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Krausz, A. S.; Harron, B.; Litvan, G. G.

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TUBULAR ICE CRYSTALS

BY

A. S. KRAUSZ, B. HARRON AND G. G. LITVAN

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Tubular Ice Crystals

It has been found that on very rare occasions long, thin ice needles grow into the air from the solid surface of water frozen in an open container[1–4]. In the course of supercooling experiments, Dorsey[5] observed a similar phenomenon in the laboratory. He assumed that growth occurred when, because of the increase in volume during solidification, water was forced through an opening in the ice covering the surface. Dorsey also suggested that a tube formed, through which water flowed and which "grew" at its tip. Recently, Hayward[6] reported a method for growing such spikes and obtained experimental evidence in support of Dorsey's mechanism.

This communication describes a simple method of growing hollow tubes or needles of controlled size, suitable for physical testing; some of the crystallographic characteristics are also reported. We present evidence in support of Dorsey's mechanism, elaborate on it, and suggest a necessary extension. Finally, we indicate how these results can be used for growing tubular bi- or tri-crystals other than ice.

The apparatus used in these experiments consisted of a cell, a cold trap and a rotary vacuum pump. The cell was cylindrical in shape, with a cold finger protruding from the bottom which contained about 20 cm^3 water (Fig. 1). The trap was placed in a mixture of dry ice and acetone or in liquid air and the system was evacuated to a pressure of 10^{-1} mm of mercury. Soon after the cell was immersed in the cold bath ($-15°$ to $-35°$ C) dendrite branches started to grow on the water surface. Before it was completely covered with a crust of ice the water surface became hemispherical in shape. Solidification then continued around the edge of the hemisphere and a short section of the tube was thus formed. The continuous flow of water maintained the droplet at the tip of the tube resulting in steady growth.

Some of the tubes were longer than 100 mm and were slightly tapered toward the tip (Fig. 2*a*). The average diameter varied between 1 and 3 mm with a wall thickness of about 0·2 mm. It was frequently found that the diameter decreased abruptly once or twice during growth. Both the diameter and the length of the secondary tubes were about one order of magnitude smaller than the same dimensions of the primary tubes (Fig. 2*b*).

Crystallographic orientation was determined in polarized light and with the etch pit technique developed by Higuchi[7]. The specimens were found to be single, bi-, or tri-crystals of random orientation. In all cases investigated the grain boundaries in the bi- and tri-crystals were parallel to the main axis over the entire length of the

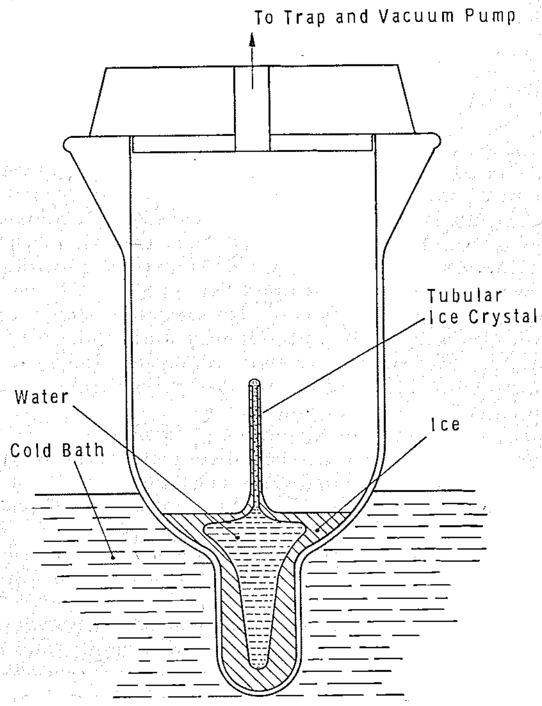
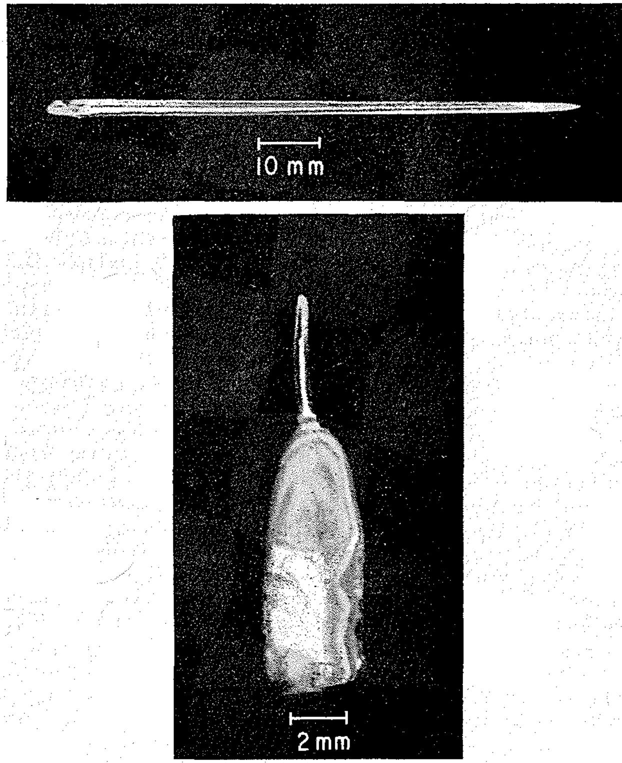


Fig. 1. Diagram of the cell showing growth of tubular ice crystal.

specimen. Microscope observations showed that the wall of the tube was clear, but the frozen core occasionally contained small bubbles of air or vapour.

With this technique it was possible to observe the process of growth in great detail. The formation of the ice cover, the flow of water through the tube, and growth at the tip were observed visually. The existence of a high water pressure due to freezing was demonstrated by reversing the process which supplied the water flow. When, during tube formation, the cell was lifted from the bath and the ice crust inside the cold finger wall melted, the consequent volume contraction drained the water from the tube of ice. Incidentally, this technique was used to produce hollow tubes. These observations support Dorsey's theory and provide further insight into the mechanism. In general, the rate of extraction of heat from the reservoir (controlled in the present experiments by the temperature and geometry of the bath) determines the rate of flow of water through the tube. The water transported to the tip of the tube has, however, to be frozen with an appropriate speed which is governed by the evaporation rate (pumping speed and trap temperature). The vapour pressure of the water droplet is greater than that of the ice because of its higher temperature and a



b

Fig. 2. *a*, Typical ice needle. *b*, Typical primary and secondary needle formation viewed in polarized light.

convex surface. Cooling by evaporation is thus concentrated on the water droplet and this method of heat extraction is preferable.

In steady state the amount of water transported from the reservoir in unit time is

$$V = r_i^2 \pi l + (r_o^2 - r_i^2) \pi l s + 2\pi r_o^2 a \qquad (1)$$

where r_i and r_o are the inside and outside radii of the tube, respectively; l is the tube length grown in unit time; s is the density of ice; and a is the amount of water evaporated from unit area in unit time. The condition of steady growth, not considering radiation and conduction, is that

$$2\pi r_o^2 a L_e = (r_o^2 - r_i^2) \pi l s L_f \qquad (2)$$

where L_e and L_f are the specific heats of evaporation and freezing, respectively. From equations 1 and 2 the following expression is obtained

$$\frac{V}{\pi}=r_i^2l+2r_o^2a\left(\frac{L_e}{L_f}+l\right) \tag{3}$$

The relatively wide range of conditions under which growth can take place shows that the hemispherical drop at the tip of the tube can accommodate significant changes in V and in a. Thus when V becomes greater than that corresponding to the established equilibrium, the surplus amount of water increases the droplet size and growth continues with increasing r_o until the steady growth condition described by equations 1 and 2 is again satisfied.

The predictions of equations 1 and 2 were substantiated by experiments, but it is realized that in practice the process is made feasible only by the high surface tension of water and the apparently low polarity of the ice surface[8] which prevents overflow. It follows from our observations that a mechanism composed of water flow and heat flow alone is not sufficient to explain the process and that the introduction of a third component, the surface tension, is necessary. The realization of the essential features of the mechanism leads to the conclusion that tubes from substances other than water could be grown if an experimental technique could be devised to create a suitable mass flow and heat extraction and a balance between them. Indeed, tubes of benzene were grown with a mechanically controlled liquid flow at atmospheric pressure and $-10°$ C. In this instance, mass flow was created by artificially forcing benzene through the orifice of a syringe. The surface tension of benzene was high enough to maintain a droplet at the tip when growth was directed downward. The successful growth of benzene tubes is considered good evidence in support of the suggested mechanism. This mechanism thus explains all the previously reported tube formations under various conditions (open air[1-3], vacuum[5,6], undercooled[6]) and all the present observations. The recognition of the essential mechanism, furthermore, makes it possible to use this technique to grow tubes of a wide variety of materials.

A. S. KRAUSZ
B. HARRON
G. G. LITVAN

Division of Building Research,
National Research Council,
Ottawa.

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