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AN EVALUATION OF ETCHANTS AND TECHNIQUES USED TO PRODUCE DISLOCATION ETCH PITS ON SODIUM CHLORIDE

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SUMMARY

A comparison of the six most commonly used etchants for sodium chloride has been made together with an evaluation of various etching and observation techniques. All six etchants were found to produce usable pyramidal etch pits when special techniques were employed. A one-to-one correspondence in number and location has been established for the etch pits produced by all six etchants. On the basis of this correspondence, the only advantage in using one etchant in preference to another to study dislocations in sodium chloride appears to be ease of observation.

INTRODUCTION

The successful use of etch pits to study dislocations in sodium chloride single crystals depends appreciably on the etchant and the experimental techniques employed. In view of the many recently developed etchants for sodium chloride and the number of reported comments concerning the etching of this material (refs. 1 to 4), a comprehensive evaluation was undertaken. The purpose of the work reported herein was to compare six of the most commonly used sodium chloride etchants and evaluate various techniques employed.

ETCHING TECHNIQUE

To study etchants properly, all variables except the action of the etchant should be held constant. Such variables as dislocation density, cleavage damage, and purity are difficult to hold constant, but other factors can be controlled by adopting good techniques. A standardized technique was developed after the etching and observation processes were investigated. The results of this investigation are given first since this was prerequisite to studying the etchants.

Handling

During the etching and observation process, manipulation of the specimen is obviously essential. This manipulation must be accomplished in a manner such that dislocations are not generated or caused to move. This is an especially difficult task when the specimen is sodium chloride because dislocations in this material can move at stresses below 25 grams per square millimeter (unpublished NASA data), and such stresses can be generated by forceps, fingers, and other conventional holding devices. Successive etching of a single specimen or the matching of etched cleavage halves shows that even the most careful handling of the specimen produces unwanted effects. For example, figure 1

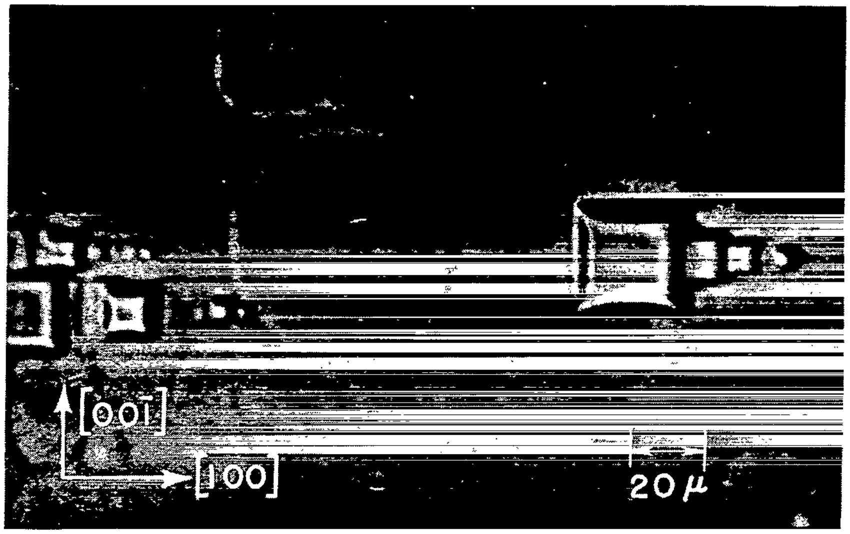

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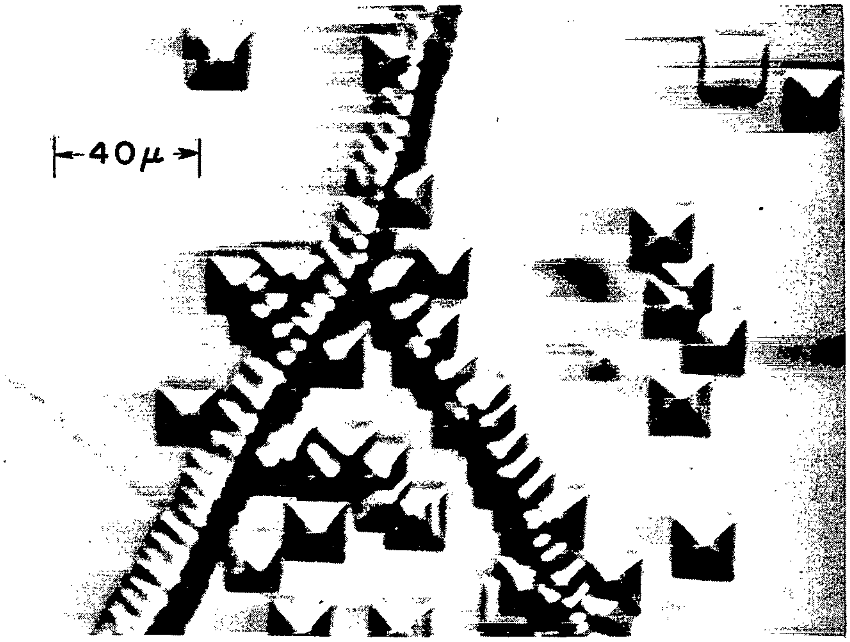
Figure 1. - Etched sodium chloride surface showing movement of dislocations during etching process. Etched 30 seconds in etchant E and 25 seconds in etchant D.

shows the movement of dislocations produced by holding the specimen with polytetrafluorethylene-coated forceps during etching. From figure 2 it can be seen that there is not an exact correspondence between etch pits on the cleavage halves. The differences might possibly be due to the way each half was handled, even though extreme care was exercised.

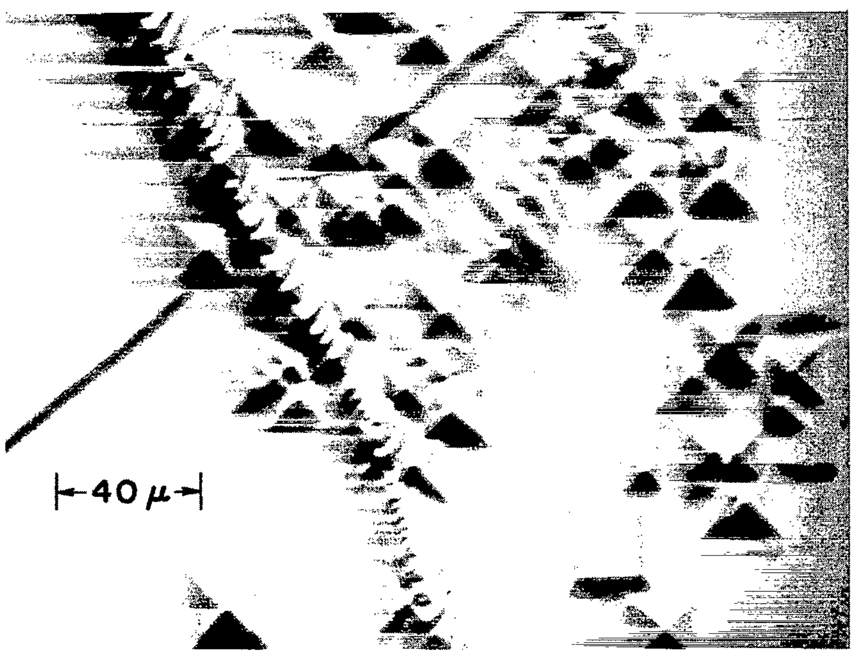
A technique for manipulating specimens, found to be superior, consists of cementing the specimen to a glass slide so that it can be manipulated without direct contact. With the specimen affixed to a slide, any area can quickly be relocated by noting the coordinates from a mechanical stage. For cementing the specimen to its "handle," methyl-alpha-cyanoacrylate adhesive has proved most suitable because (1) no heat or pressure is required to facilitate curing, (2) no shrinkage occurs upon curing, (3) the cement is insoluble in all etchants and rinses employed, and (4) an excellent bond is attained in seconds.

Polishing

Polishing of sodium chloride surfaces to be used in dislocation etch pit studies requires a solvent whose surface dissolution rate is low enough to allow controlled removal of surface material. Water is unsatisfactory because



(a) Etched 30 seconds in etchant D.



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(b) Etched 50 seconds in etchant B.

Figure 2. - Cleavage halves of etched sodium chloride.

its dissolution rate is much too high, and other solvents in which sodium chloride is less soluble (e.g., alcohols) produce slight etching action. Hydrochloric acid when diluted with water produces suitable dissolution rates without causing etching. When used with slow, rocking agitation, a solution of one part water and four parts concentrated hydrochloric acid has a surface dissolution rate of 1 micron per minute. Other rates can be attained by changing the proportions.

Postetch Rinsing, Drying, and Storing

As expected, the etched surface of a highly water-soluble material, such as sodium chloride, becomes marred by exposure to excessive moisture, and, as shown in reference 2, the etch pits on sodium chloride are all but obliterated by high humidity. Consequently, care must be taken to protect the etched surface, and this care necessarily begins with the postetch rinsing. The rinse must remove the etchant without adding water to the surface; however, water can be added to the surface if the rinse has a strong tendency to absorb water or if it evaporates so rapidly that it cools the surface sufficiently to cause condensation. Many rinses have been suggested, namely, pyridine (ref. 4), petroleum ether (ref. 3), carbon tetrachloride (ref. 1), and acetone (ref. 2). The last possesses the advantages of mild odor and low toxicity, it does not absorb sufficient water to cause marring of the etched surface, and its rate of evaporation is low enough not to cause condensation.

Drying with forced or hot air requires extreme caution because of the possibility of causing thermal shock. When acetone is used as a postetch rinse, forced drying is not required. Successive etching experiments have not revealed etch pits that could be attributed to thermal shock caused by rapid evaporation of the acetone.

Etched sodium chloride specimens, rinsed with acetone, have been stored for up to 1 month under a watch glass in a dessicator or for up to 1 year in sealed vials. The etch pits on these specimens were still of good quality, and photomicrographs of these specimens were as good as those taken immediately after etching.

Observation

The particular observation mode used to view etch pits depends on (1) the type and quality of etch pits and (2) the micrographic equipment available. For almost all etch pits ordinary bright-field illumination is unsatisfactory because it does not yield sufficient contrast to reveal clearly all etch pits. Generally, oblique incident illumination is most suitable, and the shallower the etch pits the more oblique the illumination must be. For very shallow etch pits or for high magnifications, sufficiently oblique illumination is difficult to obtain without special equipment, such as the Leitz Ultropak. When such equipment is not available, incident light phase contrast or other interference techniques can be used with various degrees of success, as shown in figures 3 and 4.

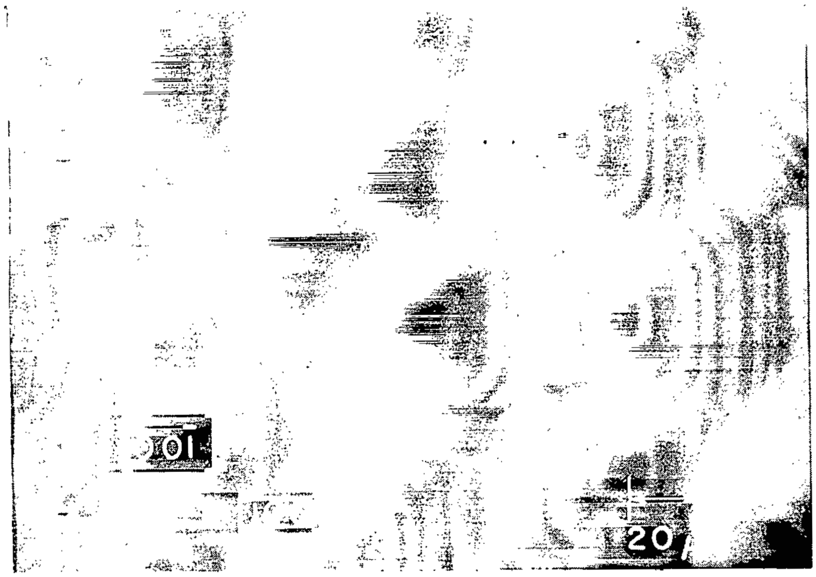

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Figure 3. - Phase contrast photograph showing etch pits on sodium chloride produced by etchant A. Etching time, approximately 2 seconds.

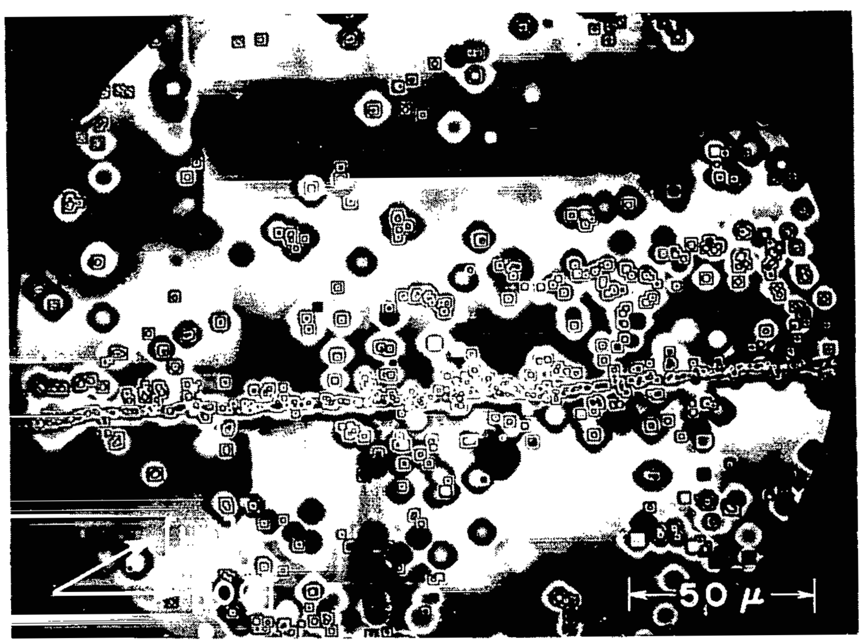

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Figure 4. - Interference photograph of sodium chloride surface successively etched in etchant E for 30 seconds and etchant D for 20 seconds.

With a little adjustment, the conventional metallurgical microscope can be used to observe several types of etch pits produced on sodium chloride. By closing down the aperture diaphragm and moving it slightly off center, a degree of oblique illumination can be obtained that produces adequate contrast to magnifications of approximately 450. Of course, this procedure results in some loss of uniformity of illumination over the entire field of view, and, hence, nonuniform negatives result when photographs are being taken.

As far as observation of etch pits is concerned, there is no substitute for sharpness and a suitable depth-to-width ratio, of which 0.15 is the optimum value.

COMPARISON OF ETCHANTS

The following table gives the six etchants investigated together with the associated etch-pit properties.

Etchant	Composition	Etching time, sec	Etch-pit orientation (a)	Ratio of depth to width (b)	Reference
A	Anhydrous methyl alcohol	<1	[100]	0.050	5
B, for sodium chloride	3 grams of mercuric chloride per liter of absolute ethyl alcohol	30	[100]	0.100	1
C	4 grams of ferric chloride per liter of glacial acetic acid	30	[100]	0.150	2
D	50 parts glacial acetic acid plus 1 part hydrochloric acid saturated with ferric chloride plus 1 part water	30	[100]	0.150	4
E, for potassium chloride-potassium bromide	95 parts ethanol[c] 25 percent saturated with barium bromide plus 5 parts methanol containing 100 grams per liter of barium bromide	15	[110]	0.070	1
F	1.75 percent by weight barium carbonate in propionic acid	40	[100]	0.135	3

[a]Defined as direction parallel to base of etch pit.
[b]Determined with two-beam interference microscope.
[c]95 percent ethyl alcohol.

Anhydrous methyl alcohol (etchant A) took the shortest time to etch and produced by far the shallowest etch pits, which are very difficult to observe. Figure 3 is a phase contrast view of etch pits on sodium chloride produced by methyl alcohol; with bright field illumination, these pits are not recognizable. Also, when methyl alcohol is used as an etchant, so much dissolution takes place that many shallow dislocation half loops are etched completely out of the specimen, and etch pits overlap to such an extent that a confusing scene results.

The sodium chloride etchant of reference 1 (etchant B) produces greater dissolution and shallower etch pits than the etchants based on acetic or propionic acids, but good quality pits can be obtained with etching times from 10 to 40 seconds, as shown in figure 5. While additions of 1 to 2 percent of water to the etchant results in shorter etching times and shallower etch pits, the excessive sensitivity to atmospheric variables (viz., relative humidity) reported in the literature (refs. 2 and 3) has not been noted. Letting the etchant stand for several hours in an open vessel on a day when the relative humidity was 90 percent did not alter the etching time or the quality of the etch pits produced.

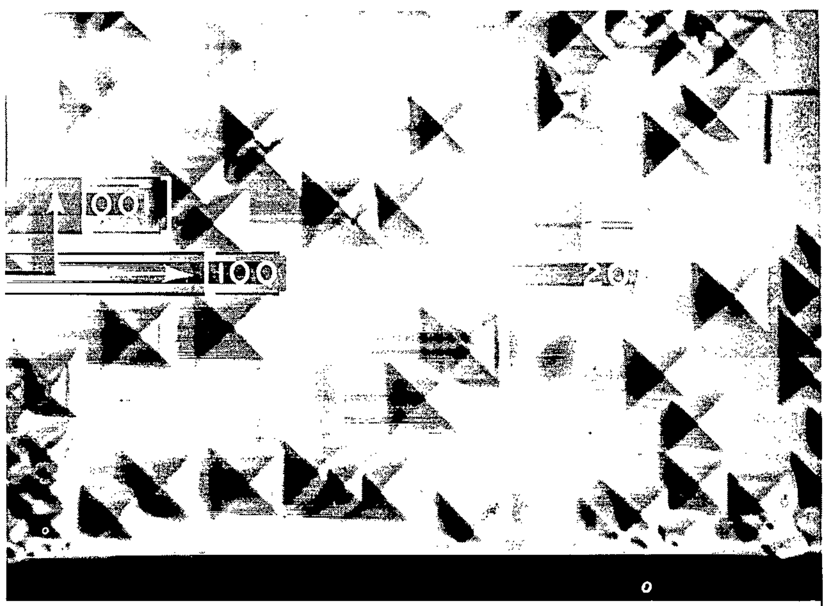

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Figure 5. - Sodium chloride cleavage face etched 30 seconds in etchant B. Edge of specimen establishes orientation of etch pits.

The etchants of references 2 and 4 (etchants C and D, respectively), based on acetic acid, produce the best quality etch pits for ease of observation in etching times of about 30 seconds. The observations of reference 2 regarding small quantities of water in etchant C have been found to apply equally to etchant D; water reduces the etching time and produces a shallower pit with somewhat rounded edges.

Etchant E (ref. 1), when used on sodium chloride with etching times of 15 to 25 seconds, produces a shallow etch pit that requires very oblique illumination for viewing. This etchant possesses a serious disadvantage because, during the etching process, crystallization, which greatly hinders observation of the etch pits, takes place on the surface. Diluting the etchant with an equal volume of 95 percent ethyl alcohol minimizes crystallization on the surface without affecting the etch pits. At best, however, only small areas are free from crystallites, which limits the usefulness of this etchant.

Etchant F (ref. 3), based on propionic acid, produces well-defined etch pits on sodium chloride. Best results were obtained with this etchant when etching times of 40 seconds were employed. Like the other etchants investigated, this etchant was found to produce shallower etch pits when water was added.

All six etchants investigated etched fresh and aged dislocations equally well. It was reported in reference 5 that methyl alcohol attacks the "grown in" dislocations somewhat better, but in this study no such preferential action was detected.

In figures 2(a) and (b) of reference 4, the author shows matching cleavage faces (of a material not specified) etched with etchant D and an unspecified etchant used in the study of reference 1, respectively. From these figures it is readily seen that the etch pits produced by the etchant of reference 1 have the edge of their base inclined 45° to the edge of the base of the etch pits produced by etchant D (ref. 4). (Hereinafter the edge of the base of the etch pits will be used to define the orientation of the etch pits.) The author of reference 4 gives the orientation for the etch pits produced by etchant D as [100] (i.e., the edge of the base is parallel to the [100] direction) and the orientation of the etch pits produced by the etchant of reference 1 as [110]. In the reference cited by Barber, Moran describes etchants for sodium chloride, potassium chloride - potassium bromide, and potassium iodide, respectively, and Barber does not state specifically which of these etchants he employed. Etchant B produces etch pits with a [100] orientation. Figure 5 shows a sodium chloride cleavage face etched with etchant B together with a [100] edge of the specimen. It can be seen from figure 5 that the etch pits have a [100] orientation. Furthermore, figure 2 shows matching cleavage faces of sodium chloride etched with etchants D and B, respectively. Each set of etch pits is identically oriented. Those produced by etchant E were found to have a [110] orientation, and presumably this is the etchant used to obtain figure 2(b) of reference 4.

In the course of this investigation, it was discovered that, if absolute ethyl alcohol (instead of 95 percent) and anhydrous barium bromide were used to compound etchant E, the etch pits produced by this "dry" etchant had a [100] orientation. Since barium bromide is quite insoluble in absolute ethyl alcohol, it might be concluded that an insufficient amount went into solution to produce the [110] etching action; however, additions of about 2 percent water to the "dry" compounded etchant caused the desired [110] etching action, while higher saturation values had no effect. Apparently, then, the barium bromide concentration is not as critical in producing an etch-pit orientation as the presence of some water.

Figure 4 shows the cleavage face of a sodium chloride crystal first etched in etchant E for 30 seconds, rinsed in acetone, and then immediately etched in etchant D for 20 seconds. (A two-beam interference microscope was used in making this photograph.) In this figure can be seen remnants of the original [110] etch pit and inside it the newly created [100] etch pit.

While figure 4 does show a few of what appear to be single-type etch pits, actual microscopic examination at a different focus and/or interference band interval, reveals that a [100] pit is associated with each [110] remnant. Similar successive etching experiments have revealed that there is a one-to-one correspondence between the etch pits produced on sodium chloride by all six etchants studied.

The author of reference 4 has pointed out that Moran's etchant (presumably etchant E) also produces some rounded etch pits not revealed by other etchants. Similar rounded etch pits have been observed on occasion when other etchants were used, but attempts to establish their correspondence to crystal imperfections have not been successful. At present it is felt that these rounded pits are an artifact of the etching process.

CONCLUSIONS

An investigation conducted to evaluate etchants and etching techniques that produce dislocation etch pits on sodium chloride yielded the following conclusions:

1. By employing suitable etching and observation techniques, all six etchants investigated can be used to produce etch pits on sodium chloride.

2. The etchants based on acetic acid produce the most easily observed etch pits on sodium chloride.

3. A one-to-one correspondence between the etch pits produced by all six etchants has been established by successive etching with two etchants.

4. All six etchants produce etch pits at both fresh and aged dislocations.

5. On the basis of the one-to-one correspondence between etch pits produced by the various etchants and the fact that all etchants etch both fresh and aged dislocations equally well, there does not appear to be any advantage, except ease of observation, in using one etchant in preference to another.

6. The fact that different etchants produce differently oriented etch pits implies that a difference in etching mechanism exists. Considering proposed etching mechanisms based on the adsorption of cations at kinks, and simple geometric aspects of size, there appears to be no reason why different cations (e.g., barium and mercury) of about the same size should produce differently oriented etch pits. Furthermore, the fact that the addition of water to the "dry" compounded potassium chloride-potassium bromide etchant changes the ori-

entation of the etch pits implies a more complex etching mechanism. Certainly further study along these lines is warranted.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, March 2, 1964

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