CHAPTER II

A BRIEF REVIEW OF CRYSTAL GROWTH

This review does not attempt on a comprehensive discussion on the growth of crystals. It is presented as a brief discussion of the recent developments in the field of crystal growth. More emphasis is made on the growth of crystals from melt, the discussion on the vapour phase growth being limited to a presentation of the observation on various metals of the growth spirals in support of Frank's theory. The results of non metals are presented only when it is necessary to keep up the continuity of discussion.

The conventional crystal growth theory starts from the observation that usually, low index crystallographic planes of a crystal exhibit a much lower surface energy than other planes owing to the high density of atoms in the former. At absolute zero of temperature, therefore, the crystal tends to be bordered by the low index plane only as smoothly as possible since this represents a state of lowest energy. At high temperatures atoms are continuously emitted and absorbed on the surface, and can diffuse out of the bulk into that surface, thereby leaving a vacancy in the interior. Steps and isolated atoms will thus form and disappear continuously on the surface in great numbers and all kinds of lattice planes will be exhibited as bounding planes. If now the vapour pressure is increased above the equilibrium vapour pressure at the temperature of the system, more atoms will, on an average arrive at the surface, than leaving it and the crystal grows. However, the addition of the new atom somewhere arbitrarily at the surface, where there is no kink or steps, is energetically a very unfavourable process. Only when an atom once arrived can, by migration over the surface reach a kink, before it is evaporated, does it have any chance to become permanently attached to the crystal. When all the kinks are filled by such an addition the surface becomes smooth and the crystal growth can proceed only by the accidental formation of a new island of absorbed molecules and the addition of molecules or atoms to the kinks formed. The critical size of such a nucleus is found to depend on the vapour pressure p as,

$$R_c = \frac{\gamma a^3}{K\,T \log p/p_o} \qquad \cdots \qquad \cdots \qquad (1)$$

γ is the surface tension, a, the lattice parameter, and po, the equilibrium vapour pressure. The critical nucleus represents an increase in the surface free energy of $2\pi\gamma a R_c$ and accordingly their formation under the action of thermal fluctuation can be expected to occur at a rate proportional to - exp $(2\pi\gamma a R_c/KT)$ which is usually an extremely small factor. In fact, according to this theory, observable growth rate cannot be expected to occur below excess vapour pressure of 25%. Actually, however, growth is often observed under very low super-saturation of the order 1% .

To explain this discrepancy Frank[1] introduced the idea of nucleation in presence of dislocation. The step formed on a surface where a screw dislocation emerges, provides a self-perpetuating edge where atoms can be accommodated without the necessity of two-dimensional nucleation, each time a new layer is completed. Such a step will not remain straight during the process, for, that would require its speed of motion to be proportional to its distance from the dislocation, whereas it will be more or less uniform. As a results it trails behind at the outside and winds itself into a spiral. The rate of growth is equal to the number of times per second the spiral makes a complete turn and hence directly proportional to the square of the degree of supersaturation. This fact has been confirmed by many experiments.

The shape of the spiral generally varies with the type and structure of the crystal on which it grows. Owing to the variation of growth rate with crystallographic direction, the turns often assume a polygonal shape. The emergence of two or more dislocation near each other can give rise to various combined spiral structures or even closed loops of growth steps due to two dislocations, of which some have a configuration which generally resembles that of the dislocation arrangement around Frank - Read source. Others are double pitch spirals due to close dislocations of equal sign.

Spiral markings on the surfaces of crystals of paraffin precepitated from commercial oil have been observed by Heck[2] as early as 1937 and on Silicon Carbide by Miller[3] (1924) and Menzes and Sloat (1929)[4] and few others, much earlier than the dislocation theory was proposed. But no satisfactory explanation could be offered by these authors. The first experimental observation published in support of the theory of crystal growth by spiral mechanism was by Griffin. Using bright field microscopy he observed fine markings on the $(10\bar{1}0)$ face of beryl crystals, which, there are reason to believe, are edges of growth layers. Patterns originating from single and double screw dislocations observed by him correspond with the theoritically predicted shape.

The volume of experimental observations in support of the spiral mechanism of crystal growth has since grown considerably. A detailed account of various growth spirals and their significance is given by Verma[6]. Frank[7] has discussed the development of the theory. Another review article by Forty[8] gives an account of the growth spirals observed on various crystals. SiC and CdI_2 are the crystals studied in greater detail.

Direct experimental observation of screw dislocations in metal crystals has been obtained by Amelinckx and others[9,10] on chemically deposited gold. However, these steps are of large heights and should be considered as anomalous because there is no evidence for expecting such large dislocations in metals. Forty[11] has grown crystals of the hexagonal metals

Mg, Cd and Zn from their vapour in vacuo or in inert atmosphere. Crystals grown on the cooler parts of the tube containing the stock metal usually present facets which are true to the crystallographic orientation within a few seconds of arc. Crystals of Magnesium and Cadmium showed faint growth spirals curvilinear in shape which, as could be inferred from their low visibility, are probably monomolecular. A few examples of growth hills with step lines are closed loops were observed, but there was no terrace at the centre of these. In each of these crystals evidences for two or more screw dislocations were not observed. Rather surprisingly no growth spirals could be observed on zinc crystals. But a large number of closed loops with a speck of material at the centre could be observed. Forty suggested that this could be due to the growth by two dimensional nucleation catalysed by the crystalline overgrowth of zinc oxide. However, this explanations cannot be considered as conclusive, since one fails to understand why the growth of Mg is not catalysed by M_gO. Dawson[12] has suggested that these growth hills are produced by pairs of dislocations of opposite sign which have since moved together to complete the inner loop. However, it is unlikely that this should happen so completely in every case.

Forty & Frank[13] have observed growth spirals on both cubic and octahedral faces of silver crystals grown from vapour. This is the first observation of screw dislocation of unit

Burger's vector in a cubic crystal. Previously a major criticism of the dislocation theory of crystal growth was that spirals have been observed only on crystals grown in the form of thin plates with layered structure such as cadmium and crystals of complex structure such as beryl.

Subsequent to the publications by Verma[6] and Forty[8], growth spirals have been observed on many crystals. They have been observed on Platinum crystals grown from the $PtCl_4$[14]. Growth spirals have been observed on Titanium crystals also[15]. Excellent loop-patterns, not on the surface, but entirely within the crystals, were disclosed by Dash[16] on silicon crystals using a microscope fitted with an infra-red image tube. Anne Williams[17,18] have studied the growth of lead nitrate crystals from solutions on the effect of local deformation on the crystal surface during the growth. She has been able to show that new growth centres are formed at the deformed regions and these may be initiated whenever desired and if these are strong enough, they do dominate over the existing centres. Raynolds & Grene[19] have reported spiral patterns on cadmium sulphide crystals grown from vapour.

Unique growth patterns with closed loops, partly concentric and partly eccentric with large step height between the ledges of the order of micron have been observed on the microblisters of copper films sputtered on to a glass substrate by Henschke[20]. A special kind of two alternately active growth mechanism, analogous to the Frank-Read sources has been proposed to explain the large step height without assuming dislocations of large Burger's vector.

Dukova,[21] has studied the effect of supersaturation on the form of spirals using paratoludine and other organic crystals and observes the following sequence from low to high supersaturation: (1) polygonised spiral layer (2) Rounded spiral layer (3) disintegration of the spiral layer to concentric loops and (4) layers of dendritic form.

Testuya et.al.[22] have observed recently, three-fold symmetrical pyramids developed from the deposition of germanium vapours produced by decomposition of ~~germanium~~ GeI_2 onto the (iii) surface of germanium crystals, and have suggested that these are formed due to the more rapid growth rates at sites of dislocations, as suggested by the Frank's theory. They further suggest that a self perpetuating step can be provided not only by a pure screw dislocation but also by an edge dislocation obliquely inclined to the surface.

Lang[23] points out that periodical bunching of advancing or retreating atomic sheets occur on the crystal surface inclined at small angle to the densely packed atomic plane and it causes microscopically observable steps to appear. Such steps usually form concentric rings and a simple mistake in the early stages of step formation can produce, instead of rings, a continuous spiral steps and no screw dislocation is required for the production of the spiral.

The discussion presented above form the uptodate data on the spirals and closeloop patterns observed on the crystals. To assess the present day situation in brief, it can be stated that spiral growth is the only possible mechanism of growth from vapour and dilute solution under lower supersaturation. Impurities and other factors can also effectively provide suitable steps in crystal growth as observed for zinc by Forty. Macroscopic spiral layers can also be formed without screw dislocation. The analysis of the spirals and closed loops should be made very carefully, and only when there are indications of the presence of dislocation detectable by other means, can we attribute the spirals of large step height to the dislocations.

During the last few years, a good amount of information has been obtained on the mechanism of crystal growth from melt. Much of the work on metals has been carried out by Chalmers and his co-workers; and on the semi conducting elements, germanium and silicon by members of the major electrical establishments and government institutions in the United States and Great Britain. Keen interest in the problem has been evinced in the U.S.S.R. and other nations recently. Though the growth process can be pictured as an atom-to-atom addition to the lattice, similar to the growth from vapour the experimental evidences of recent years rules out the necessity of a screw dislocation to promote the growth of metal crystals from melt. This conclusion has been arrived at from a number of observations. Firstly Dash[24] has successfully grown large areas of single crystals of silicon free from dislocation. A few other metal crystals have also been grown without observable dislocation. Secondly the high symmetry of the dendritic growth cannot be accounted for, if the dislocation are necessary to promote growth. Again, the theoretical calculation of growth rates of crystals on a screw dislocation has been carried out by Hillig and Turnbul[25] and the results do not agree for metals like tin, where as it agrees for some organic liquids. Hence the conclusion that nucleation at the re-entrant edge of a screw dislocation is not important for metal crystals growing from melt. Chalmers and Maritus[26] have proposed a step-like interface which provides permanent re-entrant steps which are not propagated by dislocation and evidence for the existence of such steps have been obtained.

Basically, the production of single crystals from melt involves the arrangement of the conditions such that a progressive freezing of the liquid takes place in a controlled manner, which can be considered as the motion of the interface connecting the solid and the liquid phases. The rate at which the interface moves in a direction perpendicular to iself is the growth rate of the crystal. At the freezing solid-liquid interface latent heat is continuously evolved and if the crystal is to grow at the expense of the liquid the latent heat must be removed by conduction along the solid charge, for which a temperature gradient must exist along the solid. More frequently, there exists a temperature gradient in the liquid with the temperature increasing away from the interface, in which case there is a net flow of heat thro' the interface from melt which also must be conducted down the solid. The heat transferequation may be written as

$$K_s A_s \left(\frac{dT}{dx}\right)_s - K_l A_l \left(\frac{dT}{dx}\right)_l = A\ L\ P\ \frac{dx}{dt} \quad \ldots \quad (2)$$

where,

K = Thermal conductivity
A = Cross sectional areas of the charge
T = temperature
x = co-ordinates of the interface measured along the charge
P = density of the metal and
l = Latent heat of metal.

The suffixes s and l relate to the solid and liquid respectively. Since A_s,A_l,A are equal. Equation (2) can be rewritten as

$$K_s\ G_s - K_l\ G_l = R\ L\ P \quad \ldots \quad \ldots \quad (3)$$

where G = Temperature gradient
R = Rate of growth

Thus the temperature gradient and rate of growth are two main factors controlling the growth of crystals from melt.

The interest in the field of investigations on the mechanism of crystal growth from melt has been mainly on the following lines : (1) Study of the morphology of the interface and the effect of the various growth parameters on it. (2) Study of the substructures observed on the crystals grown from melt. (3) Study of imperfections, their formation and distribution in the crystals (4) Study of the preferred orientation and the influence of the various parameters responsible for this property. The main factors that influence the growth are temperature-gradient along the solid, the rate of growth and the impurities. A number of review articles have been published on the growth of crystals from melt. The review by Holden[27] clearly indicates that our knowledge about the conditions governing the successful growth of metal single crystals is but meagre and very often contradictory. Another review is by Maritus[28]. At the International Conference on growth and perfection of crystal[29] the various problems were well-discussed. The latest review available in literature on the mechanism of growth of metal crystals from melt is by Hurle[30].

The actual process of crystal growth is usually accomplished by one of the three basic techniques or by some modifications thereof, namely Czochralski method, Bridgman's method and Chalmers method. In Czochralski method a seed crystal is put in contact with the surface of the melt, maintained at a temperature near the melting point. The seed is pulled up vertically at the rate at which the crystal solidifies, while remaining in contact with the liquid. The crystal or the containing crucible is sometimes rotated around its vertical axis for the purpose of maintaing a uniform temperature distribution. This technique has not been used widely for metals. But it is extensively used for the production of silicon and germanium single crystals. Recently it has been used for the production of Bismuth single crystals[31,32].

In Bridgman's method, a container filled with the melt is lowered vertically under an externally imposed gradient. The melt solidifies from the bottom upwards. The rate of freezing is determined by the rate of heat flow from the solid, which in turn depends on the rate of travel thro' the gradient.

The Chalmers method is the modification of the Bridgman's method, in which the container is made to travel horizontally. Seed crystals are used whenever necessary. The advantage of this technique over the Bridgman's method lies primarily in the fact that the upper surface of both solid and the liquid can be observed.

The understanding of the nature of the solid liquid interface is the key to the solution of the problem of crystal growth and no apology is required for the interest on the morphology of the interface. The actual topography of the interface is governed by the thermal pattern, solute distribution and the crystallographic character of the specimen. The interface develops a variety of microstructure, depending on the degree of supercooling. In the absence of supercooling the interface is either planar or step-like. Such cases are obtained in high purity metals, such as the zone-refined specimens. In the presence of small amount of constitutional supercooling, the interface develops small projections and presents a cellular appearance and when large supercooling is present the cellular structure breaks into dendritic. The interface structure has been studied in detail using the decanting technique.

Elbaum and Chalmers[33] have observed~~[33]~~ on the decanted interface of oriented single crystals and bicrystals of lead growing with $\{111\}$ or $\{001\}$, planes parallel or nearly parallel to the interface. When these planes are coincident with the interface the steps became large and wide terraces were observed. No such structure was observed when the crystals were not growing with the $\{111\}$ or $\{001\}$ planes nearly parallel to the interface. No systematic variation of these were observed by varying the growth conditions. Similar results have observed by Rosenberg and Tiller[34] who use the term platelet structure for this feature. Elbaum and Chalmers have explained this phenomenon in terms of creation and migration of steps when the interface is tilted to the close-packed planes. Jackson[35] states the low index platelet represent a type of faceted growth which occurs when the interface is parallel to the isotherm.

Detailed investigation of the cellular structure was first carried out by Rutter and Chalmers using Tin by decanting technique. This has also been studied in a number of metals including lead, aluminium, silver, copper and zinc. The observation of corrugation on the surface of the growing crystal interested the workers, and in an attempt to study whether this phenomenon was a surface feature or a body feature, the interface was exposed by rapidly decanting. On examining the surface it was observed that the interface consisted of a number of hexagonal cells. Subsequent cutting of the crystal with a chemical saw showed that the structure remains same inside the crystal. The corrugations had been observed earlier by Goss and Weintroub[36], who termed them as "fine lines". The corrugations and cells are two perspectives of a columnar structure of the crystal growing under conditions of supercooling, caused by the rejection of the impurities at the interface. The cell boundaries are regions of solute concentration. Thus a crystal growing under conditions of supercooling, can be thought of as a close stack of pencils, the ends of the pencils representing the cellular interface and the axis of the pencil represent the axis of growth.

The nature, size and the direction of the cells and corrugations have been studied in detail as the function of growth rate, impurity content, temperature gradient and the crystallographic nature of the interface. It has been observed that a steep temperature gradient and a slow rate of growth can supress the cellular growth. A large impurity content or a fast growth will result in a dendritic interface. The transition from a smooth interface to that of a cellular one is always characterised by the appearance of a pox-like structure of the interface[37-40]. Hulme[39] has observed that the shape of the cell boundaries of zinc single crystals grown in horizontal boat under conditions of constitutional supercooling depend markedly on the orientation of the crystal.

Rutter and Chalmers[41] have developed theory for the formation of the cellular structure, which can be qualitatively outlined as follow: The accumulation of impurities near the interface results in the formation of a liquid layer adjacent to the interface, which is below its equilibrium liquidus temperature and hence is in an unstable state. A spontaneous nucleation is initiated in this zone which results in the formation of a projection in the interface which was initially plane. The diffusion of impurities at the tip of the projection to the surrounding liquid occurs. This allows the solidification at the tip to proceed at higher temperature of the plane interface, and forces solidification round the bases of the projection at low temperature than at the plane interface. The rise in temperature at the tip of the projection produces the favourable thermal condition of the latent heat flow from the projection to the surrounding liquid and solid, promoting growth of the projection. This favourable condition is maintained only if the projection does not extend into the liquid beyond a certain amount, provided that the temperature increases away from the interface. These factors result in the formation of an array of pprojection in initially smooth interface during non-equilibrium solidification.

Dendritic interface, as has already been mentioned, is the result of a large supercooling whether thermal or constitutional. Dendrites are common features on crystals grown from melt and solutions and has been investigated by Weinberg and Chalmers[42,43] and various other workers. The transition from cellular to dendritic interface has also been studied[44,45]. The growth of strip dendrites of Germanium has been reported by Billig and Holmes[46,47,48] and other workers. Detailed accounts of dendritic growth have been published by Maritus[28], Jackson[35] and others. It must be pointed out that the morphology of dendrites is not completely understood. Little is known about the secondary dendritic arms.

Striations or lineage structure are another prominent substructures of metals and have been studied in some detail by Chalmers and others[49-54]. The striations are body phenomena and are in general, parallel to the crystal axis or, at fast rates, along certain close-packed direction. They divide the crystal into a number of different regions differing in orientations by 0.25° to 5°. The lineage boundaries are low angle boundaries, characterised by a conglomeration of dislocations. Chalmers and Tegstoonian[50] have proposed that the boundaries are formed by the condensation of vacancies at, or behind, the interface. The vacancy condensation theory is now subject to open criticism, and Chalmers[55] has reviewed the situation recently.

The development of preferred orientation in metals has been observed since long. Goss and Weintroub[36] have observed during their growth studies on single crystal that for metals, cadmium, tin and bismuth, the preferred orientation was that for which the direction of maximum thermal conductivity lay along the axis of the specimen. At fast rates the preferred orientation was found to be different than for the slow. Tammann has used the theory of anisotropy of growth to account for the preferred orientation. But this theory cannot explain the preferred orientation in cubic crystals which are not anisotropic. The development of the platelet system, the growth direction of dendrites, are cases of preferred orientation.

It has been shown by Rosenberg and Tiller[34] that the orientation of the crystal in columnar castings are directly related to the morphology of the interface. Tiller has explained how, by competitive growth of the platelets, the growth of grains of certain orientation is supressed by grains of other orientation. However the experimental results of Rosenberg and Tiller[34] and those of Walton and Chalmers[57] are contradictory and these must be resolved before any firm conclusions can be drawn on the development of preferred orientation in cubic crystals. Further work is required in case of metals of other symmetry also. Recently Grinberg[58] has observed that in Cadmium, the angle made by the basal plane with the crystal axis is dependant on the rate of travel of mould in a fixed temperature gradient.

The origin of dislocations in as grown crystals is not clearly understood. Theory of vacancy condensation[50] can be ruled out as has already been explained. Propagation of dislocations from the seed, multiplication of dislocation by thermal shock, generation due to poor epitaxy between the seed and the crystal are the possibilities proposed by Dash[24]. Tiller[59] has proposed a mechanism by which edge dislocations are produced at the platelet structure and cell structure. The dislocations are produced, according to him, due to the microseggregation of impurities which produce local changes in the lattice parameter and their density may be of the order of 10^5 - 10^6 lines/cm^2 in case the interface shows a platelet structure, and may be as much as 10^7 lines/cm^2 in case the interface is cellular.

The above review, has already been mentioned, is neither comprehensive nor exhaustive. The present day situation of the theory of crystal growth can be briefly outlined as follows:

The growth of crystals from vapour or from dilute solution, under conditions of low supersaturation is facilitated by screw dislocations. The growth of metals from melt do not require the nucleation at the re-entrant corner of a screw dislocations. The actual topography of the solid-liquid interface is governed by solute distribution, thermal pattern and crystallo-graphic features of the crystals. The same factors influence the orientation of the crystal also. The problem of the development of preferred orientation and the production of dislocations during growth are not yet solved satisfactory.

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