CHAPTER XI
REVIEW OF THE OBSERVATIONS OF ETCH-METHOD

Widmannstatten (1808) was the first person who produced the characteristic etch patterns on polished faces of meteorites by the corrosive action of acids. It was treated merely as a curiosity rather than as a scientific investigation. The results of the experimental work on meteoric iron from Brazil were published by Wollaston (1816). Daniel (1816) was a pioneer worker to correlate the nature of the etch patterns with the molecular structure of the crystalline solids. In 1824 Moh pointed out the differential solution patterns exhibited by rock salt when kept in damp atmosphere. Brewster (1837) had observed etch-patterns on a Brazilian topaz and had drawn the attention to the so-called "Licht figuren" which were subsequently studied by several workers. Leydolt (1854), as a result of etching of rhombohedral faces of quartz crystals arrived at the conclusion that the shape of the etch figure is related to the crystal molecule. Von Kobell (1862) and Hanshoffer (1865) have, however, shown that no definite relation existed between etch figures and molecular structures. Keen interest in the phenomena of etching is attributed mainly to the efforts of German investigators in the later half of the nineteenth
century. The notable contributions made to the theory and application of the etch-method are due to Baumhauer (1889), Traube (1896), Hufn (1894) and Beckenkamp (1900). The general contents of these papers comprise a theoretical study of the etch figures obtained on many of the common minerals. The importance of the etch figures in isomorphism, the topics related to the differential solution as exhibited by natural crystals and ground spheres, anomalous etching, the relation of etch patterns to the crystalline molecule, and their relation to the symmetry of the crystal are fully discussed by Baumhauer.

In the first two decades of twentieth century, a lively interest has been created in the etching of crystals and important contributions have been made by several investigators as Goldschmit, Wright, Koller, Mc Nairn and others. Attention has been drawn by them to the new possibilities arising from goniometric and projection studies of the etch figures. The discovery and the development of the x-ray analysis of the crystal structure created further interest in the method of etching. The extensive and evergrowing literature of the method of etching as applied to obtain a more exact knowledge of various aspects of crystal symmetry is an evidence of the importance of this technique as a tool of crystallographic research.
Goldschmidt has proposed a new theory for the formation of the etch figures. According to him, both etch pits and etch hillocks are the result of the movements developed in the solvent. The chemical action between the corrosive and substance upon which it is acting gives rise to currents, some of which are directed towards and some away from the surface which is being etched. The interference of the ascending and the descending currents tends to form eddis, each of which is a starting point of a pit. The tendency of any solvent would be then to produce a regular and hemispherical excavation, but this is offset by the force of crystallization, which constantly endeavours to keep the corroded surface bounded by crystal planes. The resultant of these opposing tendencies is a typical etch pit, whose sides are neither wholly irregular, nor plane crystal faces, but as a compromise, planes of similar nature to vicinal faces appear. He suggests that:

1. 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 the etch pits takes place on the strained parts of the crystal; and
The presence of inclusions or impurities are likely to be the starting point of etching.

The explanation of the etching phenomenon offered by Goldschmit appears quite adequate at the first sight. McNairn (1916) devised special methods of investigation to check the results of Goldschmit. He observed the origin and the subsequent growth of the pits. His results are not in harmony with those of Goldschmit. 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.

A detailed account of the etch method as applied to various crystalline solids has been given by Honess (1927). His work shows beautifully how the nature of etch pits formed on various crystalline faces help to identify the symmetry of the crystal. In addition to the well defined etch pits, which are a useful tool from the viewpoint of crystallographic research, there are formed shallow depressions with ill-defined outlines which may be developed later into mature pits.

The elastic strain of the lattice round the dislocation enhances the chemical potential which in its turn facilitates the chemical attack. The presence of dislocation may
enhance the etching, yet in another way. Thus, the dislocation accumulates impurities in solution, which may provide the favourable site for chemical attack. Forty and Frank (1955) have given the following interpretation of etch pattern on aluminium. An etch pit is produced only where there is a precipitation of impurities present in the surface and that these are located on dislocations which can therefore be regarded as an indirect cause of etching. That an etch pit can be formed where a dislocation meets a crystallographic surface has been demonstrated admirably by Horn (1952), Gevers, Amelinckx and Dekeyser (1952), Lacombe and Yannaquis (1947) found that large grain boundaries in aluminium etch rapidly and appear as grooves on the surface. According to them a small angle grain boundary which is indexed due to a row of edge dislocations should appear on etching as a row of discreet etch pits. Vogel et al. (1953) found a striking evidence for the dislocation structure of small-angle boundaries in germanium. The spacing between the etch pits agreed with the spacing calculated for the measured difference in orientation of grains by X-rays. These and other evidences though indirect, strongly favour the idea that a dislocation is a probable site for an etch pit.

X-ray diffraction studies and also the observed strength of crystals have shown that in general nearly $10^3$...
dislocation lines cross per cm.$^2$. Actually, however, the studies of crystal growth indicate a low value of $10^4$ to $10^6$. This order agrees very well with the density of etch pits observed by Dekeyser (1955). Further, Tolansky and Pandya (1954) have shown that the density of etch pits inside the growth trigon is less than that outside. This difference in the density has been attributed by them to the difference in the number of dislocations.

Gilman and Johnston (1956) have beautifully shown that the etch pits correspond to line singularities (dislocations) in the crystals of LiF. The symmetric and asymmetric structures of the etch pits have been used by them to index edge and screw dislocations respectively.

Jones and Mitchell (1957) made use of etching techniques to reveal dislocations associated with both annealing and deformation structures in crystals of silver halides. Bardasley and Hill (1957) used the etching techniques to reveal the distribution of edge dislocations on the (111) faces of indium antimonide. Venables and Broudy (1958, 1959) were able to identify positive and negative dislocations on single crystals of indium antimonide by using a selective etchant. Tyler and Nash (1959) arrived at the conclusion of surface dislocations in germanium by the etching process.
Cabrera (1959) has emphasized the role of dislocation energy in the formation of pits. He has considered the formation of etch pits by evaporation. The energy of dislocation which plays its role in the nucleation of a single pit is termed as 'localised energy' near a dislocation. Such energy consists of (i) core energy, and (ii) a small fraction of the total elastic strain energy. The formation of visible pits formed at the sites of dislocations depends on the rate of motion of the steps across the crystal surface and the nucleation rate of the unit pit. It is difficult to account for the up to date work of etching techniques employed by several investigators to locate the sites and behaviour of dislocations in the crystals. The reason for this is the increasing interest in this branch of study.

The above given general review indicates that under suitable conditions etch methods are reliable, easy in operation and powerful in revealing the lattice defects when associated with other experiments. One should be cautious regarding the interpretation of the etch patterns obtained on crystal faces.