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SURFACE FEATURES OBSERVED DURING THERMAL
ETCHING OF ICE

BY

A. S. KRAUSZ AND L. W. GOLD

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CARACTERISTIQUES SUPERFICIELLES DES CRISTAUX
DE GLACE EXPOSES A LA CHALEUR

SOMMAIRE

Les auteurs ont soumis des éprouvettes monocristallines et polycristallines de glace à l'attaque de la chaleur dans une atmosphère d'air saturé d'humidité. Les observations ont été réalisées sous un grossissement de 50 après une durée d'attaque allant de quelques minutes à plusieurs semaines. Les joints de forte désorientation sont devenus visibles sous forme de sillons après les premières minutes. Des joints rectilignes de faible désorientation, formés au cours de la solidification ou de la déformation plastique, ont été aussi observés. Les auteurs ont prouvé que les joints à forte désorientation s'étaient déplacés et déformés en zigzag au cours du fluage, tandis que les joints à faible désorientation étaient restés rectilignes. Les auteurs ont souvent observé de courtes crêtes rectilignes, bien délimitées, apparaissant en relief à la surface de l'éprouvette, et s'y sont intéressés en détail. Ces marques apparaissaient au bout de quelques minutes et demeuraient très stables, retenant leur aspect initial après plusieurs heures d'exposition à la chaleur. Les crêtes formaient un dessin triangulaire ou rectangulaire, dépendant de l'orientation des cristaux de la face attaquée. Les auteurs ont prouvé qu'une partie de ces crêtes était parallèle à l'axe sénnaire et que l'autre partie lui était perpendiculaire. De temps en temps de petits mamelons, creusés au sommet d'une dépression en forme de cratère, se formaient au cours de l'attaque thermique. Ces mamelons paraissaient s'aligner principalement au long des sous-joints. Les auteurs observèrent parfois un réseau hexagonal de ces mamelons, ainsi que certains mamelons de forme triangulaire à la surface de quelques cristaux. La bissectrice de l'angle aigu au sommet de la pyramide était normale à la base du cristal. Une attaque thermique poussée produisit des dépressions rectangulaires aux facettes bien formées. Les auteurs ont employé cette technique d'attaque thermique pour étudier les changements structuraux de la glace au cours d'essais de fluage et de rupture.

Surface Features Observed during Thermal Etching of Ice¹

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Polycrystalline- and single-crystal ice specimens were etched in a saturated air atmosphere. Observations were made at about 50x magnification after etching times of a few minutes to several weeks.

High-angle boundaries became visible as grooves within the first few minutes. Straight low-angle boundaries, which formed during solidification or in the course of plastic deformation, were also observed.

Sharply defined short straight lines, raised above the surface of the specimen, were frequently observed and have been investigated in detail. These features developed within a few minutes and were very stable, retaining their initial appearance for as long as several hours of etching time. The lines formed either a triangular or a rectangular pattern that was related to the crystallographic orientation of the exposed surface. It was established that one family of these lines was parallel and a second was perpendicular to the C axis.

Occasionally small round hillocks with a small central feature that appeared to be a crater formed during etching. The concentration of hillocks appeared to be greatest along subboundaries. A honeycomb-like network of hillocks was sometimes observed. Triangular hillocks were observed to form on the surface of some grains. The bisector of the acute angle associated with the raised part of the triangle was perpendicular to the basal plane. After extensive thermal etching, rectangular pits with well-developed facets appeared.

The etching technique was used to study structural changes that occurred in ice during creep and fracture experiments.

INTRODUCTION

In association with a study of the influence of structure on the plastic deformation behavior of ice, a thermal etching method was developed for observing grain boundary migration and the formation of low-angle boundaries (1). The etching process brought out other features that were considered to be of general interest. This paper reports these features, as they may be

relevant to the understanding of the properties and behavior of ice at its surface.

EXPERIMENTAL TECHNIQUE

Transparent, air-bubble-free ice plates were grown from deaerated tap water by slow, unidirectional freezing. Columnar-ice with grains of cross-sectional area about 0.015 sq. in. was obtained by seeding the cooled water with fine ice particles. Large single crystals were obtained by freezing without seeding.

The surface of specimens was prepared by melting briefly on a plate kept at a temperature slightly above 0°C. or by pouring alcohol over it. Some specimens were subsequently polished to a "mirror" surface with tissue paper or soft leather. The specimen

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FIG. 1. Sketch of profiles of high-angle grain boundaries: (a) symmetrical; (b) asymmetrical.

was then placed with the prepared surface facing upwards in an air-tight plastic box filled with crushed ice to ensure a saturated atmosphere. Observations were made through the transparent top of the box using a binocular microscope at magnification of not greater than $\times 80$. The period of time over which observations were made on a surface varied from specimen to specimen, beginning as soon as 1 minute after placing it within the box and extending at times over several weeks.

Both the preparation of specimens and the observations were made in a cold room at a temperature of $-10^{\circ}\text{C.} \pm 0.5^{\circ}$. Under the conditions existing in the cold room, a difference in temperature developed between the inside top and bottom surfaces of the box amounting to about $2 \times 10^{-2}^{\circ}\text{C.}$ over a distance of 9 cm. The specimens were supported on a platform about 2 cm. above the bottom of the box, and their upper surface was usually within about 1 cm. of the top of the box.

Surface features were usually illuminated by transmitted light by reflecting the light off a sheet of white paper placed under the specimen. The focus of the light was adjusted to give maximum contrast.

OBSERVATIONS

Thermal etching of ice at -10°C. in the conditions obtained in the plastic box produced sharply defined surface features. Features observed at low magnification were high- and low-angle boundaries and net-

works of crystallographically oriented short straight lines and hillocks of various regular shapes. It is appreciated that sublimation and deposition of water vapor on the surface at high energy sites, as well as surface or bulk migration, may all play a part in the formation of these features. The observations indicated that the solidification of a thin layer of water that formed when the surface was prepared played a significant role in the formation of some of the features, as will be pointed out later.

Grain Boundary Observations. The etching technique proved to be well suited for grain boundary studies; high-angle boundaries could always be observed within a few minutes as clearly defined lines. The profile of grain boundary grooves was similar to that observed at high temperatures in metals. Observations showed that the cross-sectional shape of grooves was dependent on the orientation of the grain boundary relative to the crystallographic orientation. The familiar symmetrical profile developed only when the angle between the boundary and the trace of the basal plane on the surface was significantly different from 0° (Fig. 1a). When the trace of the basal plane was approximately parallel, an asymmetrical profile developed as shown in Fig. 1b. Etching over long periods of time usually caused the boundary region to become steeper and to be elevated above the surface of the adjacent grains.

Low-angle boundaries could be observed within a few minutes after the initiation of etching. The grooves associated with these boundaries were distinctly shallower. When formed in surfaces almost perpendicular to basal planes low-angle boundaries were straight, and those within the same grain were usually parallel. An example of this is shown in Fig. 3a. When formed in surfaces almost parallel to the basal plane, these boundaries were not usually straight and those in the same grain were not parallel.

Line Features. Thermal etching frequently produced a triangular or rectangular pattern of short straight lines (Fig. 2). Observations showed that the lines were raised above the surface. Studies made on single crystals of known orientation, and on polycrystalline specimens for which the orientation of in-

FIG. 2. Typical examples of patterns of short straight lines: (a) triangular; (b) rectangular.

dividual grains was determined using the plastic film technique of Higuchi (2), established that the rectangular pattern developed on surfaces that were perpendicular to the basal plane; the lines being parallel to the basal and prismatic planes. If the C axis was inclined to the surface, a triangular pattern developed, the lines being parallel to the edges of the characteristic triangular etch

pits formed for this orientation using the plastic film technique. This indicated that the lines were again parallel to the basal and prism planes.

The line features were quite stable. They formed shortly after the initiation of the etching process and retained their appearance for several days. Prolonged etching coarsened the pattern by increasing the

FIGURE 3(b)

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FIG. 3. Example of the secondary set of short lines. (Note low-angle boundaries parallel to one of the primary sets of short line features.) (b) Sketch illustrating the geometrical relationship between the primary and secondary sets.

width of the lines. Lines gradually disappeared in an area swept through by a migrating boundary as would be expected from the change in crystallographic orientation. New lines, corresponding to the new orientation, were not observed to develop. Except for this observation, plastic deformation of up to about 2% did not appear to have any effect on the line features.

It was observed that sometimes a shorter and denser system of lines covered the slope of grain boundary grooves. The grain boundary region was often a preferred site for the

development of both the rectangular and triangular patterns.

A secondary set of lines, at an angle to the families parallel to the basal and prismatic planes, was occasionally observed. In a few cases it was found on closer inspection that the secondary set was made up of very short lines parallel to the primary set as shown in Fig. 3.

Hillock Formation. Round hillocks were observed to form on the surface of some grains. These hillocks appeared to be initiated during the freezing of the thin film of water

FIG. 4. (a) Example of cell-like arrangement of hillocks. (b) Example of randomly distributed hillocks with higher concentration along subboundary. Notice dark, crater-like, central region.

formed when preparing a surface on the warm plate.

Two distinctly different types of hillock systems were observed. One type consisted of a cell-like arrangement as shown in Fig. 4a. The second had a more random distribution of the hillocks, with a higher than average concentration along subboundaries

(Fig. 4b). In both types, the hillocks had a small dark central region that had the appearance of a crater.

After etching for a period of about 24 hr., triangular-shaped hillocks were sometimes observed, as shown in Fig. 5. These features were so oriented that the plane bisecting the apex angle was parallel to the C axis.

FIG. 5. Example of triangular hillocks. (Note orientation of rectangular etch pits formed by plastic film technique.)

FIG. 6. Example of prismatic pits formed after extensive etching. (Note rectangular pits formed by the plastic film technique, boundary region elevated above surface containing etch pits.)

This can be seen in Fig. 5, where the bisecting plane is perpendicular to one edge of the rectangular etch pits formed over part of the surface of the grain by the plastic film technique. There were some indications that

the triangular hillocks developed from hillocks that were round initially.

Miscellaneous Observations. There appeared to be a tendency for thermal etching to produce a smooth surface if the C axis was

Fig. 7. Example of threadlike feature observed at some grain boundary triple points.

inclined to the surface, and to produce a rough surface if the C axis was parallel to the surface. The rough surface appeared to be raised above the surface of grains that etched smooth. Etching over a period of several weeks produced prismatic pits, whose shape and orientation were related to the crystallographic orientation. An example is shown in Fig. 6, where the rectangular pits formed by the plastic film technique show that in this case the C axis is parallel to the surface.

An interesting "threadlike" feature was observed to form at some grain boundary triple points; an example is shown in Fig. 7. This feature had no apparent dependence on crystallographic orientation. Observations with the microscope showed a line of cavities extending into the specimen almost vertical to the surface at the site where the feature joined to the triple point. For one case observed, the thread feature terminated at a boundary well away from the triple point. A column of cavities extended into the ice at the intersection of the feature and the boundary in this case as well.

The authors are not prepared to offer at this time an explanation for the line and thread features that have been observed. It

is of interest that no line features were observed to form on surfaces that had been prepared by careful machining only, without subsequent melting or dissolving with alcohol. This suggests that the features may be associated with the formation and subsequent freezing of a thin film of water formed when the surface was being prepared. On the other hand, the similarity between some of the observations reported here and the appearance of impurity segregation in metals is striking (3).

Hillocks, similar in appearance to those discussed in this paper, have been observed by Bryant and Mason (4) on the basal plane of ice crystals grown from the vapor. At present there is not enough information available to correlate the two observations.

No observations were undertaken to determine how the development of the thermal etch features was affected by changing such factors as temperature, temperature difference between the top and bottom of the box, and the degree of saturation of the air.

Thermal etching proved to be a very convenient technique for studying certain structural features that play a role in the deformation behavior of ice. Experience has shown that, in addition, it is a potentially

useful method for determining crystallographic orientation and for studies of the surface of ice, such as determining the dependence of surface energy on crystallographic orientation. It is hoped that the observations reported here will provide a stimulus for such investigations.

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REFERENCES

1. KRAUSZ, A. S., "Etching technique to study plastic deformation of ice," *J. Glaciology* **3**, 30, 1003-1005 (1961).
2. HIGUCHI, K., "The etching of ice crystals," *Acta Met.* **6**, 636 (1958).
3. KIEVITS, F. J., "The ageing characteristics of aluminium-magnesium alloys containing silver and cadmium," *J. Inst. Metals* **93**, 517 (1965).
4. BRYANT, G. W., AND MASON, B. J., "Etch pits and dislocations in ice crystals," *Phil Mag.* **1221** (1960).