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Publisher's version / Version de l'éditeur:

Philosophical Magazine, 36, 6, pp. 1385-1404, 1977

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DISLOCATIONS IN ICE AS REVEALED BY ETCHING

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ANALYZED

by N.K. Sinha

Reprinted, from
Philosophical Magazine
Vol. 36, No. 6, 1977
p. 1385 - 1404

DBR Paper No. 762
Division of Building Research

SOMMAIRE

Le processus d'attaque et de reproduction des surfaces de glace a été étudié. Il a été démontré que ce processus peut être appliqué pour fins particulières en préparant la surface à l'aide d'un microtome et en faisant varier la concentration et l'épaisseur du corrosif caustique, la température et le temps de séchage. Il a été possible de reproduire les figures de corrosion sous forme de stries pour les dislocations sur les plans de base et autres, établissant ainsi directement le rapport entre les figures de corrosion et les défauts de ligne. Cette technique a servi à étudier le mouvement des dislocations autres que sur le plan de base dans des champs de contraintes uniformes et non uniformes. Cette méthode permet de déceler les défauts inhérents et les dislocations autres que sur le plan de base.

Dislocations in ice as revealed by etching

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[Received 28 June 1977]

ABSTRACT

The process of etching and replicating ice surfaces has been investigated. It has been shown that the process can be made selective for specific purposes by preparing the surface with a microtome and by varying the concentration of the etchant, thickness of the etchant, temperature and drying time. Replication of etch-pits in the form of whiskers was possible for both basal and non-basal dislocations, thereby directly establishing the correspondence of etch-pits to line defects. The technique was used to study the movement of non-basal dislocations under uniform and non-uniform stress fields. Grown-in defects and non-basal dislocations could be revealed by the method.

§ 1. INTRODUCTION

The etching of crystal surfaces is widely accepted as a powerful method of observing lattice defects and their behaviour. In recent years this has been extended to ice. The problems encountered in ice, however, are different from those in other materials, mainly because the working temperatures are so close to its melting-point.

The present investigation was carried out to develop a better appreciation of the processes involved in etching of ice. It was hoped that a technique could be developed that would allow dislocations to be identified without ambiguity. The technique would be of great value for the interpretation of the role of dislocations in the processes of deformation and fracture of single as well as polycrystalline ice. This report covers mainly the development of an etching and replicating technique and its application to the study of non-basal dislocations and etch-pits on the (0001) plane. The application of the technique to the study of glide dislocations and etch-pits on the first prismatic faces $\{10\bar{1}0\}$, second prismatic faces $\{11\bar{2}0\}$ and other faces is mentioned briefly.

1.1. *Review of literature*

Higuchi (1957, 1958) presented a technique of developing etch-pits on the surface of ice by applying a dilute solution (1%) of polyvinyl formar (Formvar) in ethylene dichloride and allowing the plastic film to dry. Kuroiwa and Hamilton (1963) showed that the etch-pits produced by Higuchi's method had no direct correlation with crystal imperfections but were produced by evaporation through tiny holes in the film. The shape of the evaporation pits depends on crystallographic orientation of the etched surface; the method has been widely used for petrographic analysis.

Kuroiwa and Hamilton (1963) also showed that a more concentrated solution of Formvar (5 to 6% in ethylene dichloride) was a suitable etchant for developing etch-pits on the basal plane corresponding to the emergence of non-basal dislocations on this surface. Dislocation etch-pits on the (0001) plane were found to be hexagonal pyramidal, in agreement with the earlier observations of Muguruma (1961).

The earlier investigators' conclusions on the association of etch-pits with dislocations were based on indirect though convincing evidence, whereas later work provided direct evidence by the movement of dislocations under stress. Some of these observations were later confirmed by Levi, De Achaval and Suraski (1965). Further progress was made by Kuroiwa (1969), who looked at Formvar replicas with a scanning electron microscope with the resolution and depth of field required for investigating the three-dimensional topography of etched surfaces of ice.

A review of the literature shows that there are still many unanswered questions. For example, the dimensions of the etch-pits were reported by Muguruma (1961) to be 0.2 to 6 μ , whereas the corresponding sizes obtained by Kuroiwa and Hamilton (1963) were 50 to 100 μ , and the diameters of the pits presented in the photographs of Levi *et al.* (1965) varied from 10 to 15 μ . Muguruma (1961) observed many stepped and spiralling etch-pits, whereas the others did not. Etch channels have been observed by Kuroiwa and Hamilton (1963), Muguruma and Higashi (1963), and Levi *et al.* (1965). The length of the channels varied from a fraction of a micron to several microns, and both tapered and non-tapered channels have been observed. No explanation is yet available on the geometric features of these channels in ice.

Glide dislocations in the basal plane are considered to take the dominating role in the viscoelastic flow of ice. These dislocations emerge on the prism planes of the crystal, and etch-pits ascribed to them have been indistinct. They have been observed only by X-ray techniques (Fukuda and Higashi 1973, Jones and Gilra 1973) in carefully prepared single crystals of ice of low dislocation density. These techniques cannot be applied readily to ordinary polycrystalline ice because of the limitations imposed by the resolution of the method and other inherent difficulties. It was realized that the etching technique would require further development in order to be used to reveal glide dislocations in the basal plane.

§ 2. ANALYSIS OF THE ETCHING PROCESS

The preferential dissolution of water molecules from ice to the surrounding medium is the basic factor that controls the etching process. This preferential removal is governed by the difference in free energy between the undisturbed surface and the site of an imperfection. The surface free energy, as a measure of the difference between the energy of an atom at the surface and one in the interior, is a function of temperature and of the medium to which the surface is exposed.

Theoretical analysis of the phenomena of preferred dissolution at dislocation emergence sites in solids has been discussed by Cabrera (1956). He came to the conclusion that the success of forming good etch-pits at the sites of imperfections would depend on how much the surface energy was decreased near

the defects by the imposed conditions of etching. The analysis bears close resemblance of the description of crystal growth and preferred evaporation by a dislocation mechanism given by Frank (1952). This description appears to be reasonable for the case of thermal etching of ice under saturated conditions as can be appreciated from a study by Krausz and Gold (1967).

The difference in free energy between the point of emergence of individual dislocation lines and the surface is small in comparison with differences associated with grain boundaries, well-developed slip planes, and relatively small-angle boundaries containing numerous dislocations (Weertman and Weertman 1964). Saturating the environment surrounding the ice specimen appears to have controlled the surface energy to a sufficient degree as to allow Krausz and Gold (1967) to observe etch features corresponding to large linear imperfections at -10°C , but not dislocations. Observations made by the present author at -30°C suggested that dislocation bundles and grown-in dislocations could be revealed by this method. It was apparent that the thermal etching of ice in air depends on both relative humidity and temperature.

The specific free energy for the ice-water interface, γ_{SL} (30 erg/cm^2), is less than one-third of the ice-vapour interface, γ_{SV} (109 erg/cm^2) at 0°C (Ketchum and Hobbs 1969, Hesstvedt 1964, Fletcher 1975). There is, therefore, a possibility of using water as the medium for etching. The method is not practical for most cases, but the possibility was demonstrated by the fact that Truby (1955) observed etch-pits on the basal plane of growing ice surfaces. Drost-Hansen (1967) considered such pits to be due to dislocations.

Surface-water molecules in ice dissociate in ethylene dichloride. Formvar dissolved in it should act as the retarding agent and the concentration of the solution should affect the rate of dissociation. In practice, etch-pits are obtained by pouring a thin layer of the solution on the surface and allowing the solvent to evaporate under the ambient conditions of a cold room. The process not only etches the surface but makes a Formvar replica at the same time; this is a great advantage and explains its continued use. This dual use for the etchant, however, complicates the process of dissociation. The rate of removal of water molecules from the ice surface to the solution depends upon the concentration of water already in the solution. This concentration changes during etching owing to the evaporation of the solvent.

The lack of understanding of this dual etching and replicating process seems to have misled previous workers and indirectly retarded development and application of this powerful method. A few examples will be cited here for clarification. Truby (1955) claimed to have developed a procedure of etching ice surface by a blast of cold and dry air at -15°C for 20 min. He demonstrated his etching technique by replicating the surface with 1% Formvar solution and observing the replica with a transmission electron microscope. Muguruma (1961) also made a similar claim of developing thermal etch-pits by allowing a surface with a mirror finish obtained by the Higuchi method to evaporate slowly for a few minutes at -25°C and then replicating the surface with a 0.5% Formvar solution. The two procedures used by these authors do not act in the way that was attributed to them. Observation by the present author of an ice surface with a mirror finish under a high-resolution optical microscope indicated that neither of the procedures for etching in air was successful in developing pits corresponding to micro-defects. Both

investigators, however, replicated the surface with a Formvar solution. The present author has found that pits developed within 20 to 30 sec after pouring such a solution on the surface. In another experiment, Ketchum and Hobbs (1969) measured equilibrium grain-boundary groove angles after maintaining the ice at -3°C for a period of two days, by making a replica of the grain boundary with 5% Formvar solution. It is possible that the replicating process could have transformed the equilibrium state into a metastable condition and changed the groove angles. This possibility was apparent from the work of Suzuki and Kuroiwa (1972) in which measurable differences were demonstrated between the grain-boundary groove angles measured by replica and metallic foil methods.

The foregoing discussion suggests that more information can be obtained by the Formvar etching and replicating process than has been obtained to date by manipulating the conditions of the process, such as the concentration of the solution, the temperature and humidity of the surrounding environment, the thickness of the etchant poured on the surface, and the drying time.

2.1. *Role of surface preparation*

Another factor that has hindered progress in the application of the etching technique to ice has been surface preparation prior to etching. Muguruma (1961) could use his method only on very small areas, less than 0.5 mm in diameter, at the bottom of evaporation etch-pits developed by the Higuchi method. He showed that for lake ice the densities of etch-pits in these small areas ($6.5 \times 10^6 \text{ cm}^{-2}$) were an order of magnitude less than the densities ($6.5 \times 10^7 \text{ cm}^{-2}$) on the original surface prepared by polishing with emery paper. It was considered by Muguruma (1961) that polishing generated many dislocations. He used this assumption, in fact, as an argument for the correspondence of etch-pits to dislocations. The increase in dislocation density by mechanical polishing was the reason that led Kuroiwa and Hamilton (1963), Levi *et al.* (1965) and Kuroiwa (1969) to limit their experiments to dendritic crystals, fresh cleavage and fracture surfaces, and surfaces produced by evaporation etch-pits. Krausz and Gold (1967) prepared their surfaces by melting briefly on a brass plate kept at a temperature slightly above 0°C , followed by polishing with soft leather or by chemical dissolution using alcohol. The surface melting method, however, cannot be used for the detection of dislocations produced in previously deformed ice if the ice is to be maintained at a constant temperature. Moreover, surface melting could introduce certain undesirable morphological changes (Krausz and Gold 1967).

§ 3. EXPERIMENTAL PROCEDURE

The following surface preparation, etching and replicating techniques were found to successfully reproduce dislocations and other imperfections at an ice surface. Their flexibility of application will be illustrated by a few specific examples.

3.1. *Preparation of the surface*

Thick sections (up to 2 cm) of required orientations were cut with a band saw. Each was mounted on a clear glass plate by freezing a few drops of water at the edge, making certain that no water entered the space between

the glass and the specimen. The latter condition can be obtained by using water precooled to just above 0°C . The exposed surface of the section was then microtomed to a mirror finish in three stages. First $1500\ \mu$ ($1.5\ \text{mm}$) was removed from the surface, $10\ \mu$ at a time. This was followed by removal of the next $500\ \mu$ in $5\ \mu$ layers, cleaning the microtome blade with a soft tissue paper after every pass. The final step was to finish the surface by removing another $100\ \mu$ in 1 to $2\ \mu$ layers, ensuring that the blade was clean before each pass. The quality of the surface was examined visually, using reflected light from a distant source, and also with an optical microscope. This procedure was used to prepare surface areas up to $8 \times 12\ \text{cm}$ with a mirror finish. On several occasions both surfaces were finished in this way to provide a thin section $0.4\ \text{mm}$ thick for analysis with transmitted polarized light. In these cases the initial thickness was $5\ \text{mm}$. After preparing the first surface, a specimen was removed from the glass plate by careful cutting of the bonding ice with a sharp razor blade. It was then remounted on another clean glass plate with the prepared surfaces facing the glass, and microtomed until the second surface had a mirror finish.

3.2. Etching and replicating procedure

A freshly prepared specimen was kept in a horizontal position inside a transparent plastic or glass box containing crushed ice. Formvar solution was placed slowly on the prepared surface with an eye-dropper and the surface coated with the desired thickness of etchant. The overflowing of the solution was prevented by building a wall of ice with water around the edges of the specimen.

The vapour pressure inside the box was controlled qualitatively by varying the degree of closure of the top of the box and providing a gentle flow of air around the box. Transparency of the box allowed the specimen to be observed externally with an optical microscope without disturbing the environment inside the chamber. For the observations reported in this paper, concentrations of the etchant were varied from 0.05 to 10%, temperatures from -5 to -40°C , the thickness of solution was up to $5\ \text{mm}$ and the humidity varied to obtain a period of drying from a few minutes to several days.

Replicas were removed by three different methods:

- (a) peeling, when the replica was to be examined immediately to evaluate a particular etching procedure;
- (b) melting of the ice in water just above the melting-point and allowing the film to float; and
- (c) allowing the ice to sublime.

The last procedure was time-consuming and took up to 15 days when the temperature was below -35°C , but it did provide undamaged replicas.

3.3. Method of observation

The replicas were carefully mounted on large glass slides with the replicated surface facing upwards, and observed with a good quality optical microscope. Selected areas were then prepared for examination with a scanning electron microscope by vacuum deposition of a layer of carbon followed by a plating of gold.

§ 4. EXPERIMENTAL RESULTS AND APPLICATIONS

4.1. *Quality of the prepared surface*

The success of the microtoming procedure depends on how effective it is in producing a flat and smooth surface without introducing undesirable effects, particularly a modification of the density of dislocations. Examination of non-basal dislocations was carried out in the following manner. Evaporation pits were produced on a microtomed (0001) plane of laboratory-grown ice by applying a thin layer of 1% Formvar solution and exposing it to the low humidity (about 15%) atmosphere of the cold room at -10°C . This caused the film to dry within 15 min. Large hexagonal evaporation pits developed subsequently after the film was dry. The evaporation pits were allowed to grow to about 0.5 mm in diameter. The plastic film was then removed by peeling and the surface recoated with a 2% solution, and the specimen placed in a box closed with an air-tight cover. This retarded the evaporation rate of the solvent and provided an opportunity for etch-pits to develop over the entire surface to the desired degree. The box was then opened and the solution allowed to dry quickly.

An optical photomicrograph of the large hexagonal evaporation pits and numerous minute dislocation etch-pits are shown in fig. 1 (a). A scanning electron micrograph of the same area is presented in fig. 1 (b). The distribution of etch-pits on the original microtomed surface (A) and at the bottom of the evaporation pit (B), about 60μ below the microtomed surface, are shown in figs. 1 (c) and 1 (d) respectively. The corresponding densities of dislocations, after correction for the tilt of the SEM stage, were found to be $4.04 \times 10^6\text{ cm}^{-2}$ and $3.37 \times 10^6\text{ cm}^{-2}$ respectively. Whether the difference in the two densities was due to inhomogeneity in the existing density or was introduced by the microtoming process was difficult to ascertain. The measurement indicates, however, that the process of microtoming did not appreciably affect the density of dislocations that originally existed in the ice crystal in non-basal planes.

Fig. 1

Fig. 1 (continued)

- (a) Optical micrograph of a replica of hexagonal evaporation etch-pits on basal plane.
 (b) Scanning electron micrograph of the same area as shown in (a). (c) Dislocation etch-pits on the original microtomed surface, marked (A) in (b).
 (d) Dislocation etch-pits at the bottom of evaporation pit, marked (B) in (b).

The above results compare well with the dislocation density of $6.5 \times 10^6 \text{ cm}^{-2}$ found by Muguruma (1961) at the bottom of large evaporation etch-pits in similar ice.

The success of microtoming depends upon the condition of the microtoming blade and the care with which the surface is prepared. Slight damage to the blade can cause the formation of rows of dislocations in the microtoming direction. The procedures used were found to be more critical for the preparation of prism surfaces for etching of basal plane dislocations.

4.2. Pits on basal plane

An example of etch-pits on the (0001) plane of a laboratory-grown large single crystal is shown in fig. 2. The replica was made at -10°C with a thick layer of 5% solution. The sizes of the pits vary from 20 to 100μ in diameter and the average density was determined to be $2.1 \times 10^4 \text{ cm}^{-2}$. Distribution of these pits was more or less homogeneous over the surface. Similar pits were also obtained for a large single crystal, about 8 cm in diameter and 40 cm long (obtained from a pond frozen under calm conditions) with a [0001] axis parallel to the growth direction. There was a noticeable difference, however, in the distribution of these pits in natural ice. The density of the pits varied greatly (10^4 to 10^5 cm^{-2}), with local concentrations around inclusions. Many sub-boundaries were also observed. The nature of pits in natural ice seemed to bear a close resemblance to that observed by Kuroiwa and Hamilton (1963) for pits on the surface of freshly frozen dendritic crystals. They used essentially the same process for preparing their pits.

It was felt that the foregoing conditions of etching would make visible only major defects having relatively large free energies. According to the principles stated earlier, it might be possible to successfully etch minor defects with free energy close to that of the free surface by using a more dilute solution

Fig. 2

Optical micrograph of a replica of large etch-pits on basal plane, made at -10°C with 5% Formvar solution under ambient conditions of the cold room.

Fig. 3

Two types of etch-pit on the same specimen used in fig. 2, but etched and replicated at -30°C with 3% Formvar solution under sub-saturated condition.

and carrying out the etching at lower temperatures. In order to test this hypothesis on the same specimens, the temperature of the cold room was decreased to -30°C over a period of 24 hours (to avoid excessive thermal stresses), and the corresponding surfaces were microtomed again. The etching-replicating process was repeated with a 3% solution under sub-saturated conditions. The results for the laboratory-grown single crystal are shown in fig. 3. Two distinct types of etch-pits are now visible. The majority of etch-pits were small, 1 to $4\text{ }\mu$ in diameter, with a pointed bottom. In addition, there were a number of large pits varying in diameter from 20 to $100\text{ }\mu$ which had some sub-structure (i.e. step-like features). The average density of these large pits was determined to be $2.0 \times 10^4\text{ cm}^{-2}$ in the laboratory-grown single crystal and was similar, therefore, to the density of the pits formed at the higher temperature. The density of the small pits, determined from a SEM micrograph, was found to be $3.2 \times 10^6\text{ cm}^{-2}$, of the same order as those given in § 4.1. Scanning electron micrography revealed (figs. 4 (a), (b)) that the large pits consisted of well-defined concentric as well as apparently spiralling steps of regular hexagonal, six-sided star and segmented shapes. The boundaries of these steps were observed to be parallel to $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions, thereby forming angles of 30, 60, 90, 120 and 150 degrees. Step heights were found to be less than $0.3\text{ }\mu$ in most cases. Pits with similar characteristics were also observed on natural ice surfaces.

A stepped layer formation at etch-pits was also observed by Truby (1955) in replicas of the (0001) surface of ice. Observations by Muguruma (1961) also indicate such stepped structures, which he thought developed at screw dislocations. From the reports of these investigators it was noticed that both replicated the surface at -20°C or lower and both used dilute solutions of 0.5 to 0.7% concentration consistent, therefore, with our observations on the action of the etchant on the ice surface. Repeating the experiments described

Stepped and spiralling sub-structures associated with large etch-pits of fig. 3: (a) showing concentric steps and spirals with irregular boundaries, (b) illustrates the symmetrical steps and star-shaped spirals.

in § 4.1 confirmed that both of these types of dislocations could be obtained at higher temperatures if the etching is carried out under enclosed conditions. Stepped structures were visible, but only at high magnification, otherwise the pits were indistinguishable as shown in figs. 1 (c), (d).

Comparison between the distribution of large pits in laboratory-grown and natural ice and the association of a stepped structure with these pits prompted the thought that the large pits correspond to grown-in dislocations and the small pits to dislocations introduced by post-freezing processes, and to thermal stress and mechanical loading during handling and storage. This possibility will be explored further in the next section.

4.3. *Glide direction of non-basal dislocations*

4.3.1. *General*

Deformation processes in ice are often explained on the basis of the mobility of glide dislocations in (0001) plane. Non-basal glide has also been shown to be possible and etch-tracks caused by the movement of non-basal dislocations have been formed on the basal plane. Gilra (1974) discussed this glide from the viewpoint of splitting of $\langle 11\bar{2}0 \rangle$ dislocations into $\langle 10\bar{1}0 \rangle$ partials in the basal plane. The present study was undertaken to determine more about the etch-tracks corresponding to this glide and explain their development.

It is known from investigations on metals (e.g. Gilman and Johnston 1957) that well-developed, point-bottomed etch-pits form at stationary dislocations, but flat-bottomed pits are formed if the dislocations move some time after the first application of the etchant. Grooves or tracks are expected to form if the dislocations move slowly during the etching process. Since the etchant is also used for making the replica in the case of ice, the conditions influencing the etching rate and drying time also determine the quality of the etch-tracks. Thus any explanation of the nature of etch-tracks in ice should take into account the factors governing this dual process of etching and replicating.

Observations were made first on the time required for the development of etch-pits under various conditions of solution concentration, humidity, temperature and thickness of the applied film. This was done by observing the surface with a high-resolution optical microscope during the etching process.

It was observed, for example, that 20 s were required to develop etch-pits of about 3μ diameter for a layer of 0.5% Formvar solution about 0.5 mm thick exposed directly to the cold room atmosphere at -10°C . The corresponding time was about 120 sec for a 5% solution. The former film dried in 10 min, whereas the latter took 2 hours.

If a moving dislocation is to result in a track 3μ wide under the action of the first etchant condition, then its speed must be about 3μ in 20 s, i.e. a velocity of 1.5×10^{-5} cm/s. Moreover, if it travels at constant velocity, then the travel path will be about 90μ in the 10 min drying time, neglecting the decrease in etching rate as the film dries. The corresponding velocity required for the 5% solution is 2.5×10^{-6} cm/s and the track length 180μ . The former velocity is a realistic velocity for basal plane dislocations under a resolved shear stress in the range of 0.2 to 0.5 kg/cm², and the latter corresponds to stresses in the range of 0.05 to 0.07 kg/cm² (Fukuda and Higashi 1973, Jones and Gilra 1973). The stress dependence of the velocities of non-basal dislocations

is not known, but the foregoing discussion indicates that the etching technique can be used only for studies of dislocation movements under low stresses. It also demonstrates that changing the concentration of the etchant from 0.5 to 5% corresponds to a decrease of about one order of magnitude in capability of detecting moving dislocations.

Further generalizations can be made from the above observation. The higher the stress, the narrower the track for a given etching process. If the stress is sufficiently large there will be no track. The tracks will be tapered if the velocity changes during the etching process. The tracks may be tapered if the etching action decreases, owing to the drying of the film. If a dislocation moves during a portion of the etching time and then stops, the track will end in a well-developed etch-pit. If the dislocation starts moving from a stationary position, then the track will have a flat-bottomed pit at the starting-point. Thus the characteristics of the tracks can provide information on the nature of the movements.

4.3.2. *Etch-tracks under non-uniform stress field*

Examples of etch-tracks in a specimen under non-uniform stress are given in fig. 5. These etch-patterns were developed when one side of the glass plate holding the specimen was kept in a slightly bent position during the etching process. All the tracks were observed to be tapered. Clear areas were produced by the movement of dislocations too rapid to leave any visible tracks. The visible tracks were found to be along $\langle 10\bar{1}0 \rangle$ as in fig. 5 (c) or along $\langle 11\bar{2}0 \rangle$

Fig. 5

(a)

(b)

Fig. 5 (*continued*)

Scanning electron micrograph (*a*) and optical micrograph (*b*), exhibiting etched tracks caused under non-uniform stress field. Scanning electron micrography show the running directions to be $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ respectively in (*c*) and (*d*).

as in fig. 5 (*d*), indicating the predominant slip directions. Serrated tracks were also observed, which could indicate the presence of obstacles in the path of the dislocations.

4.3.3. *Etch-tracks under uniform stress field*

In another experiment, the specimen was subjected to a uniform thermal stress. The specimen chosen was the laboratory-grown single crystal thick section that had been etched earlier. Prior to the reapplication of the etchant, the surface was remicrotomed at -10°C and the edges of the specimen were frozen uniformly to a glass plate, taking care to allow no water between the glass and the bottom surface of ice. The specimen was transferred quickly to a chamber kept at -30°C and the surface was coated immediately with an etchant. The thermal stress generated in the specimen could be estimated using thermoelastic stress theory and the boundary condition of constraint at the edges (Johns 1965, Carslaw and Jaeger 1959). The transient stress was large in the early period, but disappeared gradually, owing to removal of the thermal gradient as the specimen attained the temperature of the chamber. Thus the major stress in the later part of the etching process was due to the edge constraint and the differential thermal expansion of glass and ice. It is expected to decrease with time, owing to the relaxation processes associated with the dislocation movements. The drying time for the film was about 30 hours in this case. An earlier study by the author, of the stress relaxation processes in ice, indicated that the stress remaining after this period would be negligible if not zero. Thus the tracks would develop only during the later part of the etching process and it is conceivable that many dislocations would have stopped before the end of the process, forming stable etch-pits. Any

dislocations that did not move during the entire process would produce large pits. In this way, grown-in dislocations could also be identified, because these defects are not expected to move (see Gilman and Johnston (1957) for experiments on LiF).

Figure 6 shows a small area that was typical of the replica obtained from this experiment. The 3μ wide uniform track was found to be more than 1200μ in total length. The direction of the track was found to be mostly parallel to the $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions, but certain sections indicated directions parallel to the bisectrics and trisectrics of the angle between the $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions. The presence of the track appears to block the passage of other dislocations, or new dislocations were generated during its formation. This is indicated by a series of point-bottomed intermediate size ($2\text{--}5\mu$) etch-pits adjacent to the track. There is a uniform distribution of smaller pits of less than 1.5μ in diameter. These pits could have been produced by the stoppage of the rapidly moving dislocations near the end of the etching process. The density of these pits was found to be $3.8 \times 10^6 \text{ cm}^{-2}$, which agrees with the density of dislocations in the crystal before the application of thermal stress. The large pits of 50 to 100μ size appeared to be stationary during the entire process and thereby developed to large dimensions. The average density of these pits was found to be $2.0 \times 10^4 \text{ cm}^{-2}$, which is close to

Fig. 6

Optical micrograph of a long and uniform etch-track, large asymmetric etch-pits, and minute etch-pits.

the density of the large pits with a stepped structure found earlier in this crystal. This supports the hypothesis that they are grown-in dislocations. The large pits in fig. 6 were not symmetric. Since the surface was cut parallel to the basal plane within an error of a few degrees, the asymmetry was too great to be explained by the tilt of the basal to the sectional surface. The non-symmetric characteristics of these pits can, however, be explained by the tilt of the grown-in dislocation lines with the $\langle 0001 \rangle$ axis as shown in fig. 7.

The influence of large pits and the condition of the surface on the movement of dislocations is indicated in fig. 8 (a). The track directions on the left-hand side of the photograph are all parallel to $\langle 11\bar{2}0 \rangle$ directions, thereby forming semi-hexagonal patterns around a large pit. The width in the track appears to be wider where the tracks are parallel to $\langle 10\bar{1}0 \rangle$ directions, on the right-hand side of the photograph. The apparent increase in track width was found by scanning electron microscopy to be due to the formation of minute etch-pits on both sides of the tracks (fig. 8 (b)).

Fig. 7

Schematic diagram of symmetrical and asymmetric etch-pits depending upon the tilt of the surface or dislocation lines with respect to the c -axis and the a -axes.

Fig. 8

- (a) Surface conditions influence the movement of dislocations as seen in the left near a large pit. The width of the tracks on the left, parallel to $\langle 11\bar{2}0 \rangle$ directions, appear to be narrower than on the right, parallel to $\langle 10\bar{1}0 \rangle$. (b) The change in width of the track, seen in (a), is due to the formation of large number of small pits around the track, as shown by SEM.

4.4. Size of etch-pits

The energy change associated with the mechanical balance between the line tension of a dislocation and the tension at the surface is responsible for the differential dissolution at the intersection of the line defects with the surface. The dissolution at these junctions proceeds both along the line defects and parallel to the surface because of the strain field of dislocations, until equilibrium is achieved. The boundary of an etch-pit on the surface therefore, would extend a maximum distance determined by the strain field at the dislocation end of neighbouring dislocations. The dislocation density, therefore, should determine the maximum size of an etch-pit.

The maximum size of the etch-pits could be calculated from the average dislocation density. If d is the average density expressed in cm^{-2} , then the average area per dislocation will be given by $1/d$. This area would be equivalent to a circular area of radius

$$R = (1/\pi d)^{1/2} \text{ cm.} \quad (1)$$

Equation (1) can be used to calculate the approximate maximum size of etch-pits for both grown-in and other dislocations. For a density of $2 \times 10^4 \text{ cm}^{-2}$ for grown-in dislocations mentioned earlier, eqn. (1) gives a maximum diameter of about 80μ . Kuroiwa and Hamilton (1963) reported a density of etch-pits of $2 \times 10^5 \text{ cm}^{-2}$. Equation (1) gives an average diameter of 25μ for this density, which agrees with the size seen in their photograph. Both our observations and those of Muguruma (1961) showed that the density of other

dislocations was in the range of 10^6 cm^{-2} . The diameter of the etch-pits, as calculated from eqn. (1), are 11μ and 5μ respectively for densities of $1 \times 10^6 \text{ cm}^{-2}$ and $5 \times 10^6 \text{ cm}^{-2}$, which again agrees with the respective experimental observations.

4.5. Direct evidence of correspondence of etch-pits to dislocations

If the conditions of etching are such that the dissolution can continue into the crystal along the dislocation lines, then, if the energy of the dislocation core is neglected, the radius r of the etched capillary is given by

$$2\pi r\gamma = Kb^2 \ln(R/r_0) \quad (2)$$

where γ is the surface free energy of ice with respect to the etchant. The right-hand side is the elastic energy stored per unit length of the dislocation line assuming linear elasticity, where b is the Burgers vector, R is the outer extent of the strain field given by eqn. (1), r_0 is an inner cut-off radius inside which the approximation of linear elasticity theory does not apply, and K is a function of the elastic constants, orientation of the dislocation line, and the Burgers vector.

Teutonico (1970) has shown that K may be computed analytically for dislocations in crystals belonging to the hexagonal system. Tyson (1971) has calculated the elastic strain energies of dislocations in Ih ice (ordinary ice) on the basis of Teutonico's formulas.

Using the following values in eqn. (2),

$$Kb^2 = 9.85 \times 10^{-5} \text{ ergs/cm at } 0^\circ\text{C; Tyson (1971),}$$

$$b = 4.523 \times 10^{-8} \text{ cm,}$$

$$r_0 = 5b = 22.615 \times 10^{-8}; \text{ assumption (Weertman and Weertman 1964),}$$

$$R = 5.64 \times 10^{-4} \text{ cm for a dislocation density of } 1 \times 10^6; \text{ eqn. (1)}$$

$$\gamma = 20 \text{ ergs/cm}^2 \text{ (assumption),}$$

the diameter, $2r$, is computed to be 0.12μ .

The strain energy of dislocations and the value of K increase slightly with a decrease of temperature and the value chosen for r_0 also slightly influences the result, but the greatest uncertainty in the preceding calculation is the assumed value of the surface free energy of ice with respect to the etchant. The value used corresponds to that of ice with respect to water in the temperature range of -30°C to -40°C .

Equation (2) indicates that capillaries of measurable size could be developed under appropriate etching conditions. These conditions include as low a value of surface free energy as possible, and an etchant of sufficient fluidity to penetrate the capillaries produced by the dissolution. Experiments indicated that the conditions could be satisfied by the Formvar solution at low temperatures.

Figure 9(a) shows a general view of whiskers on a replica of the (0001) plane of laboratory-grown ice. The length of the whiskers was 60 to 70μ and the diameter, as shown in the SEM micrograph, was about 0.25μ . A separate measurement of the thickness of the coatings of carbon and gold, following

Fig. 9

(a) Non-basal dislocation whiskers in ice revealed by the scanning electron micrograph.
 (b) Pyramidal hexagonal etch-pits on a (0001) plane with whiskers representing the dislocation lines.

the same procedures of vacuum deposition, indicated that they were 350 and 250 Å respectively, giving a total thickness of coating of 600 Å. The correction to the observed diameter was 1200 Å or $0.12\ \mu$, assuming the whiskers were coated uniformly, which may not be true. The corrected diameter of the whiskers was $0.13\ \mu$, which agrees well with the value calculated from eqn. (2). Isolated etch-pits with small whiskers are shown in fig. 9 (b) and clearly show the relationship of the whiskers to the base of etch-pits on a (0001) plane. These observations directly correlated the etch-pits to the line defects in a three-dimensional sense more strongly than achieved earlier in any material. (See, however, Dash (1957) on his technique of decorating dislocations in silicon.)

4.6. Observations of basal plane dislocations

Tyson (1971) computed the elastic strain energies of dislocations for basal and non-basal planes, and showed that they are the same. This means that the whiskers' diameter for basal plane dislocations will be the same as for non-basal dislocations provided the surface free energies do not differ appreciably between the basal and the prismatic surfaces.

Figure 10 (a) shows whiskers produced at the bottom and side surfaces of an evaporation etch-pit on a (0001) plane. The schematic in fig. 10 (b) shows their relationship to the crystallographic orientation. It shows that both basal and non-basal dislocations can be replicated simultaneously for the same crystal of ice. The whisker diameters for both basal and non-basal

Fig. 10

(a) Scanning electron micrograph of whiskers corresponding to basal and non-basal dislocations. Whiskers in the horizontal direction are related to the basal dislocations. (b) Schematic diagram of the formation of whiskers at the bottom and side surfaces of an evaporation etch-pit on a (0001) plane.

dislocations were found to be about the same, indicating that the ice etchant interface free energies $\gamma_{(0001)}$ and $\gamma_{(1010)}$ might not differ significantly. Thus it confirms indirectly a similar conclusion arrived at by Fletcher (1975) for free energies at the ice—water interface.

An example of a replica of a forest of glide dislocations intersecting the $\{11\bar{2}0\}$ surface is shown in fig. 11 (a). The whiskers were found to be as long as 30 to 40 μ and the diameters about 0.14 μ . Figure 10 (b) shows the relationship between elongated etch-pits formed on the $\{10\bar{1}0\}$ surface and the whiskers. The replica in this case was purposely peeled off to break the whiskers so that their base could be seen more clearly.

This method of etching and obtaining replicas of glide dislocations responsible for the basal slip in ice has provided a number of possibilities for further investigation of deformation processes in ice. The technique has been applied successfully to study simultaneous basal and non-basal glide in polycrystalline ice, the effect of strain rate on microcrystalline deformation, the development of glide dislocations and pile-ups, and other deformation features. This work is to be reported in future publications.

Fig. 11

(a) Forest of basal-plane dislocations represented by the corresponding whiskers on a $\{11\bar{2}0\}$ surface. (b) Broken whiskers on a $\{10\bar{1}0\}$ surface showing the elongated pits parallel to $[0001]$ at their bases.

§ 5. CONCLUSIONS

It was well established that the dual process of etching and replicating ice surfaces with solutions of Formvar in ethylene dichloride could be improved and made more selective by controlling concentration, temperature, thickness of the film applied, and the vapour pressure of the environment. Careful microtoming was found to produce a surface condition suitable for etching and replicating dislocations. By appropriate choice of conditions, etching can be made to occur not only at the point of emergence of dislocations on the surface, but also into the crystal along the line imperfections, resulting in replicas in the form of whiskers of uniform diameter. Both non-basal and basal dislocations can be etched in this way. The technique has removed the ambiguity sometimes associated with the correspondence of etch-pits to dislocations. A relationship developed for the diameter of the etched dislocation strain cores gave values in agreement with the observed values. The ability to replicate whiskers corresponding to the dislocation lines opens up many possibilities for the application of the method to the study of deformation processes in ice.

Grown-in dislocations amongst other non-basal dislocations can be identified by the proper choice of etching conditions. Grown-in dislocations were found to have marked concentric and spiralling step features. Tracks caused by the movement of dislocations during etching are tapered for a non-uniform stress field and non-tapered when the stress was uniform. Because of the time to form measurable etch-pits and tracks, the etching technique can be used for the study of dislocation movements only for low stresses. The predominant direction of glide for non-basal dislocations was found to be along $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$. The movement of non-basal dislocations leaves a trail of new non-basal dislocations, point defects, or the etch-track is a barrier to the movement

of other dislocations. A simple relationship between the density of dislocations and the maximum size of the etch-pits is in agreement with experimental observations.

ACKNOWLEDGMENTS

The author gratefully acknowledges many helpful discussions with and the advice of Dr. L. W. Gold in the preparation of this paper, and the expert assistance of E. G. Quinn who prepared all the scanning electron micrographs. This paper is a contribution from the Division of Building Research of the National Research Council of Canada and is published with the approval of the Director of the Division.

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