PART III

THERMAL ETCHING OF CALCITE CLEAVAGES.

CHAPTER 7

THERMAL ETCHING (GENERAL)

7.1 Introduction:

It is well known from the theory of growth of perfect crystals that the time required to grow a crystal of ordinary, normal size in a laboratory is abnormally very high. However, in actual practice, this time is very small; of the order of a few minutes or a few hours. This therefore, clearly suggests that real crystals are imperfect. In nature and even under controlled conditions in laboratories, it is not possible to obtain crystals free from all defects. Thus all crystals whether grown in the laboratory or obtained in nature invariably contain some kind of defects. There are a large number of methods now available for detecting and studying ~~these~~ various types of defects. In this chapter work on thermal etching will be briefly reviewed and salient features of this method will be compared with those of others.

7.2 Experimental method for defect studies:

The methods to reveal lattice defects and in particular dislocations in crystals are as follows: (1) Chemical etching, (2) Decoration technique, (3) Ionic etching, (4) X-ray diffraction, (5) Electron microscopy, (6) Field ion microscopy and (7) Thermal etching.

Chemical etching is extensively used for a large number of crystals for revealing dislocations and is discussed in detail in the earlier chapter.

7.21 Decoration technique:

In this technique impurities are added to the crystal ~~of~~ at high temperature. The experimental conditions are so adjusted that impurities diffuse toward dislocations, thereby facilitating detections of dislocations in transparent crystals. Amelinckx (1959) had used this technique to reveal dislocations in rock-salt crystals. Infra-red illumination permits the use of decoration technique for opaque substances. Dash (1956) observed precipitates formed by diffusion of copper into opaque silicon crystal surfaces and identified its linear aggregates with dislocations. By the addition of a suitable impurity dislocations become immobile. This spoils the crystal for further investigation. Hence this technique is less useful for studying the motion and multiplication of dislocations in crystals.

7.22 Ionic etching:

Disturbed place of a crystal lattice can be easily attacked by ions and so dislocations or defect sites may be observed by selective sputtering of ions. Oxidation does not take place during ionic etching which can therefore be studied at higher temperatures also. Ionic etching is used mostly for metals and semiconductors. Dillon and Oman (1960) bombarded silicon and germanium surfaces by argon ions for prolonged period at high and low current density. They reported that pits produced due to high current density are associated with screw dislocations. Sirotenka and Spivak (1961) detected edge dislocation in germanium by heavy ion sputtering while Wehner (1958) concluded from his observations on above crystals that etch pits on germanium surface had no correspondence with dislocation pits produced by selective chemical etching except for a 6^o low angle boundary. Yurasova (1957) used this method for metallic crystals and correlated etch pits with dislocations.

7.23 X-ray diffraction:

The region of a disturbed lattice which surrounds a dislocation is large enough to produce a shadow with a minimum absorption of X-radiation, thereby increasing contrast of the picture. Narliker and Dew - Huges (1963) used X-ray reflection technique to study MgO crystal and concluded that this technique could not be used to study individual dislocations. Lang (1959) applied X-ray diffraction technique to observe individual dislocations in non-metallic crystals and found the direction of Burger's vector. Brummer (1964) reviewed X-ray method for detection of dislocation in mosaic crystals, ionic crystals and polycrystalline materials. This method is non-destructive and can be used for any orientation of the surface.

7.24 Electron microscopy:

Electron microscopy provides much higher resolution (lateral) than that obtained by any other commonly used method. The specimen to be studied is prepared in the form of a thin foil with a thickness of about 1000 A°. The process of converting a sample into above thickness is considered as a destructive process.

Further it should be noted that mechanical behaviour of foil is not necessarily the same as that of bulk crystal.

Hirsch (1959) has used the technique to study fundamental properties of dislocations and the distribution of defects as a function of treatment of the specimens. Menter (1956) observed the crystal lattice by transmission electron microscopy and directly observed imperfections in the lattice in thin crystals of copper and platinum phtaloganine.

7.25 Field-ion microscopy:

Müller (1957) invented the field ion microscope in which fine metal tip of very small radius is subjected to high electric field. The ions used for depicting the tip surface may be hydrogen or helium. He could resolve the atomic lattice of tungsten and rhodium. Surface resolution of the method depends upon the field, hopping height of rebounding gas, radius of tip and its temperature. A paired screw dislocations in iron whisker were observed by this technique (Müller, 1959). Interpretation from field-ion micrograph is quite complicated. However, this method is useful in studying the positions of atoms on a surface.

7.26 Thermal etching:

The principle of this method is that the evaporation of a crystal would take place at defect sites and in particular at dislocation sites, which possess high chemical potential. At elevated temperatures atom movement may take place to establish a mechanical balance between the surface tension and the line tension of dislocation (defect). Movement of molecules is likely to be rapid at defects in crystals raised to a temperature near the decomposition temperature or melting point. Hence etch pits may form at these sites. Thermal etching is employed to reveal and study dislocation patterns in crystals though correlation between thermal etch pits and dislocations has not yet been successfully well established for all crystals.

In a number of cases the observations on the same crystal surfaces by two or more different methods (such as X-ray, etching etc.) have been well correlated. Dislocations in Si and Ge surfaces were revealed by chemical etching. Dash had used decoration technique to study the same surface of Si crystal by diffusing impurities at higher temperatures. He had also used X-ray methods to study this surface, and could obtain good correlation ~~between~~ by these methods. Espange (1961) has used transmission electron microscopy to find spacing between crystal planes, whose value is in accordance with X-ray determination. Spivak et al (1957) preferred ionic etching to the chemical etching because ionic bombardment can be used over wide range of temperature. Further chemical etching is usually applied to a heat treated sample on the assumption that no change in the crystal structure of metal due to this treatment is introduced. The thermal etch treatment for a number of single crystals of metals has been extensively studied by many workers. The low index faces of metal crystals develop a hill and valley structure when heated in a desired atmosphere. Such changes in surface topography (usually called faceting) together with the development of grain and twin boundaries and grooves are the usual patterns produced by thermal etching. When a crystal surface is heated, there is a possibility of evaporation or decomposition or polymorphic transformation of the surface. Evaporation of a crystal may be more at defect sites than at perfect lattice regions. There is a finite probability for etch pit formation on faces similar to chemical etch pit formation. Thermal etch pits are also observed in polymorphic transformation. Thermal decomposition of the crystal also produces etch pits. All these processes usually come under the general term'thermal etching'.

In proper sense thermal etching may be termed as the spontaneous change of the topography of a planar solid surface at elevated temperatures.

Before the concept of dislocations was introduced in the defect study of crystals, review on thermal etching of metal crystals was given by Shuttleworth (1948). He has suggested that the boundary grooves and striations are formed mainly by the surface migration of metallic ions until an equilibrium surface of minimum energy is attained. Hendrickson and Machlin (1955) developed thermal etching technique for revealing dislocations in silver single crystals. A large number of microscopic thermal etch pits were formed whose density is constant and is independent of etching time. When a silver crystal was bent, it was found that density of excess thermal etch figures was dependent invesely upon the radius of bending. Hirth and Vassamillet (1958) have concluded from their observations, that there is not an exact correlation between thermal etch pits and dislocations. In addition, it is shown that the size and distribution of etch pits is a function of orientation of silver single crystals. In other metals such as antimony Shigeta and Hiramatsu (1958) found thermal etching technique to be unsatisfactory for revealing dislocations. This was based on the observation of lower density of thermal etch pits than that of chemical etch pits which revealed dislocations. Recently Bunten and Weintroub (1968) has described sensitive thermal etching technique for revealing the grain size structure of the antimony single crystal, It is clear from above observations on various crystals that thermal etching is not likely to be an exact method to reveal dislocations in metal crystals.

During the past few years much work on thermal etching of ionic crystals in general and on alkali halide crystals in particular has been carried out. Smakula and Klein (1953) observed that thermal etching carried out in vacuum occurred preferentially at distorted points in Thalium halide crystals. They observed that etching proceeded in regular manner, forming pits bound by $\{110\}$ planes. They noted that high temperature produced disordered etching and surface striations.

Freshly cleaved surfaces of NaCl single crystals thermally etched at 750°C in air showed circular etch pits produced at the sites of dislocations ending on the faces (Patel et al 1965). They also observed ~~same~~ some correspondence of thermal etch patterns on matched halves. Evaporation spiral and circular terraced pits were observed on cleavage faces of KCl single crystal.(Patel et al 1966). They attributed the formation of terraces of etch pits at two dislocations very near to etch other. Budke (1968) observed three types of etch pits produced by thermal etching of NaCl in vacuum (10^{-5} torr). (i) Crystallographically oriented square pits, (ii) pits with edges rounded and (iii) shallow pits having no observable fine structure except at their centers.

Takeda and Kondoh (1962) used thermal etch technique to reveal dislocations in nickle oxide in the temperature range of 1550°-1650°C. They found square and rectangular crystallographic etch pits, and a good correspondence of thermal etch pits with chemical etch pits, thereby suggesting the formation of these pits at dislocations. Voitsekhovskii (1968) reported evaporation figures on corundum crystals. It is suggested that the mechanism of crystal evaporation is in all probability similar to that of crystal dissolution and that evaporation figures might be used for finding orientation of crystals. Another oxide which is very well-known is ice which melts at low temperature (0°C). Thermal etching of ice crystals at about -15°C in a low vacuum (10^{-2} torr) was reported by Michelli et al (1964). They suggested the stepwise propagation of etching.

Decomposition of the crystal is also due to thermal etching. Here crystals dissociate into new substances. In evaporation there is only a phase change i.e. from solid to the vapour. Thermal treatment may give rise to polymorphic transformation. Kennedy and Patterson (1962) worked on Thallous nitrate and observed thermal etch pits after polymorphic transformation. They concluded that preferential thermal etching occurred around dislocations in the polymorphic transformation.

When intermetallic compound surfaces are heated up to a decomposition temperature of one constituent the decomposition rate of both the cleaved surfaces may not be the same. Due to different decomposition rates thermal etch pits are formed on a fast evaporating surface at relatively low temperature. Millea and Kyser (1965) reported thermal decomposition of GaAs surfaces. As (111) face decomposes at a higher rate than the Ga (111) surface at a temperature of 750°C. At 800°C the decomposition rates of both faces are nearly equal. In the above process dislocations do not appear to act as nucleation sites. Surface kinks, mechanical scratches and unknown microtopography of surface produced by chemical etching have been observed to act as nucleation sites for thermal decomposition. Regular tetrahedron whose sides are

Ga < 111 > are formed on AS <111 > surfaces. The decomposition rate of the (110) face is intermediate between the As (111) and Ga (111) faces. Density of thermal etch pits is also found to depend on the temperature of decomposition. Hillocks are formed along with thermal etch pits in the above compound. The temperature at which hillocks are formed is usually higher than the temperature at which etch pits are formed. The octahedron (111) faces of Indium antimonide appear to be an exceptional case in which hillocks are formed at temperatures lower than those required for etch pit formation. They are explained on the basis of braking of bonds. In the above cases compound decomposes into their constituents. In the following cases solid A decomposes into solid B + gas C which usually goes to the atmosphere. Singh (1956) studied the decomposition phenomenon of mercury fulminate in which critical size was needed for explosive decomposition. He observed the preferential decomposition along (010) and (110) planes as well as along the growth mark on the surface of crystals. He suggested sites of nuclei to be probable points of emergence of dislocations on the surface. Jach (1962) has studied thermal decomposition of dehydrated nickle oxalate and suggested preferential decomposition at dislocations. He remarked that linear kinetics resulted from the preferential decomposition and this type of mode was energetically more favourable than at regular reactant product interfaces. Electron microscopic study was carried out on the partly decomposed crystals of CdI_2 (Bristow & Rees, 1963). They observed white patches on partly decomposed faces of above crystals, which were associated with dislocation lines. CdI_2 decomposes into cadmium and iodine vapour. The same type of reaction was observed in calcite crystals. Calcite decomposes fully at 850°C into solid calcium oxide and carbon dioxide gas. Impurity within a crystal sometimes plays a dominant role in the process of thermal etching, e.g. it lowers the temperature at which thermal etching commences. Varshavskii (1965) observed that a pure diamond crystals could be etched in air at 850°C while for thermal etching of ~~for~~ impure crystals took~~e~~ place at a lower temperature. In thermal etching decomposition process should be unidirectional otherwise growth features along with etch figures may be observed and it is difficult to differentiate both features if they are of the same form. Neutron irradiation favours the unidirectional decomposition (Jach 1962).

7.3 Theoretical developement:

Thermal etching may initiate at the imperfections in crystals. Microtopographical changes of surfaces are of two types: (1) Formation of thermal etch pits and/or (2) formation of thermal grooving. The kinetics of atomic migration on a crystal surface, experiencing unbalanced exchange of material with its environment may produce etch pits. The reduction in surface energy with the orientation of the plane may create faceting in the crystal. Faceting is generally observed on a low index plane. The progressive widening of the facets was due to the seperate action of evaporation and condensation. Imperfections are associated with strain field and the local free energy of the crystal surface is greater near the neighborhood of imperfections than for the perfect surface region. In above cases formation of etch pits is similar to that of chemical etch pits. If the rate of evaporation is same for imperfect and perfect surfaces, general evaporation takes place. In this case dislocations may or may not act as nucleation sites for production of thermal etch pits. It may be due to higher amount of thermal energy than dislocation energy or dislocation is mobile and its free energy becomes less when dislocation is at a higher temperature.

It is clear from the above information that controversial results are found in cases of thermal etching of metal crystals which are revealed by thermal etch pits [see e.g. papers by Hendrickson et al (loc. cit.) and Hirth et al (loc. cit.)] on silver crystals . For most of the ionic crystals (such as NaCl, KCl, Cu_2O), thermal etch pits due to evaporation of material at high temperatures are formed at dislocations but it appears that all thermal etch pits donot reveal dislocations. Spiral etch pits formed on NaCl or KCl (Patel et al 1965, 1966) have no correlation with screw dislocations. Thermal decomposition of intermetallic compound does not initiate at dislocations. It starts at highly strained part of surface and also at surface irregularities. Jach (loc. cit.) reported thermal decomposition at dislocations in dehydrated nickle oxalate. Little work is available in literature on the thermal decomposition of crystals. In the present work calcite is chosen for the study of thermal decomposition. Further calcite decomposes at temperature 850°C. It can be easily attainable in ordinary muffle furnace so above crystal was selected for thermal etching work.

The properties used to find correlation between thermal etch pits and dislocations are similar to those used in chemical etching. Matching of thermal etch patterns on the counterparts is a principal test. Further if thermal etching reveals dislocations correlations can be observed for matched surfaces; one of which is chemically etched and other is thermally etched or both are thermally etched. In addition there should be no increase of etch pit density in successive etching. Besides, movement of dislocations can be revealed by thermal etching if thermal etch pits are preferentially produced at dislocations.

The process of crystal evaporation is apparently similar to the process of crystal dissolution. The unsaturated conditions were determined for the evaporation from the difference in temperature of condensate and evaporator, whereas in chemical etching unsaturated solution plays almost the same role. Dissolution and evaporations are physical changes. Some authors termed evaporation as a process of chemical etching. There are certain differences between thermal and chemical etching. Chemical etching effect (where double decomposition takes place) is determined by the chemical reaction between crystal surface and etchant. In thermal decomposition, no chemical etchant is used.

Product/s formed during thermal etching remain/s on the crystal itself whereas in chemical etching these are dissolved in the etchant. Internal structure of etch pits produced by chemical etching is usually well defined than that produced by thermal decomposition which is initiated by thermal energy at a high temperature which bring crystal into an excited state. In chemical etching (where double decomposition takes place) chemical reaction energy is responsible for etching and crystal is not in excited state. Thermal etching is a process similar to chemical etching so far as destruction of surface is concerned.

Chemical etching is well defined method to reveal dislocations sites in calcite. Many organic and inorganic, optically active and inactive, etchants were used successfully to reveal dislocations. Dislocation thermal etch pits due to evaporation of material from the surface at high temperatures were formed in many ionic crystals. However this does not happen in the case of calcite which decomposes at higher temperatures.

Systemic study of thermal decomposition of natural calcite crystals is reported in next chapter.