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Etch Pits on Prism Planes of Plastically Deformed Ice Crystals

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Applying chemical etching technique to ice crystals, the nature of dislocation etch pits on prism planes of the crystals was investigated by comparing plastically deformed and undeformed samples of natural single crystals. Appearance of dislocation etch pits caused by applied stress was interpreted as a result of mechanical polygonization which means the formation of small angle boundary segments. It was found that no thermally activated polygonization took place under the condition of 24 hours aging at $-15°C$. Pits at a small angle boundary appeared as a row of indiscrete pits. This makes it difficult to calculate the misfit angle by Burgers equation making use of the separation of the pits from one another. Microslip lines in ice crystals were revealed for the first time and their wavy shape suggests the occurrence of cross slips. Microstructure of slip bands was also clarified by the densely lined up trigonal etch pits on lines between which separation is about 10 μ.

1. Introduction

It is believed etch pits on a well finished crystal surface are formed at the points of emergence of dislocations. Such a correspondence of etch pits and dislocations in ice crystals was first ascertained by the present author[1,2] in observing with electron microscope the minute etch pits procuced on a mirror finished smooth (0001) plane. Though it was thought at the time of that investigation that the etching process of the formation of minute pits was thermal, it has been made clear by KUROIWA and HAMILTON[3] that the process is chemical. Ethylendichloride is a good etchant of which the action is decelerated by the mixing of Formvar. Replicas for electron- or optical microscope observation are produced with this Formvar.

This technique of producing etch pits in conjunction with electron- or optical microscope observation was used to reveal the nature of dislocations in ice crystals. Observation of etch channels on the (0001) plane of ice crystals produced by nonbasal glides has been described in a separate paper[4]. One reason that the observation on the (0001) plane has advanced more rapidly than on the other crystallographic planes lies in the fact that etch pits on the other planes were not so clear and sharp as those on the (0001) plane. Generally, chemical etching technique used in metallic or non metallic crystals suffer the disadvantage that the etchant works only on those surfaces nearly parallel to certain crystallographic planes of high atomic density. Though the etchant used in the present study produces etch pits on any surface of arbitrary crystallographic orientation, there is a tendency for the pits on crystallographic planes of low atomic density do not to appear clearly.

However, the technique of producing better etch pits on prism planes of ice crystal is in the way of improvement and some interesting results have been obtained through electron microscope observations on the deformed and undeformed ice crystals. This paper describes the nature of etch pits thus observed and its interpretation in terms of dislocations in crystals. Small angle boundary and slip traces which are caused to appear by plastic deformation were also observed and described in this paper.

2. Experimental Procedure

Ice samples were cut from large natural single crystals which were brought from the Mendenhall Glacier, Alaska. The goodness of qualities was described in HIGASHI and SAKAI's[5] paper. Preparation of specimens with reference to the crystallographic axis was done by the method described in the same paper. Deformations were mainly made with three points bending at a constant load of 4 kg. The bending axis was taken parallel to the basal plane so as to give basal glide. Some tensile tests were made in order to reveal slip traces. Temperature at which the deformation was performed was about $-8°C$.

After completion of a certain amount of deformation, large thermal etch pits were produced on the surface of the crystals by the method of coating the surface with plastic film[6]. Since the procedure took about 24 hours at $-15°C$, aging effect in this interval between bending and succeeding chemical etching must be noted. This procedure was to obtain very smooth prism planes only where the etch pits corresponding to dislocations were observable. After the plastic film was removed, the ice surface was again coated with a solution of Formval in ethylenedichloride. Dissolution through the etchant of ethylenedichloride took place during the drying time of the solution within approximately a few minutes. Etching rate could be controlled roughly by changing the thickness of coating of Formvar solution with which the ice surface was coated. Etch pits thus produced on the smooth prism plane of ice crystal were reproduced in a replica film formed according to drying of this solution. After the film had dried completely, the ice specimen was melted in water. The replica film floating on water surface was scooped up and the usual procedures of mounting replicas for electron microscope observation were followed.

3. Results of Observation

a) Density of etch pits

The distribution of etch pits on a prism plane had the same nature as that on the basal plane; that is, etch pits appear separately at the bottom of a large thermal etch pit whereas they do overlap on the surface around it. The density of etch pits of undeformed crystal at the bottom area was of the order of $10^5/cm^2$ which was the same order of magnitude as that on the basal plane[4]. Though such an overlapping made it difficult to meassure the density of distribution, values of about 10^6–$10^7/cm^2$ which was obtained for the basal plane would be resonable in the area outside of large etch pits.

Mechanical polishing of the crystal surface before thermal etch pits were made have generated many dislocations in the surface layer. Large thermal etch pits of the depth of about 100 μ are considered to penetrate this layer of surface irregularity. Therefore, individual etch pits on the bottom plane of a large thermal pit are considered to correspond to as-grown dislocations emerging to the plane from the interior of the crystal.

b) Shape of etch pits

The shapes of large thermal etch pits with respect to various planes of the ice crystal were studied by HIGUCHI[6] and found to be useful as a simple method of determining the orientation of the a-axes as well as of the c-axis. Thermal etch pits appearing on either $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ surfaces have rectangular shape with three prism planes on the former and with two prism planes on the latter. When etching proceeds, the planes inside the pits become no more distinguishable, and only the plane left at the bottom of thermal etch pit is distinguishable.

Chemical etch pits produced on each surface described above also have the same rectangular shape as that of a thermal pit described above. Etch pits on $\{11\bar{2}0\}$ planes should comprise two prism planes; this feature is shown in Fig. 1. It should be noticed that pyramidal planes appear at both upper and lower ends of the pits. Pyramidal planes which appear on the pits in Fig. 1 were roughly estimated to be $\{11\bar{2}2\}$ planes which were considered to operate as one of nonbasal glide planes[3].

It was found, however, that most of the etch pits which appeared on prism planes had a spindle shape with an apex as is shown in Fig. 2. The fact that every pit has an apex is another evidence that the pits can be considered to correspond to dislocations which are emerging from the interior of the ice crystal. Etch pits of spindle shap on the surface on $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ prism

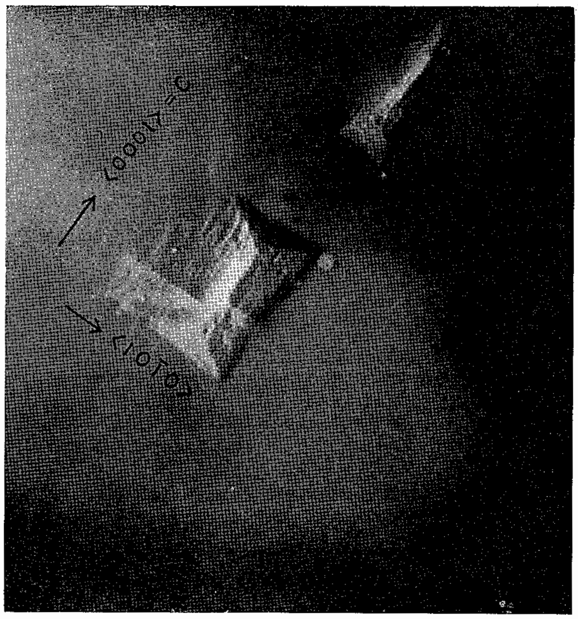

Fig. 1. Etch pits on (11$\bar{2}$0) plane on ice crystal. Comprising two prism planes are visible as well as two pyramidal planes. Electron photomicrograph.

Fig. 2. Etch pits of spindle shape on a prism plane of ice crystal. Electron photomicrograph.

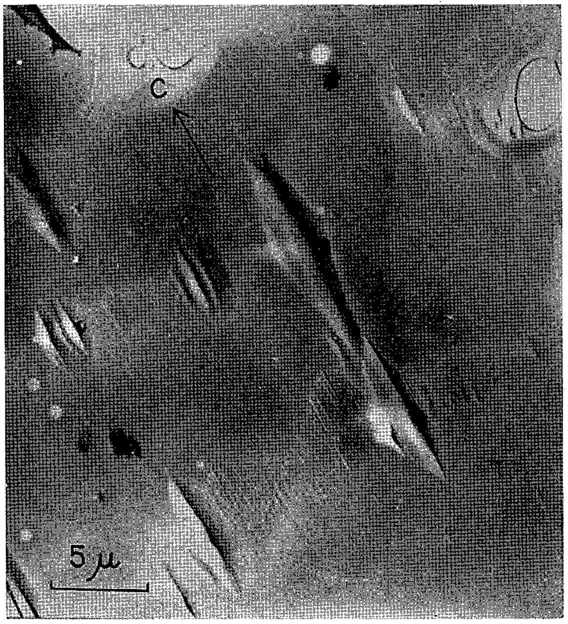

Fig. 3. Elongated spindle shape of etch pits on a prism plane caused by deformation of ice crystal. Notice that dislocations pile up on the basal plane. Electron photomicrograph.

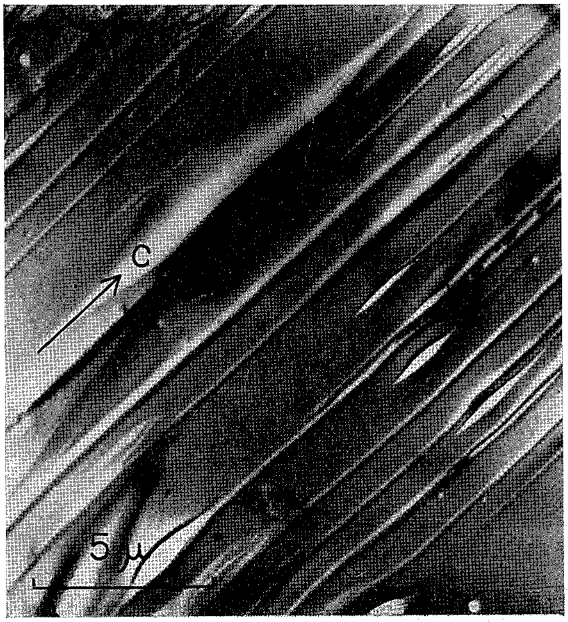

Fig. 4. Further developed stage of spindle shape of etch pits with strong deformation. Electron photomicrograph.

planes were quite similar in shape, so that the plane on which the pits were formed was hard to identify. Dislocations responsible for the formation of pits on prism planes should be lying on the basal plane and should play a role in basal slip.

c) Change of the shape of etch pits due to plastic deformation

When the crystal was deformed, the spindle shape of etch pits became elongated along the directions of ⟨0001⟩ as is shown in Fig. 3. Some of them had a Y-shape end as can be seen at the center of Fig. 3. Fig. 4 shows a further developed stage of the spindle with strong deformation. SINHA and BECK[7] observed such rows of elongated etch pits on the $(0\bar{1}10)$ face of Zn crystal as similar to those in Fig. 4 and concluded that they were resulted from mechanical polygonization. Therefore, it can be concluded that the elongated

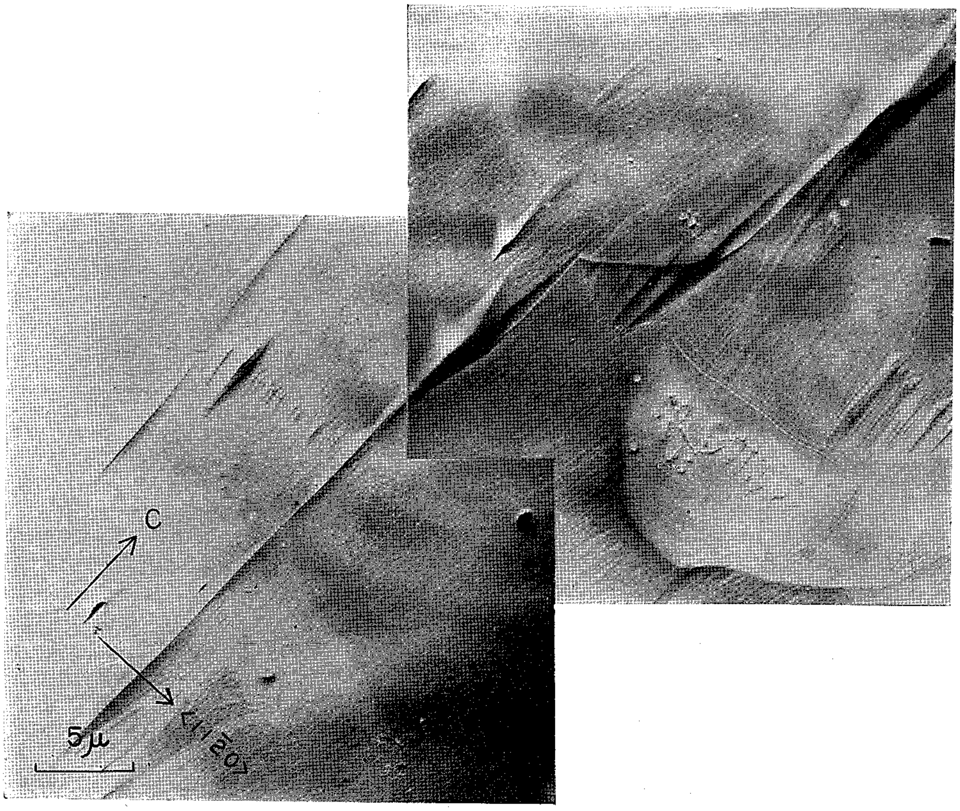

Fig. 5. Arrangement of etch pits on a prism plane along a small angle boundary. Notice a row of elongated etch pits in center is shifting and also the pile up of dislocations on the basal plane. Electron photomicrograph.

pits consist of many undistinguishable pits which are lying in rows. Mechanical polygonization mechanism as an interpretation of this feature of elongated etch pits in ice crystals will be presented later under discussion. Stress dependence of density of etch pits was hard to obtain because of the indiscreteness on elongated pits as described. It should be noted that there can be seen in Figs. 3 and 5 several short rows of etch pits in the direction perpendicular to c-axis which seem to be a dislocation pile up.

d) Dispositions of etch pits along the small angle boundary

Small angle boundaries in the ice crystal are formed at the points of supporting and loading wedges in the present bending experiment. Formation and increase in number of the boundaries at such bending experiments were first investigated by NAKAYA[8] with his beautiful shadow photomicrographs. Detailed study of the stress induced movement of small angle boundary was carried out by HIGASHI and SAKAI[5], with an interpretation of activation energy of the movement in terms of dislocations. In their paper, it was implicitly accepted, without any direct proof, that the boundary was constructed in accordance with BURGERS model[9]. It is expected that a small angle boundary in ice crystal should be constructed of a row of edge dislocations just as in the other kinds of crystals. If so, this row of dislocations should appear as a row of discrete etch pits on a plane which is perpendicular to the boundary. Observation of etch pits on the prism plane along a small angle boundary was carried out to test this expectation. Specimens for observation were prepared in such a way that the direction of length coincides with a-axis of the crystal. In this way, dislocations on the small angle boundary must lie normal to the Burgers vector $\frac{1}{2}\langle 11\bar{2}0\rangle$ in basal glide with the result that the dislocations are pure edge. The electron photomicrograph of Fig. 5 shows the arrangement of etch pits at a small angle boundary. Since there appears a tendency of elongation of pits as noted above, it is hard to identify a row of separated each pits corresponding with each of the dislocations on the boundary. Attention should be directed to the fact that in this photograph the row of pits does not lie on a straight line but it shifts from one line to another at several places but keepes continuously directed to $\langle 0001\rangle$. This suggests the existence of climb motion of dislocations. Pile up of dislocations also can be seen clearly near the small angle boundary in Fig. 5. Fig. 6 shows another photomicrograph of etch pits at the boundary of which the angle of misfit between the two sides is unknown. In this cases, etching proceeded further than in the previous case, with the results that the shape of pits had become indeterminate. However, it was

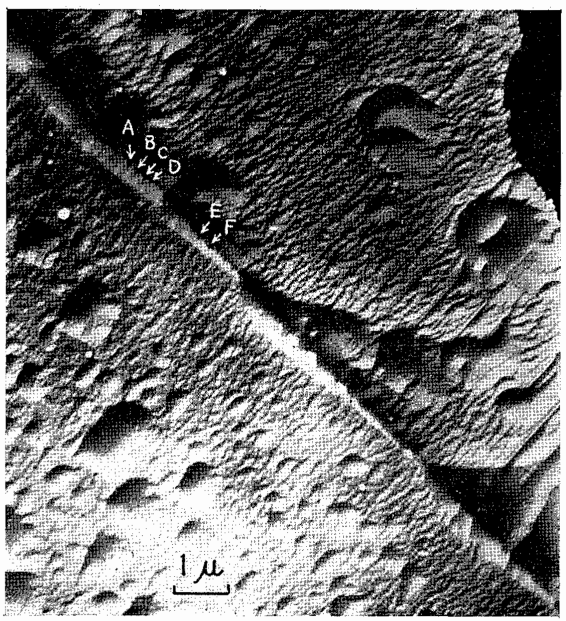

Fig. 6. A row of etch pits at a small angle boundary. Despite of overlapping, each dislocation can be distinguished with its apex as designated by A to F. Electron photomicrograph.

found that several apices of the pits are distinguishable on the photograph as designated A∼F in Fig. 6. Calculation of misfit angle θ was carried out through an approximate equation $D=\frac{b}{\theta}$ among the mean distance between dislocations D, Burgers vector b and θ. Adopting the mean distance between adjacent etch pits from A to F as the value of D, the angle of misfit at the small angle boundary was roughly estimated as 7 minutes.

e) Appearence of slip lines and etch pits

Slip lines are the visible markings on the surface of a crystal appearing as intersections of slip planes formed at deformation. Though it has been expected that also in ice crystals slip lines should appear on the surface perpendicular to the basal plane, there has been only one proof of their existence by NAKAYA[8]. However, lines parallel to the basal plane appearing in his shadow photomicrographs were rather broad; they seem to be considered as slip bands individuals of which are a several stackings of slip planes. Therefore, more precise study of slip lines about ice crystals as in the case of metals is awaited.

Using the technique described above, a first electron microscope observation on such microstructures of slip lines of deformed ice crystal was conducted in this study. Deformation was given in tension in such an arrangement that the tensile axis made a 45 degree angle with the c-axis of the ice specimen. Formation of replica films for electron microscope observation which caused etching at the beginning of coating was conducted under application of stress for a few minutes. In this case, the process of making large thermal etch pits was omitted. In the case of the specimen in Fig. 7, etching was so controlled that no clear shape of individual etch pits was produced. In this way, the slip lines were well revealed and it is evident that fine slip lines with the spacing of 0.1–0.5 μ exist among the well developed clear slip lines of which the spacing is about 10 μ. Every line has slightly wavy form and breaks which both suggest the occurrence of frequent cross slips. Since such cross slips from one basal plane to another require nonbasal slips, this photograph may be considered as presenting evidence of the existence of nonbasal slip systems such as were reported in a separate paper[4].

Another electron photomicrograph of a surface on which the etching was developed to reveal individual pits is shown in Fig. 8. Since the surface of

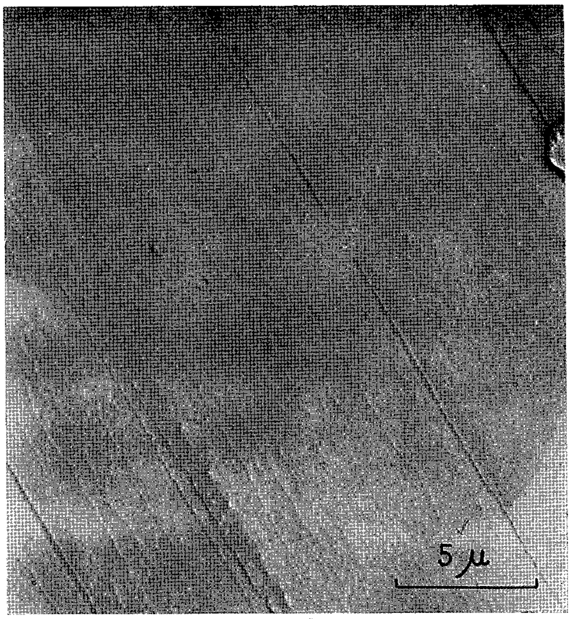

Fig. 7. Slip lines appeared on a plane making 45 degrees to the basal plane, as a result of tension in a direction perpendicular to the observed surface. Electron photomicrograph of not well developed etch pits. Notice slip bands separated about 10 μ among which many micro-slip lines are visible.

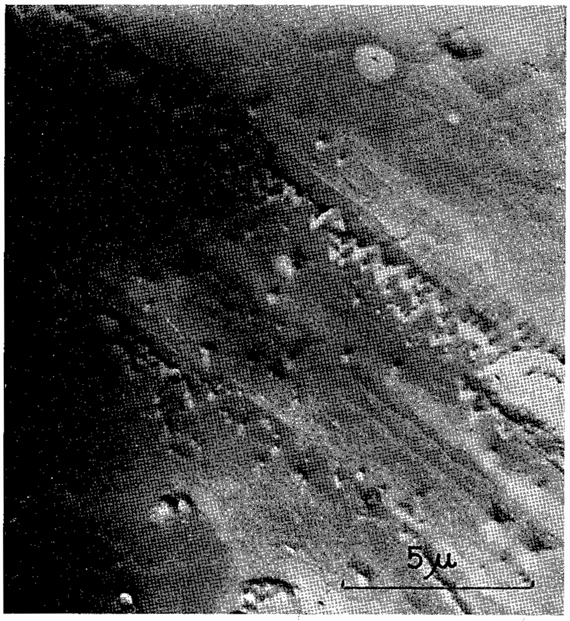

Fig. 8. Well developed trigonal etch pits along a slip band. Electron photomicrograph.

observation was at an angle of 45 degrees to the basal plane, trigonal etch pits are observed as expected from HIGUCHI's treatment[1]. Scattered etch pits along a slip plane at the top and wavy trails in the middle clearly show the microstructure of slip lines which is characterized by back and forth cross slips. A band of dense distribution of etch pits at the top in this figure may be considered a slip band in which many slip planes are stacked in layers. It is clear from Fig. 7 that such slip bands run parallel with spacings of about 10 μ. Therefore, slip lines observed under optical microscope by WAKAHAMA[10] must be these slip bands. Electron microscope observations have now revealed microslip lines with the spacing of 0.5 μ; this finding must be considered an important item of additional information for understanding dislocation structures in ice crystals.

4. Discussion

A semi-quantitative treatment is presented in order to verify the mechanical polygonization mechanism as an interpretation of the feature of elongated etch pits described in the preceding section. If thermally activated pologonization takes place, boundary separation must increase with time and temperature of annealing as was the case in Zn crystals in SINHA and BECK's[7] experiments.

It will be now shown that the separation of about 1 μ between each elongated etch pits in Fig. 4 is not resulted from thermal polygonization process during 24 hours at $-15°C$ but preserved from the time of generation of such segments of small angle boundaries. That is to say, it will be proved that the separation of 1 μ is the minimum separation which can be made under the conditions of present experiments of bending.

For this purpose, total length is calculated over which some number of dislocations generated from a source piles up against a barrier as such a segment of small angle boundary. This length must be the minimum distance along which dislocations can move on the basal plane without encountering any barrier. The total length L over which n dislocations are piling up on a slip plane is approximately given by the following equation[11]

$$L=\frac{Gbn}{\pi\sigma}$$

where G is shear modulus, b Burgers vector and σ applied stress. The maximum shear stress on the basal plane is calculated 20 kg/cm$^2 \fallingdotseq 2\times10^7$ dynes/cm^2 for the present experiment and this value is taken as that of σ in this equation. In addition, it is taken in the above equation that $G=3\times10^{10}$ dyne/cm^2, $b=4.5\times10^{-8}$ cm, $n=10$. Then one finds that $L=2\times10^{-4}$ cm. This value coincides well with the observed separation 1 μ within a factor of two. Therefore, it could be concluded that the observed separation is the minimum which can be produced by mechanical polygonization and no thermally activated polygonization takes place in 24 hours at $-15°C$.

This conclusion will lead to an important speculation that the temperature below about $-15°C$ is already sufficiently low to motivate every atomistic process in the ice crystal though the temperature itself is still near to the melting point of ice. This speculation seems to be supported by relatively the high recrystallization temperature, creep velocity etc.

5. Summary

(1) A great deal of difference of density of etch pits between that at the bottom of large thermal etch pits and that at the surface around it was recognized on the prism plane of ice crystal as well as on the basal plane. This gives evidence of the correspondence between minute etch pits at the bottom of large thermal etch pits at prism planes and dislocations in the ice crystal by the same reasoning as in the case of basal plane reported previously[2].

(2) Rectangular etch pits which appeared on prism planes were not considered to be caused by dislocations. Dislocation etch pits have a spindle

shape with an apex on each. This is another proof of the correspondence stated above. Spindles become longer and more slender with increasing applied stress. Continuous etch pits produced by the formation of connections between these long spindles were interpreted as a result of mechanical polygonization. The fact that the mechanical polygonization predominates over the thermal polygonization at temperature about $-15°C$ was concluded by a simple calculation of the minimum separation of polygon boundaries.

(3) A row of indiscrete pits appeared at a small angle boundary which was produced by applied stress. This is also understood as a result of elongation of each spindle which overlaps at the boundary.

(4) Microslip lines with the spacing of $0.5\,\mu$ between each two were found. Their wavy forms suggest occurrence of frequent cross slip on the basal slip. Concentrated etch pits along lines among which the separation is about $10\,\mu$ are considered as a slip band which can be found by optical microscope.

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