CHAPTER 3

ETCHING AND DISSOLUTION OF CRYSTAL CLEAVAGES

3.1 Historical Review of the Development of Etch Method

The first scientific application of the etch method seems to have been made by Widmannstatten in 1808, who observed that the characteristic markings may be obtained on polished faces of meteorites through the corrosive action of acids and that the etching so produced is definitely related to the molecular structure of the meteorite iron. However, the nature of the etch figures was first correlated by Daniell (1816) with the molecular structure of the crystalline solids. Since then, a large number of investigators have applied this method of etching to crystal faces.

Since then, there continued an ever growing interest in the etching of crystals as evidenced by the number and character of the publications, mainly by German Scientists. The notable contributions made to the theory and application to etch method are due to Baumhauer (1889), Wulff (1898), Walker (1898) and Beckenkamp (1900). These researches consist of theoretical studies dealing with the
questions such as, the conditions controlling the development of the etch pits, their relation to the crystalline faces and to the symmetry of the crystal.

In the first two decades of the 20th century, Goldschmidt, Wright, Kollar, Gaubert, McNairan and many others made a goniometric study of etch figures. A keen interest was developed in the methods of etch for gaining information in crystallography and mineralogy. An excellent account, covering every aspect of the subject, with detailed references and nicely illustrated by many practical examples, is given by Honess (1927). The discovery and the development of the X-ray analysis of the crystal structures created further interest in the method of etching. The extensive and ever growing literature of the method of etching as applied to obtain a more exact knowledge of the various aspects of crystal symmetry is the evidence of the importance of this technique as a means of crystallographic research.

The first attempt to provide an explanation for the process of etching is due to Goldschmidt (1904). He suggested that:

1. The etch pits are located at the places where the current starts in the corrosive.
2. Preferential etching takes place along the
scratches.

3. Small particles of dust on the substance provide the points of first attack.

4. The bunching of etch pits takes place on the strained parts of the crystal, and

4. The presence of inclusions or impurities are likely to be starting points of etching.

McNAIRAN (1916) has observed the origin and the subsequent growth of pits. He suggested that the lines of selective pitting are also the lines of weak cohesion, as for example, cleavage planes are corroded much more slowly than those of the lower degree. Desch (1934) performed etching experiments on alum and showed that explanations offered by Goldschmidt and others, regarding the origin of etch pits, are inadequate. The possible explanation for the irregularity in the density of etch pits have been given by a number of investigators but these have however proved inadequate. It may be realised that no satisfactory explanation of this difference in the density of etch pits can be given until the more fundamental problem of the origin of etch pits is solved.

The satisfactory explanation regarding the origin of the etch pits and their development has been
given on the new concept of lattice defects, known as 'dislocations'.

3.2 One-to-one Correspondence Between Etch Pits and Dislocations

That an etch pit can be formed where a dislocation meets a crystallographic surface has been demonstrated by Horn (1952), Gevers, Amelinckx and Dekeyser (1952). They have shown in a striking way, that the etch pits develop where screw dislocations emerge on the surface of silicon carbide crystals. Vogel et al. (1953) have found a striking evidence for the presence of small angle grain boundaries in germanium and showed one-to-one correspondence between etch pits and dislocations. The study of the etch patterns on both the halves of a cleaved specimen of rock salt led Amelinckx (1954) to the conclusion that there is one-to-one correspondence between the etch pits and dislocations. He inferred from his experiments that cleavage is a slipless fracture.

Gilman and Johnston (1957) in LiF, Keith and Gilman (1960) in calcite, Barber (1965) in MgF$_2$, Thyagarajar and Urusovskaya (1967) in CsI, Sagar and Faust (1967) in Bi$_2$Te$_3$, and Patel and Raju (1967) in gypsum have also shown one-to-one correspondence between etch pits and dislocations. Correlation between
spiral etch pits and screw dislocations has been shown by Johnston et. al. (1957) in silicon, Patel and Bahl (1965) in graphite, and Khukhryanskii et. al. (1967) in germanium. Amelinckx et. al. (1957) and Ellis (1957) proposed that spiral etch pits form at helical dislocations, and that the pitch of the spiral corresponds to the pitch of the helix. Dash (1957) has observed that helical dislocations in silicon do indeed cause spiral etch pits to form. Dash (1960) has pointed out that the number of spiral pits observed is sometimes much larger than the number of helical dislocations, and suggested that most spiral pits may not be associated with dislocations. Lang (1957) has suggested a simple mechanism of 'mistake' which can explain the formation of spiral etch pits, produced either by chemical or thermal etching. He has shown that no screw dislocations are necessary for the formation of spirals. Loops and spiral etch patterns have been reported by Damiano and Herman (1959) on the basal plane of zinc. This they have tentatively interpreted as the dissolution of a step in the surface with the ends of the steps pinned.

A brief review of the etch pit method by Regel et. al. (1960) presents a lengthy chronological bibliography up through the early part of 1959 and a
complete table of dislocation etchants. Johnston (1962) has presented a detailed review of etching of non-metallic crystals. Amelinckx (1964) has written an excellent review work on the direct observations on dislocations, wherein he has fully discussed the usefulness of the etch methods.

Faust (1960) and Johnston (loc. cit.) have stated that acceptable techniques for showing one-to-one correspondence between etch pits and dislocations are:

1. Following of line defects for long distances by continued etching, or by alternately etching and polishing chemically (Gilman and Johnston, loc. cit.).

2. Correspondence of etch pits on the matched faces (Amelinckx, loc. cit.).

3. Comparison of measured distances between pits on a lineage line to those calculated from X-ray orientation differences across the boundary (Vogel et. al., loc. cit.).

4. Count of pits on intersecting lineage lines. (Amelinckx, loc. cit.) and

5. Comparison between calculated and observed etch pit densities on plastically deformed samples (Hendrickson and Machlir, 1955, and
3.3 Shape of the Etch Pits

The profile of a pit, depends on the rate at which it deepens by nucleation of steps at the dislocation, $V_n$, and the velocity of steps across the surface, $V_s$. In readily observable pits the slope of the sides exceeds several degrees so that $V_s/V_n \approx 10$. In some cases this ratio can be deliberately varied by changing $V_s$ or $V_n$, thereby altering the visibility of the etch pits. Evans and Sauter (1961) have given an explanation for the different shapes of the etch pits. According to them the sides of the resultant pit have the outline parallel to the direction in which the atomic steps are moving at the slower rate. If the rate of local dissolution is less than the general dissolution then hillocks will be produced as explained by Batterman (1957).

Gilman and Johnston (1956) are of the opinion that complex chemical reaction is responsible for the rotation of etch pits, observed in LiF. Ives (1963) has explained the variation in shape of etch pits in LiF by considering the nucleation of kinks and inhibiting action caused by the poison present in the etchant.
3.4 Previous Work Reported on Etching of Alkali Halide Crystals

(a) KCl

Several investigators [Slack (1957), Moran (1958), Sakamato and Kobyashi (1958), Barr et al. (1960), Cook (1961), Shaskolskaya et al. (1961), Lebenets and Kostin (1962), Queisser (1964), Hari Babu and Bansigir (1967) and Keerti and Dubov (1968)] have reported different etchants, to produce well-defined etch pits on KCl cleavages. Lubenets and Kostin (loc. cit.) and Sakamato and Kobyashi (loc. cit) have reported several chemical polishing solutions for these crystals.

One-to-one correspondence of dislocations and etch pits has been reported by Sakamato and Kobyashi (loc. cit.). Amselinckx (1957, 1958) has reported the evidence for the occurrence of segments of dislocation with Burgers vector \( \langle 100 \rangle \), and dislocation net-work in decorated KCl crystals. Direct observation of crystal imperfections by electron microscope has been reported by Hibi and Yada (1962). Formation of dislocation structure in alkali halide crystals during plastic deformation has been reported by Komnik (1968). Schonherr (1968) has
described a method for growing KCl single crystals from melt with dislocation densities lower than $10^3$ cm$^{-2}$ and completely free from grain boundaries.

(b) NaCl

Quite appreciable work has also been done on the study of dislocations in NaCl crystals by etching and decoration techniques. Amelinckx (loc. cit.), Moran (loc. cit.), Jeszensky (1958), Cook (loc. cit.), Barber (1962), Shaskalskaya and Fang (1960), Hyder and Bansigir (1963), and Hari Babu and Bansigir (1966, 1967) have reported several etchants which are capable of producing well-defined etch pits on (100) cleavages of these crystals. Formation of etch pits and the change in shape of etch pits due to the variation in the concentration of poison in the etchant have been reported by Rozhanskii et. al. (1962), Kostin et. al. (1962), Barber (loc. cit.) and Hari Babu and Bansigir (loc. cit.). Deo and Sharma (1964) have reported dissolution structures in NaCl crystals.

Formation of shallow etch pits along glide bands due to debris was reported by Davidge and Whitworth (1961). Dislocation glide bands, dislocations and plastic flow have been studied by Amelinckx (loc. cit.), Bhide and Khosla (1965) and Mendelson (1962). Strom and McCarthy (1966) showed dislocation
distribution along the cleavage cracks. Garber and Polyakov (1935) reported that when ionic crystals are subjected to plastic compression, the density of the crystals changes. Amelinckx (1956) attributed the splitting of a pit into two to the branching of a dislocation line. Amelinckx (1957) studied the geometry of grain boundaries in NaCl. Gegnzin and Matsokin (1967) and Finkel et. al. (1967) observed 'dispersion' and puncturing of large angle grain boundaries by dislocation pile-ups respectively. Finkel et. al. (1965) studied the interaction of a crack with dislocation boundaries, Rozhanskii et. al. (1963) and Gutmanas et. al. (1963) have studied motion of dislocations and the velocity of dislocations in NaCl crystals.

(c) NaF

Cook (loc. cit.) has suggested an etchant for NaF cleavages for the first time. The etching of the disclosed structural effects due to proton bombardment of these crystals has been reported by Kubo (1966a). Kubo (1966b) reported a colloidally coloured lamina produced by electrolytic coloration in which Na decorated loops and net-works of dislocations were observed. Davidson and Levinson (1966) have reported the etchant which reveals the
sites of new edge dislocations. By changing the concentration of $\text{Mn}^{2+}$ ions in the etchant, they have studied the structure of etch pits. They (1967) have also reported a universal etchant which does not distinguish between the fresh and old dislocations.

Identification of dislocations by electrolytic coloration and chemical etching has been reported by Kubo (1959).

3.5 **Thermal Etching**

As chemical etch pits reveal the sites of dislocations in crystals, when the crystal faces are heated near to their melting points, thermal etch pits are produced at the sites of dislocations due to thermal evaporation of the material. The theory of evaporation at the sites of dislocations in crystals has been given by Cabrera and Levine (1956). Correlation between the thermal etch pits and dislocations on silver, and thermal etch pits and chemical etch pits on NaCl has been reported by Hirth and Vassamillet (1958) and Patel et al. (1965) respectively. Thermal etching at the sites of dislocations has also been described by Suzkii (1957). Kern and Pick (1953), and Turchanyi and Horvath (1960) have reported evaporation figures produced on NaCl cleavages. Bethe and Schmidt (1959), and Bethe and Keller (1960) have
reported evaporation spirals on thermally etched NaCl crystals. Relation between evaporation spirals and structure of grain boundaries has been reported by Amelinckx and Votava (1954) in NaCl. Motion of dislocation on heated NaCl cleavages has been reported by Dee and Sharma (1965). Patel et. al. (1966a) have reported evaporation loops and spirals in NaCl. Optical and interferometric studies on thermal etch patterns have been made by Patel et. al. (1966b) on thermally etched KCl cleavages. Recently Toress et. al. (1968) have reported thermal etch patterns on NaCl crystals, when heated in air and in vacuum.