CHAPTER VI

STUDIES ON CHEMICAL ETCHING OF ANTIMONY CRYSTALS

The work reported in this chapter deals with the results from the etching of antimony crystals. Chemical etching is an extremely complex phenomenon and is often influenced by a large number of factors. Among these are the nature of the individual crystals, crystalline perfection, crystallographic orientation, type and concentration of impurities in the crystals as well as in the etchant, the temperature and the hydrodynamics of the solid-liquid interface. Factors of importance to chemical etching can be distinguished as those predominently affecting the over-all (macroscopic) rate of etching and those affecting primarily the microscopic nature of etching that is the resulting microscopic nature of the surface. It is the latter phenomenon which is of interest in the present context.

Etching is often employed for the determination of dislocation densities and thus for assessing the crystal perfection. But as has been pointed out in Chapter III, the one-to-one correspondence between etch pits and dislocations has not yet been established conclusively and it is an accepted fact that etch pits should not be attributed exclusively to dislocations without further verification. Such verification often poses many problems. For example, it may not be always possible to observe lineage boundary long enough to facilitate the measurement of the tilt angle by X-ray diffraction, as has been employed by Vogel et al[1]. X-ray topography if employed reveals often the dislocations lying on the plane under observation, whereas etch pits indicate dislocations running perpendicular to the plane of observation. Differential etching being often anisotropic cannot be employed in all planes and the anisotropy of dislocation densities is a major obstacle for the use of this method for verification.

For the formation of etch pits at dislocation sites, it is necessary that the etching rate along the dislocation line be greater than that on the rest of the surface. It has been proposed that the increased etching rate along a dislocation line is due to the strain field associated with the dislocation. Alternatively the increased activity of dislocation lines is attributed to the presence of the impurities preferentially seggregated near the dislocation. Results of Lacombe et al[2,3,4,5] indicate that dislocations are revealed by etching only if they are decorated by impurities. Similar results have been obtained with certain etchants on germanium crystals[6].

The impurity mechanism for the dislocation pit formation is quite plausible and consistent with electrochemical mechanism of dissolution[6,7] i.e. the impurities along the dislocation serve as localised anode thus leading to the formation of pits. It is not plausible, however, that strain fields of dislocation constitute a necessary or sufficient prerequisite for the enhanced attack. There are no strain fields present in an array of dislocations forming a low angle boundary. Yet individual dislocations along such boundaries are as readily revealed by etching as are isolated dislocations. Similarly there are no strain fields at the intersection of screw dislocations with the surface and yet this type of dislocations are readily revealed by etching. Thus it is evident that the etching of dislocation poses quite a number of problems both in theoretical as well as practical aspects.

Nevertheless, etching is a valuable tool in revealing dislocations. Etching methods have been successfully developed for germanium[8], silicon[9,10], silicon-iron, aluminium containing critical impurities[5], zinc[11], lithium fluoride[12], sodium chloride[13] etc. to mention only a few. In applying this technique various methods have been employed to establish the correspondence between the etch pits and the dislocations. They are:

(1) Perfect matching of etch pits on cleaved surfaces;

(2) Repetition of the pattern on successive grinding and etching which allows the tracing of dislocations to some distance in the lattice;

(3) Introducing various types of plastic deformations and establishing the agreement between theoretically estimated dislocation density with the measured etch pit densities.

Etching of antimony crystals has been attempted by a number of workers[14-21]. The reagents used by these workers are summarised in Table VI-1.

Wernick et al[14] have studied etching of antimony crystals using CP-4 reagent and superoxol. Etch pits are triangular in shape and randomly distributed over

TABLE VI-1

Reagent No.	Author	Composition
1	Wernick J.H. et al	CP-4 3 parts HF 5 parts fuming HNO_3 3 parts glacial CH_3COOH 1 part Br_2
2	Kosevich V.M.	Modified CP-4 23 parts glacial CH_3COOH 5 parts fuming HNO_3 4 parts HF 3 parts Br_2
3	Shigetta J. et al.	10 grms $FeCl_3$ 30 c.c. HCl 120 c.c. H_2O
4	Pandya N.S. and Bhatt V.P.	3 parts HNO_3 9 parts Tartaric acid 1 part H_2O
5	Wernick J.H. et al.	Superoxol 1 part HF 1 part H_2O_2(30%) 4 parts H_2O

the surface. Closely spaced rows of etch pits suggestive of low angle boundaries similar to those observed on germanium and silicon were observed. These boundaries were not long enough to permit X-ray orientation measurements. However, these authors have derived a mathematical relation for the spacing of dislocation along intersecting low angle boundaries. It can be shown from Frank's boundary equation that a model having minimum free energy, for dislocation tilt boundary must consist of an array of two kinds of parallel edge dislocations which utilize two of the three a/2 [110] Burgers' vectors lying in the (111) planes. Thus if the boundary traces make an angle ϕ with the nearest Burgers' vector, then the other two Burgers' vectors are used and the number of dislocations per unit length of the boundary is given by

$$n = \frac{\theta}{\sqrt{3}b} \cos \phi \quad \ldots \quad \ldots \quad (1)$$

where θ is the angle of the tilt boundary. Considering the intersection of three boundaries, in order that the sum of the three tilt angles may be zero, one boundary, say A, must have an opposite sense of tilt from other two, say B and C, so that

$$\theta_A = \theta_B + \theta_C \quad \ldots \quad \ldots \quad (2)$$

Combining equations (1) and (2)

$$\frac{n_A}{\cos \phi_A} = \frac{n_B}{\cos \phi_B} + \frac{n_C}{\cos \phi_C} \qquad \ldots \qquad \ldots \qquad (3)$$

The angle ϕ is defined as that between the boundary trace and the nearest Burgers's vector, and hence cannot be greater than 30°, so that cos ϕ is not very different from unity.

Therefore,

$$n_A = n_B + n_C \qquad \ldots \qquad \ldots \qquad (4)$$

i.e. the dislocation density in one row is the sum of the dislocation densities in the other two. When two boundaries meet at a point, $n_C = 0$, hence

$$n_A = n_B \qquad \ldots \qquad \ldots \qquad (5)$$

Etch pit densities along intersecting boundaries were shown to satisfy the above relations (4) and (5) and hence it is reasonable to conclude that they are formed at the sites of the dislocations. In addition to this, distribution of etch pits along slip lines and in bent and annealed crystals confirms the above result. Superoxol is found to give spiral etch pits on the cleavage plane.

Kosevich[15] reports that CP-4 fails to produce etch pits on the crystals made from commercial purity metal. He modified the reagent for the successful production of etch pits and observed three different forms of etch pits viz.,

(1) Symmetrical pyramids indicating that dislocation lines are perpendicular to the cleavage plane,

(2) eccentric pyramidal pits corresponding to the slip dislocations lying along the [112] direction of Burgers' vector a[1$\bar{1}$0] and

(3) flat bottomed pits indicating that dislocations have moved away from the slip.

In a subsequent publication, Kosevich[16] reports about etch grooves formed of small triangular pits arranged on the cleavage surface, the implication of which is not clearly known. Shigetta and Hirmastu[17] have used a solution containing $FeCl_3$, HCl and H_2O. Pandya et al[18,21] have tried a solution of tartaric acid and nitric acid for the purpose, with the advantage that the surface remains bright even after prolonged etching. Etch pit method has been used to study motion of dislocation, their multiplication and polygonization by Soifer and others[19,20].

A number of reagents have been used by the author which includes those used by the earlier workers and a few other reagents with a view to establish the relative merits of these reagents in revealing dislocations. In attributing the etch pits to dislocations, the following criteria are adopted.

(1) Matching of pits on cleavage counter parts should be reasonably good.

(2) Pit density should remain constant and should not increase after repeated etching.

(3) Wherever possible the density calculation should show reasonable agreement with theoretical estimate.

(4) The nature and distribution of pits should agree with the earlier results which have been conclusively proved to be the dislocation sites.

A summary of the results is shown in Table VI-2.

Results of etching with CP-4 are comparable with those of Wernick et al. The etching is fast and produces point-bottomed triangular pits on the (111) planes. Matching of cleavage counter parts is reasonably perfect. The etching time is of the order of 1-2 seconds and longer

TABLE VI-2

Reagent symbol	Composition	Etch pit density	Shape of the pits	Matching on cleavage counter parts	Surface after etching	After deep etching	Etching rate	Remarks
A	CP-4 3 parts HF 5 parts HNO_3 (F) 3 parts CH_3COOH 1 part Br_2	10^5-10^6	Triangular	Good	Occassionally coloured	Corroded	Fast	Pit size is smaller than those obtained by earlier workers
B	Modified CP-4 4 parts HF 5 parts HNO_3 28 parts CH_3COOH 3 parts Br_2	$>10^8$	Triangular	-	Corroded	-	Fast	Not satisfactory. Results are contradictory to those of earlier workers
C	CP-4 - A 3 parts HF 5 parts HNO_3 3 parts CH_3COOH	10^5-10^6	Triangular, well defined	Good	Bright	Surface remains bright. Etch pits become large	Fast	Very useful

TABLE VI-2 (contd.)

Reagent symbol	Composition	Etch pit density	Shape of the pits	Matching on cleavage counter parts	Surface after etching	After deep etching	Etching rate	Remarks
D	10 gms $FeCl_3$ 30 c.c. HCl 120 c.c. H_2O	-	-	-	-	-	Slow	No pits produced even after prolonged etching. Results are contradictory to those of earlier workers.
E	3 parts HNO_3 9 parts tartaric acid 1 part H_2O	10^5-10^6	Triangular	Good	Bright	Surface remains bright	Moderate	Very useful.
F	Superoxol 1 part HF 1 part H_2O_2 4 parts H_2O	10^4-10^5	Large, triangular shallow, terraced pits	Reasonable after short etching time	Bright	Corroded	Fast	No spirals have been observed contradicting the earlier results
G	Dash Etchant 1 part HF 3 parts HNO_3 12 parts CH_3COOH	-	Small triangular pits	Not very good	Dull and coloured	Corroded	Fast	Used as dislocation-etch for silicon and as a chemical polish for Sb. Results contradictory.

TABLE VI-2 (contd.)

Reagent symbol	Composition	Etch pit density	Shape of the pits	Matching on cleavage counter parts	Surface after etching	After deep etching	Etching rate	Remarks
H	White etch 1 part HF 3 parts HNO_3	10^4-10^5	Triangular	Not satisfactory	Bright	Bright	Fast	-
I	1 part HF 3 parts HNO_3 4 parts CH_3COOH saturated with citric acid	10^5-10^6	Triangular	-	Bright	Bright, old pits disappeared and fresh ones observed	Fast	This is a chemical polish for InSb.
J	1 part HCl 3 parts $Na_2S_2O_3$ saturated solution.	-	Pits are not produced	-	-	-	-	This is a dislocation-etch for CdS and PbS.
K	1 cc [illegible] H_2SO_4 100 cc [illegible] H_2O 0.08 gm. Cr_2O_3	-	Pits are not produced	-	-	-	-	Reagent of dislocation-etch for CdS.

etching makes the surface over-etched. Frequently the surface gets covered with a brown layer and becomes irregular. Pit density is of the order of 10^5-10^6 cm^{-2}. Pits are generally small in size compared to those obtained by Wernick et al. The observed differences may be due to the difference in purity of the metal used. Whereas Wernick et al have grown the crystals after zone-refining 99.999% purity metal, 99.99% purity metal is used for the present investigation. Fig. 1 is a photomicrograph of an etched surface. In addition to the small triangular etch pits, there are a few extraordinarily large pits seen near the twin lamella.

The cleavage counterpart of this surface is etched with reagent E for comparison. It is seen in Fig. 2 that the pits are better defined in this case. There is a reasonable correspondence between the etch pits in these two figures. The large pits in Fig. 1, however, do not show any correspondence and it is likely that these may be sites of impurities and not connected with dislocations. Etching with reagent E requires a good length of time and hence can be conveniently used. Figs. 3 and 4 represent the surface of Fig.2 after etching for 3 mins. and 5 mins. respectively. It is seen that the size of etch pits

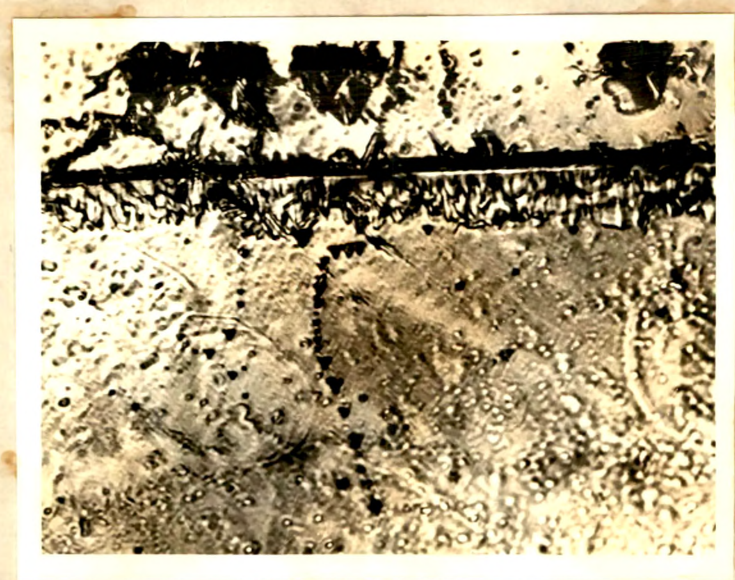

Fig. 1 X 680

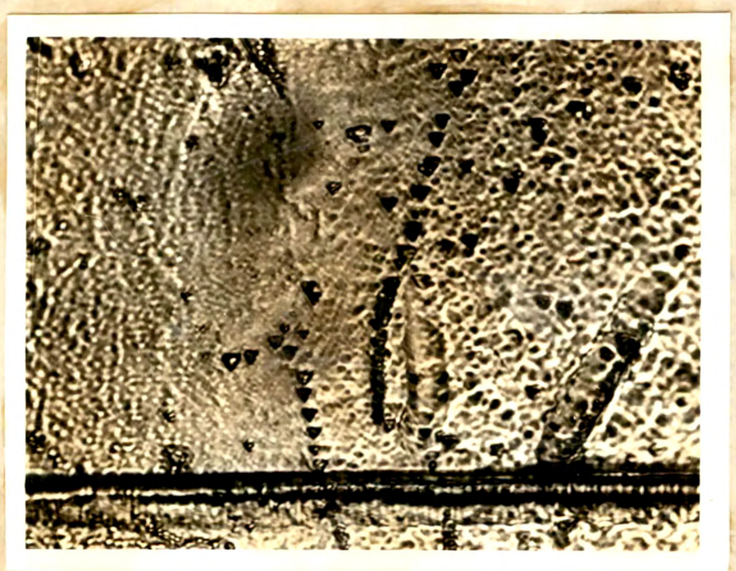

Fig. 2 X 680

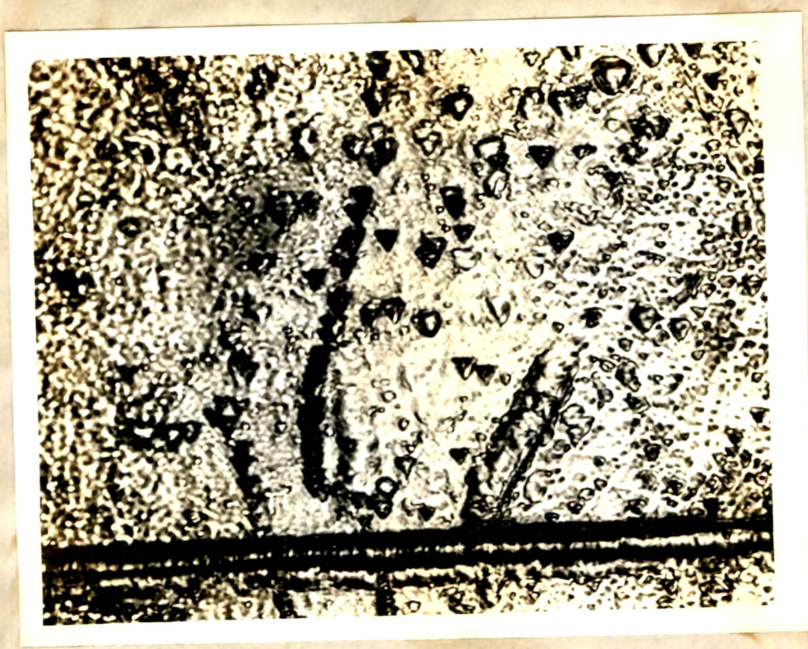

Fig. 3 X 680

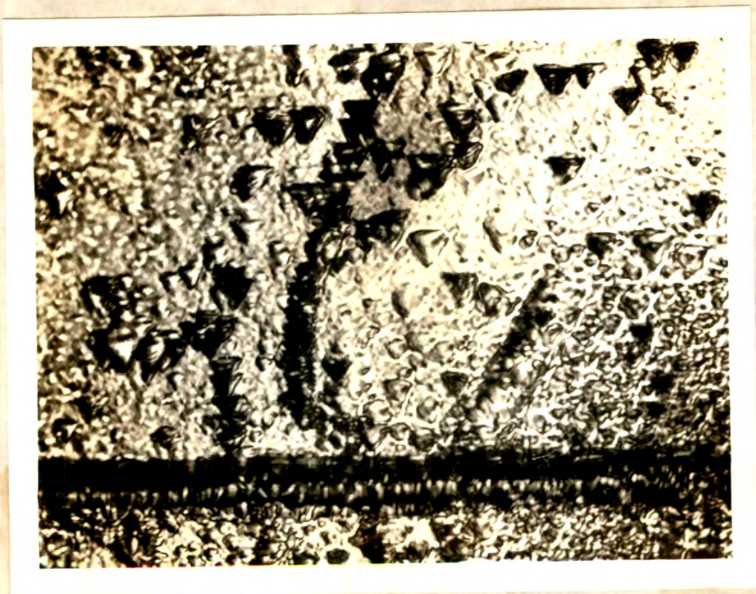

Fig. 4 X 680

increases, while the distribution, density and nature of the pits remain the same. Rows of etch pits representing sub-boundary are also revealed by this reagent. One such example is shown in Fig. 5.

The behaviour of the surface on successive etching is likely to give useful information. Reagent E has got the advantage that the surface remains bright and the etching rate is slow. A preliminary study on the rate of etching has been made by cutting a specimen 500 microns thick, and measuring the thickness of the specimen using a millimesh after successive etching for one minute each. It is estimated that the rate of etching is roughly 60 to 80 microns per minute. Microcrystals have been used for the purpose so that the establishment of the correspondence of the pits under the microscope becomes easier. Figs. 6 and 7 represent the crystal surface after 1 minute and 3 minutes etching respectively. Thus Fig. 7 represents the features at a depth of about 150 microns from Fig.6. The following features are noteworthy. A, B, C are point-bottomed etch pits and these have corresponding pits in both figures. These pits are connected by etch grooves similar to those reported by Kosevich. Whereas A and B retain their positions, pit C which is away from the etch

Fig. 5 X 450

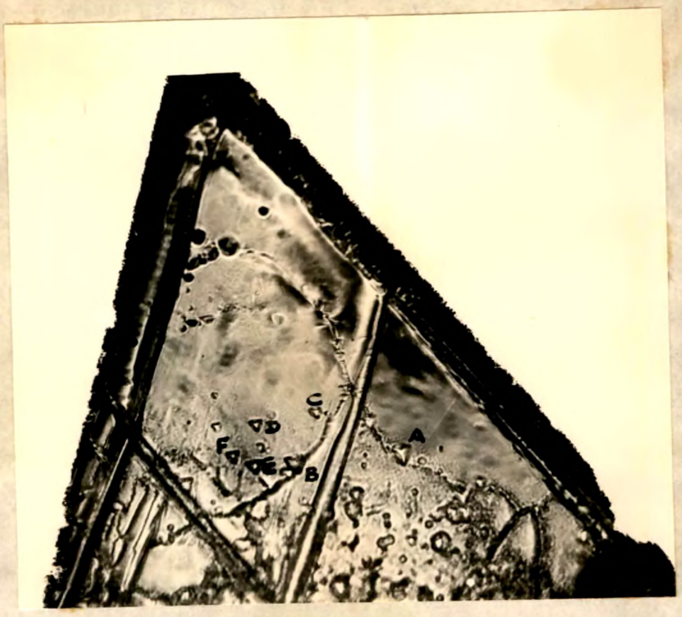

Fig. 6 X 340

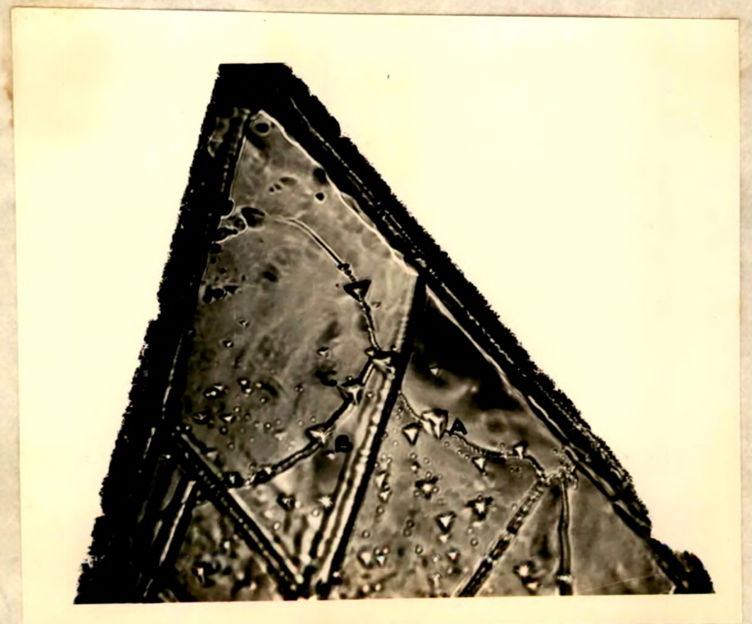

Fig. 7 X 340

groove in Fig.6 has moved towards the etch groove in Fig.7. This may be due to that the dislocation at C is not perfectly normal to the surface, but makes a small angle to the surface whereas the dislocations at A and B are normal to the surface. Pits marked D,E,F in Fig.6 have disappeared in Fig. 7. It has been shown by Gilman[12] that in LiF when a dislocation moves away from its place due to any applied stress, the original pit becomes flat bottomed and a fresh pit is developed. Interpretation of the results in Fig. 6, in a similar way, is that the pits D,E,F may represent places where a dislocation line terminates or alternatively they may not be dislocations, but possibly some other defects like impurity sites.

Modified CP-4 used by Kosevich, (reagent B), does not give satisfactory results. Fig. 8 shows a surface etched with this reagent. The surface is corroded and the unusually large number of pits on the surface is not likely to be dislocation sites. Reagent D used by Shigetta et al[17] does not produce pits even after etching the surface for 5 minutes. Fig. 9 is one such surface showing no etch pits. The same surface was etched in reagent E to see whether etch pits are produced. It is

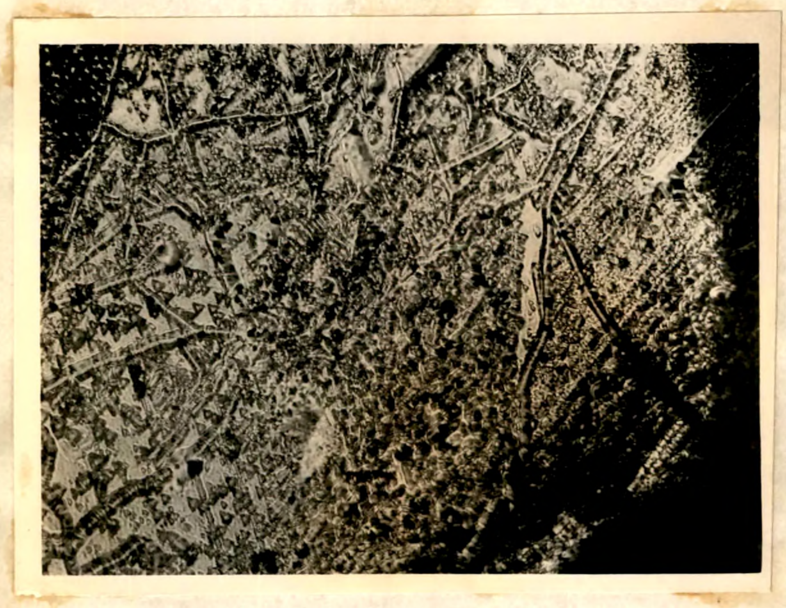

Fig. 8 X 340

Fig. 9 X 360

Fig. 10 X 360

seen from Fig. 10 that large number of pits is produced, but now the pits tend to be shallow and are much larger than the pits produced by the same reagent as shown in Figs. 2 to 7. This observation shows that etching is very sensitive to the nature of the surface. In Fig. 11 the intersection of three low angle boundaries revealed by using CP-4 - A is seen. The linear density of etch pits along these boundaries satisfies the equation (4) and are thus due to dislocations. The surface etched with this reagent remained bright. Figs. 12 and 13 are two cleavage counterparts etched with this reagent. Matching of etch pits is reasonably good and pits are well defined. In certain regions lack of matching exists which can be attributed to the dislocation rearrangements that might have taken place due to the nonuniform distribution of the cleavage stress. This is evident from the fact that the twin lamellae do not show correspondence. Matching of pits in regions shown in Figs. 12 and 13 are shown at a higher magnification in Fig. 14, whereas Fig. 15 shows a light profile running across the pits, indicating the point bottomed pits, the depth measured being about 10 microns.

Etching of twin bands gives results similar to those observed by Wernick et al. Fig. 16 shows the fine structure

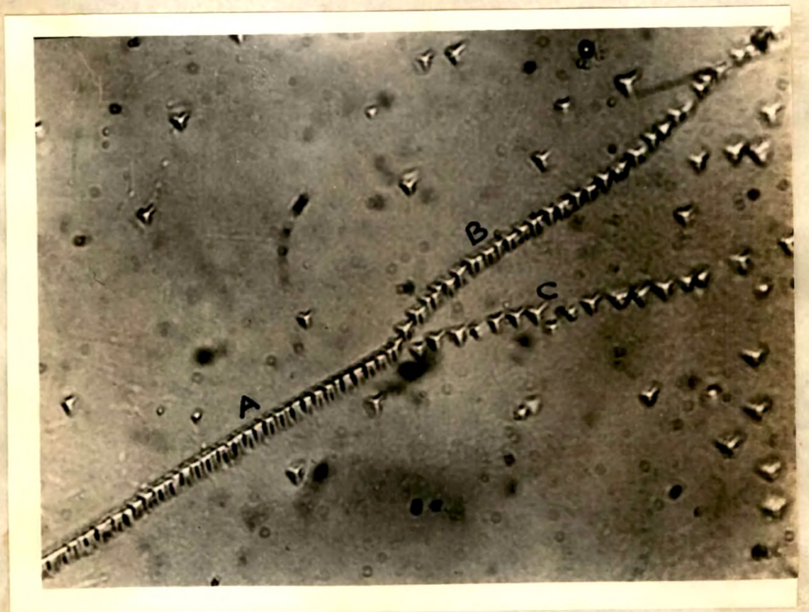

Fig. 11 X 450

Fig. 12

X 340

Fig. 13

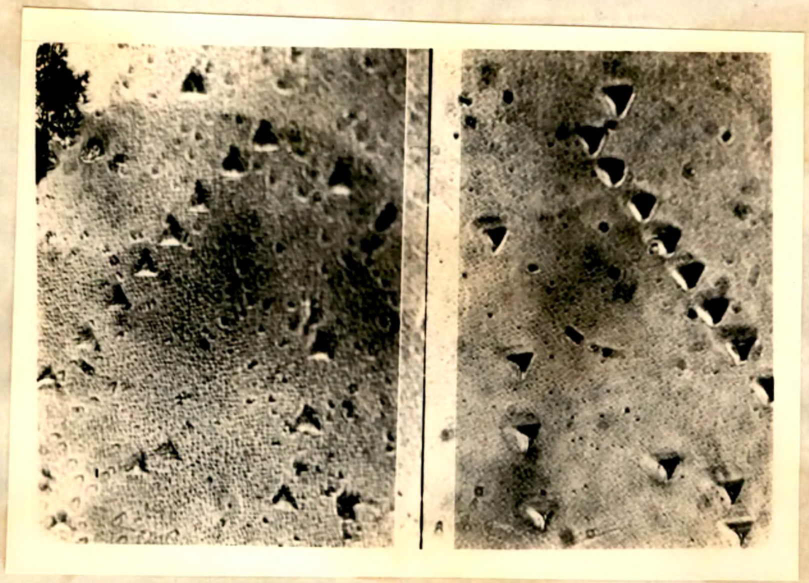

Fig. 14 X 850

Fig. 15 X 540

observed along the sides of the band. No etch pits are formed on the twin band itself. Frequently the tip of the twin band terminates in an etch pit or sometimes in a row of etch pits. Fig.17 shows one such example. Similar observations have been reported in zinc crystals[22]. Wernick et al[14] have observed spiral terraces and closed-loops using a modified form of superoxol. In the present study, reagent superoxol gives pits as shown in Figs. 18 and 19. A number of terraced pits, triangular in shape and point bottomed have been observed. Pits are shallow, the lateral dimensions being much larger compared to depth. Dash reagent is reported[14] to polish the surface without producing etch pits. In the present experiments it has been observed that small triangular pits are produced. This reagent is used for revealing the dislocations in silicon[23].

Well defined spiral etch pits have been attributed to screw dislocations by various workers[24-28], though doubts have been expressed by some workers[29]. Kraupa[30] has evolved a mechanism to explain how screw dislocations of small Burgers' vectors can give rise to large step height. The author wishes to point out that throughout these investigations involving a large number of crystals and various reagents, it has not been possible to observe etch spirals

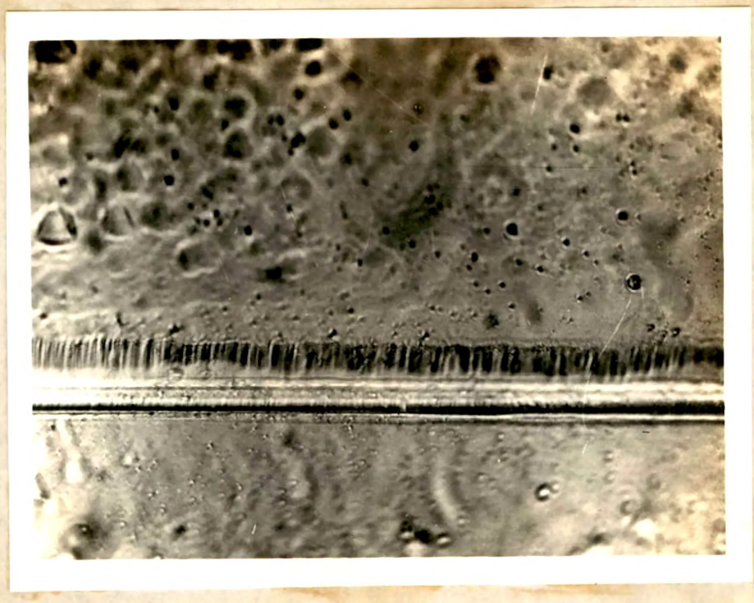

Fig. 16 X 360

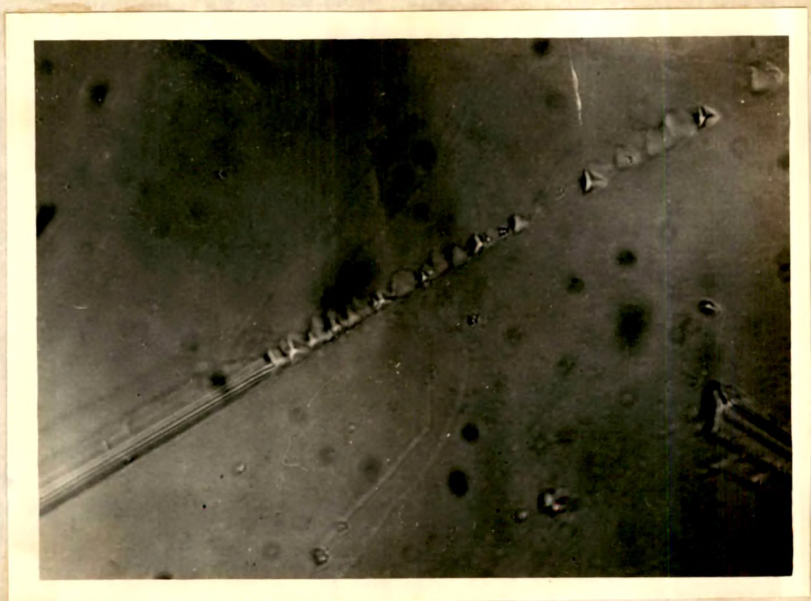

Fig. 17 X 540

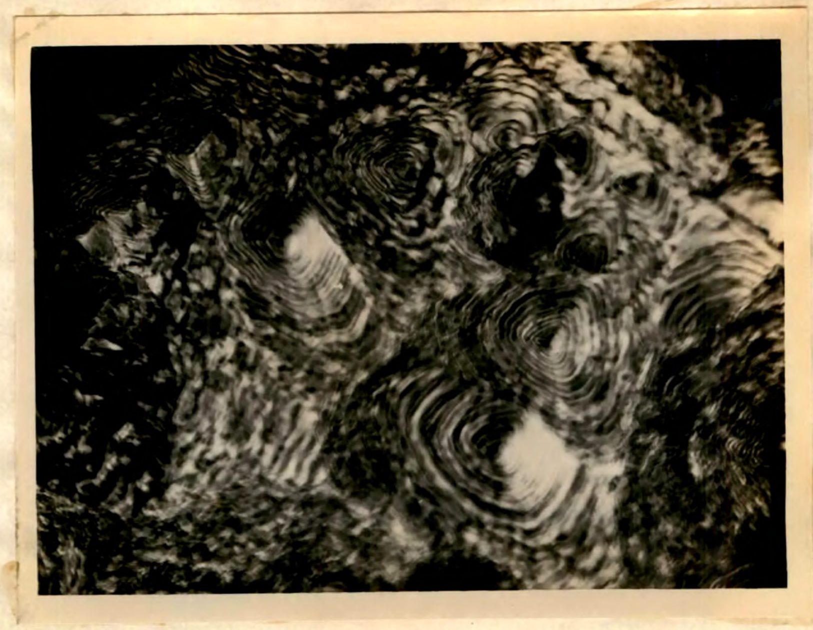

Fig. 18 X 340

Fig. 19 X 450

on the surface. While it is difficult to conceive that all the crystals are devoid of screw dislocations, the absence of spirals may be due to the fact that formation of etch spirals is very sensitive to the purity of the crystal as well as the reagent. Unfortunately few workers specify the purity of the reagents used by them. The author has throughout the work employed reagenets from BDH, analar quality and E.Merck. In addition to this, the phenomena may be very sensitive to the nature of the surface. This has been shown by Wernick et al[14] using modified superoxol, which does not produce spiral terraces on a polished specimen.

It is well known that when the motion of the dislocations is impeded by an obstacle, pile-ups are observed. The final arrangement of these dislocations in a pile-up is such that forces on them from the applied stresses, the obstacle, and their mutual interaction are in equilibrium[31,32]. Assuming such an equilibrium and that dislocations are parallel, the stress on the ith dislocation in a pile-up is given by

$$\sigma_p \propto \sum_{\substack{i=1 \\ j \neq i}}^{n} (x_i - x_j)^{-1} \quad \ldots \quad \ldots \qquad (6)$$

A plot of the summation against x_i should be a straight line of zero slope. Young[33,34] has made a detailed study of the spacing of etch pits in pile-ups in copper single crystals and has shown that this spacing does not conform to the theoretical estimate. He has suggested that this may be due to the fact that the barrier may not be in the plane of observation and negative result should not be considered as a failure of the theory. A number of dislocation pile-ups on the cleavage surfaces of antimony has been observed[35] during the course of this investigation. Fig.20 shows one such pile-up along the $[1\bar{1}0]$ slip direction and s_i vs x_i plot is shown in Fig. 21. Fig. 22 is another pile-up near a cleavage crack and the corresponding plot is shown in Fig. 23. The nature of the curves is in general agreement with those obtained by Young. Similar results have been obtained by Shah[36] on bismuth.

In establishing the correspondence between etch pits and dislocations various forms of plastic deformations are employed. Bending of crystals upto a known radius of curvature and comparing the distribution and the density of etch pits with those calculated using Nye formula has been employed by many workers[8,21,37,38]. In the present case deformation of the crystals was not successful due to

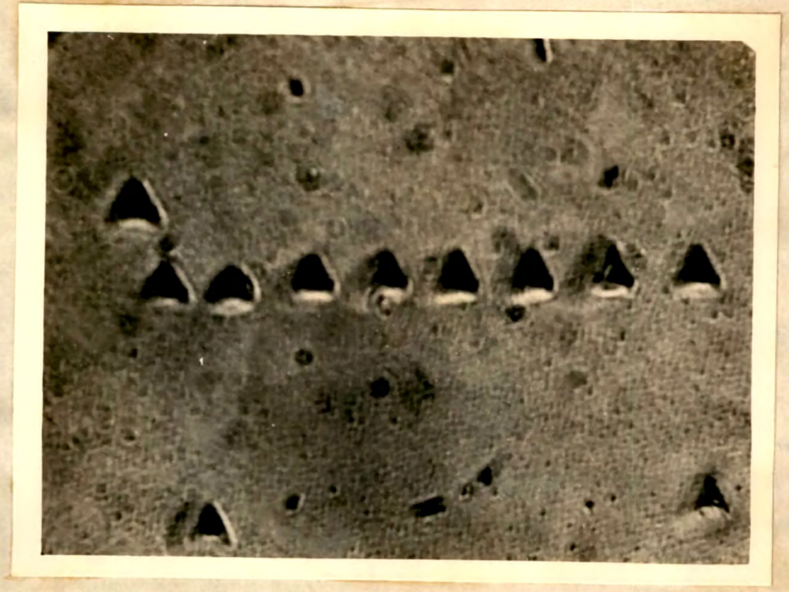

Fig. 20 X 940

Fig. 22 X 450

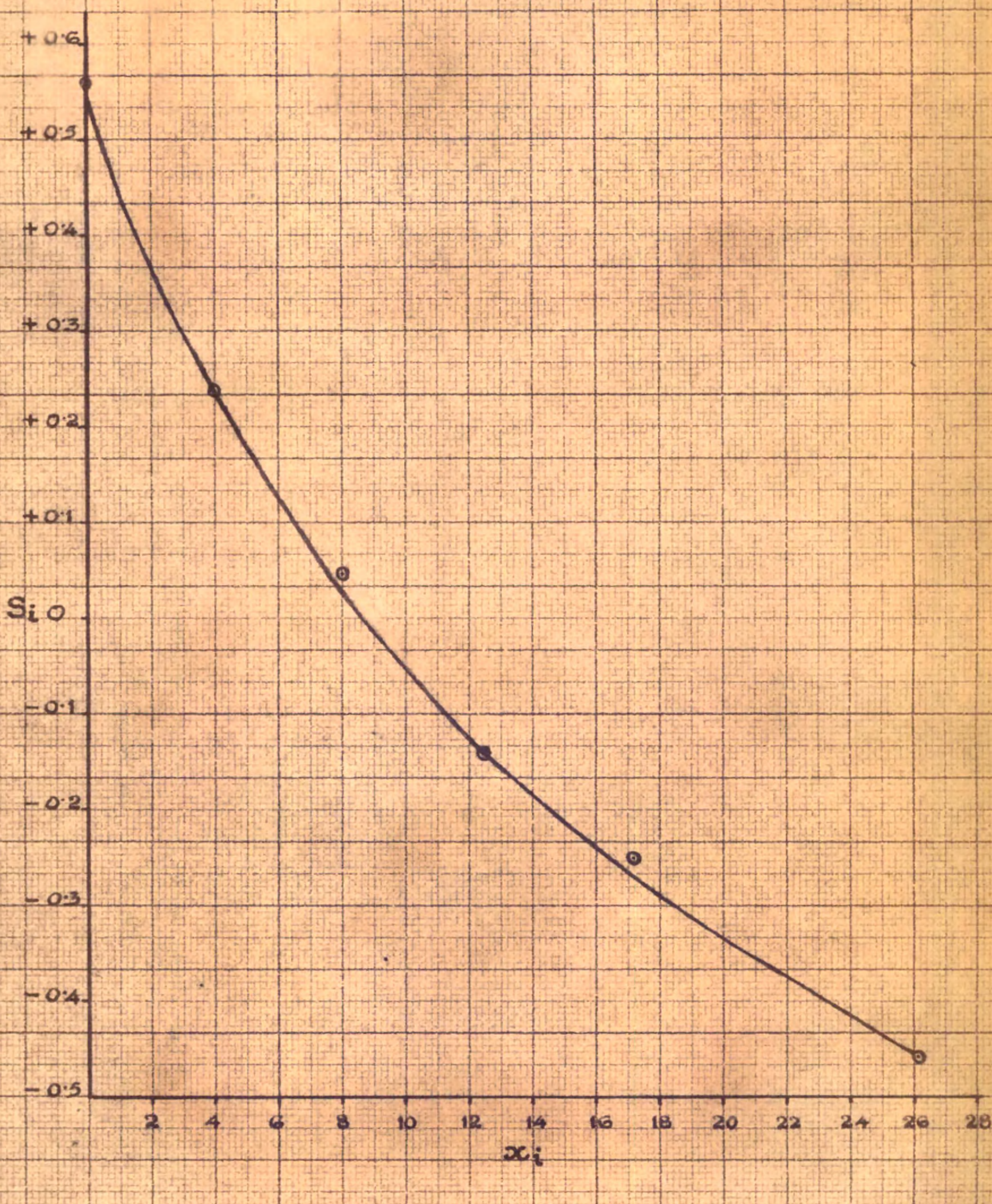
+0·6
+0·5
+0·4
+0·3
+0·2
+0·1
Si 0
−0·1
−0·2
−0·3
−0·4
−0·5
2 4 6 8 10 12 14 16 18 20 22 24 26 28
x_i

FIG. 21.

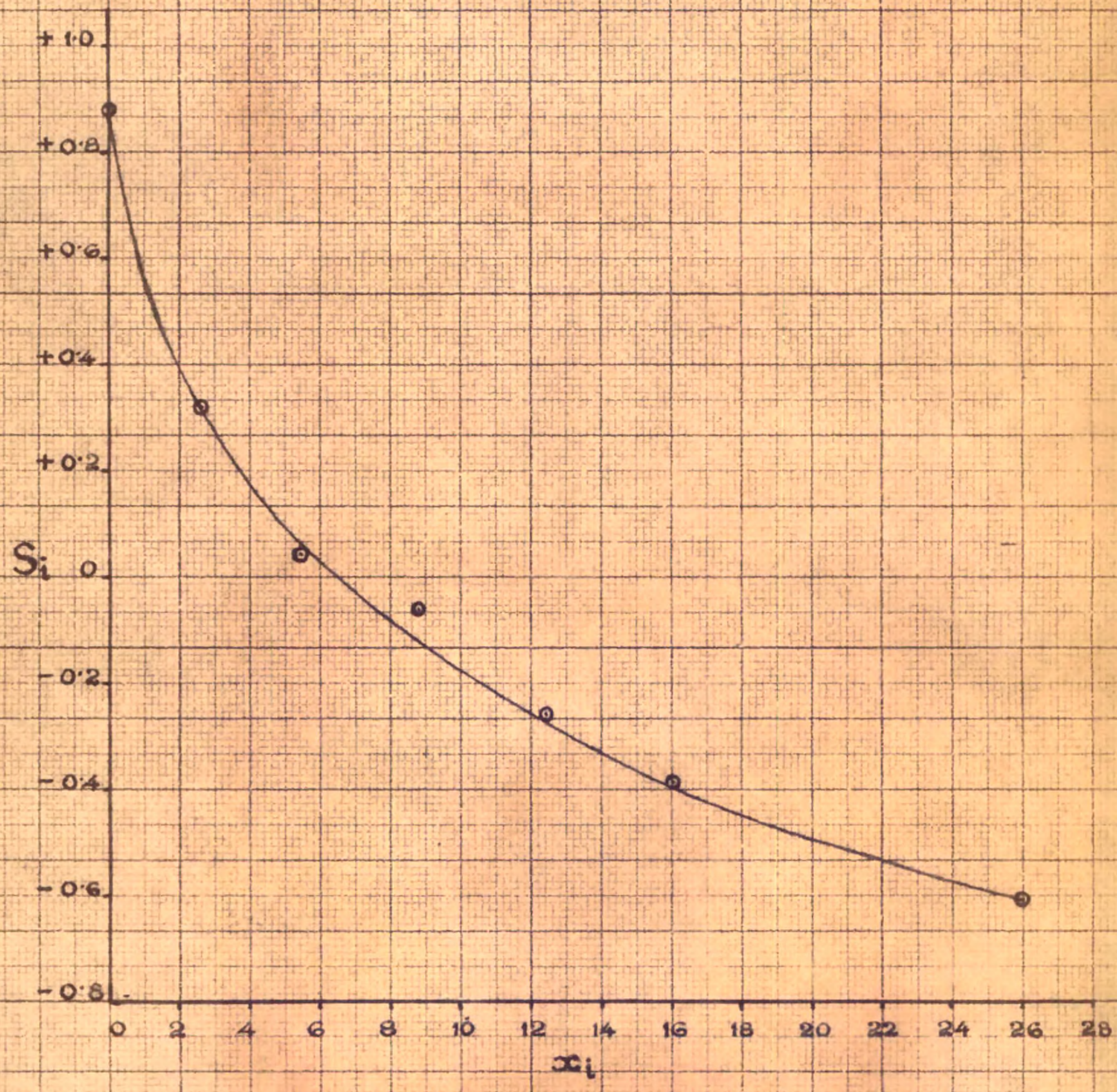

FIG. 23.

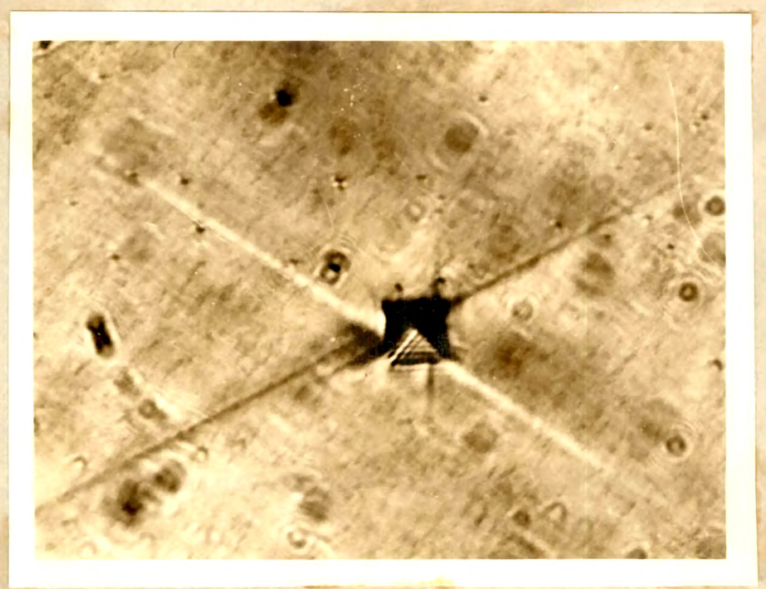

Fig. 24 X 450

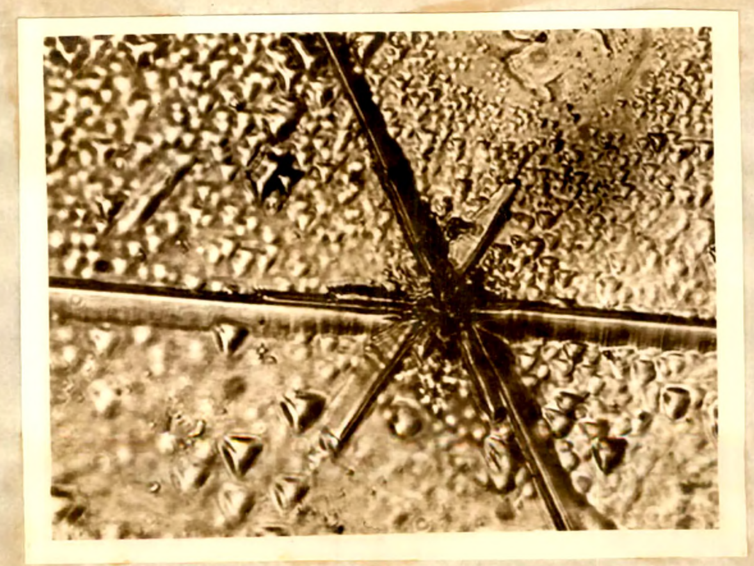

Fig. 25 X 540

the brittleness of the metal. However, with a view to find whether the fresh dislocations produced by deformation can be revealed by etching, indentation of the crystal surfaces using the diamond pyramidal indentor has been done. Fig. 24 shows an indented surface showing the twin bands from the indent mark. The etching of this surface is done and is shown in Fig. 25. A large number of pits around the indentation is observed showing thereby that fresh dislocations can also be revealed by etching. Results are again similar to those observed on bismuth[36].

CONCLUSIONS:

The following conclusions can be drawn from the results presented above:

(1) Judging from the matching of cleavage counterparts, distribution along pile-ups, low angle boundaries, etc., etch pits can reasonably be attributed to dislocations.

(2) However, there is no doubt that etch pits are occassionally nucleated at other sites also.

(3) While the results agree well with many of the earlier workers, there are instances of disagreement also.

(4) This suggests that etching is sensitive to the purity of the metal, reagents and the composition of etch.

(5) No etch spirals have been observed.

(6) Fresh dislocations can also be revealed by etch method.

(7) The reagents produce pits only on the cleavage plane and cannot be used for other planes.

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