CHAPTER IV

DISLOCATION ETCH TUNNELS, ETCH GROOVES & WHISKERS

The possible mechanisms by which dislocations are formed in crystals grown from the melt have been discussed briefly in the previous chapter. A number of methods exist for the observation of these dislocations in crystals. Chemical etching has been extensively used for revealing the sites of emergence of dislocations in crystals. Due to the simplicity and the reliability of the method much data on dislocations have been obtained with its help. This method, however, has not been largely used for the direct observation of dislocation lines. Recently, successful chemical etching of dislocation lines has been reported in a few cases. Low and Guard (1969) have produced etch grooves in Fe 4% Si in which the dislocations were decorated with carbon. Tyler and Bash (1967) have reported etch grooves in germanium decorated with lithium, whereas Bash (1968) obtained such grooves in pure silicon crystals.

In the work reported in this chapter, the chemical etching of sodium chloride crystals has been carried and normally the usual type of etch pits are observed at the sites of dislocations. However, in a very few cases, subject to certain conditions, etch tunnels have also been observed in sodium chloride single crystals. This chapter reports these, rather rare observations and their possible interpretation.
Fig. 1. Etch tunnels on (100) face of sodium chloride single crystal. (x125)
Experimental

The specimens used were cleaved from 99.9% pure single crystals of sodium chloride procured from the National Physical Laboratory, New Delhi. The etchant used consisted of 1 part of glacial acetic acid and 20 parts of methanol. Distilled water and methyl alcohol were used as the polishing agent. The crystals were later dried either by placing on a filter paper or by blowing a stream of dry air on to them. The observations were made with Reichtets MeF universal camera microscope.

Results and Discussion

It is well known that very good etch pits can be obtained on the surface of sodium chloride crystals. The usual etch pits are pyramidal in shape. Versilyea (1958) and Gilman et al (1958) have discussed the formation of etch pits in details. The shape of an etch pit depends on $V_n$, the rate at which it deepens and $V_s$, the velocity of steps along the surface. For well defined etch pits the ratio $V_s/V_n$ is of the order of 10. During the present investigation, chemical etching of (100) surface of sodium chloride produced usual pyramidal etch pits in most of the cases. In very few cases, using the above mentioned diluted etchant, rather unusual types of etch pits have been observed. Such pits are shown in figure 1.
and these are much deeper as compared to their surface dimensions. Such etch pits, called etch tunnels, are obtained very rarely and only on particular crystals. The tunnels resemble somewhat with the profile of sharp beaks which have been mentioned in the description of etch figures on minerals (Honess, 1927). These earlier descriptions sometimes included observation of beaks and canals which have a similar nature. Dash (1967) has obtained etch pits before and after copper precipitation of dislocations in silicon. Johnston (1961) has pointed out that some of the etch pits observed by Dash in silicon would resemble dislocation beaks if these were to be viewed normal to the etched surface. The tunnels in the present case have been obtained on 99.9% pure sodium chloride crystals. The unetched crystal did not show any trace of decoration at the dislocation lines. Moreover, these tunnels were seen to vanish gradually with the depth from the etched surface which is not the case with decoration which continues all along the dislocation lines.

Recently, Westwood and Rubin (1982) have reported the formation of etch channels in LiF after immersing a freshly cleaved crystal face down in distilled water for two weeks and attributed the formation of etch tunnels mainly to the strongly absorbed step poison which was introduced deliberately. According
Fig. 2. Same field as in Fig. 1 but at a few hundred microns below the etched surface. (7125)

Fig. 3. Pits of Fig. 2 superimposed on pits of Fig. 1. Pairs of dots represent positions of tunnels of Fig. 1 and shifted positions of tunnels of Fig. 2.
to these authors the tunnels are equivalent to negative whiskers or platelets and some of these may even be formed at non-dislocation sites. However, the observation of etch tunnels on sodium chloride in the present case (vide infra) indicates that the tunnels are formed along dislocations which make near normal angles with the etched surface. The strain energy and the core energy of the dislocation will certainly assist tunnel growth and will cause the tunnel to grow in the direction of the dislocation.

It was seen in the case of figure 1 that the tunnels were not exactly along [100] direction but are inclined to it. Sodium chloride crystals being transparent, the tunnels could be seen extending into the crystal by bringing the objective of the microscope closer to the specimen. It was seen that some of the tunnels were as deep as $10^3$ microns. Figure 2 represents the same field, as in figure 1 but at a level a few hundred microns deeper inside the crystal. The positions of the dots, representing the position of the tunnels at a particular depth, in figure 2 have shifted from those of in figure 1 for most of the tunnels which shows that tunnels are inclined to [100] directions. The lateral shifting of the dots can be seen clearly in figure 3 which has been obtained by superimposing figure 2 on figure 1., and the pairs
of dots represent the positions of the dots of figure 1 and the shifted positions of dots of figure 2. The shift of the position of dots is of the order of a few microns. The lateral shift at a particular depth for a certain etch tunnel was measured by using a calibrated eye piece and the higher refractive index of sodium chloride was taken into account in measuring these distances. Knowing the shift at a particular depth, the inclination of the tunnels was calculated. Calculation of this angle for a number of etch tunnels revealed that the tunnels were making near normal angles with the etched surface and the average angle was of the order of $30^\circ$ with (001) etched surface. These tunnels have been attributed to the preferential etching at dislocations.

**Tunnels and Etch Pit Formation**

It looks that the formation of tunnels is a typical case of etch pit formation. The theory of preferential etching has been presented by Cabrera (1956). He has demonstrated the existence of a region of undersaturation such that dissolution should proceed preferentially at dislocations as opposed to perfect surfaces. Recent work on selective etching of crystals has provided the experimental verification to Cabrera's conclusions but this is
subject to one modification i.e. it is insufficient to preferentially create dissolution steps at dislocation sites to obtain sharply defined etch pits. It is also necessary to have a poison present in the etching solution that adsorbs at the advancing dissolution steps. Before discussing the present results it would be helpful to briefly review the Cahn's theory of dissolution at a dislocation. The formulation used by Cahn (1957) is followed.

The dissolution nucleus is taken as a cylindrical hole in the crystal surface with the dislocation normal to the surface. The depth of the hole, \( a \), is one atom deep and its radius is taken as \( r \). The free energy of nucleation, \( \Delta f \), consists of a strain energy term, \( \Delta f_B \), a surface energy term, \( \Delta f_s \), and a volume energy term \( \Delta f_v \).

Therefore,

\[
\Delta f = \Delta f_B + \Delta f_s = \Delta f_v
\]  \hspace{1cm} (1)

Now strain energy is given by,

\[
\Delta f_B = -A \ln \left( \frac{r}{r_0} \right) + B \left( r - r_0 \right) \]  \hspace{1cm} (2)

where \( A \) and \( B \) are dependent on the nature of dislocation and the amount of solute absorption at the dislocation. For a clean edge dislocation

\[
A = G b^2 / 4 \pi \left( 1 - \nu \right)
\]

and for a clean screw dislocation

\[
A = G b^2 / 4 \pi
\]

where \( G \) is the shear modulus, \( \nu \) is the poisson ratio and \( b \) is the Burgers vector.
of the dislocation. Thus the equation (1) can be rewritten as

\[ \Delta f = -a A \ln \left( \frac{r}{r_0} \right) + 2 \pi a \gamma f - \pi r^2 a f + B \]  

where \( \gamma \) is the appropriate interfacial energy and \( f \) is the negative of volume free energy of dissolution i.e. \( f > 0 \) for dissolution to occur.

The behaviour of the free energy curve is determined by considering the first two derivatives of \( \Delta f \)

\[ \frac{d}{dr} \Delta f = -a/r + 2 \pi a \gamma - 2 \pi a r f \]  

\[ \frac{d^2}{dr^2} \Delta f = a/\gamma - 2 \pi a f \]  

Equating the first derivative to zero gives a quadratic equation having the roots,

\[ \begin{align*} 
 r^+ & = \frac{\gamma}{2f} \left\{ 1 + \left( 1 - \frac{\gamma}{2f} \right)^{1/2} \right\} 
 r^- & = \frac{\gamma}{2f} \left\{ 1 - \left( 1 - \frac{\gamma}{2f} \right)^{1/2} \right\} 
\end{align*} \]  

where \( \frac{\gamma}{2f} \) when \( 0 < \frac{\gamma}{2f} < 1 \), there are two real roots, \( r^+ \) corresponds to a maximum and \( r^- \) corresponds to a minimum. When \( \frac{\gamma}{2f} = 1 \), there is a double root \( r^+ = r^- = \gamma/2f \), when \( \frac{\gamma}{2f} > 1 \) there are no real roots i.e. there is no nucleation barrier to the formation of a dissolution nucleus.

When the second derivative is equated to zero, there is a single positive real root.

\[ r^* = \frac{\gamma}{2f} \left( \frac{\gamma}{2f} \right) \]
Thus every free energy curve has an inflection point. For $\xi = 1$ the slope of the free energy is zero at the inflection point. The equation for the slope of the inflection point is obtained by combining equations (4 a) and (6) and it gives,

$$(d\Delta f/dr)^* = (d\Delta f/dr)_r = 2\pi a \delta (1 - \xi)^{1/2}$$ (7)

For $\xi < 1$ the slope is positive at the inflection point and for $\xi > 1$ the slope is negative at the inflection.

This undersaturation in the immediate neighborhood of surface site is pertinent in determining the nucleation rate of monolayer holes in that area. For a given solute solvent system $\xi$ can be changed only by altering the undersaturation in the etching solution i.e. by changing the free energy of dissolution.

For $\xi < 1$ the critical free energy for nucleation of the hole at a dislocation is given by

$$\Delta f^* = \Delta f (r+) - \Delta f (r-)$$ (8)

Combining equation (3), (5) and (8), we get,

$$\Delta f^* = (\pi a \gamma^2/\rho)(1 - \xi)^{1/2} + \rho a \ln \frac{1 - (1 - \xi)^{1/2}}{1 + (1 - \xi)^{1/2}}$$ (9)

which is valid for $r \gg r_0$ and $\xi \leq 1$

when $\xi \to 1$, $\Delta f^* \to 0$ (10a)

or when $\xi \to 0$, $\Delta f^* \to 0$ (10b)

For $\xi \to 1$, the second term on the right hand side of equation (9) approaches zero more rapidly than the
first term and can be neglected. Therefore,

\[ \Delta f_0 \sim (\pi a \gamma^2/\xi^n)(1 - \xi^n)^{1/2}, \text{ for } \xi \approx 1 \]  

(11)

The competing process of nucleating the hole in a perfect crystal surface has a critical free energy \( \Delta f_0 \) given by,

\[ \Delta f_0 = \pi a \gamma^2/\xi^n \]

It is apparent for \( \xi > 1 \) i.e. \( f > \pi \gamma^2/2 a \), that there is no barrier to the formation of a dissolution nucleus at a dislocation, while there is a nucleation barrier at a site on a perfect surface. For \( \xi \approx 1 \) the nucleation barrier is smaller by the factor \( (1 - \xi^n)^{1/2} \) at a dislocation than at a perfect surface site.

It is thus clear that the dissolution rate at a dislocation must exceed the net dissolution rate on the surrounding perfect surface and there is a region of undersaturation in which dissolution pits at dislocations are created with no nucleation barrier, whereas nucleation does not occur on a perfect surface at an appropriate rate.

**Dislocations and Etch Tunnels**

The tunnels observed in the present case are attributed to preferential etching at the sites of dislocations. This is in agreement with the ideas of Sears (1960) whereas Westwood and Rubin (1962) have pointed out that all the tunnels may not
correspond to dislocations. In the present case the
time of etching is much smaller as compared to the
earlier investigations and tunnels are inclined at
small angles to \(\langle 100\rangle\) directions. The etchant used
in the study did not have any deliberate addition of
poison and so it is assumed that the poison was
provided by the dissolving crystal itself or by the
unintentional impurities present in the etchant. The
effect of the poison is to inhibit the dissolution
process. It has been shown that severe hindrance
(Sears, 1958) of growth and solution at a step is
associated with complete coverage of the adsorption
sites on the steps. An originally clean step moving
across a crystal surface can be poisoned by diffusion
of the poison from the etching solution and for the
explanation of the etch tunnels observed, it is
essential to have a poison in the etchant, otherwise,
the solution would become sufficiently saturated in
the neighborhood of the crystal and preferential
formation of monolayer holes at the dislocations
would not occur. A simple procedure can be used to
make an estimate of the time required to poison an
originally clean step. Assuming the interstep spacing
to be of the order of \(10^{-3}\) cm, the sites available
for the adsorption of poison would be approximately
\(10^{13}\) cm\(^{-2}\). This quantity of poison would be contained
in the solution within $10^{-7}$ cm of the surface if the poison concentration was $10^{-3}$ mole fraction. Taking the diffusion coefficient, $D$, for poison to be $\sim 10^5$ cm$^2$ sec$^{-1}$, the Einstein's equation

$$2D\gamma = \lambda_x$$

relating mean free path to diffusion $\lambda_x$ and diffusion time $\gamma$ can be solved to give a poisoning time of $10^{-9}$ sec. Even including a generous allowance for a material accommodation coefficient of less than unity, a poisoning time greater than 1 micron second is not conceivable.

The comparison of the profile of etch tunnels to that of usual etch pits shows that in the case of the latter the ratio $V_s/V_n$ becomes very small. $V_s$ can be decreased by the presence of the inhibitor or the step poison. The poison may be provided by the dissolving crystal or it may be added deliberately. The difference in the dissolution rate is probably caused by the differential concentration of the poison, the poison concentration being lesser at the growing end of the tunnels. The velocity of steps along the surface of a freshly nucleated pit is retarded by the readily available poison, as calculated the poison would not take a time more than one micron second to reach the steps, and because of the reduced poison concentration at the end of a tunnel, a unit pit nucleated there is able
to expand over a considerable distance before it is inhibited. It also means that the length of the tunnel is likely to increase with decrease in the poison concentration in which case it will take more time for the poison to reach the tunnel end. Indeed it can be expected that tunnel formation would not be favoured if the poison concentration were to be above an unknown critical value. This is supported by much greater length of tunnels, of the order of $10^3$ microns, in sodium chloride as compared to $10^2$ microns obtained by Westwood and Rubin (1963) by deliberate addition of the long chain fatty acids as the step poison. In case of sodium chloride the poison is provided by the unintentional impurities present in the etchant or the crystal itself and so the concentration of the poison is likely to be less as compared to that in lithium fluoride and this has possibly resulted in comparatively longer tunnels in sodium chloride. The time of etching for sodium chloride was only a few minutes as compared to many hours for LiF to obtain the tunnels. This may be due to comparatively higher dissolution rate in the etchant of the sodium chloride. It is also believed that originally short tunnels are produced at dislocation sites by etching the crystal for a short duration. Even after drying the crystal surface, some etchant remains in the pits and the attack
continue along the dislocation lines which may give rise to the observed length of the etch tunnels.

The density of the tunnels observed is of the order of $10^5$/cm$^2$ and these tunnels are making large and random angles with (100) etched surface which indicates that the tunnels are formed at the grown-in-dislocations making near normal angles with the (100) etched surface and that the poison may be mainly responsible for their formation.

Earlier, the etch tunnels have been reported only in LiF crystals. Sears (1960) has pointed out that preferential etching of LiF occurs at undersaturation ratios in the solution in the immediate neighborhood of the crystal surface such that steps are generated spontaneously at dislocations and not at all at perfect surface pits. Accordingly, he has attributed the formation of long narrow channels in $\langle 100 \rangle$ directions to preferential etching along dislocations in the presence of a poison contributed by the dissolving crystal phase. This view is confirmed by the present observation of etch tunnels on sodium chloride and the observation of etch tunnels inclined to $\langle 100 \rangle$ directions strongly indicates the presence of dislocations at the tunnel sites, as only a linear defect can cause this deviation from the normal direction. However, Westwood and Rubin (1952) have attributed the observation of $\alpha$-type
tunnels to nucleation at perfect surface sites. This is not understandable especially at the undersaturation concentration of the solution at which such tunnels were formed. Cabrera's etching theory, as discussed above, does not favour the formation of unit pits at the perfect surface sites at low undersaturations. Furthermore, the probability of a unit pit created at a perfect site, to grow to a critical size cannot be much. Westwood et al (1962) have observed that once nucleated R-type of tunnels grow at a similar rate to that of D-type of tunnels which have been attributed to dislocations. This is again contrary to the Cabrera's theory of dissolution according to which nucleation barrier would always be smaller at a dislocation site and therefore normal rate of etching cannot be same for dislocations and perfect surface sites. In view of these contradictions the association of R-type tunnels with the prismatic dislocation loops, which tend to be confined to [100] direction, appears to be more probable.

**Dislocations and Etch Grooves**

The observation of the tunnels also indicated the possibility of the etchant in attacking along the dislocation lines which lie parallel to and just below the etched surface. In some of the observations of the (100) etched surface, etch grooves as shown in figure 4 were observed. The apparent resemblance of
Fig. 4. Etch grooves on (100) face of a sodium chloride crystal. (×375)
these grooves to networks reported by Amelinkx (1957) and Rozhanskii (1960) in decorated sodium chloride crystals, indicates that these grooves can not be associated with sub-boundaries as these in as grown crystal usually have too large an orientation difference to give well resolved nets. As suggested by Amelinkx, the network of figure 4 can result from two basic sets of dislocations.

If a dislocation line lying parallel to and just below the etched surface has an impurity atmosphere and the rate of dissolution is high in the impure region, etch grooves may be formed at the sites of dislocation lines. Low and Guard (1959) and Tyler and Dash (1957) have observed dislocation grooves in Fe 4% Si and germanium respectively. In these cases the enhanced rate of attack may be due to the presence of impurities because the impurity atoms may go into the solution more easily than do the normal atoms or because the impure material has a low surface energy. Dash (1958) however, has also observed these dislocation grooves in case of pure material. In such cases the enhanced rate of attack may be due to the elastic strain energy of dislocations. The appearance of figure 4 suggests that it has resulted by the preferential etching of the cores of dislocations. The depth and ease of observation of these dislocation
Fig. 5. Coarsened network showing loss of dislocations at the surface. (x375)
grooves are seen to vary from specimen to specimen. This indicates that up to certain extent, impurities are responsible for the etching of these grooves.

The network of figure 4 represents three-fold nodes. If the stable dislocations have a Burgers vector \( \frac{a}{\sqrt{2}} \) (110), three-fold nodes result when Burgers vector encloses angles of 60° or 120°. From the considerations of energy and probability, theory also predicts the possibility of three-fold nodes as the maximum. The nets observed in figure 4 are not perfectly hexagonal. This is in accordance with Frank's (1957) theory which indicates that the perfectly hexagonal nets should lie in the (111) plane, all dislocations being pure screws. A change of the contact plane would change the shape of the nets. Further, the nets are not free to adopt the shape and position of minimum energy as these are bound to others building up the cellular structure of the polygonized crystals. It has also been observed that the nets are not even necessarily planar. The network is coarsened except at a few odd places. It may be due to the loss of dislocations at the surface. Figure 5 represents such a state of affairs. Some of the dislocations of the network may also have been lost due to the slight unevenness of the surface.

It is therefore, seen that all the evidence
indicates that the etch grooves are formed at the site of dislocations.

**Sodium Chloride Whiskers**

The phenomenon of dissolution has often been treated as the reciprocal of crystal growth. Dislocation etch tunnels, discussed earlier in this chapter, are thought to be a process just opposite to that of whisker growth (Sears, 1960, Westwood and Rubin, 1942) and have been called as negative whiskers. In this section the growth of sodium chloride whiskers from solution at very low supersaturations, so that the whiskers grew in several days, and from vapours in which case the whiskers grew much faster would be considered. The whiskers from the solution were grown in a manner that has not been reported in the literature to the best knowledge of the author. Cleaved sodium chloride crystals were placed in humid atmosphere for several days and the whiskers up to 10 mm long appeared on the crystals lying on the glass substrate. Accordingly, it is expected that the supersaturation was very low and as discussed in the previous section if the growth phenomenon is to be just the reverse of the dissolution process the whiskers should grow at the sites of dislocations. The observations of whiskers at such small supersaturations do indicate the definite
Fig. 6. A sodium chloride whisker grown from the solution. (x250)
Complicated sodium chloride whiskers grown from the solution.

Fig. 7.  

Fig. 8.  

Figs. 7 & 8. Complicated sodium chloride whiskers grown from the solution.
Fig. 9. Thick rod type NaCl whisker grown from solution. (x250)

Fig. 10. Chemical etch pits on a thick NaCl whisker. (x250)
Fig. 11. A number of vapour grown NaCl whiskers extending from the bulk crystal. (x200)

Fig. 12. Thickening of a whisker by the appearance of a large number of branches. (x500)
Figs. 13 & 14. Vapour grown Fe21 whiskers showing a large number of branches and sub-branches.
requirement of dislocations for the phenomenon of whisker growth.

The whiskers observed have been cylindrical as well as rectangular in cross section. Figures 6 - 10 depict the whiskers grown from solution. Etching of these whiskers showed that thinner whiskers were either free from dislocations or contained very few dislocations, whereas bigger whiskers contained a dislocation density comparable to bulk crystals. This is shown by the etch pits in figure 10.

Sodium chloride whiskers were also obtained by vapour deposition at near melting point temperature. Commonly NaCl whiskers are grown either by crystallization in air from aqueous films on porous substrates or by crystallization in poisoned aqueous solutions. The growth from the vapour has been reported only very recently. Such whiskers are shown in figures 11 - 14. The branching of whiskers can be seen in these figures. It appears that most of the whiskers in a clump form nearly simultaneously and all grow at approximately the same rate regardless of the thickness or morphology. The rate of growth seems to be virtually unaffected by branching or its number.

A large number of workers have studied the whisker growth in various substances. Whisker growth from the vapour and solution was explained by postulating an
axial screw dislocation in the whiskers (Sears, 1955, Newkirk and Sears, 1955, Esbelby, 1963, Frank, 1953, Amelinckx et al., 1967, Sears, 1953, Branner, 1966, Piper and Roth, 1953). The presence of the screw dislocation has been reported in sapphire (A12O3), sometimes in palladium, once in silver, but never in other metal crystals (Webb et al., 1957). The non-metallic whiskers containing axial screw dislocation have been found (Webb, 1960, Amelinckx, 1958, Webb et al., 1960, Hamilton, 1960, Amelinckx et al., 1960), and Price (1960) has established the complete absence of dislocations in some zinc and cadmium whiskers grown from the vapour. Several workers (Coleman and Sears, 1957, Gorsuch, 1959) have questioned recently the description of the growth of whiskers based on a screw dislocation mechanism. Initially it was proposed that the axial screw dislocations may be lost by climb after the whiskers are formed or that the dislocations may be equal numbers of parallel screws with equal magnitude and opposite sign (Webb et al., 1957). The possibility of slip mechanism has also been considered but excludes for whiskers more than 5000 Å thick.

The growth mechanism of platelets is more complicated than those of whiskers. Sears and Coleman (1956) showed that platelets grow by the action of a set of crossed screw dislocations. Sears (1956) proposed a
mechanism for the vapour deposition of mercury platelets by a single screw dislocation. Wagner (1960) suggested that coherent twin planes played an important role in dendritic growth process of germanium. Hirth and Frank (1968) predicted theoretically that a dislocation in a metal whisker with edge components with respect to the whisker axis will slip out of the whisker axis more easily than a pure dislocation and by this slip new growth will proceed perpendicular to the whisker axis. However, broadly speaking, the growth mechanism of platelets is not yet fully clear. The etch pit observation of platelets of sodium chloride, figure 13, shows the presence of a large number of dislocations in these and this at least points that a number of dislocations may be responsible for the growth of platelets.

Recently Chickawa et al. (1964) have reported the growth of cadmium sulfide whiskers. They came to the conclusion that a $[10\bar{1}0]$ whisker of cadmium sulfide has two parallel dislocations along its axis; one has a Burgers vector $1/3 [21\bar{1}0]$ and seems to be responsible for the axial growth, and the other is an edge dislocation with a Burgers vector $[0001]$. Each dislocation is considered to slip out of the whisker surface in the direction perpendicular to the whisker axis. By slipping of the edge dislocation out of the $[10\bar{1}0]$
Whisker, an array of dislocation half loops is formed along one of the \{0001\} surfaces of the [10\overline{1}0] whisker. These half loops contribute to thickening of the [10\overline{1}0] whisker in one of the \langle0001\rangle directions and platelet is formed. A similar mechanism can be applicable for sodium chloride platelets and it would explain as well the observation of large dislocation density which may be due to half loops created by slip.

Weib (1945) has discussed the dislocation mechanism in the growth of palladium whiskers and has shown the operation of the often predicted screw dislocation mechanism in the growth of a metal whisker and climb of dislocations during growth.

It is thus clear that a number of mechanisms are involved in the various processes of whisker growth. Indeed it even appears that in one case two mechanisms can operate simultaneously. Each case has to be studied individually to recognize the effective growth mechanism, the role of dislocations and the resulting structures.

In case of whiskers grown from the vapour it was observed that the whiskers are favoured if the crystal is cleaved and allowed a few days in the open. This would imply that surface would be contaminated with impurities from the atmosphere and these impurities would later act as step poisons. A probable mechanism
for the formation of whiskers and their subsequent branching can be as follows (Spencer and Dragadorf, 1962).

At an elevated temperature $T$, the percentage of vacancies in the whisker is given by,

$$f = \exp \left(-\frac{U_v}{2kT}\right),$$

where $U_v$ is the energy of formation of a vacancy pair in NaCl. The mixed axial dislocation will serve as a sink for the vacancies. As the vacancies diffuse to the dislocation core, the dislocation will begin to climb and a helix will be formed. As the dislocation continues to climb, it will reach a stage where its configuration becomes unstable and it will then be attracted to the surface (Cottrell, 1953). After intersection with the surface, there will be a component of the Burgers vector perpendicular to the primary whisker face which would produce the sites for secondary whisker growth. Every turn of the original helical dislocation will produce a growth site on each of the four primary whisker faces and so the observed branching is understood.

Whiskers which did not produce secondary growth probably had paired screw dislocations (Webb, 1930). At high temperatures these would annihilate each other if the Burgers vectors of the dislocations were equal in magnitude and opposite in direction.
This mechanism would also explain the absence of branching in whiskers produced in the first case at lower temperature as at this temperature number of vacancies available would be very small and climb would not be possible.

The role of impurity atoms may be understood as hindrance to dislocation slipping and in this way a single axial dislocation can be responsible for the whisker growth. If the growth rate is large the whiskers are observed in freshly cleaved crystals as well i.e. without impurity and this can again be explained on a single dislocation in agreement with the ideas of Chickava et al (1964).

Summary

The process of chemical etching has been employed for the direct observation of dislocations in sodium chloride single crystals. Etch tunnels as deep as $10^3$ microns have been observed and their inclination with the (100) etched surface has been measured. The formation of etch tunnels has been considered as a typical case of etch pit formation. The presence of the poison is thought to be essential in the formation of tunnels. Earlier the etch tunnels have been reported only in LiF crystals and some of these have been attributed to non-dislocation sites. In the
present case the tunnels have been attributed to the sites of dislocations. Preferential etching theory, the observed inclination and the density of the tunnels support this view. In a few cases etching of (100) surface also resulted in the formation of etch grooves which apparently correspond to dislocation networks. The coarsening of the network is attributed to the loss of dislocations at the surface and to the slight unevenness of the etched surface. It is believed that the impurities are partly responsible for the formation of etch grooves along the dislocation lines of the network.

Whiskers, which are thought to be a process just opposite to etch tunnels, of sodium chloride have been grown from solution and vapour phase. Thinner whiskers contain one or no dislocation whereas thick whiskers have a dislocation density comparable to the bulk crystal. The branching of the whiskers have been observed and it is seen that most of the whiskers in a clump form nearly simultaneously and all grow at approximately the same rate. Existing theories of whisker growth have been discussed briefly and the whisker growth in the present case has been explained on the basis of a single axial dislocation.
Bibliography


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