Chapter

II

Crystal growth and solidification

II-1. Introduction

The properties of metallic materials, whether in a pure state or as a mixture of two or more elements, depend on the phase transformations they undergo. 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 present in the system under consideration, we distinguish between two main categories: transformation from the liquid phase to the solid phase, and transformation from one solid phase to another. In this chapter, we will study the first category of these transformations (liquid ↔ solid), specifically focusing on the phenomenon of solidification.

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

The structures formed after solidification influence the mechanical properties of castings and partially determine the type of treatment required to achieve desired properties. Specifically, the size and shape of grains depend on solidification conditions.

II-2. Liquid state and solid state

In the crystalline solid state, at the atomic scale, atoms are considered to have well-defined average positions held together by cohesive forces, arranged in a motif (unit cell). Moreover, the structure of solids typically includes a significant number of defects such as vacancies, dislocations, and stacking faults, etc...

Crystalline materials exist in either monocrystalline or polycrystalline forms. Commonly used metallic materials typically have a polycrystalline structure composed of numerous microcrystals (grains) interconnected by less ordered regions known as grain boundaries. Each grain in a metallic material is a single crystal. Decreasing the grain size leads to an increase in material strength at room temperature.

In the liquid state, atoms no longer have well-defined positions. The first neighboring atoms of a given atom occupy positions close to those they occupy in a crystal, while the positions of second and third neighbors are less well-defined, and beyond that, order does not exist. 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 key fact is the sudden change in certain physical characteristics when transitioning between different physical states.

- Liquids are generally less dense (except for certain elements: Bi, Ge, Ga, Si, water, and cast iron). This results in a volume loss or shrinkage during solidification (e.g., copper experiences a 4.8% shrinkage).
- Atom mobility (diffusivity) is greater in liquids (self-diffusion and chemical diffusion of alloying elements and impurities are slower in solids compared to liquids).

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, with a thickness typically only a few atoms of the material. Once the solid phase nucleus forms, its growth continues and is limited by:

- The kinetics of atom attachment at the solid-liquid interface,
- Heat diffusion from atoms in both the solid and liquid phases. The significance of each of these factors depends on the substance under study and the conditions of solidification.

In general, creating an interface is a process that requires energy and is thermodynamically unfavorable. The presence of interfaces increases the free energy of a material. Similar to phase boundaries, grain boundaries represent a specific type of interface as they delineate the boundary between two crystalline grains of the same composition and structure but different orientations. Fine-grain systems, characterized by numerous interfaces, possess higher free energy compared to coarse-grained systems.

From a thermodynamic standpoint, an interface is characterized by its specific interfacial energy, denoted as γ. This energy is independent of the interface area and can be determined by measuring the work required to create a unit area of the interface.

❖ Interfacial structures

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

At low solidification rates, with a fixed temperature gradient in the liquid, the solid-liquid interface remains flat. Achieving this ideal growth state is practically challenging because heat exchange between the molten material and the sample creates a temperature gradient in the liquid region. The planar interface becomes unstable beyond a critical value of the growth rate or temperature gradient.

However, if the growth rate is increased beyond a critical value Vc, and the temperature gradient is reduced, the solid-liquid interface becomes unstable. This instability leads to the formation of a cellular morphology, where the spacing λ typically ranges from tens to hundreds of micrometers. At even higher growth rates, this cellular structure can transform into a dendritic form. These different cases are illustrated in Figure II-1.

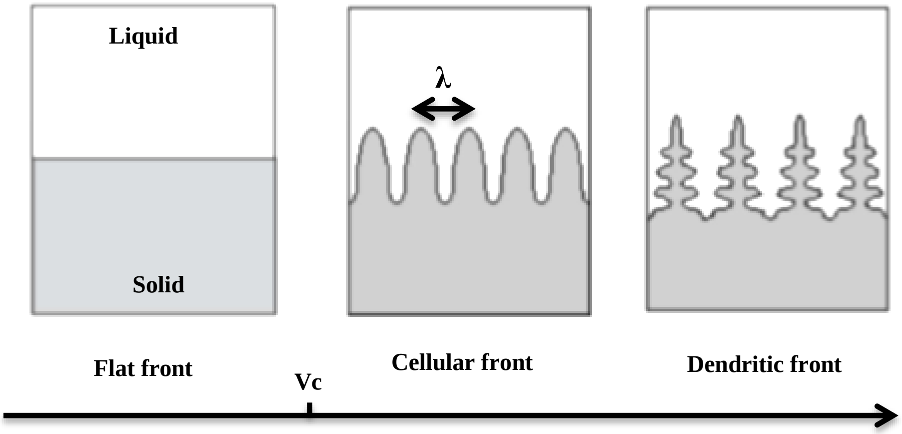


Fig. II-1- : Schematic representation of the different morphologies of the solid-liquid interface.

Solidification occurs in two stages: nucleation and growth. Nucleation is the stage where many small solid particles (nuclei) form from the liquid. Each of these solid nuclei must reach a certain critical size to remain stable. Growth then occurs as the solid nuclei increase in size at the expense of the surrounding liquid until the liquid phase is completely consumed.

II-3-1. Nucleation

There are two types of nucleation: homogeneous nucleation, where solid nuclei form within the liquid without contact with walls or impurities, and heterogeneous nucleation, where nuclei form on foreign particles submerged in the liquid or on the cold walls of the mold.

II-3-1-1. Homogeneous nucleation

Some nuclei can form within the liquid without any solid support (such as mold walls or inclusions). These nuclei are called homogeneous nuclei, and their formation requires very high supercooling—typically around 20% of the melting temperature (T_f).

a. Latent heat and volume free energy

The change in free energy per unit volume (ΔG) that accompanies solidification of a pure substance A can be expressed as:

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

where:

- G_v^l is the free energy per unit volume in the liquid state,
- G_v^s is the free energy per unit volume in the solid state.
- H and S are respectively the enthalpy and the entropy per unit volume of A at the considered temperature.

This expression represents the difference in free energy per unit volume between the liquid state G_v^l and the solid state G_v^s of substance A during solidification.

For a pure metal, the transformation from liquid to solid occurs at a specific temperature characteristic of the metal. This temperature is where the free energies of the solid (G_v^s) and liquid (G_v^l) phases are equal: $G_v^s = G_v^l$. The latent heat (L) is defined as the amount of heat released during solidification or absorbed during fusion, where $L = \Delta H$.

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

- At $T=T_F$, the two phases, liquid and solid, coexist in equilibrium, with their free energies being equal: $G_V^s = G_V^l$.
- For $T>T_F$, the liquid phase is stable, so $G_V^l < G_V^s$.
- For $T<T_F$, the solid phase is stable, so $G_V^s < G_V^l$.

In summary, T_F represents the temperature at which the solid and liquid phases of the material are in equilibrium, and the stability of each phase relative to the other depends on whether the temperature is above or below T_F.

Figure II-2 schematically represents 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 phase with the lowest free energy is the most stable, or equivalently, the phase whose formation reduces the free energy of the system.

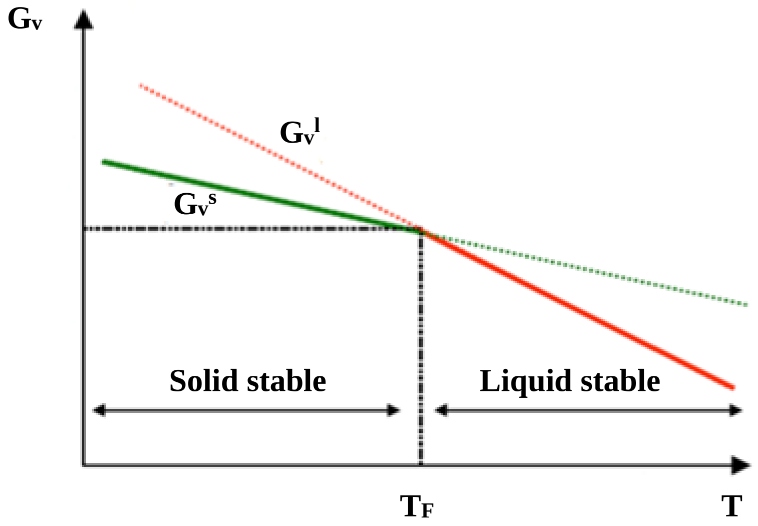


Fig. II-2- : Variations of free energy per unit volume as a function of temperature.

Consider the solidification of a pure metal initially maintained at a temperature above its melting point to keep it in the liquid state. The metal is then cooled to a temperature T well below its melting point. For solidification to occur, ΔG_V must be less than zero ($\Delta G_V<0$).

This clarifies that solidification will only occur when the Gibbs free energy change per unit volume (ΔG_V) is negative, indicating that the solid phase is more stable than the liquid phase under the given conditions.

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

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

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

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

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

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

If the temperature T differs from T_F, the change in free energy ΔG_v is not zero, and it can be evaluated assuming that ΔH and ΔS are not significantly affected by temperature.

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

Where:

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

For solidification to occur ($\Delta G_v < 0$), the term ($T_F - T$) must be positive, indicating $T_F > T$. The difference ($T_F - T$) is referred to as *supercooling*.

The minus sign in the ΔG_v relation indicates that the liquid → solid transformation occurs with a decrease 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 nucleus (germ):

$$\Delta G_1 = \Delta G_v * V \qquad \text{(II-8)}$$

b. Supercooling and surface energy

During cooling under equilibrium conditions (i.e., at very low rates), the thermal analysis curve T=f(t) typically resembles that shown in Figure II-3-(a): the isothermal plateau indicates solidification occurring at a constant temperature for the pure metal. However, under usual cooling conditions in industrial settings, it is observed that the liquid phase does not immediately solidify just below the equilibrium temperature T_F.

In practice, the thermal analysis curve obtained resembles that shown in Figure II-3-(b). Solidification initiates at a temperature T_B significantly lower than T_F, requiring an 'undercooling' ΔT, also known as supercooling (portion AB of the curve). Once the first nuclei (germs) form, the release of latent heat causes a temperature increase (portion BC of the curve).

In the case of an alloy (solid solution), the thermal analysis curve corresponds to that shown in Figure II-3-(c), where one can determine the starting temperature of solidification, T_S , by extrapolation. Supercooling reflects a delay in solidification. This delay is explained by the formation of an interface between the solid nuclei and the liquid. This interface consumes an amount of energy ΔG_S per unit area of interface created ($\Delta G_S>0$, indicating that interface formation is an endothermic process). The presence of nuclei increases the free energy of the system by an amount ΔG_2 proportional to the surface area of the nuclei, where:

$$\Delta G_2 = \Delta G_S * S \qquad \text{(II-9)}$$

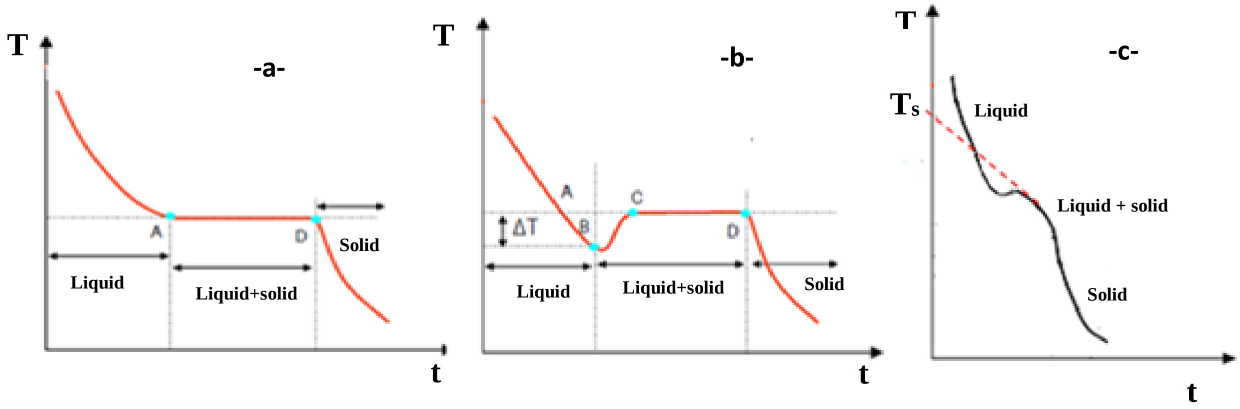


Fig. II-3- : Cooling curves for:
(a) a pure metal without supercooling,
(b) a pure metal with supercooling,
(c) a supercooled binary alloy.

c. Free energy of nucleus formation

Consider an initial volume of liquid undergoing solidification. When a solid nucleus forms with volume V and surface area S, the total change in free energy of nucleus formation (ΔG_g^f) is the sum of two components: the free energy related to volume and the free energy related to surface area:

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

The formation of this nucleus will only be possible if $\Delta G_g^f < 0$. The first term, being negative, drives the solidification process, while the second term, being positive, opposes it. The most probable shape of the nucleus will therefore correspond to minimizing surface energy consumption (minimum surface area) and maximizing volume energy release (maximum volume). The spherical shape satisfies this condition (see Figure II-4).

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

$$\Delta G_g^f = \Delta G_1 + \Delta G_2 \qquad \text{(II-111)}$$

$$\Delta G_g^f = \Delta G_v * V + \Delta G_s * S \qquad \text{(II-12)}$$

$$\Delta G_g^f = \Delta G_v * (4/3\ \pi\ r^3) + \gamma_{s\text{-}l} * (4\pi r^2) \qquad \text{(II-13)}$$

So, the total change in free energy of nucleus formation (ΔG_g^f) is:

$$\Delta G_g^f = -\frac{4}{3}\frac{\pi L \Delta T}{T_F} r^3 + 4\pi\gamma r^2 \qquad \text{(II-14)}$$

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

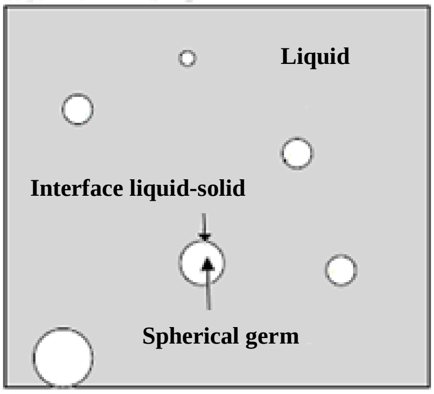


Fig. II-4- : Formation of the spherical solid nucleus

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

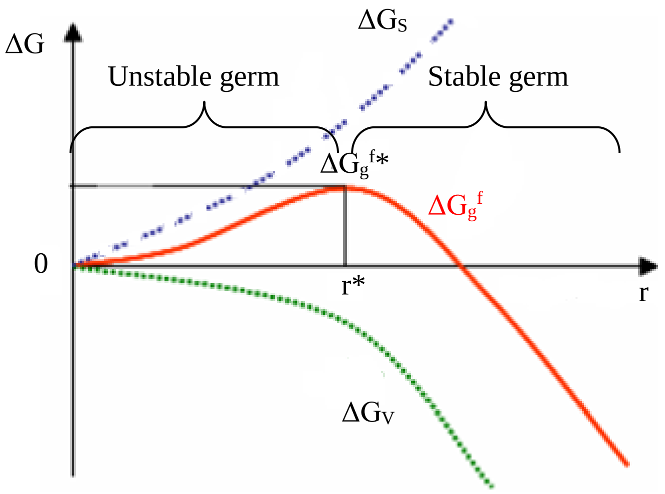


Fig. II-5- : Free energy variation curves as a function of nucleus size.

- **Influence of germ size**

As the size of the nuclei increases, the free energy first increases before reaching a maximum ΔG_g^{f*} at a critical size r = r*, then decreases for larger values of r. The critical size r* can be determined by setting the derivative of ΔG_g^f equal to zero at r*:

$$\frac{d\Delta G_g^f}{dr} = 0 \tag{II-15}$$

$$-\Delta G_v 4\pi r^2 + \gamma_{s\text{-}l} 8\pi r = 0 \tag{II-16}$$

$$r^* = \frac{2\gamma T_F}{L\Delta T} \tag{II-17}$$

The critical value of the free energy is:

$$\Delta G_g^{f*} = \frac{16\pi\gamma^3 T_F^2}{3L^2\Delta T^2} \tag{II-18}$$

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

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

$$\Delta G_g^f{}_{3\rightarrow4} = \Delta G_g^f{}_4 - \Delta G_g^f{}_3 \tag{II-19}$$

As $\Delta G_g{}^f{}_4 < \Delta G_g{}^f{}_3$, we will therefore have $\Delta G_g{}^f{}_{3\rightarrow4} < 0$.

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

$$\Delta G_g{}^f{}_{1\rightarrow2} = \Delta G_g{}^f{}_2 - \Delta G_g{}^f{}_1 > 0 \qquad \text{(II-20)}$$

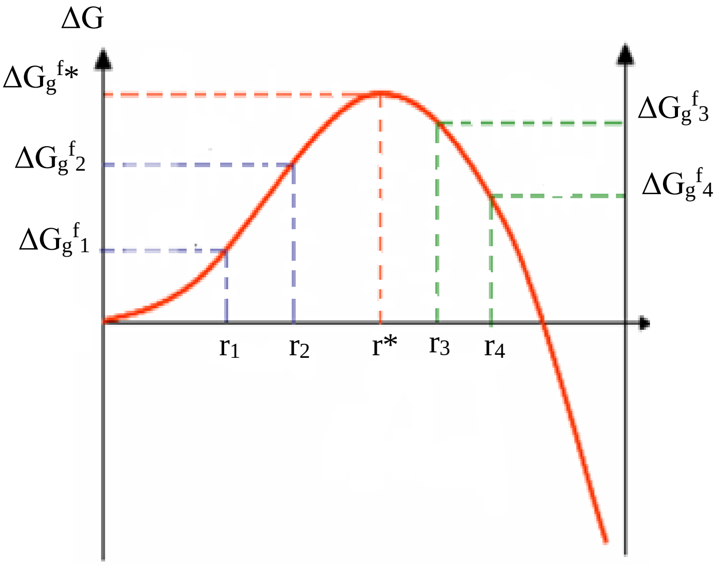


Fig. II-6- : The variation of the free energy of nucleus formation according to its radius r shows the stability domain of the nucleus.

- **Influence of temperature**

The influence of temperature can be deduced from the previous relations; that is, the potential barrier decreases when the supercooling ΔT increases (up to moderate values), and the same applies for r^* (the critical size and the energy barrier are lower as the supercooling increases). This means that increasing supercooling allows smaller nuclei to stabilize. In other words, the number of stable nuclei increases, and solidification is favored when supercooling is high.

II-3-1-2. Heterogeneous nucleation

In practice, there are supports that provide a surface on which the metal can solidify. These supports consist of either insoluble impurities (see Fig. II-7) or the walls of the mold or crucible. Under these conditions, a nucleus with a radius of curvature greater than the critical radius forms with a minimal liquid-solid surface area. Moreover, the number of atoms required to form a nucleus of critical size is much smaller compared to that of a homogeneous nucleus.

The nucleus assumes the shape of *a spherical cap* with radius r. Various contact surfaces contribute with their interface energies: γ_{gl} (the interface energy between the liquid and the nucleus), γ_{gs} (the interface energy between the nucleus and the support), γ_{sl} (the interface energy between the support and the liquid).

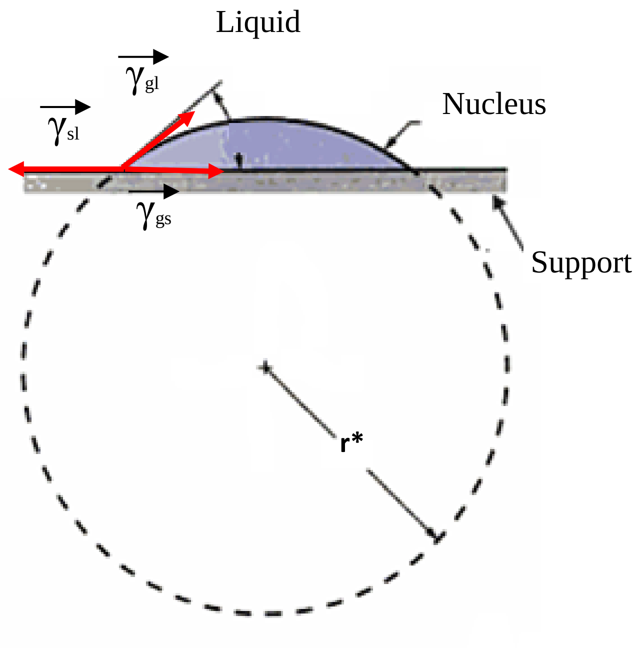


Fig. II-7- : Heterogeneous nucleation on a solid support.

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

$$\vec{\gamma}_{sl} + \vec{\gamma}_{gl} + \vec{\gamma}_{gs} = 0 \qquad \text{(II-21)}$$

By projection on the axis of the support:

$$\gamma_{sl} = \gamma_{gl} \cos\theta + \gamma_{gs} \qquad \text{(II-22)}$$

In this case, the total change in free energy of nucleus formation (ΔG_g^f) is:

$$\Delta G_{het} = \Delta G_{hom}\, f(\theta) \qquad \text{(II-23)}$$

Where:

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \qquad \text{(II-24)}$$

II-3-1-3. Nucleation rate

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

$$n^* = N.exp\left(-\frac{\Delta G_g^{f*}}{KT}\right) \qquad \text{(II-25)}$$

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

It is observed that the number of nuclei reaching the critical size increases with the degree of supercooling. However, nuclei of critical size become stable only if they capture additional atoms. This condition depends on the ability of these atoms to diffuse toward the nucleus. This phenomenon involves an activation energy for diffusion in the liquid, ΔG_d (the potential barrier that must be overcome for an atom to attach itself to the growing nucleus). We can introduce the concept of nucleation rate, which can be expressed by the following relationship:

$$V_G = C.exp\left[-\frac{\left(\Delta G_g^{f*}+\Delta G_d\right)}{KT}\right] germ.m^{-3}.s^{-1} \qquad \text{(II-26)}$$

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

- The nucleation rate is zero when:
  - $T=T_F$: Few nuclei 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 reach the nucleus to enhance its stability.

- The nucleation rate is higher for moderate supercoolings, which allows for the presence of a large number of critical nuclei and facilitates their subsequent growth due to reasonable diffusion.

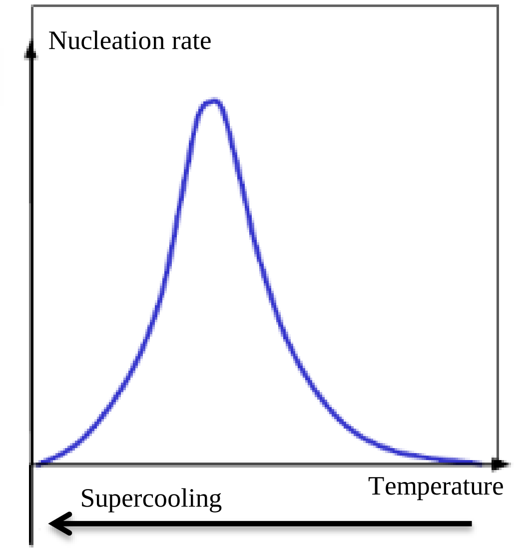


Fig. II-8- : Influence of supercooling on the nucleation rate.

The heterogeneous nucleation rate can be expressed similarly, but in this case:

$$\Delta G_g^{f\,*}{}_{het} = \Delta G_g^{f\,*}{}_{hom}\, f(\theta) \qquad \text{(II-27)}$$

II-3-2. Growth

As soon as a stable nucleus is formed, its growth begins with the addition of atoms to its surface. This growth is determined by the rate at which atoms arrive at the interface and by their ability to adhere 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 nucleus is controlled by the ability of its surface to capture new atoms. Growth is therefore favored by an irregular surface containing sites on which atoms can easily attach themselves (vacancies...).

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

For a pure metal, once the initial nuclei are formed, growth continues through their development. These nuclei assume a regular geometric form during their growth. However, when they come into contact with other nuclei during growth, their regular form is disrupted, and the initial crystals become irregular, forming what are known as grains.

If the cooling of the pure metal is very slow (under equilibrium conditions), as a layer of solid forms, the thickness of the solidified layer increases as heat diffuses outward. It is at the interface where the release of latent heat occurs and where a discontinuity in thermal gradients is established between the liquid and the solid. At this stage, growth occurs with a flat front.

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

$$Q_S = Q_L + Q^* \qquad \text{(II-28)}$$

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:

$$Q_S = J_S.A.dt \qquad \text{(II-29)}$$

$$Q_L = J_L.A.dt \qquad \text{(II-30)}$$

$$Q^* = -L.A\ .dx \qquad \text{(II-31)}$$

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 area 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):

$$J = -KG \qquad \text{(II-32)}$$

$$J_S.A.dt = J_L.A.dt - L.A\ .dx \qquad \text{(II-33)}$$

$$-K_S T'_S\, dt = -K_L T'_L dt - L\ dx \qquad \text{(II-34)}$$

Which gives the solidification rate as follows:

$$V_s = \frac{(K_S T'_S - k_L T'_L)}{L} \qquad \text{(II-35)}$$

In reality, this front is subject to disturbances that result in the presence of a protuberance (an advanced part of the solid) ahead of the interface (see Figure II-9).

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

Heat tends to concentrate on the protuberance that develops at the interface. This results in a local increase in the temperature gradient, T'_L, which slows down the solidification rate. The protrusion's growth is then halted until the remainder of the interface has advanced to catch up. This mechanism is known as *planar growth*, which happens as a smooth interface progressively advances through the liquid.

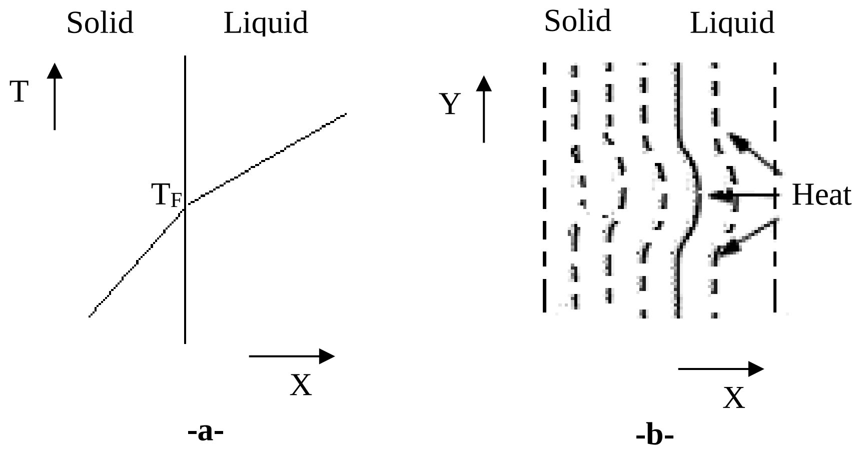


Fig. II-9- : Mechanism of protrusion development at the solid/liquid interface, with the liquid at a higher temperature than the solid:
(a) Temperature distribution curve
(b) Formation of a protrusion.

- ❖ If a pure metal cools rapidly, the liquid near the interface can reach a temperature lower than T_F before many nuclei form. In these circumstances, a solid protrusion that forms ahead of the interface will immediately find itself in a region of supercooling. This leads to an exaggerated growth of the protrusion ahead of the interface.

The latent heat of solidification L initially flows towards the supercooled liquid, causing its temperature to increase. Secondary and tertiary branches then form on the primary trunk (this assembly of trunk + branches is called a dendrite) to accelerate the removal of the latent heat of solidification (Fig. II-10). In the solidification of pure metals, these dendrites are referred to as thermal dendrites to distinguish them from dendrites formed in alloys.

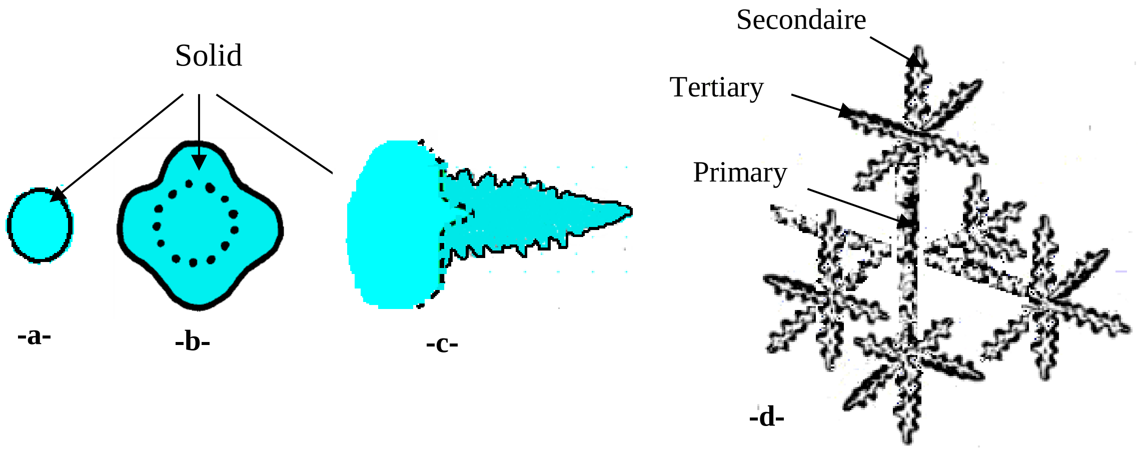


Fig. II-10- : Mechanisms of dendrite development: (a) spherical germ crystal, (b) development of protuberance on the crystal surface, (c) first stage of dendrite formation; (d) developing dendrite.

Fig. II-11 shows a dendrite during growth more clearly. The size of dendrites is typically characterized by the distance between the axes of the secondary branches, denoted as λ\lambdaλ. This distance is smaller when the liquid solidifies more rapidly.

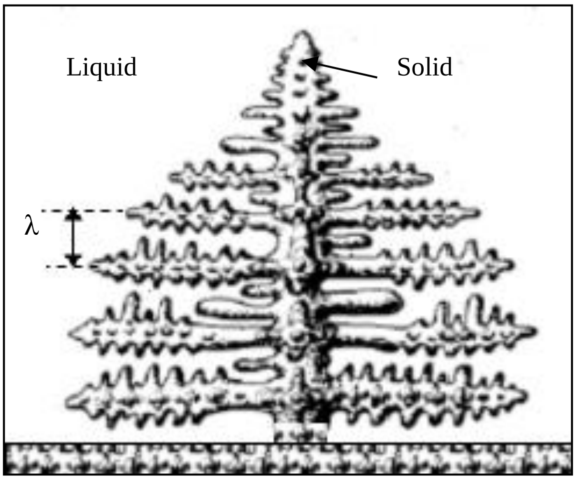


Fig. II-11-: Dendrite during growth.

III-3-2-2. Solidification Process in Alloys

In practice, the solidification of pure solids is rare because pure metals typically contain impurities that alter their solidification characteristics, effectively transforming them into alloys. Therefore, solidification of alloys is more commonly encountered in industry.

What we have just described for a pure metal also applies to alloys: before solidification begins, there must be nucleation. Solidification must also involve simultaneous redistribution of solute between the solid and the liquid.

A- Case of a single-phase alloy

❖ Solidification of a single-phase alloy under equilibrium conditions

Consider an alloy A-B with a nominal composition C_0 of element B (Fig. II-12-a). Under equilibrium conditions, cooling a liquid alloy of composition C_0 from temperature T′ results in progressive solidification within the temperature interval between T_0 and T_f . At a specific temperature T, the solid phase formed has composition C_s, while the remaining liquid phase has composition C_L. Once solidification is complete, the cooled alloy is homogeneous, and its composition throughout is C_0.

At a given temperature within the solidification interval, there is coexistence of both liquid and solid phases, with their masses following the law of conservation. This occurs under the assumption that the solid phase forming has sufficient time to continuously homogenize through the diffusion of alloying elements in the solid state.

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

In practice, the cooling rates used (such as cooling in air outside the furnace) are high, and diffusion in the solid state remains extremely limited. However, diffusion is always possible in the residual liquid that has not yet solidified. These factors mean that the composition of the solid and the liquid does not evolve as described in the equilibrium diagram.

We consider the binary alloy A-B with composition C_0 (Fig. II-12-a). If this alloy is cooled under equilibrium conditions (i.e., with a very slow cooling rate) as described in the previous paragraph, the point representing the overall composition of the solid follows the solidus curve from S_0 to S_f. In this scenario, the time required for the solid composition to become uniformly continuous through solute diffusion would be extensive.

Due to the slow diffusion in the solid state (when the alloy is cooled at a rate such that diffusion is negligible in the solid phase but still possible in the remaining liquid), the actual situation often resembles the following:

- The initial nuclei deposited at T_0 have a composition close to their equilibrium composition C_{S0}.
- During cooling, these nuclei maintain a composition closer to their initial values rather than reaching equilibrium values, i.e., richer in A (point B in Fig. II-12-a).

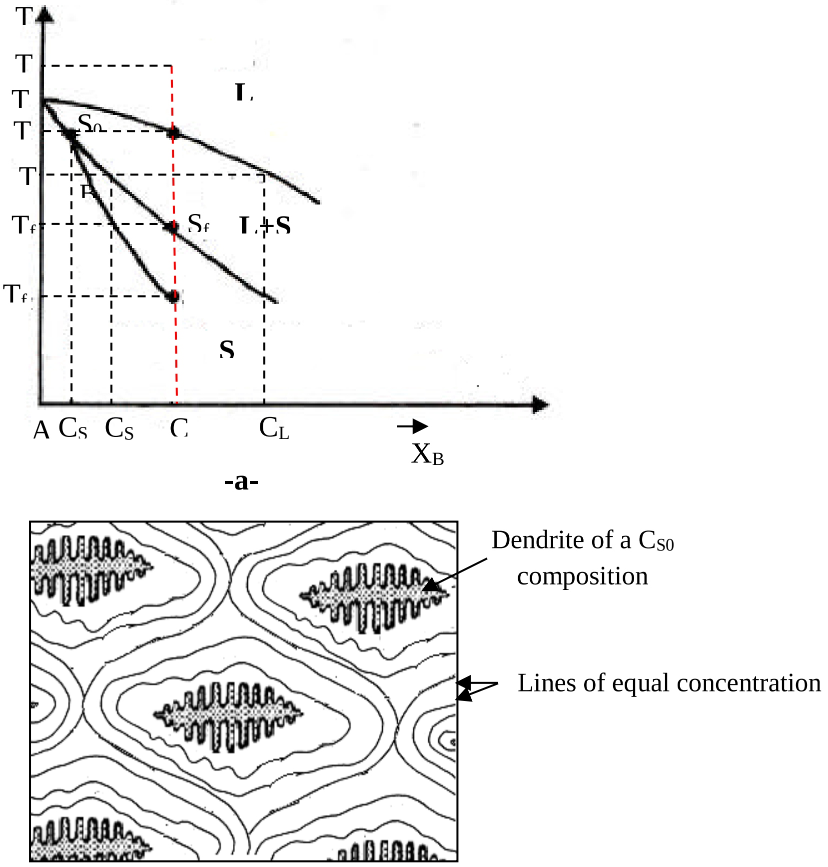
As a result, the overall composition of the solid is positioned in Fig. II-12-a- to the left of the ideal solidus line. Solute B is rejected from the centers of the solid grains towards their boundaries (grain boundaries). This heterogeneity in composition is known as *minor segregation*: the clustering of solute atoms along the grain boundaries of a material.

Solidification therefore ends at a temperature $T_{f'}$, which is below the steady-state solidification temperature T_f.

From a microstructural perspective, the initial nuclei formed at temperature T_0 with concentration C_{S0} exhibit a dendritic morphology (Fig. II-12-b). As temperature decreases, solidification progresses along the dendrite branches, forming lines that represent surfaces of equal concentration, with each line corresponding to a different concentration (Fig. II-12-b). The solidification interval expands from T_0 to T_f , rather than from T_0 to $T_{f'}$.

This phenomenon can be observed in alloys with a eutectic point. The shift in the solidus can cause the eutectic phase to appear at the grain boundaries (Fig. II-13) for compositions that theoretically lie outside the eutectic range. This results in the unexpected appearance of a phase with a lower melting point, posing a risk of local melting under conditions of use that were initially considered safe (melting at the grain boundary leading to material failure).

We also distinguish segregation on the scale of the piece, known as major segregation: during the solidification of a metal part, the center solidifies last and is therefore richer in solute compared to zones that solidified first.



-a-

Dendrite of a C_{S0} composition

Lines of equal concentration

-b-

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

(a) Portion of the phase diagram illustrating deviations from equilibrium during the solidification of a single-phase binary alloy.

(b) Lines of equal concentration in a single-phase alloy exhibiting minor segregation.

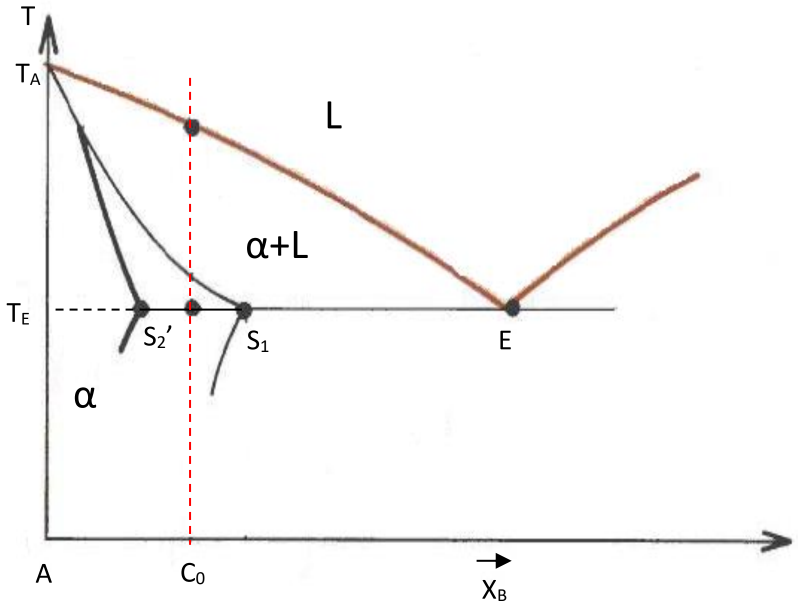


Fig. II-13- : Part of the Phase Diagram with Eutectic Point: Illustration of Deviations from Equilibrium during Solidification of a Binary Alloy.

B- Case of a two-phase alloy:

❖ Eutectic growth:

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

The redistribution of solute in the liquid destabilizes the planar interface during the growth of a single-phase solid and promotes the proximity of solid phases during eutectic growth. Various eutectic microstructures have been observed and are classified as regular (in lamellar or rod forms) and irregular (Fig. II-15).

If, during coupled growth, the two solid phases are characterized by isotropic interfacial energy, the eutectic lamellae grow parallel to the heat flow. This results in a regular structure of the eutectic after solidification. The lamellar structure of eutectics can be described as the periodic and alternating stacking of parallel ribbons of the two phases.

In some alloys, irregular structures are observed where the lamellae or fibers are not evenly spaced. In these eutectics, the interlamellar spacings are disorderly and vary significantly throughout.

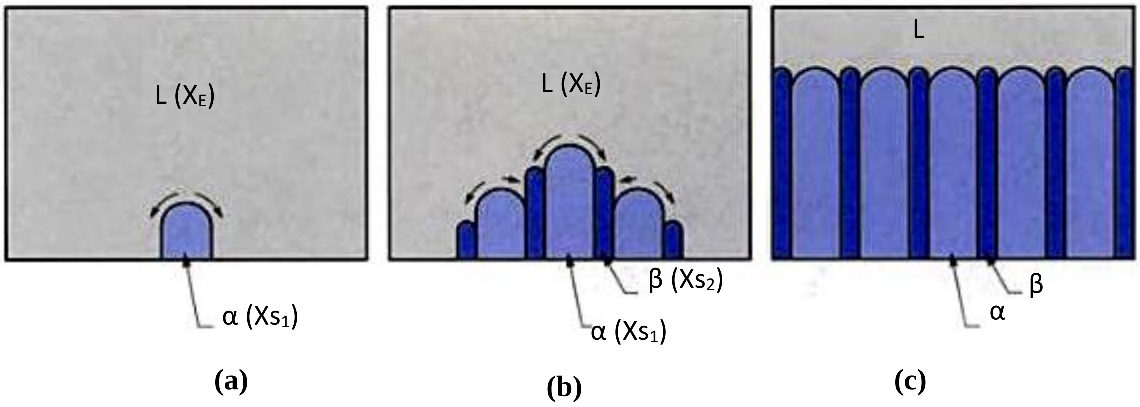


Fig. II-15 : Formation and growth of eutectic constituent :

(a) Formation of a nucleus of the α phase with composition Xs_1 within the liquid of composition X_E . The arrows indicate the rejection of solute in front of the α nucleus.

(b) Lateral growth of the eutectic by formation of the β phase.

(c) Planar growth of the solidification front.

- **Peritectic growth**

Alloys with a peritectic phase transition are commonly observed in metals such as steels and copper-based alloys. A peritectic transformation involves the combination of a solid phase and a liquid phase to form a new single solid phase.

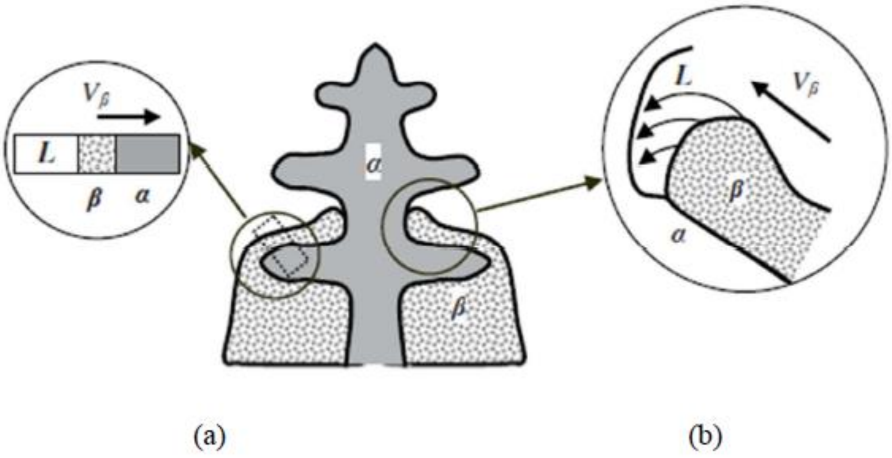


Fig. II-16-: Peritectic growth mechanism:
(a) Peritectic transformation
(b) The peritectic reaction

III-4. Solidification structures

During the development of an alloy, the material is melted to a liquid state and then cast into a mold to obtain a shaped piece. In the case of static casting in an ingot mold, the macroscopic structure of the alloy depends on both the nucleation rate and the rate of heat exchange (determined by the nature and thickness of the ingot mold wall). If we consider a cross-section at the mid-height of the ingot mold, typically three distinct crystallization zones can be observed (Fig. II-14):

- ***Chill zone of equiaxed crystals (coating zone):*** When molten metal comes into contact with a mold significantly cooler than its liquidus temperature, it undergoes rapid cooling and nucleation occurs immediately (quenched from high temperature to ambient). The substantial supercooling in this zone facilitates the initial formation of solid nuclei through heterogeneous nucleation (aided by the mold walls), with a high density of nuclei preventing each other from further growth.

- ***Basaltic zone (columnar zone):*** Once the coating zone is established, the temperature gradient within the liquid decreases. Dendritic growth of grains continues, but those with dendrites aligned parallel to the heat flux grow more rapidly. In the basaltic zone, grains exhibit nearly uniform orientation and cross-sectional area. The length of basaltic grains can extend several centimeters, with this zone being thicker than the first zone.

- ***Equiaxial zone:*** Towards the end of solidification, the evolution from the basaltic zone is constrained by the nucleation of numerous crystals within the remaining supercooled liquid. This nucleation is heterogeneous and frequently occurs on dendrite remnants. In this zone, grains are randomly oriented and grow uniformly in all directions.

We can observe that not all of these zones are necessarily present in a foundry piece. In addition to structural heterogeneity, there is chemical heterogeneity observed at the center of the ingot: elements with lower melting points segregate towards the center, known as the major segregation phenomenon.

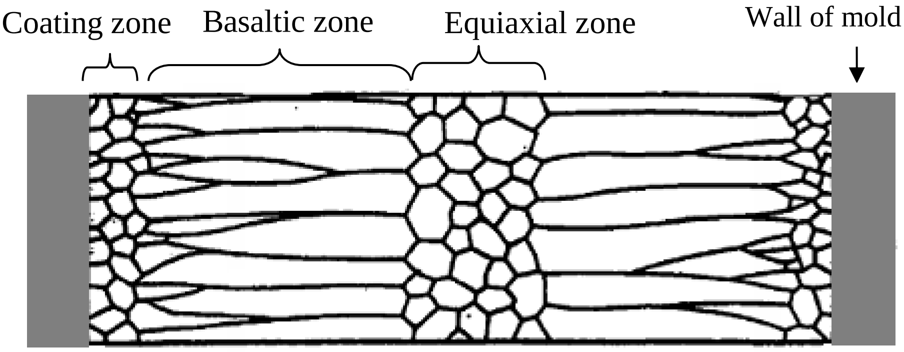


Fig. II-14- : Schematic representation of the different zones formed during solidification.

Practice exercises

Exercise 1:

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

What are the consequences for the dendritic microstructure?

Exercise 2:

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

Exercise 3:

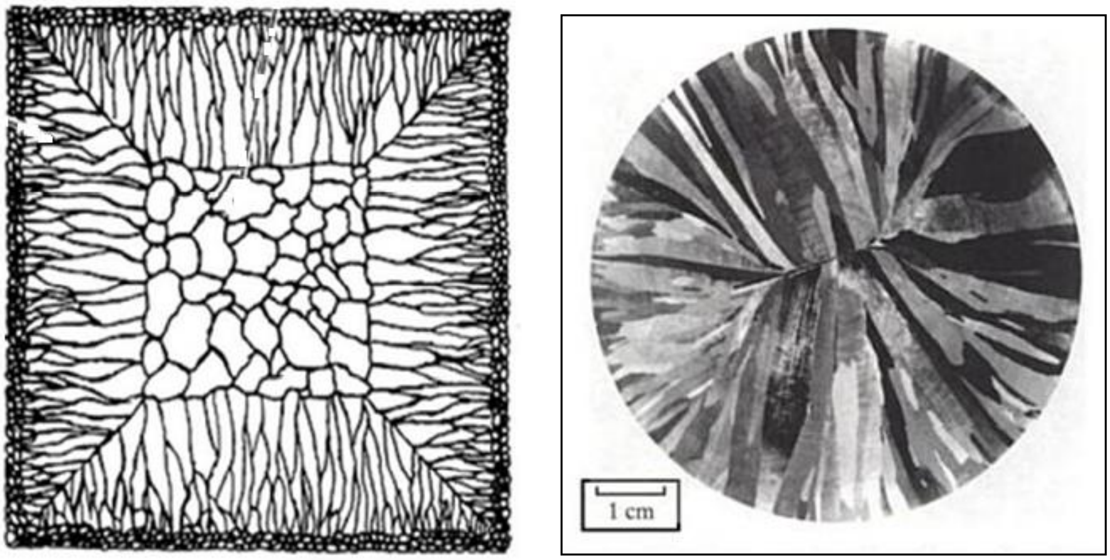
Calculate the dimensions and the free enthalpy of the critical germ formed during solidification of a pure metallic material. ΔG_v called the free enthalpy per unit volume and γ the interface energy.

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 nucleation in this case?
- Remake the calculations of dimensions and critical germ free enthalpy.
- Under what conditions is nucleation easier?

Exercise 4:

1- Explain why, under a given pressure, a pure substance is solid at low temperatures and liquid at high temperatures.
2- We consider a section of an ingot represented in Figure II-15-(a)-. Describe what you observe in this figure.
3- Figure II-15-(b)- shows a section of a commercially pure copper ingot. Compare the two figures (a) and (b) and highlight the differences between them.



-(a)- Section of an ingot *(Amarican Society for Metals, Metals Handbook, Volume 8: Metallography, Structures and Phase Diagrams, 8th Edition, 1973).*

-(b)- Section of a commercially pure copper ingot *(J.P. Bailon, J.M. Dorlot, Des matériaux, presses internationales polytechnique de Montérial, 3^{eme} édition, 2000).*

Fig. II-15

<u>Answers</u>

Answers for Exercise 1

The issue highlighted in this exercise is *minor segregation*.

Consider the binary alloy A-B with composition C_0 (Fig. II-16-). If this alloy is cooled under equilibrium conditions (i.e., with a very slow cooling rate), the point representing the overall composition of the solid follows the solidus curve from S_0 to S_f. In such cases, the time required for the solid's composition to uniformly homogenize through solute diffusion would be extensive.

As a result, the global composition of the solid is shown in Fig. II-16, positioned to the left of the ideal solidus line. Solute B was rejected from the center of the solid grains toward the boundaries (grain boundaries). This variation in composition is referred to as *minor segregation*: it is the accumulation of solute atoms at the grain boundaries of a material.

N.B. For more details, refer to the section in this chapter titled "Solid Growth in the Case of Alloys (Solidification of a Single-Phase Alloy Under Non-Equilibrium Conditions).

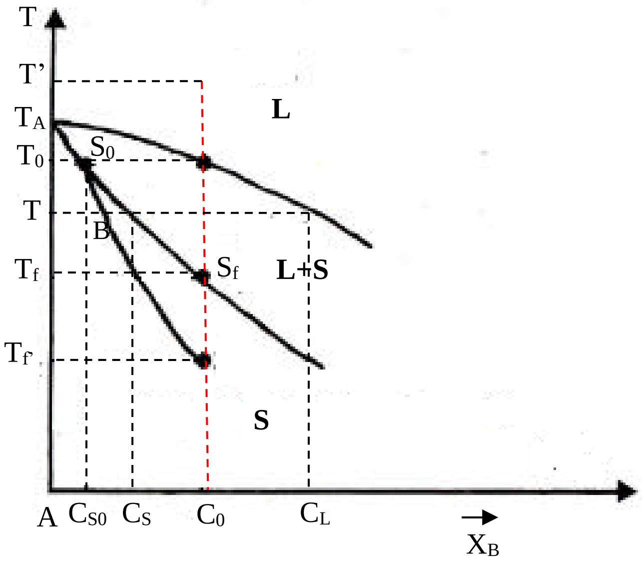


Fig. II-16-: Part of the phase diagram illustrates the deviation from equilibrium during the solidification of a single-phase binary alloy.

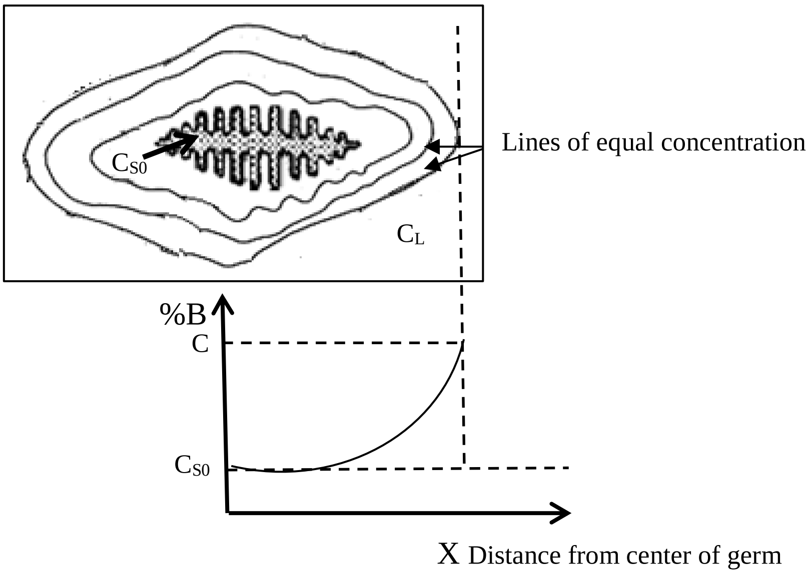


Fig. II-17-: Lines of equal concentration in a single-phase alloy exhibiting minor segregation.

Answers for Exercise 2

ΔG_g^{f*} corresponds to a critical size $r = r^*$,

The derivative of $\Delta G_g^f = 0$ for the value r^*:

$$\frac{d\Delta G_g^f}{dr} = 0 \qquad \text{(II-15)}$$

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

$$r^* = \frac{2\gamma T_F}{L\Delta T}$$

The critical value of the free energy is:

$$\Delta G_g^{f*} = \frac{16\pi\gamma^3 T_F^2}{3L^2\Delta T^2}$$

Answers for Exercise 3

1. Assuming the germ is spherical in shape:

$$r^* = \frac{2\gamma T_F}{L\Delta T}$$

$$\Delta G(r^*) = \frac{16\pi\gamma^3 T_F^2}{3\Delta G_v^2}$$

2. Addition of inclusions ⇒ heterogeneous germination

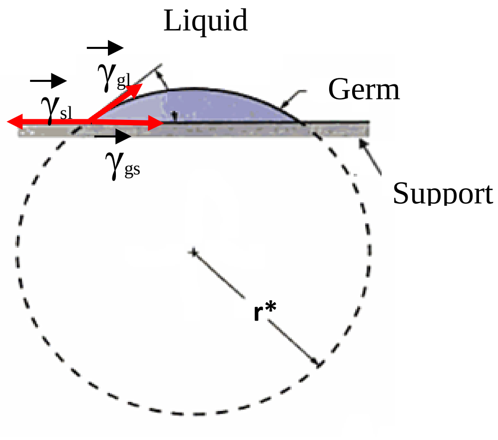


Fig. II-18- : Heterogeneous germination on a solid support.

To calculate the free energy of heterogeneous nucleation it is necessary to to consider the following:

- The volume contribution associated with solidification $V_g\Delta G_v$
- The removal of an interface between the particle and the liquid, with energy γ_{sl}
- The formation of the interfaces between the particle and the solid, and the solid and the liquid, with energies γ_{gs} and γ_{gl} respectively

$$\Delta G_{het} = V_g \Delta G_v + A_{gl}\gamma_{gl} + A_{gs}\gamma_{gs} - A_{sl}\gamma_{sl}$$

Where: $\vec{\gamma}_{sl} + \vec{\gamma}_{gl} + \vec{\gamma}_{gs} = 0$

By projection on the axis of the support:

$$\gamma_{sl} = \gamma_{gl} \cos\theta + \gamma_{gs}$$

- To calculate the volume of the spherical cap, we compute the surface integral of disks with radius r′ along the z-axis over the entire height of the cap (i.e. between z = rcosθ and z=r)

$$V_g = \int_{r\cos\theta}^{r} \pi r'^2\,(z)dz$$

$$V_g = \pi r^3 \left[\frac{(2+\cos\theta)(1-\cos\theta)}{3}\right]$$

- The contact surface between the solid and the support can be determined very easily:

$$A_{gs} = \pi r^2 sin^2\theta$$

- To calculate the surface area between the solid and the liquid, you need to use a curvilinear integral:

$$A_{gl} = 2\pi r^2(1 - \cos\theta)$$

Thus, the total change in the free energy of germ formation (ΔG_g^f) is given by :

$$\Delta G_{het} = \Delta G_{hom}\, f(\theta)$$

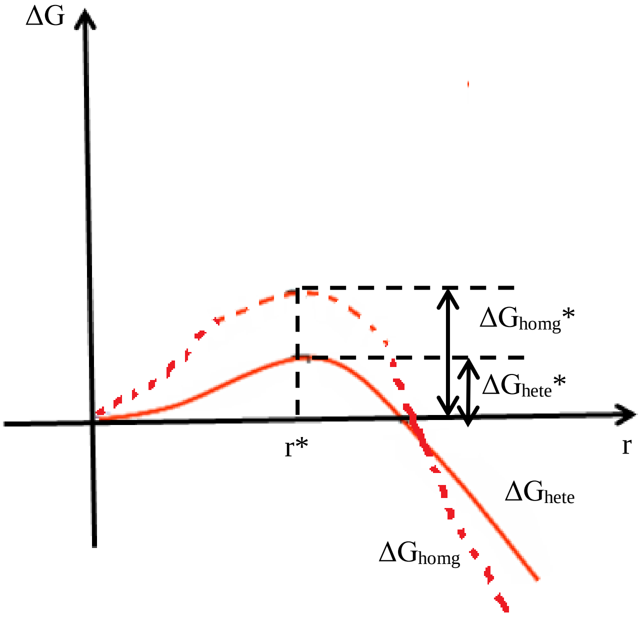
Where:

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

In our case, we are interested in $\Delta G(r^*)$, which represents the energy barrier to form a critical nucleus with radius r* where r^*_{het}=$r^*_{homg} = r^*$.

So: $\Delta G^*_{het} = \Delta G^*_{hom} * f(\theta)$

- $\Delta G_{hete}^* < \Delta G_{homg}^*$ ⇒ Heterogeneous nucleation is easier than homogeneous nucleation.



Answers for Exercise 4

1- $\Delta G = G_s - G_L = \frac{-L(T_f - T)}{T_f}$

For solidification to occur (i.e., for the formation of a solid phase), ΔG must be less than 0. Therefore when $T >> T_f \Rightarrow \Delta G > 0 \Rightarrow G_s - G_L > 0$

This means $G_s > G_L$ ⇒ indicating that the liquid phase is stable, and vice versa

2. For a description of the ingot and its three different crystallization zones, refer to the section titled "Solidification Structures" in the course material.
3. The difference between the two figures is the absence of an equiaxed zone in the copper ingot