Phase transformations in solids

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Phase transformations in solids

- In metallurgy, phase transformations of interest are **typically among solid phases**. A solid-solid phase transformation is a change from one crystalline structure to another within the solid phase. This can occur due to changes in temperature or pressure and is common in metals and alloys

- There is one obvious exception: **solidification**.

- **Most, but not all, phase transformations require diffusion**.

- There are **several possible classifications of phase transformations** from the point of view of thermodynamics, mechanisms, the phases involved, etc.

First order: discontinuity in first derivative of free energy. There is latent heat. Ex. solidification.

Second order: discontinuity in second derivative of free energy. There is step in specific heat. Ex. magnetic transition (ferro<->para).
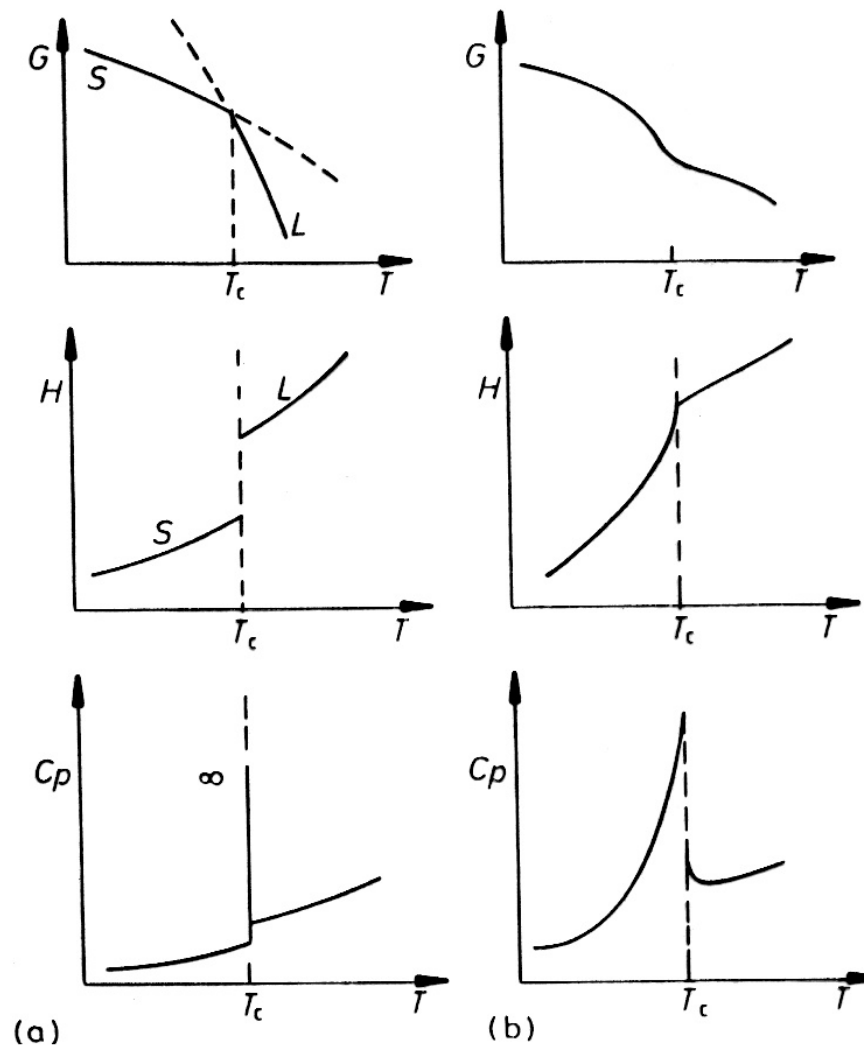

The thermodynamic characteristics of (a) first-order and (b) second-order phase transformations.

• **Diffusional Transformations**: These **involve the long-range movement of atoms** and are typically slower. Most phase transformation in metallurgy are diffusional. They can be further distinguished in:
  • **heterogeneous**: **occur via nucleation and growth** of one or more new phases.
  • **homogeneous**: **occur only via diffusion**. Example: spinodal decomposition.

• **Displacive Transformations**: These involve a change in the material's structure **through the shift of atoms over relatively short distances** and can be much faster. Example: martensitic transformations in steel.

a) *precipitation*

A solute exceeds its solubility limit in the solvent at a given temperature, leading to **the formation of a new phase (precipitates) within the original solid matrix.**
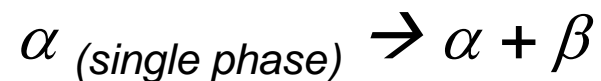
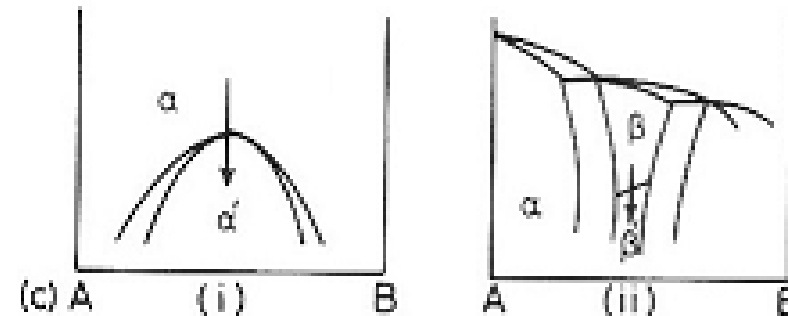$$\alpha \text{ (single phase)} \rightarrow \alpha + \beta$$

b) *eutectoid*

A eutectoid transformation is a type of phase transformation in which **a single solid phase transforms into two different solid phases upon cooling**. This transformation occurs at a specific composition and temperature, known as the eutectoid composition and the eutectoid temperature, respectively. The eutectoid reaction is reversible, meaning the two solid products can transform back into the original solid phase upon reheating to the eutectoid temperature.

$$\gamma \rightarrow \alpha + \beta$$
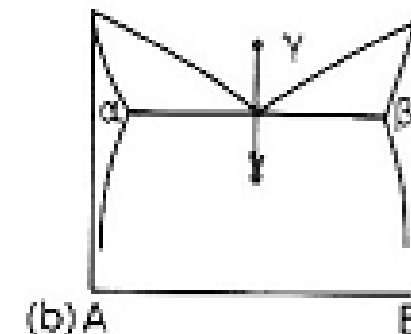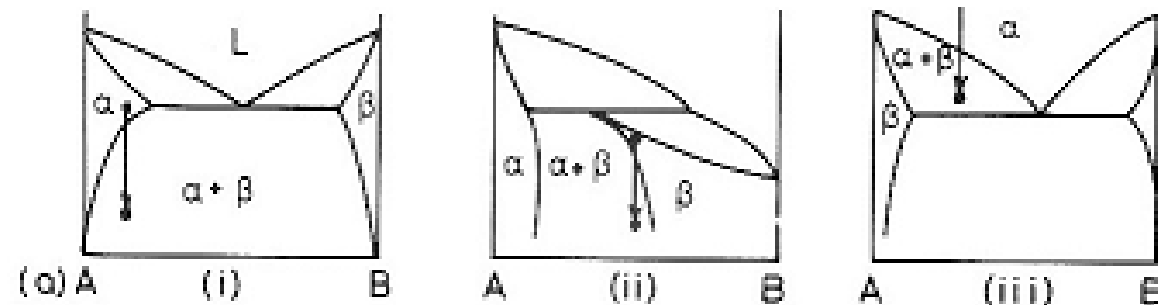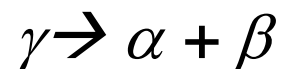
c) *ordering reaction*

Refers to the process by **which atoms in a solid solution rearrange themselves into a more ordered structure without changing the overall composition of the alloy**. This transformation results in a decrease in the material's entropy but an increase in its internal order, leading to the formation of a new phase with a distinct crystal structure.

$$\alpha \rightarrow \alpha'$$

d) *massive*

Characterized by **the formation of a new, single-phase microstructure from the parent phase, without the diffusion of the major alloying elements.** This transformation is typically rapid and occurs under conditions of high undercooling below the equilibrium transformation temperature. The term "massive" refers to the relatively large, featureless grains of the product phase that form during the transformation.

$$\beta \rightarrow \alpha$$
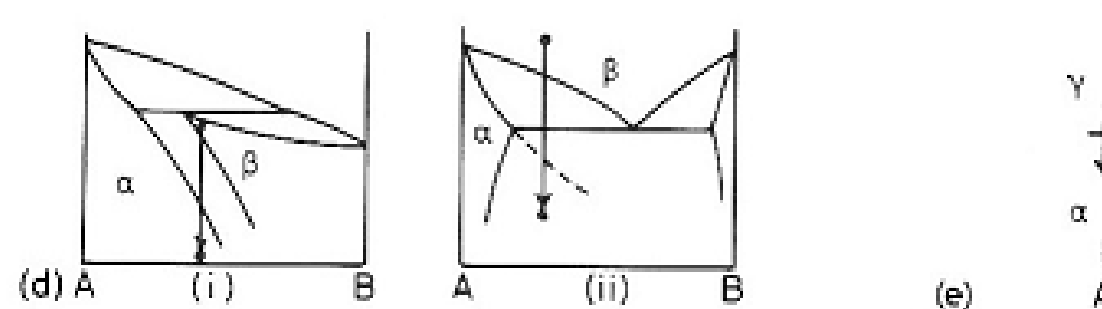
e) *Polymorphic (or polymorphous)*

Solid-state transformation in which **a material changes its crystal structure without changing its chemical composition** (pure elements or compounds). This transformation occurs in materials that can exist in more than one crystallographic form, known as polymorphs, depending on temperature, pressure, or other external conditions. The process involves a rearrangement of the atoms within the material to form a new crystal structure. Examples: pure iron austenite (fcc) to ferrite (bcc).

$$\gamma \rightarrow \alpha$$

(e)
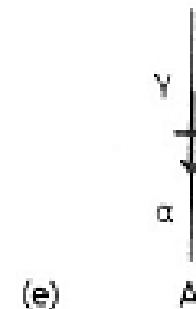
Reminder: homogeneous nucleation is a process that occurs in phase transformations where nuclei (the initial phase of the new structure β) form spontaneously within a uniform parent phase α, without any preferential sites or impurities acting as nucleation points. This type of nucleation is considered "homogeneous" because it happens uniformly throughout the parent phase, rather than at specific locations such as grain boundaries, impurities, or surfaces, which would be characteristic of heterogeneous nucleation.

Energy contributions due to: β volume formed $(-V\Delta G_V)$, formation of interface $(A\gamma)$, misfit strain* $(V\Delta G_s)$

Nucleation free energy change:
$$\Delta G = (G_\alpha - G_{\alpha+\beta}) = -V\Delta G_V + A\gamma + V\Delta G_s$$

For a spherical nucleus
$$\Delta G = -\frac{4}{3}\pi r^3(\Delta G_V - \Delta G_s) + 4\pi r^2\gamma$$

*Misfit strain arises due to the difference in lattice parameters (size and shape) between two different phases

Posing the derivative = 0 to obtain the condition
of metastable equilibrium

$$r^* = \frac{2\gamma}{(\Delta G_V - \Delta G_s)}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V - \Delta G_s)^2}$$

For nucleation to occur, **a critical energy barrier ($\boldsymbol{\Delta G^*}$) must be
overcome**. This barrier is associated with the formation of new
surfaces between the new phase (nuclei) and the parent phase.

There is a specific size, called the **critical nucleus size (r^*),** below
which nuclei are unstable and tend to dissolve back into the
parent phase, and above which they are stable and can grow to
form the new phase.
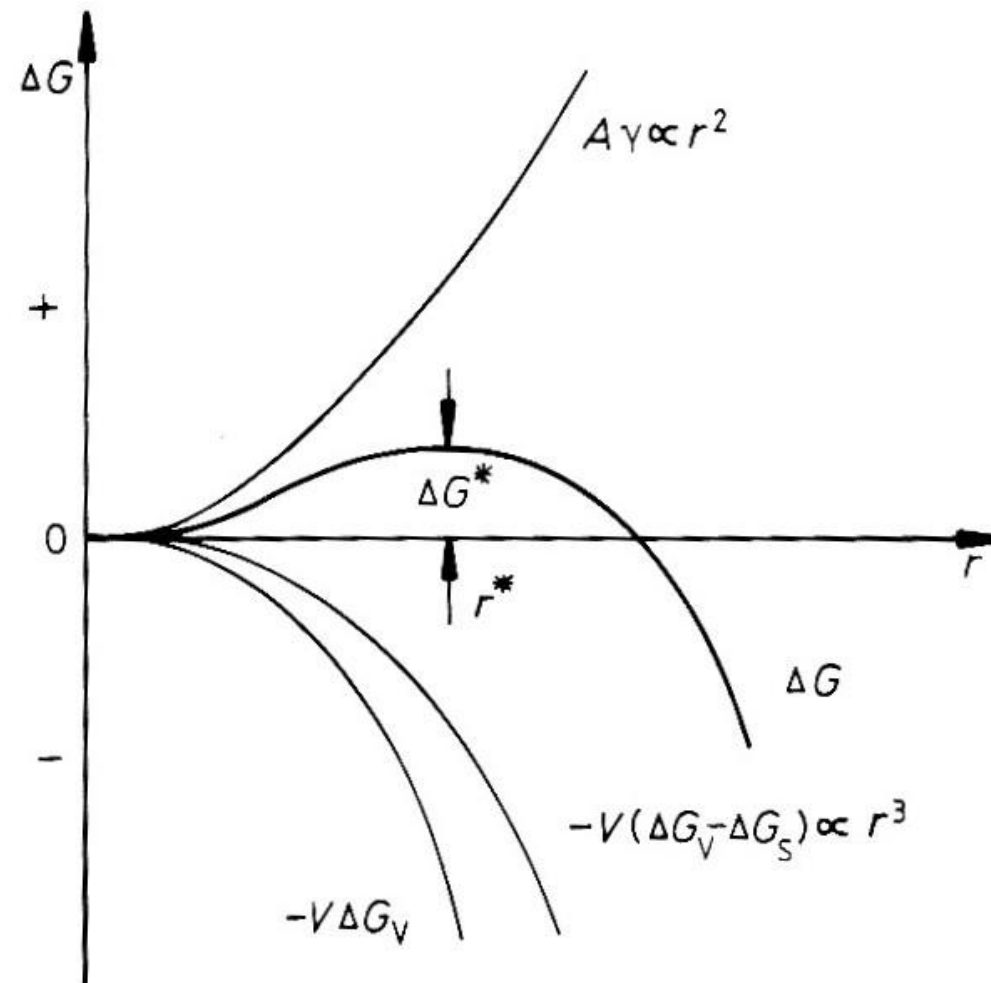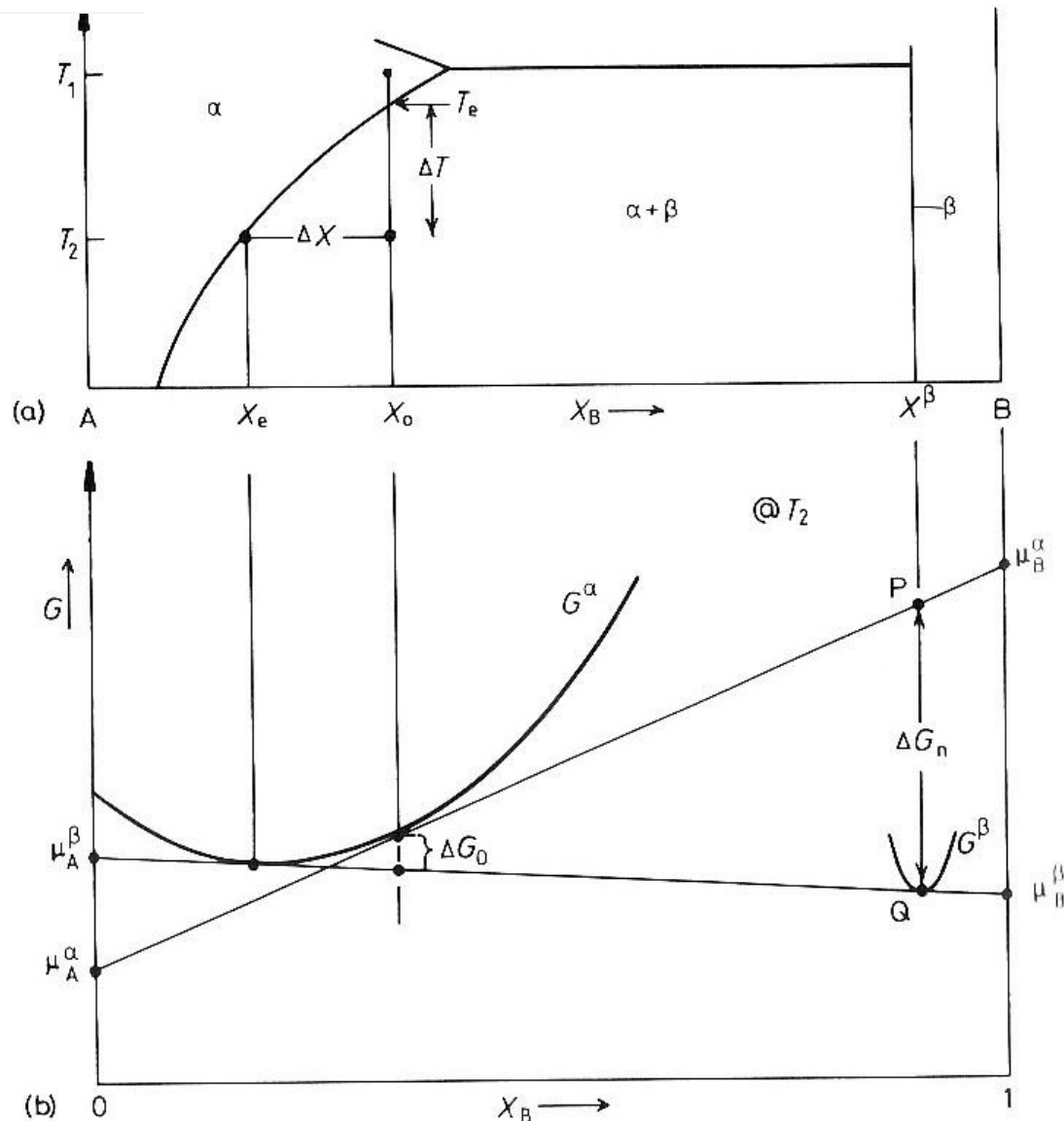
Example: precipitation of β (stoichiometric compound) from a matrix α.

Alloy is supersaturated (ΔX) when quenching from T_1 to T_2 (ΔT)

ΔG_0, total driving force of precipitation process (formation of a β in bulk, at the end of the process).

However, when the first nucleus form, the matrix composition does not change composition (only a little).
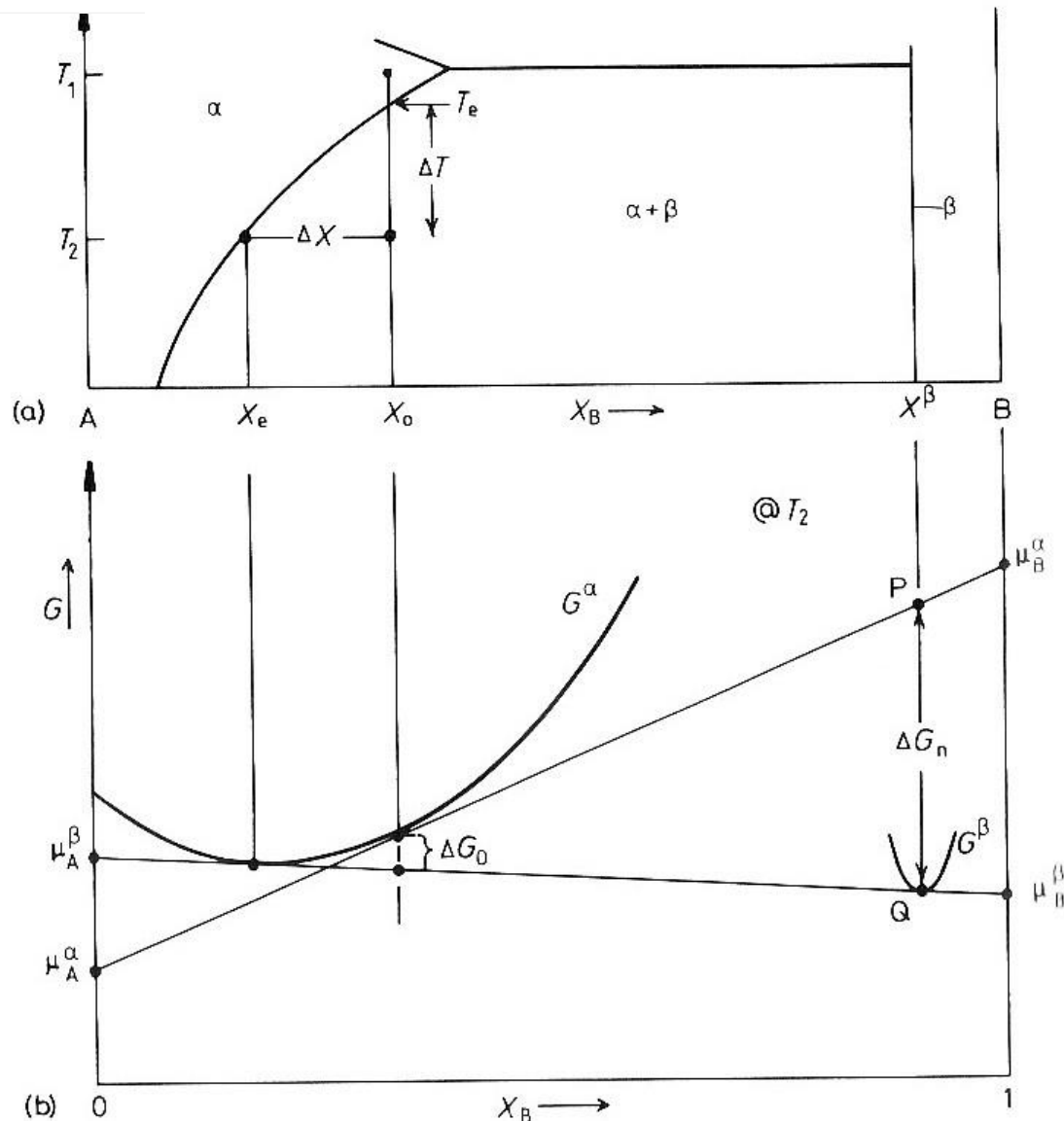
Considering the definition of chemical potential in α and β phases, the free energy scheme provides ΔG_n, the driving force for formation of a small nucleus (point P).

(ΔG_n to be divided by V_m to get ΔG_V).

ΔG_V can be obtained from the knowledge of the free energies of α and β phases.

Rate of homogeneous nucleation is $\qquad N_{\text{hom}} = fC^*$

$$C^* = C_0 \exp(-\frac{\Delta G^*}{kT})$$ is the concentration of nuclei of critical size

$$f = \omega \exp(-\frac{\Delta G_m}{kT})$$ is the frequency of atomic migration

C_0 number of atoms/unit volume

ω vibration frequency factor

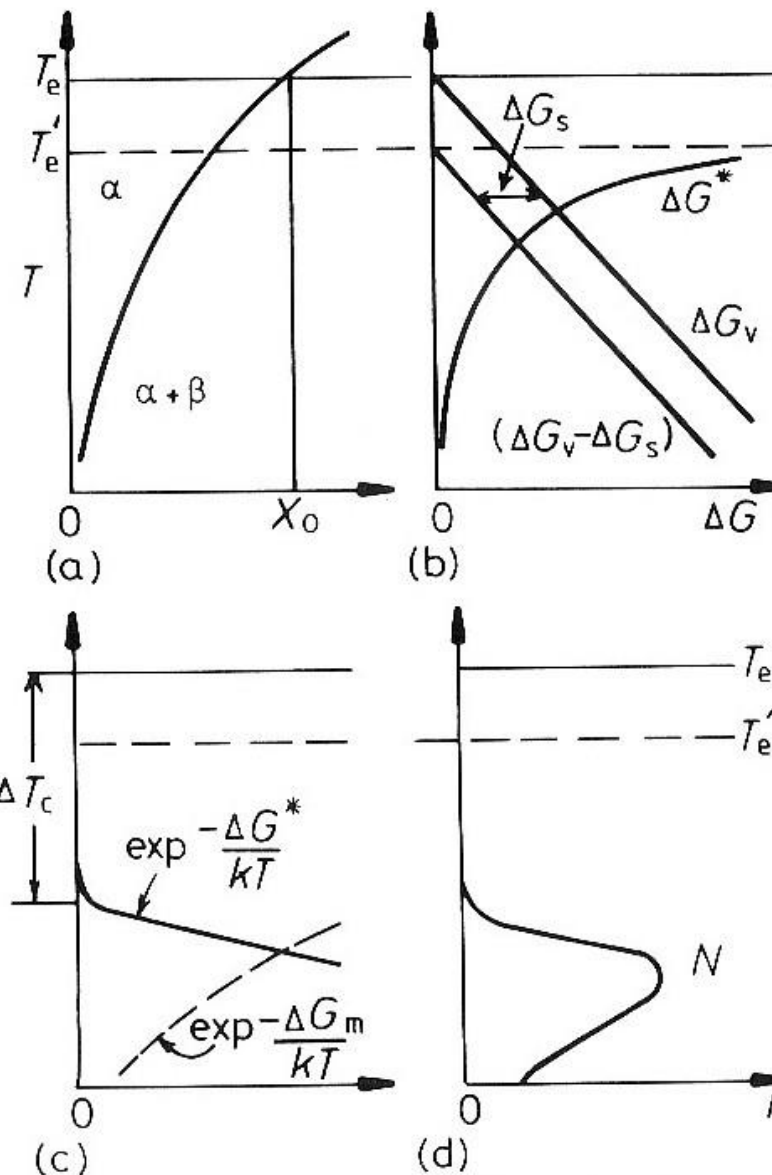ΔG_m energetic barrier for atomic migration

The outcome is

- opposite trend of exponential functions

- maximum of N_{hom}
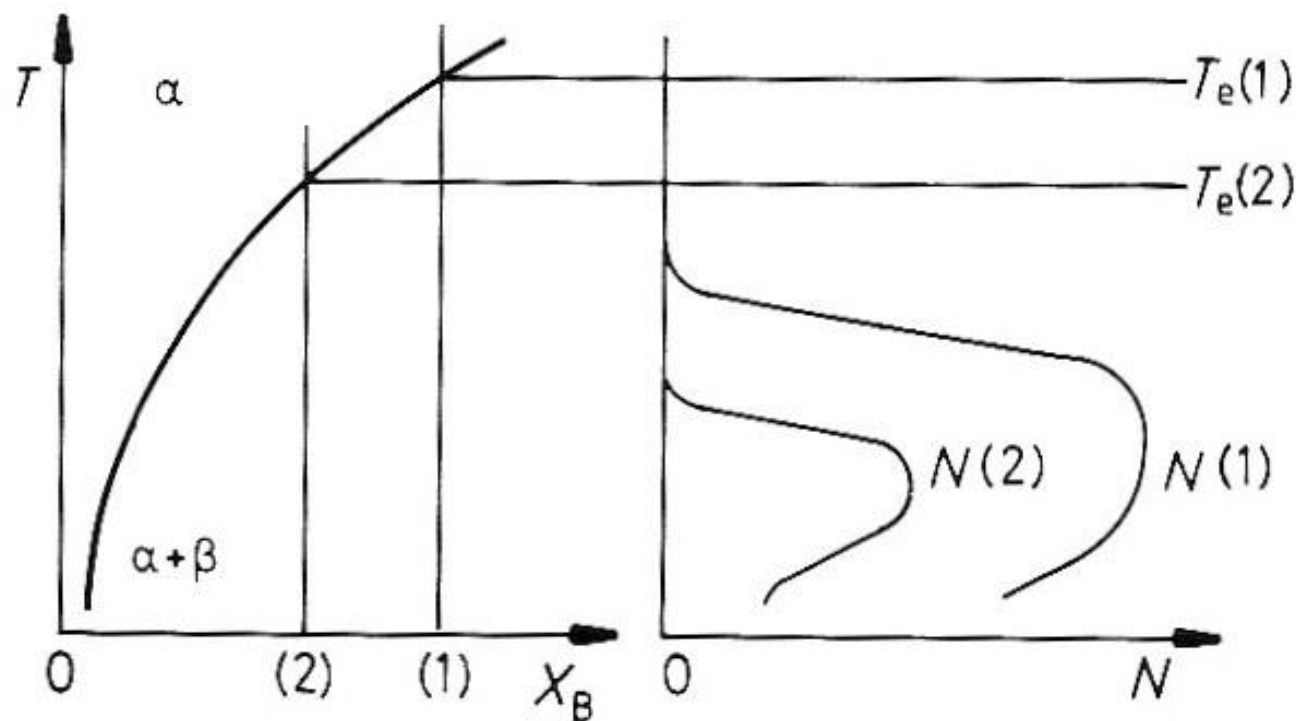
Effect of additional free energy term for misfit strain:

• at T'_e equilibrium solvus accounts for ΔG_S

• ΔG_S imposes undercooling

High values of N_{hom} at T well below T_e

The equilibrium temperature of composition (2) is less than that of (1), therefore N is lower because of less undercooling and reduced atomic mobility.

Reminder: occurs preferentially at specific sites rather than uniformly throughout the parent material. These sites can include surfaces, interfaces, impurities, grain boundaries, or other structural inhomogeneities within the material. Heterogeneous nucleation is more common in practice than homogeneous nucleation because pure materials and perfect conditions are rare in real-world situations.

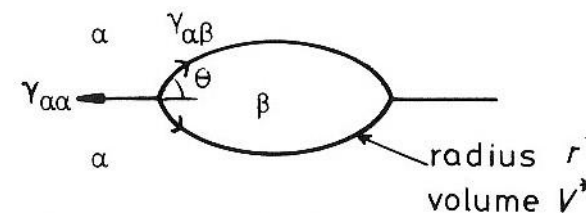**Lower nucleation ΔG** (with respect to homogeneous nucl.)

$$\Delta G = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

Energy contribution from defects (ΔG_d)

For example at grain boundaries, neglecting misfit strain (ΔG_S=0)

Nucleation ΔG at grain boundaries

$$\Delta G = -V\Delta G_V + A_{\alpha\beta}\gamma_{\alpha\beta} - A_{\alpha\alpha}\gamma_{\alpha\alpha}$$
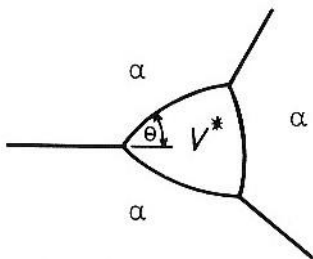
It can be proved that:

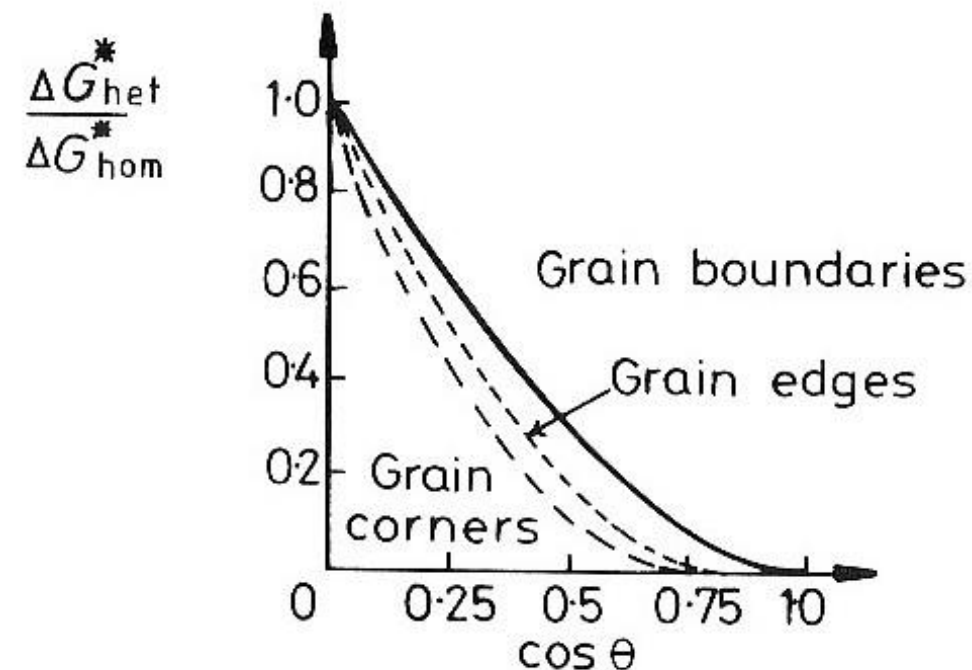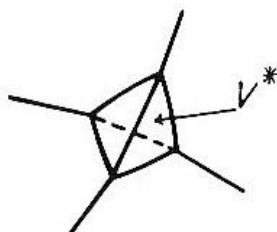$$\frac{\Delta G^*_{het}}{\Delta G^*_{hom}} = S(\theta) = \frac{1}{2}(2 + \cos\theta)(1 - \cos\theta)^2$$

θ is the angle between αα and αβ interfaces (as in picture at previous slide)
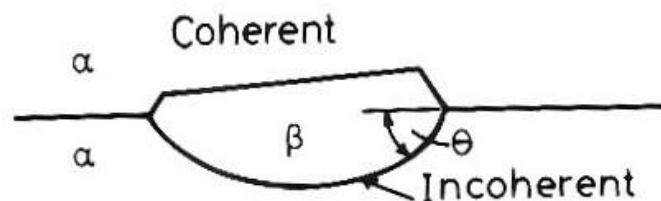
Nucleation can also occur at:

grain edges

grain corners

High angle gb's are effective nucleation sites because of high $\gamma_{\alpha\alpha}$.

If low energy interfaces is formed (ex. coherent, lower critical volume, V^*), nucleus has orientation to grain. After nucleation it will grow faster on incoherent, mobile interface.

Stacking faults less potent sites (except for hcp in fcc) because of lower γ.

Dislocations reduce ΔG_S , enhance diffusivity and provide segregated solute.

Excess vacancies help with coherent nuclei reducing strain energy.

Precipitates growth

Reminder: After nucleation, growth must occur for the phase transformation to proceed. Growth refers to the increase in size of the newly formed nuclei after they have successfully nucleated. Growth occurs through atom migration across the interface between the new and old phases, the interface between the new and old phases moves as atoms or molecules from the parent phase are incorporated into the growing phase. The rate at which this interface moves can be influenced by the chemical potential difference between the two phases, the mobility of the atoms or molecules, and the presence of any barriers to growth, such as impurities or defects.

Precipitate shape satisfies criterion of minimum surface free energy:

- **planar for coherent or semi-coherent interfaces** (required for coherency)

- **curved for incoherent** (spherical shape minimizes interfacial energy for a given volume)

Mobility: **low for semi-coherent, high for incoherent interfaces**.

Interface mobility affects the final shape.

Example in the figure on the right:

- Horizontal interfaces are coherent (slow growth)

- Vertical interfaces are incoherent (fast growth)
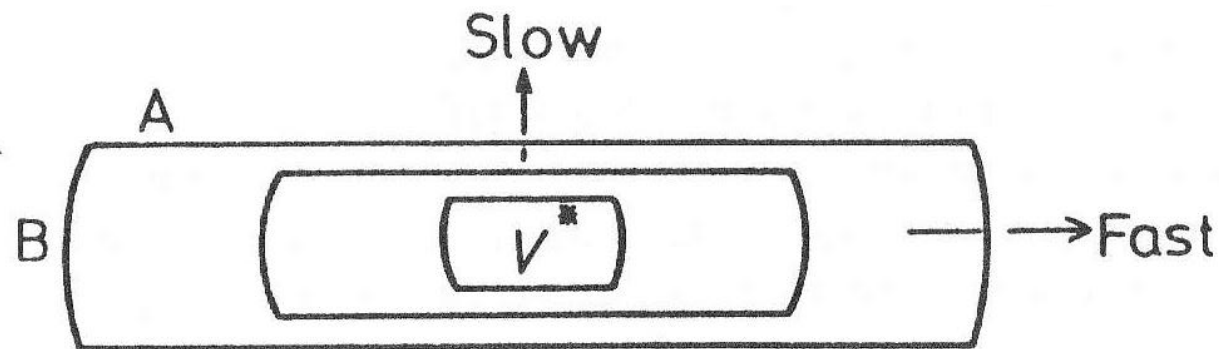
This can lead for example to the Widmanstätten morphology (more in a future lecture).

Consider the **diffusional growth of a β precipitate into α matrix with a planar incoherent interface**.

Growth rate is $v=dx/dt$.

The matrix close to β will be depleted of diffusing solute. Solute concentrations per unit volume: C_β in β, C_e at interface as per phase diagram, C_0 in alloy.
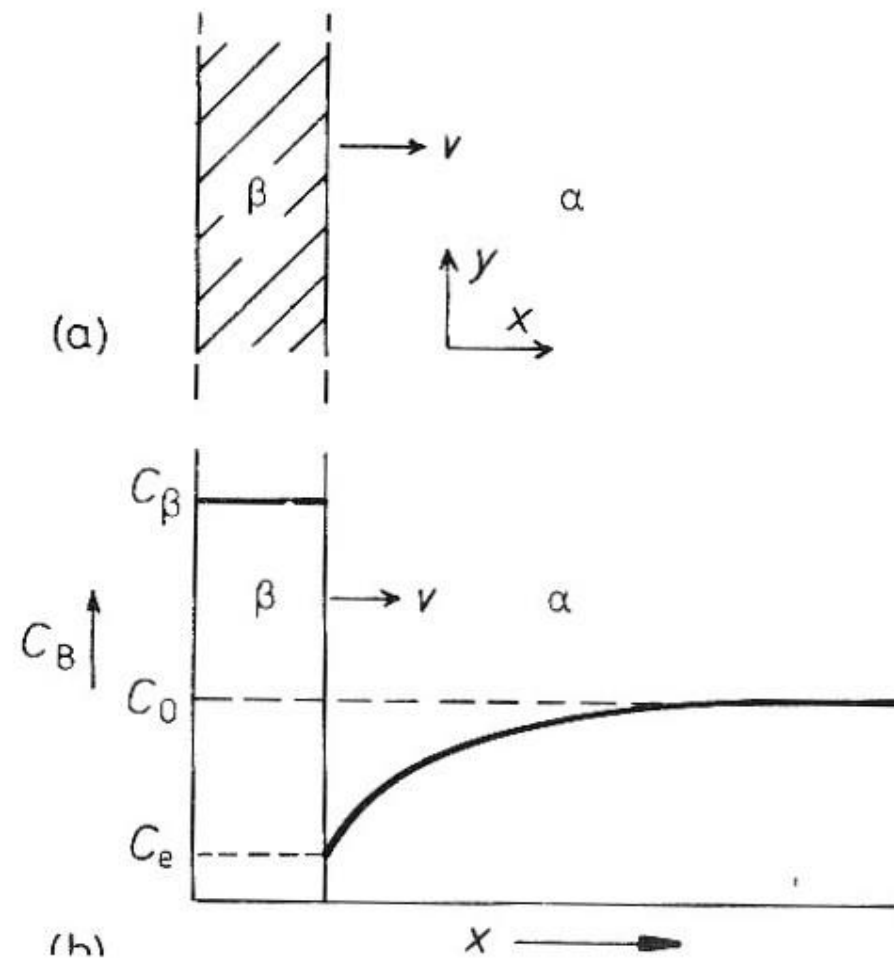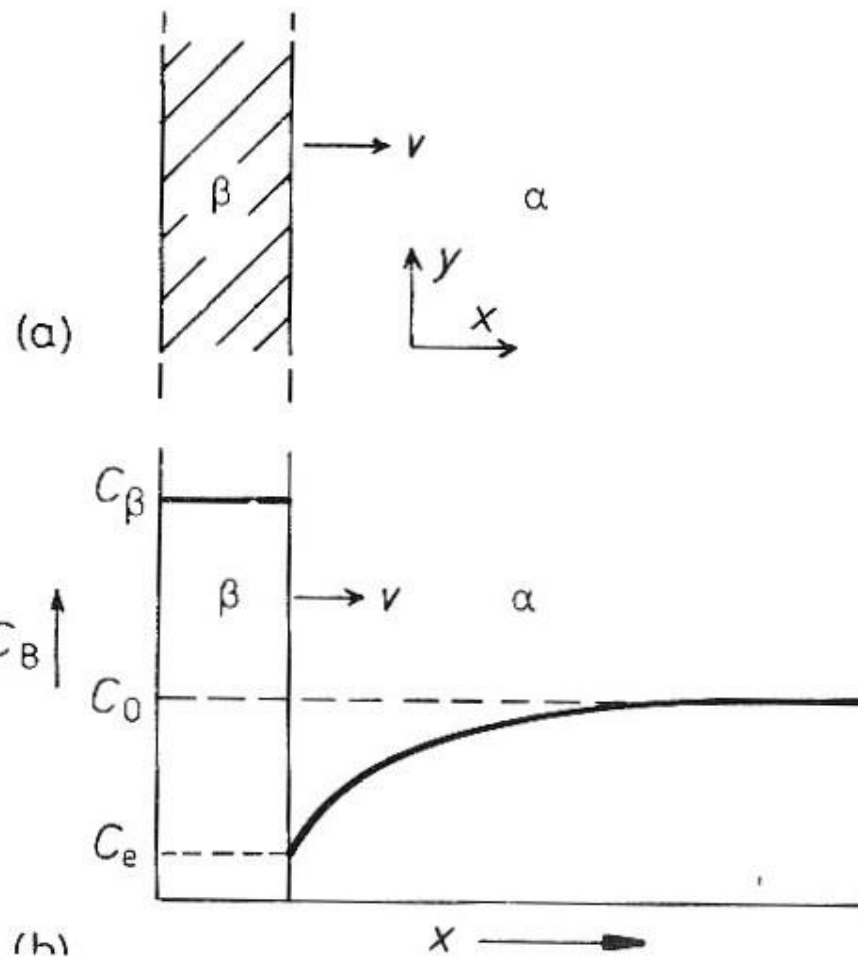
Mass conservation of B implies:

amount of B for thickening precipitate of *dx*
= amount of B in diffusion flux, i. e.

$(C_\beta - C_e)dx = D(dC/dx)dt$

therefore

$$v = \frac{dx}{dt} = \frac{D}{C_\beta - C_e}\frac{dC}{dx}$$

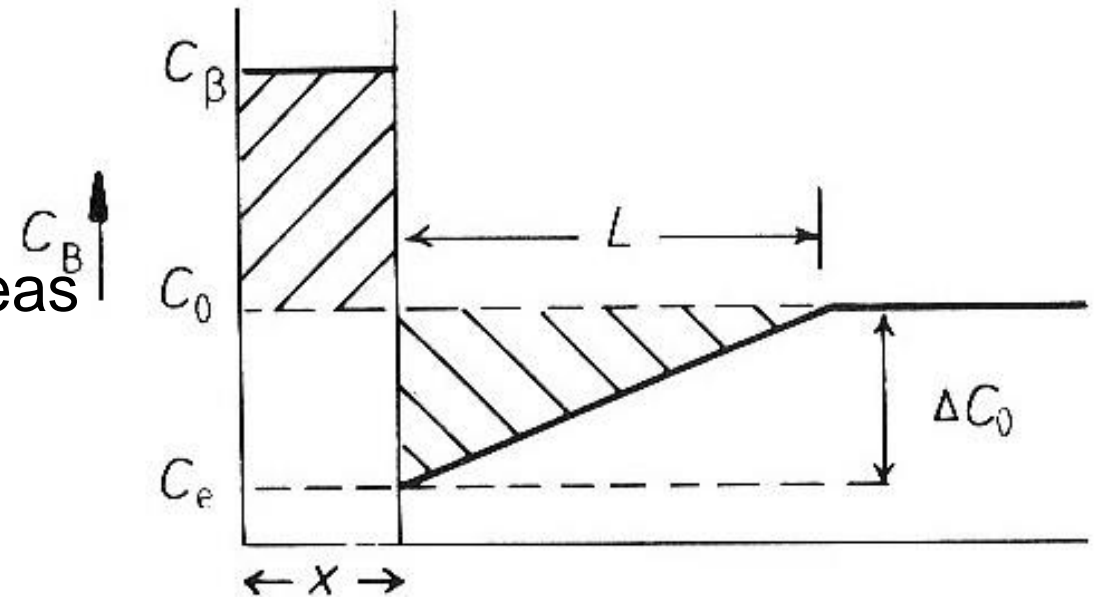The gradient $\frac{dC}{dx}$ is general is complex and the equation can be solved only numerically.

Zener model with simplified concentration profile:

$dC/dx = \Delta C_0/L$

Applying mass conservation (equality of areas of triangle and rectangle) gives

$(C_\beta - C_0)x = L\, \Delta C_0/2$.

Substituting the latter two equations into v=dx/dt gives the growth rate as:
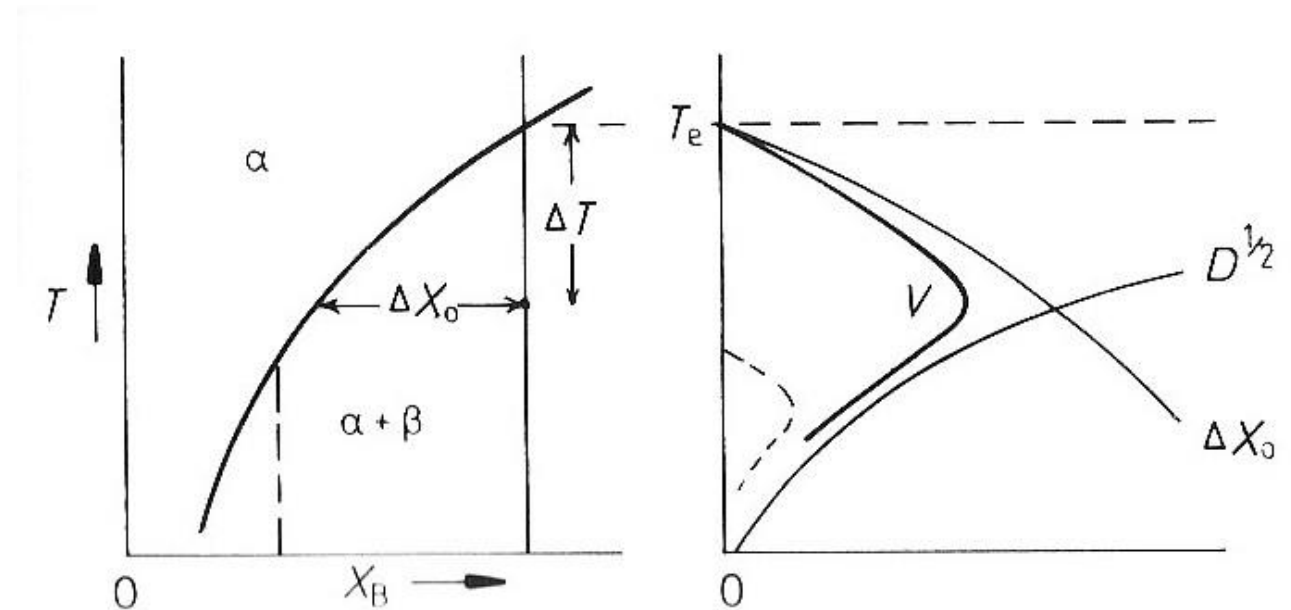
$$v = \frac{D(\Delta C_0)^2}{2(C_\beta - C_e)(C_\beta - C_0)x}$$

Using mole fraction $X_i = C_i V_m$, *approximating* $(C_\beta - C_0) = (C_\beta - C_e)$ and integrating gives

$$x \cong \frac{\Delta X_0}{(X_\beta - X_e)} \sqrt{Dt}$$

$$v \cong \frac{\Delta X_0}{2(X_\beta - X_e)} \sqrt{\frac{D}{t}}$$

with ΔX_0 the supersaturation.

v reaches a maximum due to increase in supersaturation on undercooling (ΔT) and decrease of diffusivity.

In Zener model, growth never stops. It does not consider that at a certain point growing grains will start interacting (impingment).

When diffusion fields impinge (late stage of growth), Zener model (implying steady state profile) is not valid anymore.

Growth decelerates until full equilibrium is reached.
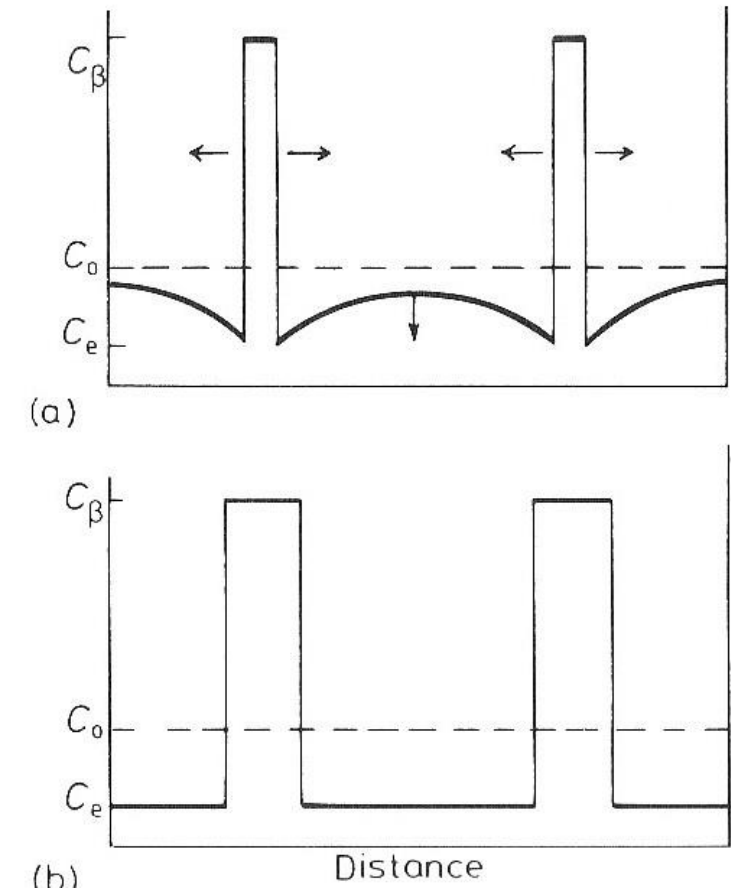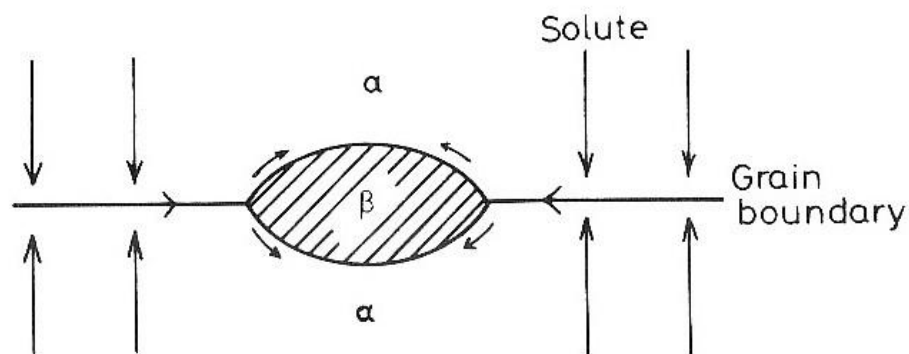
For precipitates at grain boundaries faster growth occurs because of gb and α-β interfacial diffusion.

Consider the **thickening of plate-like precipitates β precipitate into α matrix with a planar semicoherent interface**.

Mechanism is migration via lateral movement of ledges, which are incoherent (higher mobility).
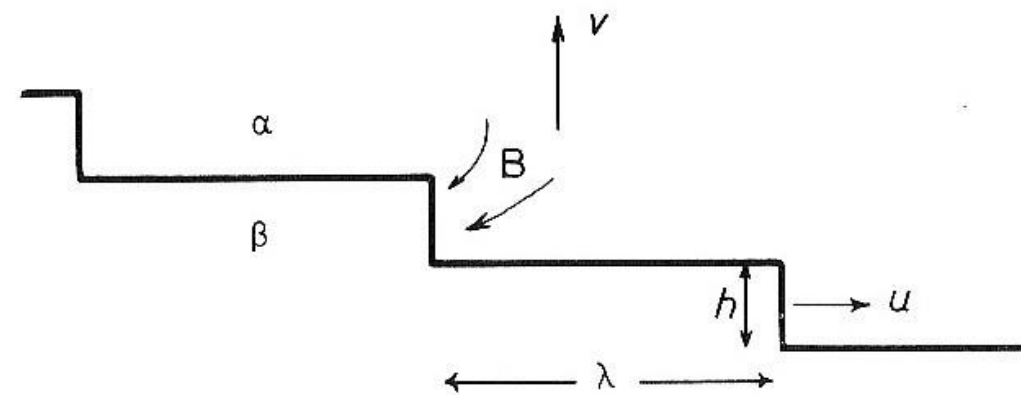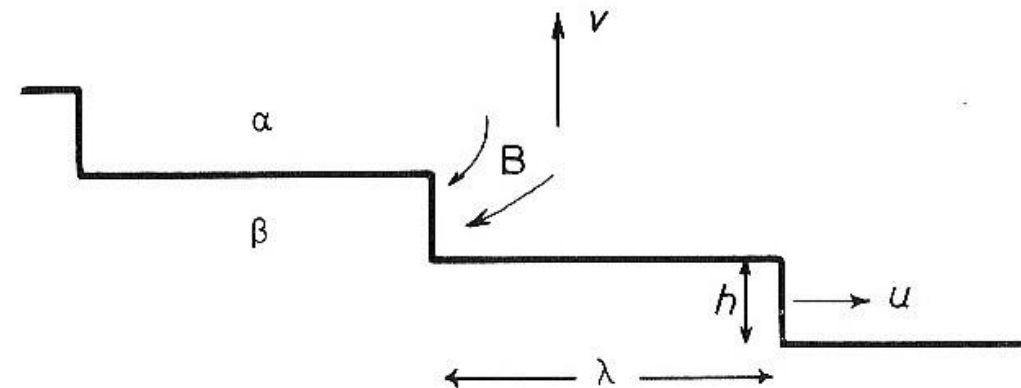

Rate of thickening $v = \dfrac{uh}{\lambda}$

When the vertical incoherent interface growth to the right creating a new volume uh of β, the horizontal semicoherent interface moves upward creating the same volume $v\lambda$ of β.

The lateral growth rate is as in previous slides (planar incoherent interface):

$$u = \frac{D}{C_\beta - C_e}\frac{dC}{dx} \cong \frac{D}{C_\beta - C_e}\frac{\Delta C}{h}$$

therefore

$$\nu \cong \frac{D\Delta X_0}{(X_\beta - X_e)\lambda}$$

In order to have growth, there must be supply of ledges (e. g. by re-nucleation at surface or edge. Spiral growth keeps ledge number constant).

Rates can vary greatly.

Theory of transformed fraction f(t,T)

The "transformed fraction" f(t,T) during a phase transformation refers to **the proportion of the material that has successfully transformed from the initial phase to the new phase at any given point in time during the process**. This fraction can range from 0 (no transformation has occurred) to 1 (the transformation is complete, and the entire material has changed to the new phase).

It is a function of time and temperature, especially in diffusion-controlled transformations like nucleation and growth processes. The kinetics of these transformations can be described by models such as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation, which predicts the fraction transformed as a function of time for a given temperature.

The transformed fraction is essential for controlling and optimizing phase transformations to achieve specific material properties. By understanding and controlling the rate of transformation and the final transformed fraction, materials scientists and engineers can design materials with tailored properties for various applications.

Volume, ω, of a single spherical nucleus at time t

$$\omega = \frac{4\pi}{3} r^3 = \frac{4\pi}{3} v^3 (t - \tau)^3$$

τ is the time at which each nucleus appears.

With N the nucleation rate and Ω the original volume of the matrix, the number of nuclei formed during time $d\tau$ is

$$N\Omega \, d\tau$$

If there is no impingement (f ≪ 1)

$$f = \frac{\sum \omega}{\Omega} = \frac{4\pi}{3} \int_0^t N v^3 (t - \tau)^3 d\tau = \frac{\pi}{3} N v^3 t^4$$

Considering reduction in available volume for nucleation and impingement occurs, the transformed fraction, *f*, becomes (Johnson-Mehl-Avrami equation)

$$-\ln(1-f) = \frac{4\pi}{3}\int_0^t N\nu^3(t-\tau)^3 d\tau \qquad f = 1-\exp(-\frac{\pi}{3}N\nu^3 t^4)$$

For short times, $f = 1 - \exp(-\frac{\pi}{3}N\nu^3 t^4) \cong \frac{\pi}{3}N\nu^3 t^4$ as in the previous slide.

For long times, $t \to \infty, f \to 1$

According to nucleation and growth mechanism (e. g. growth on pre-existing nuclei, different shape of crystals,...)

$$f = 1-\exp(-kt^n) \qquad \text{with} \sim 1 < n < 4$$

The transformed fraction, *f*, vs time increase generally with sigmoidal function (see plot b and previous slide) at constant temperature. As a function of temperature a TTT diagram is obtained.
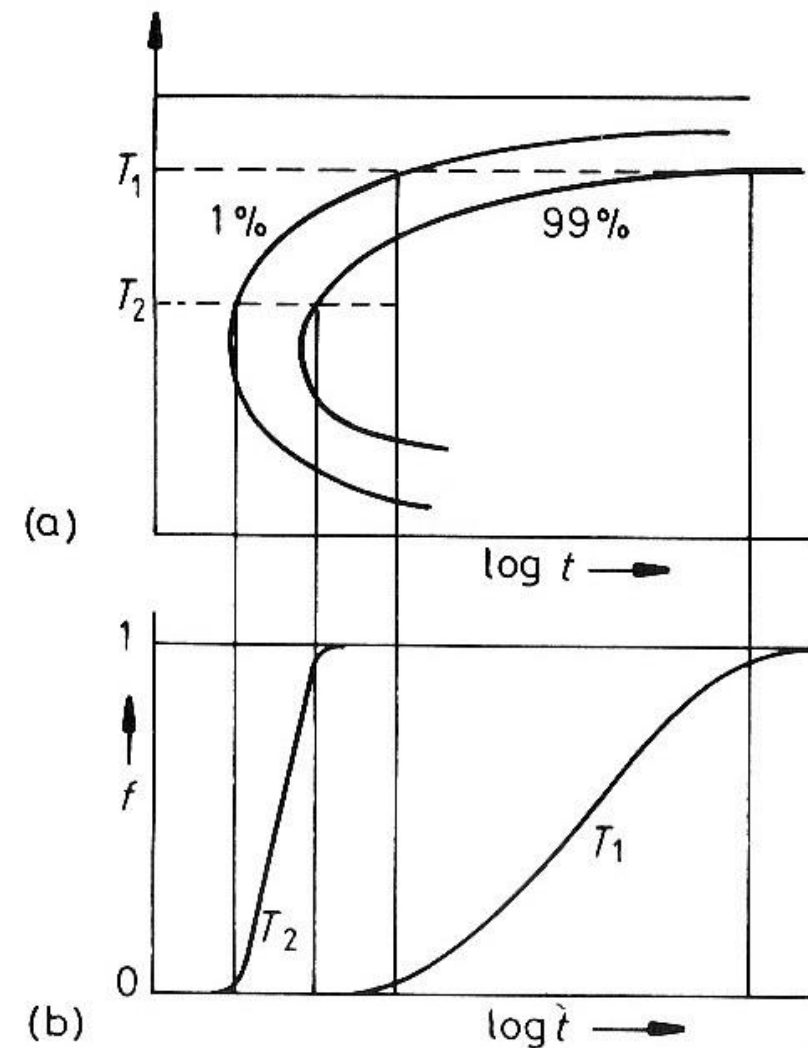
The *f(t, T)* function can refer to different cases:

a) nucleation + growth (nucleation over the entire process)

b) growth on limited nucleation sites (site saturation)

c) parent phase completely consumed (recrystallization, massive transformation, pearlite, etc.).
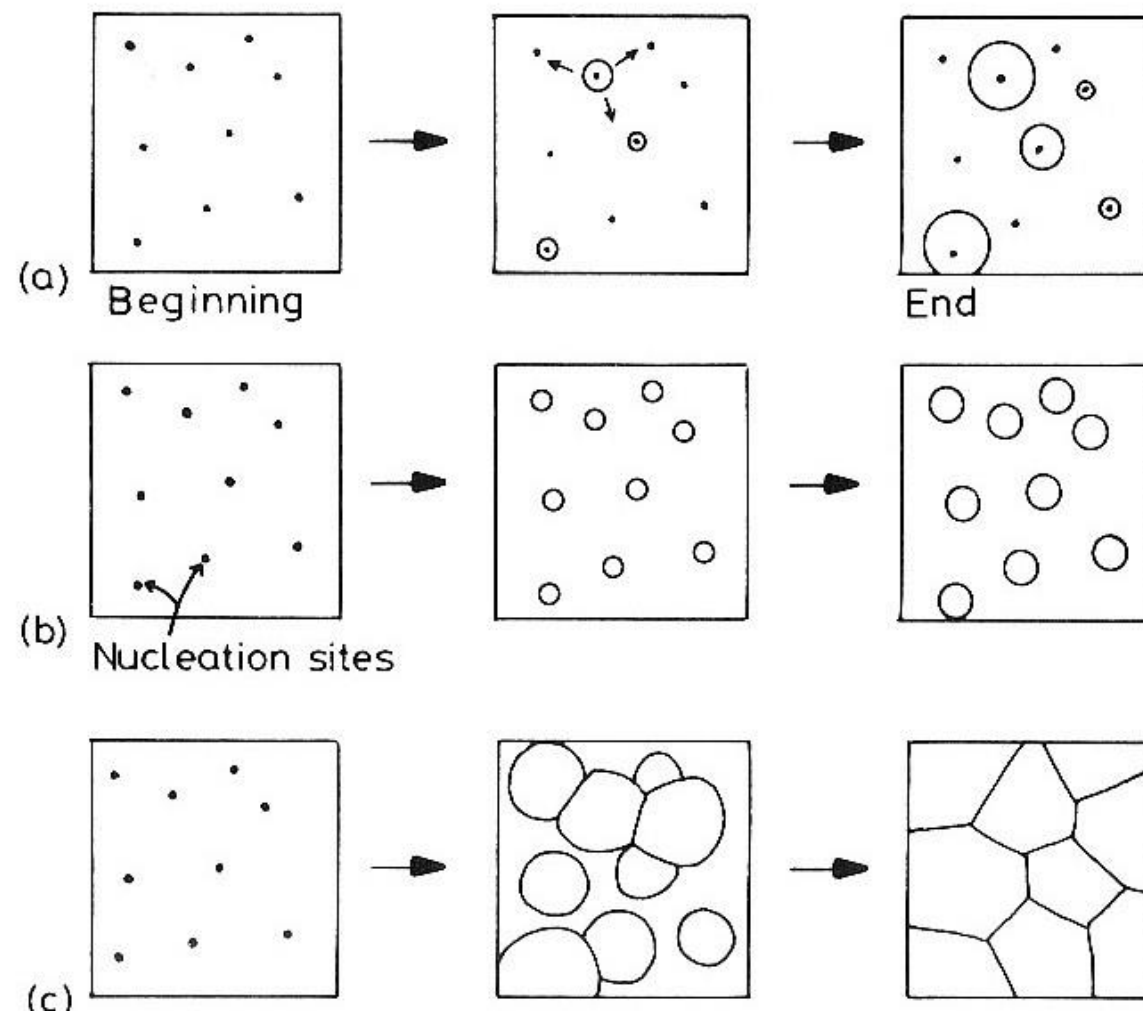
Need for microstructure observation.