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Citation	Physics of Snow and Ice : proceedings, 1(1), 259-266
Issue Date	1967
Doc URL	http://hdl.handle.net/2115/20301
Type	bulletin (article)
Note	International Conference on Low Temperature Science. I. Conference on Physics of Snow and Ice, II. Conference on Cryobiology. (August, 14-19, 1966, Sapporo, Japan)
File Information	1_p259-266.pdf

Experimental Study of the Evaporation of Ice in Controlled Conditions of Subsaturation

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Abstract

The evaporation rate and the surface morphology obtained by thermal etching on (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes are studied at about −20°C over a range between 25% and 76% of R. H. (taken with respect to the solid). Except for free evaporations, etch pits and facets are formed their characteristics being related to the surface symmetry. In these cases the evaporation rate and the depth of the thermal attack are in relation with the R. H. values. On the contrary, in free evaporations, only smooth surfaces are observed and the values of the evaporation rate are lower than those expected according to the subsaturation conditions. The results show that the presence of O_2 is not essential for the ice facetting. On the other hand, the thermal attack appears greatly increased in the presence of traces of silicone, without any modification in the evaporation rate. These features are compared with some results of the thermal etching on metals.

I. Introduction

Investigations about thermal etching of ice indicate that crystallographic planes are formed when the evaporation process takes place either very near or quite far from equilibrium conditions.

In fact, thermal pits limited by low index planes are produced by an inhibited process, their shape depending on the orientation of the surface. These features were found when a slow evaporation of ice was allowed maintaining the samples in fairly hermetic enclosures (Levi *et al.*, 1964). Analogous results have been obtained when the ice surface evaporates through a plastic film (Higuchi and Muguruma, 1958). Recently, experiments performed in this laboratory on thermal etching of ice "in vacuo", indicate that geometrical pits also form by a large increase in the evaporation rate (De Micheli and Lubart, 1964).

On the contrary, ice crystals freely evaporating during many days in a cold chamber usually have smooth surfaces which are only crossed by traces of boundaries and subboundaries.

This experimental evidence does not allow to establish a clear correspondence between the characteristics of thermal attack and vapour pressure of ice in contact with the evaporating surface.

In the present paper, we intend to initiate a systematic study of the most important parameters controlling the evaporation process. For this purpose, thermal etching of

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ice single crystals was carried out under measured conditions of relative humidity and the morphology of the evaporating surface was followed by optical microscopy. The evaporation was performed in the following conditions: low vacuum, 540 torr., free and inhibited conditions and in air currents. The rate of evaporation was determined by measuring the mass loss of the samples. In addition, nitrogen currents were used in order to determine whether the presence of oxygen modifies the kinetics of evaporation. Finally, we have evaporated samples of ice in the presence of silicone in order to test the influence of this water repellent on thermal etching.

II. Results and Discussion

Experimental procedure

Single crystals of ice were grown in "Pyrex" glass tubes and the crystal orientation was determined by Higuchi's method (Higuchi and Muguruma, 1958). By suitable fusions, the (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes were easily obtained.

Individual samples were sawn from the ice rod to standard dimensions $10 \times 15 \times 12$ mm. The lateral surfaces and the base of the sample were respectively wrapped in aluminium and transparent cellophan foils. Finally, the surface to be evaporated was carefully polished with a silk cloth.

After and before evaporation, the samples were weighed to 0.1 mg in a small container of styropor. These operations were performed in similar conditions in order to reduce the errors due to condensation of water during the weighing of the sample.

The evaporation was carried out in a small box where the bottom and cover were parallel glass plates. This device was mounted on the travelling stage of a microscope placed within a cold chamber. The observations were made by transmitted light.

The temperature of the environment in contact with the sample was determined by means of a thermocouple. The evaporation trials were performed between -20 and -22°C according to the temperature conditions in the cold chamber. Usually, oscillations of about 1°C were found during the experiences.

The relative humidity was measured with an electro-humidity transducer placed within the evaporation box.

For measurements performed at low and intermediate values of the R. H. the evaporation box was continuously pumped to about 10^{-1} and 540 torr. respectively. The lower pressure was obtained with a vacuum pump that operates at 10^{-2} torr. Some experiences were performed with a vacuum pump operating at 10^{-3} torr. The actual pressure of 10^{-1} torr. was calculated from the R. H. measurements by supposing the absence of air in the box.

Currents of dry and cold gases were used for measurements involving air and nitrogen (quoted O_2 concentration 1%). For experiments with nitrogen, the specimens were placed into the evaporation box after passing a stream of this gas during about 30 minutes.

Inhibited conditions were obtained by enclosing the sample in the box and free evaporation was performed in the cold chamber under measured conditions of subsaturation.

Evaporation rate and relative humidity

Table 1 shows the values of the evaporation rate and R. H. obtained in different

Table 1

Evaporation conditions	Evaporation rate $g \cdot cm^{-2} \cdot sec^{-1}$	R. H. %	Temperature °C
Low vacuum	$(1.2 \pm 0.2) \times 10^{-5}$	<25	-22 ± 1
Low vacuum with traces of silicone	$(1.2 \pm 0.2) \times 10^{-5}$	—	-22 ± 1
Pumping at 540 torr.	$(4 \pm 2) \times 10^{-6}$	52 ± 2	-20 ± 1
Nitrogen and air currents	$(4 \pm 2) \times 10^{-7}$	71 ± 2	-20 ± 1
Inhibited evaporation	$(4 \pm 2) \times 10^{-8}$	76 ± 2	-21 ± 1
Free evaporation	$(4 \pm 2) \times 10^{-8}$	50 ± 2	-20 ± 1

conditions.

The experimental error in the values of the evaporation rate was evaluated as follows according to the work conditions: 1) for evaporations "in vacuo" the results are mainly affected by the uncertainty in the total area due to the change of the surface produced during the thermal attack. This change was estimated to be 15% and the experimental results were corrected accordingly. In addition, only the upper limit of the relative humidity can be assured owing to the uncertainty in the determination of high subsaturations; 2) for lower evaporation rates, in which the average weight loss in each experience was of about 0.03 g the error involved in the manipulation of the samples (up to 50%) must be considered as the most important one.

Similar values are found for the rates of evaporation obtained with vacuum pumps operating at 10^{-2} or 10^{-3} torr. In some experiences performed "in vacuo" the specimens could be weighed at intervals of 30 minutes. The results indicate that in these conditions, the rate of evaporation does not depend on time. In all evaporation methods and within the experimental error, no differences were found for the evaporation rate of (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes.

Surface morphology

Our results indicate that, except for free evaporation the surface of ice is always modified, though, for comparable intervals the depth of the thermal attack is generally in direct correspondence to the relative humidity.

a) Low vacuum. The samples were evaporated during about 2 hours. As a general rule, the surface roughens as soon as the vacuum is established and geometrical pits appear after 5–15 minutes on some regions of the sample.

On (0001) and $(10\bar{1}0)$ planes, a layer structure is frequently found consisting of thermal pits arrayed as steps of quite different depth (Figs. 1 and 2). As evaporation goes on some layers disappear due to a faster evaporation of the shallower steps. This behaviour may be determined by a bunching of the thinner layers; similar features were found when ice crystals grow from the vapour (Mason, Bryant and Van den Heuvel, 1963).

On some regions of $(11\bar{2}0)$ planes, intersecting prismatic faces form striations along ⟨0001⟩ direction (Fig. 3). In addition, a secondary facetting normal to the *c*-axis is formed in prismatic faces etched during the the evaporation from $(11\bar{2}0)$ and $(10\bar{1}0)$ planes (Fig. 3).

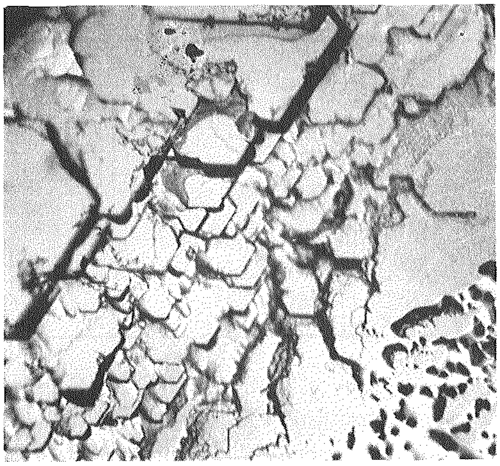

Fig. 1. Layer structure on a (0001) plane. (Low vacuum; 30 min; ×50)

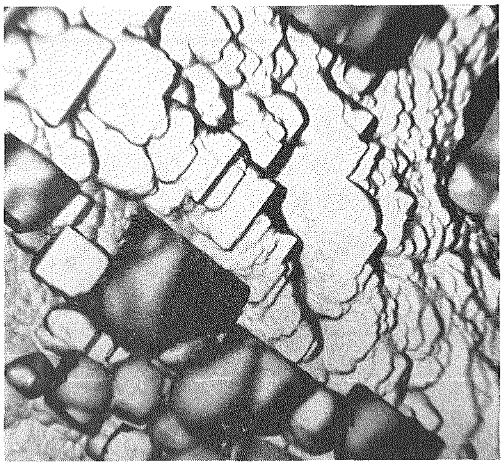

Fig. 2. Layer structure on a $(10\bar{1}0)$ plane. (Low vaccum; 2 h; ×25)

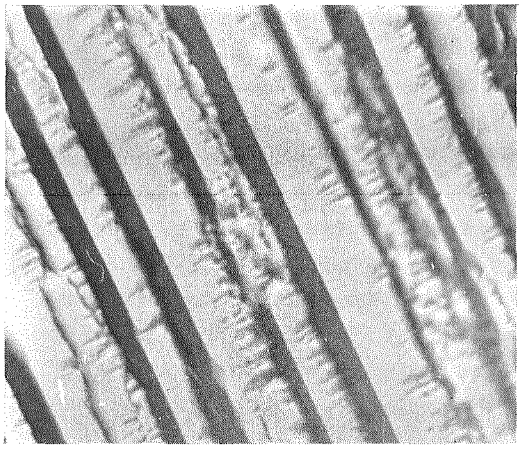

Fig. 3. Thermal etching on a $(11\bar{2}0)$ plane showing striations along the ⟨0001⟩ direction and the secondary facetting normal to the *c*-axis. (Low vacuum; 5 h; ×50)

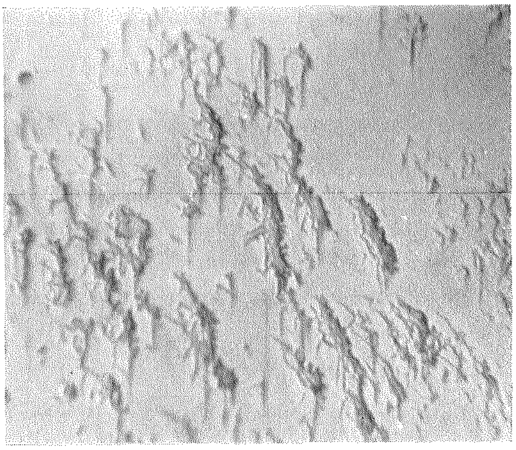

Fig. 4. Facetting on a (0001) plane. (Evaporation at 540 torr.; 2 h; ×80)

b) Pumping at 540 torr. The specimens were evaporated during 4–5 hours. After this lapse of time thermal pits did not form but a weak facetting slowly developed following the crystal symmetry. This facetting might be interpreted as a first stage of the evaporation process (Fig. 4). On prismatic planes, $(10\bar{1}0)$ faces are formed along the *c*-axis. In some cases, on the etched $(10\bar{1}0)$ surfaces, a secondary facetting normal to the ⟨0001⟩ direction was observed.

c) Nitrogen and air currents. During the evaporation experiences (4–5 hours) in N_2 and air currents analogous results were obtained: after about 2 hours a primary and secondary facetting and prismatic pits appeared on $(11\bar{2}0)$ and $(10\bar{1}0)$ planes respectively (Figs. 5 and 6) and hexagonal pits slowly developed on (0001) faces (Fig. 7).

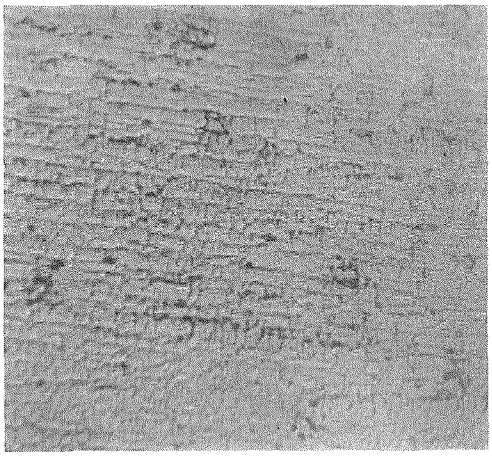

Fig. 5. Primary and secondary facetting on a $(11\bar{2}0)$ plane. (Evaporation in N_2; 1 h 30 min; ×80)

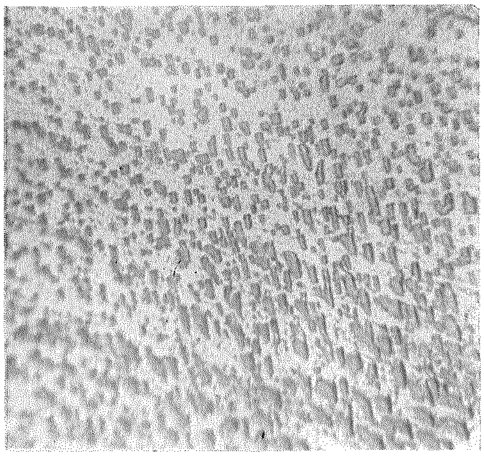

Fig. 6. Prismatic pits on a $(10\bar{1}0)$ face. (Evaporation in N_2; 1 h 30 min; ×80)

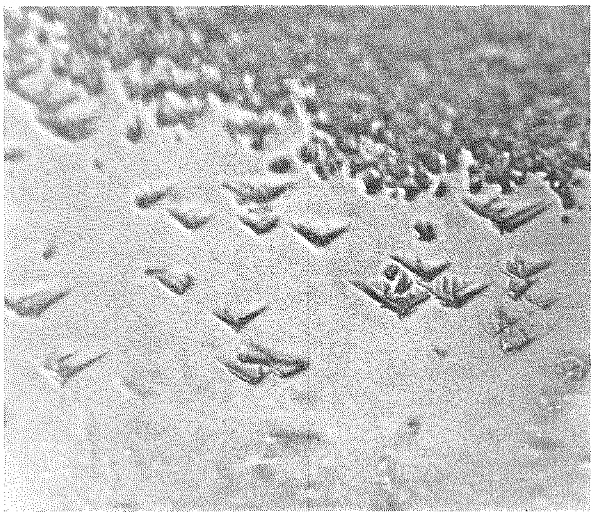

Fig. 7. First stage in the formation of hexagonal pits on a basal plane. (Evaporation in N_2; 3 h 30 min; ×80)

In some cases, isolated grooves of about 50–100 μ in length were also obtained on basal planes. Similar features have already been observed in free evaporation. (Kuroiwa and Hamilton, 1963). A subsequent evaporation "in vacuo" of the reground surface allowed to determine that the observed grooves did not follow clear crystallographic directions.

d) Inhibited evaporation. The results obtained in these conditions are similar to that already observed (Levi *et al.*, 1964): geometrical pits are formed after few days of evaporation.

Inhibited process was also performed in ice surfaces etched during a previous faster evaporation. Etch patterns illustrated in Fig. 8 were obtained in inhibited conditions on

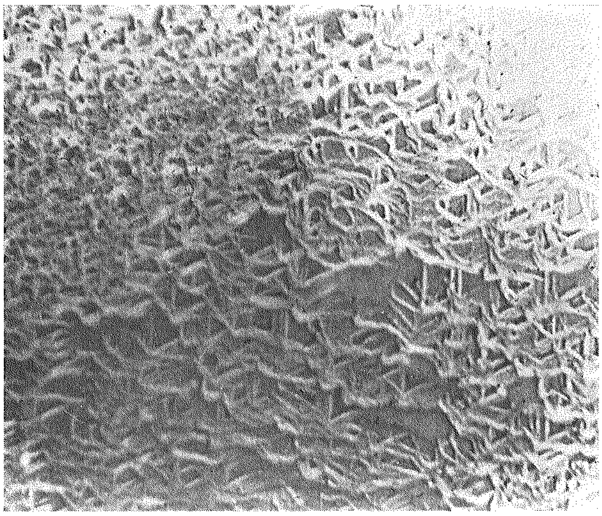

Fig. 8. Hexagonal arrangement on a basal plane showing the emergence of $(11\bar{2}0)$ planes. (Inhibited conditions; 20 h; ×80)

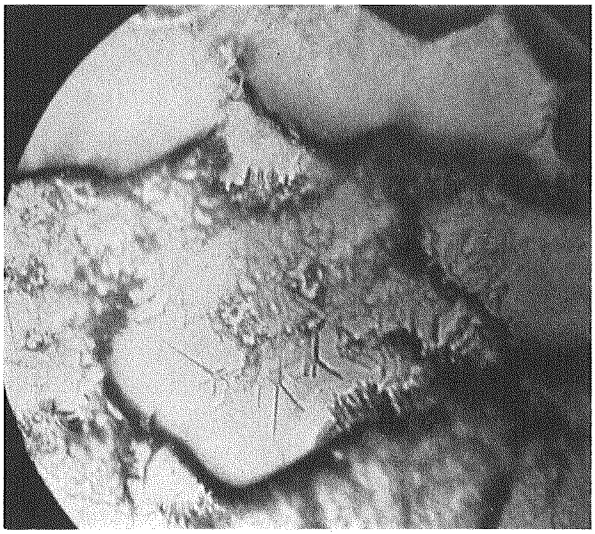

Fig. 9. Terraces obtained by an inhibited evaporation on a basal plane formed *in vacuo*. (48 h; ×50)

a (0001) plane in which the formation of hexagonal pits had been initiated by evaporation in a N_2 current. As it is shown, intersecting lines appear generally in $\langle 11\bar{2}0\rangle$ directions. However, some lines cut each other at angles of 90° indicating the eventual emergence of $(11\bar{2}0)$ planes. Figure 9 shows the features observed on a basal plane previously etched "in vacuo". As it can be seen, the pits already formed become deeper through the formation of new terraces starting from the corner of the (0001) surface.

e) Evaporation with traces of silicone. Preliminary experiments in this laboratory had shown that the depth of the thermal attack of ice is severely increased when the

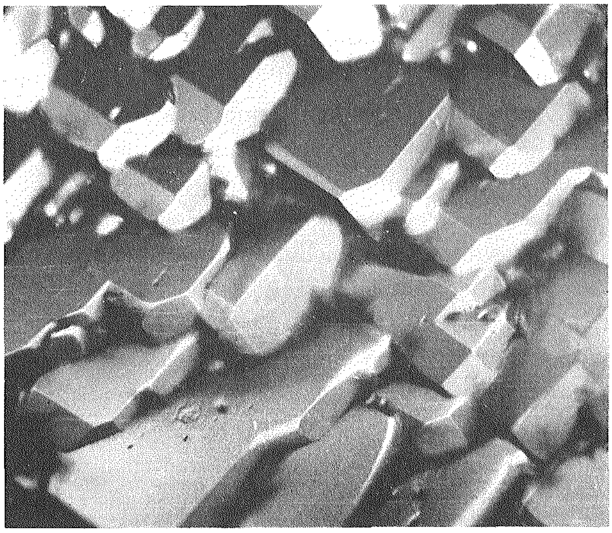

Fig. 10. Etch pits on a near $(11\bar{2}0)$ plane after an evaporatin with silicone. (40 min ; ×50)

evaporating sample is in contact with silicone oil. Subsequently, analogous features were found when solid silicone was used as high vacuum grease during evaporations "in vacuo".

As a general rule, thermal pits are formed on almost the whole surface as soon as the pump is connected to the system and after few minutes the sample become deeply attacked. Figure 10 shows a typical etch pattern on a nearly prismatic plane. The surface is covered by pits up to 1 mm in length along the *c*-axis. They are limited by $(10\bar{1}0)$ faces and in some regions higher index planes, probably $(40\bar{4}1)$, are also formed. In some cases such planes were also found by Higuchi and Muguruma, (1958).

Discussion

Our results show that etch pits or facets can be obtained over a wide range of relative humidity. Thus, the equilibrium in the vapour-solid interfase is not a necessary condition for crystallographic planes to be formed.

A correlation can be established between the vapour pressure of ice and the depth of the thermal attack obtained in comparable lapses of time. Actually, the weak facetting observed between 52–71% of R. H. may be considered as the initiation of an evaporation process which, developed with time would probably produce the surface morphology obtained in a few days in inhibited conditions (76% R. H.). In addition, deeply modified surfaces are formed in a few hours at the highest subsaturations.

Furthermore the same crystallographic planes are found by evaporations "in vacuo" and in N_2 or air at atmospheric pressure. This fact indicates that neither the total pressure nor the presence of O_2 in contact with the sample modify the characteristics of the ice thermal etching though it might be supposed that O_2 could be easily adsorbed on the ice surface.

Our results of thermal etching of ice may be compared with some features of the thermal etching in metals. As it is known, it is under discussion whether thermal facetting on many metals heated in presence of oxygen is determined by a minimization of the surface energy or by the kinetics of the evaporation process.

Recently, experiments on silver performed "in vacuo" and in atmospheres of N_2 and O_2, have shown that the same activation energies are found under non-facetting and facetting conditions (Lowe, 1964). These results support the hypothesis that the phenomenon is due to a minimization of the surface energy.

The features obtained in presence of silicone show that the facetting "in vacuo" appears greatly increased without any modification in the correspondent value of the evaporation rate. Similarly, the thermal etching in free and inhibited conditions, produces quite different surface morphologies with comparable rates of evaporation (Table 1). This behaviour would suggest that also in the present case, the characteristics of thermal etched surfaces are not determined by the kinetics of the process but by the minimization of the surface energy.

Finally, it must be noticed that in free and inhibited conditions, the thermal etching is performed without a compelled removal of the molecules of water near the solid surface as existing in the other cases. Therefore, in these conditions a layer of vapour near saturation is probably formed in contact with the surface its thickness depending on the R. H. at the environment. This fact would explain the similitude between the rates of evaporation found in both cases, though, no clear interpretation can be made for the differences in the surface morphology.

Likely, the thermal facetting is favoured when gas currents or pumping are produced explaining that, for the free process, thermal pits do not form. However, under this assumption, a new hypothesis must be made in order to explain the surface morphology in the inhibited process.

Our experimental evidence is not enough to state concluding results about the evaporation process in ice; it is our project to determine the energy of activation for the different conditions and its relation with the energy of subsaturation.

The authors should like to express their indebtness to Dr. Laura Levi for helpful discussions and suggestions on this paper.

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