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Thermal Etching and Whisker Growth on Sodium Chloride Single Crystals

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When freshly cleaved faces of single crystals of sodium chloride are thermally etched at 750 °C in air, circular etch pits, indicating the sites of dislocations, are produced. Some correspondence in thermal etch patterns on matched cleavage faces has been established. When the crystal cleavages are heated between 765° and 785 °C etching and growth proceed simultaneously on the same crystal face. The etching produces the pits while the growth produces whiskers. The whiskers in some cases extend up to 4 mm in length. They are of nearly rectangular parallelopiped shapes, their tops being perfect squares. Phase-contrast microscopy has revealed rectangular growth spirals on the whisker tops. When these whiskers are etched, a deep circular pit on the top of each whisker is produced. The implications are discussed.

Introduction

When crystals are heated to a temperature very near to their melting points, in a suitable atmosphere, thermal etch pits are formed due to evaporation. Cabrera & Levine (1956) have given a dislocation theory of evaporation for crystals. Hirth & Vassamillet (1958) have reported a correlation between dislocations and the thermal etch pits for silver single crystals. Thermal etching of dislocations has also been described by Suzuki (1957). Bethge & Schmidt (1959) and Bethge & Keller (1960) have produced etch spirals on sodium chloride by thermal etching. Deo & Sharma (1964) have described dislocation motions in sodium chloride obtained by thermal etching. Turchanyi & Horvath (1960) have reported evaporation figures and Mendelson (1961) has also described dislocation etch pits on sodium chloride. Although a considerable amount of work has been reported on the thermal etching of metal crystals, not much detailed information is available with regard to the thermal etching of non-metallic crystals. In present work we have made a systematic study of the thermal etch patterns produced on the cleavage faces of sodium chloride single crystals.

Experimental

Freshly cleaved sections of sodium chloride were heated on a platinum lid. The thermal etch patterns produced were studied optically. Studies were made on (i) thermal etch patterns produced on isolated cleavages, (ii) thermal etch patterns produced by successively heating the same cleavage for different periods, (iii) thermal etch patterns produced on matched cleavage faces, (iv) comparision of thermal etch patterns with chemical etch patterns and (v) growth of whiskers from the vapour of sodium chloride on the parent crystal.

Thermal etch pattern on isolated cleavages

Fig. 1(*a*) represents the thermal etch pattern produced on a sodium chloride cleavage by heating at 750 °C for 2½ hours. To compare this with the etch pattern produced by chemical etching, a freshly cleaved sodium chloride cleavage was etched in a mixture of glacial acetic acid and methyl alcohol (proportion 2:1) for 25 seconds. Fig. 1(*b*) represents the etch pattern produced. Attention is drawn to the following:

(1) Both etch patterns show point-bottomed and flat-bottomed pits.

(2) The chemical etch pits are square, the thermal pits circular.

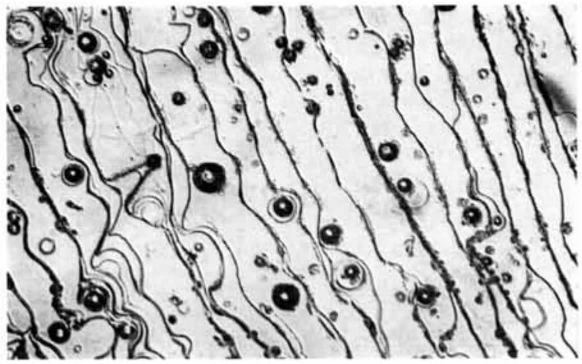
(3) The square pits are more or less of uniform size but there is a wider size range in the circular pits.

(4) The black lines in Fig. 1(*a*) are the edges of layers receding on the surface from the edges of the crystal owing to evaporation of the material.

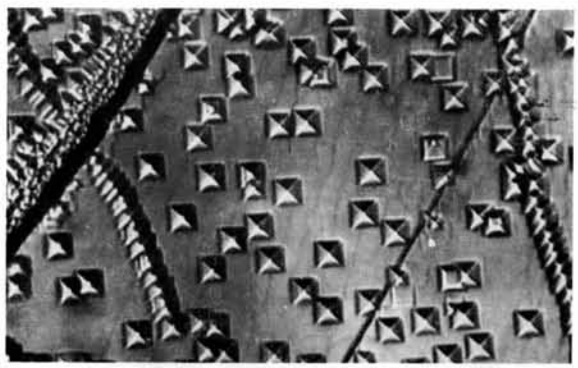
(5) In both the patterns, the point-bottomed pits are not always symmetrical.

(6) The density of square pits exceeds that of circular pits.

(7) In thermal etching, it appears that evaporation is more pronounced at the edges of the layers on the crystal face than at the sites of the dislocations. Because of this the cleavage lines on the crystal face are rapidly destroyed, and moreover from the four edges of the crystal new layer-lines move rapidly on the crystal face inwards giving rise to the black lines observed in Fig. 1(*a*). The result is to make the crystal somewhat convex after etching, as shown in Fig. 2, which is a multiple-beam interferogram (Tolansky, 1948) on a thermally etched surface. The non-uniformity in the pit size as observed in the thermal etch pattern may possibly be due to new surfaces being exposed continuously giving shallow sites. The evaporation process appears to be very rapid and hence the pits produced are circular. Because of the rapid removal of the layers in thermal etching, many of the pits nucleated at the ends of dislocation half-loops, which are confined to a few atomic layers near the surface and produced during the process of cleaving, may be destroyed, thus giving rise to a lower density of pits in the thermal etch patterns as observed. The symmetric and asymmetric structures of the pits suggest that dislocation lines run at various inclinations to the surface.



(a)



(b)

Fig. 1. Etch patterns produced on freshly cleaved sodium chloride surfaces by (a) heating at 750°C for $2\frac{1}{2}$ hr (×33), (b) glacial acetic acid: methyl alcohol (2:1) for 25 sec (×324).

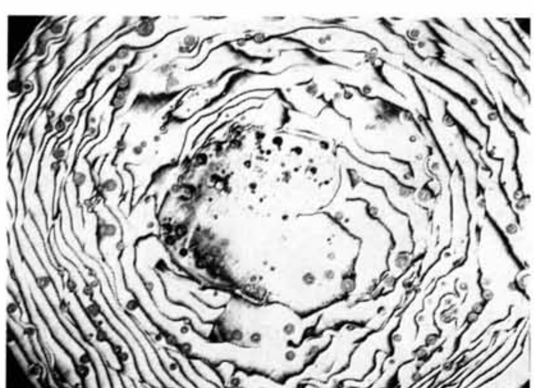
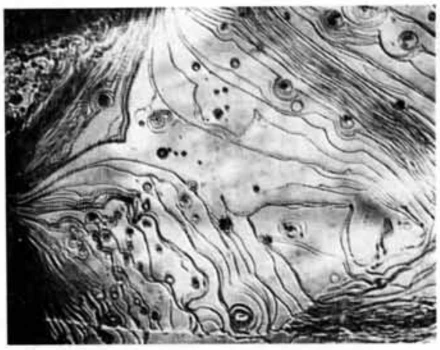


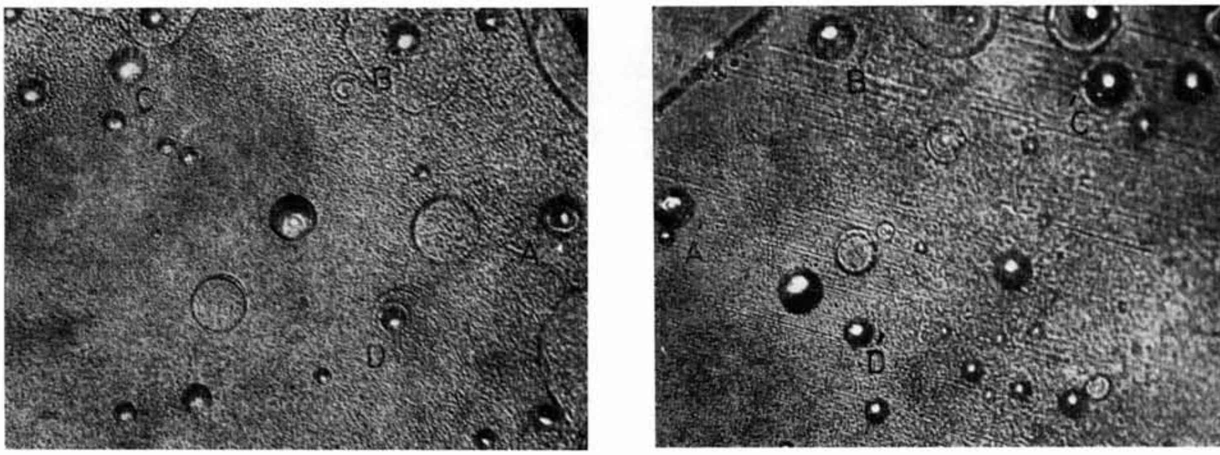
Fig. 2. Multiple-beam interferogram on a thermally etched sodium chloride surface (×45).



(a)

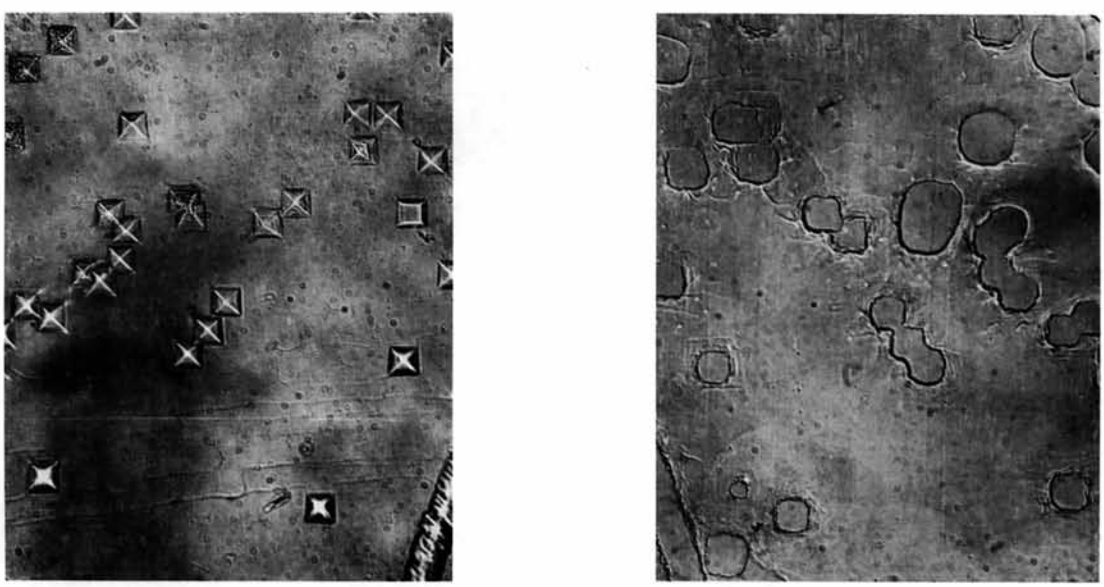
(b)

Fig. 3. Thermal etch patterns produced on one region of a crystal face at 750°C after (a) 3hr, (b) 4hr (× 100).



(a) (b)

Fig. 4. Thermal etch patterns produced on matched cleavages by heating in air at 750 °C for 2 hr (× 440).



(a) (b)

Fig. 5. Etch patterns produced on matched cleavage faces, one of which (a) was chemically etched and the other (b) thermally etched (× 160).

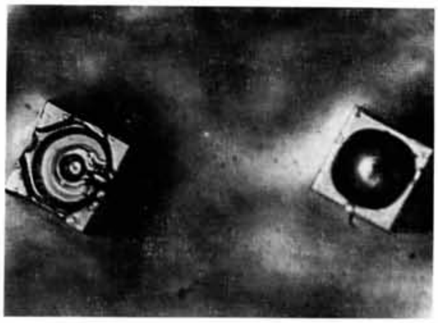


Fig. 6. Hillocks produced by thermal etching at 765–785 °C (× 264).

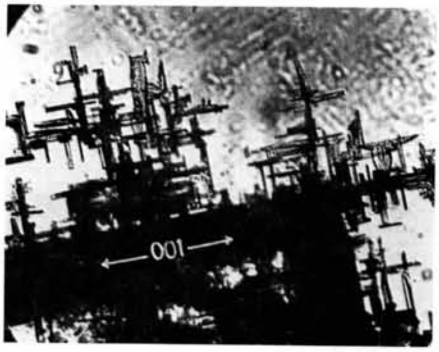


Fig. 7. Whiskers observed after thermal etching (× 33).

Fig. 8. Anticlockwise spiral on top of a whisker (× 510).

Thermal etch patterns produced by successive heating

A freshly cleaved crystal was successively etched for different periods. Figs. 3(*a*) and 3(*b*) thus represent thermal etch patterns produced on the same region of the crystal face after 3 and 4 hours of heating at 750 °C respectively. There is movement of the edges of layers owing to evaporation, the nucleation of small pits on the new face exposed, and only few pits can be identified as present in both. Some of the pits vanish owing to the removal of surface layers. Successive heating does not necessarily increase the size of the existing pits. (This is quite contrary to chemical etching.) This may be due to the removal of the surface layers.

Thermal etching of matched pairs

The thermal etch pits probably reveal dislocation sites. A number of matched pairs of sodium chloride cleavages were simultaneously thermally etched and the etch patterns compared to see if there were correspondences in the number and position of the etch pits on the matched faces. Many pairs failed to reveal any correlation. This may be due to the rapid removal of the layers from both the faces, leading to the exposure of new layers which in fact are not matched faces. However, if matched pairs are heated for only a comparatively short period some correspondence is established in the thermal etch patterns. Thus Figs. 4(*a*) and (*b*) represent the thermal etch patterns produced by heating the cleavages in air at 750 °C for two hours. There is some correspondence, *e.g.* in those marked *A*, *B*, *C*, *D*, *etc.* in the Figure. This supports the conjucture that some thermal etch pits reveal dislocation or impurity sites.

Comparision of thermal and chemical etch patterns on matched faces

Matched cleavage faces were etched, one chemically and the other thermally. Figs. 5(*a*) and (*b*) represent such etch patterns produced by chemical etching and thermal etching respectively. There is one to one correspondence in the number and positioning of the pits on the matched faces, although only the chemically etched pits have regular shape and size. The cleavage lines are missing on the thermally etched face.

Growth of whiskers on the parent crystal

During the experiments on thermal etching, when the crystal cleavages were heated at temperatures between 765 and 785 °C, in addition to the normal thermal etch patterns raised hillocks were observed. The heights of the hillocks were measured by the depth of focus method and range from 0·15 to 0·17 mm. Fig. 6 shows some of the hillocks, whose tops are square with sides parallel to the cubic edges of the crystal. In each square is a circular pit region. It is conjectured that the numerous hillocks observed may be whiskers of sodium chloride, grown from the sodium chloride vapour. In some of our experiments whiskers as large as 4 mm in height appeared (Fig. 7).

That the thermal etch pattern and the whisker growth are produced simultaneously on the sodium chloride cleavages appears rather strange. It indicates that both dissolution and growth take place simultaneously. This may be explained by assuming the existence of some screw dislocations on the crystal faces. When the crystal is heated, evaporation at the edges of the layers may take place, and hence an atmosphere of sodium chloride vapour is created in the vicinity of the crystal surface. Now if a screw dislocation is present on the surface the conditions may be favourable for a whisker to grow at the site of the dislocation as explained by Amelinckx (1958). As the whiskers grow on the parent crystal the sides of their square tops should be parallel to the cube edges as observed. Now during the experiments, if the conditions change, one might expect etching on the surface of the whiskers. As the whiskers are assumed to be grown at the sites of screw dislocations, the centres of the tops of the whiskers are the sites of the screw dislocations and hence they will be etched there preferentially, producing a central pit on the square tops of the whiskers as observed.

If the whiskers do grow at screw dislocations it may then be possible to observe a spiral on the top. A large number of whiskers were examined with a phase-contrast microscope. Spirals on the tops of some were found. Fig. 8 represents one example on which an anticlockwise spiral is seen.

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