by the advancing ice-water interface. But no such phenomenon was observed in our experiment. The existence of the supercooled water on an ice surface must be a very interesting problem, but there is no evidence indicating whether the layer of water is the same as proposed by Weyl (1951), Nakaya and Matsumoto (1954) and Fletcher (1962).

When an ice block was annealed under an isothermal condition, the contained air bubbles were observed to split or shrink into smaller ones. The mechanism of the phenomenon does not seem to be simple. The evaporation-condensation process is a possible one, but may be too slow to explain the phenomenon; according to Yosida's calculation it would take 6 years at 0°C for a 5 μ thinning in radius of an ice cylinder (100 μ in diameter) to grow to 10 μ through evaporation-condensation due to the difference in curvature (Yosida, 1954).

The shrinkage of air bubbles may be explained in two ways: through the dissolution of molecules of air or through the diffusion of some kind of defects in the ice crystal. Many chemical analyses revealed the existence of air or other gas in ice crystals, and the author observed the appearance of tiny air bubbles from a block of commercial or glacier ice melting in kerosene under a microscope; so that the former process would no doubt occur. The latter is a process which can be accomplished by a diffusion of some kind of defects such as vacancies. The two processes are quite probable in such an open lattice configuration of ice crystal, and have been recently discussed for the shrinkage of air bubbles in snow crystals by Maeno and Kuroiwa (1967).

Acknowledgments

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