

CHAPTER 2GROWTH AND DISSOLUTION OF CRYSTALS

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## 2.1 INTRODUCTION

As the work reported in the thesis concerns detailed studies of the growth and characterization of calcium molybdate single crystals, it is quite relevant to discuss briefly how and with what driving force actually the crystal grows and dissolves. Hence the existing theories and mechanisms of both the growth and the dissolution of crystals have been discussed in this chapter.

One of the characteristic features of crystals is their ability to grow in predetermined geometrical shapes bounded by plane faces. Since the rates of growth of crystals are, in general, functions of the supersaturation of the melt or any fluid from which they grow, it may be questioned as to how the surface of a crystal can grow truly plane, while in many cases conditions of supersaturation may vary from point to point on the surface. When the fluid is unsaturated or undersaturated, the dissolution of crystal takes place. Depending on the degree of solution undersaturation, the dissolution proceeds on the crystal surface as a whole or on some isolated points on the crystal surface. The question then naturally emerges : how does a crystal dissolve ?

## 2.2 THEORIES OF CRYSTAL GROWTH

Crystallization can be regarded as a two stage process, viz. nucleation and growth. A complete understanding of crystal growth would require the knowledge of many a discipline, e.g., equilibrium thermodynamics, irreversible thermodynamics, chemistry, surface sciences, heat transfer, mass transfer, crystallography, etc. There is a voluminous literature on the various existing theories of crystal growth covered extensively by Buckley (1), Verma and Krishna (2), Strickland-Constable (3), Brice (4), Elwell and Scheel (5) and others (6-12). Kinetics of nucleation from solution have been reviewed by Hirth and Pound (13), Nielsen (14) and Zettlemoyer (15). In most systems used for the growth of crystals, nucleation occurs heterogeneously, that is at favourable sites within the solution such as the crucible wall or the surface of the solution. Nucleation theory, however, normally describes the process of homogeneous nucleation in which the nuclei are considered to form at random throughout the solution, although estimates of heterogeneous nucleation can also be made.

### 2.2.1 Nucleation kinetics

Fluctuations occurring within a supersaturated

solution are likely to give rise to small clusters of molecules, known as "embryos". The probability that an embryo grows to form a stable nucleus would depend on the change in free energy associated with its growth or decay. The change in Gibbs free energy associated with the formation of a spherical embryo of radius 'r' is given by

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \Delta G_v + \Delta G_e + \Delta G_c \quad (2.1)$$

where  $\gamma$  is the interfacial surface energy of the solid phase,

$\Delta G_v$  is the difference in the Gibbs free energy per unit volume between the solid and the liquid phases,

$\Delta G_e$  and  $\Delta G_c$  represent respectively the change in Gibbs free energy due to the strain energy

and to the configurational entropy change associated with the replacement of internal degrees of freedom of bulk crystal by rotational and translational degrees of freedom of isolated embryos (16) and these are normally neglected as a first approximation.

With 'r' increasing from zero, the Gibbs

free energy increases upto a critical value  $r^*$  and later it decreases, implying that  $r^*$  represents the critical minimum size of stable nucleus, whose value is obtained by differentiating equation(2.1), yielding thereby

$$r^* = \frac{2\gamma}{\Delta G_v} \quad (2.2)$$

The critical radius  $r^*$  may be related to the super-saturation if the free-energy change is written in terms of the heat of crystallization as :

$$\Delta G_v = - S_v \Delta T = \frac{\phi v}{T} \Delta T \quad (2.3)$$

where  $\phi v$  is the heat of crystallization per unit volume, and

$\Delta T$  is the magnitude of the supercooling at constant pressure.

For an ideal solution, the equilibrium solute concentration is given by,

$$n_e = n_\infty \exp(-\phi/RT)$$

where  $\phi$  ( $= \Delta H_f$ ) is the molar heat of solution, so that  $\phi = V_M \phi v$ , with  $V_M$  the molar volume. The

relative supersaturation for small values of  $\Delta T$  is

$$\sigma = \frac{\Delta n}{n_e} = \frac{\phi \Delta T}{RT^2} \quad (2.4)$$

so that

$$\Delta G_V = \frac{\phi v \Delta T}{T^2} = \frac{\phi \Delta T}{V_M T} = \frac{RT\sigma}{V_M} \quad (2.5)$$

substituting the value of  $\Delta G_V$  from equation(2.5) into equation(2.2), gives

$$r^* = \frac{2\gamma V_M}{RT\sigma} \quad (2.6)$$

revealing that any increase in supersaturation will entail decrease in  $r^*$  and will therefore favour nucleation.

The value of  $\Delta G$  in equation(2.1) for a nucleus of critical size is

$$\Delta G^* = \frac{16\pi\gamma^2}{3\Delta G_V^2} = \frac{16\pi\gamma^3 V_M^2}{3R^2 T^2 \sigma^2} \quad (2.7)$$

If the solution contains  $n$  molecules per unit volume, the concentration of critical sized nuclei is

$$r^* = n \exp(-\Delta G^*/kT) \quad (2.8)$$

The nucleation rate  $I$ , defined as the number of critical nuclei generated in unit volume per second, is given by the product of concentration of nuclei of critical size and the rate at which molecules join such nuclei, as

$$I = n^* z^* A^* = 4\pi n^* z^* r^{*2} \quad (2.9)$$

Here  $z^*$  is the frequency of attachment of single molecules to unit area of nuclei and  $A^*$  is the area of a critical nucleus.

Putting for  $r^*$  and  $n^*$  into equation(2.9) gives

$$I = \frac{16\pi z^* \gamma^2 n V_M^2}{R^2 T^2 \sigma^2} \exp\left(-\frac{16\gamma^2 V_M^2}{3kR^2 T^3 \sigma^2}\right) \quad (2.10)$$

It is apparent that  $I$  will vary rapidly with the supersaturation  $\sigma$ , mainly through the exponential term.

The above treatment assumed that the probability of growth of the nuclei undergoes a sharp

discontinuity (17) at the critical radius  $r^*$ . Actually embryos of subcritical size will have a finite probability of growing and those of supercritical size may shrink. A correction for such behaviour was applied by Becker and Doring (18), but the resulting expression for  $I$  still varies rapidly with the driving force for crystal growth, which is represented by  $\sigma$  .

#### 2.2.2 Growth mechanism

Once a crystal has nucleated in a solution, the growth process involves the transport of solute molecules from the solution to some point on the crystal surface where they become part of that surface. Of critical importance is the nature of the crystal-solution interface and we consider first the atomic models of the surfaces of crystals.

To the unaided eye, many crystals grown from solution have perfectly flat faces. The important question which will determine the growth kinetics of the crystal is whether this flatness persists down to the atomic level. Without going much into mathematical intrications, all theories of crystal growth may be summed up to have been divided into two parts : the growth

of an ideally perfect crystals and that of real ones. By an ideal crystal is meant a crystal, in which each atom is symmetrically surrounded by neighbouring atoms in a regular geometrical configuration. An imperfect, or a real crystal is one in which the relative positions of atoms differ from those of an ideal lattice by amounts comparable to interatomic spacing.

### 2.2.3 Growth of a perfect crystal

In the first quantitative theory of crystal growth, given by Gibbs (19), based on thermodynamic grounds, an analogy is made between the growth of a water droplet in a mist and the growth of crystal. It is agreed that only those faces develop which would lead to a minimum surface free energy for a given volume. Curie (20) calculated the shape and the end forms of the crystal in equilibrium with solution or vapour, consistent with the conditions of possessing a minimum sum total of surface energies. Wulff (21) further extended the Curie's theory by measuring growth velocities of different faces. Marc and Ritzel (22) modified the Curie's theory by considering the influence of surface tension and solution pressure i.e. solubility. When the differences in solubility are small, growth is influenced

by surface energy and an increase in the surface of one form occurs necessarily at the expense of the other. The idea that different forms might exhibit difference in solubility was urged as a possibility by Lecoq de Boisbaudran (23).

Berthand (24) and Valetton (25) assailed Curie's theory on the ground that greater supersaturation would cause rapider growth and consequently, the crystal habit ought to approximate to the spherical shape, a contradiction to the commonly observed fact. The more rapid the growth, the simpler the crystal becomes usually until one single form predominates to the practical exclusion of all others.

The growth problem remained, for a long time, an obscure problem until it was realised that the atomic structure of matter had to be first introduced. Kossel (26) analysed the atomic inhomogeneity of a crystal surface and emphasised the importance to the growth process of molecular kinks along the steps. Between 1920 and 1940 Kossel (26), Stranski (27), Volmer (28) built up a conventional theory on the mechanism of crystal growth.

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Figure 2.1(a) shows a section through an idealized crystal having atomically flat faces in which the atoms, all identical, have been represented as small cubes. Inside the crystal any atom will have six neighbours and, if the binding energy per atom pair is  $W_B$ , the energy with which the atom is bound into the crystal is  $3W_B$ , since each bond is shared between two atoms. For simplicity, only nearest-neighbour interactions are considered. If a single extra atom is to be added to the crystal, it can form a bond with only one nearest neighbour and so its binding energy is only  $W_B$ . Further atoms may, of course, form extra bonds with this first additional atom (adatom) and so constitute a stable cluster, but the small energy with which the first atom is attached is clearly a major barrier to the growth of this crystal.

An atomically rough crystal interface will have a cross-section such as that shown diagrammatically in Fig. 2.1(b). An atom added at the sites labelled A will form bonds with two atoms in the same plane and atoms arriving at sites labelled B will form bonds with three atoms in this plane. It is clear that any atom incident on this "rough" surface will have a much greater probability of becoming part of that

surface than in the case of the smooth surface. This probability will, however, depend on the binding energy  $W_B$ ,  $2W_B$ ,  $3W_B$ , etc., not linearly but through terms  $\exp(W_B/kT)$ ,  $\exp(2W_B/kT)$ , etc., where  $T$  is the interface temperature and  $k$  the Boltzmann's constant.

It may thus be concluded that atomically rough surfaces have a much higher rate of growth than atomically flat surfaces. Rough surfaces tend to remain rough as long as adatoms which become attached at sites such as those labelled A in Fig. 2.1(b) create new "corner" or "kink" for the attachment of subsequent atoms. However, on a smooth surface, the rate-limiting step will be the addition of a new atom or group of atoms on that surface, since this group will form a layer with a "rough" edge at which atoms can be integrated relatively easily until the layer covers the whole crystal face and the surface is again smooth.

Figure 2.2 exhibits the schematic growth of a three dimensional simple cubic crystal, by the addition of molecules at A, the so-called repeatable step or kink. The molecule joining the surface at any other positions, viz. B or C will be held by two bonds or one bond. When a complete line of molecule has been

added to the molecular ledge, the starting of a new line will be a difficult process, for the first molecule to be added will be held by two bonds. Finally, when a whole molecule ledge has been completed, the next molecule will be held only by one bond and launching of a new layer will involve an even longer delay than starting a fresh line. This is so because the starting process of a new layer (known as surface nucleation) involves the simultaneous arrival of a number of molecules on adjacent sites.

This mechanism described above results in the formation of monomolecular layers, similar to that of layer by layer growth. Both the theories suggest that growth occurs by the spreading of layers of constant thickness across the face and the thickness of the layers must be very small as compared with the distance between the advancing fronts. The repeatable step theory is based on a particular molecular mechanism for the attachment of molecules, whereas the layer-by-layer theory is of general nature, since nothing is assumed here.

Experiments, however, indicate that in the growth from solution or vapour, the rate of direct arrival of molecules at any particular point on the

crystal surface is generally smaller compared to the rate of indirect arrival through surface migration. So, Volmer (28) suggested that the absorbed molecules would be able to migrate freely over the surface and might change the sites a larger number of times before evaporating. Layer mechanism of growth has been extensively studied by Bunn and Emmett (29), Griffin (30), Forty (31), and Sunagawa and co-workers (32,33).

### 2.3 DISCREPANCY IN GROWTH THEORY

The theory of growth at kink sites, even-though assisted by surface migration, becomes less satisfactory to account for the observed, practical rate of spreading of layers and still less to explain the rate of surface nucleation. Calculations for the concentration of kinks in steps and the rate of diffusion of molecules led Burton et al (34) to conclude that at normal supersaturation the rate of surface nucleation would be immensely small, and to obtain an observable growth rate a large supersaturation of at least 25 - 50 % is required. Above this value of supersaturation, the growth is not limited by nucleation and an ideal crystal will be able to grow layer by layer. Real crystals do, however, grow at observable rates at supersaturation of

1 % or lower (35); indeed the crystals grown at such low supersaturation are almost well faceted and of high quality with respect to the concentration of normal defects. The theoretical prediction of the rate with which a crystal should grow at this saturation turned out to be smaller by a factor  $10^{1,200}$ . Since there is an appreciable disagreement between theoretical and experimental growth rates, nucleation theory was rechecked, but was found to be correct. This was, however, not enough to provide a complete basis for understanding the problem of crystal growth.

### 2.3.1 Growth of real (Imperfect) crystals

In an attempt to explain the disparity between the theory and the experiment, Frank (36) drew attention to the probable role of screw dislocations in furthering the growth process, retaining many features of older theory. Grown-in dislocations were thought capable of providing the sources of steps required for continuous, perpetual growth of a crystal. He propounded that the emergence of screw dislocation on a crystal face produces a ledge of height equal to the Burgers vector. If the crystal is to be pictured as growing by the attachment of molecules to the edge of this

ledge, then no surface nucleation is necessary, since the ledge itself is a self perpetuating one and continues to be present on the surface so long as the dislocation line intersects the surface. As the growth proceeds on the surface, the ledge winds itself upto a spiral centred on the dislocation itself. Several stages in the development of the spiral are shown in Fig. 2.3. Further, since the turns of the spiral will be close together, a large portion of the molecules absorbed will reach the ledge before re-evaporation.

Direct evidence of the occurrence of spiral on grown faces were obtained by Griffin (30) on beryl and subsequently by Verma (37), Verma and Amelinckx (38), Forty (39) and others (40-43).

### 2.3.2 Criticism of screw dislocation theory

Though the experimental observations in support of the theory of spiral growth increased considerably, there were workers who expressed their doubts about several aspects of it. The step-height of growth-spirals, e.g. in SiC, are often too large to be understood in terms of screw-dislocation, and Buckley (44,45) suggested their formation to be connected with macroscopic events occurring in the vapour adjacent to the

surface at the moment of solidification. Lang (46), Arora and Rao (47) and others (48-50) have also reported and attributed the formation of macroscopic spirals on different crystals to creation of "mistake" and to bunching of layers. Jagodzinski (51) and Schneer (52) agreed 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 will, therefore, play a role only in the later stages of growth, thereby determining the surface structure but not the crystal structure. This was further supported by Knippinberg's (53) observations.

Nonetheless, it appears that the screw dislocation mechanism, despite many setbacks, explains well several facts associated with polytypism in crystals (37,50).

#### 2.4 VAPOUR-LIQUID-SOLID MECHANISM

In this mechanism, put forth by Wagner et al (54-56) atoms are dissolved in a molten metal alloy phase from the vapour and condense in turn from the liquid phase onto the crystal surface. Growth from vapour has been excellently reviewed by Chernov (57) and

by Hirth and Pound (13).

## 2.5 DENDRITIC GROWTH MECHANISM

The name "dendrite" comes from the Greek word for "tree" and denotes any tree like branched structure (58). Dendritic growth, therefore, is characterized by treelike, or branching, non-faceted crystals. This is one of the most common modes of growth which crystals of every possible internal symmetry and chemical composition take up. This is almost invariably the rule in metals and is common in crystals from solution, melt and vapour.

A typical dendrite consists of a primary stem onto which secondary branches grow and on their secondary branches grow the tertiary branches. This frequently occurs in one plane but three dimensional dendrites are also observed (59). In later stages, the dendrites often fill in and the filling-in process is indistinguishable from the type of growth which produces uniform crystals.

Dendrites are normally single crystals and the branches are often regularly spaced, and opposite side of the dendrite show marked symmetry. It has been suggested that the spacing of branches is decided by the

supersaturation of the mother solution. Originally, a dendrite was thought to be the result of a growth protrusion on a crystal surface. It was felt that the protrusion would collect more material and hence grow more rapidly than the rest of the crystal surface (60). Though the cause of such an abnormal growth is known to be the large supersaturation or rapid deposition, no definite explanation regarding the regularity of dendritic branching has been completely accepted. Buckley (1) gives a detailed account of the theories of dendritic growth.

At times, dendrites whose limbs are not related to definite crystallographic directions are also observed. The exact growth mechanism in operation depends on the crystallographic orientation of the surface, growth rate, defects in crystals, the behaviour of foreign atoms on the surface, the presence of guest crystals and probably several other factors as yet unknown or unproved.

## 2.6 CRYSTAL DISSOLUTION

Crystal dissolution and evaporation both have been known to take place by the retreat of

monomolecular steps across the crystal surface, a process reverse of growth. In the dissolution of a smooth face, atoms or molecules must be removed from crystal steps just as they must be added to a step during growth. In crystal growth new steps may be added by two-dimensional nucleation or at a screw dislocation. During dissolution, steps may also be initiated at the edges of a crystal (Fig. 2.4) or edge dislocations. Therefore, dissolution is often found to be controlled by mass transfer, particularly for polycrystalline materials which have plentiful sites for initiation of steps (61,62). With slight under-saturation, there is a tendency for pits to form at emergent sites of dislocations. This tendency is often amplified by the presence of impurities, which are thought to absorb on the steps and greatly retard the removal of atoms (63-65).

## 2.7 NUCLEATION OF ETCH PITS

According to Cabrera and Levine (66) all structural imperfections are strained regions and have some extra energy localized around them. This decreases the activation energy needed for nucleation and motion of the steps, resulting thereby into rapid formation of / etch pits at dislocations. In the case of screw dislocations,

the surface can not sustain stress and hence to relieve the stress the atoms must rearrange themselves. In doing so, their bonds become strained and this causes nucleation of a pit at screw dislocation. This screw dislocation pit is believed to nucleate due to resolving retreat of a perpetual step it makes with the surface. Gilman (67) questioned this theory and suggested that the very core of a dislocation is the most important in the nucleation process. Addition of poison can inhibit or enhance the motion of steps from the sites of nucleation centres as shown by Gilman et al (68) and Ives and Hirth (69). Frank (11) inferred that all etchants that produce well defined pits contain a poison either by chance or by design.

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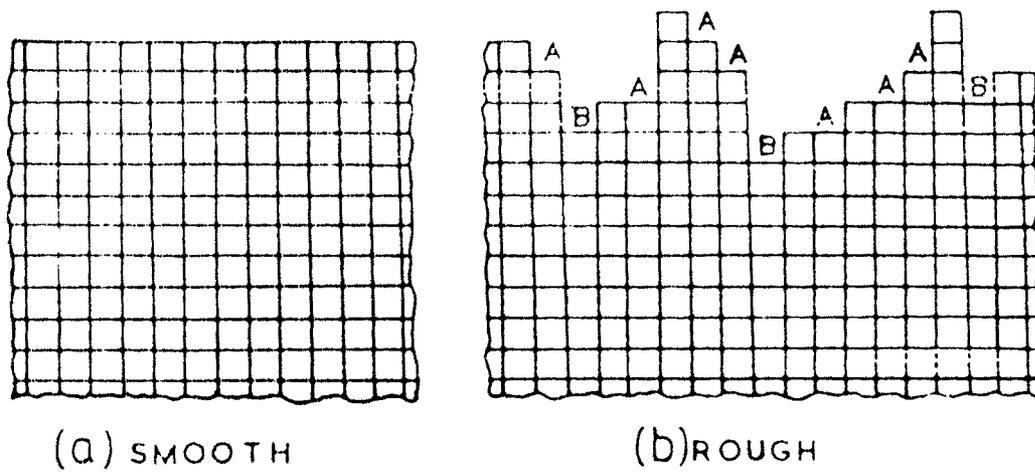


Fig. 2.1 Crystal interfaces (a) flat (b) rough.  
(a, b)

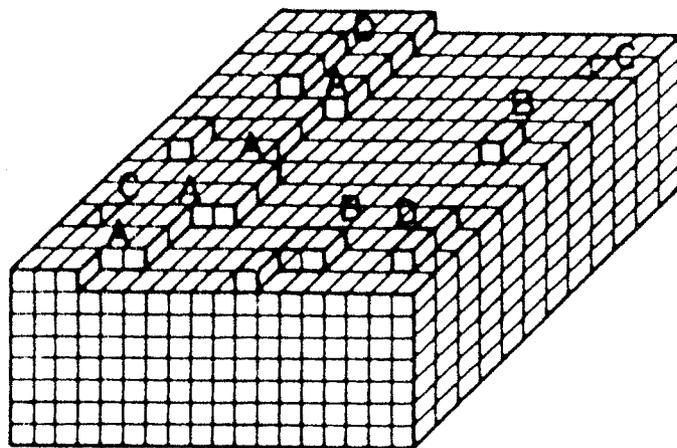


Fig. 2.2 Growth on (100) face of a cubic crystal by the repeatable step mechanism.

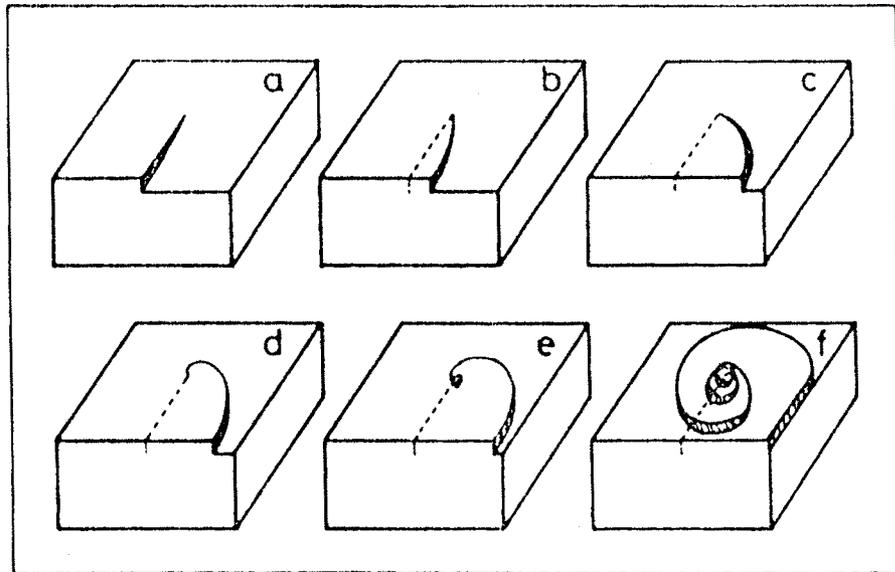


Fig. 2.3 Different stages of the formation of growth spiral at a screw dislocation.

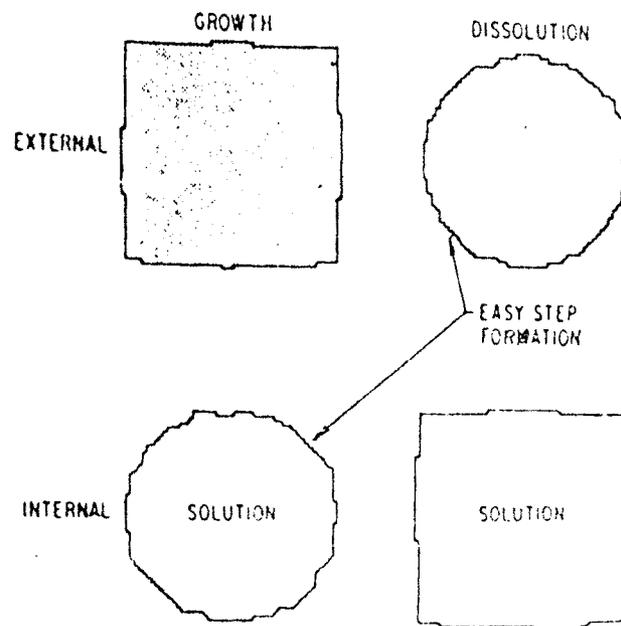


Fig. 2.4 Schematic formation of steps during growth and dissolution.