CHAPTER 3

GROWTH AND DISSOLUTION OF CRYSTALS

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3.1 Introduction

As the observations recorded in this thesis are mainly interpreted using the theories of growth and dissolution it appears relevant to give a brief description of the salient points of these two phenomena. Accordingly they find their place in this chapter.

3.2 Growth of Crystals

Interest in crystal growth has, of recent years, been greatly enhanced by the need for the industrial production of single crystals for electronic and optical purposes. One of the most characteristic features of the crystals is their ability to grow in predetermined
geometrical shapes bounded by plane faces. Since rates of growth of crystal faces are in general, functions of supersaturation of the fluid phase from which they are growing it is pertinent to ask how the face of a crystal can grow truly plane when in many cases the conditions of supersaturation may vary from point to point on the face.

3.2.1 Earlier theories of crystal growth

The first quantitative theory of crystal growth was given by Gibbs on thermodynamic grounds. He made use of the analogy between the growth of a liquid droplet in a mist and that of a crystal and argued that only those faces would develop in the crystal which would lead to a minimum total surface energy for a given volume. However, Gibbs realised the essential difference between the random arrangement of molecules or atoms in a liquid drop and the regular arrangement of them in a crystal. Curie calculated the shape and end forms of the crystal in equilibrium with solution or vapour, consistent with the conditions of possessing a minimum total of surface free energies. Wulff further extended Curie's theory and deduced a simple relation between the velocities of growth of different faces in the directions of their normals and the appropriate specific surface free energies. Marc
and Bitzel modified the Curie's theory by considering the influence of surface tension and solution pressure (solubility) and proposed that the crystals will assume an equilibrium form which takes into account both these tendencies.

3.2.2 Growth by surface nucleation and the repeatable step mechanism

Between 1920 and 1940 Kossel, Stranski, Volmer and others had built up a conventional theory of the mechanism of growth of crystals. One of its principal ideas can be illustrated in fig. 3.1 which represents the surface of a simple cubic crystal. The crystal will grow by the addition of molecules at A the so called repeatable step, because the binding energy is the greatest at this point; the molecule joining the surface at any other positions B, C or D will be held by a smaller number of bonds. When a whole line of molecules has been added to the monomolecular ledge, starting of a new line will be a difficult process, since the first molecule to be added will be held by only two bonds. Finally, when a whole monomolecular layer has been completed the next molecule will be held by only one bond and launching of a new layer will involve an even longer delay than the
starting of a fresh line. The process of starting a new layer is known as surface nucleation and involves the simultaneous arrival of a number of molecules on a small group of adjacent sites.

The mechanism of growth described above results in the formation of a succession of monomolecular layers similar to the principle of layer-by-layer growth. In this mechanism the crystal grows by the spreading of layers of constant thickness across the face and the thickness of the layers must be very small as compared to the distance between the advancing fronts. This argument does not depend on assumptions about the detailed mechanism by which the molecules are built into the crystal.

Experiments indicate that in growth from vapour, the rate of direct arrival of molecules at any particular point on the crystal surface is generally small compared to the rate of indirect arrival by surface migration. So Volmer suggested that adsorbed molecules would be able to migrate freely over the surface and might take on an average a very large number of steps on the surfaces before re-evaporating and thus enormously facilitate the rate of growth of the crystal by the
repeatable step mechanism.

Growth by layer deposition has been extensively studied by many workers such as Bunn and Emmet, Griffin, Forty, Williams, Buckley, Seager and Sunagawa.

Discrepancy with the observations

The theory of growth at the kink sites even when assisted by surface diffusion becomes less satisfactory to account for the observed rate of spreading of layers, and still less to explain the rate of surface nucleation. The calculations of the concentration of kinks in a step and the rate of diffusion of molecules by Burton et al led to the conclusion that at normal supersaturation the rate of surface nucleation would be prohibitively slow and for an observable growth rate a supersaturation of at least 25-50% is required. Above this saturation the growth process is not limited by nucleation and an ideally perfect crystal will therefore be able to grow layer-by-layer. But Volmer and Schultze found that crystals do grow at observable rates at supersaturations down to a value of 1% or lower; indeed most regular and well faceted crystals are observed at lower supersaturations. The nucleation theory was
re-checked and found to be essentially correct. The reason for the incapability of the theory to account for the large disparity between the theoretically calculated and the experimentally determined growth rates was yet to be traced out.

3.2.4 Screw dislocation theory of growth

At this stage Frank\(^{18}\) in an attempt to explain this big disparity between the theory and the experiment drew the attention to the probable role of screw dislocation in furthering the growth process, retaining many features of the older theory. He pointed out that the emergence of a screw dislocation on a face of a crystal produces on that face a ledge of height equal to the Burgers vector. If the crystal is pictured as growing by the attachment of molecules to the edge of this ledge then no surface nucleation is necessary, since the ledge in question is self-perpetuating and continues to be present on the surface so long as the dislocation line intersects the surface. The ledge winds itself up into a close spiral centered on the dislocation and as growth proceeds the spiral apparently revolves as shown in fig. 3.2. Further, since the turns of the spiral will be close together a large proportion of the molecules
adsorbed in the surface will reach the ledge before re-evaporating.

The first experimental observation published in support of the spiral growth mechanism of crystals was by Griffin\textsuperscript{9} on beryl. The steps in his case were concluded to be a unit cell high and thus the observed spiral was interpreted as a 'growth spiral'. Verma\textsuperscript{19} and Amelnickx\textsuperscript{20} also simultaneously observed spiral growth steps on SiC.

3.2.5 Criticism of screw dislocation theory

The volume of experimental observations in support of the theory of spiral growth of crystals has increased quite considerably. A collected account of these observations can be got from Buckley\textsuperscript{12}, Verma\textsuperscript{21}, Forty\textsuperscript{22}, and Amelnickx\textsuperscript{23}. However there were workers who expressed their doubts about several aspects of it. The step heights of growth spirals are often too large to be understood in terms of screw dislocations and their developments on the slow growing faces. Buckley\textsuperscript{24,25} suggested that the formation of spirals is connected with macroscopic events occurring in the vapour adjacent to the surface at the moment of solidification. Jagodzinski\textsuperscript{26,27} suggested that the high energy required for the creation of
a screw dislocation cannot come from the crystal structure until the crystal has grown to a considerable volume. The screw dislocation, hence, will play a role only in the later stages of growth of a crystal thereby determining its surface structure but not its crystal structure. This was further supported by Knippenberg's\textsuperscript{28} observations on SiC.

It appears that screw dislocation theory, despite of many set backs explains several facts associated with polytypism in crystals.

3.2.6 Vapour-liquid-solid mechanism

Another mechanism of importance is the vapour-liquid-solid (V.L.S.) mechanism. It differs from the layer nucleation mechanism in that a molten alloy phase is present. Atoms are dissolved in the metal from the vapour and condense in turn from the liquid phase on to the crystal surface. The mechanism was suggested by Wagner et al.\textsuperscript{29-31}

3.2.7 Dendritic growth

One of the commonest modes of growth by which crystals of every possible internal symmetry and chemical composition grow is by the formation of dendrites. They are almost invariably a rule in metals and are common in
crystals grown from solution, melt and vapour.

A typical dendrite consists of a primary stem on to which secondary branches grow and on these grow the tertiary branching. This commonly occurs in one plane but three-dimensional dendrites are also observed. In later stages however the dendrites often fill in and the filling-in process is indistinguishable from the type of growth which produces uniform crystals. The existence of inclusions in the centre of many crystals illustrates the above view that many good specimens grow in this way.

Dendrites are normally single crystals and the branches follow definite crystallographic directions. The branches are often regularly spaced and the opposite sides of dendrites show marked symmetry. Eventhough the cause of this abnormal growth is known to be high supersaturation (rapid deposition) no definite explanation regarding the regularity of dendritic branching has been arrived at so far. However, it has been suggested that the spacing of the branches is decided by the supersaturation of the solution. Buckley has given a detailed account of the theories of dendritic growth.

At times dendrites whose limbs are not related to definite crystallographic directions are also
3.3 Crystal Dissolution

The heterogeneous nature of the reactivity of crystal surfaces has been known for very long time. However, the existence of an inter-relation between the heterogeneities and the dislocations in crystals was suggested by Read and Shockley\textsuperscript{33} particularly in the case of etch pits.

Since dissolution and evaporation are the phenomena which are the reverse of growth, the same concepts of crystal growth can be considered in these phenomena also. Dissolution presumably takes place under conditions of low supersaturation by the retreat of surface steps which have kinks at the active sites. Normal surface steps will disappear in the process. Similarly when a perfect crystal is exposed to a solvent, dissolution probably begins by the nucleation of unit pits of one molecular depth. These unit pits grow as steps retreat across the crystal face through the action of kinks.

3.3.1 Nucleation of etch pits

According to Cabrera and Levine\textsuperscript{34} all structural defects are strained regions and hence have some extra energy localised around these regions. This will
decrease the activation energy required for the nucleation of steps and their motion. Therefore a repeated and rapid nucleation process at the sites of dislocations, which are line defects, will occur as a result of which etch pits will be formed. In the case of a screw dislocation the surface cannot sustain the stress; however to relieve the stress the atoms must re-arrange themselves. In doing so their bonds become strained and it is this strain which may cause nucleation of a pit at a screw dislocation. An etch pit at a screw dislocation can be nucleated due to the revolving retreat of a perpetual step it makes with the surface. For an edge dislocation that intersects a free surface mostly the strain energy remains. Hence the etch pits nucleate two dimensionally at the dislocations due to the localised strain energy.

Besides these facts there are many controlling factors in the etch pit formation. In many metals some impurity segregation is necessary before dislocations can be reliably etched. Addition of poison can inhibit or enhance the motion of steps from the site of nucleation centre as shown by Gilman and Johnston and Ives and Hirth. Frank inferred that all etchants that produce well defined etch pits contain a poison 'either by chance or by design'.
3.3.2 **Mechanism of etching**

The formation of a visible dislocation etch pit depends on the nucleation rate for unit pit at the dislocation and the rate of motion of steps across the crystal surface. These two quantities are reflected in \( v_n \) and \( v_s \) respectively, where \( v_n \) is the linear solution rate normal to the surface at dislocation and \( v_s \) that parallel to the surface. In readily observable pits \( v_n/v_s > 0.1 \). The ratio \( v_n/v_s \) can be increased by (a) increasing \( v_n \) as has been done in the etchants of several metals (b) decreasing \( v_s \) by the addition of an inhibitor as in LiF and (c) by varying the temperature to take the advantage of the difference in activation energy of \( v_n \) and \( v_s \). Gilman et al.\(^{39}\) have shown that \( v_s \) depends very much on the inhibitor concentration whereas \( v_n \) remains almost independent of it. In the case of LiF, Al\(^{3+}\) and Fe\(^{3+}\) were found to be effective ions for slowing down the motion of steps across the surface by forming strong complexes with fluorine. The importance of the complex forming properties of additive cations has subsequently been stressed by several workers such as Urusovskaya\(^{40}\), Gutumanas and Nadgornyi\(^{41}\), Haribabu and Bansigir\(^{42}\) but their views widely differ from those of Gilman et al.\(^{39}\). Hence it can be said that, by and large, the reason why the emergence
points of dislocations are preferentially attacked is not well understood yet. Nonetheless the fact that the pits are produced at dislocation sites is verified by a large number of workers. The first direct proof was independently given by Gevers et al.\textsuperscript{43} and Horn\textsuperscript{44} who showed that etch pits are developed at the centres of growth spirals in SiC. Later many workers employed this technique to study dislocations and these works have been reviewed several times by Forty\textsuperscript{22}, Faust\textsuperscript{45}, Johnston\textsuperscript{46} and Amelinckx\textsuperscript{47}.

3.3.3 Information obtainable from etch pits

Etch pits essentially reveal the emergence points of dislocations in the surface and they, therefore, give a direct measure of dislocation density. Since they are having a certain depth they may also give some information about the kind\textsuperscript{39}, configuration\textsuperscript{48} and inclination\textsuperscript{49} of dislocations. Further, the etching technique has been used to study (a) the stress velocity relations for individual dislocations\textsuperscript{50} (b) movement of dislocations\textsuperscript{50} (c) deformation patterns like pile ups, polygon walls\textsuperscript{51} (d) origin of dislocations in as-grown crystals\textsuperscript{52,53} (e) fresh and as-grown dislocations\textsuperscript{39} (f) radiation hardening\textsuperscript{54} (g) fracture and dislocations\textsuperscript{55} (h) polarity of crystals\textsuperscript{51} (i) reaction mechanism\textsuperscript{56-58} (j) grain
boundaries \( (k) \) distribution of dislocations around indentation \( ^{36,60} \) and (1) effect due to dynamic impacts \( ^{36,61} \)

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