PART TWO

CHEMICAL DISSOLUTION OF CALCITE CLEAVAGES

CHAPTER - III

DISSOLUTION (GENERAL)

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3.1 INTRODUCTION

When a crystal is attacked by an appropriate solvent which chemically or physically dissolves it, the initial dissolution begins at certain preferential points. This phenomenon is known as etching, which is as old as the art and science of metallography. It gives rise to various types of geometrical features on a crystal surface. The production of conical depressions with regular geometrical outlines on crystal surfaces are usually known as etch pits, etch figures or etch marks. The form and symmetry of etch pits were used by mineralogists to determine crystal planes and their orientation with one another. At that time the production of etch pits on a crystal surface was not understood satisfactorily. Dissolution of crystal surface is now thought to occur by retreat of monomolecular steps, being reverse to that of growth, which takes place due to the motion of steps on a surface. It is believed that when a crystal is exposed to a solvent, the dissolution usually begins by a nucleation of unit pit of one molecular depth at relatively weak spot on the surface. The unit pit grows as steps retreat across the crystal surfaces through the action of kinks.

The understanding of etch phenomenon was enhanced by the recognization of various types of imperfections in a crystal. The defect points are relatively weakly bound with the crystal surface. They need less energy to dissociate than that required by points (atoms) in regular structure. If chemical or physical change gives sufficient energy to dissociate imperfections from the exposed surface, etch pits or etch figures are observed on it. It is not necessary that the solvent should be present at the time of etching, other appropriate physical conditions such as ionic bombardment, temperature etc. also help to form etch pits at preferential points on a crystal surface. Following are the ways of obtaining preferential dissolution on a crystal surface (i) Chemical dissolution (ii) Thermal dissolution (iii) Ionic dissolution (iv) Electrolytic dissolution and (v) Dissolution by dehydration. The chemical etching usually produces a few or all features on a crystal surface mentioned below :

(i) Etch pits, terraced, flat-bottomed and point-bottomed, (ii) Shallow pits, pits with beaks, (iii) linear etch rows, (iv) Tunnels and dendritic etch figures (v) Etch hillocks, (vi) Etch spirals etc.

3.2 DISLOCATION DELINEATION BY ETCHING :

The study of topographical features on crystal surfaces has assumed increasing importance due to the information it provides for defect structure and under favourable circumstances the history of the growth of crystals. There are several methods of studying surface for revealing dislocations ending on the surface. They are (i) Etching technique, (ii) Decoration method, (iii) X-rays and (iv) Electron microscopy. Important experimental studies on microtopographical features were made by utilizing the above techniques. In the present chapter studies of delineation of dislocation by characteristic etch features and also of growth features on crystal surfaces by high resolution optical techniques are reviewed.

The number of papers on observations of dislocations which have been published by now is so large that it is impossible to do justice to each one of them with a few pages of this chapter. It should be emphasized that all methods have contributed and are still contributing valuable information on dislocations in crystals. The experimental investigation of dislocations in any crystalline substance should not be considered as completed until studies based by all four methods have been saturated. It is particularly desirable to employ more than one method of observation of the same distribution of dislocations to establish whether all dislocations are visible and whether the configurations are modified by the method used for observation. Examples of this are etching and decoration, or either etching or decoration and one of the X-ray diffraction contrast methods or electron microscopy.

The essential background of the dislocation theory of the strength of materials was reasonably well established in 1949 although much remained to be done in developing the fundamental ideas for particular application. Heck (1937) had observed Spiral terraces on single crystals of paraffin, and Hemmlein (1945) and others had observed similar terraces on carborundum crystals. Honess (1927) had published a book on etch pits on habit faces of minerals and Lacombe and Beaujard (1944) had reported arrays of etch pits on aluminium crystals. Siedentopf (1905), Rexer (1931) and Edner (1932) had described the decoration on linear imperfections in crystals. Heidenreich (1949) had observed imperfections in thin foils of aluminium by using electron microscope. ~~Apart from specu~~

Apart from speculations by shockley and Read (1949) on the possibility that the etch pits on the surfaces of aluminium crystals observed by Lacombe and Beaujard (1944) were associated with dislocations, there appeared to be no experimental support for dislocation theory. The discussion on crystal growth which was organized by Faraday society and held at University of Bristol in April 1949 (" Crystal growth " Discussions Faraday Society) marked the begining of the first phase of rapid development of experimental knowledge of the properties, behaviour and interaction of dislocations in crystals. This represents one of the outstanding advances in physics and chemistry of the solid state. At this conference, Frank (1949) pointed out that it was not possible to explain the observed rates of growth of crystals under conditions of low supersaturation unless some crystal defect was present which would facilitate or eliminate the need for the formation of two dimensional nuclei on the surfaces of growing crystals. According to theoretical calculations, (Burton and Cabrera (1949), supersaturations far in excess of those under which crystals are observed to grow would be required for this. Frank (Loc. cit) proposed that crystal imperfection which played important role in crystal growth was screw dislocation. He showed that even the presence of one screw dislocation would eliminate the need for the formation of successive two dimensional nuclei during growth because the crystal would then have only helicoidal surface. He concluded that participation of single screw dislocation in growth of crystals would be made evident by the appearance of spiral terraces on the surfaces while pairs of screw dislocations of opposite hand would be associated with succession of closed loops. However, no experimental evidence was immediately forthcoming to support his ideas. Later, Griffin (1951) found such features on beryl crystals and his photomicrographs provided confirmation of the validity of the mechanisms proposed by Frank (Loc. cit). Spiral terraces on surfaces of carborundum crystals were then extensively studied by Verma (1951 a, b, c, 1952 a, b) and Amelinckx (1951, 1952 a, b, 1953) and shadowed replicas of spiral terraces on the surfaces of crystals of paraffin were then examined in the electron microscope by Dawson and Vand (1951 a, b). All these observations provided the evidence for occurrence of dislocations with component of Burger vector normal to the surface and this represents a serious limitation of the method of determining presence and distribution of dislocations by the studies of topography of habit and cleavage surfaces of crystals.

The work on the correspondence between etch pits and dislocations arose as a natural sequel to the studies of relationship between spiral growth terraces and screw dislocations. The fact that the dissolution of a crystal occurs preferentially at the site of screw dislocations was first established by Horn (1952). Gilman and Johnston (1956) studied the behaviour of dislocations in Lithium fluoride crystals and found that well defined etch pits were formed at the points in which dislocations intersected the cleavage surfaces, when Lithium fluoride crystals were immersed in a very dilute aqueous solution of ferric fluoride or in a solution containing this substance and hydrofluoric acid. They were able to distinguish between dislocations already present in the crystals and dislocations freshly introduced by plastic deformation and also between edge and screw dislocations.

The first theoretical treatment of the nucleation of etch pits at dislocations was given by Cabrera (1956), Cabrera and Lavine (1956). They postulated that the strain energy localized in the vicinity of a dislocation, lowered the free energy required for the nucleation of a cavity of unit depth at the site of intersection of dislocation with a crystal surface. This leads to the preferential dissolution of dislocation sites on the surface. Gilman (1960) has criticized this model because elastic strain energy of a pure screw dislocation is zero at the surface and both types of dislocations (having some finite energy at the surface) seem to be etched in almost identical fashion. He has suggested that the dislocation core energy is more important than the elastic strain energy for nucleation of etch pits. This is supported by the following observations :- (i) The dislocations in metals are more difficult to etch than those in ionic or covalent crystals (ii) The core energies of dislocations in metals are less than in other types of materials while the elastic strain energies of dislocations are about the same for all materials. (iii) Since overlapping strain fields of dislocations closed together tend to cancel out, it would be expected on the basis of cabrera's model that widely separated dislocations would etch at different rates than ones closely spaced. Contrary to this, it is observed that etch pits at isolated dislocations within the subgrains of a crystal are of the same size as the etch pits in the sub-boundries. (iv) Dislocations having quite different rates (Gatos and Lavine 1960). Schaarwachter (1965) has modified Cabrera's treatment taking due care of core energy suggested by Gilman. He distinguished three cases depending on the relative importance of the contributions of the dislocation core energy and elastic energy. (a) Only the core energy is important in lowering G (change in free energy of a two dimensional nucleus formed at dislocations). This is probably the case for metals. (b) Both the core and strain energy contribute to lowering of G; this is possibly the case for ionic and covalent crystals with small

Burger vector. (c) only the strain energy of dislocation is significant and the cabrera's model is valid. This case applies to materials having large Burger vectors e.g. Organic materials.

3.3 FORMATION OF VISIBLE ETCH PITS :

The necessary condition for the formation of visible etch pits is governed by the kinetics of dissolution ledges as they move across the crystal surface during dissolution. Successive monomolecular ledges usually sweep across closed packed surface. In order for an etch pit to be visible under an optical microscope, the slope of the etch planes should be at least about 3° with respect to a close packed surface. Experimentally measured etch pit slopes for several successful dislocation etching solutions have indeed, been found to lie in the range of 5-12°. For an etch pit to have a sufficiently steep slope the ratio of dissolution velocity Vn (normal to surface) to Vl (lateral or ledge dissolution velocity parallel to surface) must be greater than a certain value, 0.1. In addition to this, the normal dissolution velocity at a dislocation (V_{nd}) be greater than the average vertical dissolution velocity (V_{ndf}) of a dislocation free portion of the surface. The necessary conditions can thus be written as :

$$Vn / Vl \geqslant 0.1 , \quad V_{nd} > V_{ndf}$$

Recently, Shah (1976) found that for better quality of etch pits, on calcite cleavages, the ratio of tangential velocity Vt (or Vl) to V_{ndf} should be greater than 10 and the value of activation energy for tangential movement of steps away from the source, E_t, should be greater than activation energy for surface dissolution, Es. i.e.

$$Vt / V_{ndf} > 10 , \quad Et / Es > 1$$

For a symmetrical pit, all planes forming a pit are equally inclined, while slopes of these planes are different for asymmetric pits. A detailed study of slopes of etch pits was systematically carried out by Ives and Moausland (1968). They have classified pits into three categories, depending upon the various ranges of slopes of pits on (0001) surface of zinc crystals. They reported that planes of the etch pits were vicinal faces.

Impurity may segregate around dislocations in impure crystals. Impurity may enhance greater chemical reactivity, ~~respectively,~~ giving rise to preferential two dimensional nucleation in metal crystals. It is normally observed that etch pitting solutions for most of the metals and semiconductors studied so far are strong oxidizing agents. It is presumed that the first step in the dissolution process is an oxidation of crystal surface. This is followed by the removal of oxide layers. It was observed that oxide nuclei were formed on pure copper crystals (Young, 1960) and on Ge crystals (Faust, 1963). However, these oxide nuclei were not related to dislocations. The influence exerted by impurities on and around dislocations has been discussed in detail by Gilman et al, (1958) on LiF crystals which was etched by water with addition of impurities such as FeF_3, AlF_3 etc. They found that nature of etch pits was dependent on the concentration of FeF_3 solution. The function of FeF_3 is to inhibit the ledge motion. It means that Vl depends upon Fe^{+++} concentration. The Fe^{+++} ion (and such others in about 30 compounds) retards the step motion, apparently by adsorption on the steps, but does not seem to effect V_{nd}. Cations (Fe^{+++}, Al^{+++} etc.) are believed to have strong tendency to form (FeF_6), (AlF_6) complexes and that is why they play a major role and anions do not effect the pit formation. Cabrera (1956) examined theoretically the conditions for the formation of etch pits and oxide nuclei at dislocations. He observed that the energy associated with dislocations having large Burger vector, is sufficient to cause etch pit or oxide nuclei. Sears (1960) reviewed theory of

Cabrera and modified it by including the effect of solution poison. Step poison increases the rate of two dimensional nucleation at fixed supersaturations but markedly decreases the rate of step motion or of spreading of newly formed layers. Ives and Hirth (1960) studied the etch pit profile as a function of concentration of LiF and FeF_3 in the etching solution. The results were consistent with a mechanistic theory involving dissociation of LiF from unimolecular steps on it and subsequent diffusion into solution if a time dependent adsorption of FeF_3 poison at the receding unimolecular steps was involved. The above theory deals with ' part diffusion part inhibitor control of ledge kinetics '. It explains very well other results except slope of pits. According to this theory, the slope of a dislocation pit should decrease with decreasing under-saturation of LiF. Experiment showed the pit slope to be essentially independent of LiF concentration. The explanation given for the discripancy was that the accumulation of an inhibitor on a given ledge increased as the distance between ledge and surface increased i.e. it was a time-dependent process. Westwood (1961) used aqueous solutions of a long chain fatty acids to reveal the point of emergence of dislocations in LiF. This shows that fatty acid may provide a ready source of potential inhibitors for a variety of crystal-etchant systems. Chemisorption and complex formation in this process is likely to affect the core energy available for the nucleation of kinks. Ives and Ramchandran (1967) studied the morphology of etched LiF surface with an electron microscope. It reveals complex structure of surface ledges on (100) cleavege face of this crystal. The ledge structure is complex due to irregular inhibition by ferric ions. Haribabu and Bansigir (1969) after studying the role of poison and undersaturation of the etching mechanism, concluded that the stability of the complexes formed at the kink site and those formed in the solvent layer very close to the crystal surface played an important role in the formation of etch pit. Frank (1958) and also Cabrera and Vermilyea (1958) then applied the theory of kinematic waves to the localized dissolution process. They showed that the role of adsorbed impurity was to promote the bunching of the outward spreading dissolution terraces so that sharp edge depressions were formed which were clearly visible in microscope.

It is known that the optical resolution of a microscope is inadequate to observe the atomic steps or the small bunches of steps in the pit nucleation and early stages of growth. How do steps move during the etching of a crystal ? Where does a ' poison ' act ? How does it act for inhibiting the motion of steps ? What is the exact role of a poison ? The present theory is not yet developed to the extent of answering convincingly these questions.

3.4 ETCH PITS AND THEIR CHARACTERISTICS :

The most noticable feature on a chemically etched surface consists of etch pits. They represent early stages of crystal dissolution and subsequent information concerning the origin, distribution and other important aspects of pits is sought by many workers. Etch pits are used to locate dislocations terminating on a crystal surface. Density of etch pits usually remains constant for different periods of etching. Generally it is higher in metal crystals (10^5 to $10^7/cm^2$), than in ionic crystals (10^3 to $10^5/cm^2$). Crystals with low dislocation density are desirable for the study of indivisual dislocations by etch pit technique. Whether all etch pits reveal dislocations or all dislocations give rise to etch pits is a question, which is not yet fully answered. Dislocation etch pits are usually of same size and shape but may be of different depth. The difference in the depth may be due to inclination of dislocation line or energy of a dislocation. Patel and Ramnathan (1964) observed oppositely oriented triangular etch pits as well as hexagonal etch pits on octahedral cleavages of diamond. They explained these observations by assuming different energies of various dislocations inside the crystal. It is well known that dislocation line never ends within a crystal. However, if it remains inside the crystal it must form a closed loop. The distance between the positions of depth points of a pair of point bottomed etch pits produced on a dislocation loop are varying with etching time and when the loop is exhausted pits coalesce with each other and form a single etch pit. Due to non-existence of dislocation line it becomes shallower on further etching.

The different types of dislocation etch pits (symmetric and asymmetric) were produced on cleavage surfaces of NaCl[Amelinckx (1956)] and LiF by Gilman and Johnston (1956). This is found to be due to different inclinations of edge and screw dislocations. Gilman and Johnston have shown that edge dislocation lines lie normal to the plane of observations in LiF crystals, hence symmetric pits arise after heavy etch by CP-4 etchant, while screw dislocations lie 45° to the plane of observation and etching of screw dislocations gives rise to asymmetric etch pits though symmetrical etchant was used in both cases. They could also distinguish between aged and fresh dislocations. Etch pits formed at aged dislocations are shallower than those formed at fresh dislocations. The different types of etch pits corresponding to edge and screw dislocations terminating on grain boundries were distinguished by their varying depths on surface of NaCl crystals (Amelinckx,Loc.cit), Livingstone (1962) developed etching technique to distinguish between positive and negative edge dislocations in copper. He found two different types of pits (light and dark) on (111) surface of copper single crystals, Marukuwa (1967) also observed dark and light pits on Cu(111) surface. He concluded that pits at screw dislocations had dark appearence.

It is now known that shapes of etch pits are functions of concentration of etchants, etching time, temperature and other conditions of etching. The shapes of etch pits produced by various etchants of different concentrations on calcite cleavages were studied by Honess and Jones (1937), Keith and Gilman (1960), Patel and Goswamin (1962), Pandya and Pandya (1961), Mehta (1972) and Shah (1976). The bounding side of a pit may be rectilinear or curvilinear depending upon the energy of an etchant. Tolansky and Patel (1957) observed rectilinear etch pits when etching was carried out on octahedral faces of diamond by fused potassium nitrate at a temperature below 475°C while at 525°C, etching was much faster and the sides of pits become rounded. Pandya (1969) has also studied the aspects of curvilinearity of etch pits for various crystals, such as calcite and Mica.

Etch pits are usually of three types (1) Flat-bottomed, (2) Point-bottomed and (3) Terraced etch pits. The third type may be further subdivided into (a) flat-bottomed with terraced structure (b) Point-bottomed and terraced with closed layers or with spiral formation. Flat-bottomed pits occur on etched surfaces at the sites of point defects. This is due to formation of chemically highly resistant layers after certain dissolution at point defects, where V_n has extremely small value, nearing zero. However rate of surface dissolution, V_s, does not become zero thereby increasing shallowness of flat-bottomed pits. Point-bottomed pits are observed at line defects intersecting the plane of observation. Depth of point-bottomed etch pit usually increases with etching time. There is also variation of normal velocity of dissolution, V_n, with etching time. Hanke (1961) observed different slopes of same etch pits for different periods of etching by the same etchant. Terraced etch pits are formed at the dislocations associated with impurities (Gilman, 1960). Some times the distance between any two successive layers of terraces are unequal. This was explained on the basis of unequal distribution of impurities around dislocations.

Hanke (loc.cit) has also observed stepped structure of etch pits on cleavage faces of calcite crystals etched by low concentration of glacial acetic acid. He explained that dissociation constant of the etchant at low concentration was more while reaction product was considerably less giving rise to a stepped structure of etch pits.

The eccentricity of an etch pit arises due to the non-coincidence of geometrical centre with depth point, in the plane figure of an etch pit. It is reported in many cases (e.g. on NaCl by Amelinckx 1956, on diamond by Patel 1960, on Calcium floride by Patel and Desai 1965, on Gypsum by Patel and Raju 1967). They had explained the formation of the eccentric pits at the site of inclined dislocations ending on the surface and found no effect on eccentricity due to etchant concentration. Recently Mehta (1972) showed very clearly that besides other factors concentration of an etchant does affect the eccentricity of an etch pit on calcite cleavages.

Etch technique has been utilized to study dislocations and various properties controlled by them. Etch pits essentially reveal the emergent points of dislocations on a surface and therefore, they give a direct measure of dislocation density. Since they have a definite depth, they may also give some useful information about the kind, configuration and inclination of dislocations. Further, etching is also applied to study

(1) Stress velocity for individual dislocations,

(2) Deformation patterns like pile ups, polygonal walls,

(3) Configuration of dislocations in as-grown crystals,

(4) Dislocation multiplication and movements,

(5) Fresh and grown-in dislocations,

(6) Plastic flow around dislocation,

(7) Radiation hardening,

(8) Fracture and dislocation,

(9) Surface orientation determination,

(10) Polarity of crystal lattice,

(11) Reaction mechanism, and

(12) Grain boundry.

3.5 KINETICS AND MECHANISM OF DISSOLUTION :

Inspite of continued efforts over a number of years the exact mechanism of dissolution is not yet well understood. Notwithstanding the formation of guidelines and generalizations in choosing an etchant of the crystal, the selection of an etchant is usually based on a tedious trial and error method. It is often found that many solutions, quite different in composition of their constituents, may give similar results, while with minor changes in the composition or temperature, an etchant which earlier formed dislocation etch pits, may not reveal dislocations or may behave as a polishing solution or vice-versa. Hence a detailed systematic study of reactions occuring on a crystal surface is necessary.

In order to understand the complex reactions occurring on a surface during etching process, one has to consider Laidler's theory of heterogeneous reactions which deals with the dissolution of a solid in a liquid forming products. According to this theory a reaction occurring at the surface may, in general, be separated into five steps, the slowest of which will determine the rate of the overall process. The five steps are : (Gerasimov etal 1974).

(1) Transportation of reactants to the surface (diffusion),

(2) Adsorption of reactants on the surface,

(3) Reaction on the surface,

(4) Desorption of products and

(5) Transportation of products into the bulk.

Depending on the conditions under which the process is conducted and its features, any of the five steps may be the slowest one. Hence the rate of catalytic reaction may be limited by one of them. The rate of diffusion grows with the temperature according to the law similar to the Arrhenius equation, (Gerasimov et al 1974)

$$D = K\exp\left(- E/RT\right)$$

It should be noted that the value of E rarely exceeds 1000 - 2000 calories/mole. (.05ev - 0.15ev) i.e. it is only a small fraction of the activation energies of most of the chemical reactions. Consequently, the increase in the rate of diffusion will considerably be slower than the rate of chemical process in most of the reactions. The surface reactions generally have activation energies of the order of 30 Kcal (or 1.4ev) whereas for the diffusion processes the values are very small. Diffusion is also frequently the rate determining step in the case of solid-liquid reactions owing to its relatively slow rate in solution. In general, the processes 2 and 4 may be expected to be slow steps in heterogenious reaction, provided the activation energy of adsorption and desorption is high. Because of low activation energy the surface reaction 3 is rapid. Such a rapid reaction is to be expected if the adsorbed particles are atoms, the combination of which requires little or no energy. According to the proposed mechanism, it is very probable that the actual combination of atoms on the surface will be rapid, and hence the slow stage in the reaction should be adsorption of the reactant or desorption of the product.

Viscosity (δ) and diffusion (D) are considered in a chemical process to decide its nature. For liquids having low viscosity at room temperature, the value of its activation energy, E_δ , is about 0.14ev. For denser solutions the graph of $\log\delta$ versus 1/T is split into two straight lines with different slopes (Sangwal and Arora 1978). If E_δ and activation energies of dissolution happen to be equal, the dissolution kinetics are fully diffusion controlled (Sangwal and Patel, 1978, Bogenschultz _et al_ 1967). Further the value of activation energy for a diffusion controlled mechansim is usually less than that of kinetically controlled one. (Abramson and King, 1939).

The nature of heterogeneous process is greatly affected by its temperature, pressures of the reactants, rate of flow and porosity of the catalyst. When the temperature changes by 10^{o}K, the rate of diffusion changes approximately by 1.2 times while the rate of a reaction by 3 to 4 times. For this reason when the temperature is reduced, the rate of chemical reaction will decrease faster than that of diffusion (Gerasimov et al. loc.cit). Hence the process may have high values of activation energy at low temperatures and conversely. Such behaviour is observed for porus catalysts.

The rate of dissolution depends on the nature of the etchant, temperature and concentration of the etchant. In particular the concentration dependence of the etch rate is quite complex showing a maximum at particular concentration. Such peaks in the curves of etch rate versus $CuCl_2.2H_2O$ concentration in alcohols were observed in CsI crystals (Sangwal and Urusovskaya 1977, Sangwal et al, 1978) and subsequently in the curves of etch rate versus acid concentration on MgO crystals (Sangwal and Arora loc.cit.). The maxima corresponded to a particular etchant concentration ($CuCl_2.2H_2O$) or HNO_3 and HCl) which formed octagonal or circular etch pits on $\{100\}$ faces of MgO crystals. In case of CsI this behaviour was explained on the basis of the influence of copper complexes on the nucleation and movement of dissolution steps. On $\{100\}$ surfaces of MgO the appearence of maximum was attributed to the adsorption of acid and reaction product. (Sangwal & Arora loc.cit, Sangwal, Patel & Kotak 1979).

A Model for dissolution was proposed by Sangwal (1980). The dissolution of crystal surface on crystal-etchant interface involves the following consequetive steps :

(1) Availability of H^+ and an anion, An^-, on the surface.

(2) Capture and migration of H^+ and An^- ions on the surface.

(3) Formation of a complex.

(4) Adsorption of the complex onto the surface.

(5) Formation of an activated complex on the surface.

(6) Adsorption of the activated complex.

(7) Dissociation of the activated complex into reaction products.

(8) Adsorption of reaction products on the surface.

(9) Transport of the reaction products into etchant.

Steps 1 and 9 of the transport of the reacting species are determined by diffusion kinetics while other steps may be regarded to be limited by the reaction rate between acid and the solid. On the basis of this model, it was argued (Sangwal 1980) that experimental results obtained from their studies on MgO could be understood if adsorption of the reactants and the complexes formed during the dissolution on a perfect surface and at dislocation sites were taken into consideration. It was concluded that the adsorption processes played an important role in the formation of good, contrasting dislocation etch pits and that the adsorption of the activated complex at defect site caused the nucleation of an etch pit (Sangwal, Patel and Kotak, loc.cit).

3.6 FACET FORMATION OF ETCH PIT :

Faust (1969) studied the reactivity of germanium in various oxidizing and complexing agents and suggested that the shape of a pit was controlled by oxidizing agent and the complexing agent controlled by the rate of attack. Vaghari and Shah (1974) studied the effect of different concentrations of oxidizing agents on Bi-single crystals and suggested that the shape of an etch pit was dependent on the strength of the defects and reactivity of etchants. In contrast to them Bhatt et al, (1974) observed that the shape of etch pit was neither dependent on the type of oxident used in the etchant nor on apparent activation energy associated with etching process. Shah (1976) concluded that the shape of an etch pit was dependent on the apparent activation energy. Sangwal and Sutaria (1976) found that the formation of pits of different morphologies was associated with different effective undersaturations developed very close to dislocation sites whereas spherulites and hillocks result when effective supersaturation developed at the crystal surface. The formation of spherulites and hillocks is considered to be a process similar to overgrowth of MgO itself on its cleavages. They also concluded that etch pits were produced under conditions when the solutions have a low viscosity and the reaction products were moderately soluble and that highly viscous etchant led to the formation of spherulites and hillocks.

Several workers have developed dislocation etchants for calcite but the present author has not come across any systematic study on kinetics of entire etching process determining etch pit shapes. Hence optical study of kinetics and mechanism of dissolution of calcite cleavages by organic acids is made to correlate the results with morphology of etch pits.