AN APPLICATION OF THE REPLICA METHOD FOR SEM-STUDY OF THE ICE CRYSTAL INSTABILITY

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AN APPLICATION OF THE REPLICA METHOD FOR SEM-STUDY OF THE ICE CRYSTAL INSTABILITY

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RÉSUMÉ
On a étudié les étapes initiales de l'instabilité morphologique des cristaux de glace, obtenus â partir de la phase vapeur, en utilisant une méthode de réplique et la SEM. On a observé différentes sortes d'instabilités dont l'apparition est probablement due â divers mecanismes.

ABSTRACT
By using replica techniques and SEM the initial stages of morphological instability of ice crystals grown from vapours are studied. Different kinds of instabilities are observed which suggest that probably different mechanisms are responsible for their appearance.

In Nature very often ice crystals can be found as unstable growth forms with a complicated morphology. Their experimental investigation puts many questions, some of which are discussed in the present paper.

The morphological instability of vapour-grown ice is usually interpreted using either the common theory of dendrite formation of crystals /1-4/ or the specific peculiarities of ice /5/. Numerous optical-microscope investigations /6-10/ support the idea that the diffusion inhomogeneity of supersaturation of the parent phase destabilizes the growth of the ice crystal. On the other hand the processes on the crystal surface (step distribution, surface diffusion etc.) are the possible stabilizing factors.

The initial stages of instability are of the main significance for its experimental study, as the available theories deal with these stages or more specifically with the transition from stable to unstable growth. Combining replica techniques with an observation using Scanning Elecron Microscopy (SEM) we have investigated in detailes these initial stages of instability appearance on vapour-grown ice crystals. The obtained resultes hardly can be interpreted in the framework of available theories /1-5/ from common point of view.

Ice crystals are received in a fog chamber as a result of freezing of supercooled water droplets by means of a shock wave /11/. An advantage of this method is the possibility for a simultaneous creation near the melting point of a large number of ice crystals without using ice forming nuclei or a substrate. One of the techniques, developed by Schaefer /12/ is used to prepare formvar replicas from crystals during the first seconds of their

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growth. The free fallen crystals are caught on glass slides covered with a thin dry formvar film. Immediately we replicated them by means of cold chloroform vapours. Thus the initial stages of development of their instability are fixed. After drying the film and evaporating of ice, the samples are metallized with Au and investigated by SEM JEOL T-200. The growth temperature is maintained with an accuracy of $1^{\circ}C$ in the range from -1 to $-26^{\circ}C$. The growth conditions in the chamber are close to those in the clouds. However the supersaturation cannot be strictly measured.

The observed ice crystal habit changes with temperature approximately in accordance to the four regions of the Nakaya-Kobayashi diagram /13/. The free falling crystals lay down on the formvar surface with the most developed face. As a result ice plates are replicated as hexagons (Fig.1) and ice columns - as rectangles (Fig.2).

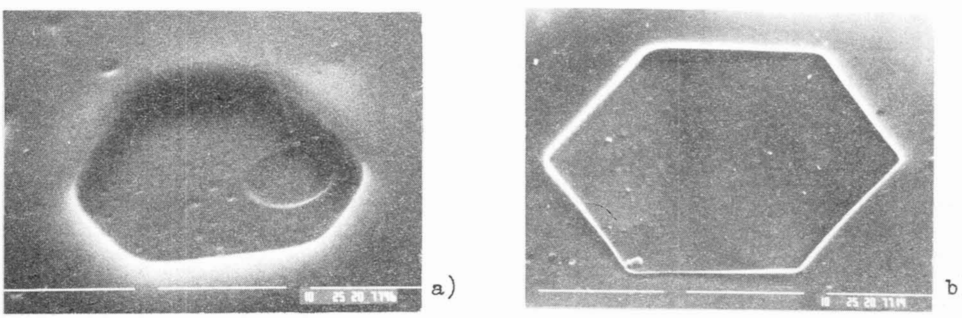


Fig.1-a,b
Stable hexagonal ice plates with rounded (a) and sharp (b) edges and corners.

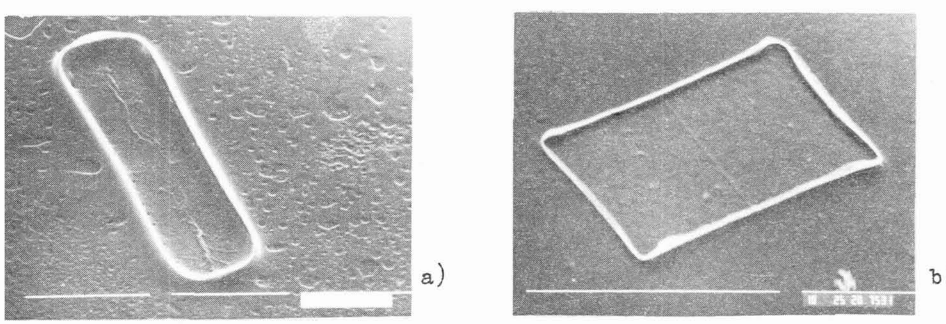


Fig.2-a,b
Stable hexagonal ice columns with rounded (a) and sharp (b) edges and corners.

Ice crystals grown at normal air pressure are morphologically stable under about 20 microns (Figs.1,2). Their initial size is determined by the size of the frozen water droplets (approximately 10 microns diameter). Moreover, in order to be observed this instability experimentally a sufficient aditional quantity of ice should crystallize from the vapours. Hence, the size of about 20 microns should be considered as an upper limit for the critical size. This limit is considerably lower than the expected one according to the theory of Chernov /1/ as well as that given by Fletcher /2/.

Generally, we can divide the observed instabilities into two different kinds from morphological point of view: i) lacunary-like instability and ii) dendrite-like instability.

Morphologically the lacunary-like instability is characterized by a growth retardation in the advancement of the central part of the crystal face - prismatic (Fig.3) or basal (Fig.4) one.

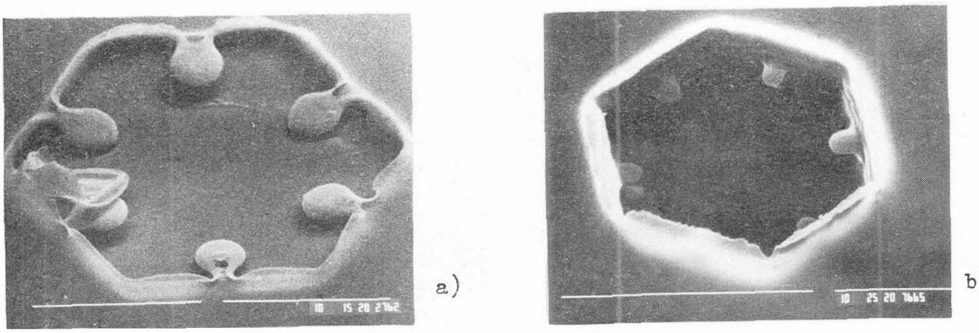


Fig.3-a,b
Unstable ice plates with initial stages of a lacunary-like instability on their prismatic faces.

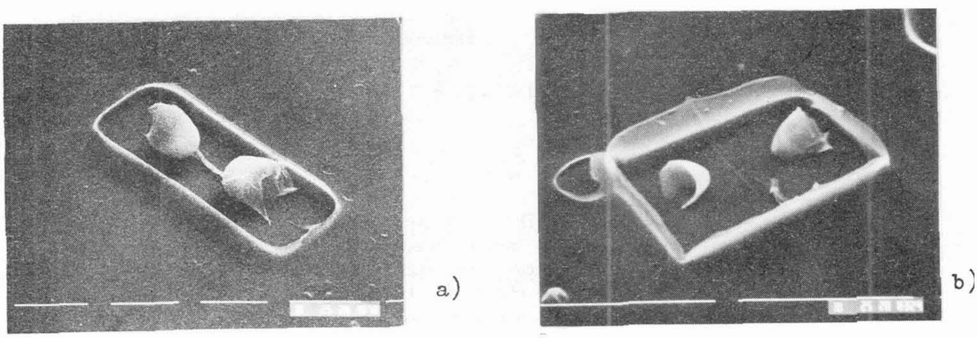
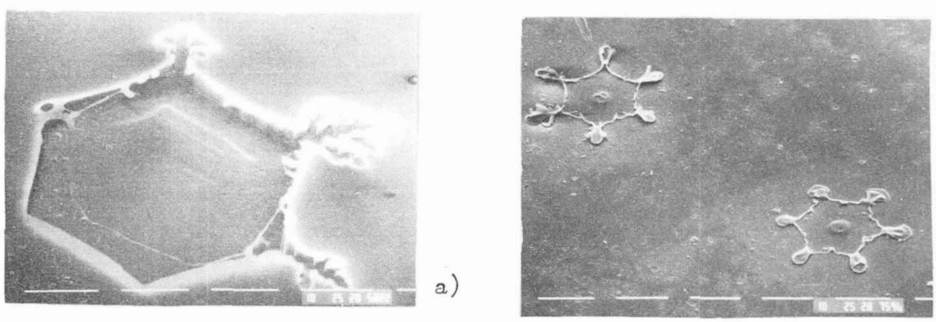


Fig.4-a,b
Initial stages of a lacunary-like instability on the basal faces of ice columns with rounded (a) and sharp edges and corners.

It is observed in the whole temperature range investigated on both sharp- and rounded-edge crystals. In the case of hexagonal plates in the regions I and III of the Nakaya-Kobayashi diagram its initial appearance is observed on the prismatic faces (Fig.3), whereas in the case of column crystals (region II) it appears initially on the basal faces (Fig.4). Since the habit of the crystals is determined by the ratio of the growth rates of the basal and prismatic faces, this leads us to the conclusion that the lacunary-like instability appears initially on the faster growing face. This result is in agreement with the implications of the theory of morphological instability of polygonal crystals of Chernov /1/ as well as with the numerical calculation for hexagonal crystals of Kuroda et al. /4/. The same result is observed at -30 °C by Gonda and Koike /10/. From our experiments such conclusions cannot be made for the low temperature region IV because the crystals in this case are often replicated either with disturbed stability on both faces (basal and prismatic) or separately without any order.

At lower temperatures below -10 °C (regions III and IV) dendrite-like instability appears. It is characterized morphologically by a preferential growth of a narrow region around the corners of the crystal. As a result thin dendrite branches are formed out at the sharpened corners of the crystal (Fig.5). The dendrite-like instability can be observed both combined with lacunary-like instability on one and the same crystal or independently. In our experiments intermediate forms between these two kinds of instability are not observed. For this reason we consider that it is rather unlikely the different supersaturation to be responsible for their different morphology.



a) b)

Fig.5-a,b
Initial stages of a dendrite-like instability on ice plate crystals.

The available theories /1-5/ can propose some explanation or of the first or of the second mentioned kind of instability but they cannot explane from common point of view the observed morphological difference. It seems quite possible in the case of ice crystals that different mechanisms are responsible for the observed different instabilities. The theoretical interpretation of this question remaines unclear up to now.

At lower temperatures (regions III and IV) we observed crystals with sharp edges and corners (Figs.1b,2b). At the highest temperatures (regions I and II) we have found a considerable rounding of the edges and the corners (Figs.1a,2a) which decreases with lowering the temperature. This fact is in agreement with our previous optical-microscope investigations /14/ at a lower air pressure (0.00005 mm Hg) as well as with the resultes of Keller et al./15/ and Colbeck /16/. This appearance of rounded (nonsingular) surfaces near below the melting point of ice have been considered by us /14, 17/ as an effect of surface roughening. The appearance of morphological instability on such crystals with strongly rounded (nonsingular) edges is experimentally established fact. This is the lacunary-like instability in regions I and II

(Fig.4a). This result is unexpected from the point of view of the theory of morphological instability of Chernov /1/ which concerns crystals with well developed sharp edges and corners. Indeed, it is difficult to accept that the rounded edge is an effective source of steps. It is clear also that one can hardly speak about inhomogenious supersaturation along the surface of such small rounded crystals.

A modification of a lacunary-like instability on plate crystals is shown in Fig.6. The increase of such instability on the prismatic surface surrounding the crystal leads to the appearance of an unstable crystal with a shape similar to those of the so called Tzusumi-crystal. In the latter case two hexagonal plates grow from the edges of the basal face of a hexagonal column. Theoretically the possibility for the appearance of such kind of unstable crystal was previously discussed by Frank /3/.

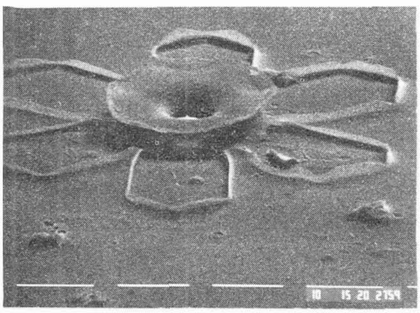


Fig.6
An unstable ice crystal.

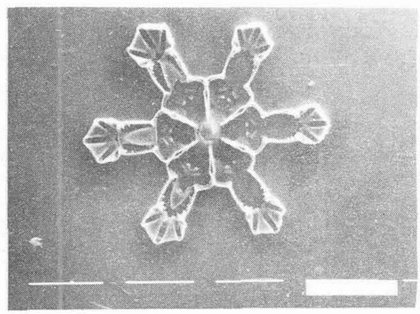


Fig.7
An electron-microscopy image of the formvar replica of a snow crystal (the latter stage of instability development).

In conclusion we will emphasize that the replica method and the Scanning Electron Microscopy offer excelent possibilities for investigation of different morphologically unstable forms at their initial stages. Their interpretation is hardly possible without suggestion of different mechanisms of formation of the instability. This technique allows also a detailed investigation on latter stages of the growth of ice crystals with a complicated morphology (Fig.7).

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COMMENTS

Remark of J.W. GLEN

I would welcome hearing the view of Dr Kuroda on the extent to which these observations are now theoretically understood.

Anwser of T.KURODA :

The driving force of morphological instability of polyhedral crystals is non-uniformity of supersaturation along the crystal surface. It is highest at crystal corners and lowest at center of surface. And degree of the non-uniformity is proportional to crystal size and normal gradient of supersaturation at surface which increases with increasing supersaturation σ_∞ at infinity. Therefore, as shown by Mrs. Stoyanova, morphological instability occurs when σ_∞ exceeds critical value.

Remark of N. FUKUTA :

Vapor method of Formvar seems to cause a number of problems. The surface features seem to be lost and corners and edges appear dissolved. I would suggest you to try better combination of plastic and solvent which I will present later.

Answer :

The observed transition from rounded to sharp edges and corners of ice appears in a narrow temperature interval less than 20°C. It is hardly believed that replication possibility of formvar at these temperatures will be changed so much. This result is in accordance also with other direct observations. I think that this method is good enough for investigation of the morphological instability of ice and I am thankful to Dr Fukuta for the proposed new replicating materials and solvents.