# CHAPTER VIII

## A DETAILED STUDY OF THE ETCH PHENOMENA IN ZINC SINGLE CRYSTALS

The techniques of etching to study dislocations has been used widely in zinc single crystals by various authors. A large number of reagents have been developed for this purpose. The easy methods of growing single crystals, the availability of the metal in sufficiently pure form and the existence of a perfect basal cleavage offer many advantages in this metal to study the dislocations. A brief report of the work done in this field has already been presented in chaptef III. The inconsistency of the results, and the contradictory views of the various workers have provoked the interest of the present author, in the study of the etch phenomena in this metal. These will be outlined briefly with the relevant references before the results are presented.

The early reports of Abodu[1] and Meleka[2] do not mention the plane of the observation. However from the nature of the results it is apparent that these are the cylindrical surfaces of the crystal. The pits do not have any definite shape and hence no information of the plane can be obtained from these also. The etch figures observed by Meleka using 0.1% iodine has been attributed to oriented precipites of salts formed by the reaction by Stepenov and Urusokaya[3]. Recent studies of Rosenbaum and Saffren[4] with 0.1% - 1.0% iodine in alcohol on the basal plane have failed to produce pits attributable

to dislocations even after several minutes of etching. Kosevich and Soldatov[5] hold the view that these oriented precipitates, square or rectangular in shape are distributed more densely in regions which are deformed and can be used for a qualitative study of the distribution of plastic deformation. Other reagents, according to the authors, which produce oriented precipitates are weak solutions (0.1%) of nitric acid and sulphuric acid in alcohol and 1% aqueous solution of ammonium persulphate and these solutions are not useful in locating individual dislocations.

Servi[6] using a reagent consisting of 200 gms $CrO_3$, 15 grms $Na_2SO_4$, 50 c.c Conc $HNO_3$ made up to 1000 c.c with water, has observed on a face nearly parallel to the basal plane several complex spirals after etching for 1 hour and has attributed them to screw dislocations. Their observations have been interpreted by Frank and Vreeland[7] Damiano and Hermon[8], using 32 grms of $CrO_3$ and 10 grms $Na_2SO_4$ in 1000 c.c of water, have also observed loops and spiral pattern on a face nearly parallel to the basal plane and have suggested the presence of screw dislocations and Frank-Read sources. In both the cases the steps are large, about a micron. Using the same reagent Gilman[9] observed on cast specimens and monocrystals, various patterns such as low angle tilt boundaries, complex boundaries, pile-ups, etc. attributable to edge

dislocations; but no spirals or closed loops are reported by him. Kosevich and Soldatov[5] state that the formation of spiral pattern is evidently due to the etching kinetics and has little to do with the dislocation structure. Spiral pattern have been reported using CP-4 as well as during electrolytic polishing of zinc.

If the contention of Kosevich and Soldatov is correct, one has to look for other reasons for the formation of etch spirals. One such suggestion has been put forward by Lang[10]. When the surface makes a small angle with the close-packed planes a small mistake in the early stages of step formation resulting from the periodic bunching of atomic sheets will lead to a continuous spiral without the presence of dislocation. Whereas Gilman has studied the basal plane, other authors have studied the surfaces nearly parallel to this plane and hence it is possible that such spirals can be formed. Howfar can this apply to the polygonal spirals, is not known. However the discrepancy is quite significant.

Another important question is whether it is necessary to decorate the crystal to reveal dislocations or not. In the earlier work of Gilman[9] about 0.1% cadmium was added to decorate the dislocations. Damiano and Hermon have used both the pure metal as well as metal containing 0.1% cadmium and there is no difference in the pattern. Results of Rosenbaum and Saffren[4]

suggest that at least in case of screw dislocation terminating in the basal plane, decoration is not required.

The present work was taken up with a view to study in detail etching of the metal using all reagents reported previously, so that an assessment of the merits of the various reagents would be possible. Another factor of interest is the capacity of a particular reagent to reveal dislocations in planes other than the basal plane so that an estimate of isotropy of density and distribution of etch pits in the various crystallographic planes can be made. No attempt is made to develop any new reagent. However, a solution of Tartaric acid has been tried to develop a slow etchant, with some success, so that the effect of temperature and rotation of the etchant on the nature of the pits can be studied.

In such a study frequent polishing of the specimens will be required to study the repetition of the etch pattern. Three reagents have been used according to convenience. A solution consisting of chromic acid, combined variously with other acids has been used by various workers to polish zinc specimens. One such combination was used in the present study, consisting of 20 grms of $CrO_3$, 5 c.c. of $HNO_3$ and 1.5 grms $Na_2SO_4$ in 100 c.c of water. The solution was stirred vigourously during the polishing. The polishing action varied among the crystallographic planes and was

poor along the basal plane. The reagent was best suited for the $(10\bar{1}0)$ plane. Twin bands were not removed by this reagent and occasionally a thin brown film remained on the surface. To remove this a reagent consisting of equal parts of $HNO_3$, $H_2O_2$, and ethenol was used. The solution was taken in a cotton swab and rubbed briskly over the surface and washed with running water. This procedure gives a bright surface free from markings. Another reagent used for polishing is a mixture of 4 parts saturated Tartaric acid solution and 1 part $HNO_3$ which was also equally effective. The various etching reagents used in this study is given in Table VIII-1. Each etchant has been assigned a symbol which is used in the text for convenience.

On a freshly cleaved surface etchant A gives small pits having the hexagonal prism shape and distributed at random. The concentration was varied from 0.05% to 0.3% of Iodine in ethenol. Good pits are observed at low concentration. At higher concentrations the surface gets corroded. These pits increase in size on increasing the etching time. The number of etch pits remain constant. In addition to these pits dark precipitates, square or rectangular in shape, could also be observed at points of stress concentration. These precipitates could be removed by boiling the specimen in distilled water. The precipitates align themselves along the body of the twin lamellae, as shown in fig.VIII-1 and other regions of stress concentration. Obviously these are the

TABLE VIII-1

LIST OF ETCHING REAGENTS

| Reagent Symbol | Authors | Composition | Reference in Text |
|---|---|---|---|
| A | Meleka A.H.A. | 0.1% iodine in Ethenol | 2 |
| B | Abodu A.H. | 20% $CrO_3$ in Water | 1 |
| C | Servi I.S. | 20 grms $CrO_3$ + 15 grms $Na_2SO_4$+5 c.c. $HNO_3$. Solution made up to 100 c.c with $H_2O$ | 6 |
| D | Gilman J.J. also Damiano V & Hermon M. | 32 grms $CrO_3$+ 10 grms $Na_2SO_4$+ 100 c.c $H_2O$ | 9,8 |
| E | Pandya N.S. & Shah C.J. | Acetic Acid | 11 |
| F | - | 1% Ammonium persulphate in water | 5 |
| G | Kosevich V.M. & Soldatov V.P. | 2-5% Fuming HCl in $CH_3COOH$ | 5 |
| H | Rosenbaum H.S. & Soffren M.M. | Chlorine bubbled through Ethenol | 4 |
| I. | " | 1 part Bromine in 5 parts Ethenol | 4 |
| J | " | HCl (0.2-0.6 M) in Ethenol | 4 |
| K | " | HI (0.2-0.6 M) in Ethenol | 4 |
| L | " | HBr (0.2-0.6 M) in Ethenol | 4 |
| M | - | 1-3 parts Tartaric acid in 10 parts water | - |

TABLE VIII-1 (CONTD.)

| Reagent Symbol | Authors | Composition | Reference in Text |
|---|---|---|---|
| CP-4 | U.S.Patent | 3 parts HF+3 parts $CH_3COOH$+5 parts $HNO_3$(F)+1 part $Br_2$ | - |
| Superoxol | H.C.Theuerer U.S.Patent 2542727 | 1 part HF+1 part $H_2O_2$(30%)+4 parts $H_2O$ | 14 |

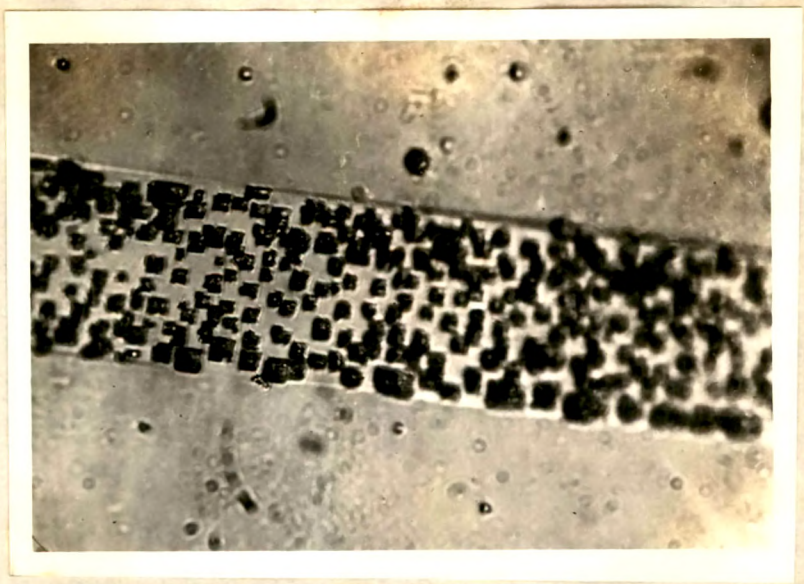

Fig. VIII -1 X 360

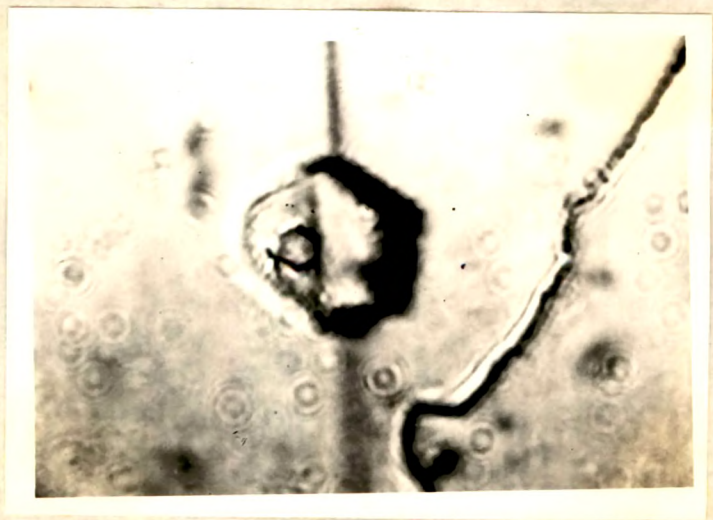

Fig. VIII -2 X 950

precipitates referred to by Stepenov and others[3,5]. The hexagonal pits are not discussed by these authors. In some cases, a small hexagon was seen at the bottom of a large hexagon. The shape of the outer hexagon and the presence of small one inside suggest that the etching is proceeding along a line inclined to the surface. Photographs were taken with light profiles and the depth of the pit 'd' measured. The inner and outer hexagons were eccentric and the eccentricity 'a' also measured. If the pits were assumed to be due to dislocations - and we have every reason to believe so - then the inclination of the dislocation line can be calculated using the formula $\tan \theta = d/a$. Strangely enough, three pits were observed on the same surface, all of them inclined at about $36^{\circ}$ to the surface. It was decided to investigate whether this was of any significance, and various specimens were tried, grown at different rate. The results were negative, though in some cases dislocation lines inclined at angles $6^{\circ}$ to $8^{\circ}$ were observed. The inclination of the dislocation is not of any special significance as it was anticepitated in the early observations[12].

Another interesting feature observed was the etching of twin bands. Along one edge of the bands, which are not accompanied by accommodation bends, a series of etch pits having a half-hexagonal shape could be observed. These pits tend to group in pairs as can be seen from fig.VIII-3.

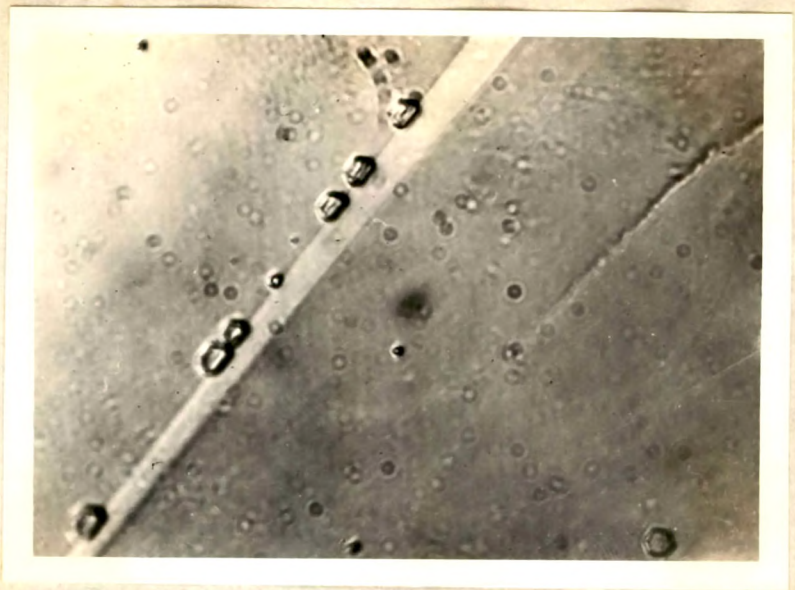

Fig. VIII -3 X 360

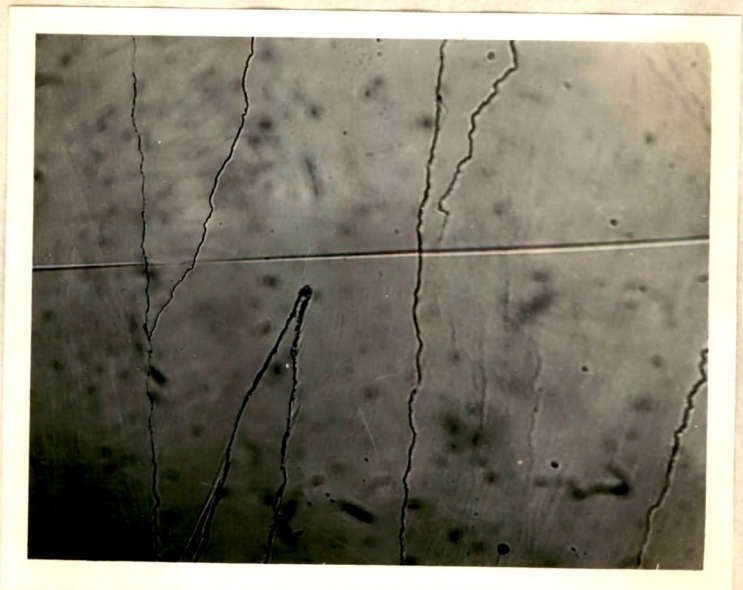

Fig. VIII -4 X 170

The peculiar shape is due to heavy distortion of the surface at the band-edge. The production in pairs suggests that they are the intersecting points of the dislocation loops on the surface etch pits are seen only on one edge of the twin band and suggest that this may be associated with the dislocation while the other edge is a simple bending of the basal plane. These observations indicate that iodine is capable of revealing dislocations by etch pits.

However, the fundamental question, as to whether all dislocations are revealed by this reagent, still remains unanswered. The observed etch pit density in the specimen is $\simeq 10^4/cm^2$, which is too low indicating that all dislocations are not revealed. It has already been mentioned that, in general, correspondence between the surface features was not always perfect and probably because of this, one to one correspondence between etch pits on the two counterparts did not exist. However, in regions where the cleavage counterparts show perfect matching one to one correspondence between etch pits could be observed. While this leaves no doubt that etch pits are dislocation sites, it appears that all dislocations do not produce etch pits.

To study the features in further detail, a speciment which was etched with reagent A was re-etched for about 8 seconds in reagent K. A large increase in the number of etch pits was observed. The features are shown in figs VIII-4,

Fig. VIII -5 X 170

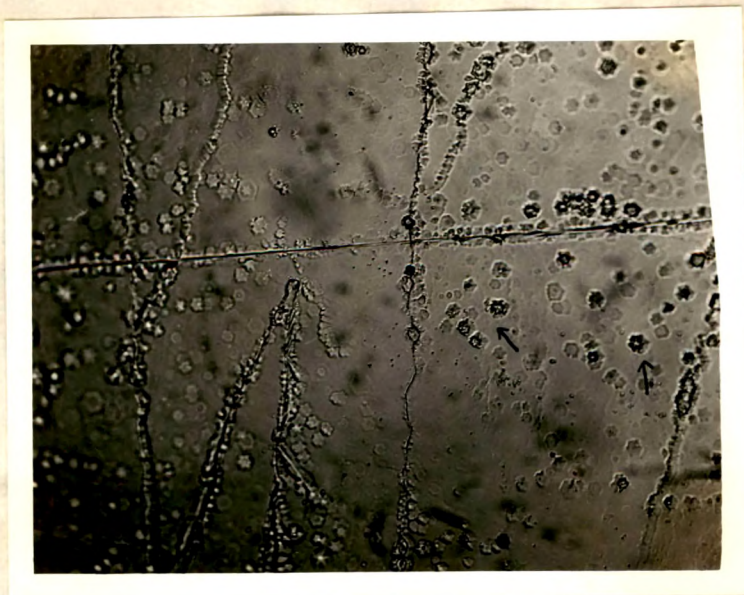

Fig. VIII -6 X 170

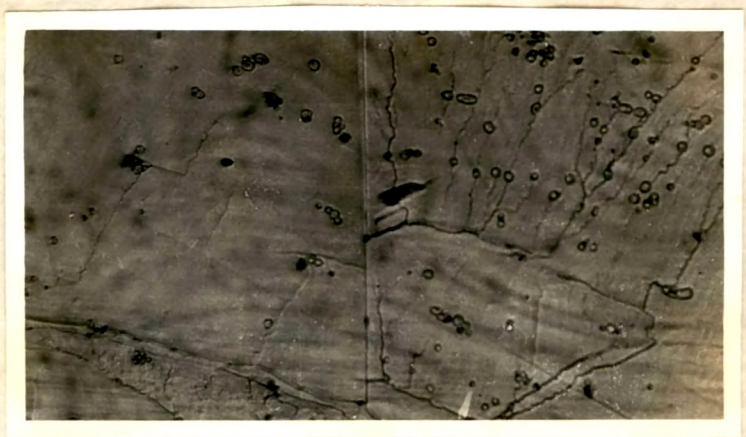

Fig. VIII -7 X 170

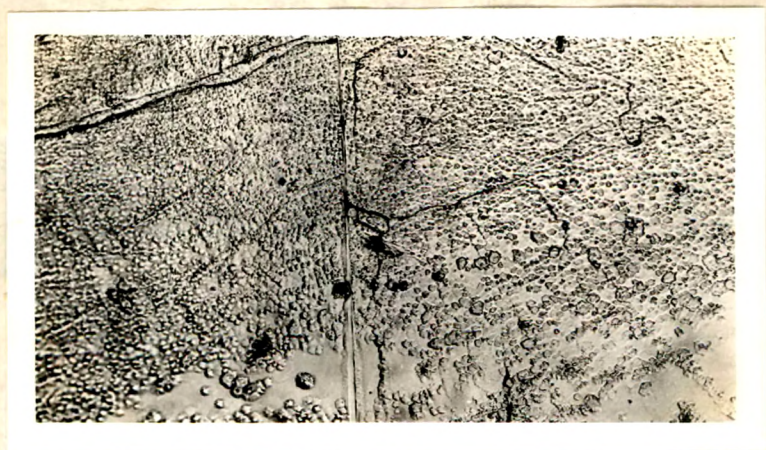

Fig. VIII -8 X 170

VIII-5 and VIII-6. Fig.VIII-4 shows a cleavage lines and the tip of a narrow twin band. The surface after etching with reagent A for 5 seconds is shown in fig.VIII-5. A few pits are developed. The pits are hexagonal and flat bottomed. The same surface after etching in reagent K is shown in fig.VIII-6. A ten-fold increase in the etch pit density can be observed. The pits are hexagonal but point, bottomed. The pits revealed by iodine are over etched, enlarged in size and take the shape of truncated hexagonal pyramids. Some of these corresponding pits in the two cases are shown by arrows in figs VIII-5 and VIII-6. Two cleavage counterparts were taken, one etched in iodine and the other parts in HI. The results were same and are shown in figs. VIII-7 and 8. In this case also the pits revealed by iodine over etched and take the shape of truncated prism. This indicate that the initial etching with iodine in the previous case is not responsible for the different shape of the pits and it is the property of the defects at these points and probably due to the large free energy at these points. This view is supported by the fact that pits are produced along twin bands which is also a region of stress concentration. It is quite probable that impurities also are responsible for this. HI being an unstable compound the energy of the reagent is more and hence this can reveal all dislocations. No distinction between the edge and screw dislocations is possible with the present results. If the views of Amelinckx, Votava, Pratt and others that the screw dislocations produce

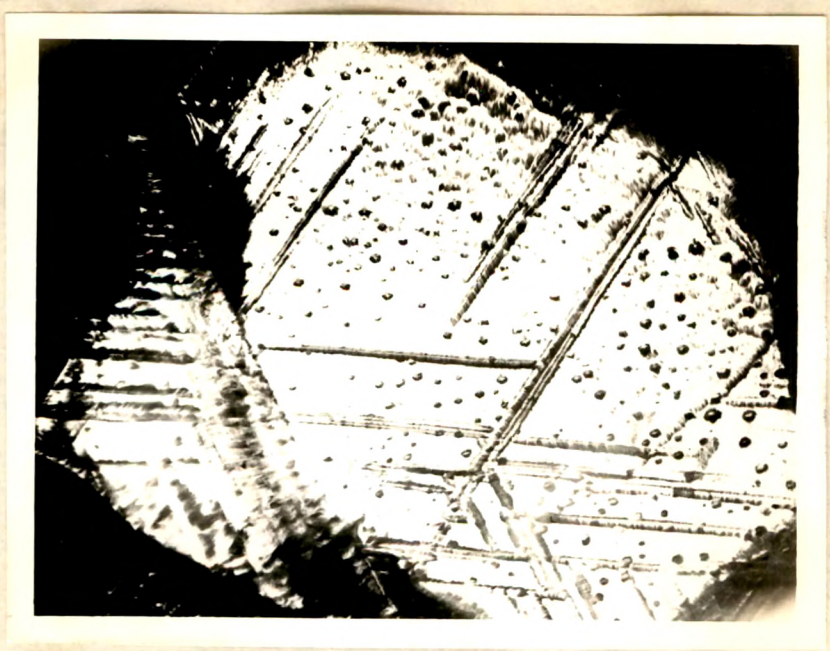

Fig. VIII -9 X 90

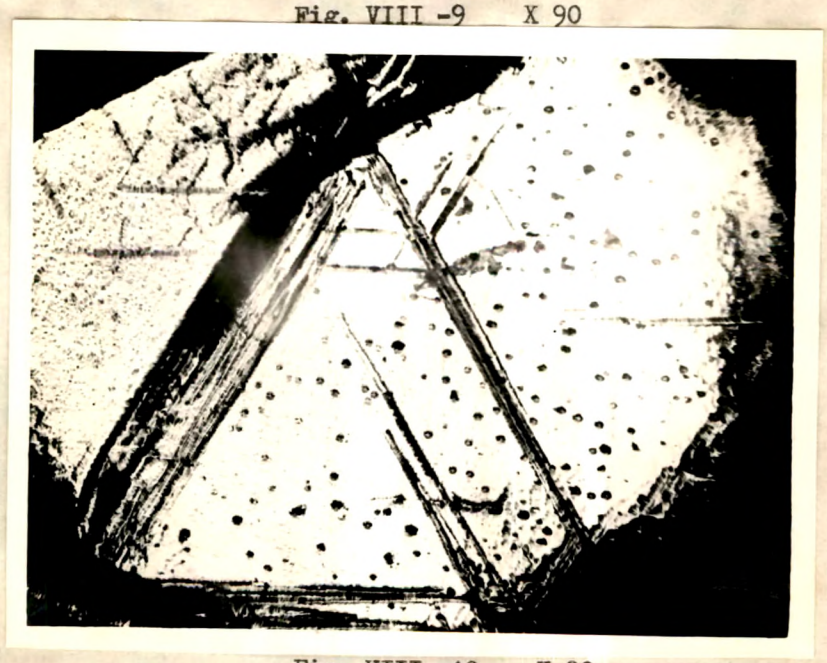

Fig. VIII -10 X 90

cleavage step one can identify the dislocations revealed in fig.VIII-7 using iodine, arranged along the cleavage line as screw dislocations. Gilman[13] has obtained evidence in support of this view. However, examination of fig.VIII-5 and VIII-6 show that all the screw dislocation also are not revealed using iodine as etchant. The only conclusion that can be derived from this experiment is that reagent A reveals only those dislocations which have an extra free energy on the surface.

Reagents B,C,D were tried on the basal plane from 1 second to 1 hour. No spirals could be observed on any of the specimen. Small pits distributed at random could be seen. The density of etch pits is quite low. Fig.VIII-9 and VIII-10 show two cleavage counterparts etched in Gilmans reagent for about 20 minites. The matching is not perfect though correspondence exists in many cases. The pits do not have any particular shape. A brownish precipitate settles on the surface of the specimen. To remove such precipitates it is necessary to dip the specimen in a solution containing $HNO_3$ & $H_2O_2$ for a second and rinse it in distilled water. The purity of the metal was 99.995%. A crystal containing 0,1% cadmium shows pattern similar to those obtained by Gilman and an increased etch pit density. Etching with servi's reagent for 1 hour with continuous rotation of the solution during the process gives an etching pattern which could be identified as the elongated cell structure

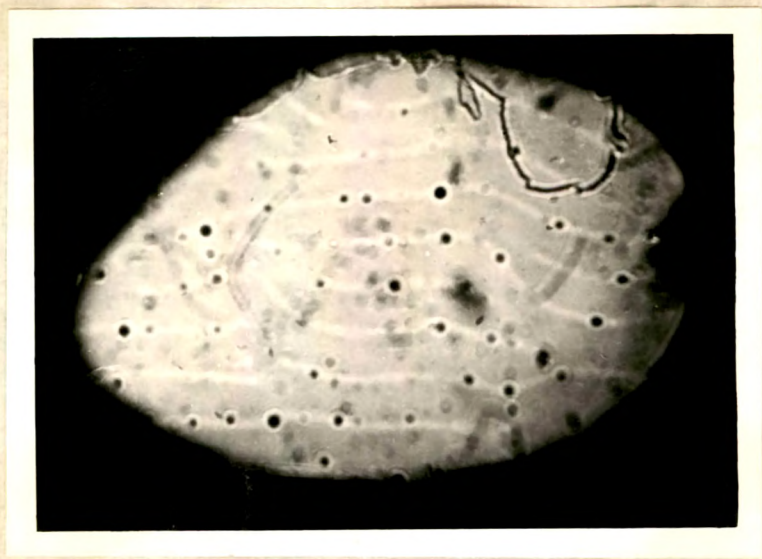

Fig. VIII -11 X 10

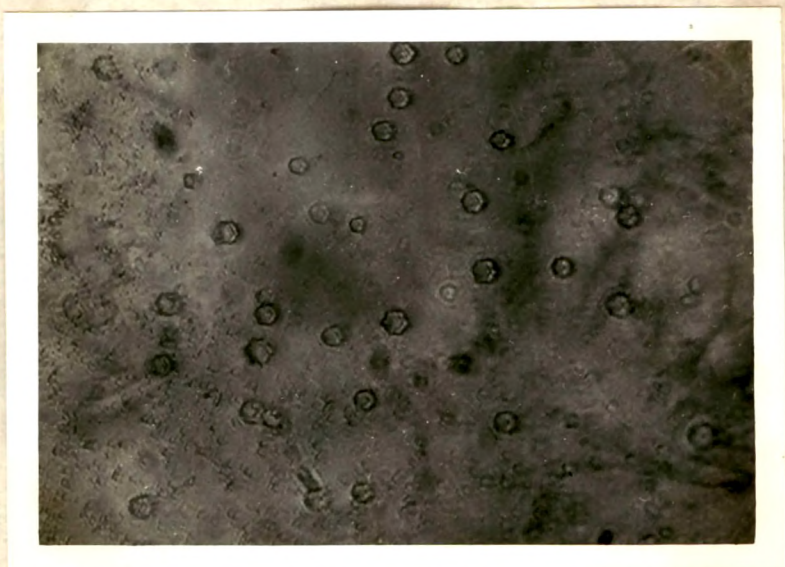

Fig. VIII -12 X 360

Fig. VIII -13 X 360

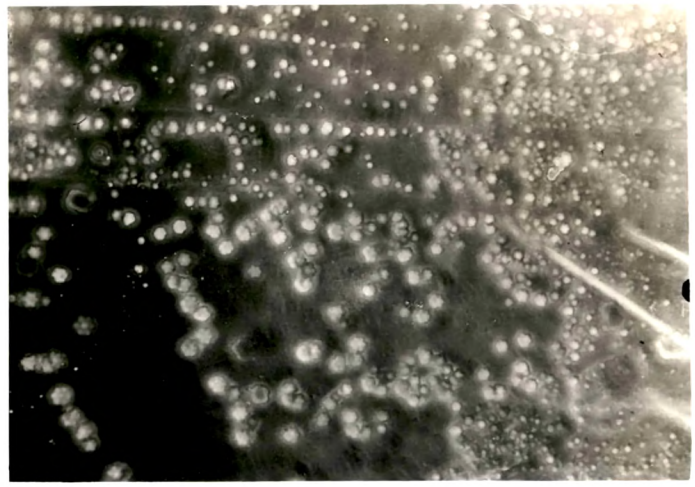

Fig. VIII -14 X 360

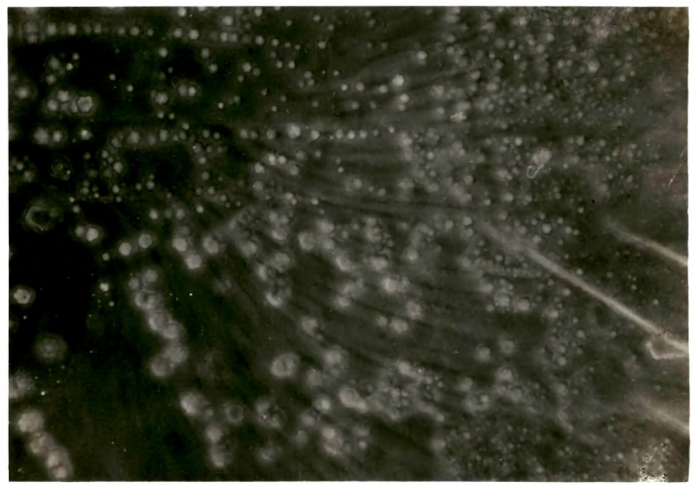

Fig. VIII -15 X 360

discussed in chapter VII. Fig.VIII-11 shows such a crystal. In this case, if the specimen is quickly transferred from the solution to water no colouration remains on the surface. It is well known that cell boundaries are region of high solute concentration and since pits are formed at these boundaries they are dislocations which have been migrated towards the cell boundaries and hence decorated. The general conclusion drawn from this is since none of the reagents have revealed spirals or similar features, they are very sensitive to the surface treatment prior to etching and to the small changes in orientation of the surface.

Etching with reagent F also produces results similar to these of iodine in ethenol. The etchant produces pits along the edges of the twin bands and oriented precipitates on the body of the twin band. A few hexagonal pits distributed at random could also be observed as shown in fig.VIII-12. Fig.VIII-13 shows a twin band after etching.

Etching with reagent G developed by Kosevich and Soldatov gives good results. One of the remarkable qualities of this reagent is the reproduction of the pits after chemical polishing. Fig.VIII-14 shows a region on the basal plane after etching for 2 seconds. The specimen was chemically polished and re-etched for 2 seconds. The resulting surface is shown in fig.VIII-15. Except for the polishing marks there is

striking repetition of the pattern. However, contrary to the observations of Kosevich and Soldatov the pits have regular hexagonal shape with point bottom as can be seen from figure VIII-14. However the depth of the pits is quite small and hence phase contrast pictures are taken. Longer times of etching cannot be used since the surface is corroded. The definition of the shape is lost as the polishing and etching are repeated. On a cleavage counterpart with perfect matching of the surface features one-to-one correspondence between etch pits is obtained. This is seen from fig.VIII-16 which is a phase contrast photograph of the matching counterparts of a region where a twin band terminate giving rise to concentration of dislocation and formation of cleavage steps. The observed etch pit density is $10^5$-$10^6$ $cm^{-2}$ which is the expected value for the crystal. That these pits are due to dislocations could be established from the following characteristics: (1) The number of etch pits do not depend on time of etching (2) On polishing the specimen and re-etching the pattern repeats (3) Etch pattern on the cleavage counterparts were symmetrical in a mirror image fashion (4) Etch pit density and distribution agreed with the theoritical estimate. This reagent therefore, offers a definite advantage over many of the other reagents mentioned above. The observed results agree well with those of Kosevich and Soldatov except in that the pits are hexagonal pyramids in shape.

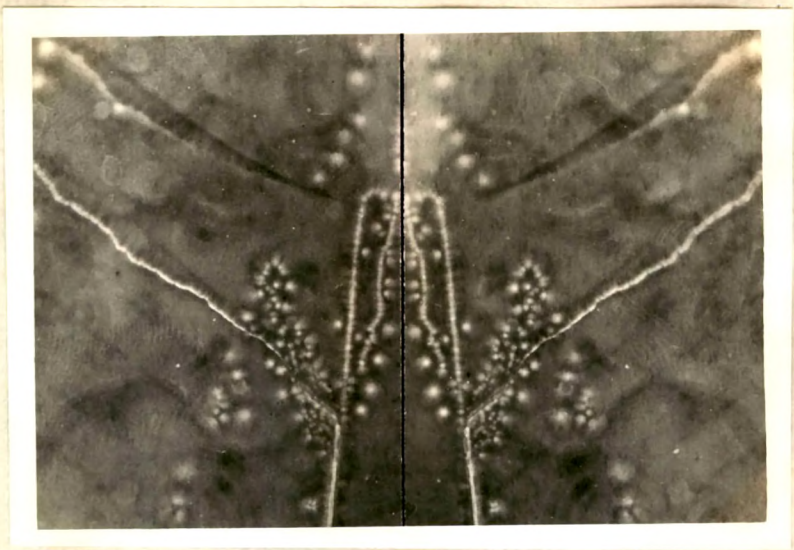

Fig. VIII -16 X 360

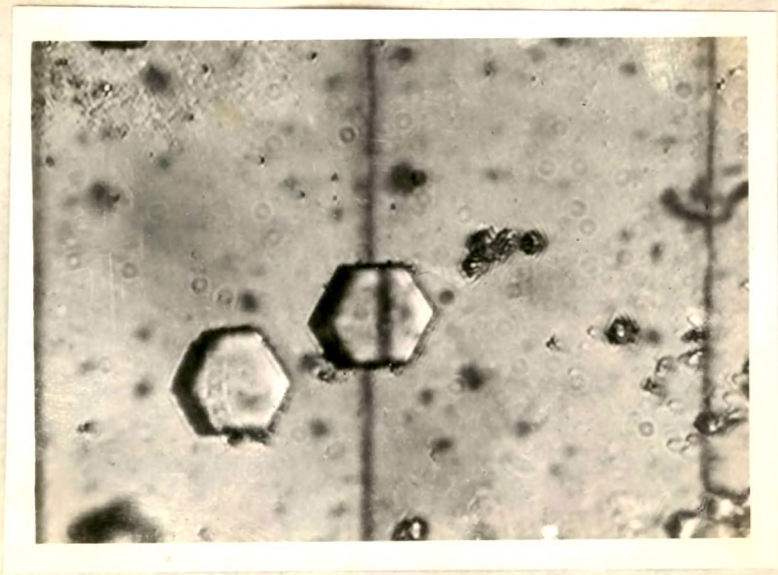

Fig. VIII -17 X 950

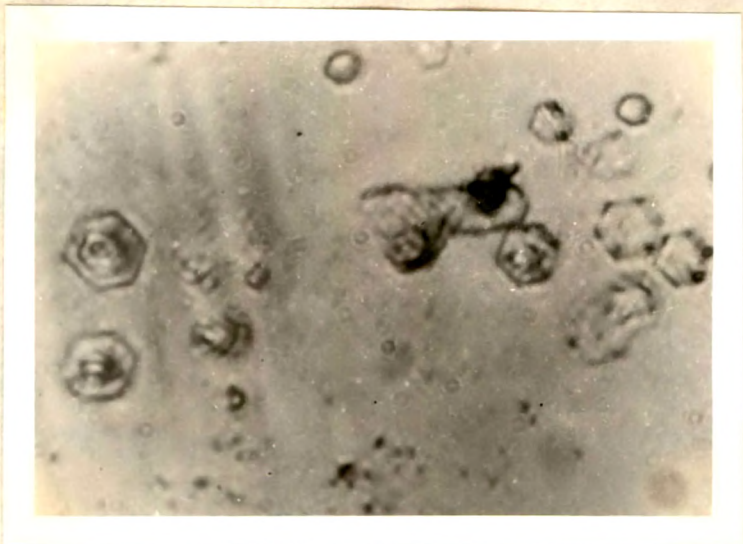

Fig. VIII -18 X360

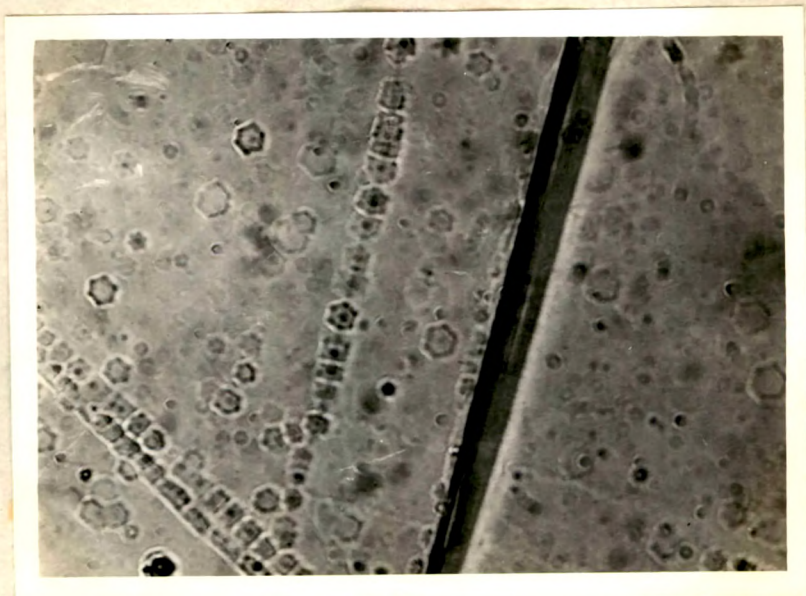

Fig. VIII -19 X 170

Etching with reagent E has been reported by Pandya and Shah[11]. Etch pits produced by this reagent are large but the surface soon gets spoiled and the pits lose their definition due to the insoluble precipitates settling on the surface. The pit density is small compared to the reagent G and the results indicate that the addition of a small amount of HCl to this greatly modifies the density and distribution of the pits.

George[14] has studied the etch pattern in zinc crystals grown from vapour. Star shaped terraced pits as well as etch pattern suggestive of growth from Frank-Read source has been observed. The present author has observed pits which are hexagonal prisms. For longer periods of etching the pits show some fine structure inside the crystal. Fig.VIII-17 shows an etch pit with light profiles running across. Fig.VIII-18 shows the inner details of some pits. Concentric hexagons suggestive of stepped structure can be seen. The observations have failed to record any spirals.

Rosenbaum and Saffren have studied the dislocation etch pits produced by Halogens and their acids dissolved in various organic solvents. The results of the studies on non basal slip and polygonization after annealing a bent crystal suggest that the screw dislocations can be revealed by etching without deliberate solute decoration. As regards edge dislocations no conclusion could be made. The present

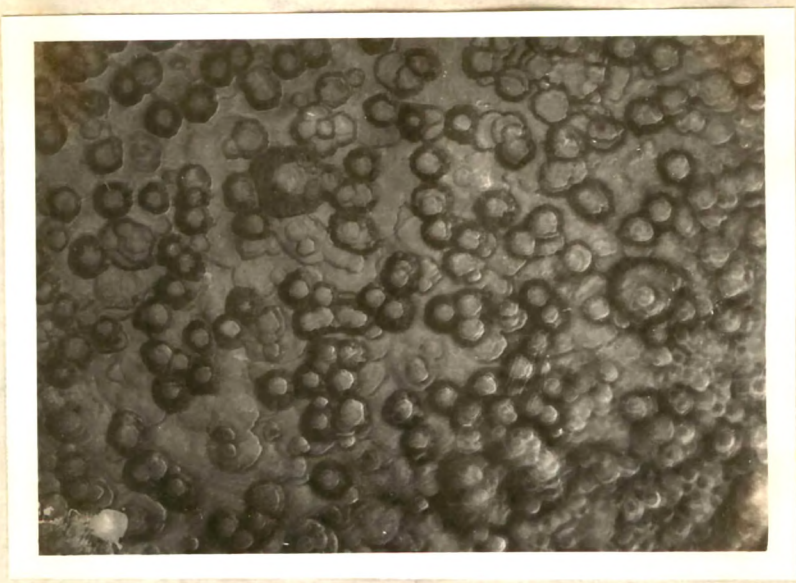

Fig. VIII -20 X 176

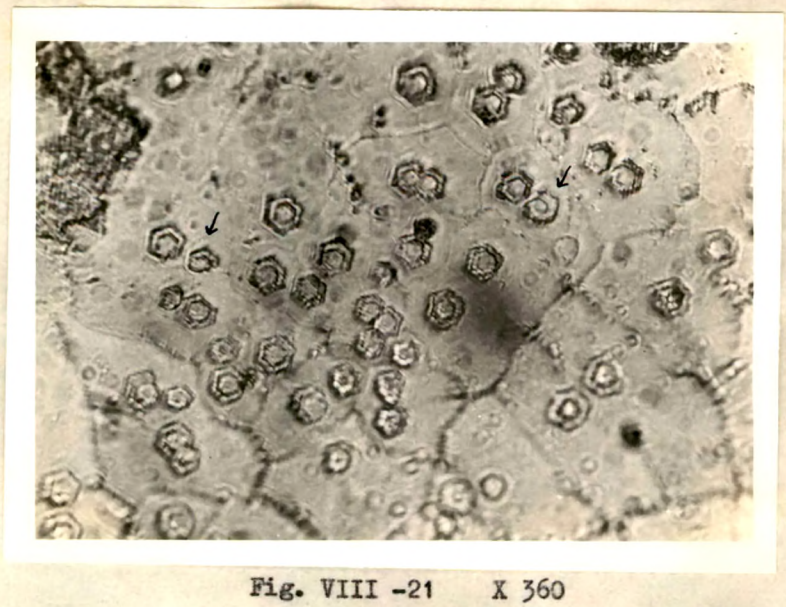

Fig. VIII -21 X 360

author has also studied in detail the etching of dislocations by these reagents. Methenol and Ethenol have been used as solvents. There is a general agreement between the present results and these of Rosenbaum and Saffren. However, some peculiar features have also been observed and these will be discussed here. Fig.VIII-19 shows etch pits aligned along the bend plane associated with the twin lamella after etching with reagent K. The pits are hexagonal pyramids. These may be sites of edge dislocation. The other features have already been discussed. Reagent H and J produce pits with their edges along $\langle 10\bar{1}0 \rangle$ direction as observed by Rosenbaum and Saffren. With longer times of etching the hexagon are rounded and when over-etched the surface gives the appearance as shown in fig.VIII-20.

Bromine produces three distinct types of pits (1) Point bottomed hexagons (2) Stepped hexagons with flat bottom (3) Star shaped pits. The last two types of pits are shown in figs.VIII-21 and VIII-22. Pits of a particular shape collect together in certain region. Longer etching the star shaped pits grow laterally and inner region of the pits become hexagonal. This pattern is similar to those observed by George and can be attributed to the preferred etching along the $\langle 11\bar{2}0 \rangle$ direction. In some cases pattern appearing as the inner portion of spirals are also observed. These are indicated by arrows in fig.VIII-21. Another important feature

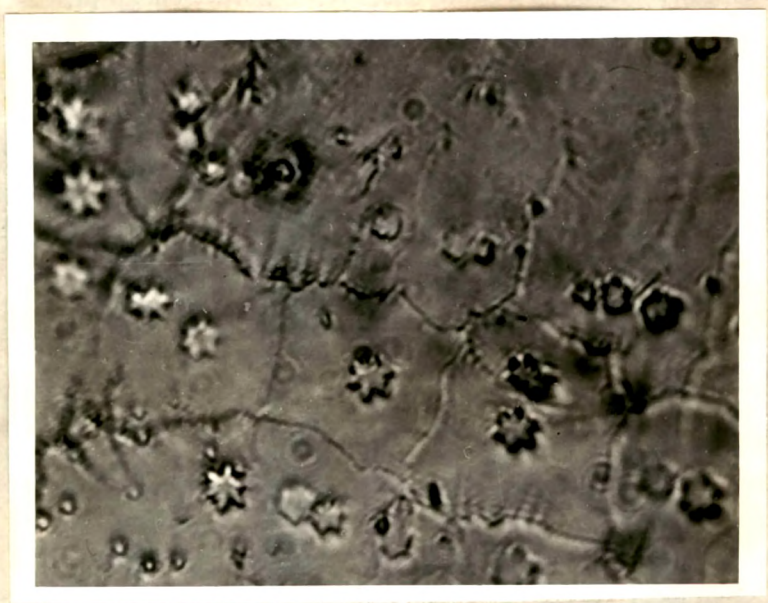

Fig. VIII -22 X 360

Fig. VIII -23 X 170

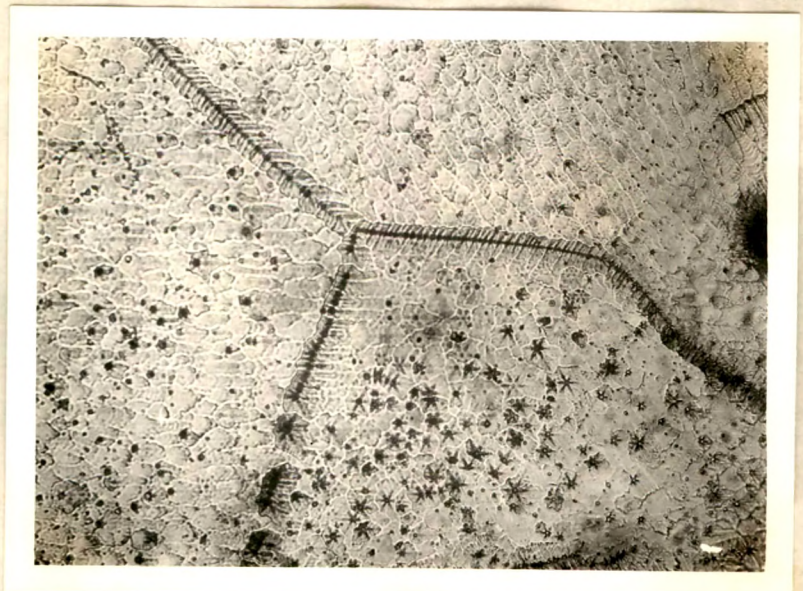

Fig. VIII -24 X 170

observed using bromine is the etch pattern associated with the cellular structure. Along the cell boundaries are seen a descrete set of regularly arranged etch pits shown in figs.VIII-23 and VIII-24. According to Tiller[15] microseggregation of impurities at the interface of a growing crystal can cause local changes in lattice parameters. Thus, in a crystal exibiting cellular structure, the cell boundaries will be rich in solute and hence there will be a change in the lattice parameter in the intercellular region with a resultant stress. This stress will be relieved with the formation of edge dislocation lines for which the dislocation lines are parallel to the columnar axis of the substructure. A cross-grid of dislocations will be formed at right angles to the crystal axis. The etch pits observed along cell boundaries are therefore edge dislocations. The observed pit density agrees well with the theoritical estimate of $10^7$ $cm^{-2}$. It can be seen from fig.VIII-23 and VIII-24 that the shape of etch pits in different cells also change.

When acetic acid is used as solvent the results hav are similar to those obtained with reagent K. The pits are smaller in size and the surface is corroded very easily. However the reagent is very useful when the dislocation density is quite high as in the case of heavily deformed metals. Behaviour of Bromine and HBr are similar.

A general feature of all the reagents made using

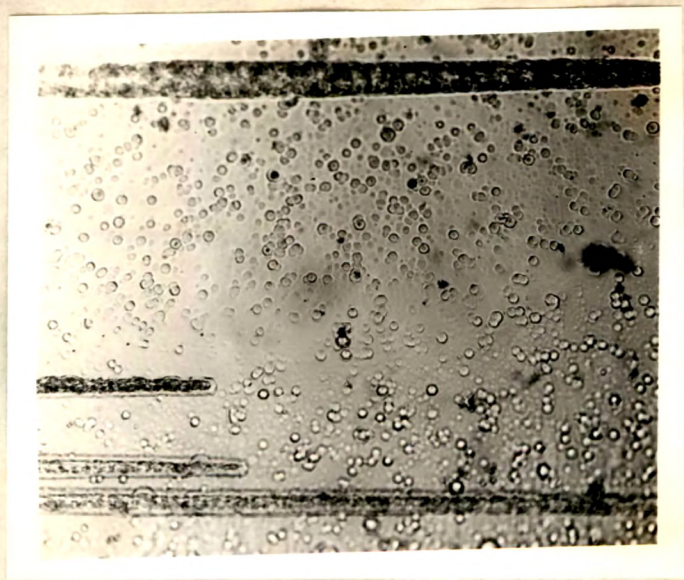

Fig. VIII -25 X 360

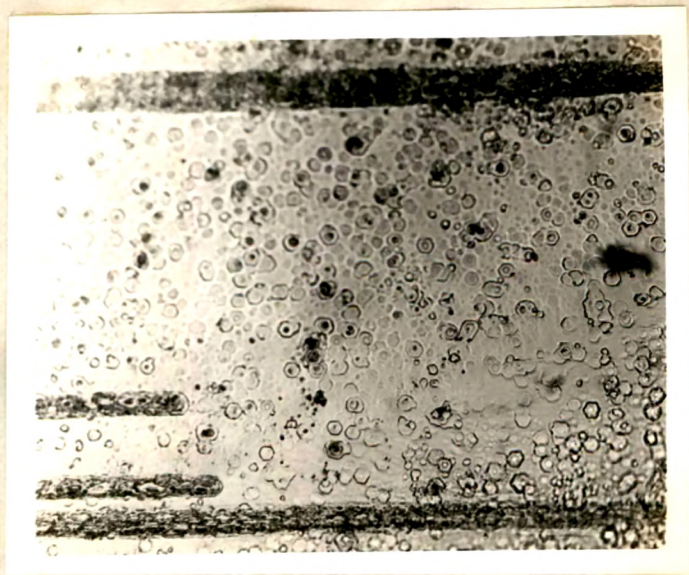

Fig. VIII -26 X 360

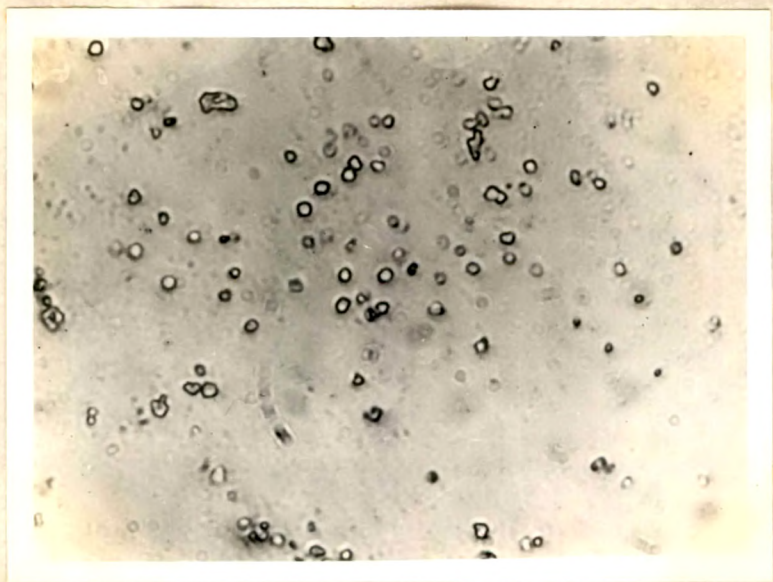

Fig. VIII-27 X 360

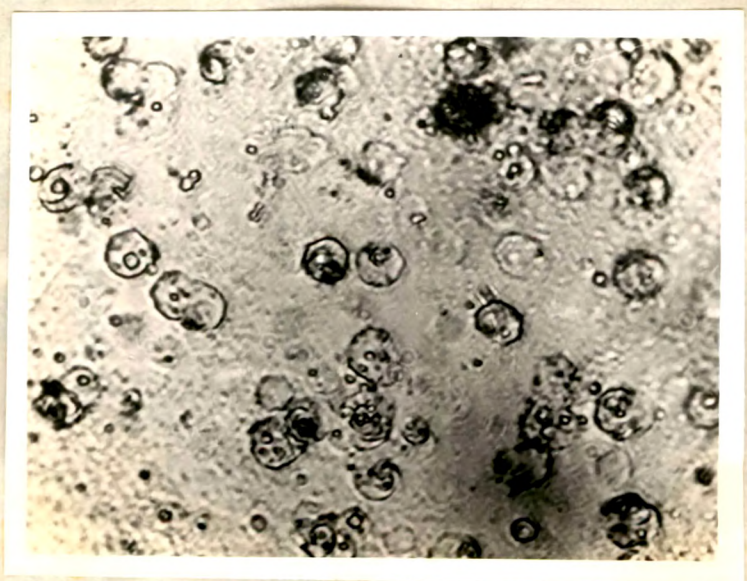

Fig. VIII -28 X 360

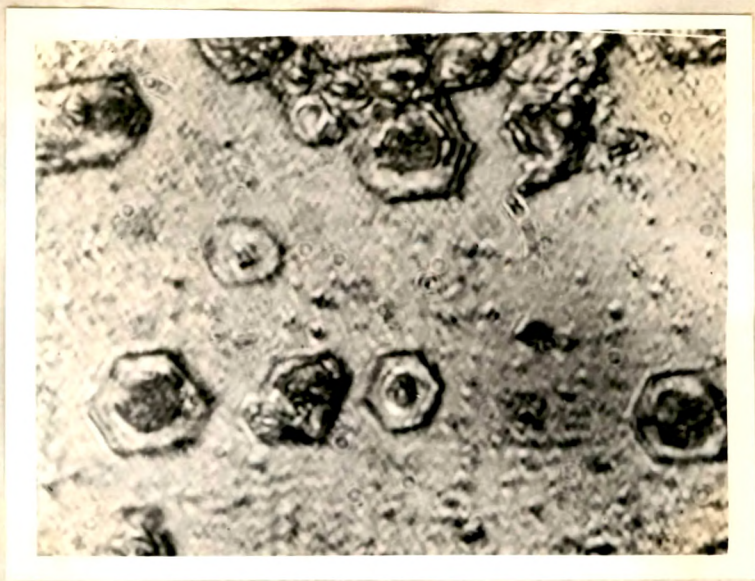

Fig. VIII - 29 X 360

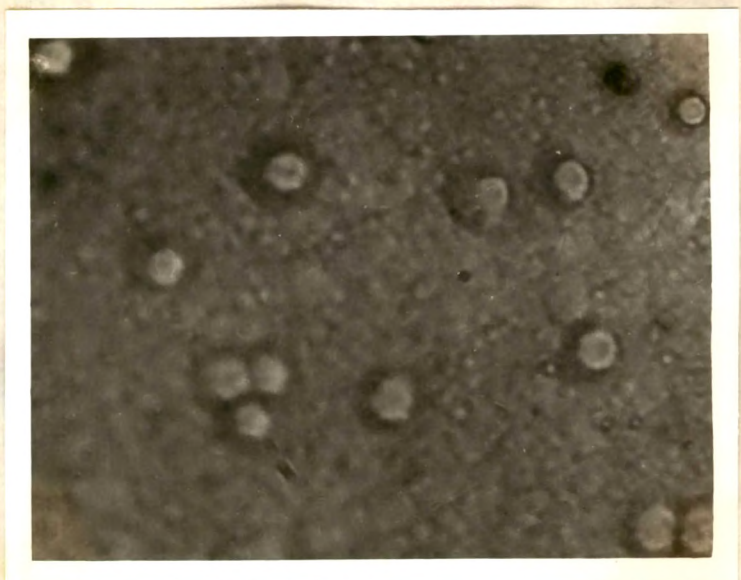

Fig. VIII -30 X 360

halogens and their acids if the solvent contains water, the pit shape tends to be conical and lose their regular hexagonal shape. The surface loses its lustre and is covered by insoluble precipitates. It is therefore necessary to avoid water in these reagents. Results obtained with HF are not encouraging. Etching with CP-4 reagent also produces etch pits having hexagonal shape. The reaction is quite vigorous. The pits obtained after etching for one second is shown in fig.VIII-25. The same region after etching for 2 seconds is shown in fig.VIII-26. The sizes of the pits are increased and pits develop steps as in case of Bromine (fig.VIII-21) but are less regular. This reagent corrodes the surface very easily.

Since the rate of a chemical reaction is very sensitive to the temperature it is worthwhile to study the effect of temperature on the etch pits. For such studies one requires a slow reagent and after some trials about 2-3 parts of saturated solution of tartaric acid in 10 parts of water, was found to be suitable. The etch pits produced at $25^{o}$, $40^{o}$ and $70^{o}C$ are shown in figures VIII-27,VIII-28, and VIII-29. The pits are formed after 3 minutes etching at $25^{o}C$ and $40^{o}C$ while pit size is very large after only 30 seconds of etching at $70^{o}C$ shown in fig.VIII-29. Fig.VIII-30 shows a specimen re-etched at $70^{o}C$ for 30 seconds after polishing where the pits take a circular shape. These observations

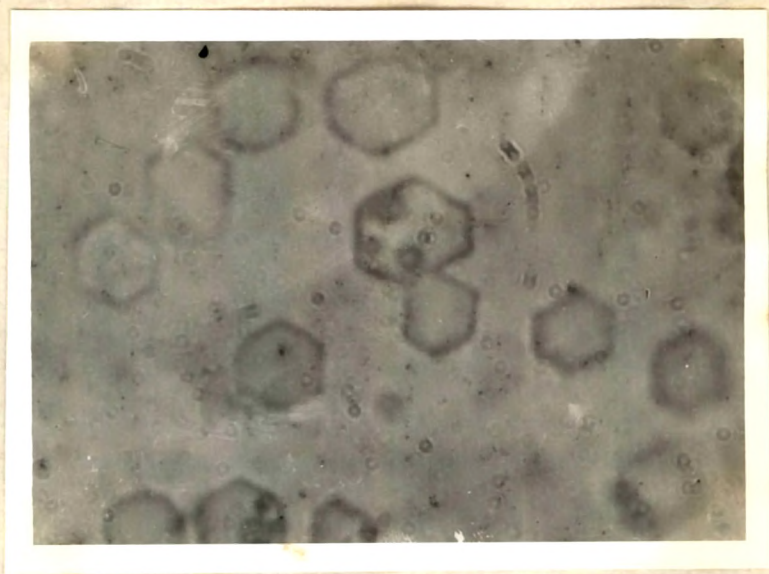

Fig. VIII -31 X 360

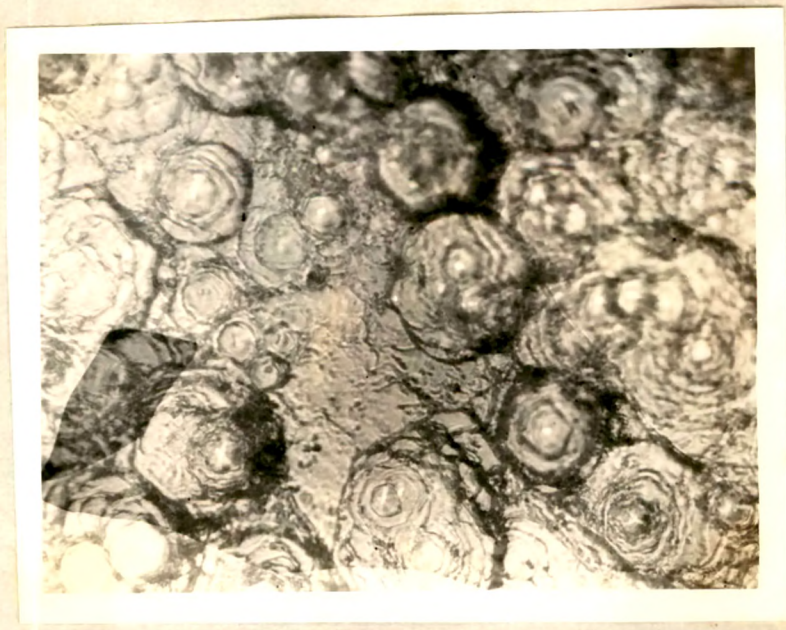

Fig. VIII -32 X 360

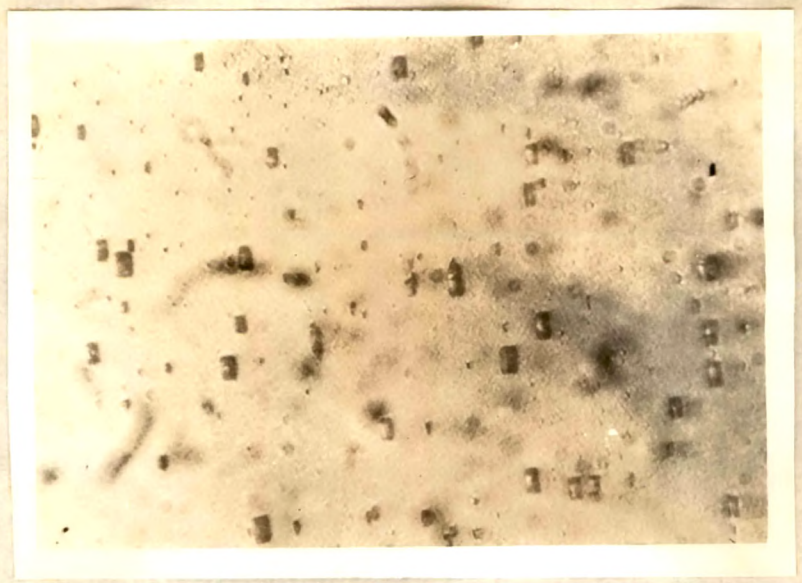

Fig. VIII -33 X 360

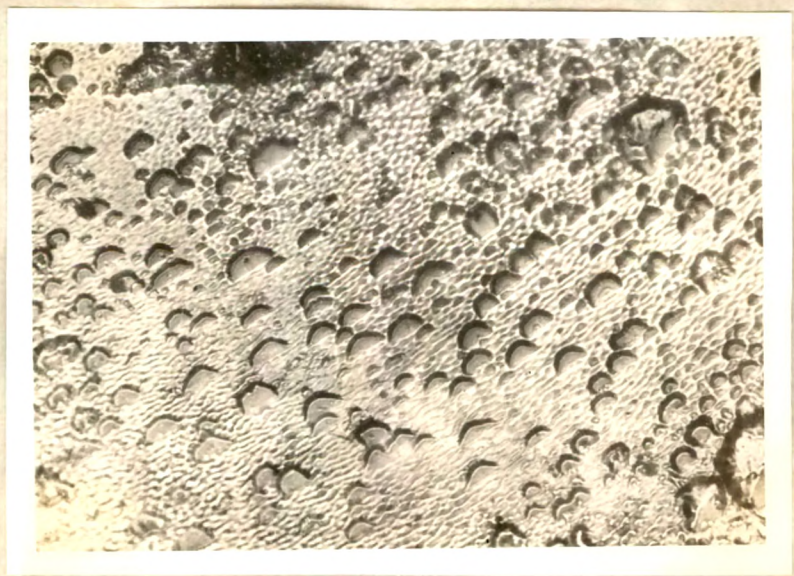

Fig. VIII -34 X 360

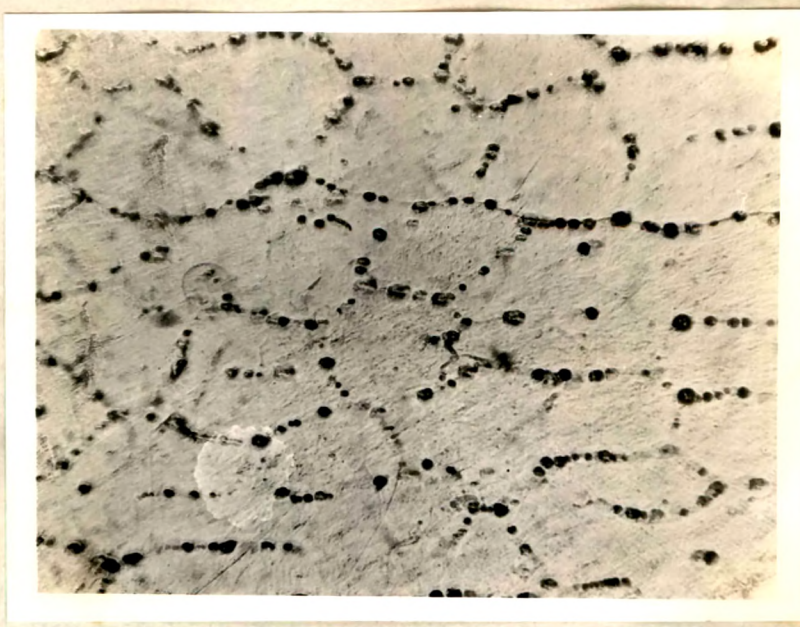

Fig. VIII -35 X 170

signify the profound effect the temperature and nature of the surface has on the etch pits. The state of the reagent is also quite significant. When a solution or the crystal is rotated the resulting pits are larger in size. This can be seen from Fig.VIII-31, where the specimen has been etched at 25°C for 30 seconds in rotating medium. A longer etching time results in an over etched surface shown in fig.VIII-32 which consists of concentric circular figures, Changing to a hexagonal figure in the inner region. It is apparent that the rotation of the liquid results in a more pronounced reaction in the lateral directions than in depth.

Of the numerous reagents used in this study most of them produce pits only on the basal plane. Investigations on the $(10\bar{1}0)$ and $(10\bar{1}2)$ planes using these reagents show that only a few of the reagents are useful. Superoxol produces rectangular pits on the $(10\bar{1}0)$ prism planes and rounded half-hexagonal pits on the $(10\bar{1}2)$ planes. These are shown in figs.VIII-33 and VIII-34. On comparision, it is found that there is no isotropy in the etch pit density and distribution in these planes. The prism plane contains minimum number of etch pits. Fig.VIII-35 is the etch pattern observed along the cell boundaries of a surface perpendicular to the crystal axis. The (0001) plane of this crystal is at 35° to the crystal axis. Individual pits are resolved along the boundaries suggesting that these are the edge dislocations. Servi's reagent and that of Gilman is effective in

the prism planes also, but the etch pits do not have any definite shape and the process requires impurity decoration. None of the reagents prepared using halogens and their acids are effective on planes other than the basal plane.

SUMMARY OF OBSERVATIONS AND CONCLUSIONS:

The results of the study of the etch phenomena may be summarised as follows:

(1) Dislocations can be revealed by etching of the various reagents, mentioned above, without deliberate decoration by solutes.

(2) Etching with iodine in alcohol do not reveal all dislocations.

(3) The pit size and shape is very sensitive to the nature of the etchants, the temperature and also the state of the reagent with respect to the crystals.

(4) The pit size is in general proportional to the pit density being small for high densities and large for low density.

(5) Most of the reagents permit the observation of pits only on the basal plane which is evidently due to the anisotropy in the solubility of the crystal in the reagent.

(6) A few reagents, superoxol for example permit the observation of etch pit on other planes.

(7) There is no isotropy in the etch pit density and distribution in different crystallographic planes.

(8) The results indicate that no differentiation could be made between edge and screw dislocations from the shape of the pits.

(9) No etch spirals have been obtained, though in a few cases a spiral like pattern is seen. It is not known whether the etch spirals correspond to dislocations or not. If they are, they are very sensitive to the small difference in orientation of the crystal.

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