PART -IV

Controlled Chemical Dissolution of d-AHT crystals

General Information on Dissolution

Chemical Dissolution of d-AHT crystals

Conclusions & Future plan of work

CHAPTER 8

Etching (General)

ETCHING GENERAL

8.1 Introduction:

When a crystal is attacked by an appropriate solvent which chemically dissolves it, the initial dissolution begins at certain preferential sites. 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 crytal 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 the crystal planes and their orientation with one another. At that time production of etch pits on a crystal surface was not understood satisfactorily. Dissolution of a crystal surface is now thought to occur by the 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 spots on the surface. The unit pit grows as steps retreat across the crystal surface through the action of kinks.

The understanding of etch phenomenon was enhanced by the recognition of various types of imperfection in a crystal. The defect points are relatively weakly bound with the crystal surface. They need lesser energy to dissociate than that required by points (atoms) in a regular structure. If a chemical or physical change gives sufficient energy to dissociate imperfections from the exposed surface, etch pits or etch figures are observed on it. A solvent is not necessary at the time of etching. Other appropriate conditions such as ionic bombardment, temperature, etc also help to form etch pits at preferential points on a crystal surface. The following are the ways of obtaining preferential dissolution on a crystal surface.

1) Chemical dissolution;
2) Thermal dissolution;
3) Ionic dissolution;
4) Electrolytic dissolution&
5) Dissolution by dehydration.

The chemical etching usually produces a few or all features on a crystal surface such as:

a) Etch-pits, terraced, flat-bottomed and point- bottomed;
b) Shallow pits, pits with beaks;
c) Linear etch rows and inter secting etch rows;
d) Tunnels and dendritic etch figures;
e) Etch hillocks &
f) Etch spirals.

8.2 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 & iv) Electron microscopy.

Important experimental studies on microtopographical features were made by utilizing the above techniques. In the present chapter studies of delineation of dislocations by characteristic etch features and also of growth features on crystal surface by high resolution optical techniques are reviewed.

The number of papers on observations of dislocations under controlled dissolution which have been published so far is so voluminous that it is impossible to do justice to each one of them in such a short review. 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 complete until qualitative studies of all facets based by all four methods are done. It is 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.

Etching and decoration, or either etching or decoration and one of the x-ray diffraction contrast methods or electron microscopy should be employed.

Heck (1,2) had observed spiral terraces on single crystals of paraffin and Hemmlein and others had observed similar terraces on carborundum crystals. Honess (3) had published a book on etch pits on habit faces of minerals and Lacombe and Beaujard (4) had reported arrays of etch pits on aluminium crystals. Siedentop (5) Rexer (6) and Edner (7) had described the decoration on linear imperfections in crystals. Heidenreich (8) had seen imperfections in thin foils of aluminium by using electron microscope.

Frank (9) reported that it was not possible to explain the observed rates of growth of crystals under conditions of low super saturation unless some crystal defect was present which would facilitate or establish the need for the formation of two dimensional nuclei on the surfaces of the growing crystals. According to theoretical calculations (10) super saturation in excess of those under which crystals are observed to grow would be required for this. He proposed real crystals to be imperfect and the crystal imperfection which played an important role in crystal growth was screw dislocation. Firm confirmation of the validity of the mechanisms proposed by Frank was provided by topographical studies of spirals on several crystal surfaces (11,12,13).

The fact that the dissolution of a crystal occurs preferentially at the site of screw dislocations was first established by Horn (14). Gilman and Johnston (15) found well defined etch pits at the points of intersections of dislocations with cleavage surfaces.

8.3 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 surfaces 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 atleast 3 with respect to a closed packed surface. Experimentally measured etch pit slopes for several successful dislocation etching solutions have indeed, been found to lie in the range of 5- 120 . For an etch pit to have sufficiently steep slope the ratio of dissolution velocity V_n (normal to the surface) to V_l (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:

$10 > V_l/V_n$ or $V_n/V_l > 0.1$

$V_{nd} > V_{ndf}$

Recently Shah (16) found that for better quality of etch pits, on calcite cleavages the ratio of tangential velocity (V_t or V_l) 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, E_s, i.e.

$V_l/V_{ndf} > 10$ $E_t/E_s > 1$

For a symmetrical etch pit, all planes forming a pit are equally inclined, while slope of these planes are different for asymmetric pits. A detailed study of slopes of etch pits was systematically carried out by Ives and Macushand (17). 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, giving rise to preferential two dimensional nucleation in metal crystals. It is considered that the first step in the dissolution process is an oxidation of the crystal surface. This is followed by the removal of oxide layers. It was observed that oxide nuclei were formed on pure copper crystals (18) and Ge crystals (19). However, these oxide nuclei were not related to dislocatons. The influence exerted by impurities on and around dislocations have been discussed in detail by Gilman (20).

Sears (21) reviewed the theory of Cabrera and modified it by including the effect of solution poison. Ives and Hirth (22) studied the etch pit profile as a function of concentration of LiF and FeF_3 in the etching solution. Westwood (23) used aqueous solutions of long chain fatty acids to reveal the point of emergence of dislocations in LiF. Ives and Ramachandran (24) studied the morphology of etched LiF surface with an electron microscope. It revealed complex structure of surface ledges on (100) cleavage face of this crystal. Haribabu and Bansigir (25) after studying the role of poison and understanding 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.

8.4 Etch Pit and their characteristics:

The most noticeable feature on a chemically etched surface is an etch pit. Etch pits are used to locate dislocations terminating on a crystal surface. Crystals with low dislocation density are desirable for the study of individual 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. Patel and Ramanathan (26) observed oppositely oriented triangular etch pits as well as hexagonal etch pits on octahedral cleavages of diamond and explained them by assuming different energies of various dislocations inside the crystal.

Different types of dislocation etch pits (symmetric and asymmetric) were produced on cleavage surfaces of NaCl (12) and LiF by Gilman and Johnstone (15) which were due to different inclination of edge and screw dislocations. Livingstone (27) 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 also observed dark and light pits on Cu (111) surface. He concluded that pits at screw dislocations had dark appearance.

Etch technique has been utilized to study dislocations and various properties controlled by them. Etch pits essentially reveal the emergent points 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 dislocation;
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 dislocations;
7) Radiation hardening;
8) Fracture and dislocation;
9) Surface orientation determination;
10) Polarity of crystal lattice;
11) Reaction mechanism &
12) Grain boundary.

8.5 Kinetics and mechanism of dissolution:

In order to understand the complex reactions occuring 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 relation 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:

1) Transportation of reactants to the surface ;
2) Adsorption of reactants on the surface;
3) Reaction on the surface;
4) Desorption of products &
5) Transportation of products into the bulk.

Depending on the conditions under which the process is conducted and its features, one of the five steps may be the slowest. Hence, the rate of the catalytic reaction may be limited by one of them. The rate of diffusion grows with temperature according to the law similar to the Arrhenius equation (28).

$$D = k \exp(- E/KT)$$

The value of E rarely exceeds 1000-2000 cals/mole (0.05 eV - 0.15 eV) 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 (1.4 eV) 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.

Viscosity (μ) and diffusion (D) are considered in a chemical process to decide its nature. For liquids having low viscosity at room temperature, the value of activation energy E is about 0.14 eV. For denser solutions the graph of log μ versus 1/T is split into two straight lines with different slopes (29). If E and activation energies of dissolution happen to be equal, the dissolution kinetics are fully diffusion controlled (30,31). Further the value of activation energy for a diffusion controlled mechanism is usually less than that of kinetically controlled one (32).

The rate of dissolution depends on the nature of the etchant, temperature and concentration of the etchant. In particular the concentration dependent etch rate is quite complex showing a maximum at a particular concentration. Such points in the curves of etch rates versus $CuCl_2.2H_2O$ concentration in alcohols were observed in CaI crystals (33,34) and also in the curves of etch rate versus acid concentration on MgO crystals (Sangwal and Arora Loc Cit). The appearance of maxima was attributed to the adsorption of acid and reaction product (35).

A model for dissolution was proposed by Sangwal (36). The dissolution of crystal surface at crystal etchant surface involves the following consecutive steps:

1) Availability of H and anion on the surface;
2) Capture and migration of H and anions on the surface;
3) Formation of a complex;
4) Adsorption of the complex into 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.

The adsorption processes played an important role in the formation of good, sharp dislocation etch pits and the adsorption of the activated complex at defect site caused the nucleation of an etch pit.

8.6 Facet formation of etch pit:

Faust (37) 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 the rate of attack. Vaghri and Shah (38) 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 the etchant. In contrast to them Bhatt et al (39) observed that the shape of etch pit was neither dependent on the type of oxidizing agent used in the etchant nor on apparent activation energy associated with the etching process. Sangwal and Sutaria (40) found that the formation of pits of different morphologies were associated with different effective undersaturations developed very close to the dislocation sites. 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.

The present author has performed the optical study of kinetics and mechanism of dissolution of d-AHT cleavages and as grown faces by different etchants.

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