PART - I

CHAPTER-1

CRYSTAL GROWTH FROM MELT

The word 'crystal' may have different meanings for a layman and for a scientist. Crystal growth concepts have been fundamental to many areas of science for quite sometime. Disciplines as diverse as mineralogy, meteorology, biology, medical science, astrophysics and chemical engineering have contributed to and benefited from the crystal growth concepts. In concerted efforts, solid state physics and crystal growth research has led to many new materials and devices. Their applications have had a great impact on modern life.

To grow a good crystal is an art as well as a science. [1] The success of a technique in obtaining good large crystals depends on various factors:

(I) nature of material itself

(II) its purity

(III) thermal environment

(IV) growth rate

(V) pressure

(VI) diffusion coefficients of the materials

(VII) impurity concentration

(VIII) homogeneity

The classification scheme of growth technique can best be an abbreviated version of that of Laudise [2] and is summarized in Table 1.

Table – 1

Crystal growth methods

Monocomponent	Polycomponent
A Solid –solid (solid growth) 1. strain annealing 2. Diversification 3.Polymorphic-phase change	A Solid-solid (solid growth) 1. precipitation from solid solution
B Liquid-Solid (melt growth) 1. Conservative (a) Directional solidification (Bridman-Stockbarger) (b) Cooled seed (Kyropouls) (c) Pulling (Czochralski) 2. Non conservative (a) Zoning (horizontal, vertical float zone, growth on a pedestal) (b) Verneuil (Flame fusion, plasma, arc image)	B Liquid-Solid (melt growth) 1. Growth from solution (evaporation, slow cooling, and temperature differential) (a) aqueous solvents (b) organic solvent (c) molten-salt solvent (d) solvents under hydrothermal condition (e) other organic solvents 2. Growth by reaction (media as above temperature change, concentration change) (a) chemical reaction electrochemical reaction
C Gas-Solid (Vapor Growth) 1. Sublimation-condensation 2. Sputtering	C Gas-Solid (Vapor Growth) 1. Growth by reversible reaction (temperature change, concentration change) (a) Van Arkel (hot wire processes) 2. Growth by irreversible reaction (a) Epitaxial processes.

Thus, as shown in table, crystals can be grown from the solid, liquid or vapour phases. Since the author has grown single crystals from the melt, only this technique will be described in this chapter.

CRYSTAL GROWTH FROM MELT:

To grow large single crystals of metals, alloys and semiconductors the most widely used method is growth from melt. Crystal growth from melt carries maximum theoretical importance also since it is directly the process of phase change from liquid to solid involving systematic aggregation of atoms or molecules into crystalline order from their random distribution in liquid state of the same substance. The basic principles of the crystal growth from melt are based on cooling of a liquid to solidification in a controlled manner. The process of solidification should be so controlled as to promote extension of single nucleus without producing new nuclei and with a minimum of nuclei. Instability of the growing surface can be eliminated by avoiding extensive zone of super-cooling in the melt. Heat transport in the solidification process plays a vital role in the success of growth. Basically the method involves transfer of heat through the solid-liquid interface. The heat transfer can be described by the equation

$$K_S G_S - K_L G_L = LV$$

where, K_S = thermal conductivity of solid

K_L = thermal conductivity of liquid

G_S = temperature gradient in solid

G_L = temperature gradient in liquid

L = latent heat of fusion per unit volume

V = growth velocity

If we required $G_L > 0$, clearly $V > 0$, we must have $G_s > 0$.We must extract heat from the growing crystal.The melt is allowed to solidify in a controlled manner. The parameters affecting the growth process, such as the temperature gradient, the growth velocity and the composition of molten charge are crucial. In the case of some alloys, if a gradient in composition is established in the liquid during growth, there results non-uniform distribution of constituents in the alloy crystal and also the constitutional super-cooling. The composition of frozen material in such a case is always different from that of liquid or the frozen charge. Tiller et [3] and Delves [4] have shown that the constitutional super-cooling can be reduced to minimum

- → by having a steep temperature gradient
- → by having slow growth rate
- → by stirring the melt to minimize solute concentration gradient

Solute segregation occurs at the solid-liquid interface due to unequal equilibrium solute concentration in the liquid and solid states of the solvent. The segregation characterized by a segregation coefficient k, which is the ratio of equilibrium solute concentration in solid to that in liquid. In most alloy systems, $k<1$. For such cases, during crystallization, the solute concentration in the liquid near the interface will increase. The solute rejected at the interface can diffuse into the bulk of the liquid and distribute itself uniformly for sufficiently slow growth rates. In practice, however, this condition is not achieved and a concentration gradient may establish in the liquid. The solute segregation may cause

1) Crystal with non-uniform solute distribution along length of crystal

2) Constitutional super-cooling. Delves [4] has defined a parameter "S" known as constitutional super-cooling parameter which is given by

$$S = mG_{LS}/G_L$$

where, G_{LS} = solute concentration gradient in liquid= $-V(C_L-C_S)/D$

V= growth speed

D= diffusivity of solute in liquid

C_L= concentration in liquid

C_S= required concentration in solid

m= slope of the liquids line at the given composition of alloy, in the phase diagram

G_L= temperature gradient in liquid

It has been shown that if $S > 1$, constitutional super-cooling will occur. Using slow growth rate, good stirring of the melt to minimize G_{LS} and using steep temperature gradient, chance of constitutional super-cooling can be greatly reduced. However, very small growth rate would require extreme care in maintaining stable thermal environment and very steep gradient would produce curved interface. The crystal growth from melt can be pictured as an atom-to-atom addition to lattice similar to the growth from vapor and the experimental evidence rule out the necessity of a screw dislocation to promote the growth of metal crystal from melt. This has been concluded from a number of observations.

Firstly Das [5] has successfully grown large single crystal of silicon free from dislocation. Chalmer et al [6] have proposed a step like interface which provides permanent reentrant steps which are not propagated by dislocation and evidence of the existence of such steps has been obtained.

Study of growth of crystals from melt mainly involves:

- → Study of imperfections, their formation and distribution in the crystal
- → Study of morphology of the interface and the effect of various growth parameters on it.
- → Study of preferred orientation and the influence of various parameters responsible for this property of crystal and
- → Study of the growth features observed on the crystal grown from melt.

Many crystals have been grown from melt by various workers and many reviews have been published [7-12].

There are three basic techniques for crystal growth from melt :

1 Bridgmann method

2 Czochralski method

3 Zone melting method.

1. BRIDGMAN METHOD :

This method was first developed by Bridgman [13] in 1925 to grow single crystals. In this method, the melt in a suitable container in moved relative to a fixed temperature gradient so that the solidification starts from one end and proceeds gradually to the other. The tip of the container, which enters the freezing temperature region first, is usually kept conical so that initially only a small volume of the melt is super-cooled. As a result, only one nucleus is formed or if at all more than one nuclei are formed, only one nucleus with favorable orientation is given the chance to grow by the tapering end. To this method, a modification was introduced successfully by Stockbarger who used two furnaces at different temperatures and separated by a baffle, instead of using a single furnace. This method is called Bridgman-Stockbarger method and provides for desired variation of the temperature gradient. The limitation of Bridgman method is that, it can be used only for low melting point element, which is overcome by the horizontal moving furnace technique given by Chalmers [14] This method is applied for three types of material:

1 Metals [15-16]
2 Semiconductor[17-18]
3 Alkali and Alkaline Earth halides[19-20]

Kumagawa et al [21] have grown ternary mixed crystal on InSb and GaSb seed crystals successfully, using the Bridgman method with high-speed rotation of about 80 to 120 rpm. The growth of $(Sb_xBi_{1-x})_2Te_3$ single crystals with programmable temperature control by vertical Bridgman method has been reported by Fang-Lang Hsu[22]. Yokota et al [23] have grown Cadmium telluride crystals by horizontal two-zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 10^{-7}. Voda et al[24] have grown pure and doped CdF_2

single crystals using Bridgman method wherein unwanted vapour reaction was avoided by using an argon atmosphere and glassy carbon crucibles. Cabric et al[25] developed a method for crystallization of several substances at different rates in a chamber furnace. Eutectic intermetallic compound SnSe has been grown by Siddiqui [26] by the Bridgman –Stockbarger method. One of the important semiconductors namely CdTe crystals are also usually grown by the Bridgman method [27].

HORIZONTAL BRIDGMAN/CHALMER TECHNIQUE:

In this method the charge is contained in a boat which is placed within a horizontal furnace tube which can be filled with the required ambient gas (or evacuated) A muffle furnace is placed around the tube and serves to melt the charge. Directional solidification is obtained by slowly withdrawing the boat from within the furnace. Hence the limitation of the Bridgman technique that it can be used only for low melting point metals is overcome by the horizontal moving furnace technique given by Chalmers [28]

2. CZOCHRALSKI METHOD:

In the year 1918, Czochralski [29] developed this method. In this technique, the material to be grown is melted in a suitable crucible. A seed crystal is then dipped slightly into the melt and slowly pulled away from the melt. The seed is simultaneously rotated also to attain thermal symmetry and to stir the melt. The diameter of the growing crystal depends on the temperature and the pulling rate while it is limited by the diameter of the crucible. Crystals of the various materials have been grown by this method [30-33]. Practical aspects of the technique have been treated in detail by Draper [34]. The excess of heat is removed by conduction and water circulation through the seed –holder which also helps in maintaining temperature gradient. The essential factors for obtaining a good crystal are

→ Pulling rate

→ Accurate control of temperature

→ Rotation rate of seed

Bi_2Te_3 single crystals have been grown by Laudise et al [35] using this method in H_2 and in inert atmospheres. Wenzl et al [36] have grown copper crystals by Czocharaski method in a hydrogen atmosphere at a pressure of 1 bar. A modification known as liquid encapsulated Czochralski technique has also been used [37].

3. ZONE MELTING METHOD:

It is a relatively a more efficient method of growth from melt discovered by Pfann [38].The technique has two important aspects: Impurity removal and uniform distribution of impurity, if any. In this method a small molten zone is created in a large solid ingot of the material to be crystallized and it is passed from one end of the ingot to the other end. The quality of the crystal depends on the relative zone length, growth velocity and temperature gradient. The smaller the zone length, the better is the quality of the crystal. The technique is capable of purifying a material to utmost sparse level of impurities by giving a large number of passes to the ingot in the same direction. This process is known as zone refining process. Impurities with segregation coefficient K>1 are collected at the end molten and frozen first, whereas the impurities with segregation coefficient K>1, are collected at the other end. The portion between the two ends of the ingot can be obtained purer and purer after each successive zone pass. An ingot doped with a known impurity can be made uniform in impurity distribution by the process known as zone – leveling. In this process, a molten zone is repeatedly passed through the length of the ingot in alternate directions. After several such repeated runs, effect of segregation of dopant can be virtually eliminated and the ingot can be made homogeneous. This can be efficiently done by the zone melting technique. This technique is dependent on the ratio of zone length to ingot length, speed of zone travel and the temperature gradient at the solid-liquid interface,.

Parr [39] and Shah [40] have discussed in detail the theoretical and practical aspects of this method. Growth of organic compound crystals by this technique has been reviewed by Herington [41]. The use of this method to grow crystal and to refine various materials has been made by different workers, e.g. Harman et al, Richards, Hamaker, Delves, Brower et al, and Swineheart [42-47].Balazyuk et al [48] have grown cadmium antimonite and zinc antimonite single crystals by zone melting method to study the effect of crystal growth condition on the structural perfection and thermal properties. Lunin et al [49] have studied the distribution in various layers of $Al_xGa_{1-x}Sb$ growing in a temperature gradient field. Shukla et al[50] have grown $CdBr_2$ single crystals by the zone melting method. Interestingly, Serra et al [51] have successfully grown large area zinc sheet crystals by using a modified zone melting method. This is a hybrid of the zone melting and the horizontal Bridgman techniques. Zhanguo et al [52] have used the zone melting method for preparing YBaCuO superconductor successfully.

A detailed account of the work on growth of $Bi_{1-x}Sb_x$ (x= 0.05,0.10,0.15,0.20,0.25 and 0.30) single crystal is given in Chapter 6.

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