

Chapter

II

Crystal growth and solidification

II-1. Introduction

The properties of metallic materials in the pure state or a mixture of two or more elements, depends on the phase transformations that have undergone. The majority of phase transformations that occur in materials are accompanied by a change in the number of phases present.

Depending on the types of phases that exist in the considered system, we distinguish the two main categories; the transformation from the liquid phase to the solid phase, and the transformation from the solid phase to another solid phase. In this chapter we will study the first category of these transformations (liquid \leftrightarrow solid), where we study the phenomenon of solidification.

Solidification is defined as the passage of material from the liquid phase to the solid phase. In metallic alloys, this phase change produces significant changes in mechanical, physical and chemical properties. The study of this phase transformation in metals has continued for several decades in order to improve the understanding of the solidification principles.

The structures produced after solidification affect the mechanical properties of castings and partly condition the type of treatment to be implemented to achieve the targeted properties; in particular, the size and shape of the grains depends on the solidification conditions.

II-2. Liquid state and solid state

In the crystalline solid state, on the scale of the atom, we can consider that the atoms have a well-defined average position linked to each other by the forces of cohesion, and that they are arranged in a motif (unit cell). In addition, the structure of the solid generally includes a large number of defects: vacancy, dislocations, stacking faults, etc...

Crystalline materials exist in a monocrystalline or polycrystalline form. The commonly used metallic materials have a polycrystalline structure which is formed of a multitude of microcrystals (grains) linked together by less ordered zones (grain boundaries), each grain of a metallic material being a single crystal. The decrease in grain size induces an increase in the material strength at room temperature.

In the liquid state, the atoms no longer have a well-defined position. The first neighboring atoms of a given atom occupy a position close to that which they occupy in a crystal, the second and third neighbors are less well located, but beyond that, the order is non-existent. This partially disordered arrangement results from the existence of empty spaces between groups of atoms or molecules. It is the mobility of these empty spaces that gives liquids their fluidity.

The essential fact is the sudden variation of certain physical characteristics when passing from one physical state to another.

- The liquid is less dense (except in the case of the following elements: Bi, Ge, Ga, Si, water, cast iron). A loss of volume or shrinkage is then recorded during solidification (shrinkage of 4.8% in the case of copper),
- The mobility of atoms (diffusivity) is greater in the liquid (self-diffusion and chemical diffusion of alloying elements and impurities are slower in the solid than in the liquid),

II-3. Solid/liquid interface

The solid-liquid interface is the intermediate zone between the last atoms constituting the solid and the atoms of the liquid phase, the thickness which is that of a few atoms of the material. Once the solid phase germ is built, it will continue its growth which is limited by:

- The atom attachment kinetics at the solid-liquid interface,
- The diffusion of heat from atoms in the two solid and liquid phases.

The importance of each of these factors depends on the substance studied and the solidification conditions.

Generally, creating an interface is a process that requires some work and is disadvantaged from a thermodynamic point of view. The presence of interfaces therefore increases the free energy of a material. As in a phase, the grain boundaries constitute a particular type of interface since they mark the limit between two crystalline grains of the same composition and the same structure, but of different orientation, the fine-grain systems which are characterized by the presence of many interfaces, have a higher free energy than coarse-grained systems.

From a thermodynamic point of view, the interface is characterized by its specific interfacial energy γ . The specific interfacial energy is independent of the interface area. It can be determined by measuring the work required to create a unitary interface.

❖ Interfacial structures

The solid-liquid interface can take different growth forms (flat, cellular or dendritic) depending on the cooling conditions (solidification). Among the parameters controlling the morphology of the solid-liquid interface, the temperature gradient in the liquid and the growth rate of the germs.

We notice that at low solidification rate, by fixing the temperature gradient in the liquid, the solid-liquid interface is flat. It is, practically, difficult to achieve such an ideal state of growth because a heat exchange between the melting-pot and the sample leads to the temperature gradient in the liquid region. The planar interface becomes unstable at some critical value of the growth rate or temperature gradient.

However, if the rate is increased beyond a certain critical value, V_c , and when the temperature gradient is lowered, the front of the interface becomes unstable and the solid-liquid interface presents a cellular form whose spacing, λ , is typically a few tens or hundreds of micrometers, which will subsequently transform into a dendritic form at high growth rates. These different cases illustrated in figure II-1-.

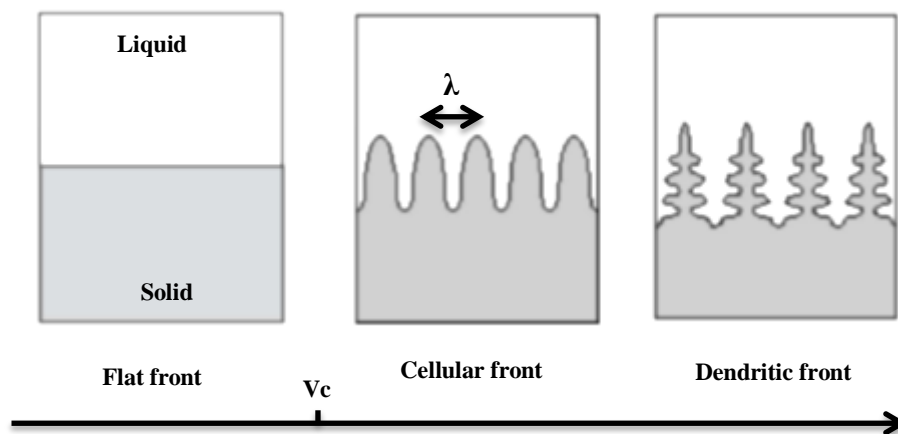


Fig. II-1- : Schematic representation of the different morphologies of the solid-liquid interface.

Solidification takes place in two stages: germination and growth. Germination is the stage in which many small solid particles (germ) are formed from the liquid. Each of these solid particles must reach a certain critical size to remain stable. Growth occurs as the solid germs increase in size at the expense of the surrounding liquid until the latter completely disappears.

II-3-1. Germination

There are two types of germination, the homogeneous germination whose solid germs are formed within the liquid without contact with walls or impurities, and the heterogeneous germination where the germs are created from foreign particles bathing in the liquid or in contact of the cold wall of the mold.

II-3-1-1. Homogeneous germination

Some germs can appear within the liquid in the absence of any solid support (walls of the mold, inclusions, etc.). Such germs are said to be homogeneous and their formation requires very high supercooling (explained below), of the order of 20% of T_f (melting temperature).

a. Latent heat and volume free energy

We study the solidification of a pure substance A: $A_{\text{liquide}} \leftrightarrow A_{\text{solide}}$. G_v^l and G_v^s the free energies per unit volume of the A substance, in the liquid state and in the solid state respectively. The change in free energy that accompanies solidification per unit volume is:

$$\Delta G_v = G_v^s - G_v^l = \Delta H - T\Delta S \quad (\text{II-1})$$

H and S are respectively the enthalpy and the entropy per unit volume of A at the considered temperature.

For a pure metal, the liquid \rightarrow solid transformation takes place at a well-defined temperature, characteristic of the metal. It is the temperature for which the free energies of the two solid and liquid phases are equal: $G_v^s = G_v^l$. The latent heat (L) is defined as the amount of heat released (at solidification) or absorbed (at fusion) where $L = \Delta H$.

Now studying the variations of free energy per unit volume as a function of temperature for this material:

- For $T = T_F$, the two liquid and solid phases coexist and they are in equilibrium; the free energies of the two phases are equal: $G_v^s = G_v^l$

- - For $T > T_F$, it is the liquid phase which is stable; so $G_v^l < G_v^s$
- - For $T < T_F$, it is the solid phase which is stable; so $G_v^s < G_v^l$

Figure II-2- represents schematically the evolution of the free energy per unit volume (G_v) of the metal as a function of temperature. This observation can be generalized to any phase transformation: the most stable phase is the one whose free energy is the lowest, or even the one whose formation produces a reduction in the free energy of the system.

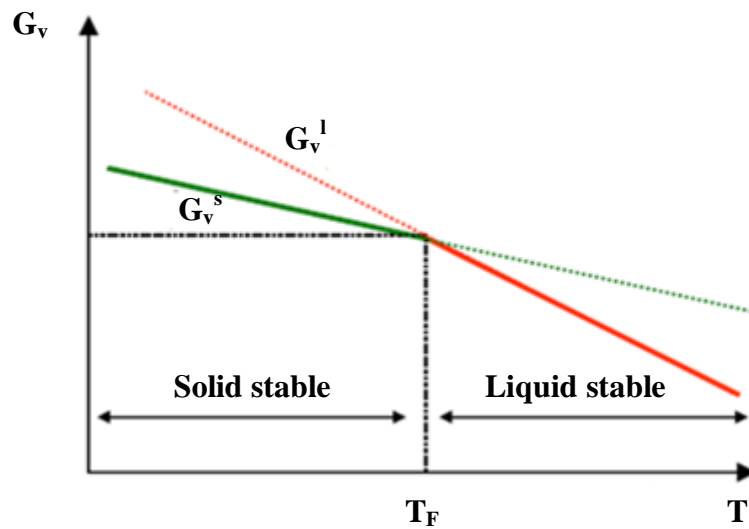


Fig. II-2- : Variations of free energy per unit volume as a function of temperature.

Consider the solidification of a pure metal initially maintained at a temperature above its melting point to make it liquid. The metal is cooled by bringing it to a temperature T well below the melting temperature. For solidification to occur, ΔG_v must be < 0 .

At a temperature T different from T_F ($T \leq T_F$), $\Delta G_v = 0$ and $\Delta H = -L$ (the minus sign means release of the latent heat of solidification):

$$\Delta G_v = 0 \quad (\text{II-2})$$

$$G_v^s - G_v^l = 0 \quad (\text{II-3})$$

$$H_v^s - T_F S_v^s = H_v^l - T_F S_v^l \quad (\text{II-4})$$

$$H_v^s - H_v^l = T_F S_v^s - T_F S_v^l \quad (\text{II-5})$$

$$-L = T_F \Delta S \text{ which give: } \Delta S = \frac{\Delta H}{T_F} = -\frac{L}{T_F}$$

If the temperature T is different from T_F , the variation of the free energy ΔG_v is not equal to zero and it can be evaluated by admitting that ΔH and ΔS are not very affected by temperature.

$$\Delta G_v = \Delta H - T\Delta S \quad (\text{II-6})$$

Where:

$$\Delta G_v = (-L) - T \left(\frac{-L}{T_F} \right) = -L \frac{T_F - T}{T_F} \quad (\text{II-7})$$

For there to be solidification ($\Delta G_v < 0$) the term $(T_F - T)$ must be positive, so $T_F > T$. The difference $(T_F - T)$ is called *supercooling*.

The sign “-” in the ΔG_v relation indicates that the liquid \rightarrow solid transformation takes place with a drop in the free energy of the system, because at $T < T_F$; $G_v^s < G_v^l$. This decrease in free energy is proportional to the volume of the germ:

$$\Delta G_l = \Delta G_v * V \quad (\text{II-8})$$

b. Supercooling and surface energy

During cooling under equilibrium conditions (i.e. at very low rate), the thermal analysis curve ($T=f(t)$) would resemble that of figure II-3-(a) : the isothermal plateau reflects the solidification at constant temperature of the pure metal. During usual cooling, under industrial conditions, it can be seen that the liquid does not turn into a solid immediately below the equilibrium temperature T_F .

In practice, the thermal analysis curve obtained is that of figure II-3-(b). Solidification begins at a temperature T_B significantly lower than T_F and therefore requires “undercooling” ΔT , also called supercooling (portion AB of the curve). As soon as the first germs are formed, the release of latent heat causes a rise in temperature (portion BC of the curve).

In the case of an alloy (solid solution) the curve of the thermal analysis corresponds to that of figure II-3-(c) where one can determine the starting temperature of solidification T_s by extrapolation. Supercooling reflects a retard in solidification. This retard in solidification is explained by the formation of an interface between the solid germs and the liquid. This interface consumes a quantity of energy ΔG_s per unit of interface created ($\Delta G_s > 0$ i.e. interface formation is an endothermic phenomenon). The presence of the germ therefore

increases the free energy of the system by a value ΔG_2 proportional to the surface of the germ where:

$$\Delta G_2 = \Delta G_s^* S \quad (\text{II-9})$$

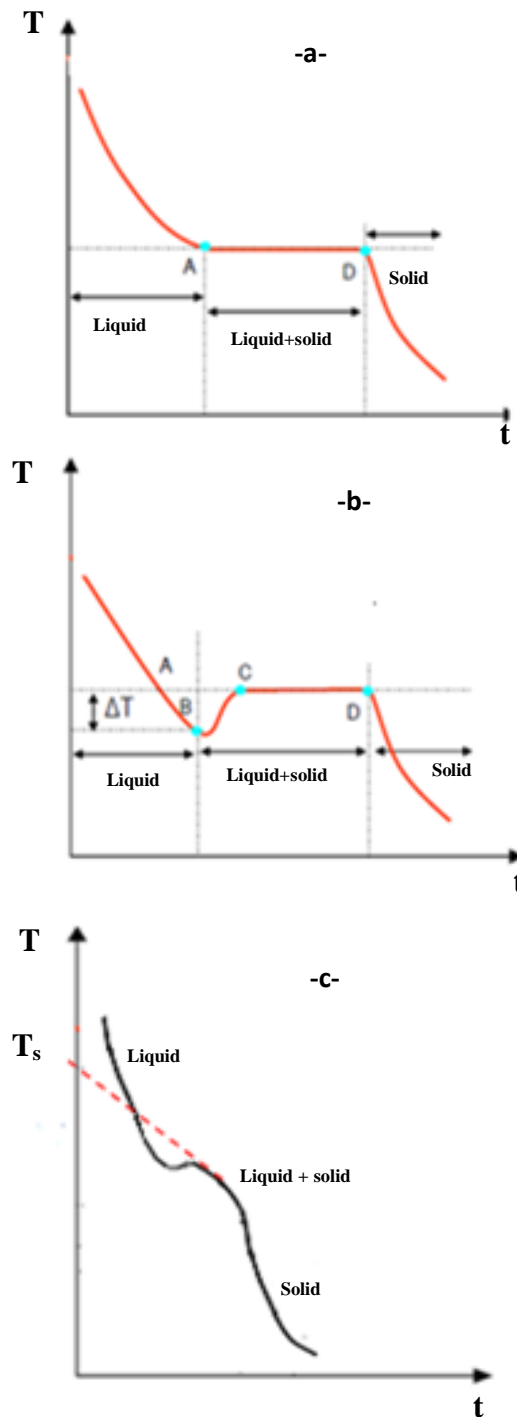


Fig. II-3- : Cooling curves for:
 (a) a pure metal without supercooling,
 (b) a pure metal with supercooling,
 (c) a supercooled binary alloy.

c. Free energy of germ formation

Consider an initial volume of liquid being solidified. When a solid germ forms of volume V and surface S , the total variation of the free energy of formation of the germ (ΔG_g^f) is the sum of the two free energies: the free energy of volume on the one hand and of surface free energy on the other hand:

$$\Delta G_g^f = \Delta G_1 + \Delta G_2 \quad (\text{II-9})$$

The formation of this germ will only be possible if $\Delta G_g^f < 0$. As the first term is negative, it plays a driving role for solidification while the second plays a braking role (positive term). The most probable shape of the germ will therefore correspond to the lowest surface energy consumption (minimum surface) and the highest volume energy release (maximum volume). It is the spherical shape that meets this condition (Fig. II-4-).

Suppose therefore that the germ is spherical in shape with radius r . We then have:

$$\Delta G_g^f = \Delta G_1 + \Delta G_2 \quad (\text{II-10})$$

$$\Delta G_g^f = \Delta G_v * V + \Delta G_s * S \quad (\text{II-11})$$

$$\Delta G_g^f = \Delta G_v * (4/3 \pi r^3) + \gamma_{s-l} * (4\pi r^2) \quad (\text{II-12})$$

So the total variation of the free energy of formation of the germ (ΔG_g^f) is:

$$\Delta G_g^f = -\frac{4 \pi L \Delta T}{3 T_F} r^3 + 4\pi \gamma r^2 \quad (\text{II-13})$$

Where: L , T_F , γ (the specific interface energy) are constants which depend only on the nature of the metal.

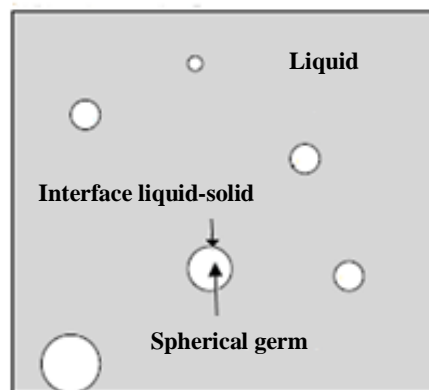


Fig. II-4- : Formation of the spherical solid germ

The free energy of germ formation then depends on two parameters: one experimental is the temperature T or the supercooling ΔT , and the other is the size of the germ. Let us fix the temperature, therefore the supercooling $\Delta T = T_F - T$ and examine the evolution of the free energy of formation as a function of the size of the germ (Figure II-5-).

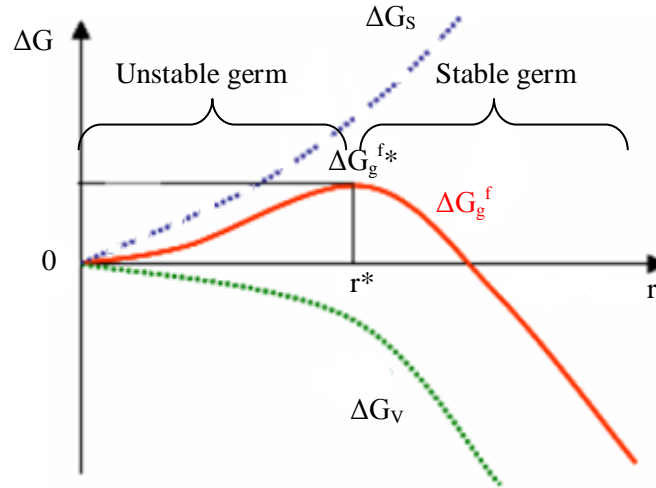


Fig. II-5- : Free energy variation curves as a function of germ size.

❖ Influence of germ size

When the size of the germs increases, the free energy first increases before passing through a maximum ΔG_g^{f*} which corresponds to a critical size $r = r^*$, then decreases for the largest values of r . The value of the critical size can be determined by writing that the derivative of ΔG_g^f is zero for the value r^* :

$$\frac{d\Delta G_g^f}{dr} = 0 \quad (\text{II-14})$$

$$-\Delta G_v 4\pi r^2 + \gamma_{s-l} 8\pi r = 0 \quad (\text{II-15})$$

$$r^* = \frac{2\gamma T_F}{L\Delta T} \quad (\text{II-16})$$

The critical value of the free energy is:

$$\Delta G_g^{f*} = \frac{16\pi\gamma^3 T_F^2}{3L^2 \Delta T^2} \quad (\text{II-17})$$

ΔG_g^{f*} is the potential barrier that a germ must cross to reach the critical size r^* .

Figure II-6- shows that only germs that have reached a critical size can be stable. Indeed, the growth of a germ of size greater than r^* (for example, a germ of radius $r = r_3$ becoming a germ of radius $r = r_4$) leads to a decrease in free energy:

$$\Delta G_{g_{3 \rightarrow 4}}^f = \Delta G_{g_4}^f - \Delta G_{g_3}^f \quad (\text{II-17})$$

As $\Delta G_{g_4}^f < \Delta G_{g_3}^f$, we will therefore have $\Delta G_{g_{3 \rightarrow 4}}^f < 0$.

On the other hand, the growth of a germ of size less than the critical size (for example, a germ of radius $r = r_1$ becoming a germ of radius $r = r_2$) implies an increase in free energy:

$$\Delta G_{g_{1 \rightarrow 2}}^f = \Delta G_{g_2}^f - \Delta G_{g_1}^f > 0 \quad (\text{II-18})$$

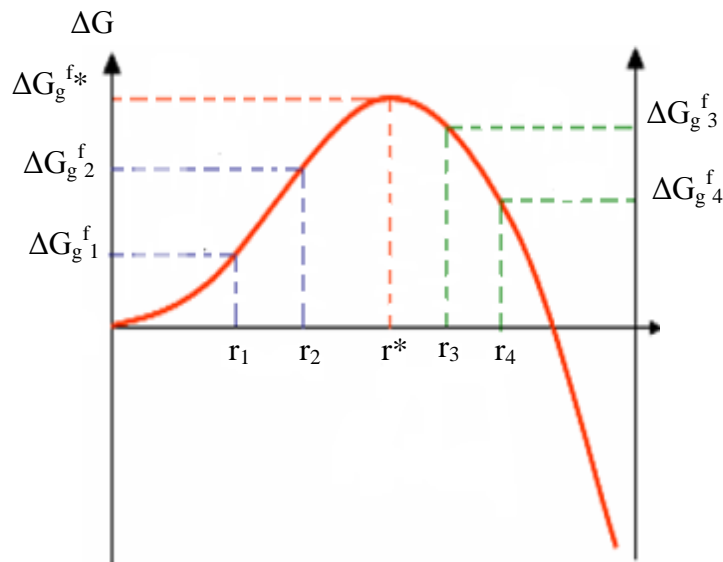


Fig. II-6- : Variation of the free energy of germ formation according to their radius r shows the domain of stability of this germ.

❖ Influence of temperature

The influence of the temperature can be deduced from the previous relations, i.e. the potential barrier decreases when the supercooling ΔT increases (up to average values) and the same for r^* (The critical size and the energy barrier are all the lower as the supercooling is higher), this means that the increase in supercooling makes it possible to stabilize smaller germs. In other words: the number of stable germs increases and solidification is favored when supercooling is high.

II-3-1-2. Heterogeneous germination

In practice, there are supports which, therefore, provide a surface on which the metal can "lean" to solidify, consist either of insoluble impurities (fig. II-7-), or of the walls of the mold or the crucible. Under these conditions, a germ whose radius of curvature is greater than the critical radius forms with a minimum liquid-solid surface. Moreover, the number of atoms necessary to obtain a germ of critical size is much smaller compared to that of a homogeneous germ.

The germ prefers the shape of a *spherical cap* of radius r . The various contact surfaces intervene with their interface energies γ : γ_{gl} (the interface energy between the liquid and the germ), γ_{gs} (the interface energy between the germ and support), γ_{sl} (the energy interface between the support and the liquid).

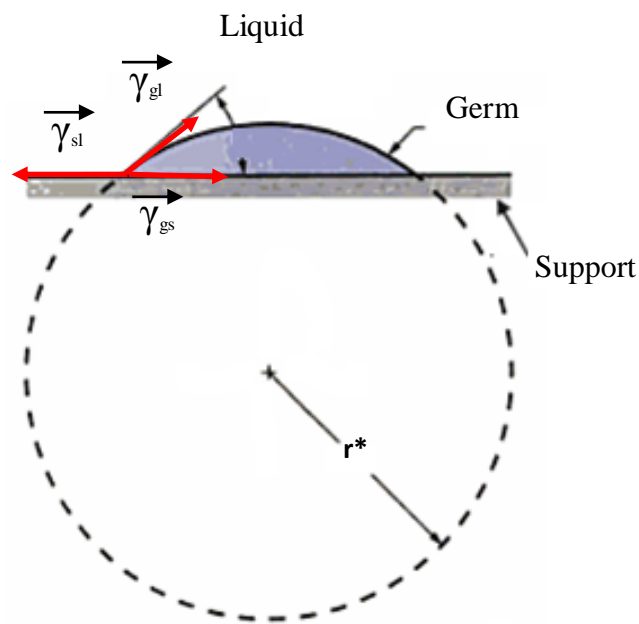


Fig. II-7- : Heterogeneous germination on a solid support.

Let θ be the contact angle between the support and the germ: this angle measures the tendency of the solid germ to spread out more or less on the support. The stability of the germ-support-liquid system requires a relationship between the surface energies, namely:

$$\vec{\gamma}_{sl} + \vec{\gamma}_{gl} + \vec{\gamma}_{gs} = 0 \quad (\text{II-19})$$

By projection on the axis of the support:

$$\gamma_{sl} = \gamma_{gl} \cos \theta + \gamma_{gs} \quad (\text{II-20})$$

In this case the total variation of the free energy of germ formation (ΔG_g^f) is:

$$\Delta G_{\text{het}} = \Delta G_{\text{hom}} f(\theta) \quad (\text{II-21})$$

Where:

$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (\text{II-22})$$

II-3-1-3. Germination rate

In the liquid, there are germs of all sizes. Each germ size corresponds to a critical formation energy ΔG_g^{f*} . We can then evaluate the number of germs (n^*) of critical size (r^*) by the following relationship:

$$n^* = N \cdot \exp\left(-\frac{\Delta G_g^{f*}}{KT}\right) \quad (\text{II-23})$$

Where N is the total number of atoms in the system.

It is observed that the number of germs reaching the critical size increases with the degree of supercooling. But the germs of critical size only become stable if they capture additional atoms. This condition depends on the possibilities of diffusion of these atoms towards the germ. This phenomenon brings into play an activation energy of the diffusion in the liquid ΔG_d (it is the potential barrier that must be crossed for an atom to attach itself to the growing germ). We can introduce the concept of germination rate which can be expressed by the following relationship:

$$V_G = C \cdot \exp\left[-\frac{(\Delta G_g^{f*} + \Delta G_d)}{KT}\right] \text{ germ} \cdot m^{-3} \cdot s^{-1} \quad (\text{II-23})$$

In the case of homogeneous germination, a simplified calculation makes it possible to establish that the germination rate strongly depends on supercooling (ΔG_g^{f*} depends on ΔT). Figure II-8- shows the evolution of the germination rate as a function of temperature. We observe that:

- The germination rate is zero when:
 - $T = T_F$: few germs reach the critical size at this temperature

- The supercooling is very high: the temperature is then too low, which greatly slows down the diffusion of the species and makes it difficult for the atoms of the liquid to be brought to the germ to reinforce the stability of the latter.
- The germination rate is higher for medium supercoolings reconciling the presence of a large number of critical germs and a reasonable diffusion allowing their subsequent growth.

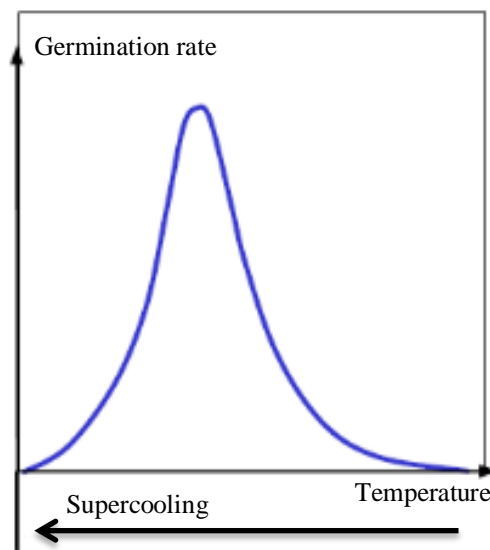


Fig. II-8- : Influence of supercooling on the germination rate.

The heterogeneous germination rate can be expressed in the same way but in this case:

$$\Delta G_g^{f*}{}_{\text{het}} = \Delta G_g^{f*}{}_{\text{hom}} f(\theta) \quad (\text{II-24})$$

II-3-2. Growth

As soon as a stable germ is formed, its growth begins with the addition of atoms to its surface. This growth is determined by the rate at which the atoms arrive at the interface and by the possibilities offered to them to cling to it. In other words, the growth rate of the solid depends on the diffusion coefficient of the atoms and the structure of the interface.

At the atomic scale, the growth of the germ is controlled by the ability of its surface to capture new atoms. Growth is therefore favored by an irregular surface containing sites on which the atoms can easily attach themselves (vacancy.....).

III-3-2-1. Growth of the solid in the case of pure metal

For a pure metal, as soon as the first germs are formed, growth continues through their development. These germs take, during their growth, a regular geometric form, but when they come into contact with other germs in the course of growth, their regular form is disturbed and the primitive crystals become irregular and take the name of grains.

- If the cooling of the pure metal is very slow (in equilibrium conditions) until a layer of solid forms, as the heat diffuses outwards, the thickness of the layer solidified increases. It is at the level of the interface that the release of latent heat will occur and that a discontinuity of the thermal gradients will be established in the liquid on the one hand and that of the solid on the other hand. At this stage, the growth presents a flat front.

The heat balance is based on the continuity of the heat fluxes at the solid/liquid interface, we can write:

$$Q_S = Q_L + Q^* \quad (\text{II-25})$$

Where Q_S : is the quantity of heat that the solid can extract,

Q_L : heat evacuated by the liquid,

Q^* : latent heat of solidification

We define:

$$Q_S = J_S \cdot A \cdot dt \quad (\text{II-26})$$

$$Q_L = J_L \cdot A \cdot dt \quad (\text{II-27})$$

$$Q^* = -L \cdot A \cdot dx \quad (\text{II-28})$$

L is the latent heat of solidification per unit volume, released, hence the sign (-).

J_S and J_L are the heat fluxes in the solid and the liquid respectively.

A is the interface section which advances with a speed dx/dt

The thickness of the solid increases by an infinitesimal quantity dx during dt , and according to Fourier's law which expresses the heat fluxes as a function of the thermal conductivities (K_S and K_L) and the temperature gradients (T_S and T_L):

$$J = -KG \quad (\text{II-29})$$

$$J_S \cdot A \cdot dt = J_L \cdot A \cdot dt - L \cdot A \cdot dx \quad (\text{II-30})$$

$$-K_S T'_S dt = -K_L T'_L dt - L dx \quad (\text{II-31})$$

Which gives the solidification rate as follows:

$$V_S = \frac{(K_S T'_S - k_L T'_L)}{L} \quad (\text{II-31})$$

In reality, this front is subjected to disturbances which result in the presence of a protuberance (an advanced part of the solid) in front of the interface (Fig. III-9-).

The solid/liquid interface is at the melting temperature T_F , while the liquid has a higher temperature as one move away from this interface.

The heat tends to concentrate on the protuberance which develops on the interface. This has the consequence of locally increasing the temperature gradient T'_L and slowing down the solidification rate. Growth of the protrusion will then be blocked until the rest of the interface has moved forward to catch up. This mechanism is called *planar growth*. It occurs globally by the progressive advance of a smooth interface in the liquid.

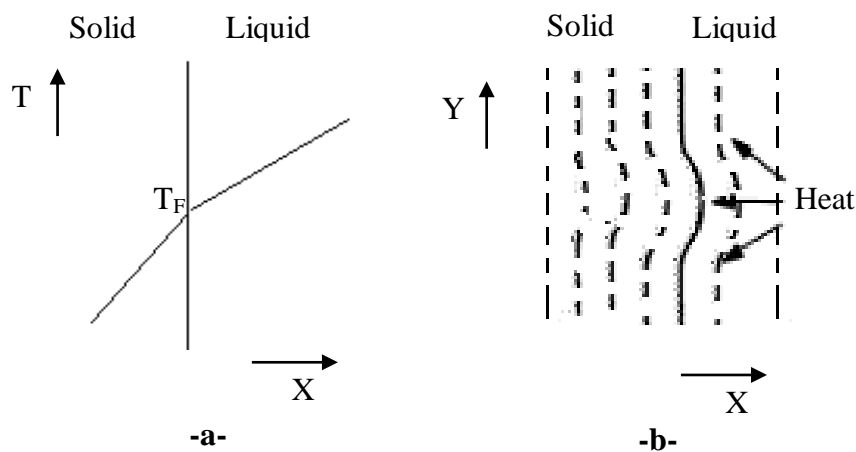


Fig. III-9- : Mechanism of development of a protrusion at the solid/liquid interface, the liquid is at a temperature higher than that of the solid:

- (a) Temperature distribution curve
- (b) Formation of a protrusion.

- ❖ If the cooling of a pure metal is rapid, the liquid close to the interface can be at a temperature lower than T_F , well before many germs are formed. Under these conditions, a solid protrusion that would appear in advance of the interface would immediately be located in a region of supercooling; the result is an exaggerated growth of this protuberance anterior to the interface.

The latent heat of solidification L first flows towards the supercooled liquid, the temperature of which will tend to increase. Secondary and tertiary branches are formed on the primary trunk (the trunk + branches assembly called dendrite) in order to accelerate the evacuation of the latent heat of solidification (Fig. III-10-). In the case of pure metal solidification the dendrites are called thermal dendrites to distinguish from that of dendrites formed in alloys.

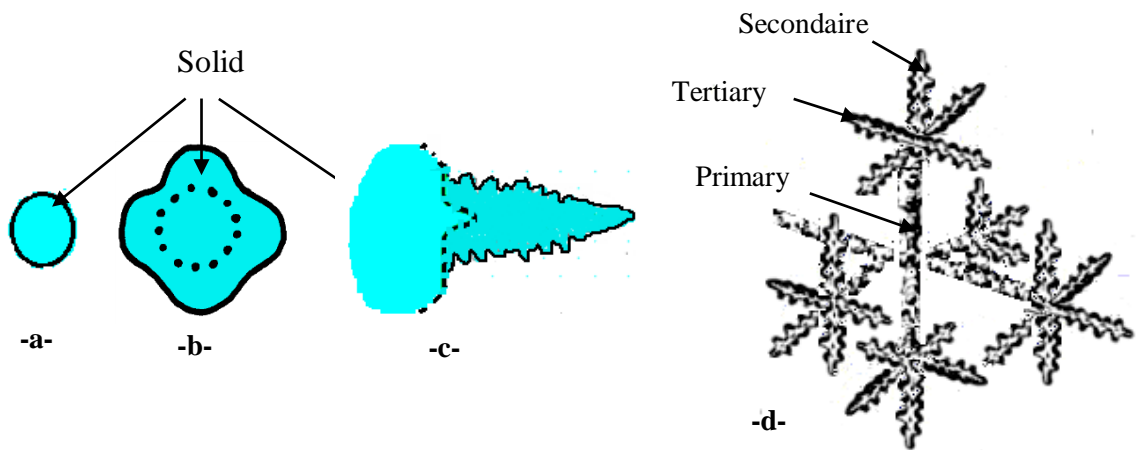


Fig. III-10- : Mechanisms of development of a dendrite: (a) spherical germ crystal, (b) development of protuberance on the crystal surface, (c) first stage of dendrite formation; (d) developing dendrite.

Figure III-11- shows more clearly a dendrite during growth, the size of the dendrites is generally characterized by the distance separating the axes of the secondary branches λ . The value of this distance is all the lower as the liquid solidifies more quickly.

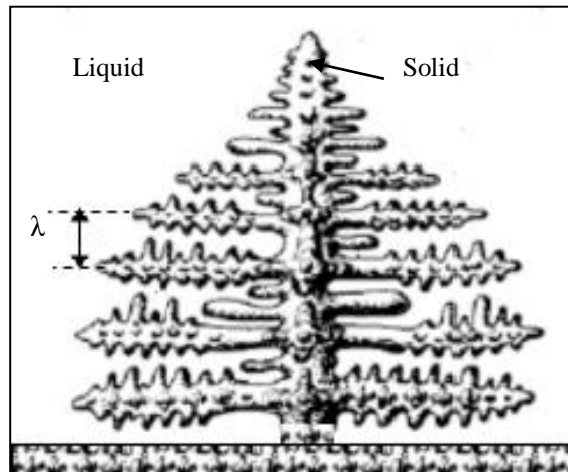


Fig. III-11-: Dendrite during growth.

III-3-2-2. Solid growth in the case of alloys

In practice, the solidification of pure solids is rarely encountered by that pure metals contain impurities which serve to change the solidification characteristics of a pure metal to an alloy, as well as the solidification of alloys is most prevalent in the industry.

What we have just described for a pure metal applies to alloys; before solidification begins; there must be germination. Solidification must simultaneously be accompanied by a redistribution of the solute between the solid and the liquid.

A- Case of a single-phase alloy

❖ Solidification of a single-phase alloy under equilibrium conditions

Let us consider an alloy A-B of nominal composition C_0 of B element (Fig. III-12-a-). Under equilibrium conditions, the cooling of a liquid alloy of composition C_0 from the temperature T' , produces its progressive solidification in the solidification interval between T_0 and T_f . At a given temperature T , the solid formed has the composition C_s and the remaining liquid has the composition C_L . Once solidification is complete, the alloy thus cooled is homogeneous and its composition at all points is equal to C_0 .

At a given temperature located in the solidification interval, there is coexistence of the liquid and the solid whose masses obey the law of conservation. This result assumes that the solid being formed has time to homogenize continuously by diffusion of alloying elements in the solid state.

❖ **Solidification of a single-phase alloy under non-equilibrium conditions**

In practice, the cooling rates implemented (cooling in air, outside the furnace) are high and diffusion in the solid state remains extremely limited. On the other hand, diffusion is always possible in the residual liquid, not yet transformed; these considerations mean that the composition of the solid and the liquid do not evolve as described in the equilibrium diagram.

We consider the binary alloy A-B of composition C_0 (Fig. III-12-a-). If the cooling of this alloy is carried out under equilibrium conditions (i.e. with a very slow cooling rate) as described in the previous paragraph, the point representative of the global composition of the solid describes the curve of solidus from S_0 to S_f . In this case the time required for the composition of the solid to become uniform continuously by diffusion of the solute would be long.

Due to the slowness of the diffusion in the solid state (cooling of the same alloy with a rate such that the diffusion is negligible in the solid formed but possible in the residual liquid), the real situation is often the following:

- The first germs deposited at T_0 have a composition close to its equilibrium composition C_{S_0} .
- During cooling, they retain a composition closer to its initial values than these equilibrium values, i.e. richer in A (point B in figure III-12-a-).

As a result, the global composition of the solid is located in Figure II-9-a- to the left of the ideal solidus line. Solute B was rejected from the center of the grains of the solid towards the boundary (grain boundary). This heterogeneity of composition is called *minor segregation*: it is the grouping of solute atoms on the grain boundaries of a material.

Solidification therefore ends at a temperature T_f below the steady-state solidification temperature T_f .

From the microstructural point of view, the first nuclei formed at the temperature T_0 of concentration C_{S_0} have a dendritic morphology (Fig. III-12-b-). With the decrease in temperature, solidification takes place on the branches of the dendrite forming lines which materialize the surfaces of equal concentration where each line has a different concentration (Fig. III-12-b-). The solidification interval is increased instead of $[T_0-T_f]$, it becomes $[T_0-T_f]$.

This phenomenon can be observed in alloys with a eutectic point. The shift in the solidus can lead to the appearance of the eutectic phase at the edge of the grain (Fig. III-13-) for compositions that are theoretically outside the eutectic, hence the unexpected appearance of a phase with a low melting point and the risk of local melting under conditions of use a priori without risk (melting at the grain boundary leading to the collapse of the material).

We also distinguish the segregation on the scale of the piece, it is the *major segregation*: during the solidification of a metal part their center solidifies last, it is therefore rich in solute that the zones which have solidified in first.

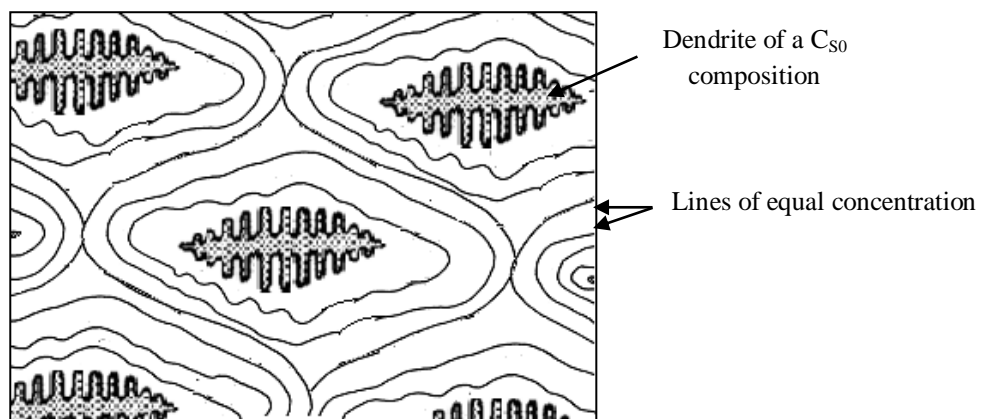
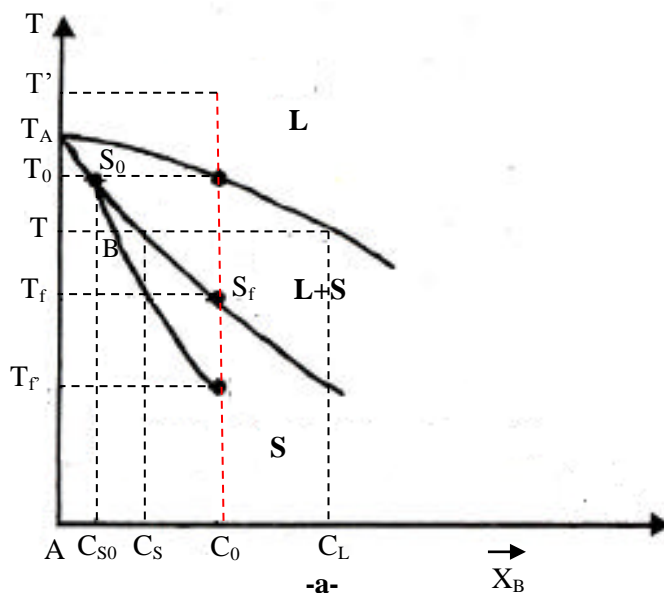


Fig. III-12-: Illustration of minor segregation:

- (a) Part of phase diagram shows the deviation from equilibrium during solidification of a single-phase binary alloy.
- (b) Lines of equal concentration in a single-phase alloy with minor segregation.

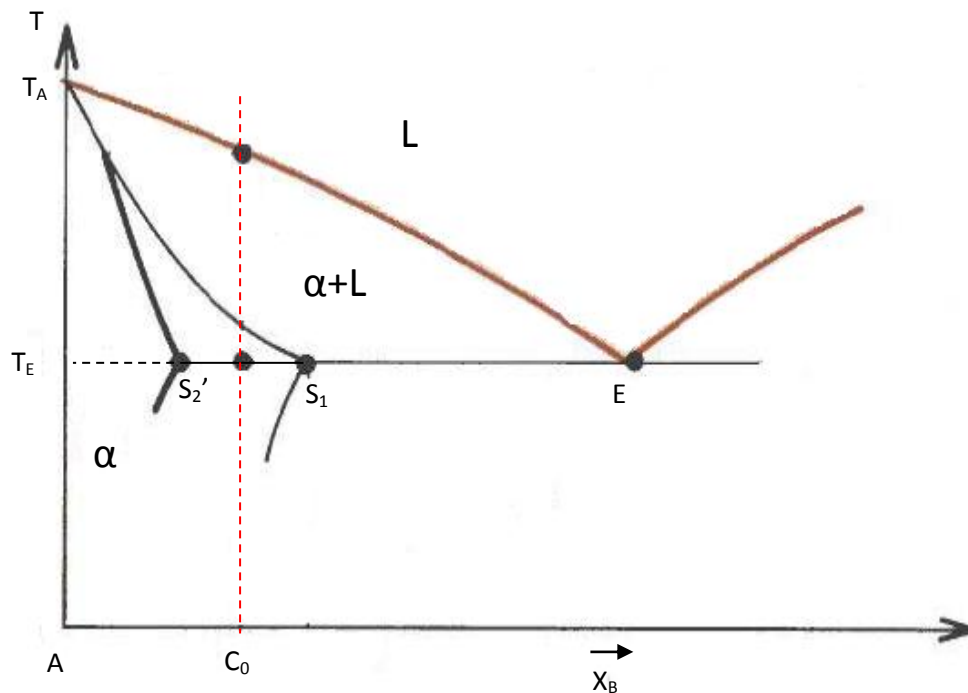


Fig. III-13- : Part of phase diagram has eutectic point shows the deviation from equilibrium during solidification of a binary alloy.

B- Case of a two-phase alloy:

❖ Eutectic growth:

Eutectic growth is a cooperative growth of two solid phases of different compositions from a single homogeneous liquid phase. During the eutectic growth, there is an accumulation of species B in the liquid in front of one phase and of species A in front of the other phase ((Fig. III-14-).

The redistribution of the solute in the liquid is a factor of destabilization of the plane interface during the growth of a single-phase solid and it is a factor of rapprochement of the solid phases during the eutectic growth. Various eutectic microstructures were observed and they are classified as regular (in lamellar or rod form) and irregular (Fig. III-15-).

If, during the coupled growth, the two solid phases present are characterized by an isotropic interfacial energy, the eutectic lamellae grow parallel to the heat flow. This leads to a regular structure of the eutectic after solidification. The lamellar structure of the eutectics

can be considered as the periodic and alternating stacking of parallel ribbons of the two phases.

Some alloys have irregular structures; the lamellae or fibers are not evenly spaced. In this type of eutectics, the interlamellar spacings are everywhere disordered and vary considerably.

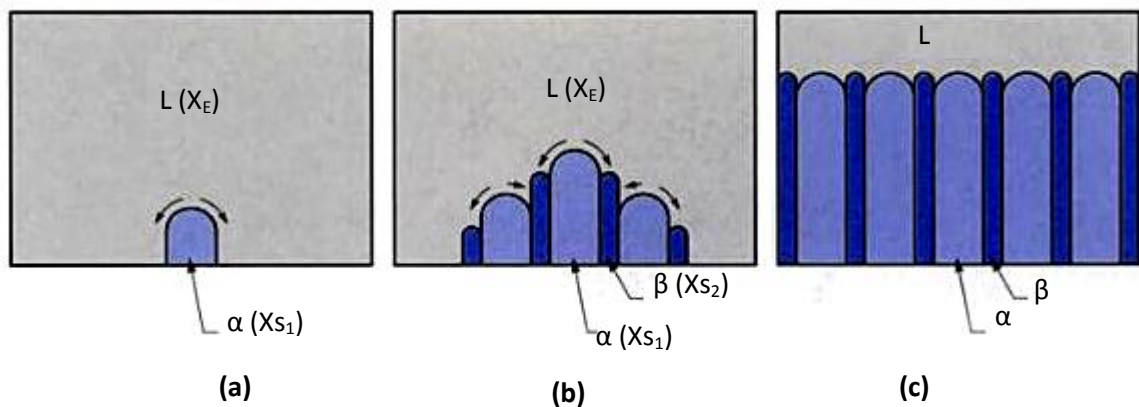


Fig. III-15 : Formation and growth of a eutectic constituent :

- (a) Formation, within the liquid of composition X_E , of a nucleus of the α phase of composition X_{S_1} . The arrows represent the rejection of the solute in front of the α germ
- (b) Lateral growth of the eutectic by formation of the β phase,
- (c) Planar growth of the solidification front

❖ Peritectic growth

Alloys with peritectic phase transition are frequently observed in metals, for example, steels, copper-based alloys. A peritectic transformation involves the transformation of a solid phase and a liquid phase into a single new solid phase.

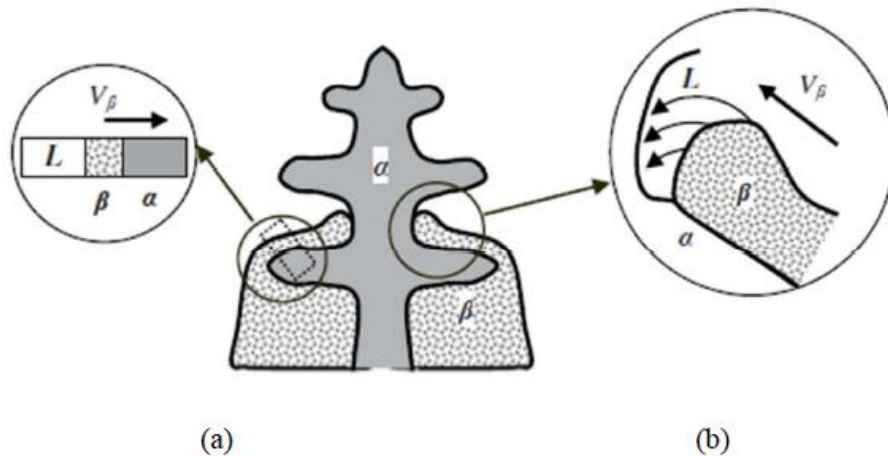


Fig. III-16-: Peritectic growth mechanism:
 (a) Peritectic transformation
 (b) The peritectic reaction

III-4. Solidification structures

During the development of an alloy, the material is taken to a liquid state then it is casted into a mold or mold to obtain a shaped piece. In the case of static casting in an ingot mold, the macroscopic structure of the alloy depends both on the rate of germination and the rate of heat exchange (nature and thickness of the wall of the ingot mold). If we consider a section at mid-height of the ingot mold, we generally observe three different crystallization zones (Fig. III-14):

- ❖ **Chill zone of equiaxed crystals (coating zone):** When the melting metal comes into contact with a mold whose temperature is far below that of liquidus, it is suddenly cooled, and germination takes place there rapidly (as it is quenched from high temperature to ambient). A significant supercooling in this zone, which allows the appearance of the first solid germs by heterogeneous germination (the support is the walls of the mold), their large number, prevent each other from developing.
- ❖ **Basaltic zone (columnar zone):** once the coating zone is formed, the temperature gradient in the liquid decreases. The dendritic growth of the grains continues, but those whose dendrites have an axis parallel to the heat flux grow more rapidly than the others, in the basaltic zone, the grains have approximately the same orientation and the same section. The length of the basaltic grains can reach several centimeters (the thickness of this zone is greater than that of the first zone).

- ❖ **Equiaxial zone:** at the end of solidification, the evolution of the basaltic zone is limited by the germination of many crystals within the remaining liquid, which is totally supercooled. This germination is heterogeneous and very often occurs on dendrite debris. In this zone, the grains are randomly oriented and grow at the same speed in all directions.

We can notice that in a foundry piece, all these zones are not necessarily present. In addition to the structural heterogeneity, there is a chemical heterogeneity observed at the center of the ingot: the elements which have a lower melting point segregate at the center; this is the major segregation phenomenon.

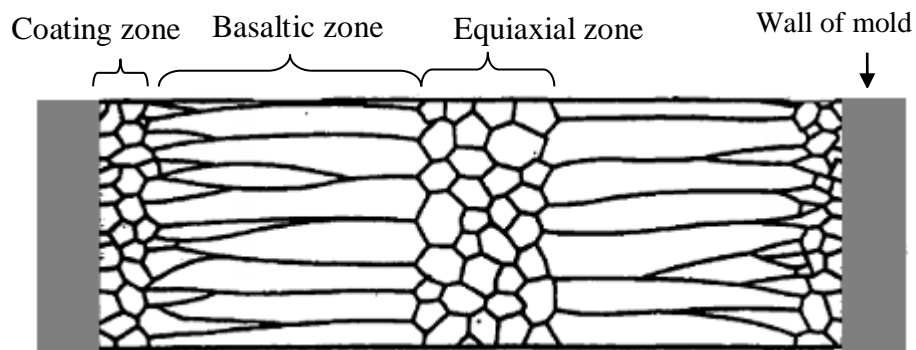


Fig. III-14- : Représentation des différents zones qui se créés lors de la solidification.

Practice exercise

Exercise 1:

Show using a phase diagram that due to the slow diffusion in the solid state, the actual solidification of a binary alloy occurs at a lower temperature than that predicted by the equilibrium diagram.

What is the consequence on the dendritic microstructure?

Exercise 2:

Determine the critical free enthalpy of germination ΔG^* of a spherical germ of critical size.

Exercise 3:

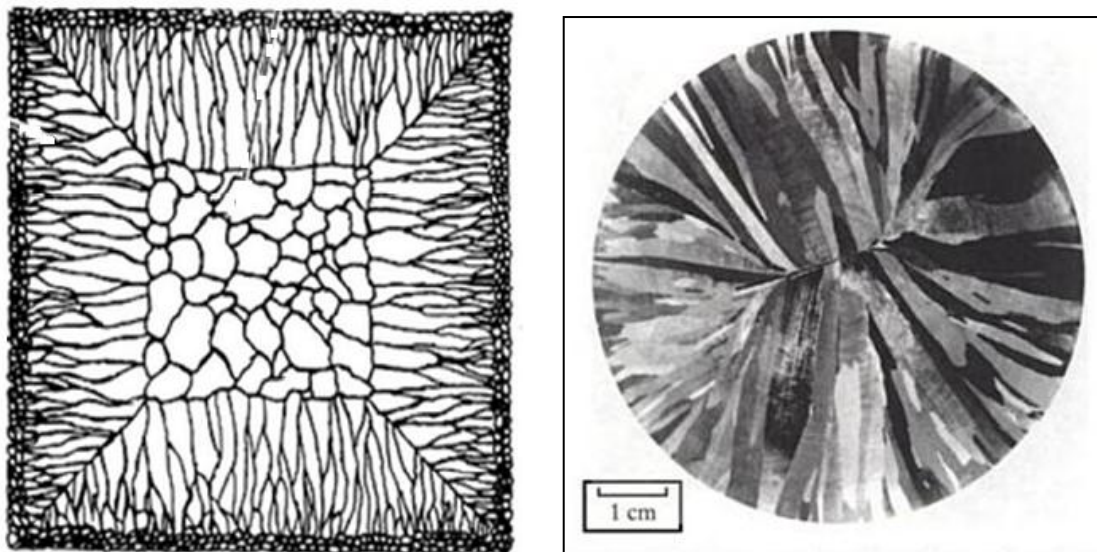
Calculate the dimensions and the free enthalpy of the critical germ formed during solidification of a pure metallic material. We will call ΔG_v the free enthalpy per unit volume and γ the interface energy.

Inclusions are very frequently added to reduce the size of the metallic grains. Germination then occurs in contact with a substrate.

- What is the type of germination in this case?
- Remake the calculations of dimensions and critical germ free enthalpy.
- When is germination easier?

Exercise 4:

- 1- Explain why, under a given pressure, a pure substance is solid at low temperature and liquid at high temperature
- 2- We consider a section of an ingot represented in figure 1 -(a)-.
 - Describe what you observe in this figure.
- 3- Figure 1 -(b)- shows a section of a commercially pure copper ingot.
 - Compare the two figures (a) and (b) and show the difference between them.



-(a)- American Society for Metals, *Metals Handbook, Volume 8: Metallography*, Structures and Phase Diagrams, 8th Edition, 1973

-(b)- J.P. Bailon, J.M. Dorlot, *Des matériaux*, presses internationales polytechnique de Montréal, 3^{ème} édition, 2000

Figure 1