

$$N_{hom} = f_0 c_0 \exp\left(-\frac{\Delta G_{hom}^*}{kT}\right) \quad (\text{number of nuclei per } m^{-3} s^{-1})$$

where  $f_0$  is the function of frequency of atomic vibrations, activation energy of diffusion in melt and the surface of critical nucleus.

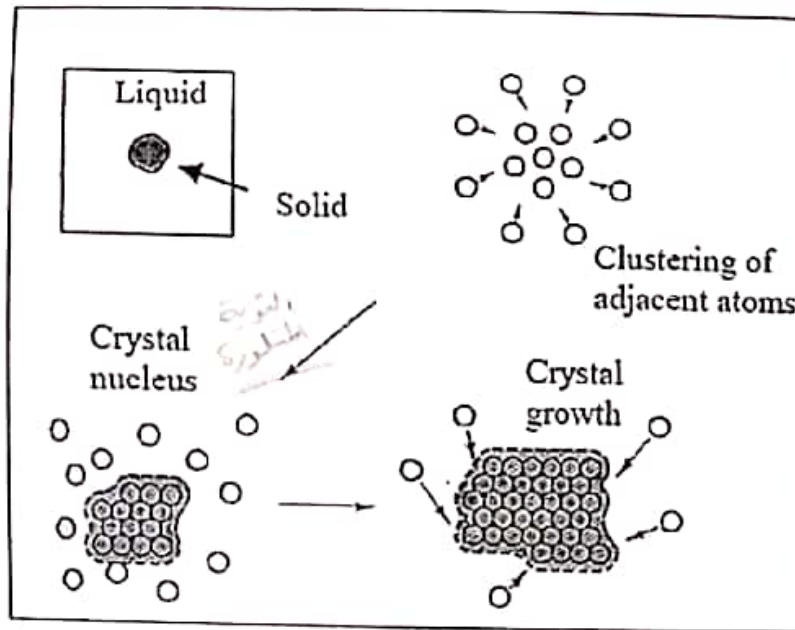


figure (11) Stages of homogeneous nucleation.

## 2) Heterogeneous nucleation:

The equation of  $\Delta G^*$  implies that easier nucleation at low undercooling levels requires a reduction of surface energy in the interface between the solid phase and the melt. Formation of nucleus on the mould surface is an easy method to achieve that. Assume formation of a nucleus on the mould surface in accordance with fig.(12). Assuming that  $\gamma_{SL}$  is isotropic, the shape of nucleus corresponding with the minimum total surface energy of the system consists of a spherical cap.

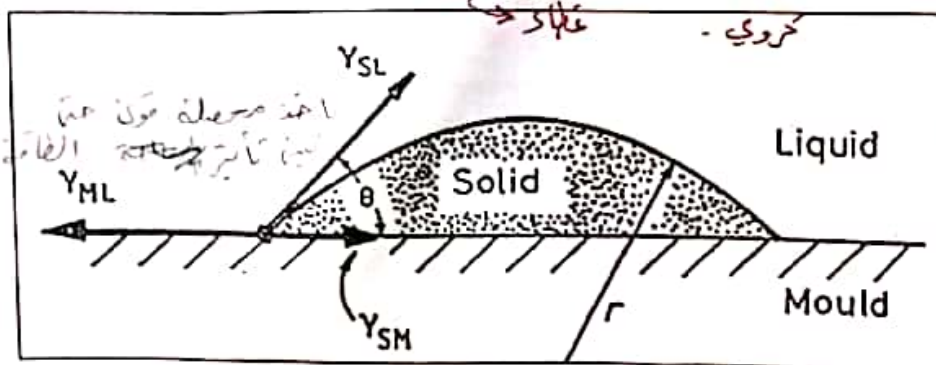


Figure (12) Heterogeneous nucleation of solid phase on a planar wall of the mould

The prerequisite for equilibrium of surface tension at the mould wall plane can be expressed as:

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL} \cos \theta$$

where:  $\gamma_{ML}$  is the surface energy of interface between the mould (M) and the melt (L),

$\gamma_{SM}$  is the surface energy of interface between the solid phase (nucleus) and the mould,

$\gamma_{SL}$  is the surface energy of interface between the solid phase (nucleus) and the melt.

The contact angle is therefore  $\theta$  equal to:

$$\cos \theta = (\gamma_{ML} - \gamma_{SM}) / \gamma_{SL}$$

The total Gibbs free energy during a heterogeneous nucleation will be defined by the formula:

$$\Delta G_{het} = -V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}$$

where:  $V_S$  is the volume of solid nucleus,

$A_{SM}$  is the area of interface between the nucleus and the mould,

$A_{SL}$  is the area of interface between the nucleus and the melt.

The equation above ( $\Delta G_{het}$ ) contains three terms relevant to the surface energy now. The first two terms are positive and they characterize the contribution of interfaces developed during nucleation. However, the third term corresponds with elimination of the interface between the mould and the melt under the nucleus and that is why it is negative, i.e. reducing the total nucleation barrier.

Substitution of values for volume  $V_S$  and areas  $A$  helps altering the equation into the following form:

$$\Delta G_{het} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma_{SL} \right\} S(\theta)$$

where:

$$S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$$

The equation above ( $\Delta G_{het}$ ) is, except for the term  $S(\theta)$ , identical to the equation  $\Delta G$ , describing the homogeneous nucleation in melt. The

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numerical value of expression  $S(\theta)$  is always lower than or equal to 1 depending on the size of the wetting angle  $\theta$ . The expression  $S(\theta)$  is therefore marked as the *shape factor*.

Fig. (13) shows the course  $\Delta G_{het}$  as well as  $\Delta G_{hom}$  for comparison purposes, depending on the radius of nucleus. Note that the actual critical radius of nucleus is independent of the nucleation type.

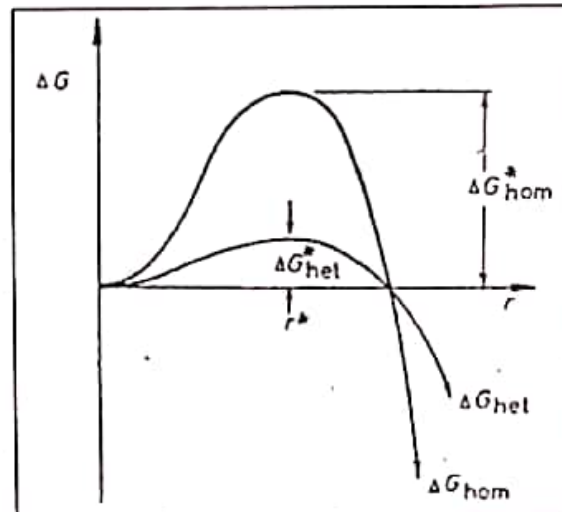


Figure (13) Changes of the Gibbs free energy during homogeneous or heterogeneous nucleation.

Formulas for calculation of critical values applicable to a heterogeneous nucleation can be obtained by derivation of the equation ( $\Delta G_{het}$ ) above:

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} S(\theta)$$

The comparison of homogeneous and heterogeneous nucleation has produced the following conclusions:

$$r_{het}^* = r_{hom}^* \quad \Delta G_{het} = S(\theta)\Delta G_{hom}^*$$

If there are  $n_1$  atoms in contact with mould walls, the number of nuclei is given by the formula:

$$n^* = n_1 \exp\left(-\frac{\Delta G_{het}^*}{kT}\right)$$

While the volume rate of heterogeneous nucleation describe by the following formula:

$$N_{het} = f_1 c_1 \exp\left(-\frac{\Delta G_{het}^*}{kT}\right)$$

Where  $f_1$  is the frequency factor similar to  $f_0$  in the equation  $N_{hom}$ ,  $c_1$  is the number of atoms touching the potential areas of heterogeneous nucleation per volume unit of melt.

### 1.5 Interfaces in solids

-What is a surface and what is an interface?

1- A cut through an infinite crystal creates two surfaces.

2- The joining of two phases creates an interface. As shown in fig. (14).

(Two orientations of the same crystalline phase joined in different orientation also creates an interface called a grain boundary).

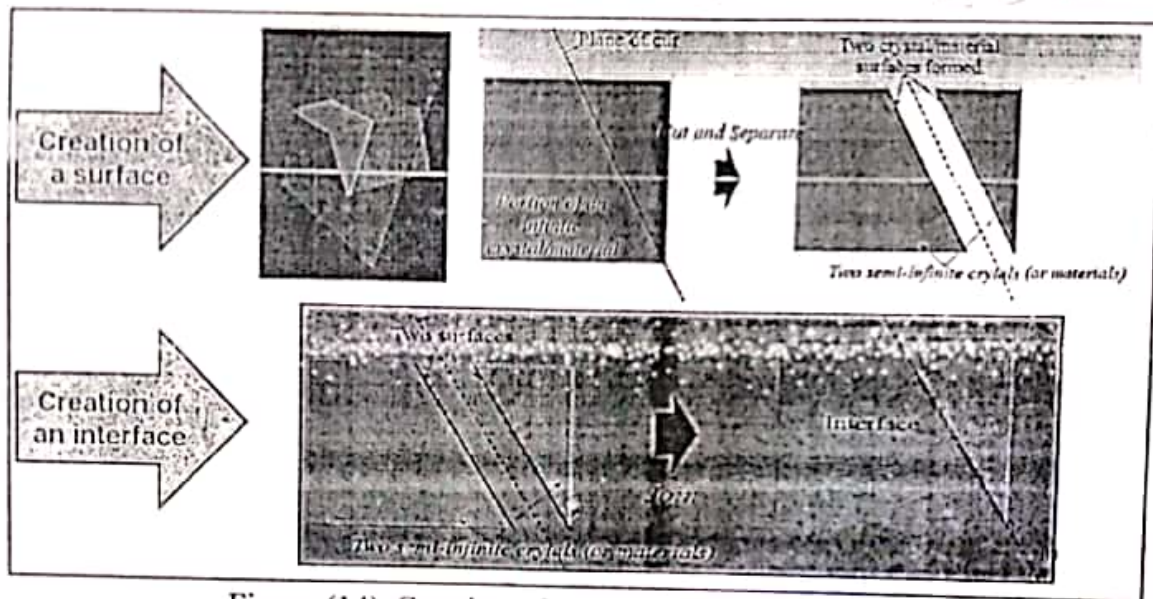


Figure (14) Creation of a surface and an interface.

- Nature of interfaces and their energies play an important role during phase transformation in materials.

- During nucleation of a new phase in a metastable parent phase, the interface created between nucleus and the parent phase contributes to an increase in Gibbs energy of the system. This leads to an activation barrier for nucleation of the new phase, whose magnitude, among other factors, also depends on the energy of such an interface.

- Interfaces between the product and parent phases also play significant role during the growth of stable nuclei. Growth occurs by movement of product/parent interfaces, and the mobility of an interface (the rate at



which an interface moves under the influence of a driving force) depends to a large extent on its structure (nature).

- Basically three different types of interface are important in materials, are:-

- 1- The free surface of a crystal (solid/vapor interface): All crystals possess this type of interface.
- 2- Grain boundaries and twin boundaries ( $\alpha/\alpha$  interface: solid/solid interface): This type separates crystals with essentially the same composition and crystal structure, but a different orientation in space.
- 3- Interphase interfaces ( $\alpha/\beta$  interfaces: solid/liquid or solid/solid interface): This type of interface separates two different phases that can have different crystal structures or compositions and therefore also includes solid/liquid interfaces.

Interfaces like the twin and grain boundaries separate the same phase are called homophase interfaces. In contrast, the solid-vapor or precipitate-matrix interface is called a heterophase interface.

Many engineering properties of interest are decided by the structure of the solid-solid interfaces in the material. Hence, a classification of solid-solid interfaces in crystalline systems according to the structure of the interface itself is important. Based on the structure of the interface, a (crystalline) solid-solid interface can be classified into three broad categories. They are as follows:

1- Coherent interface

2- Semicoherent interface

3- Incoherent interface

1- Coherent interfaces are interfaces across which the lattice planes are continuous as shown in fig.(15). In some cases, the continuity can be maintained with- out any distortion of lattice planes. However, in most of

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the coherent interfaces, the lattice planes are elastically strained to maintain continuity as shown in fig.(16); These elastic strains play a crucial role in determining the properties of the material containing such coherent interfaces.

The Ni<sub>3</sub>Al precipitates in Ni-base superalloys form coherent interfaces with the Ni-rich matrix. Al-Li and Al-Cu are some of the other systems in which coherent precipitates are seen. Certain twin boundaries can be coherent; they are known as coherent twin boundaries.

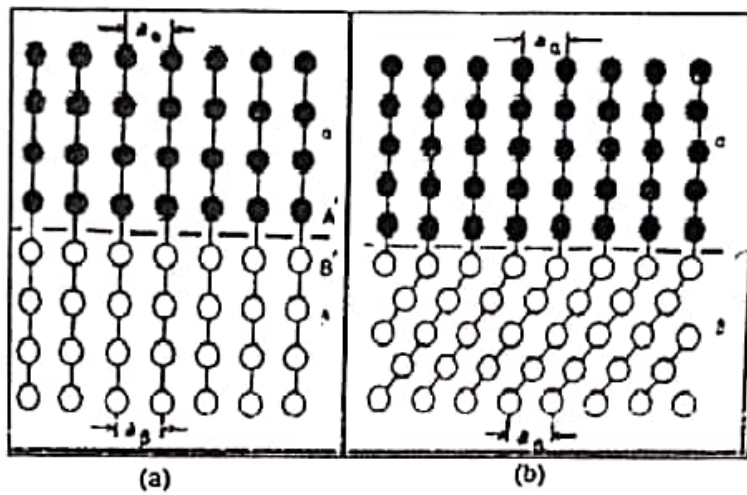


Figure (15) Coherent interfaces without strain (a) same crystal structure but different composition ( $\alpha$  and  $\beta$ ), (b) with different crystal structure

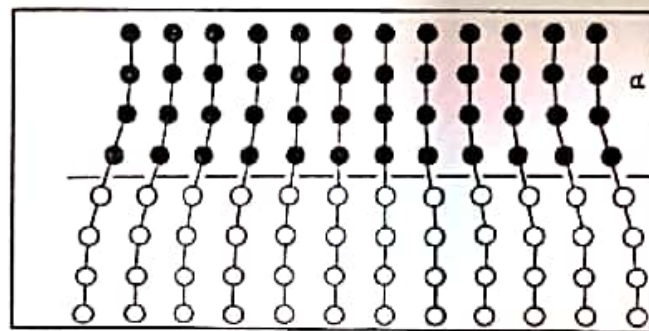


Figure (16) Coherent interface with elastic strains

2- Semicoherent interfaces are interfaces across which some planes are continuous and some are not as shown in fig.(17). Semicoherent interfaces have an array of dislocations which partially relax the misfit strains arising from the lattice mismatch across the interface between the

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two materials. The small angle grain boundaries are classic examples of semi-coherent boundaries. ازادہ بزرگی بلوریکہ

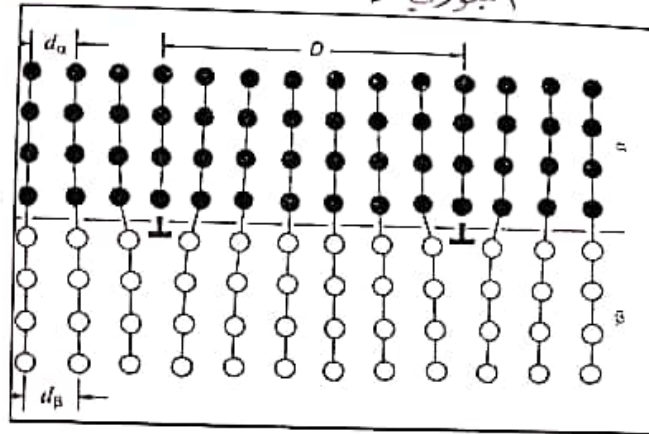


Figure (17) Semicoherent interface.

3- Incoherent interfaces are interfaces across which there is no continuity of lattice planes as shown in fig.(18). There is an elastic energy associated with incoherent boundaries, which is due to the difference in the volume of the particle without any constraints and the volume of the matrix available for the particle. Generic high angle grain boundaries are typically incoherent. Similarly, the inclusions in alloys (for example, MnS in steel) have incoherent interfaces.

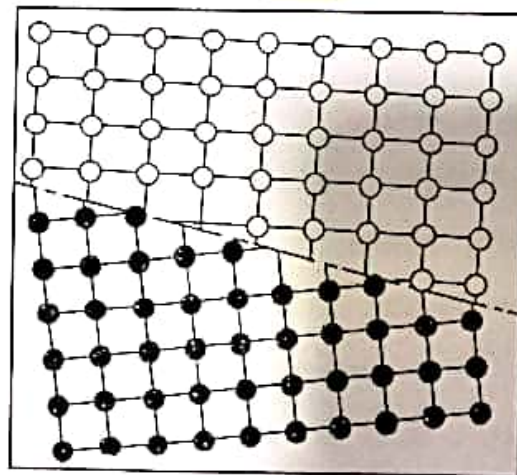


Figure (18) Incoherent Interface.

### 1.6 Interface migration ہجرت الہی

Most phase transformations in materials are conducted by means of nucleation and growth processes. An interface is created at the nucleation stage and it subsequently migrates into a metastable matrix during the

growth stage. Growth brings relocation of atoms via the moving interface. This is the heterogeneous type of transformation: the system can be split into the master and resultant phases at any moment during the transformation process.

There are two types of interfaces: glissile and non-glissile. A glissile interface migrates in terms of a coordinated sliding movement of dislocations, which induces shear transformation (deformation) of the source phase into a new phase. The movement of a glissile interface is relatively independent from temperature; it is therefore called an athermal growth. However, most of the interfaces are of non-glissile type and these migrate with more or less random atom jumps across interfaces. The additional energy required by atoms to execute a free jump from an old phase and join a new phase is supplied by means of thermal activation. That makes migration of any non-glissile interface strongly dependent on temperature.

Two major groupings can be made by dividing the transformations according to whether growth involves glissile or non-glissile interfaces.

Transformations produced by the migration of a glissile interface are referred to as military transformations. This emphasizes the analogy between the coordinated motion of atoms crossing the interface and that of soldiers moving in ranks on the parade ground. In contrast the uncoordinated transfer of atoms across a non-glissile interface results in what is known as a civilian transformation.

During a military transformation the nearest neighbours of any atom are essentially unchanged. Therefore the parent and product phases must have the same composition and no diffusion is involved in the transformation. Martensitic transformations belong to this group. Glissile interfaces are also involved in the formation of mechanical twins and twinning therefore has much in common with martensitic transformations.



During civilian transformations the parent and product may or may not have the same composition. If there is no change in composition, e.g. the  $\alpha \rightarrow \gamma$  transformation in pure iron, the new phase will be able to grow as fast as the atoms can cross the interface. Such transformations are said to be interface controlled. When the parent and product phases have different compositions, growth of the new phase will require long-range diffusion.

### 1.7 Solid phase growth in single-component system

There are basically two types of the solid phase - melt interface:

- Uneven (diffusion interface) - typical for metal systems, fig. (19-a),*
- Smooth (planar) interface - found mainly in non-metals, fig. (19-b).*

The differences in atomic structure enable these two types of interface migrate by absolutely diverse ways. The diffusion interface migrates by means of continuous growth process, whereas the flat interface migrates by means of the lateral growth process using ledges (lateral growth include surface nucleation and spiral growth).

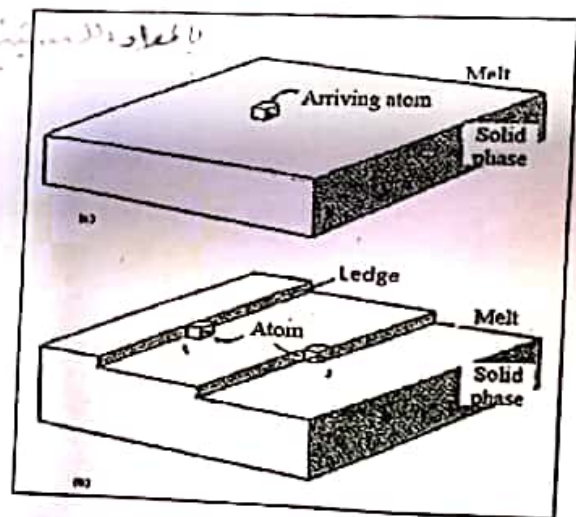
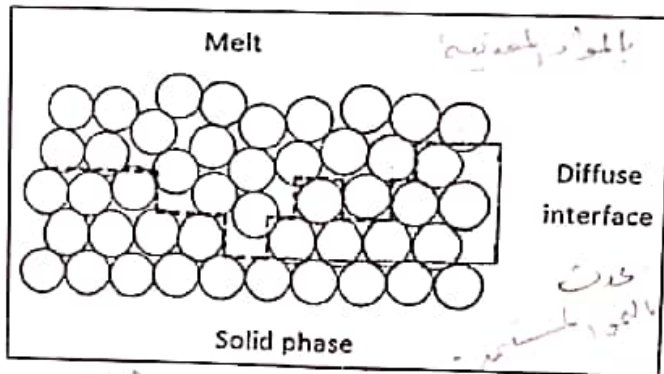


Figure (19) (a) Diffuse interface between a solid phase and melt, (b) Smooth atomic interface of solid phase/liquid containing cube-shaped atoms.

### Surface nucleation

lonely atoms "captured" on a flat surface will be unstable and they will tend to return back into the melt. However, if there is a sufficient quantity of atoms forming a disc-shaped layer, as shown in the fig.(20-a), such body can be stabilized and grow further. The problem associated with the disc formation lies in two-dimensional analogy in development of atomic cluster by means of homogeneous nucleation. The disc edge contributes with positive energy in this case; the energy must be counterbalanced by the volume free energy released during the process of disc development. The critical radius  $r^*$  associated with the two-dimensional nucleus will decrease with the increasing undercooling of the interface.

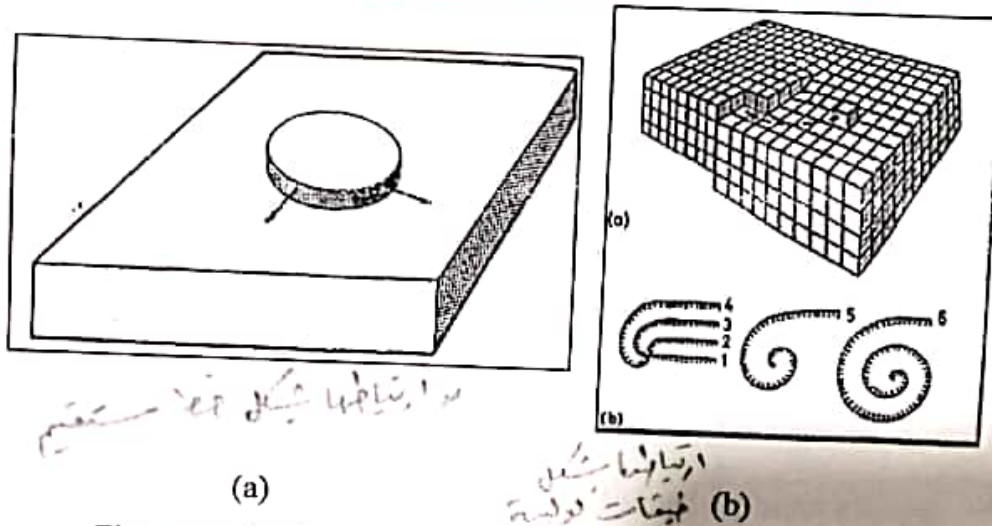


Figure (20) (a) Ledge by Surface Nucleation (b) Spiral growth.

### -Spiral Growth

In case the solid phase contains dislocations intersecting the S/L interface, spiral growth of the solid phase may occur. Let us assume a simple screw dislocation protruding out of a perfect crystal. The resultant form will be a ledge on the crystal surface, as shown in the fig.(20-b).



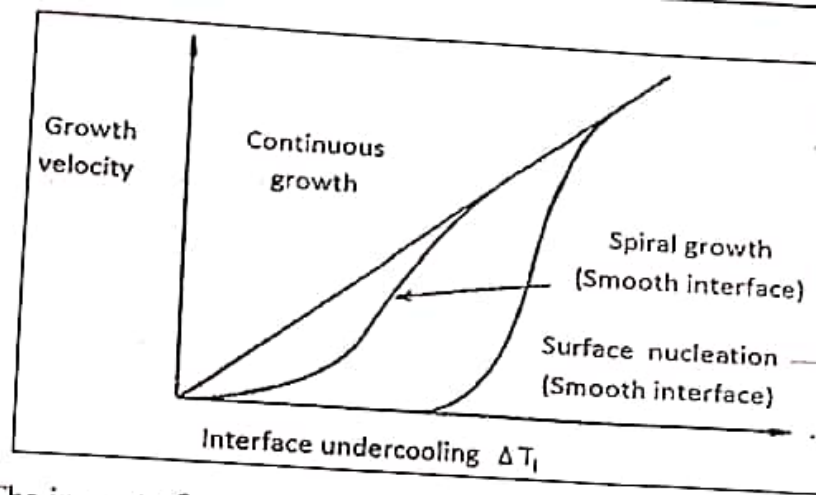


Figure (21) The impact of undercooling on the growth rate of various interface types.

## 1.8 Solidification of Binary Alloys

Solidification of pure metals occurs is a very rare event in practice. Even the commercially pure metals contain sufficient amount of impurities that turn the solidification characteristics of pure metals into behavior of alloys. The following chapters will deal with solidification of single-phase binary alloys.

### 1.8.1 Solidification of Single-Phase Alloys

Under practical circumstances, the mechanism of solidification of alloys shows complex dependency on the temperature gradient, the rate of cooling and the growth rate.

There are three cases of solidification of single-phase alloys:

- Infinitely slow (equilibrium) solidification,
- Without diffusion in the solid phase with perfect mixing in melt,
- Without diffusion in the solid phase and only diffusional mixing in melt.

### 1.8.2 Cellular and Dendritic Solidification

Cellular microstructures are stable within a particular interval of the temperature gradient only. When the temperature gradient is low enough, walls of cells or primary branches of the solid phase show a development of secondary branches and even lower temperature gradient will induce creation of the tertiary branches, i.e. formation of dendrites. The

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