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Chapter

Solidification of Metals and Alloys

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Abstract

In order to analyse the process of solidification of metals and alloys critically, it is most pertinent to understand the different modes of nucleation and the uneven rates of growth throughout the melt. It is also important to take a note of the constraints in the growth process that definitely influence the crystal structure and the structure related properties of the casting. The freezing pattern of the liquid melt decides the feeding of the mould which is instrumental in producing a complete and compact casting. For pure metals and even in case of alloys with a narrow freezing range a well defined solid–liquid macro-interface exists. Here feeding of the solidifying casting is the easiest, by the common lowering of the liquid metal surface in the mould. However, in many instances, a well defined interface is not witnessed. The solid–liquid interface could be discrete and not continuous. Here process of feeding the solidification sites that witness considerable shrinkages, may become complicated. On grounds of above it is implied, the process of solidification constitutes an important aspects in the production of a defect free casting.

Keywords: solidification processes, modes of nucleation, rate of growth, crystal structure, freezing pattern solid liquid interface

1. Introduction

The manufacture/fabrication of all men- made objects made up of metals/alloys involve the process of solidification at same stage. It processes of phase change, a liquid phase giving way to a solid phase. In metals and alloys, however, solidification involves the formation of crystals, a crystalise solid exhibiting regularity in atomic spacing over a considerable distance [1]. This is dissimilar from a process involving glasses and polymers. However, even in the case of metal/alloy, when crystals are deposited as a consequence of solidification from the melt, though, there exist certain extents of internal symmetry, there are certain irregular external forms and shapes. This tendency can be attributed to the uneven growth rates throughout the process of solidification and the constraints in the growth process during the last stages of freezing. In the ordinary general case, the solidified grain or cell representing the structure of the solid is a normal crystalline unit formed in the cast structure. However, under the specific case of eutectic freezing, the solidified cell consists of two separate crystal structures with the simultaneous growth of separate phases [2].

The most important practical applications of the process of solidification is found in the production of castings. Indeed, casting can be defined as liquid metal forming. The process consists of introducing the liquid metal of appropriate composition into the mould effecting its solidification under controlled conditions of cooling, pouring, etc. to obtain the desired cast structure [3, 4]. A molten metal has a viscosity which is about one-twentieth of the corresponding solid. Thus, instead

of spending, high energy, overcoming the high flow of stresses of a solid to shape if by adopting bulk metal forming operations of forging, extrusion, rolling, etc. a liquid metal with essentially zero shear stress is required to be handle. A detailed study of the process of solidification, therefore, enables one to know and hence control the microstructure of the casting that decides is microstructural properties.

The process of freezing of a solid from its melt is accompanied by to very important phenomena which decides the intrinsic properties of the resultant casting. At the first instance, freezing is associated with volume contractions as a consequence of the development of a more closely packed solid [5]. At the same time a reduction in the molecular motion is experienced when the randomly moving molecules in the liquid phase generate the nuclei that finally grow into the solid phase. Latent heat of crystalization is liberated at the solid/liquid interface. This liberated heat energy markedly affects the rate and mode of crystal growth. The general fall of temperature to give way to freezing causes a lowering of the solubility of the alloying elements in the melt. Solute atoms are rejected at the solid–liquid interface. The solubility of the alloying elements is further affected as a result of the changed composition of the alloy grossly affecting the final structure of the solidified melt.

Where the casting process is the last stage of fabrication or it has to be followed by further mechanical working, solidification possesses pay an important role in deciding the microstructure of the product and hence its final structure related properties. In this respect, two distinct cases can be considered:

1.1 Casting, the final operation in production

One of the major problems concerning the process of casting involves the local variation of the resultant microstructure leading to compositional variations. The above is illustrated in **Figure 1**.
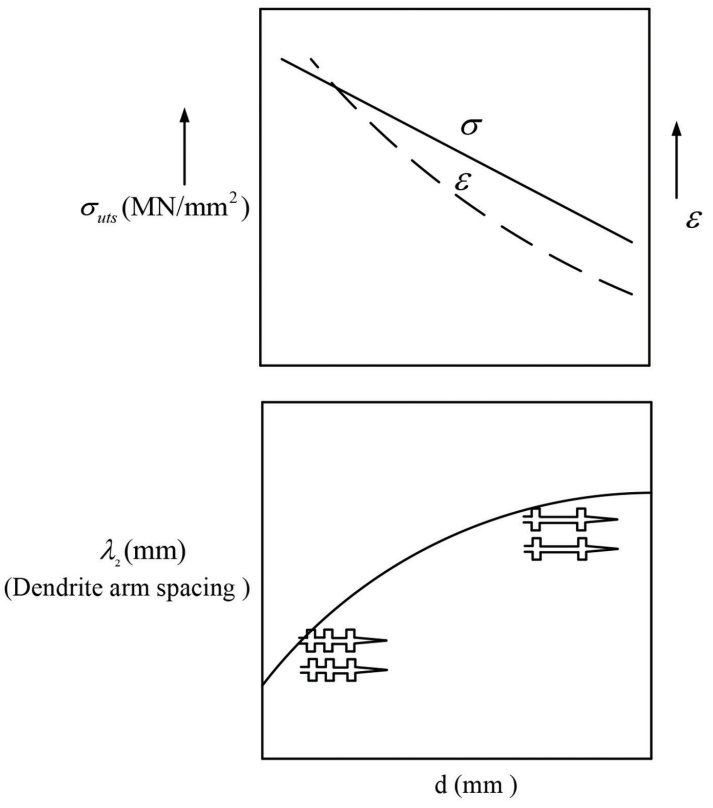

Figure 1.
Schematic presentation of alloy properties as influenced by its position in the melt.

As seen in **Figure 1**, the dendritic arm spacing (λ_2) is measured from the surface of the casting in terms of 'd'. Clearly, with the increase in 'd', i.e., when one goes further into the casting, λ_2 increases. This leads to the resultant variations in the properties of the casting, such as its strength 'σ' and elongation 'ε'. The finer microstructure, in general, exhibit superior mechanical properties. In turn these finer structures are generally formed when the rate of solidification is high. Such high rates of solidification are witnessed as or within a short distance from the surface of the mould. Thus, good combination of mechanical properties are ensured close to the mould surface. As the distance increases from the surface of the mould, into the interior of the casting, rate of solidification decreases, λ_2 increases and grain size of the casting increases rendering a poor combination of mechanical properties.

1.2 Castings with heavy mechanical working

Heavy reduction through mechanical working is not a very efficient method of modifying the edge cast structure. Any initial heterogeneously develop structure, due to the adoption of a faulty solidification process has some tendencies to persist. Therefore, it can be said with authority, any effective control of product quality must be exercised during the process of solidification itself.

The process of solidification comprises of successive stages of **Nucleation** and **Growth**. Whether, freezing is directional or adopts a discrete fashion, throughout the melt, depends on these two factors. In this regard, the location and relative rate of **Nucleation and Growth** hold the keys to the casting characteristics.

2. Concept of nucleation

Any phase change has to get initiated by the emergence of the new phase at some instant of time. Likewise, when a solid phase emerges out of the liquid metal/alloy, it begins with the appearance of Nuclei. These are the cluster of atoms which come together during their course of random motion in the melt and can be termed as the embryonic crystals. These embryonic crystals permit further sitting at atoms on their surfaces which causes the growth of the solid phase. However, many of the nuclei again disappear in the melt, the clustered atoms again moving randomly in the melt. Only those nuclei which are stable and meet the thermo-dynamic requirements, allow growth to take place on their surfaces.

Nucleation can take place in two ways.

2.1 Homogeneous nucleation

The coming together of the randomly moving atoms, from within the melt to form the embryonic crystals, the Nuclei, is known as Homogeneous Nucleation. These are smaller zones of higher density, formed by the ordered cluster of atoms [6]. Mahata et al. have conducted experiments to understand homogeneous nucleation in solidification of aluminium by molecular dynamics simulation [7]. They are of the opinion that there are many methods like X-ray scattering [8] etc., to monitor solid to liquid transformation. However, these methods are limited by several factors that make it difficult to study Homogeneous Nucleation in pure metals.

The precipitation of the group of atoms as the embryonic fresh phase in the melt, is subjected to a change in the free energy. The total free energy change comprises of two components, VOLUME FREE ENERGY CHANGE and INTERFACE FREE ENERGY CHANGE. Thus, a thermodynamic set of conditions is set up

for the formation of the Nuclei and for the Nuclei to be stable and not to dry–out prematurely, these thermodynamic conditions have to be met with.

2.1.1 Volume free energy change

Thermodynamically, when a solid comes out as a liquid, there is a negative free energy change in the system. This change of free energy is directly proportional to the new volume(solid) transformed. Thus, for a spherical solid particle formed in a liquid,

$$\Delta G\left(Volume\right) = -\tfrac{4}{3}\,\Pi\,r^3\,\Delta G_v,$$ where $\Delta G\left(Volume\right)$ - the change in free energy due to the formation of the new volume.

$'r'$ - the radius of the freshly created spherical solid and ΔG_v - the bulk free- energy change per unit volume of the spherical solid created.

2.1.2 Interface free energy change

Thermodynamically, when a new interface is generated due to the emergence of a solid from a liquid, there is a gain of free energy at the interface created. This free energy gained is gained is proportional to the surface area of the solid particle created. For the same sphere, as considered above, with a radius of $'r'$, the free energy gain can be given as:

ΔG (interface) = $4\Pi r^2\gamma$, where, all the terms have their usual meaning, $'\gamma'$ being the interfacial free energy per unit area of a spherical surface.

The volume free energy change and the interfacial free energy change are both presented graphically in **Figure 2**. The **Figure 2** also depicts the overall free energy change as a consequence of the two components when the solid volume is created in the melt.

As seen in the **Figure 2**, for small values of $'r'$, the sum of free energy changes is positive. However, as $'r'$ increases, this sum becomes negative. The peak positive value
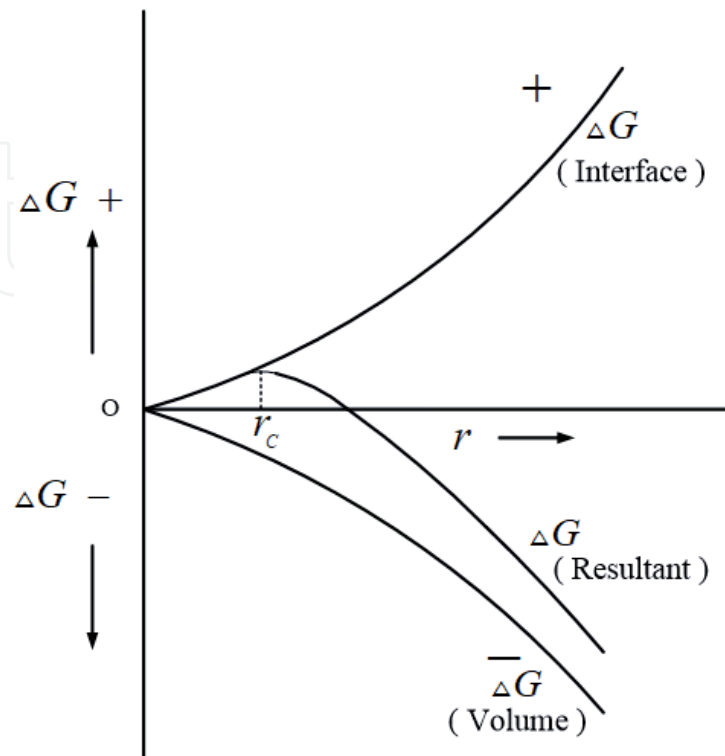

Figure 2.
Change of free energy (volume and interface) as a consequence of the creation of solid phase.

corresponds to the critical radius 'r_c' or the embryonic crystal. The radius of the embryonic crystal must be greater than 'r_c' so that the free energy change ΔG becomes negative, the embryonic crystal becomes stable and growth proceeds. On the other hand, till the 'r_c' is reached, the sum of free energy change remains positive and creates a barrier, obstructing nucleation and the consequent growth. An intent analysis reveals as the temperature falls 'r_c' goes on decreasing. This means, with the fall of temperature, more and more embryonic crystals tend to be stable and the probability of homogeneous nucleation is increased, permitting the growth process to proceed.

From the above it follows, homogeneous nucleation conditions are not favourable at the beginning for the stability of the nuclei as considerable undercooling is necessary for homogeneous nucleation to be effective. In the practical case of casting in a foundry, however, the melt need not be supercooled to make the homogeneous, stable nuclei form to start the solidification process. This is because, in the practical melt in the foundry, solidification processes are initiated by heterogeneous nucleation.

2.2 Heterogeneous nucleation

For heterogeneous nucleation, the initial interface for growth is provided by a foreign particle [9]. This foreign particle can be provided from outside or formed in the melt itself. The impurities, foreign particles or even the mould wall (the subtstate) can provide for a part of the surface energy required for nucleation. It is a known fact that less activation energy (free energy barrier) is required for nucleation. Therfore, the presence of the substate as mentioned above reduced the free energy barrier and can be very helpful in creating more growth capable nuclei. This is known as heterogeneous nucleation which need less activation energy than homogeneous nucleation [10]. This second phase to act as a nucleus, however, must be capable of being wetted by the melt forming low contact angles and also it must have some structural affinity with the crystalline solid to be formed on it. This second phase could be any one or any combination of the following:

a. impurities in the metal

b. the wall of the mould

c. deliberately added particles to encourage a particular mode of crystallisation

Once the heterogeneous nuclei meet the growth conditions, growth occurs on them. After a certain lapse of time, when the temperature of the melt is lowered, the homogeneous nuclei become stable, and more solid may get deposited on them. At the same time, fresh nucleation may occur generating further stable nuclei. These fresh nuclei may be of the same phase as the first nuclei or of a different phase.

3. Growth processes

The growth process is conceived as the sitting of further atoms on the stable nuclei which brings in the growth of individual crystal or a general growth in the mass of the solid as solidification proceeds *the latent heat of crystallisation* is liberated at the solid–liquid interface. *Zones of thermal supercooling* are generated in the liquid pool. Also, with the lowering of temperature the solubility of an alloying element in the liquid melt decreases. As a consequence, the solute is rejected at the solid–liquid interface. The equilibrium freezing temperature of the alloy is

continuously altered and a phenomenon known as *constitutional supercooling*, takes place. Both thermal and constitutional supercooling obstruct growth and alter the growth pattern.

3.1 Plane-front growth

Nucleation does not take place randomly in the metal/alloy melt throughout the liquid because in the actual case of solidification, and uniform lowering of temperature throughout the melt cannot be obtained. There exist a thermal gradient between the cool mould wall surface exposed to the ambience and the interior of the solidifying melt that would eventually form the casting. Therefore, in the practical case, nucleation is initiated at the mould surface and the growth of the solid phase proceed being directed towards the centre of the casting. This growth takes place in a preferred crystallographic direction as dictated by the characteristic of the solidifying crystal. For an example, in a cubic crystal the preferred crystallographic direction is <001>. With the aid of the temperature gradient, the grains oriented favourably grow at a faster rate than the others.

With the lapse of time, depending on the no of effective nuclei and the initial growth rate setup by the initial temperature gradient, the growth of the crystals in the lateral direction gets obstructed. This is because the laterally growing crystals impinge into each other restricting growth of the neighbouring crystals. Also any growth of any crystal ahead of the others, into the high temperature melt is inhibited due to the unfavourable temperature conditions. Such a situation gives rise to planar or plane front growth where in a seemingly plane interface proceeds into the melt causing growth [11]. The interface is plane macroscopically whereas in actual, it is a terraced structure microscopically. This is a typical condition leading to the formation of columnar grains which is often observed in cast ingots. These columnar grains grow in a direction opposite to the direction of heat-flow. This is illustrated in **Figure 3**.

The occurrence of planar growth giving rise to a columnar structure involves thermal condition present in **Figure 4**.

It is assumed, a positive temperature gradient exists at the solid–liquid interface. Here, the liberated latent heat of crystallisation is not enough to reverse the temperature gradient due to the freezing; i.e., a situation is not created when some pockets in the inside of the melt, away from the interface, are at relatively lower
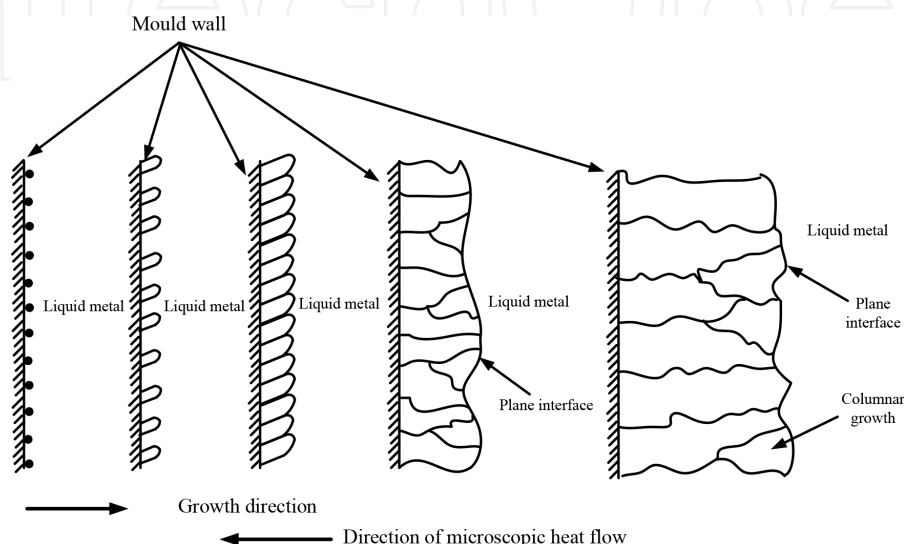

Figure 3.
Schematic presentation of planar growth giving rise to columnar dendrite.
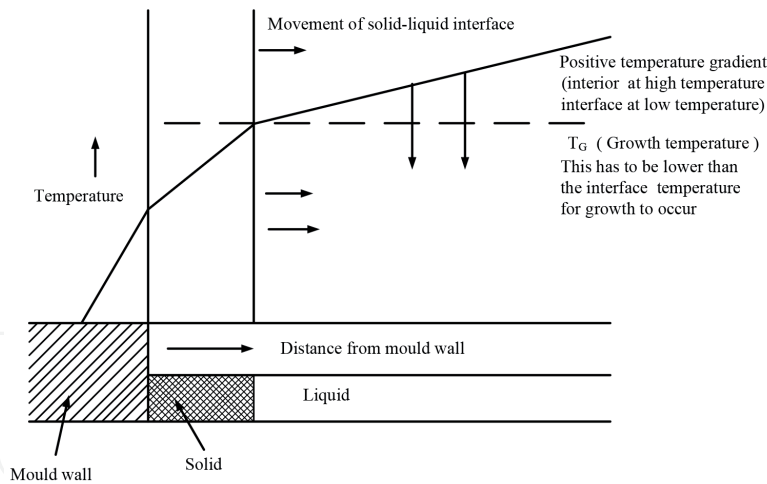
Figure 4.
Schematic presentation of the thermal condition for plane front growth.

temperature. This situation is favoured at slow cooling rates which ensure a stiff and positive temperature gradient. Under these conditions only, the interface assumes the shape of a seemingly plane surface a columnar grain-structure is favoured.

3.2 Thermal super-cooling

The thermal conditions get grossly distributed when sufficient accumulation of the liberated latent heat of crystallisation at the interface is experienced. The liberated heat now disturbs the thermal gradient. Though there is a positive thermal gradient due to the cold mould surface, the local evolution of latent heat produces a reverse temperature gradient at the interface. This is illustrated in **Figure 5**. Where a zone of thermal super cooling indicating pulls in the melt at the interface or adjacent to it at temperatures lower than the equilibrium temperature are witnessed. Obviously, growth does not occur due to the general advancement of the plane-front but by preferential growth processes in these undercooled pulls in the melt.

The planar growth pattern is disturbed as the minimum temperature in the liquid melt is not witnessed at the interface. Plane-front growth is hindered and growth occurs by other means. Depositions of further atoms on the surface of the nuclei may occur in regions of greater under cooling in preference to the interface. The thermal super cooling greatly influences the final structure of the solidified melt.
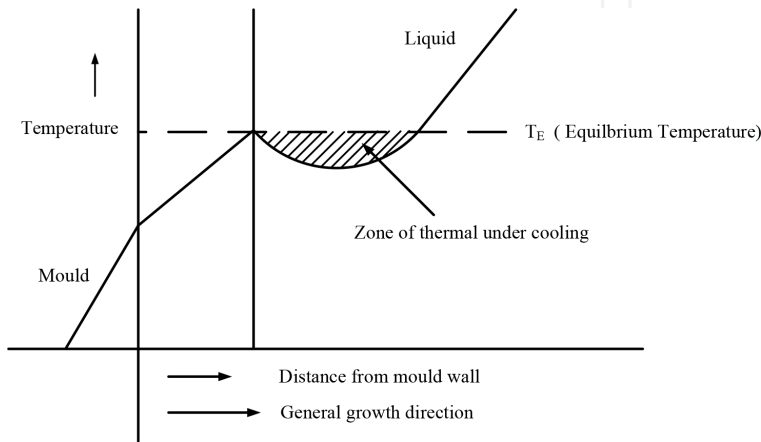

Figure 5.
Schematic presentation of generation of thermal undercooling.

3.3 Constitutional super cooling

Constitutional supercooling in an alloy is best illustrated in **Figure 6**.

The **Figure 6** presents the solidification and hence the phase changes in a simple binary alloy of 'A' and 'B'. Let us consider the alloy of C_o. The initial alloy deposited from Co has a composition confirming to 'C_1'. Obviously, 'C_1' has a composition pertaining to 'B' which is less than that of the original alloy 'Co'. Therefore, as 'C_1' is formed, the residual liquid gets slightly enriched in 'B'. Thus, as solidification proceeds 'B' is continuously rejected into the liquid. This rejection occurs at the solid–liquid interface throughout the process of freezing. A constitutional gradient is, thus, created in the liquid, solute 'B' being continuously rejected at the interface. The concentration of 'B' is maximum at the interface and gradually diminishes as one goes towards the interior of the liquid melt. This compositional variation is presented in **Figure 7(a)**. The change of composition brings in a corresponding change
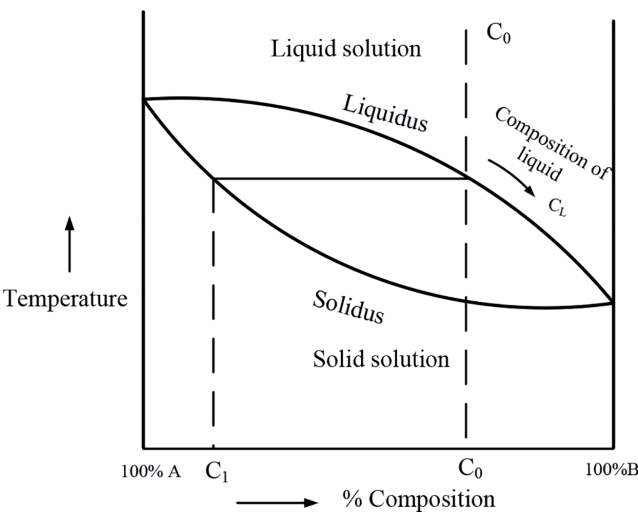

Figure 6.
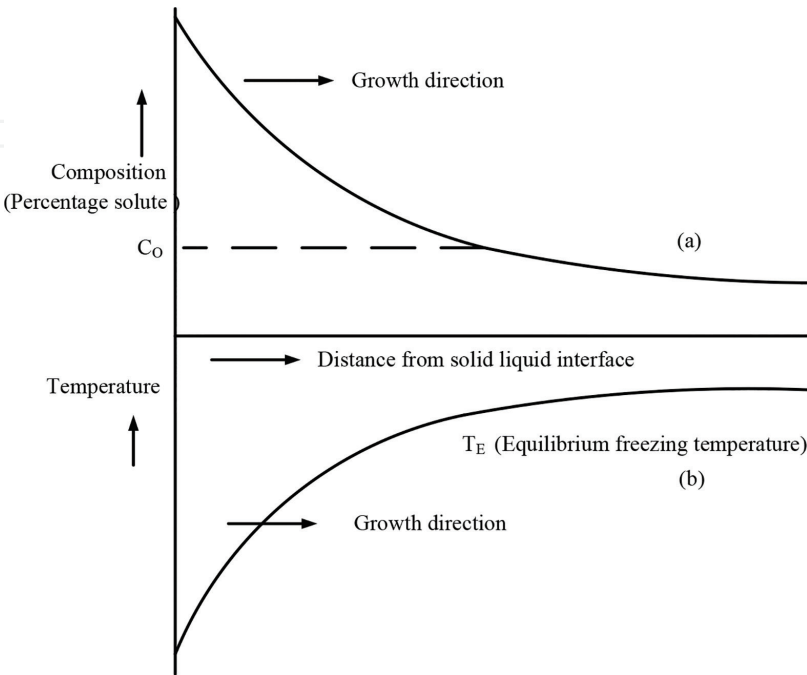*Phase diagram of a typical binary alloy.*

Figure 7.
Schematic presentation of rejection of solute at the interface (7(a)) and change of equilibrium temperature (7(b)) as a consequence of the solute accumulation.
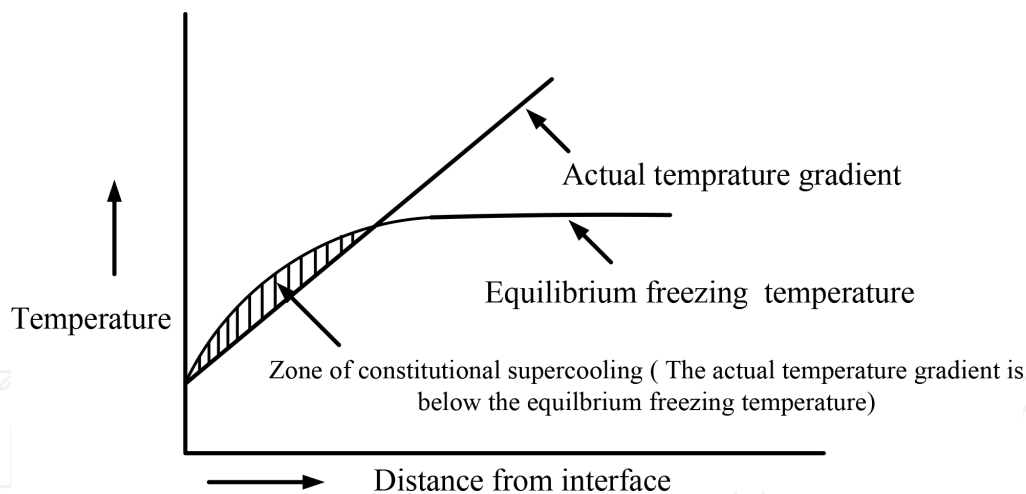
Figure 8.
Schematic presentation of constitutional supercooling as a consequence of solute rejection at the interface and the resultant alternation in the equilibrium freezing temperature.

in the equilibrium freezing temperature of the alloy as presented in **Figure 7(b)**. Each composition on the solute distribution curve has its corresponding equilibrium freezing temperature as it depends on the corresponding composition of an alloy.

The relationship between the actual (existing) temperature gradient in the melt and the equilibrium freezing temperature as a consequence of alterations in the composition of the alloy-melt, is illustrated in **Figure 8**.

Figure 8 clearly illustrates, before the actual (existing) temperature falls considerably for growth to occur, there, is a pool of melt where considerable supercooling can be witnessed at points farther within the melt. In this pool of supercooled liquid conditions are more favourable for freezing than at the interface. This condition is referred to as constitutional super-cooling.

3.4 Freezing of eutectic alloys

Alloys having Eutectic composition or containing appreciable amounts of eutectic constituents, undergo eutectic freezing. The alloy of eutectic composition solidifies at a single temperature to precipitate a mixture of two phases $'\alpha'$ and $'\beta'$ of different compositions, 'x' and 'y' [2]. Thus, two separate phases, of two different compositions are precipitated out at a single temperature as a consequence of freezing of an eutectic alloy. Here, unlike the growth of grains as in a solid solutions, each of the eutectic grains is formed by the simultaneous growth of two dissimilar phases in close association. The eutectic structure could be any one of the following:

a. Alternate laminates of the two,

b. Rod-like or globular solids of apparently discontinuous phase in the matrix of the other phase.

3.5 Other growth modes

It is the extent of undercooling and its relative location in the melt that immensely influence the mode of growth of the crystal in a solidifying melt. As suggested earlier, it can be a thermal undercooling or a constitutional undercooling. Different extents of undercooling may be found in a band of liquid adjoining the interface or even in the inside of the melt depending on the following:

i. Temperature gradient in the melt,

ii. The equilibrium freezing temperature and

iii. The nucleation temperature (which will also be dictated by heterogeneous nucleation)

Depending on the extent of under cooling growth can be Dendritic Growth, Cellular Growth or growth due to independent nucleation.

Dentric crystalline growth takes place on solidification of a metal/alloy melt when the liquid–solid interface moves into supper cooled liquid at a temperature lower than that of the interface. This is illustrated in **Figures 5** and **6** wherein the thermal supercooling or the constitutional supercooling, as the case may be, generate pools in the liquid melt with temperature less than that at the interface. To understand dendritic growth it is important to realise that any protuberance on the solid face may tend to be stable and act as a centre for further growth in preference to other locations due to undercooling. The general advancement of the interface is retarded by the liberated lateral heat of crystallisation or by a solute barrier, but the local growth centres have the possibilities to grow into the zones of supercooling. This gives rise to dendritic growth. This is characterised by commercial alloys forming solid-solutions. It can be emphasised, under rapid solidification conditions non equilibrium condition of solid –liquid interface influence the dendritic characteristics to a great extent [12].

Primary axis of the dendrite is a result of preferred growth at the edge or corner of an existing crystallite. The projection develops into a needle, an then into a plate following the general direction of heat flow. This growth direction is usually associated with a particular crystallographic direction. Again, lateral growth of the primary crystal, needle or plate, is restricted by the liberation of latent heat of crystallisation or solute accumulations that had earlier restricted the growth of the original interface. However, the secondary or tertiary branches may grow by a similar mechanism that helped the formation of the primary stem. This is presented in **Figure 9** which depicts the branch like dendritic growth.

This unidirectional dendritic growth produces columnar dendritic structure.

In a pure metal dendritic growth is detected by interrupted freezing and decantation (once a portion freezes, it is separated from the liquid, i.e., the liquid is decanted from the freezing crystal). On the other hand, in alloys dendritic growth is revealed by the characteristic cored structure. Coring is resulted from the differential freezing processes. The centre of the dendrites are deficient in solute which are rejected to the interdendritic zone, as explained earlier.
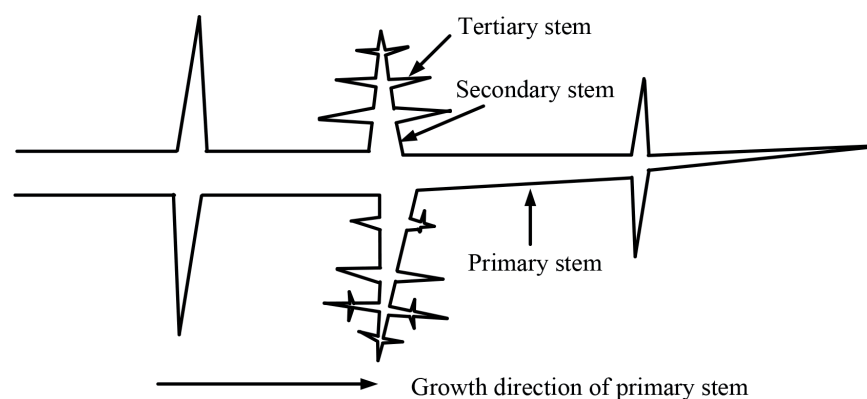

Figure 9.
Schematic diagram showing the growth of a typical dendritic arm.

Dendritic growth may be associated by crystals growing independently on independently formed nuclei, elsewhere in the melt depending on the preventing thermal conditions. This independently growing crystal within the melt has an interface on its periphery. Thus, it is capable of growing in all directions generating an approximately equiaxial grain. With a less marked undercooling, when the undercooling is not enough to form dendrites, cellular growth may still take place. Thus, cellular growth precedes dendritic growth. The cellular substructure is produced as a cluster of hexagonal rods. These rods grow into the liquid and reject solute on their boundaries at the respective interfaces. After a certain level of undercooling is achieved by both thermal and the constitutional means, cellular growth gives way to dendritic growth. This proceeds by the preferential development of some of the cells. This intermediate, rod like structure is also referred to as *Fibrous Dendrites*.

As shown in **Figure 10** when the temperature gradient is very shallow or the rate of freezing is very rapid, the undercooling achieved may be sufficient to promote nucleations at points in the melt,

distant from the main interface. In such an eventuality, the nuclei are free to grow in all directions on their periphery. An equiaxial grain structure, is thus, produced by independent nucleations. **Figure 10**, thus, exhibits the effect of increased undercooling (with the creation of different temperature gradient) on the mode of growth. It also shows the growth pattern with this different temperature gradients existing in the melt in the growth direction away from the mould wall into the interior of the liquid-melt.

3.6 The structure of the casting

Three factors have major influence on the casting structure.

3.6.1 Alloy constituents

The alloy constitution (composition) decides whether the structure will be of a simple phase or eutectic grains or both. The alloy composition also indicates the tendency of the alloy to respond to constitutional supercooling. The extent of constitutional supercooling is certain to influence the growth pattern that decides the crystallographic morphology of the casting.

3.6.2 Thermal conditions

The thermal conditions to which the liquid melt/alloy is exposed during solidification, refer to both, the rate of cooling and the temperature distribution in the
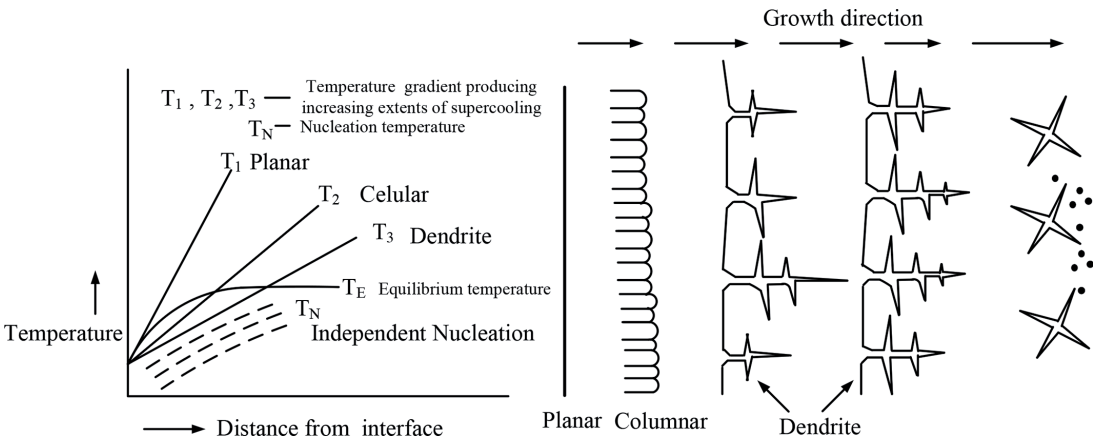

Figure 10.
Schematic representation of the influence of undercooling on the growth pattern and grain morphology.

solidifying melt. This is also related to the thermal properties of the melt as well as that of the mould. Obviously, the above would influence the cast structure by dictating the mode of growth.

3.6.3 Inherent nucleation and growth conditions in the liquid melt

The inherent nucleation and growth conditions in the melt are decided by the presence of foreign particles as well as the solute present in the melt. These solute atoms could be present as trace impurities or may be due to deliberate additions to influence nucleation. Obviously, these will influence/modify the possibilities of nucleation and growth, influencing the cast structure.

To elaborate the above we take help of **Figures 11** and **12**.

The alloys considered in these figures form a continuous range of solid solutions. The **Figures 11** and **12** illustrate the mode of crystallisation and hence the structure of the casting, as governed by the interaction of temperature and compositional gradients in the liquid.

Figures 11 and **12** depict the effect of temperature gradient and that of liquidus temperature profile, respectively on the structure of the casting. Initially when the melt is at higher temperature the existing temperature gradient is stiff [T_i (in **Figure 11**)] planar growth is encouraged and columnar grain structure is favoured. This is assisted by a slow cooling rate. This continues till the temperature gradient
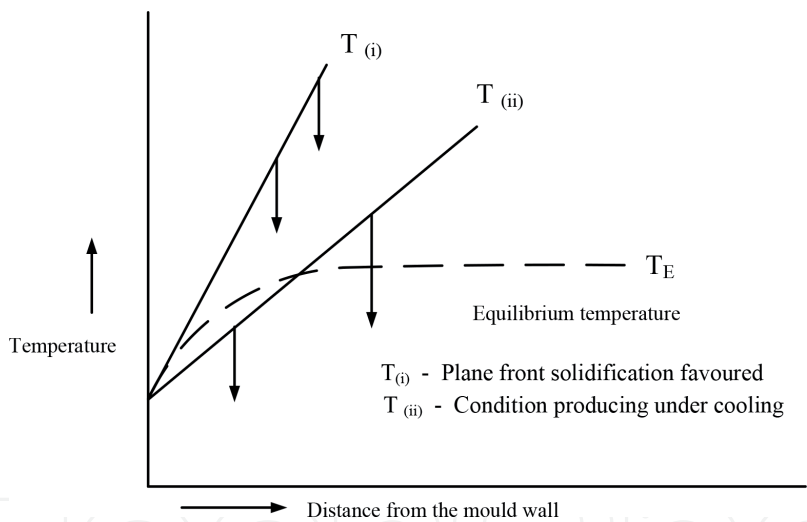
Figure 11.
Effect of temperature gradient variations on the extent of undercooling that influence the crystal structure.
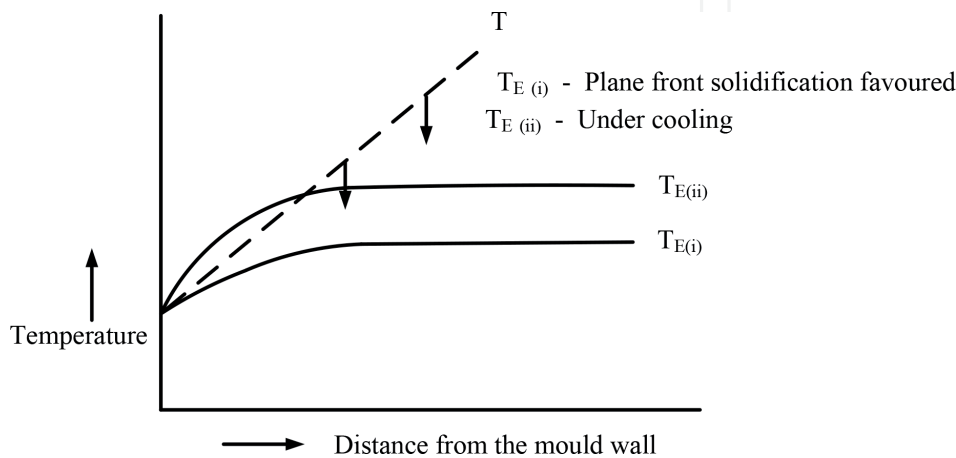
Figure 12.
Effect of liquidus temperature profile on extent of supercooling and crystal structure.

is sufficiently shallow to generate considerable undercooling which disturbs planar growth and growth proceeds adopting other modes, as explained earlier. **Figure 12** clearly indicates, with a given temperature gradient the alterations of equilibrium temperature profile, which could be due to the alterations in the solute concentration, undercooling is witnessed with liquidus profile TE (ii), with the liquidus profile TE (i) and the given temperature gradient 'T', undercooling is not witnessed and growth proceeds by plane-front growth giving rise to columnar grain structure. From the above, it can be concluded that columnar growth is promoted under stiff temperature gradients. Columnar growth is also favoured at slow cooling rates because of the following:

slow cooling rates establish low rate of nucleation in comparison to the growth rates, allowing growth to overtake nucleation.

As seen in **Figure 13** when the cooling rates are slow the solid rejected at the interface get sufficient time to migrate into the melt interior, away from the interface. The equilibrium temperature is altered.

It changes from TE (ii) to TE (i) (**Figure 13**). This is parallel to a situation as in **Figure 12** when with TE (i) the extent of undercooling are negligible or absent. Such a situation promotes columnar growth.

3.7 The temperature gradient (G) and rate of cooling (R) ratio (G/R)

In a foundry the various local factors like the extent of superheat, the extent of heterogeneous nucleation, the mould characteristics, etc. decide the variations in the thermal gradient (G) and the rate of cooling (R). Needless to say, the ratio G/R forms an important parameter to decide the mode of growth and the consequence of structure development.

Figure 14 illustrates that as the G/R ratio progressively changes from a high to a low volume the effect of undercooling becomes more and more pronounced. Columnar, plane-front growth gradually gives way to independent nucleation.

During freezing the thermal conditions prevailing in the melt continuously change. Thus separate structural zones as shown in **Figure 15** are encountered in the solidifying melt.

These zones are consequences of the continuously changing G/R ratio in the melt. Assuming of a lower value of the G/R ratio with the lapse of time results in the increasing extents of undercooling which are instrumental in the separable structural zones as preserved in **Figure 15**. The above can be made more clear with the aid of **Figures 16** and **17**.

Both **Figures 16** and **17** provide for an explanation of the mixed structure in a solidifying casting on the basis of the prevailing thermal conditions. To start with, as presented in **Figure 16**, the temperature gradient is stiff. Solidification initially occurs under this marked thermal gradient. This is often sufficient to cause
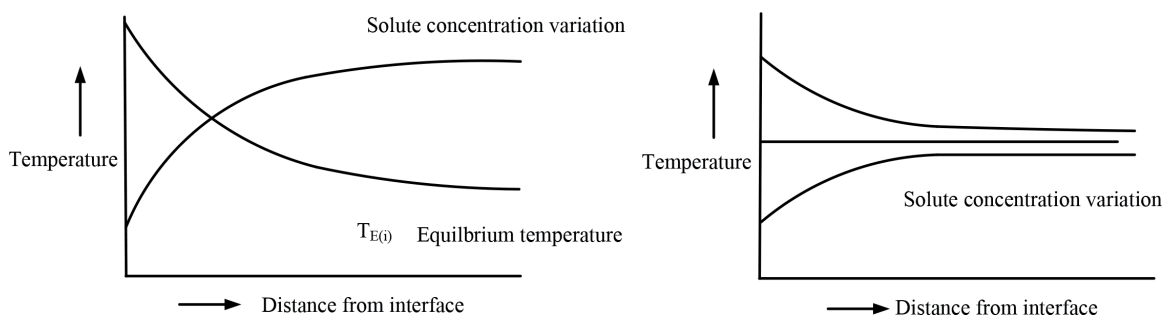
Figure 13.
Change in equilibrium temperature profile as a consequence of solute concentration crystal variation.
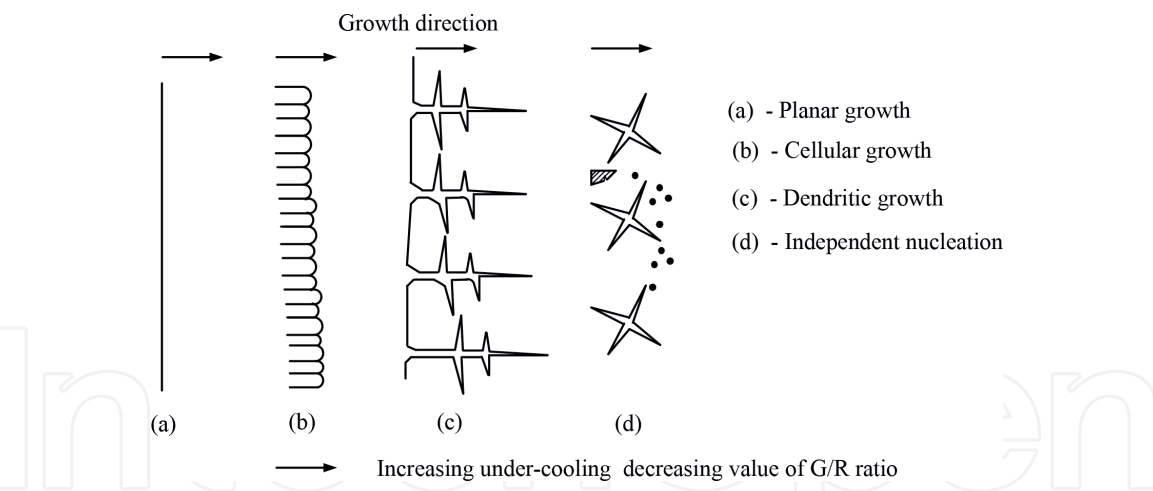
Figure 14.
Schematic presentation of G/R ratio influencing the effect of undercooling and the resultant structure.
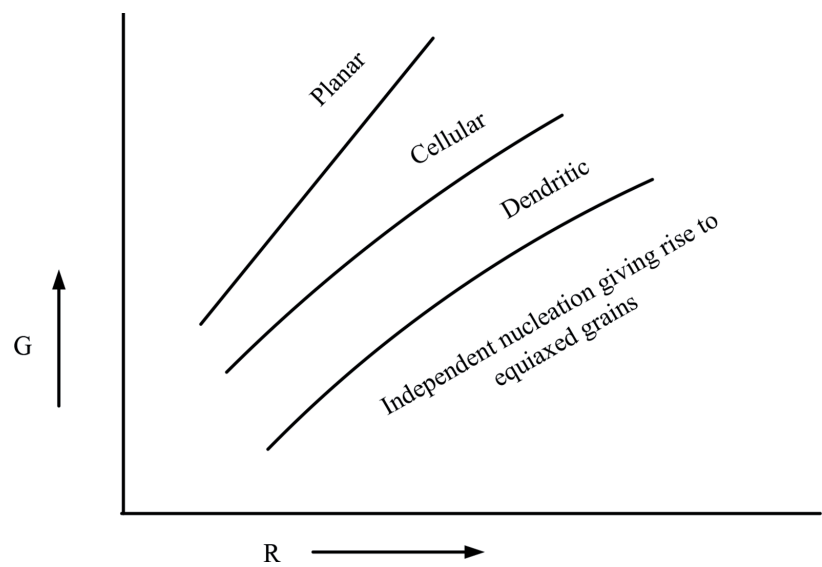

Figure 15.
Schematic presentation of critical changes in the G/R ratio during freezing and its influences on the different structural zones.
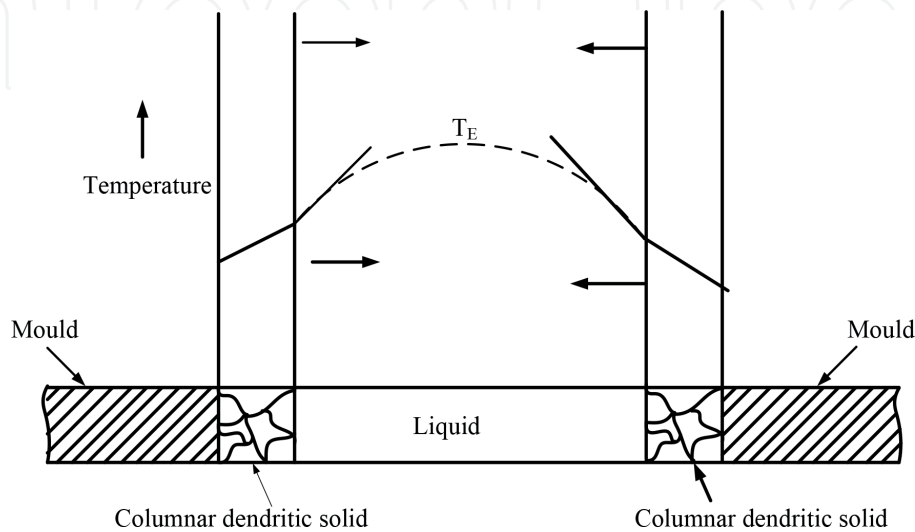

Figure 16.
Variation of undercooling with alteration in the thermal gradient showing different grain morphology.
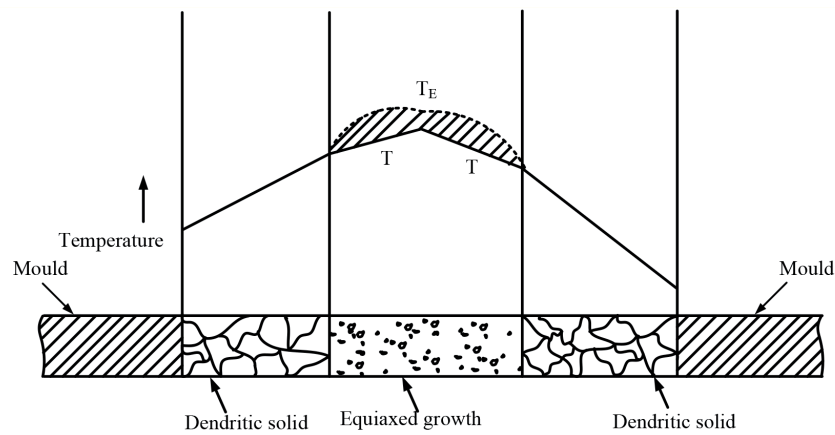
Figure 17.
Variation of undercooling with alternation in the thermal gradient showing different grain morphology.

columnar dendritic growth in the outermost region and adjacent to the mould wall as shown in **Figure 16** in this central zone (in some cases, throughout the entire solidifying melt) the temperature gradient is shallow (**Figure 17**).

This shallow gradient generates excessive undercooling. Here solidification proceeds by widespread nucleation, the rate of nucleation being very high. Independent nucleation occurs in the interior of the melt. These nuclei, without any barrier for growth across their periphery, grow into equiaxed grains. To be more specific, initially the temperature gradient is stiff. The rate of cooling is low, G/R assume high values. Initial solidification, thus, occur under a marked temperature gradient which is sufficient to cause columnar dendritic growth in the outermost layer. Gradually 'G' decreases, i.e., the temperature gradient becomes shallow and 'R' the rate of cooling increases as a consequence of increasing extents of undercooling. The shallow temperature gradient in the casting and the increasing extents of undercooling in the melt give rise to the formation of independent nucleation in the melt interior forming equiaxed grains, being free to grow on their unhindered periphery.

Schematically the practical, ideal cast structure can be presented as in **Figure 18**.

Although, the above refers to alloys forming solid solutions, analogous changes occur in alloys subject to eutectic freezing. The **Figure 18** shows small dendrites (equiaxed) in the outermost surface because of chilling effects at the cold mould wall.
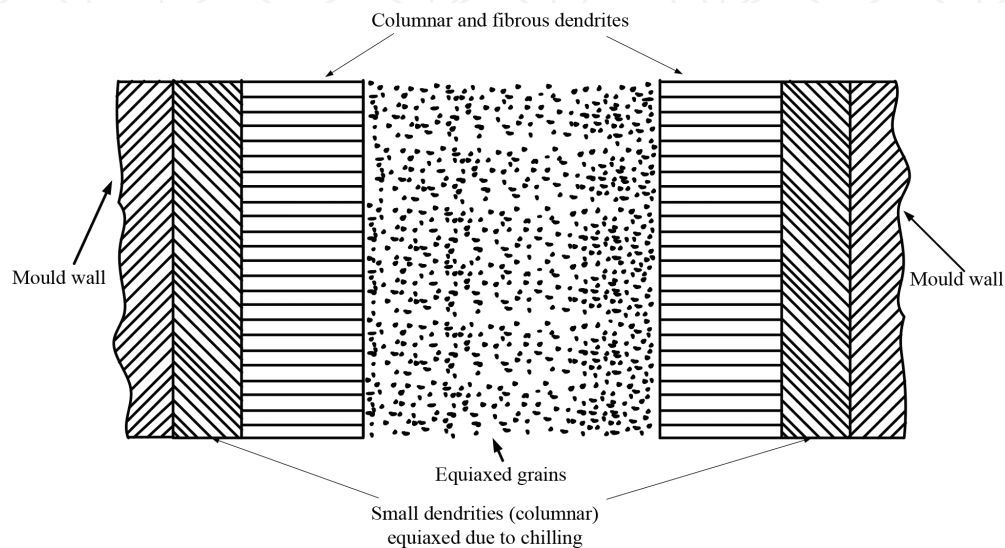

Figure 18.
Schematic presentation of a theoretical grain structure of the casting.

3.8 Further factors influencing the cast structure

Two further factors, other than the thermal and constitutional undercooling, also influence the cast structure particularly concerning the formation of equiaxed crystals. These are:

3.8.1 Crystal multiplication

Crystal multiplication is a consequence of the fragmentation of dendritic arms in the columnar zone due to local factors like thermal fluctuations and change in growth rates, etc. Also the nuclei formed on the inside of the mould wall may get washed off when further metal is being poured into the mould. Some of these detached nuclei may vanish being unstable, while some may get transported to favourable sides in the liquid and grow into equiaxed grains.

3.8.2 The transportation of these fragmented or detached crystal may occur by

 i. Turbulence during pouring

 ii. Thermal convective currents between the hot central portion and the relatively cooler surface region,

iii. Gravitational separation due to the difference in densities between the solid and the liquid. In general the fragmented dendrules in the melt tend to go to the bottom of the melt due to density differences between the solid dendrules and the surrounding liquid melt. The only exception is 'Be'. Here the density of the liquid is higher than that of the solid.

To sum up the formation of the equiaxed zone consisting of equiaxed grains, is promoted by the following:

   a. Heterogeneous nucleation in situ

   b. Crystal multiplication and

   c. Transportation of crystallites by gravity or by mass movement into the interior of the melt

Obviously, the above form certain factors which influence the crystallographic morphology of the casting.

4. Mould feeding issues

For a casting to be produced, it is essential that appropriate technique to be adopted for the liquid metal to be fed into the mould cavity. It is an issue inviting special considerations since the viscosity of the melt increases with drop of temperature making its flow sluggish and time taking which may result in considerable solidification prior to the completion of the feeding process. Also, the metal/alloy shrink on solidification producing solidification shrinkages in the casting which are discontinuities in the casting. For a healthy casting production ample facilities must be made be made available for compensating for these shrinkage. On these considerations, we can take the case of a pure metal which solidifies at a constant

temperature or even alloys having a narrow freezing range. In these cases, three are clearly defined interfaces between the solidified region and the 'still-liquid' region. Any solidification contraction has the liberty to be compensated by the 'still-liquid' melt adjacent to it. If sufficient liquid metal is available the process of compensation of the physical contraction continues by the general lowering of the free liquid surface resulting in the production of a sound casting with no solidification shrinkages. The supply of liquid metal is accomplished by the provision of liquid metal reservoir known as feeder head or riser.

However, in many cases the case is not as simple. A clearly defined solid/liquid interface does not exist. Solidification takes place through a zone simultaneously. Even in certain cases the solidification zone may extend throughout the melt entirely. In these zones crystals at different stages of growth can be seen with the residual low melting point liquid. The alloy is in a pesty zone or in a mushy stage. Contraction sites are dispersed in the casting making feeding of these contraction sites a very difficult and even impossible, for the production of sound casting.

Under these conditions, liquid metal is fed ink the contraction sites in three successive stages.

4.1 Stage I

In the early stages, growing crystal bodies are suspended in the liquid. Free movement of the liquid across the crystals is possible. Thus, any contraction can be easily compensated by a feeder head with the general lowering of the free liquid surface.

4.2 Stage II

Here, after some lapse of time, the grains grow to certain extent and form contact among themselves forming a network of solid. Liquid movement becomes confined to intergranular channels. These channels get diminished continuously. Frictional resistance to the liquid movement in these channels increases. It becomes considerably difficult for the liquid to reach the solidification sites that undergo contraction. Thus, feeding for compensating the contractions becomes progressively difficult.

4.3 Stage III

Now the final stages of solidification have reached. The intergranular channels are completely blocked by the growing crystals. Thus, isolated pockets of liquid are generated which solidify independently. The resultant contractions cannot be fed from external sources. These are always with long freezing range and cool under shallow temperature gradients. The shrinkage defects in these alloys persist resulting in spatter porosities distributed in the entire castings, even extending to the casting surface.

An external feeder head, known as the riser, is employed to compensate for the solidification shrinkages so that a sound casting results. For successful functioning of the riser the principle of directional solidification is employed. It is also known as progressive solidification in which solidification starts farthest from the riser and proceeds into the riser so that any side of shrinkage has an unfailing supply of liquid metal. The successful functioning of the riser must ensure the following:

i. Riser should be the last one to solidify in the casting system. This means throughout the process of solidification the riser must have liquid metal for feeding during freezing.

ii. Freezing must start farthest from riser and continue through the casting towards the riser.

iii. There must be a continuous path of feeding the liquid metal from the riser to the solidifying site.

The cooling rate of the casting need to be controlled for this purpose. The cooling rate on the other hand can be controlled by controlling the pouring temperature of the metal, pouring rate, promoting differential cooling by use of chills, differential heating by addition of exothermic materials, use of padding, etc. The temperature gradient and cooling rate are very important consideration in a solidifying melt. It is opined [13, 14] by setting up an appropriate temperature gradient and cooling rate by selecting the necessary pouring rate and temperature the cast structure can be controlled and the casting upgraded. A fine grain structure can be, thus, obtained by proper selection of the pouring rate and temperature. These fine grained structure can enhance the ability of the casting to inhibit the slide of the dislocations. This can result in the increase of yield strength and the ultimate strength of casting. These measures stiffen the temperature gradient assisting the setting up of a path feeding from the riser to the contraction sites in the mould.

5. Freezing characteristics of alloys

Though, no two alloys have identical feeding characteristics, on the basis of the major contrasts of solidification they can be put under three categories.

5.1 Gr.I

This group of alloys freeze with marked skin formation. These have of obvious short (narrow) freezing zone. These include Low carbon steels, Brasses, Aluminium Bronzes, Aluminium Copper, etc.

In these group of alloys progressive or directional solidification measures can be easily achieved. Sound castings can be obtained with proper feeding from the feeder head. However, the casting yield may suffer sometimes as the feeder head has to be finally discarded.

5.2 Gr.II

These are alloys with long feeding ranges. These include Medium and High carbon steels, Nickel based alloys, Gun metals, Mg alloys, Complex Al alloys, etc.

In these alloys solidification proceeds simultaneously in much of the casting, even in the entire casting. All the three stages of freezing can be clearly witnessed as explained earlier. In the third and last stage of freezing widespread porosity may occur. In such castings of alloys progressive solidification is very less unless heavy chilling is used to disturb the thermal gradient. The chilling induces very sharp temperature gradient and help formation of a sound casting by setting up of narrow freezing zones. However, the casting feeding in these alloys is not always based on directional solidification. Efforts are made to follow measures such that concentration of porosity is not localised but distributed in the casting. To achieve the above mentioned disperse porosity measures have to be adopted for equalisation of cooling

rates over the entire zone instead of going for a sharp temperature gradient. These disperse micro pores could be more acceptable than concentrated porosities [15].

5.3 Gr.III

These are the alloys which show expansion on freezing. These include Grey Cast Iron. In the Gr III hypoeutectic Grey Cast Irons freezing is initiated with the growth of austenite dendrites. Contraction on freezing occurs much like the other alloys with considerable freezing range. Then the eutectic freezing begins. Graphite precipitates out of the solid. Interdendritic liquid gets enriched with carbon. The solidification of this austenite-graphite eutectic is accompanied by volume expansion. A positive pressure is caused. In a completely rigid mould this expansion makes it virtually self-feeding. In practice, however, the positive pressure tends to cause mould-wall-movement. This movement increases the mould dimensions and sets up a tendency for contraction giving rise to an increase in the internal porosity.

To sum up, in the Gr.I alloys feeding by risers is easy. In the Gr.2 alloys feeding by riser is helped by ensuring directionality in solidifications and in the Gr.III alloys, in the contraction stage all the three stages of bulk feeding and interdendritic feeding stages may be encountered.

6. Effect of temperature gradient on the feeding range of the alloys

As mentioned earlier the temperature gradient in a casting system can be made stiff from a shallow one by adopting several means. This is illustrated in **Figures 19** and **20** [16].

A stiff temperature gradient can reduce the extent of pasty zone with the associated advantages in setting of directionality in solidification. On the other hand, a shallow temperature gradient can be set up and extensive pasty zone resulting in simultaneous freezing in an extended zone in the melt and help distribution of micropores.
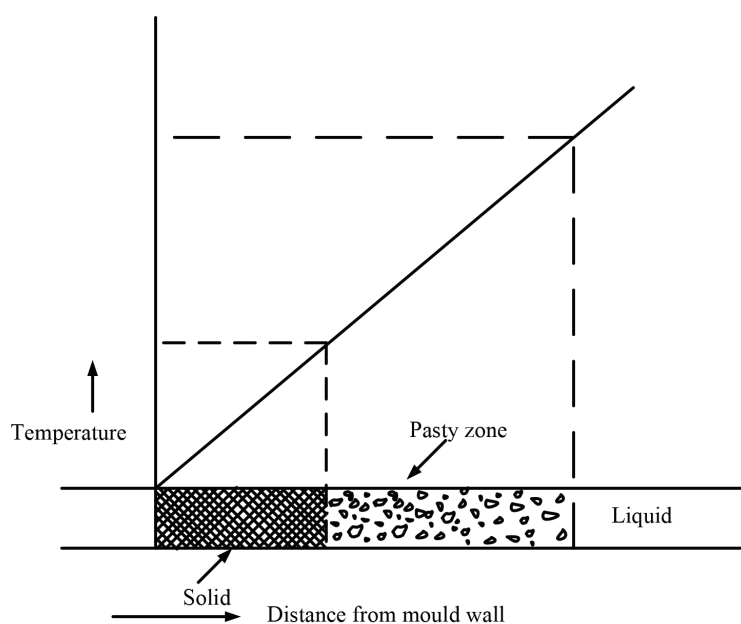

Figure 19.
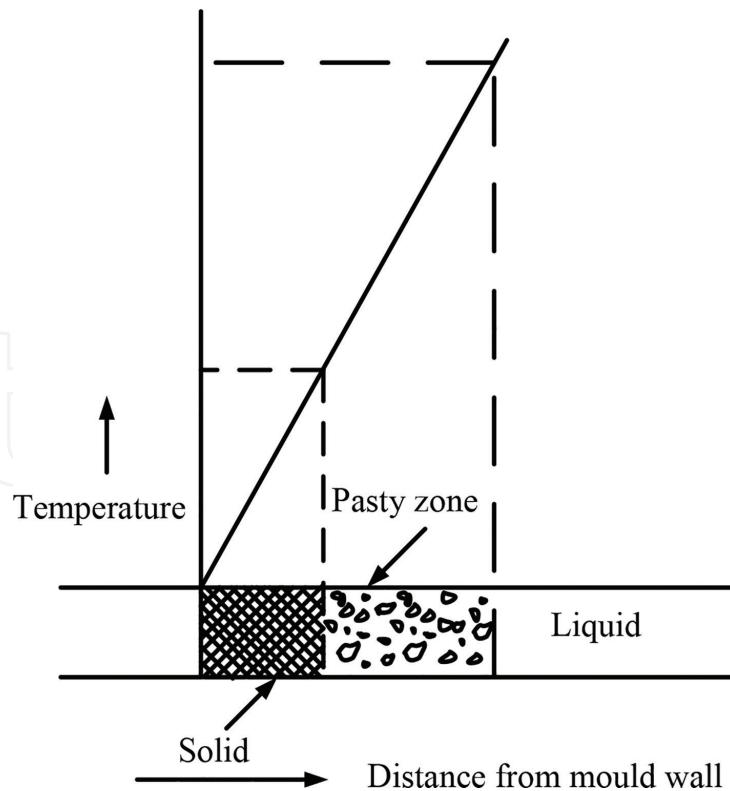*Shallow temperature gradient showing extensive pasty zone.*

Figure 20.
Effect of stiff temperature gradient on pasty zone (narrow zone of crystallisation).

7. Concluding remarks

Casting of a metal/alloy is a manufacturing process in which the liquid metal/alloy Is poured into a pre-formed mould. The liquid solidifies in the mould and the solidified liquid, known as the casting, is finally retrieved from the mould. In the whole process of producing the casting, the solidification processes play a major role in deciding the cast structure which dictate the structure related properties of the casting and decide its end-use. Throughout the entire process of solidification the metal/alloy shrink, generating discontinuities in the casting in the form of shrinkage cavities. These have to the compensated for by the supply of liquid metal from a liquid-metal-reservoir, known as the feeder-head or the riser. For efficient functioning of the riser it is desirable to ensure directionality in solidification by shaping of the necessary thermal gradient 'G' and the rate of cooling 'R'. Infact the ratio 'G/R' plays a very important role in deciding the cast structure when it changes from a high value to a low value with the lapse of time. It decides the mode of growth which can be planar, cellular dendritic or growth due to independent nucleation and dictates the consequent development of the cast structure. The extent of superheat in the melt, the extent of heterogeneous nucleation, the mould characteristics, etc. Setup the required 'G/R' ratio. External factors like the pouring rate and pouring temperature can be altered suitably to vary the 'G/R' ratio such that the desire cast structure can be obtained.

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