2017 Fall

"Phase Transformation *in* Materials"

11.27.2017

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

4.4 Solidification of Ingots and Castings

a lump of metal, usually shaped like a brick.

Later to be worked, e.g. by rolling, extrusion or forging>> blank (small)

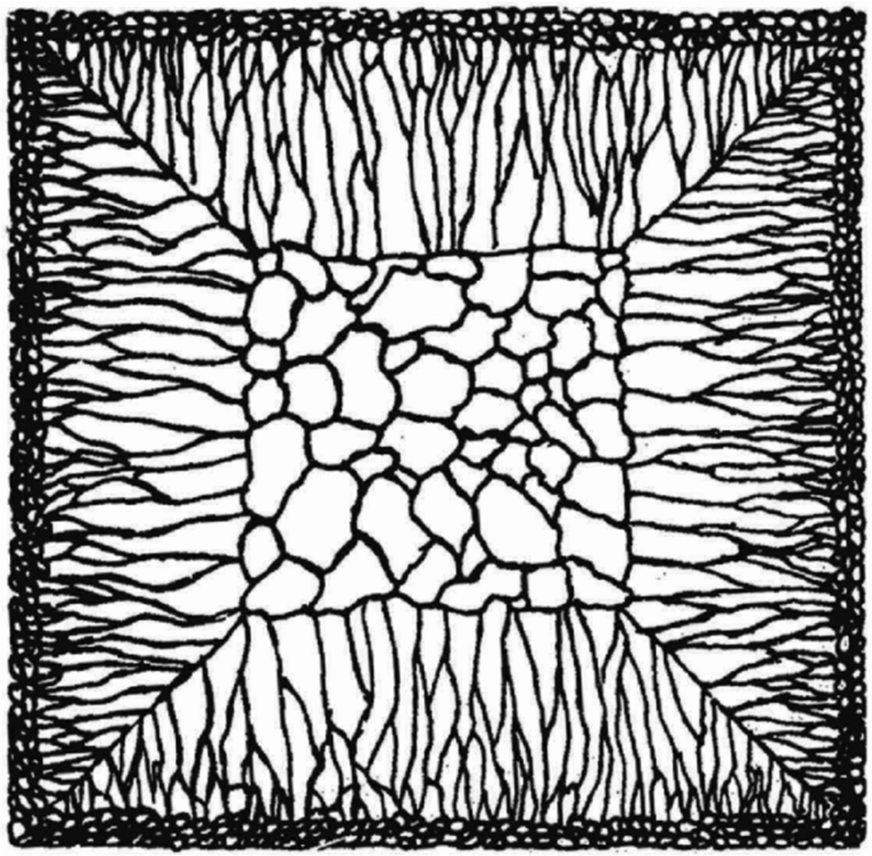
an object or piece of machinery which has been made by pouring a liquid such as hot metal into a container

Permitted to regain their shape afterwards, or reshaped by machining

Ingot Structure

- outer Chill zone
  : equiaxed crystals
- Columnar zone
  : elongated or column-like grains

  Mushy zone (or pasty zone)
  depends on temp. gradient and non-equil.
  Freezing range of the alloy
- central Equiaxed zone



1) Segregation: undesiable ~ deleterious effects on mechanical properties

→ subsequent homogenization heat treatment, but diffusion in the solid far to slow

→ good control of the solidification process

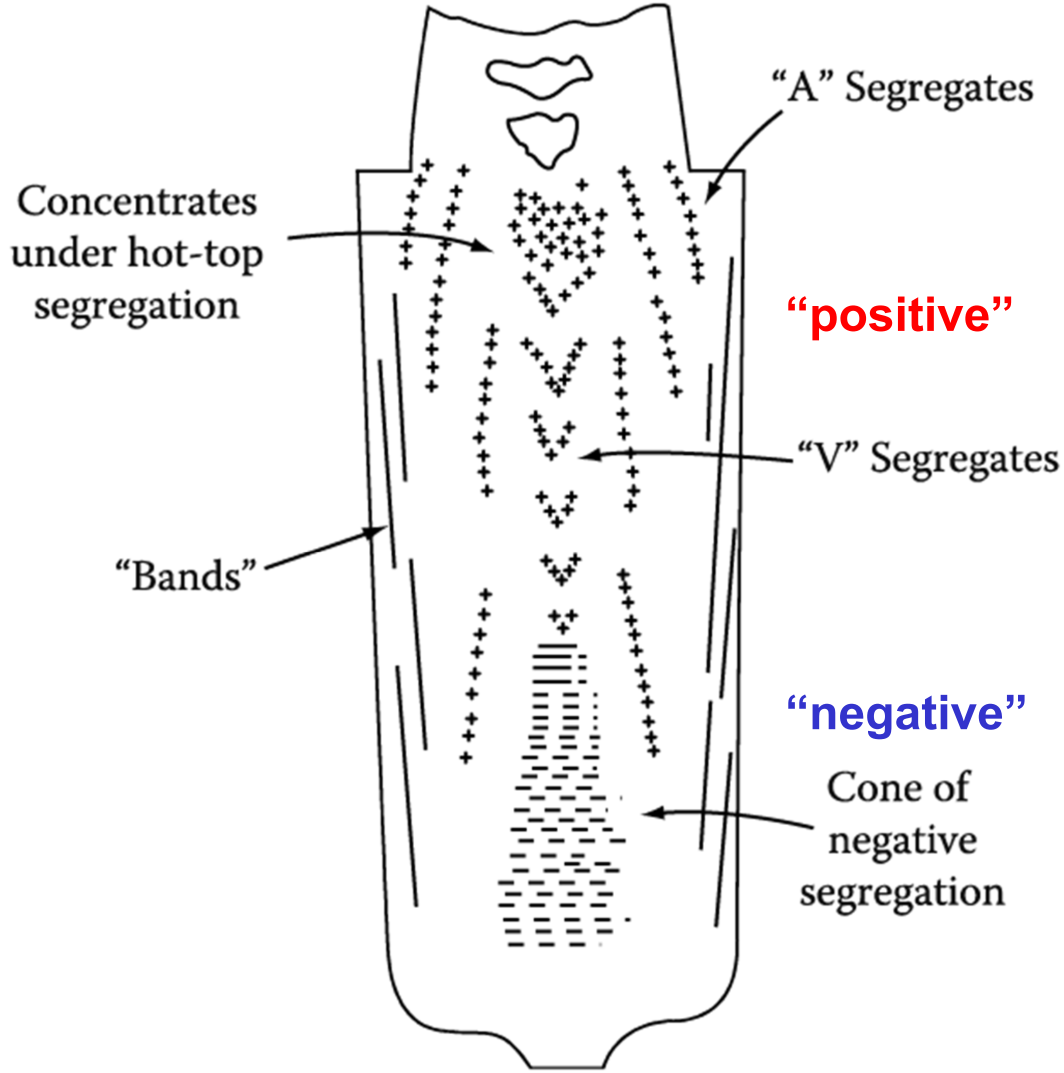


Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.)

Inverse segregation (역편석): As the columnar dendrites thicken solute-rich liquid (assuming k<1) must flow back between the dendrites to compensate for (a) shrinkage and this raises the solute content of the outer parts of the ingot relative to the center.

EX) Al-Cu and Cu-Sn alloys with a wide freezing range (relatively low k)

Negative segregation: The solid is usually denser than the liquid and sinks carrying with it less solute (초기응고고상)than the bulk composition (assuming k<1). This can, therefore, lead to a region of negative segregation near the bottom of the ingot. ((b) Gravity effects)

2) Shrinkage effect

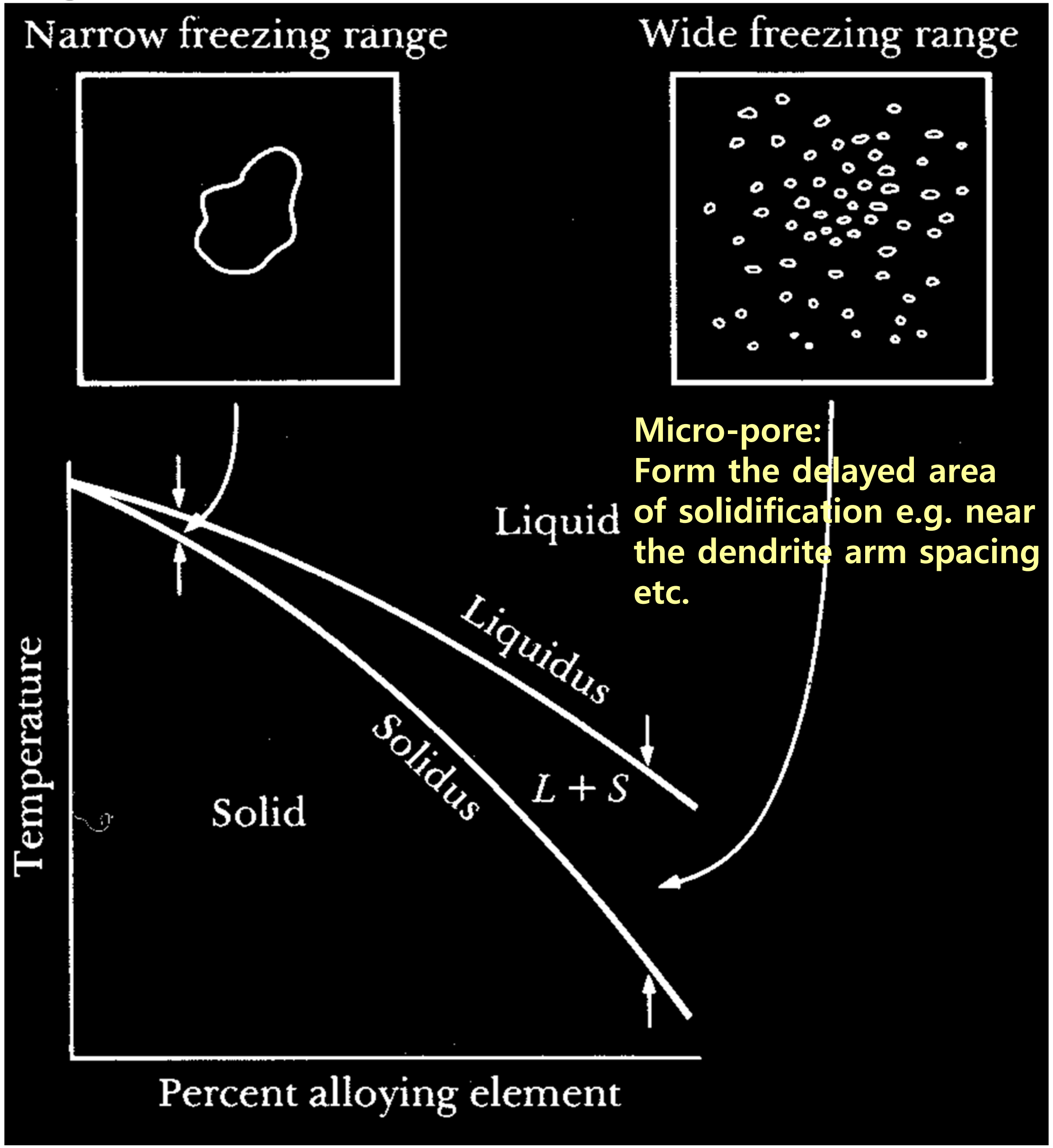
* Formation of Voids during solidification

Central shrinkage:
조성 변화가 크지 않은 주물의 응고 시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

Dispersed Micro-Pore:
상당히 넓은 범위에 분산된 미소기공

외부수축 (몰드 주위) 및 1차수축공 (표면)을 제외하면, 이러한 수축공 결함은 주로 기포 결함임

기포 내에는 철합금에서는 CO, 질소, 산소, 수소 등이, 동합금에서는 수소, 산소, 알루미늄 합금에서는 수소 등의 가스가 존재



Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

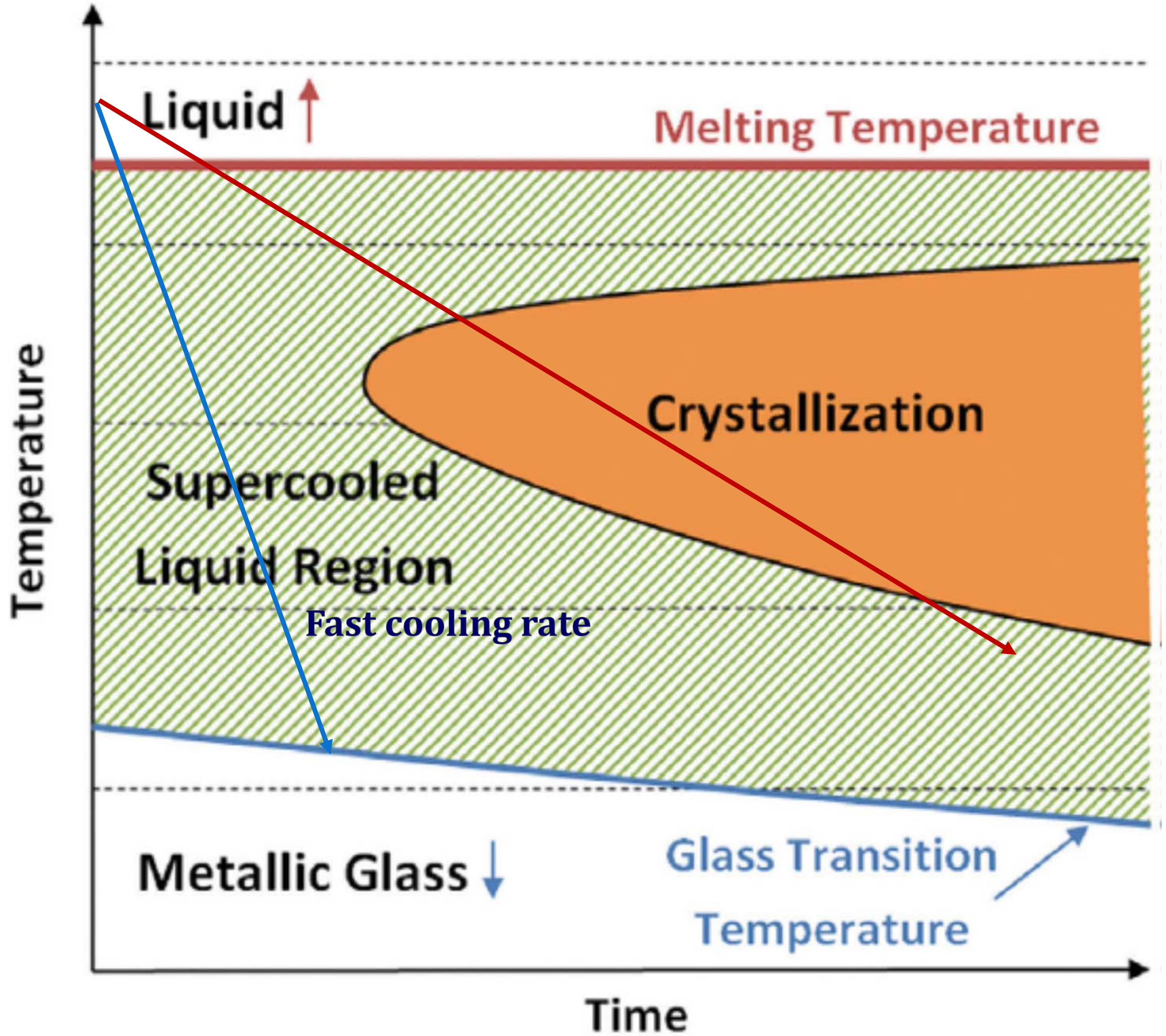
*** Volumetric solidification expansion: H_2O (10%), Si (20%), Ge**

ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

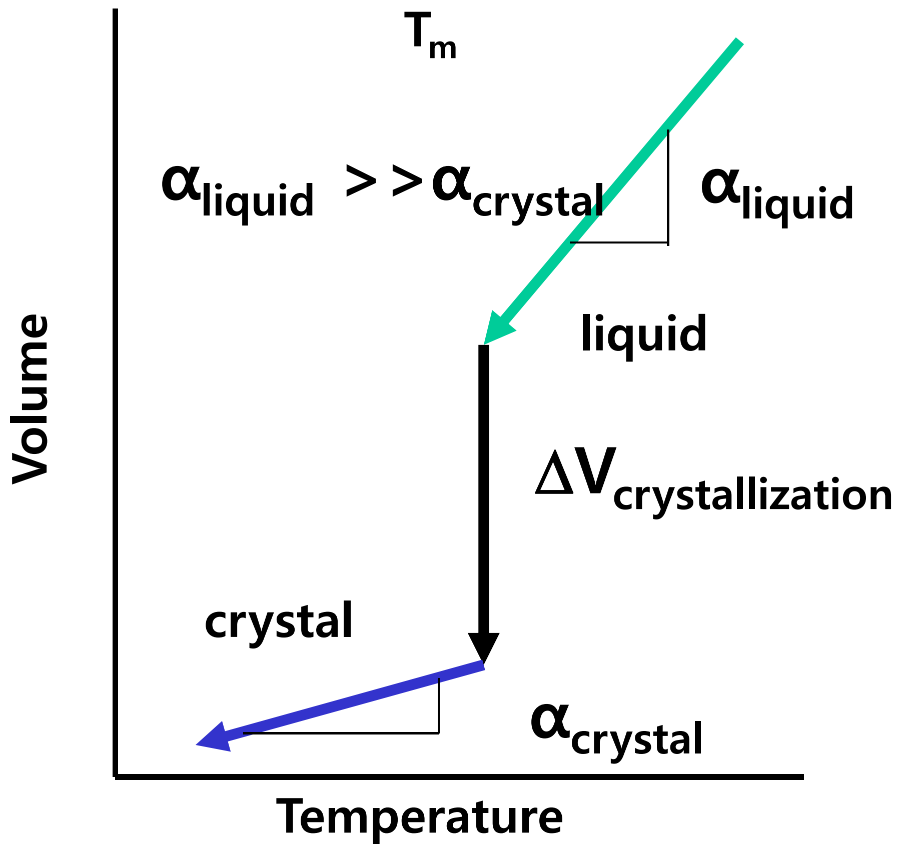
→ precipitation of graphite during solidification reduces shrinkage.

Glass formation : Fast Cooling

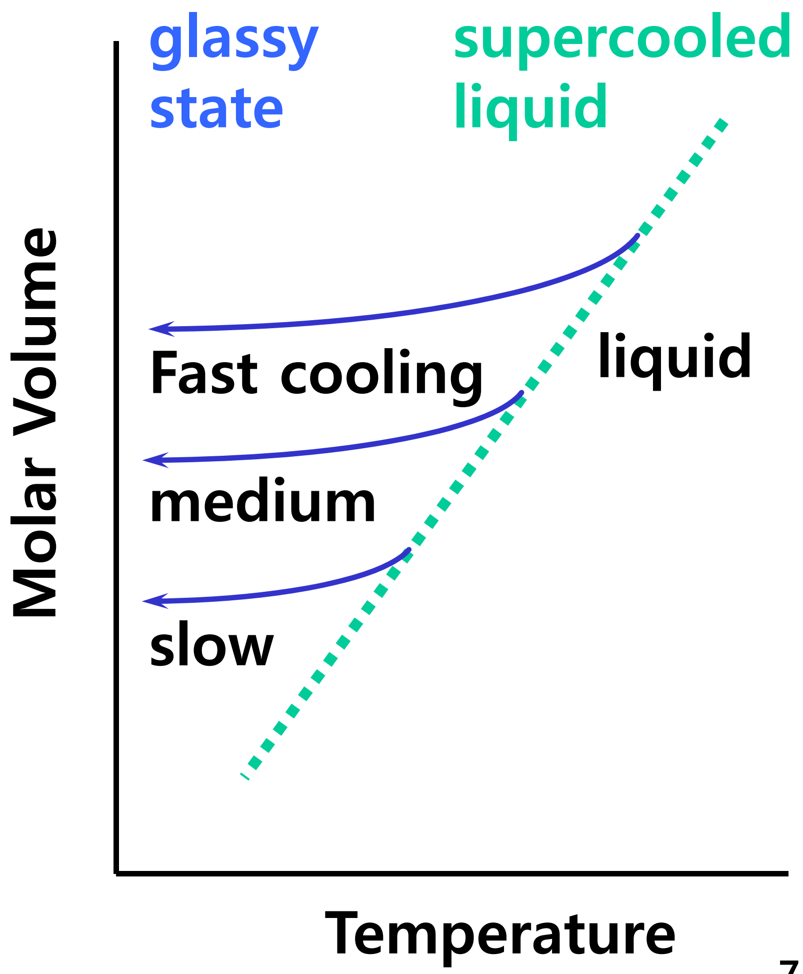


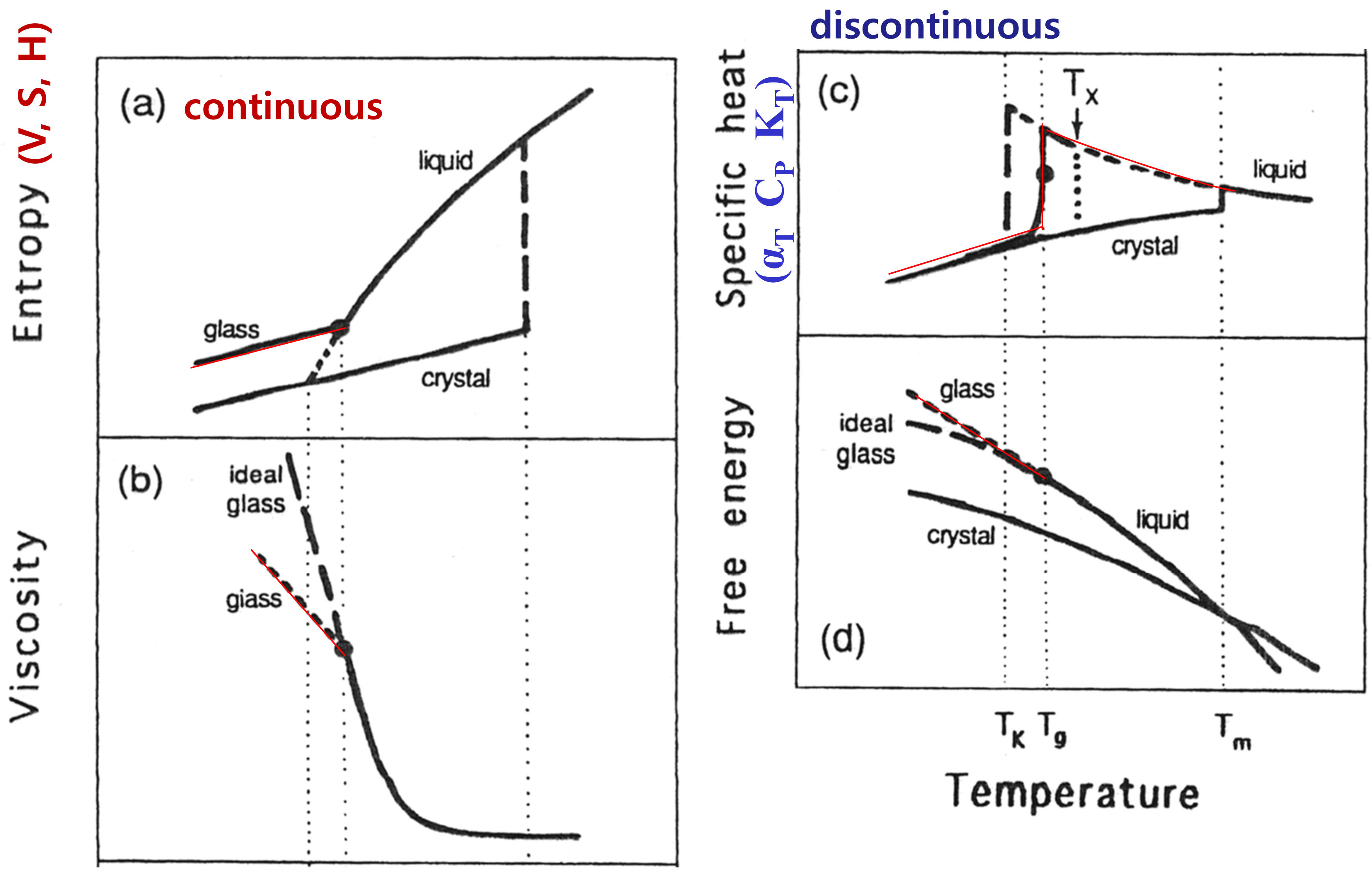
Fundamentals of the Glass Transition

- Melting and Crystallization are Thermodynamic Transitions



- The Glass Transition is a Kinetic Transition



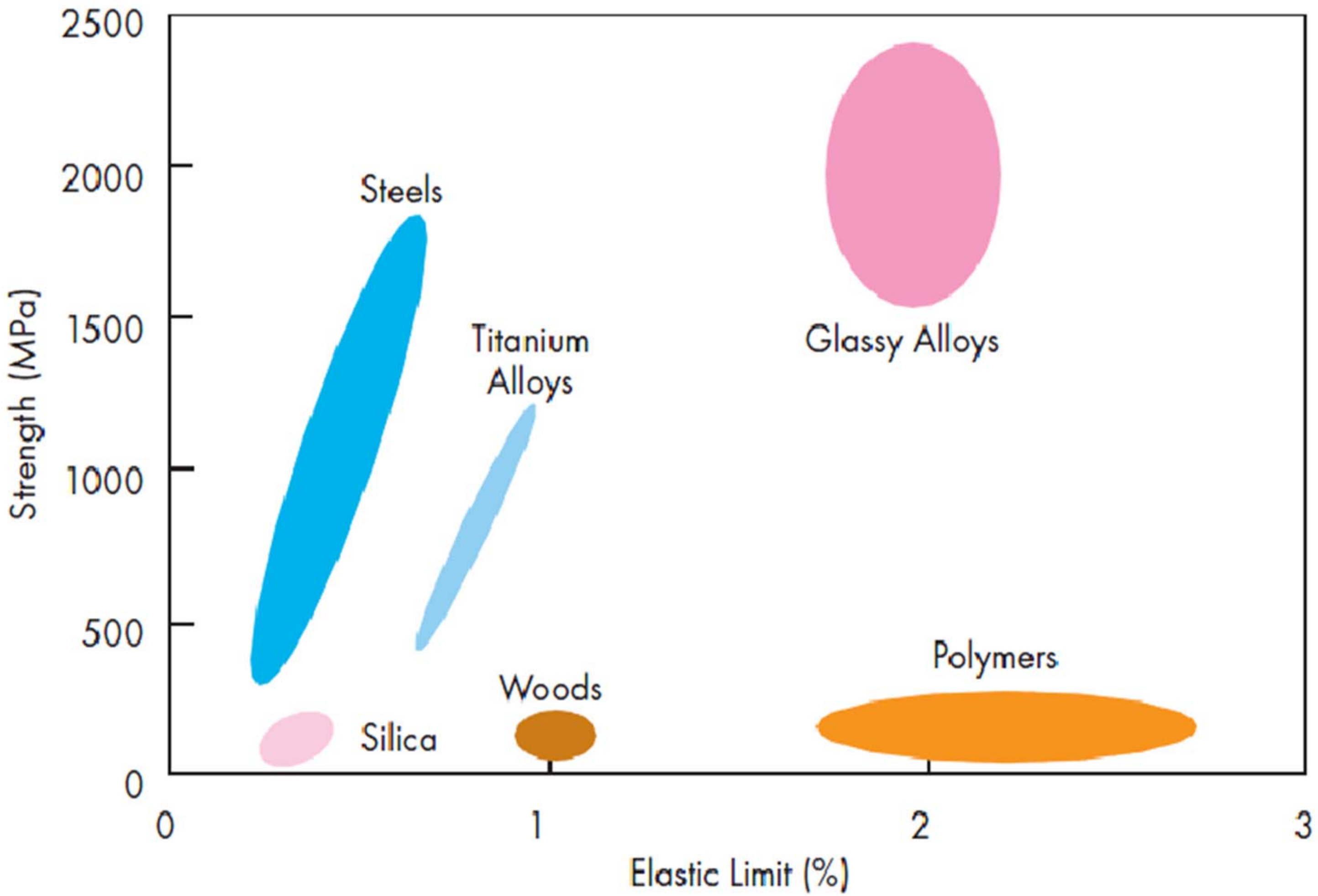


Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

BMG: The 3rd Revolution in Materials?

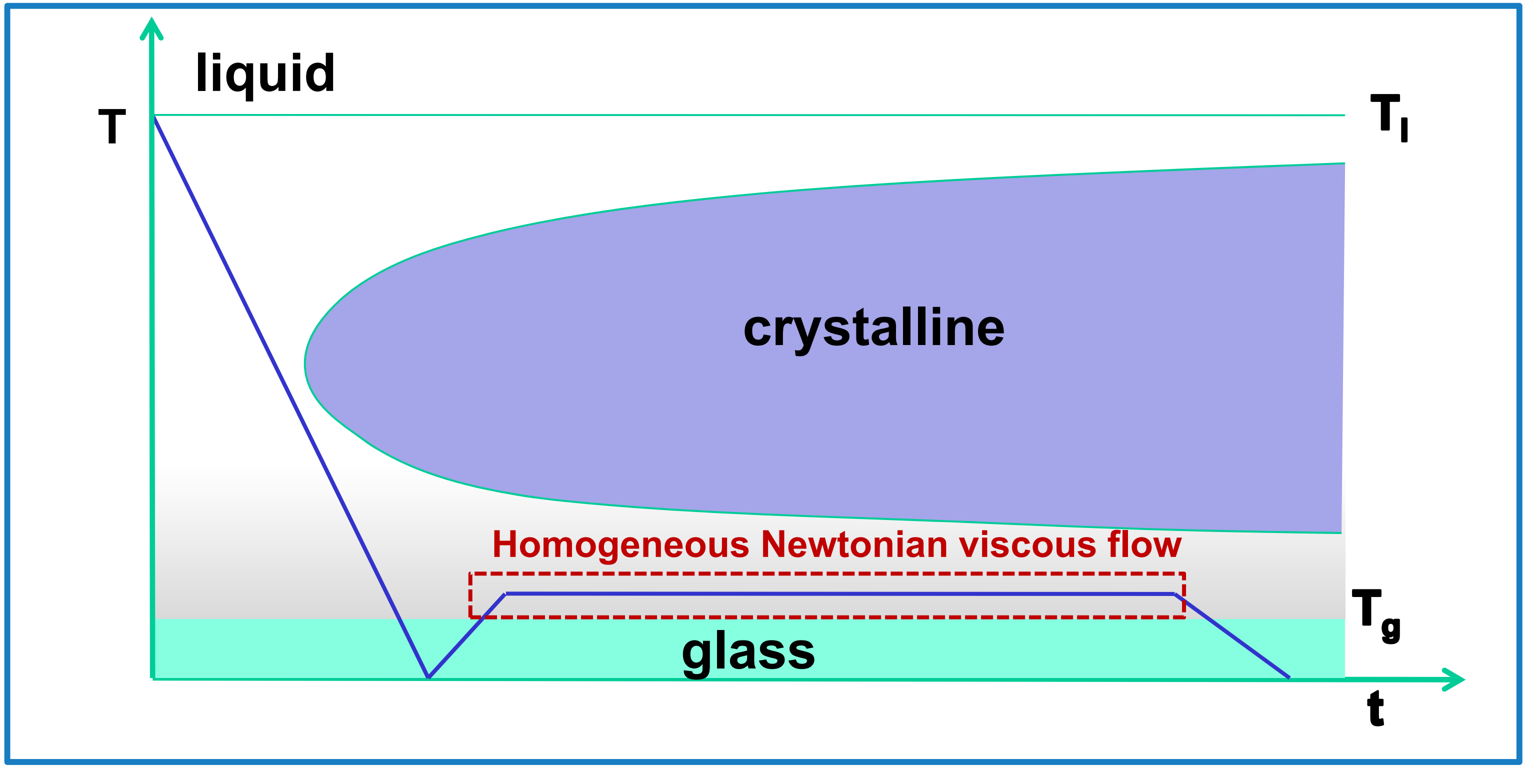
Metallic Glasses Offer

a Unique Combination of "1) High Strength" and "2) High Elastic Limit"



3) Processing metals as efficiently as plastics

*** Thermoplastic forming in SCLR**

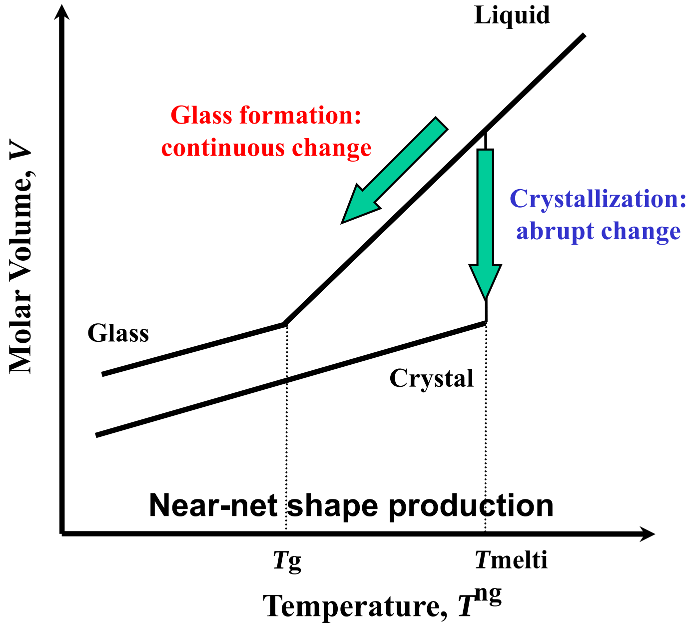


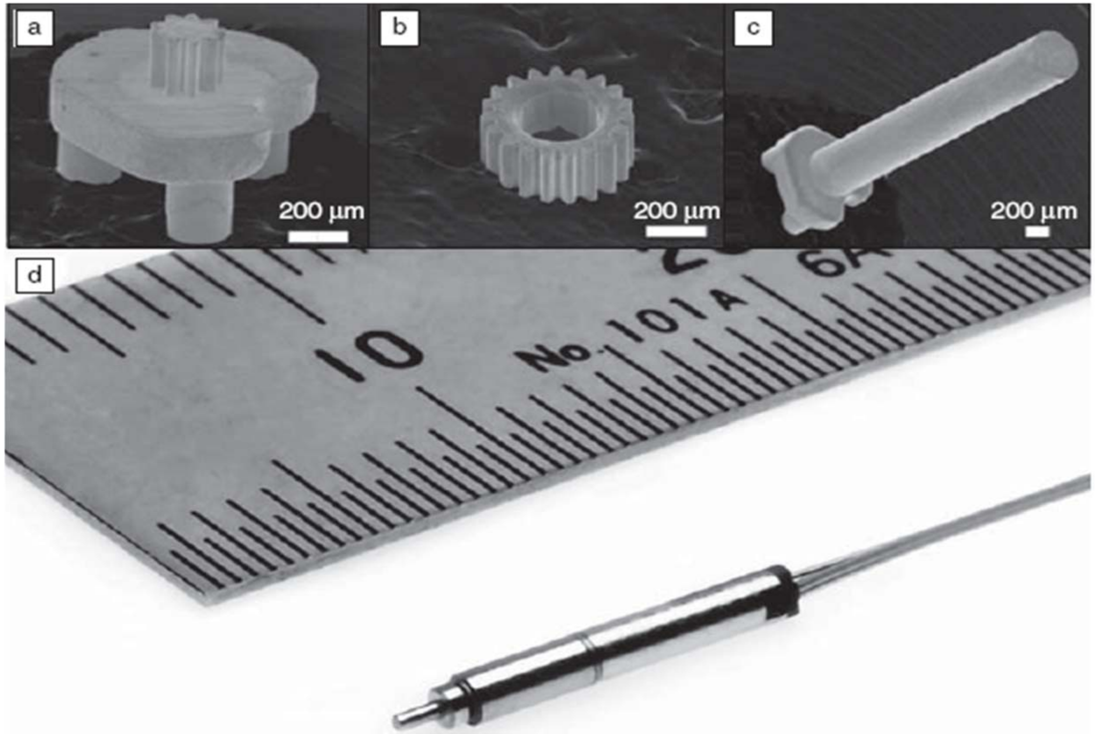
Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

➡ **Possible to deform thin and uniform in SCLR**

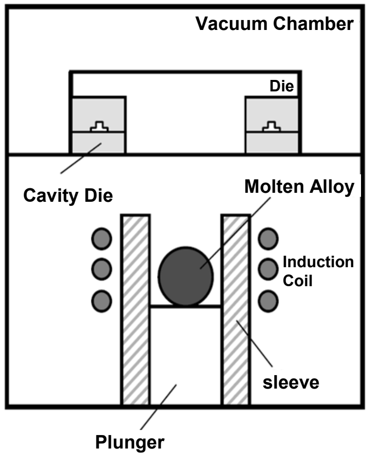
3) Processing metals as efficiently as plastics

(a) Micro-casting

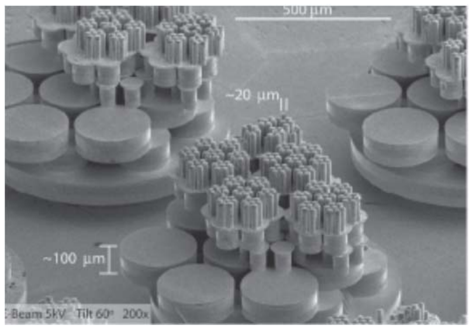




Precision Gears for Micro-motors



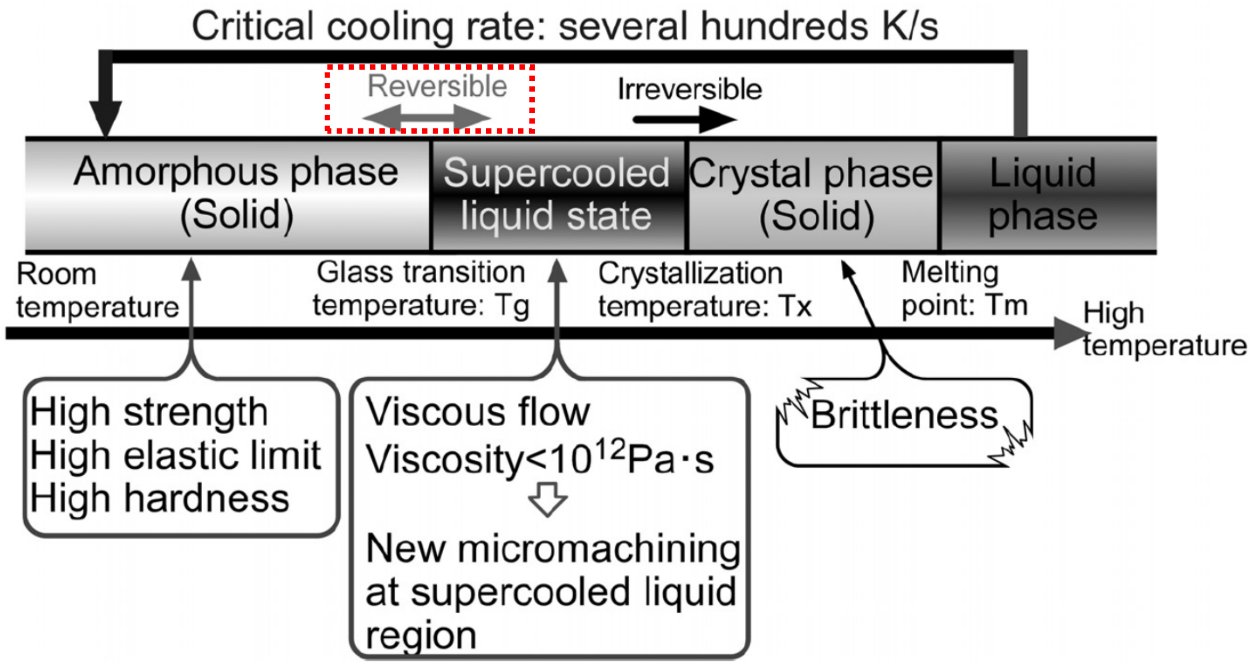
Precision die casting



*MRS BULLETIN **32** (2007)654.*

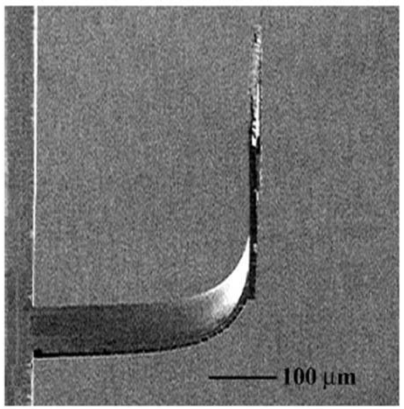
3) Processing metals as efficiently as plastics

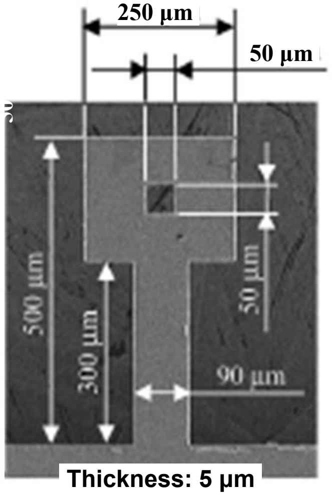
(b) Micro-forming



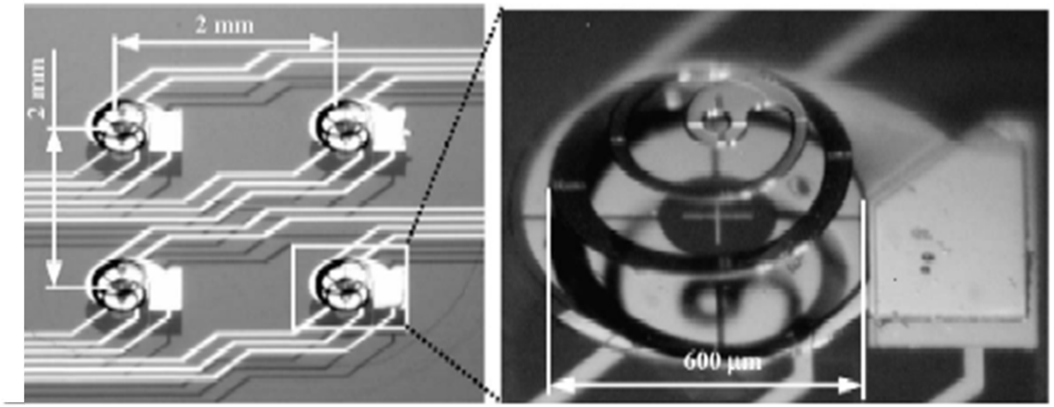
Micro-forming of three-dimensional microstructures from thin-film metallic glass

Micro-cantilever





Integrated conical spring linear actuator



Contents in Phase Transformation

Background to understand phase transformation

- (Ch1) Thermodynamics and Phase Diagrams
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase transformation

- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Contents for today's class

< Phase Transformation in Solids >

1) **Diffusional Transformation: Thermally-activated process= rate$\propto$ exp(-ΔG^*/kT)**

2) **Non-diffusional Transformation: Athermal Transformation**

- **Precipitate nucleation in solid (homogeneous/ heterogeneous)**

- **Precipitate growth**

  1) **Growth behind Planar Incoherent Interfaces**
  2) **Diffusion Controlled lengthening of Plates or Needles**
  3) **Thickening of Plate-like Precipitates by Ledge Mechanism**

- **Overall Transformation Kinetics – TTT Diagram**

  - **Johnson-Mehl-Avrami Equation**

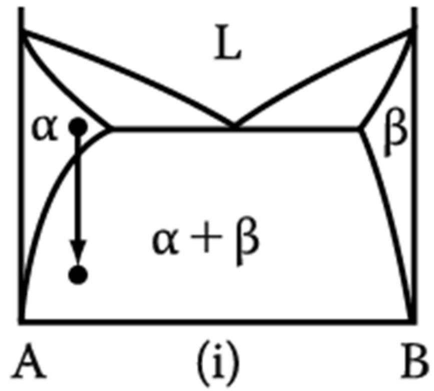
Q1: What kind of representative diffusion transformations in solid exist?

5. Diffusion Transformations in solid
: diffusional nucleation & growth

(a) Precipitation

$$\boxed{\alpha' \rightarrow \alpha + \beta}$$

Metastable supersaturated
solid solution



Homogeneous Nucleation

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

$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

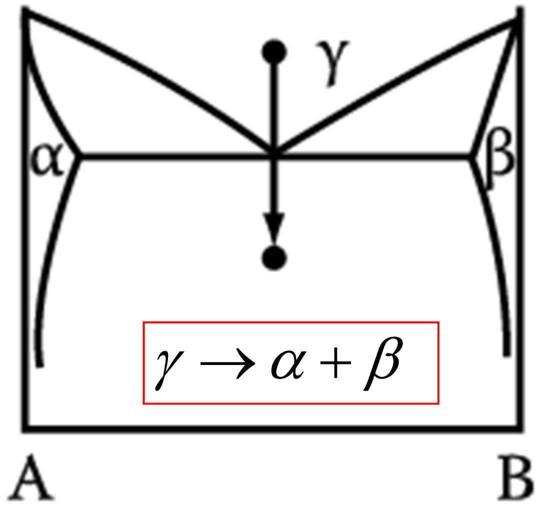
Heterogeneous Nucleation

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

➡ suitable nucleation sites ~ nonequilibrium defects
(creation of nucleus~destruction of a defect($-\Delta G_d$))

(b) Eutectoid Transformation

Composition of product phases differs from that of a parent phase.
→ long-range diffusion



$$\boxed{\gamma \rightarrow \alpha + \beta}$$

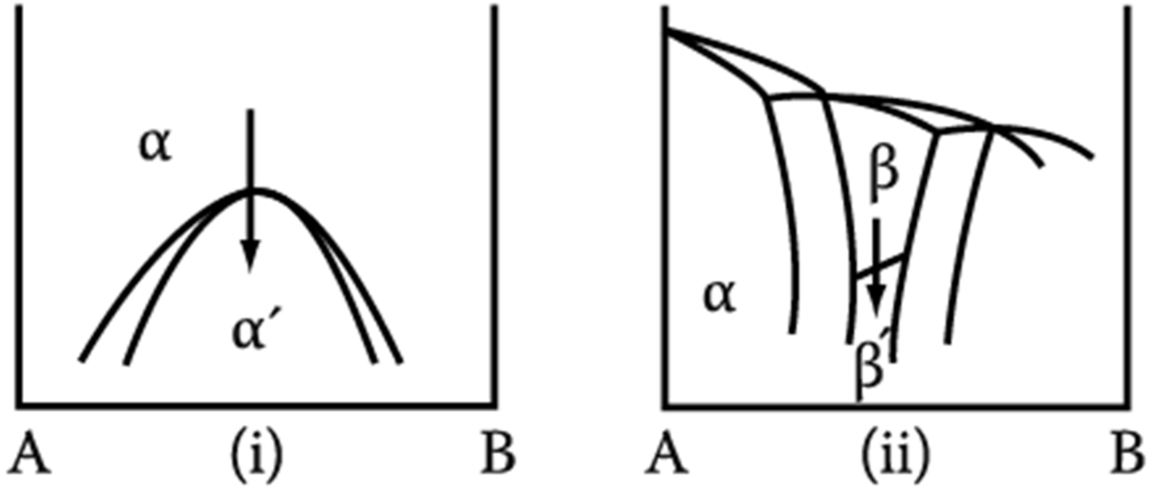
Which transformation proceeds by short-range diffusion?

5. Diffusion Transformations in solid

(c) Order-Disorder Transformation

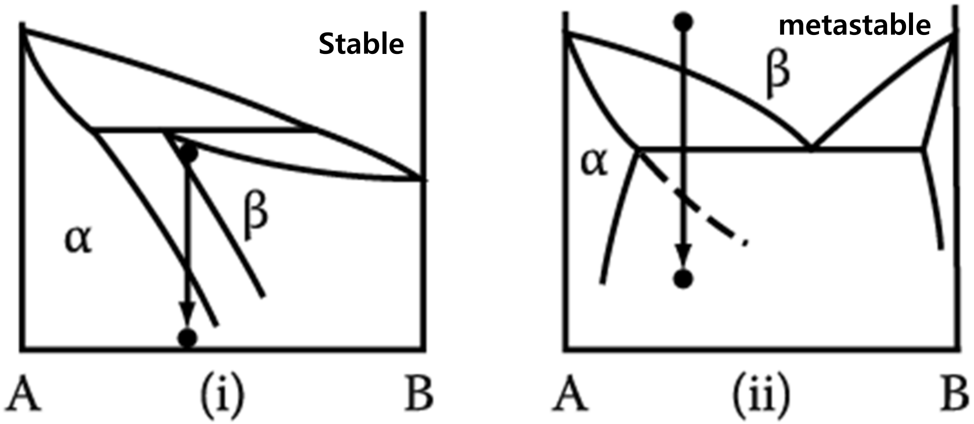
$$\boxed{\alpha \rightarrow \alpha'}$$

Disorder (high temp.) Order (low temp.)



(d) Massive Transformation

: The original phase decomposes into one or more new phases which have the <u>same composition</u> as the parent phase, but <u>different crystal structures</u>.



$$\boxed{\beta \rightarrow \alpha}$$

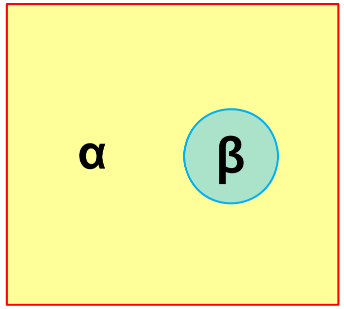
(e) Polymorphic Transformation

In single component systems, <u>different crystal structures are stable over different temperature ranges</u>.

Q2: Homogeneous nucleation in solid?

Homogeneous Nucleation in Solids

Free Energy Change Associated with the Nucleation



Negative and Positive Contributions to ΔG?

1) Volume Free Energy : $\boxed{-V\Delta G_V}$

2) Interface Energy : $A\gamma$

3) Misfit Strain Energy : $V\Delta G_S$

$$\Delta G = \boxed{-V\Delta G_V} + \boxed{A\gamma + V\Delta G_S}$$

for spherical nucleation

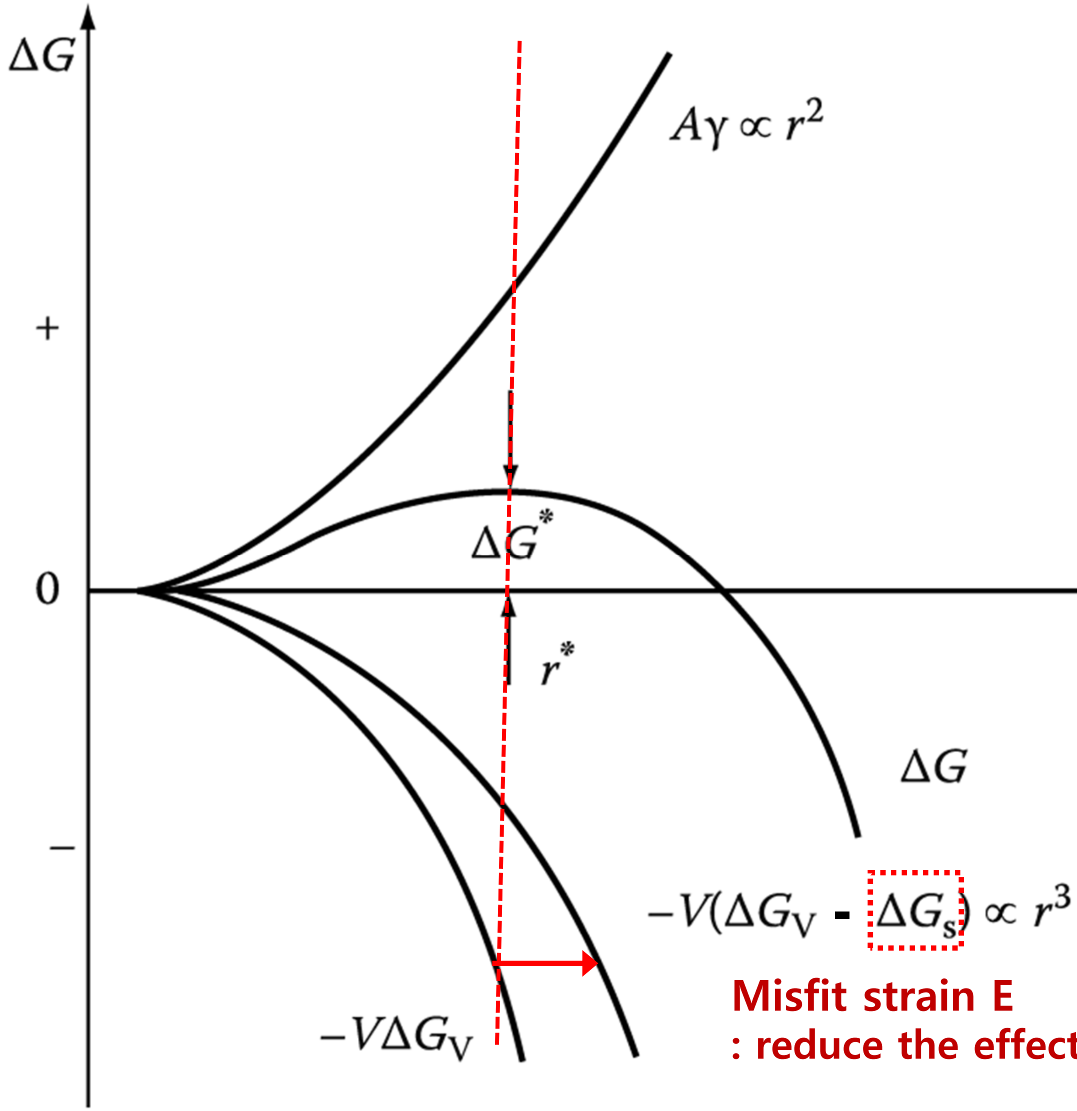
$$\Delta G = -\frac{4}{3}\pi r^3(\Delta G_V - \Delta G_S) + 4\pi r^2\gamma$$

Plot of ΔG vs r?

r* = ?

ΔG* = ?

Homogeneous Nucleation in Solids



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

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

: driving force for nucleation

Most effective way of minimizing ΔG^*

~ formation of nuclei with the smallest total interfacial E

Very similar to the expression for solidification (L→S)

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

Misfit strain E

: reduce the effective driving force for the transformation

Fig. 5.2 The variation of ΔG with r for a homogeneous nucleus. There is a activation energy barrier ΔG*.

Homogeneous Nucleation in Solids

Concentration of Critical Size Nuclei per unit volume

$$C^* = C_0 \exp(-\Delta G^* / kT)$$

C_0 : number of atoms per unit volume in the parent phase

Homogeneous Nucleation Rate

If each nucleus can be made supercritical at a rate of *f* per second,

$$N_{hom} = f\,C^*$$

$$f = \omega \exp\left(-\Delta G_m / kT\right)$$

: *f* depends on how frequently a critical nucleus can receive an atom from the α matrix.

$\omega \propto$ *vibration frequency, area of critical nucleus*

ΔG_m : *activation energy for atomic migration*

$$N_{hom} = \boxed{\omega} C_0 \exp\left(-\frac{\boxed{\Delta G_m}}{kT}\right) \exp\left(-\frac{\boxed{\Delta G^*}}{kT}\right)$$

: This eq. is basically same with eq (4.12) except considering temp. dependence of *f*.

Homogeneous Nucleation rate $\boxed{N_{hom} = f_0 C_o \exp(-\frac{\Delta G^*_{hom}}{kT})}$ **nuclei / m³·s**

$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

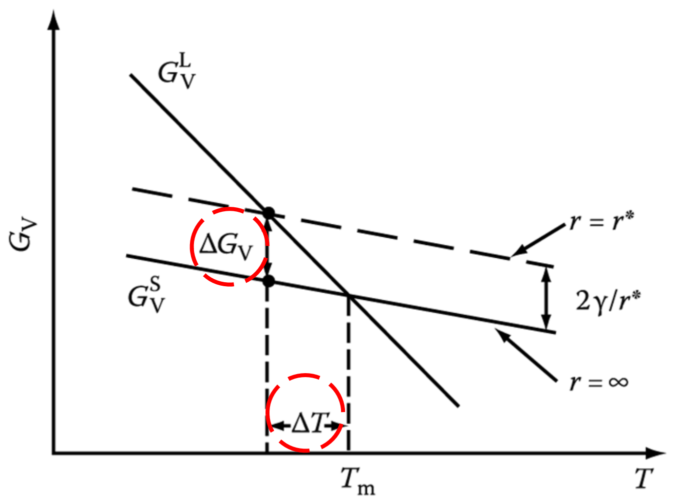
: strongly temp. dependent

ΔG*는 온도에 민감

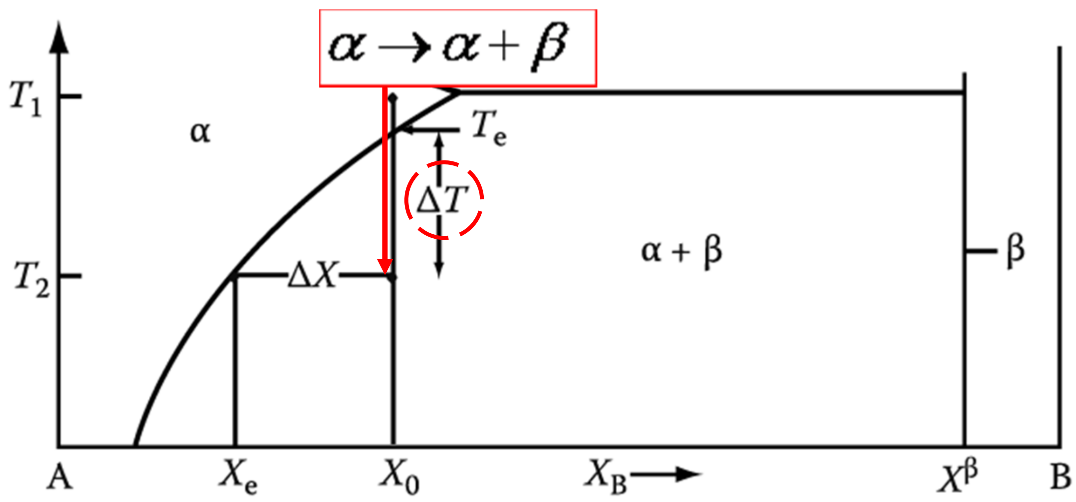
$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V - \Delta G_S)^2}$$

$\Delta G^* \propto \Delta G_V$ (driving force for precipitation_main factor)

* magnitude of ΔG_V ~ change by composition



Liquid → Solid



1) For X_0, solution treatment at T_1

2) For X_0, quenching down to T_2

α → α+β

: supersaturated α with B → β precipitation in α

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: overall driving force for transformation/ different with driving force for nucleation

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ $\Delta G_V = \dfrac{\Delta G_n}{V_m}$

$$\Delta G_1 = \mu_A^\alpha X_A^\beta + \mu_B^\alpha X_B^\beta$$

: Decrease of total free E of system
by removing a small amount of material
with the nucleus composition (X_B^β) (P point)

$$\Delta G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta$$

: Increase of total free E of system
by forming β phase with composition X_B^β
(Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}$$ (length PQ)

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m} \quad \textit{per unit volume of } \beta$$

: driving force for β precipitation

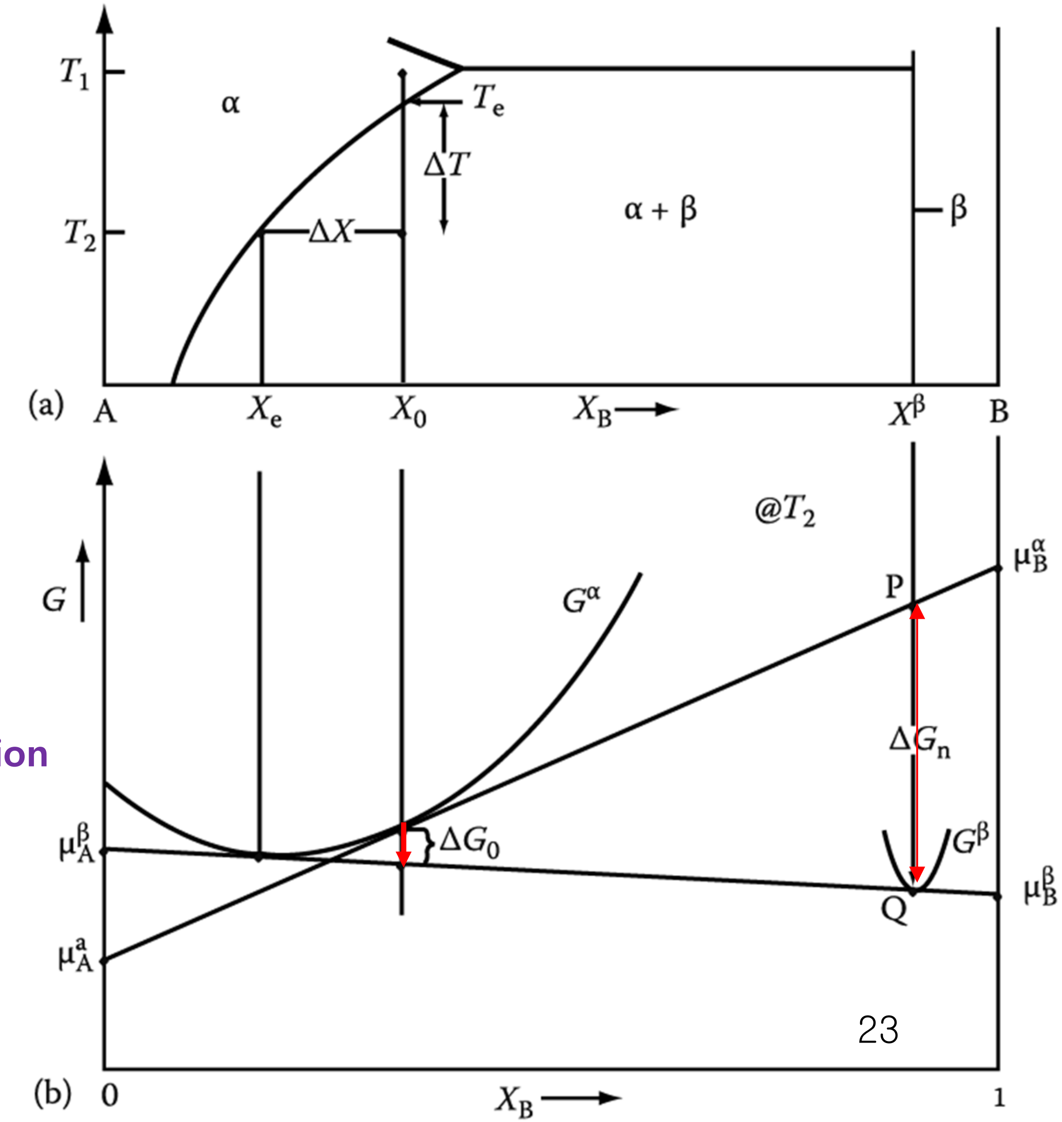
For dilute solutions,

$$\Delta G_V \propto \Delta X \quad \textit{where } \Delta X = X_0 - X_e$$

Composition dependent

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝ undercooling below T_e



Rate of Homogeneous Nucleation Varies with undercooling below T_e for alloy X_0

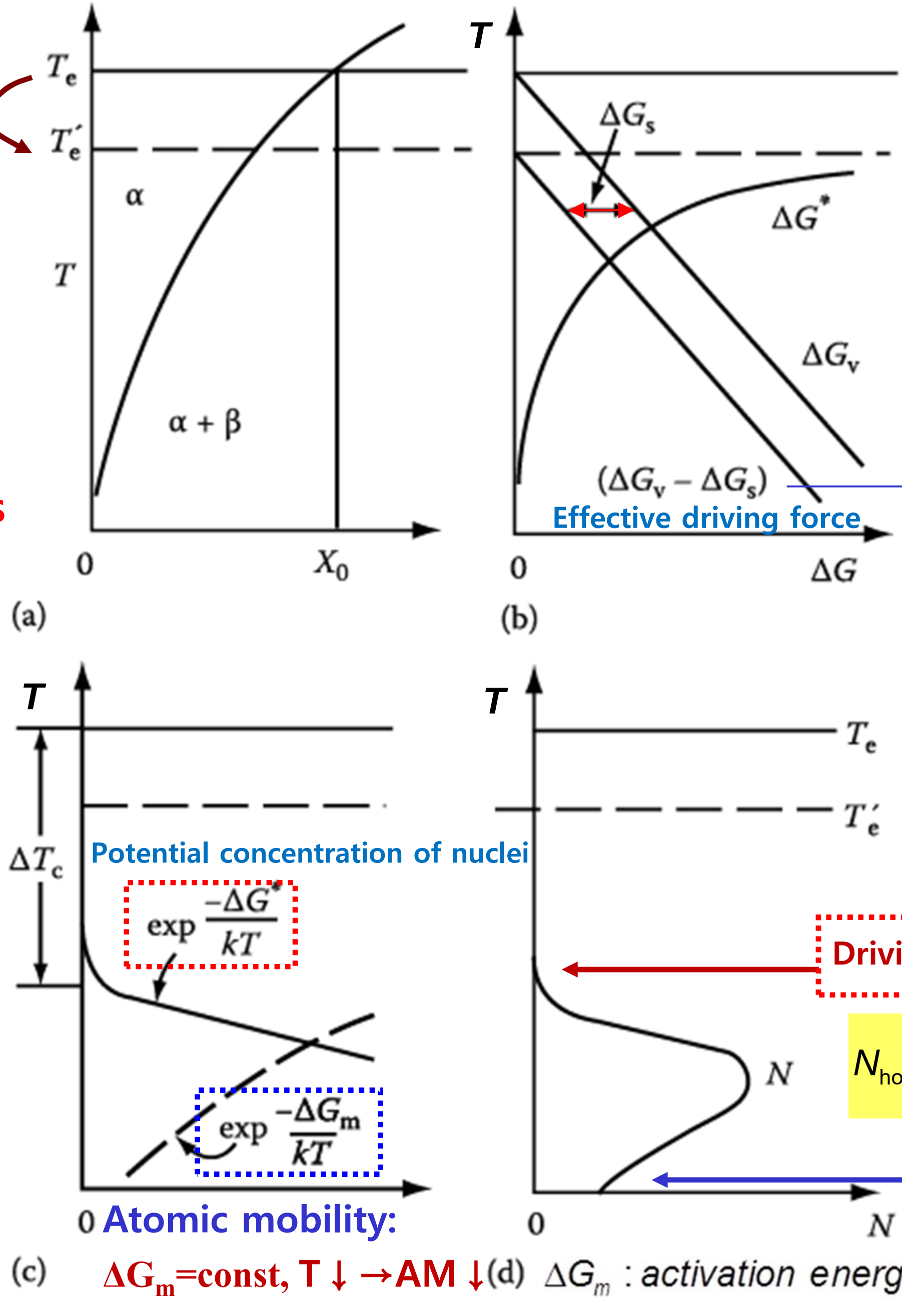
Effective equilibrium temperature is reduced by misfit strain E term, ΔGs.

Thermodynamics

vs

Kinetics

Critical undercooling



$$\Delta G_V \propto \Delta X \propto \Delta T$$

Composition dependent

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

Resultant energy barrier for nucleation

Driving force ΔG_v~too small → N~negligible

$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

Diffusion~too slow → N~negligible

ΔG_m=const, T↓ →AM↓

ΔG_m : activation energy for atomic migration

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom}?_Critical undercooling, ΔT_c

Plot ΔG^*_{het} & ΔG^*_{hom} vs ΔT and N vs ΔT.

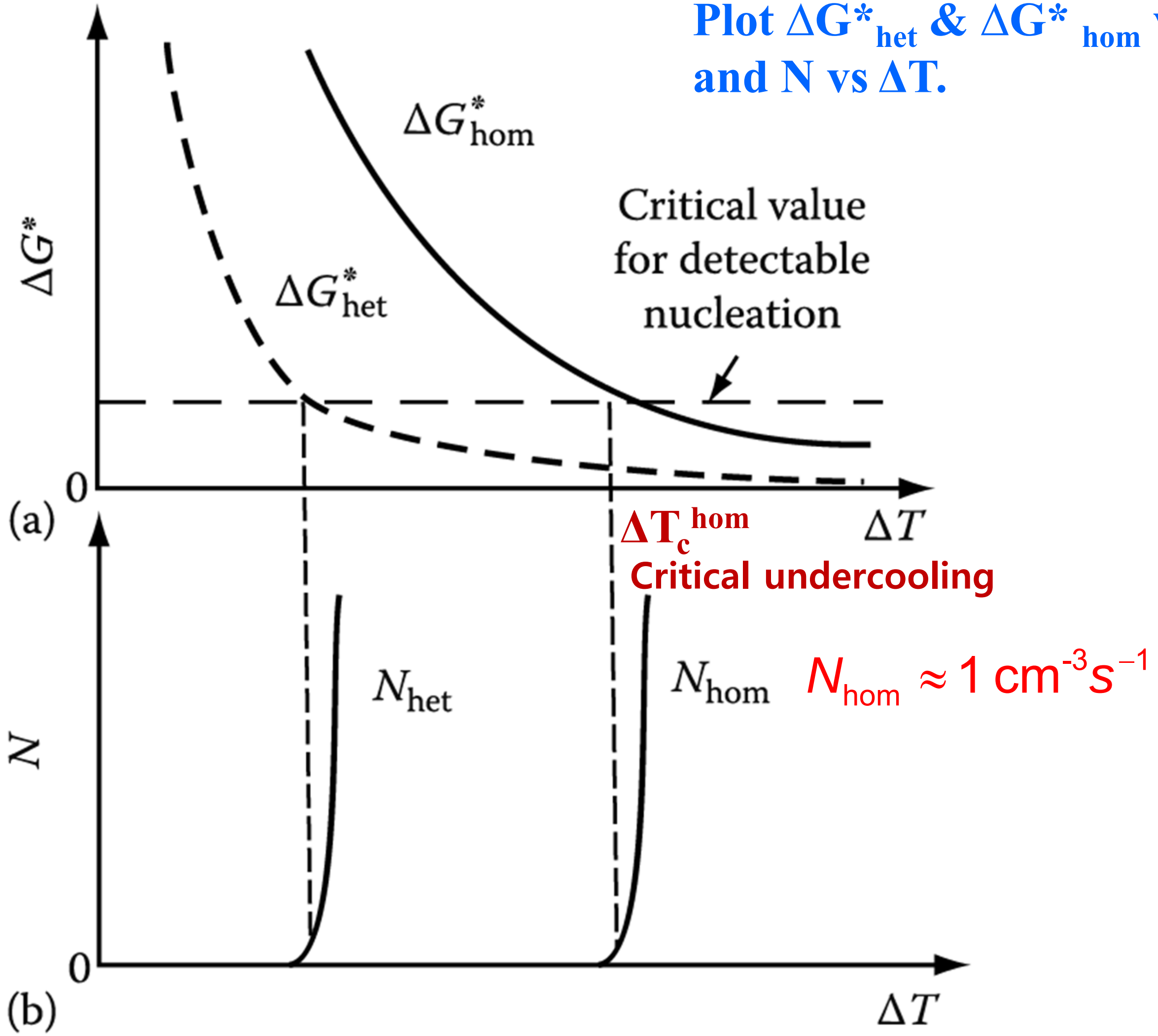


Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG*

The Effect of Alloy Composition on the Nucleation Rate

Compare the two plots of T vs N(1) and T vs N(2).

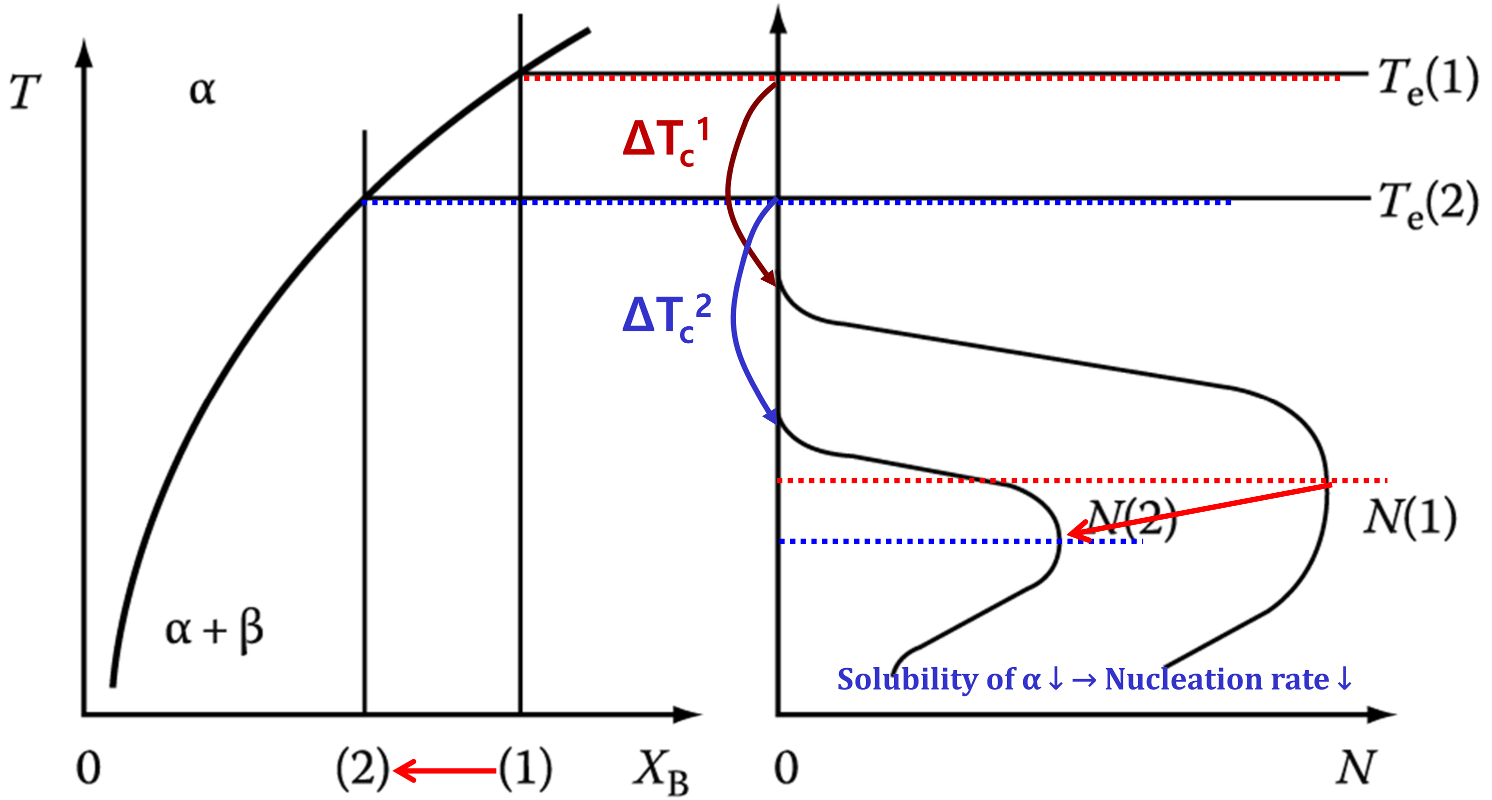


Fig. 5.5 The effect of alloy composition on the nucleation rate. The nucleation rate in alloy 2 is always less than in alloy 1.

* 어떤 핵이 형성되느냐? → 어느 경우 최소의 ΔG* 필요로 하나? → 최소의 계면에너지를 갖는 핵 생성

(a) 핵이 모상과 방위관계를 갖고 정합계면 형성하면 → ΔGs 증가 & Te' 감소
그러나, Te' 이하에서는 정합계면 생성에 의한 γ 감소가 ΔGs 증가 효과보다 더 커질 수 있음.
→ ΔG* 크게 감소 → 균일핵생성 발생

(b) In most system, α, β phase~ different crystal structure → 부정합 핵은 γ가 커서 평형 β상의 균일 핵생성 불가능 → **metastable phase β' 균일핵생성** (GP Zones, Section 5.5.1)

Q3: Heterogeneous nucleation in solid?

Heterogeneous Nucleation in Solids

➡ most cases, heterogeneous nucleation_suitable nucleation sites ~ nonequilibrium defects
(creation of nucleus~destruction of a defect($-\Delta G_d$) & reducing the activation E barrier)

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

Nucleation on Grain Boundaries

Assumption: ΔG_S (misfit strain E)= 0,

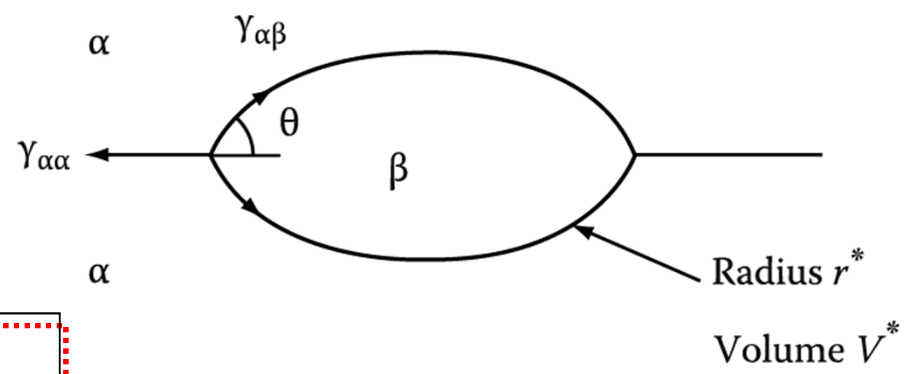
Optimum embryo shape should be that which minimizes the total interfacial free E.

$$\cos\theta = \gamma_{\alpha\alpha}/2\gamma_{\alpha\beta}$$

(by assuming $\gamma_{\alpha\beta}$ is isotropic and equal for both grains)

$$\Delta G = -V\Delta G_V + A_{\alpha\beta}\gamma_{\alpha\beta} - \boxed{A_{\alpha\alpha}\gamma_{\alpha\alpha}}$$

Critical nucleus size(V*) for grain-boundary nucleation

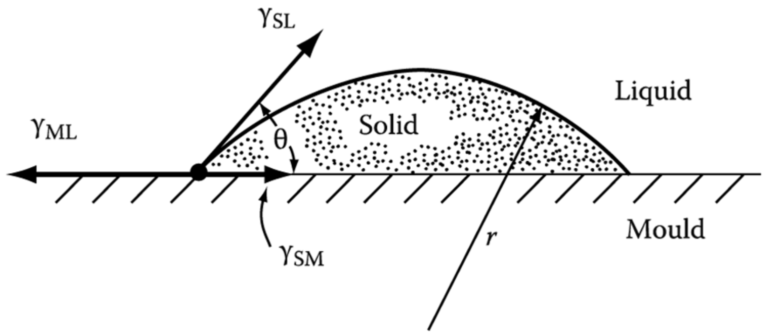


⇨ Excess free E associated with the embryo~analogous to solidification on a substrate (Section 4.1.3) (next page)

Barrier of Heterogeneous Nucleation in S→L transformation

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

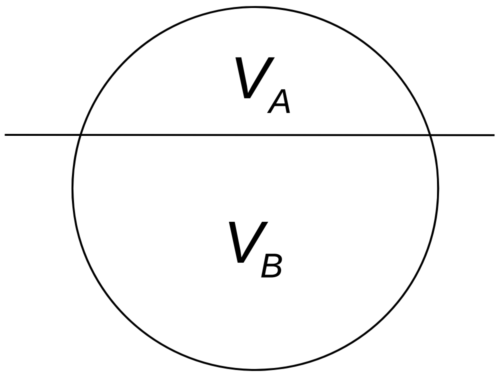
$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



Shape factor

S(θ) has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\boxed{\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*} \Rightarrow r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad and \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$



$$\Delta G_{het}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

$$\boxed{\frac{V_A}{V_A+V_B} = \frac{2-3\cos\theta+\cos^3\theta}{4} = S(\theta)}$$

Heterogeneous Nucleation in Solids

➡ most cases, heterogeneous nucleation_suitable nucleation sites ~ nonequilibrium defects
(creation of nucleus~destruction of a defect($-\Delta G_d$) & reducing the activation E barrier)

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

Nucleation on Grain Boundaries

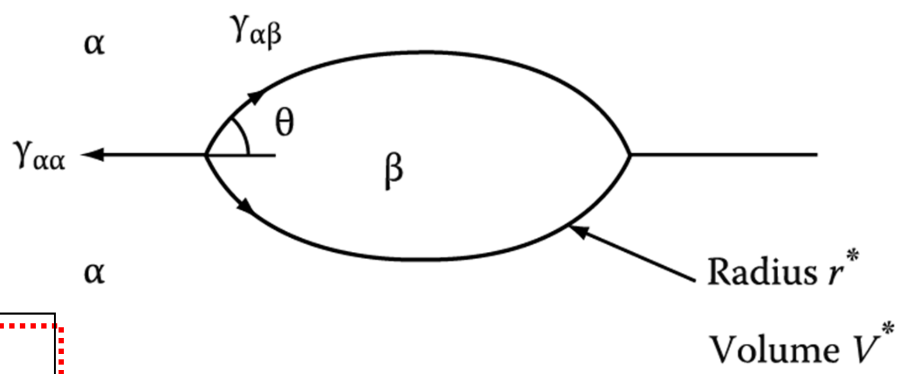
Assumption: ΔG_S (misfit strain E)= 0,

Optimum embryo shape should be that which minimizes the total interfacial free E.

$$\cos\theta = \gamma_{\alpha\alpha}/2\gamma_{\alpha\beta}$$

(by assuming $\gamma_{\alpha\beta}$ is isotropic and equal for both grains)

Critical nucleus size(V^*) for grain-boundary nucleation



$$\Delta G = -V\Delta G_V + A_{\alpha\beta}\gamma_{\alpha\beta} - \boxed{A_{\alpha\alpha}\gamma_{\alpha\alpha}}$$

⇨ Excess free E associated with the embryo~analogous to solidification on a substrate (Section 4.1.3)

Critical radius of the spherical caps

$$r^* = 2\gamma_{\alpha\beta} / \Delta G_V$$

r* is not related to $\gamma_{\alpha\alpha}$

Activation E barrier for heterogeneous nucleation

$$\frac{\Delta G^*_{het}}{\Delta G^*_{hom}} = \frac{V^*_{het}}{V^*_{hom}} = S(\theta)$$

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

Heterogeneous Nucleation in Solids

$$\boxed{\Delta G^*_{het} \sim \cos\theta \sim \gamma_{\alpha\alpha} / 2\gamma_{\alpha\beta}}$$

Reduction by boundary effect

⇨ $\gamma_{\alpha\alpha} : \gamma_{\alpha\beta} \geq 2 \rightarrow \boldsymbol{\theta} = 0$

No energy barrier for nucleation

$$\Delta G^*_{het} = \Delta G^*_{homo}\left(\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right)$$

How can V* and ΔG* be reduced even further?

→ **By nucleation on a grain edge or a grain corner.**

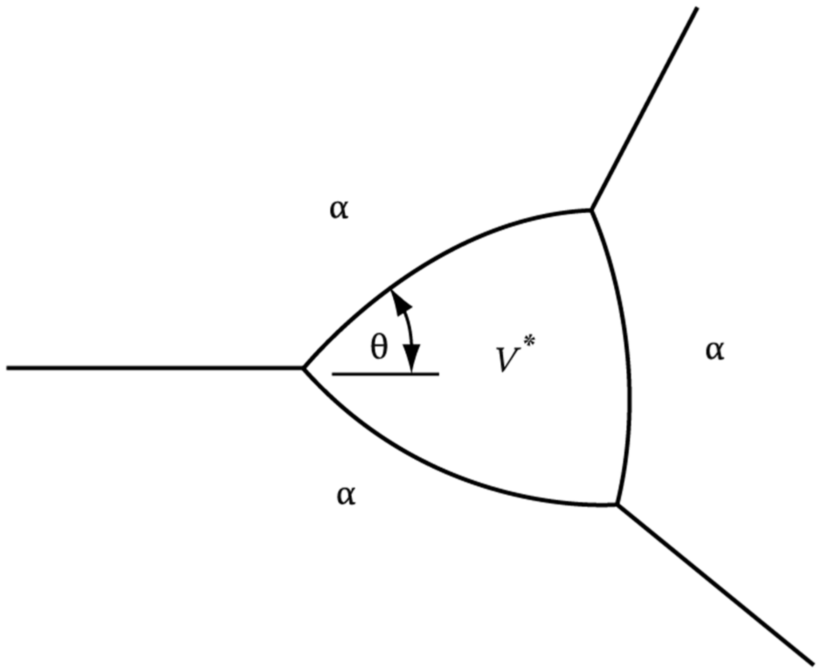


Fig. 5.7 Critical nucleus shape for nucleation on a **grain edge**.

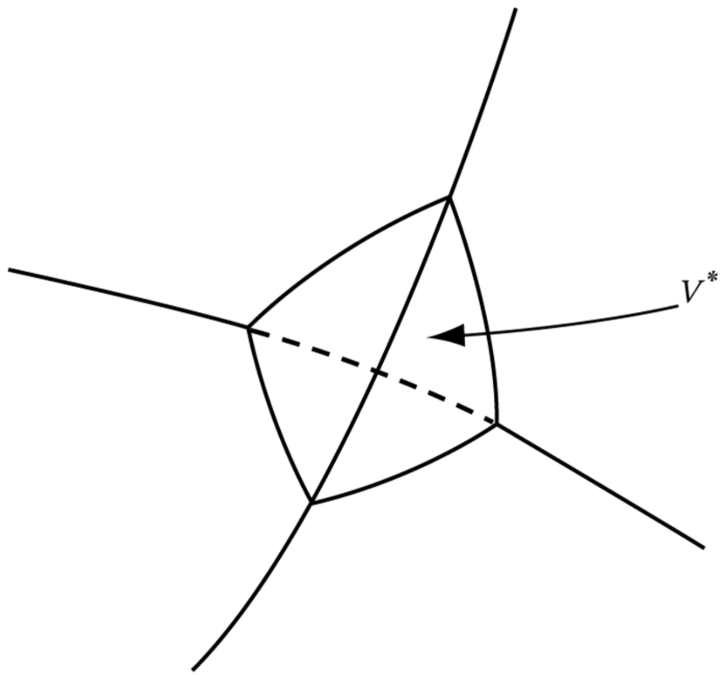


Fig. 5.8 Critical nucleus shape for nucleation on a **grain corner.**

Heterogeneous Nucleation in Solids

Compare the plots of $\Delta G^*_{het} / \Delta G^*_{\mathrm{hom}} vs \cos\theta$
for grain boundaries, edges and corners

$$S(\theta) = \frac{\Delta G^*_{\mathrm{het}}}{\Delta G^*_{\mathrm{hom}}}$$

If same **θ, 1) GB → 2) Grain edges → 3) Grain corners**
Activation E barrier ↓→ fast nucleation

Activation E Barrier

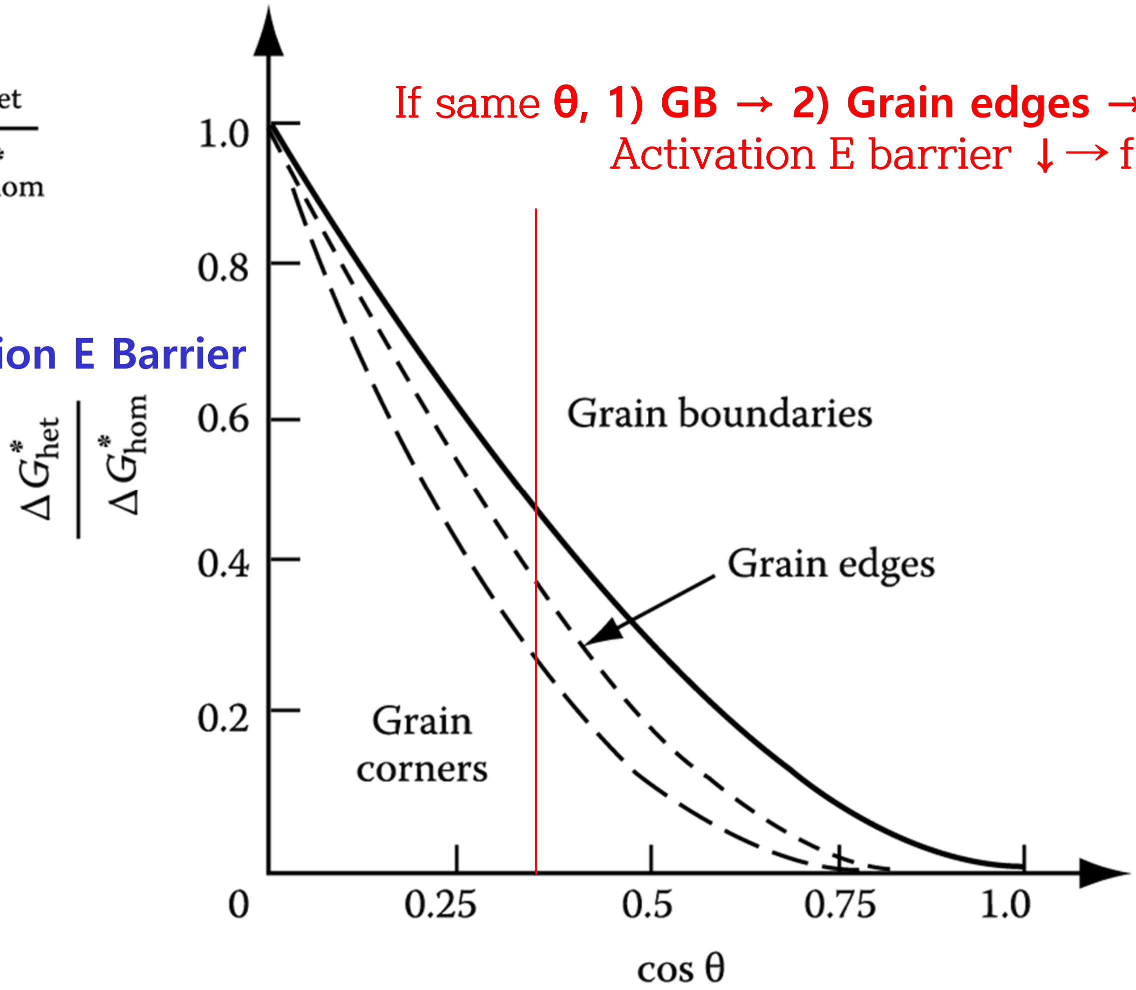


Fig. 5.9 The effect of θ on the activation energy for grain boundary nucleation relative to homogeneous nucleation.

Heterogeneous Nucleation in Solids

High-angle grain boundaries (high interfacial E) are particularly effective nucleation sites for incoherent precipitates with high $\gamma_{\alpha\beta}$.

If the matrix and precipitate make a coherent interface, V* and ΔG^* can be further reduced as shown in Fig. 5.10. The nuclei will then have an orientation relationship with one of the grains.

< Nucleus with Coherent Interface >

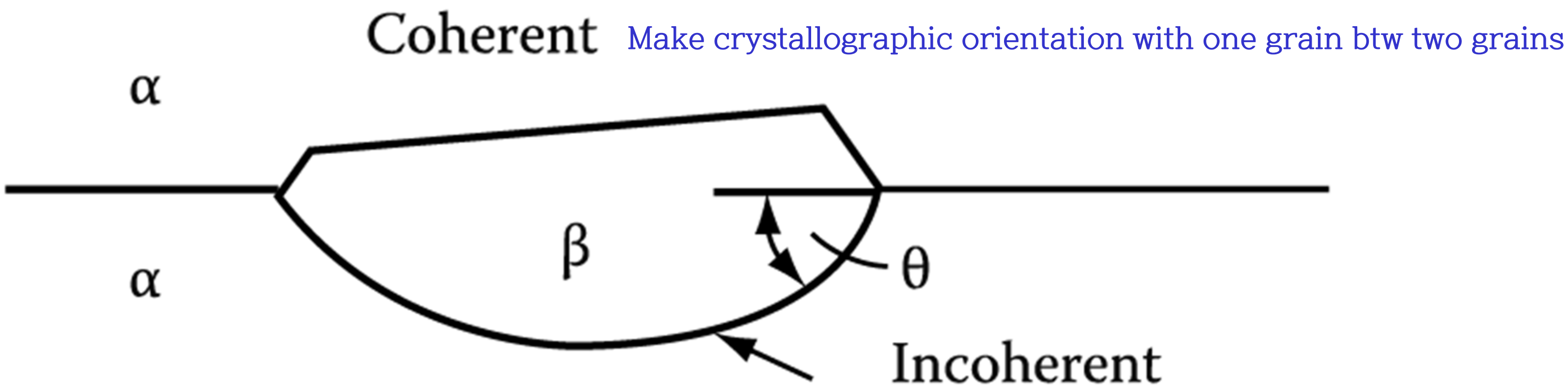


Fig. 5. 10 The critical nucleus size can be reduced even further by forming a low-energy coherent interface with one grain.

* Other planar defects, such as inclusion/matrix interfaces, stacking faults (relatively low E), and free surfaces, dislocations and excess vacancies (?) can behave in a similar way to grain boundaries in reducing ΔG^*.

Heterogeneous Nucleation in Solids

Rate of Heterogeneous Nucleation

Decreasing order of ΔG^*, i.e., increasing ΔG_d

(Activation Energy Barrier for nucleation)

1) homogeneous sites
2) vacancies 단독으로 또는 작은 군집체 상태로 핵생성에 영향/ 확산속도 증가 & 불일치 변형에너지 감소
3) dislocations 전위주위의 격자비틀림→ 핵생성시 전체변형에너지 감소 / 용질원소 편석/ 손쉬운 확산경로
4) stacking faults 매우 낮은 에너지/ 총계면에너지 ↓ 효과적이지 못함 → 강력한 불균일 핵생성처는 아님
5) grain boundaries and interphase boundaries
6) free surfaces

: Nucleation should always occur most rapidly on sites near the bottom of the list.
However, the relative importance of these sites depends on the relative concentrations of the sites, C1.

$$N_{het} = \omega C_1 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right) \quad nuclei\ m^{-3}s^{-1}$$

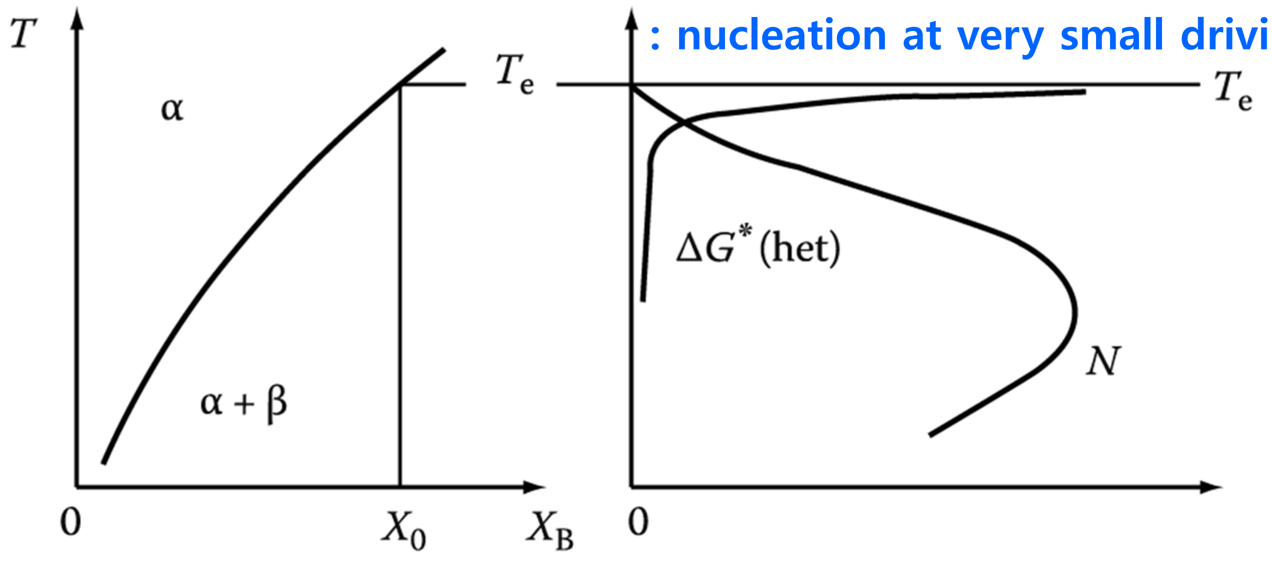
C_1 : concentration of heterogeneous nucleation sites per unit volume

$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

: number of atoms per unit volume in parent phase

Heterogeneous Nucleation in Solids

The Rate of Heterogeneous Nucleation during Precipitation



: nucleation at very small driving forces

* Relative magnitudes of the heterogeneous and homogeneous volume nucleation rates

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0} \exp\left(\frac{\boxed{\Delta G^*_{hom} - \Delta G^*_{het}}}{kT} \right)$$

Ignore ω and ΔG_m **due to small deviation**

ΔG* ~ always smallest for heterogeneous nucleation ⇨ **Exponential factor : very large quantity** ⇨ $\frac{N_{het}}{N_{hom}} > 1$ **High heterogeneous nucleation rate**

But, The factor C_1/C_0 ?

Heterogeneous Nucleation in Solids

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0}\exp\left(\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT}\right)$$

C_1/C_0 for GB nucleation?

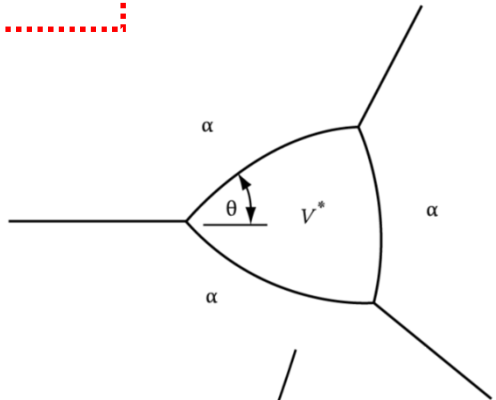
$$\frac{C_1}{C_0} = \frac{\delta(GB\ thickness)}{D(grain\ size)}$$

: the number of atoms on heterogeneous sites relative to the number within the matrix

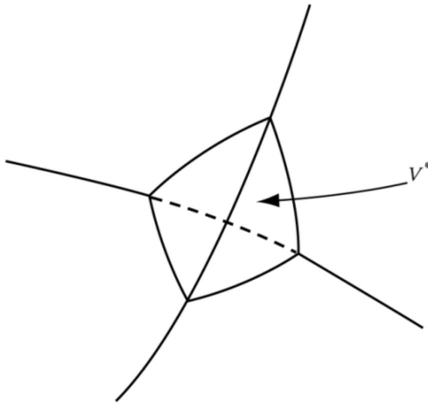
For D = 50 μm, δ = 0.5 nm

$$\frac{C_1}{C_0} = \frac{\delta}{D} \approx \boxed{10^{-5}}$$

$$\frac{C_1}{C_0} = \left(\frac{\delta}{D}\right)^2 \rightarrow for\ \ nucleation\ on\ grain\ edge$$



$$\frac{C_1}{C_0} = \left(\frac{\delta}{D}\right)^3 \rightarrow for\ \ nucleation\ on\ grain\ corner$$



C_1/C_0 for Various Heterogeneous Nucleation Sites

Grain boundary	Grain edge	Grain corner	Dislocations		Excess vacancies
$D = 50\ \mu m$	$D = 50\ \mu m$	$D = 50\ \mu m$	$10^5\ mm^{-2}$	$10^8\ mm^{-2}$	$X_v = 10^{-6}$
10^{-5}	10^{-10}	10^{-15}	10^{-8}	10^{-5}	10^{-6}

Heterogeneous Nucleation in Solids

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0} \exp\left(\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT} \right)$$

C_1/C_0 for Various Heterogeneous Nucleation Sites

각각의 핵생성처에서 경쟁적으로 핵생성 발생: 구동력 조건에 따라 전체 핵생성 속도에 dominant하게 영향을 미치는 site 변화

Grain boundary	Grain edge	Grain corner	Dislocations		Excess vacancies
$D = 50\ \mu m$	$D = 50\ \mu m$	$D = 50\ \mu m$	$10^5\ mm^{-2}$	$10^8\ mm^{-2}$	$X_v = 10^{-6}$
10^{-5}	10^{-10}	10^{-15}	10^{-8}	10^{-5}	10^{-6}

In order to make nucleation occur exclusively on the grain corner, how should the alloy be cooled?

1) At very small driving forces (ΔG_v), when activation energy barriers for nucleation are high, the highest nucleation rates will be produced by grain-corner nucleation.

핵생성 구동력

ΔG_v

↓

increase

2) dominant nucleation sites:
grain edges → grain boundaries

3) At very high driving forces it may be possible for the (C_1/C_0) term to dominate and then homogeneous nucleation provides the highest nucleation rates.

* The above comments concerned nucleation during isothermal transformations (driving force for nucleation: [isothermal] constant ↔ [continuous cooling] increase with time)

Q4: Precipitate growth:

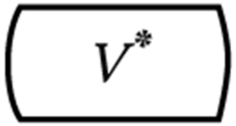
1) Growth behind Planar Incoherent Interfaces
2) Diffusion Controlled lengthening of Plates or Needles
3) Thickening of Plate-like Precipitates by Ledge Mechanism

5.3 Precipitate Growth

Initial precipitate shape
~minimizes the total interfacial free E

Precipitate growth → interface migration
: shape~determined by the relative migration rates

Coherent or semicoherent facets

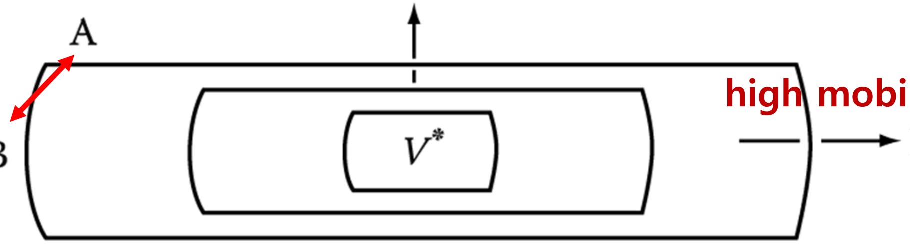


Smoothly curved incoherent interfaces

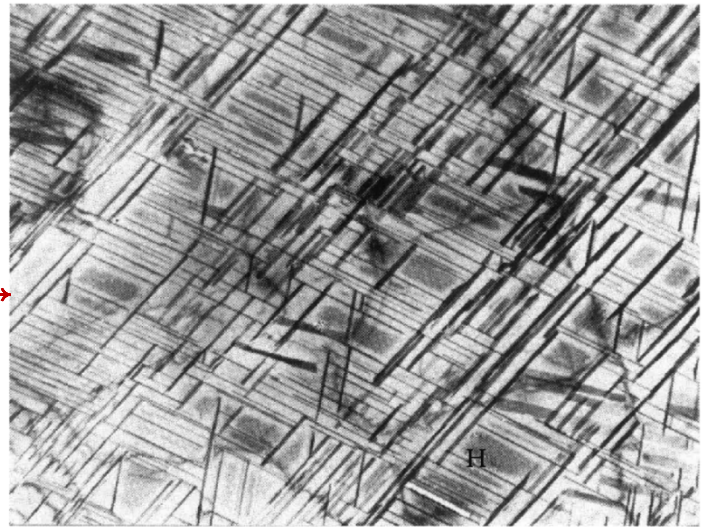
If the nucleus consists of semi-coherent and incoherent interfaces, what would be the growth shape?

Low mobility → Slow

Different crystal structures



high mobility → Fast



⇨ **Ledge mechanism**

Thin disk or plate

→ **Origin of the Widmanstätten morphology**

1) Growth behind Planar Incoherent Interfaces

Incoherent interface → **similar to rough interface**

→ **local equilibrium** → **diffusion-controlled**

Diffusion-Controlled Thickening: precipitate growth rate

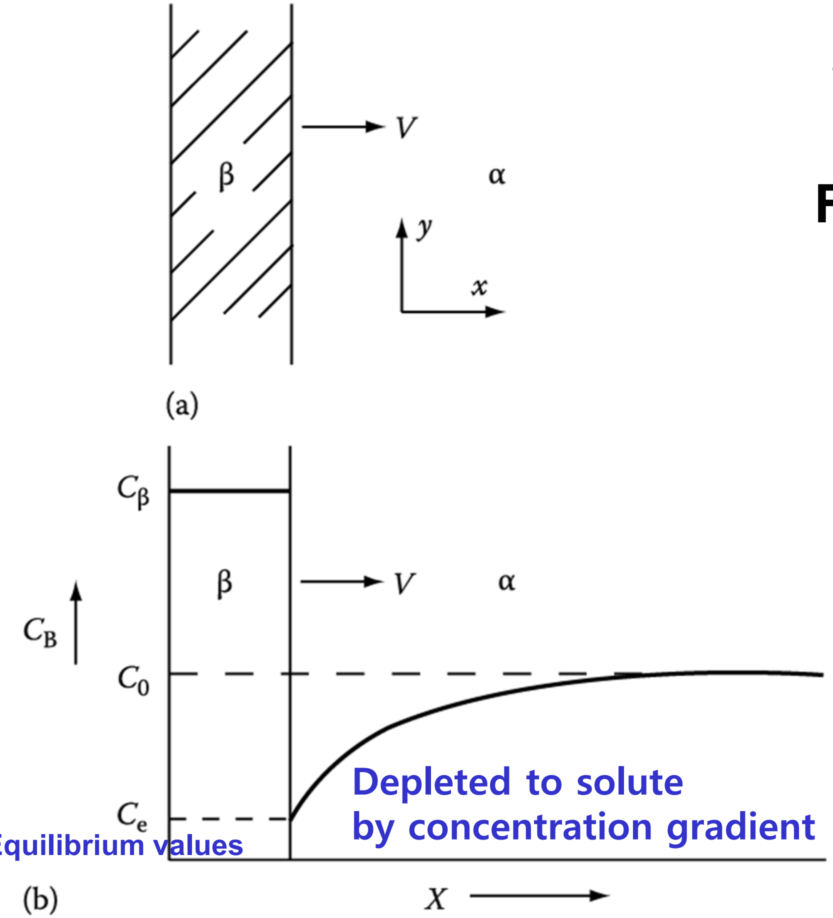


Fig. 5.14 Diffusion-controlled thickening of a precipitate plate.

$$\rightarrow v = f\,(\Delta T \text{ or } \Delta X, t)$$

From mass conservation,

$$(C_\beta - C_e)dx \text{ mole of } B$$
$$= J_B = D(dC/dx)dt$$

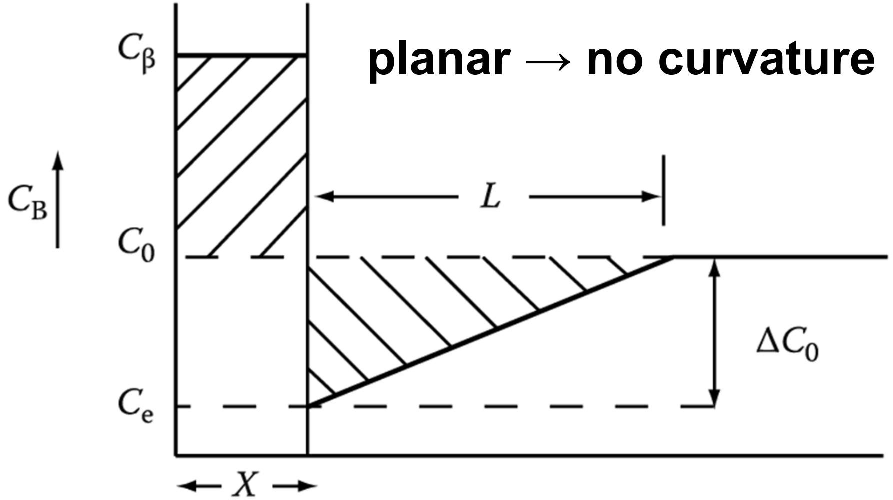
D: interdiffusion coefficient
or interstitial diffusion coeff.

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

Depends on the concentration gradient at the interface dC/dx

1) Growth behind Planar Incoherent Interfaces

Simplification of concentration profile **(Zener)**



planar → no curvature

Thickness of the slab

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

$$\boxed{dC/dx = \Delta C_0 / L} \leftarrow L = 2(C_\beta - C_0)x / \Delta C_0$$

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

(same area)

$$\boxed{v = \frac{D(\Delta C_0)^2}{2(C_\beta - C_e)(C_\beta - C_0)x}}$$

if $C_\beta - C_0 \cong C_\beta - C_e$ **and** $X = CV_m$ **,** $\quad \Delta C_0 \rightarrow \Delta X_0 = X_0 - X_e$

(simplification) Mole fractions

$$xdx = \frac{D(\Delta X_0)^2}{2(X_\beta - X_e)^2} dt \xrightarrow{\text{integral}} \boxed{x = \frac{\Delta X_0}{X_\beta - X_e}\sqrt{(Dt)}}$$

Thickness of the slab

$$x \propto \sqrt{(Dt)}$$

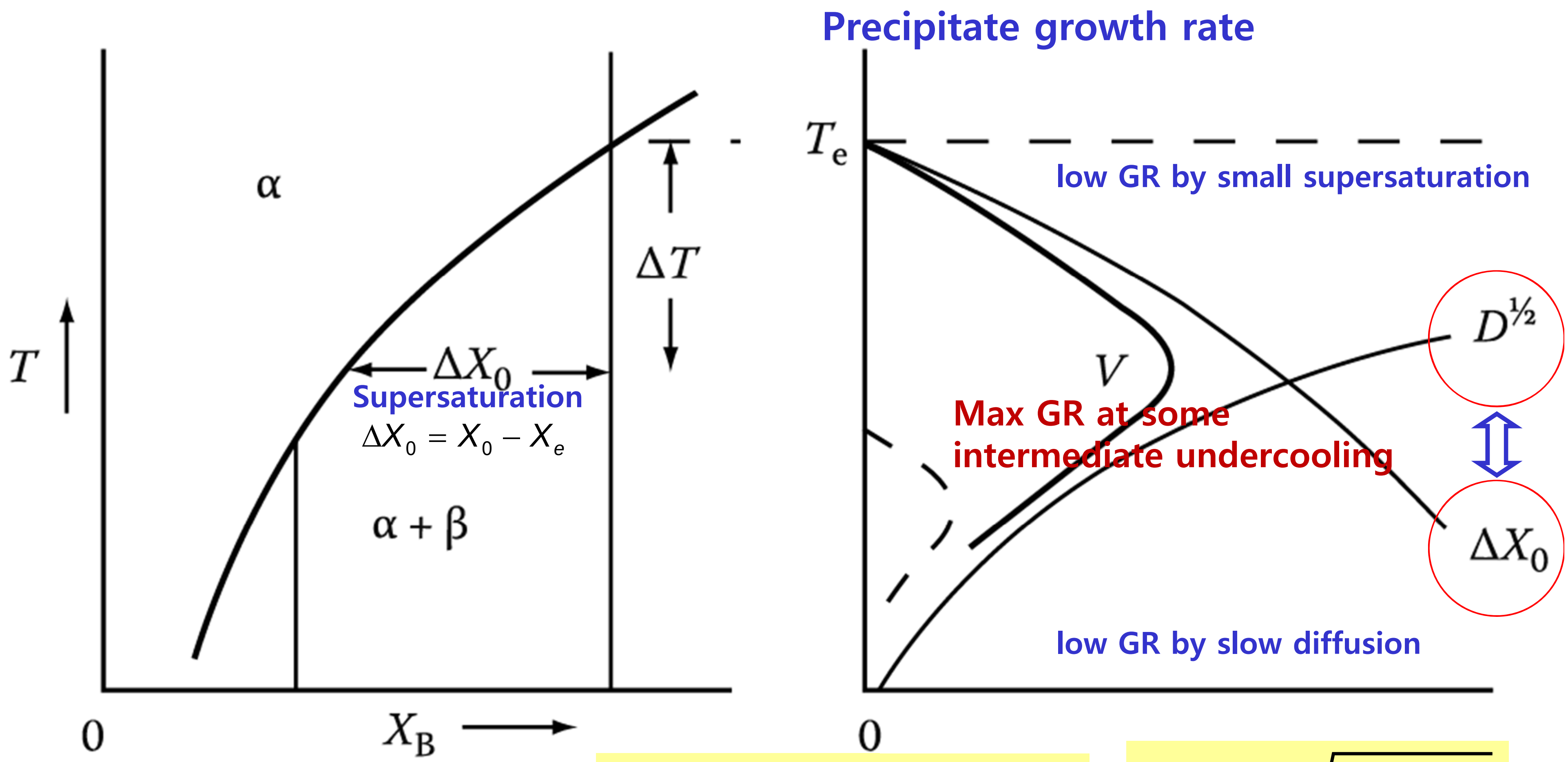
Parabolic growth

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

$$v \propto \Delta X_0, \quad v \propto \sqrt{(D/t)}$$

Growth rate ∝ supersaturation

1) Growth behind Planar Incoherent Interfaces

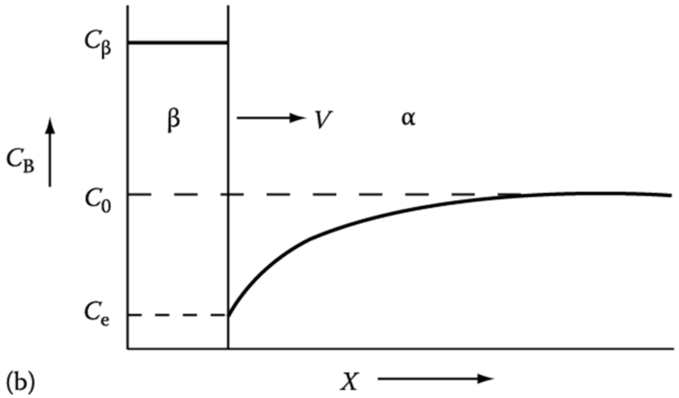


$$v \propto \Delta X_0 \propto \Delta T \qquad v \propto \sqrt{(D/t)}$$

Fig. 5.16 The effect of temperature and position on growth rate, v.

1) Growth behind Planar Incoherent Interfaces

Effect of "Overlap" of Separate Precipitates



Due to overlapping diffusion fields at later stage of growth, growth will decelerate more rapidly and finally cease when the matrix concentration is X_e everywhere.

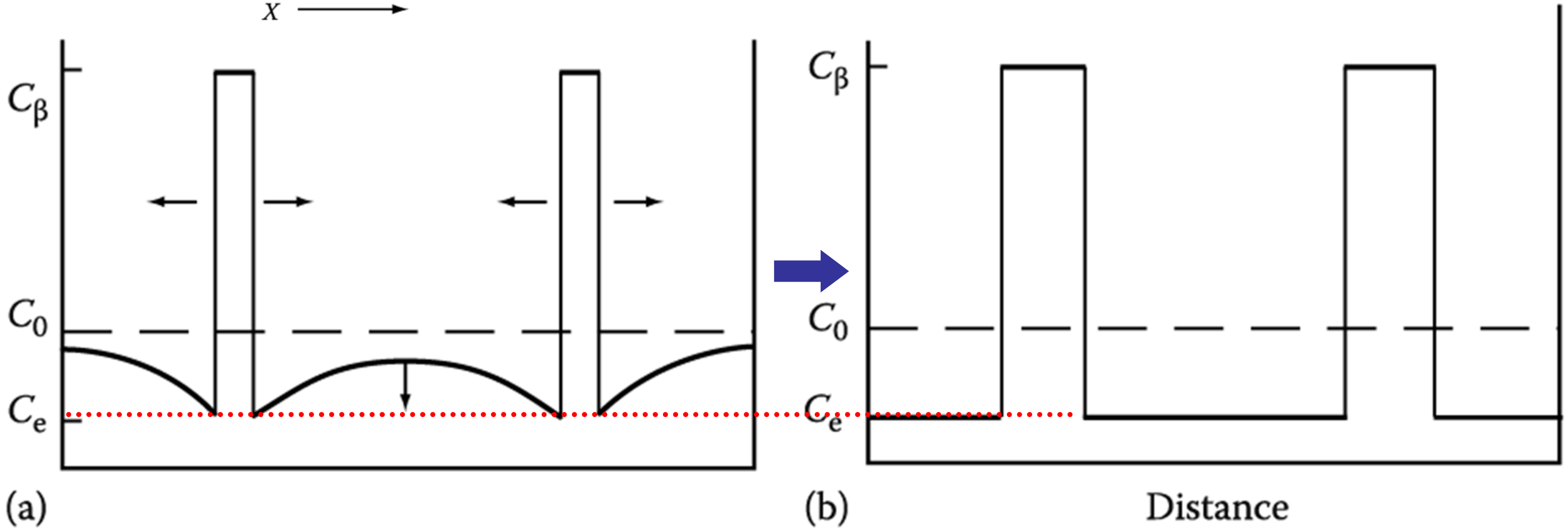
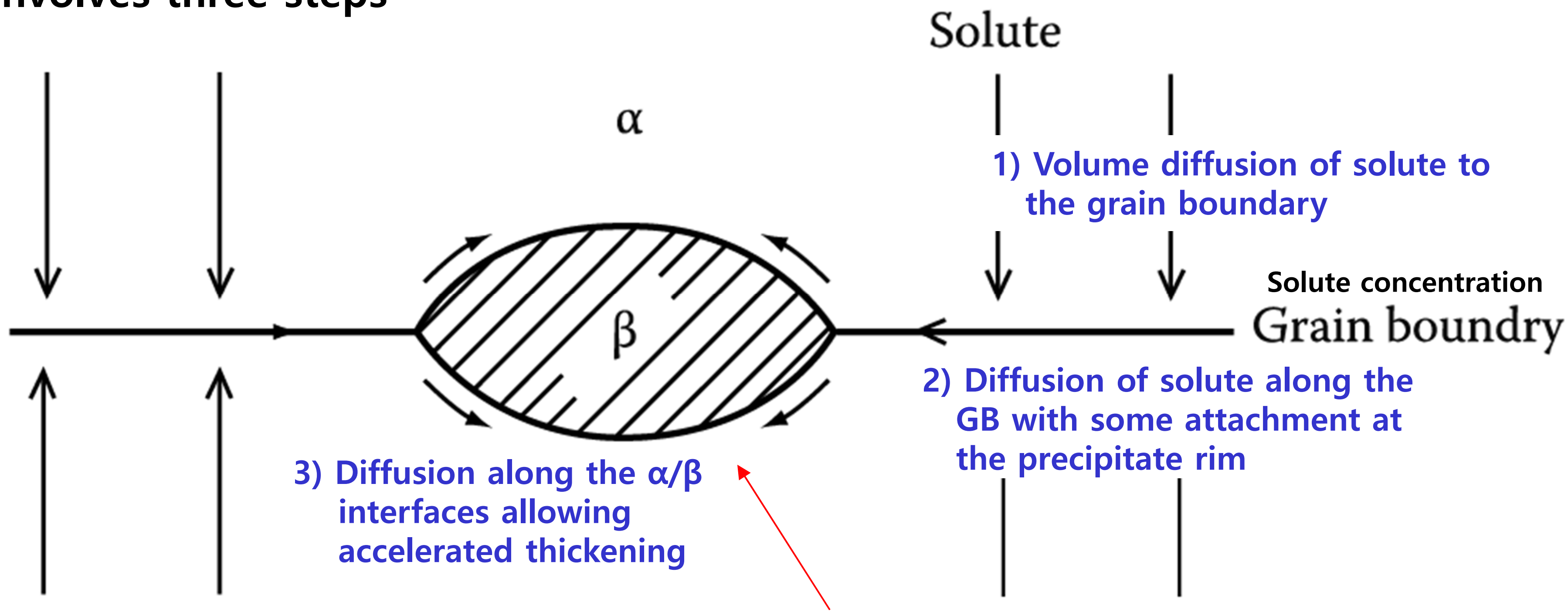


Fig. 5.17 (a) Interference of growing precipitates due to overlapping diffusion fields at later stage of growth. (b) Precipitate has stopped growing.

1) Growth behind Planar Incoherent Interfaces

Grain boundary precipitation involves three steps → **Faster than allowed by volume diffusion**



Grain boundary allotriomorph
입계타형

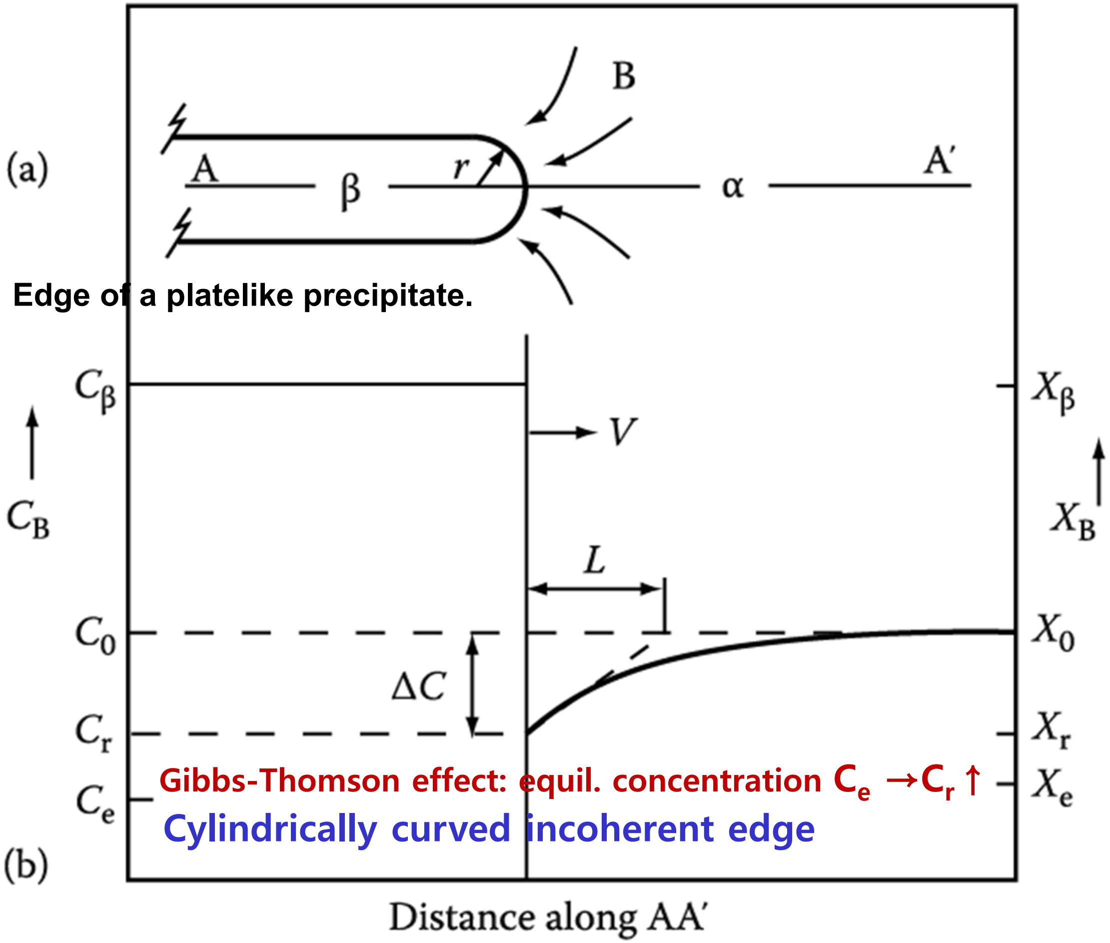
치환형 확산이 일어나는 경우 매우 중요/ 침입형 고용체에서는 체적 확산 속도가 크기 때문에
입계나 전위를 통한 단거리 확산은 상대적으로 중요하지 않음.

Fig. 5.18 Grain-boundary diffusion can lead to rapid lengthening and thickening of grain boundary precipitates, especially by substitutional diffusion.

2) Diffusion Controlled lengthening of Plates or Needles

Plate Precipitate of constant thickness

Volume diffusion-controlled continuous growth process



Edge of a platelike precipitate.

Concentration profile along AA' in (a).

From mass conservation,

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

$$\frac{dC}{dx} = \frac{\Delta C}{L} = \frac{C_0 - C_r}{kr}$$

Radial diffusion

k (const)~1

$$v = \frac{D}{C_\beta - C_r} \cdot \frac{\boxed{\Delta C}}{kr}$$

ΔX for diffusion ∝ edge radius of precipitate

(next page)

$$X = CV_m \qquad \Delta X = \Delta X_0 \left(1 - \frac{r^*}{r}\right)$$

r*=critical radius (if r=r*, ΔX→0)

$$v = \frac{D\boxed{\Delta X_0}}{k(X_\beta - X_r)} \cdot \frac{1}{r} \boxed{\left(1 - \frac{r^*}{r}\right)}$$

$v \rightarrow$ **constant** → $x \propto t$

(If t=2r, v= constant)

Linear growth

Needle → **Gibbs-Thomson increase in G = $2\gamma V_m/r$ instead of $\gamma V_m/r$**

→ **the same equation but the different value of r***

2) Diffusion Controlled lengthening of Plates or Needles

Volume diffusion-controlled continuous growth process/ curved ends

The Gobs-Thomson Effect : curvature of α/β interface~ extra pressure $\Delta P = 2\gamma/r$

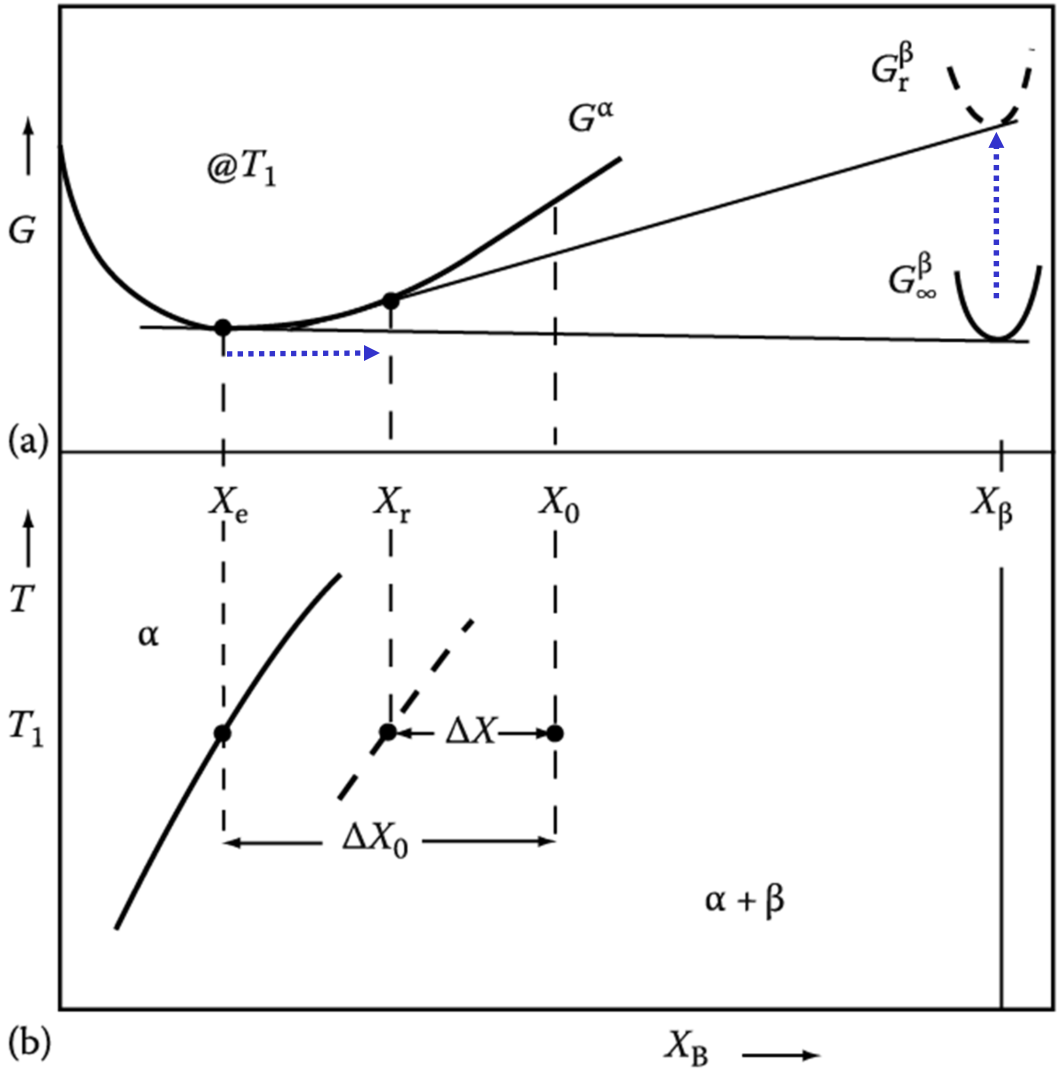


Fig. 5.20 Gibbs-Thomson effect.(a) Free E curves at T1. (b) corresponding phase diagram.

$\Delta G = \Delta P \cdot V \sim 2\gamma V_m / r$ ↑

Interfacial E → total free E ↑

$$\boxed{\Delta X = \Delta X_0 \left(1 - \frac{r^*}{r}\right)}$$

r^*: critical nucleus, radius

$$\Delta X = X_0 - X_r$$
$$\Delta X_0 = X_0 - X_e$$

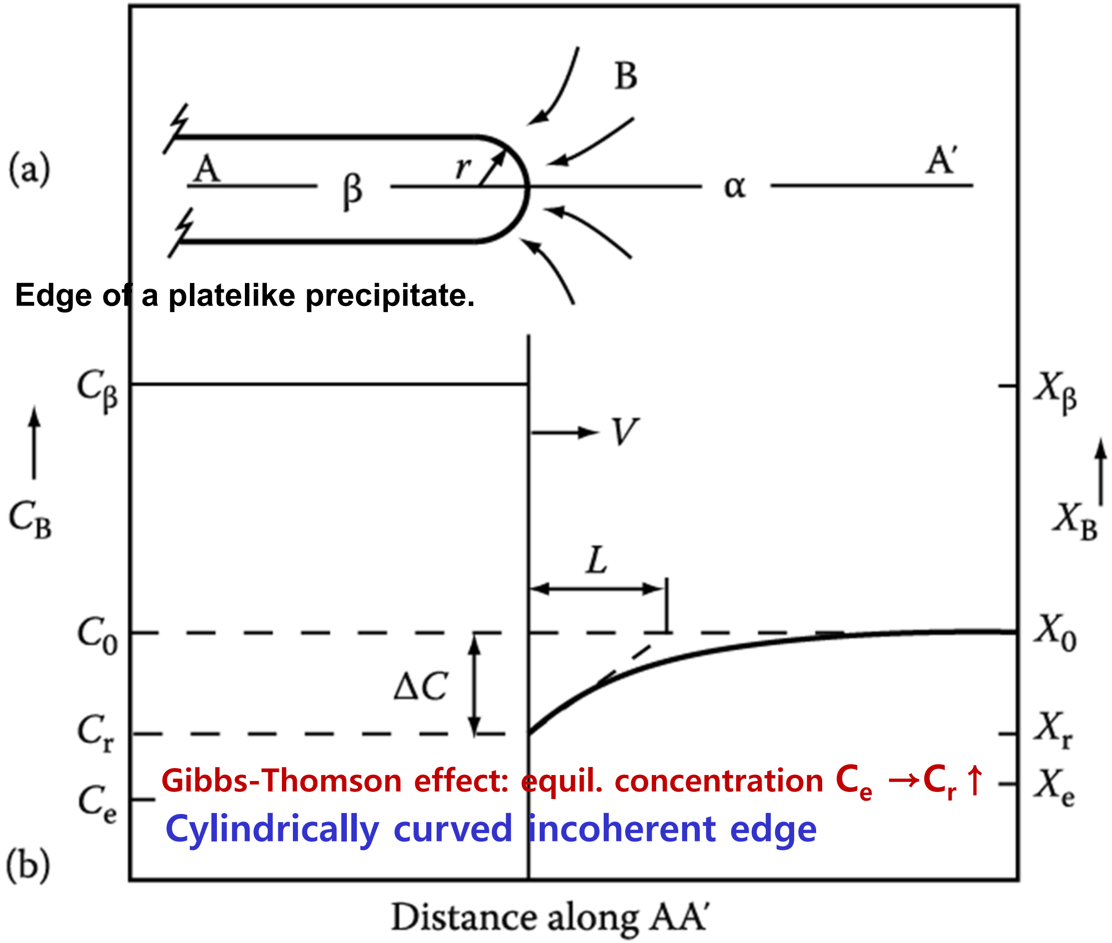
r ↑ ⟶ ΔX ↑

* In platelike precipitates, the edges are often faceted and observed to migrate by a ledge mechanism.

2) Diffusion Controlled lengthening of Plates or Needles

Plate Precipitate of constant thickness

Volume diffusion-controlled continuous growth process



Concentration profile along AA' in (a).

From mass conservation,

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

$$\frac{dC}{dx} = \frac{\Delta C}{L} = \frac{C_0 - C_r}{kr}$$

Radial diffusion
k (const)~1

$$V = \frac{D}{C_\beta - C_r} \cdot \frac{\boxed{\Delta C}}{kr}$$

ΔX for diffusion ∝ edge radius of precipitate

$$X = CV_m \qquad \Delta X = \Delta X_0 \left(1 - \frac{r^*}{r}\right)$$

r*=critical radius (if r=r*, ΔX→0)

$$\boxed{V = \frac{D\boxed{\Delta X_0}}{k(X_\beta - X_r)} \cdot \frac{1}{r} \boxed{\left(1 - \frac{r^*}{r}\right)}}$$

$V \rightarrow$ **constant** $\rightarrow$ $x \propto t$

(If t=2r, v= constant)

Linear growth

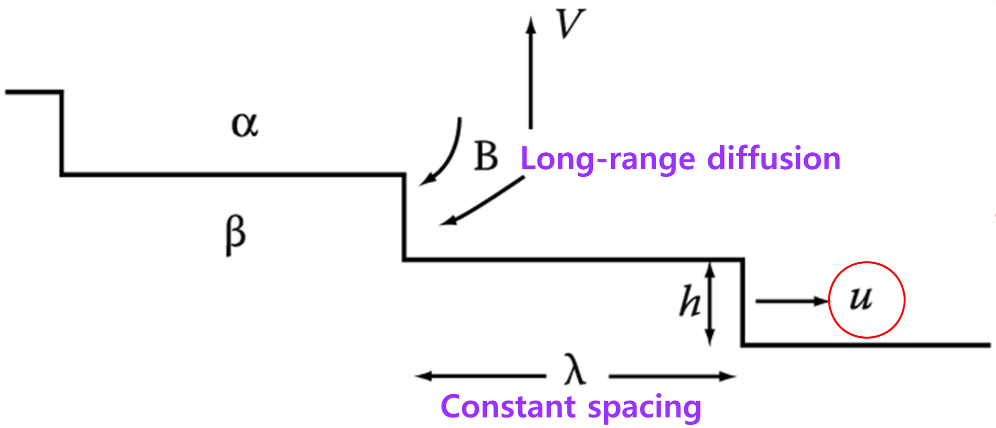
Needle → **Gibbs-Thomson increase in G = 2γV_m/r instead of γV_m/r**

→ **the same equation but the different value of r***

3) Thickening of Plate-like Precipitates

Thickening of Plate-like Precipitates by Ledge Mechanism

↔ planar incoherent interface with high accommodation factors



- For the diffusion-controlled growth, a monoatomic-height ledge should be supplied constantly.
- sources of monatomic-height ledge → spiral growth, 2-D nucleation, nucleation at the precipitate edges, or from intersections with other precipitates (heterogeneous 2-D)

Half Thickness Increase

$$v = \frac{uh}{\lambda}$$

u : rate of lateral migration

$$v = \frac{D}{C_\beta - C_r} \cdot \frac{\Delta C}{kr}$$

If the edges of the ledges are incoherent,

Assuming the diffusion-controlled growth,

very similar to that of plate lengthening

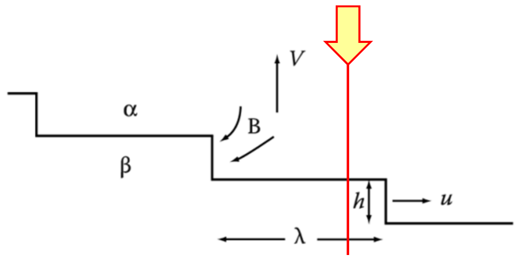
$$u = \frac{D\Delta X_0}{k(X_\beta - X_e)h} \xrightarrow{v = \frac{uh}{\lambda}} v = \frac{D\Delta X_0}{k(X_\beta - X_e)\lambda}$$

(Here, h= r and X_r = X_e, no Gibbs-Thomson effect)

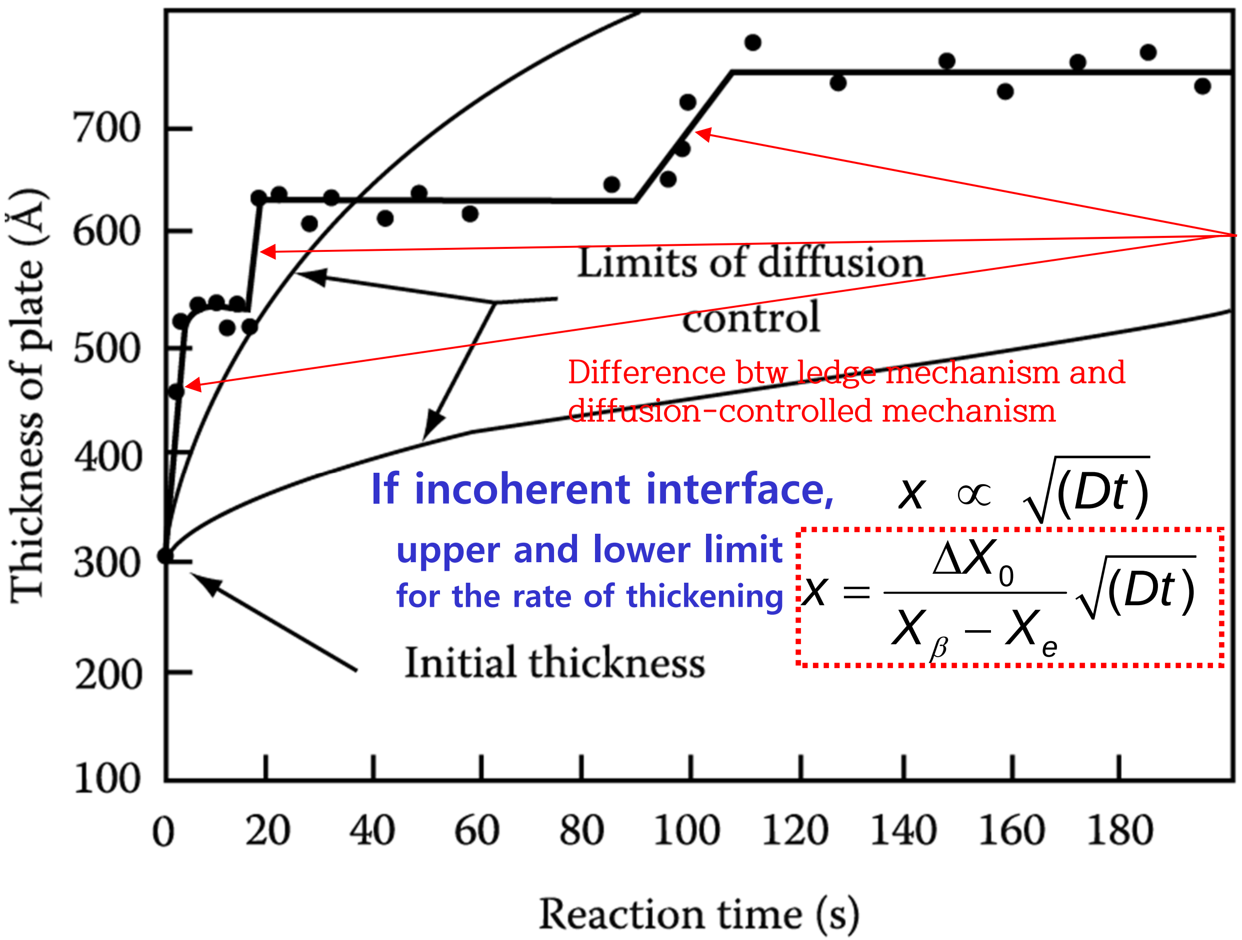
Distance btw ledges

3) Thickening of Plate-like Precipitates

Except spiral growth, supplement of ledge with constant λ is difficult.



Thickening of γ Plate in the Al-Ag system



What does this data mean?

appreciable intervals of time

(no perceptible increase in plate thickness)

& thickness increases rapidly as an interfacial ledge passes.

⬇

Evidence for the low mobility of semi-coherent interfaces

⬇

Thickening rate is not constant

"Ledge nucleation" is rate controlling.

Fig. 5. 22 The thickening of a γ plate in an Al-15 wt% Ag alloy at 400 ℃

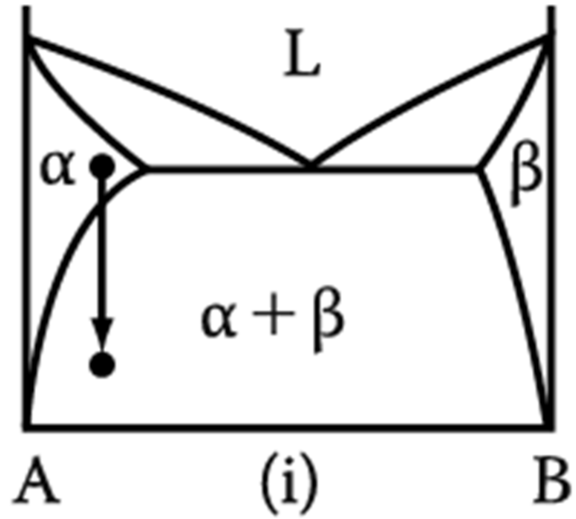
measure the thickening rates of individual precipitate plates by using hot-stage TEM.

Contents for today's class

< Phase Transformation in Solids >

1) Diffusional Transformation

(a) Precipitation



Homogeneous Nucleation

➡ Effect of misfit strain energy

$$\Delta G = \boxed{-V\Delta G_V} + \boxed{A\gamma + V\Delta G_S}$$

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

$$N_{\text{hom}} = \omega C_0 \boxed{\exp\left(-\frac{\Delta G_m}{kT}\right)} \boxed{\exp\left(-\frac{\Delta G^*}{kT}\right)}$$

Heterogeneous Nucleation

➡ suitable nucleation sites ~ nonequilibrium defects

(creation of nucleus~destruction of a defect($-\Delta G_d$))

$$\boxed{\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d}$$

$$\frac{\Delta G^*_{het}}{\Delta G^*_{\text{hom}}} = \frac{V^*_{het}}{V^*_{\text{hom}}} = S(\theta)$$

$$\boxed{\frac{N_{het}}{N_{\text{hom}}} = \frac{C_1}{C_0} \exp\left(\frac{\Delta G^*_{\text{hom}} - \Delta G^*_{het}}{kT}\right)}$$

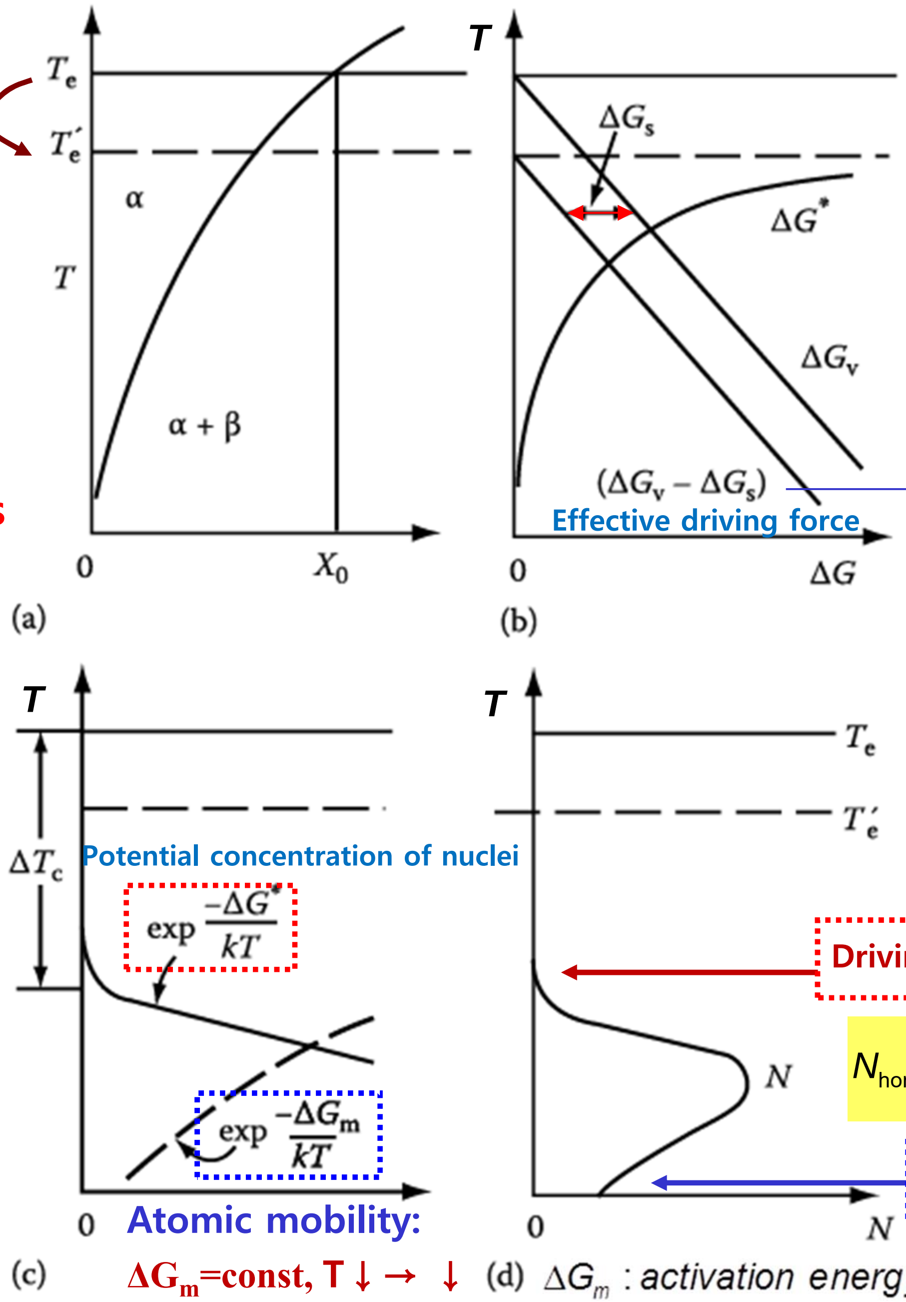
Rate of Homogeneous Nucleation Varies with undercooling below T_e for alloy X_0

Effective equilibrium temperature is reduced by misfit strain E term, ΔGs.

Thermodynamics

vs

Kinetics



$$\Delta G_V \propto \Delta X \propto \Delta T$$

Composition dependent

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

Resultant energy barrier for nucleation

Driving force ΔG_v~too small → N~negligible

$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Diffusion~too slow → N~negligible

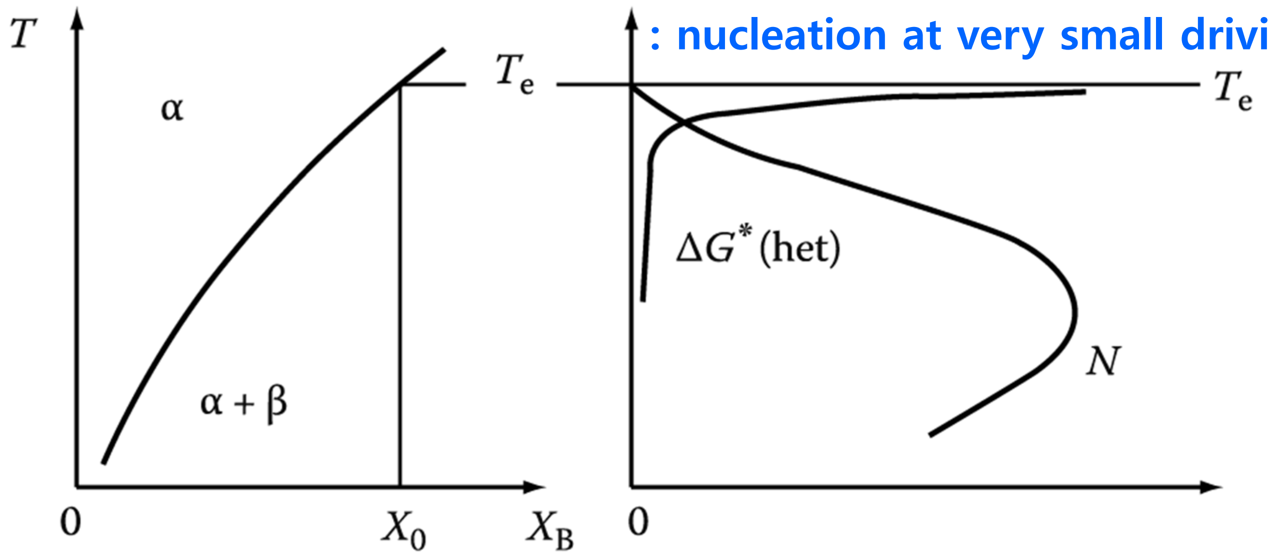
Atomic mobility:

ΔG_m=const, T ↓ → ↓

ΔG_m : *activation energy for atomic migration*

Heterogeneous Nucleation in Solids

The Rate of Heterogeneous Nucleation during Precipitation



* Relative magnitudes of the heterogeneous and homogeneous volume nucleation rates

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0}\exp\left(\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT}\right)$$

ω 와 ΔG_m의 차이는 미비하여 무시

ΔG* ~ always smallest for heterogeneous nucleation ⇨ Exponential factor : very large quantity ⇨ $\frac{N_{het}}{N_{hom}} > 1$ High heterogeneous nucleation rate

But, The factor C_1/C_0 ?

Heterogeneous Nucleation in Solids

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0}\exp\left(\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT}\right)$$

C_1/C_0 for Various Heterogeneous Nucleation Sites

각각의 핵생성처에서 경쟁적으로 핵생성 발생: 구동력 조건에 따라 전체 핵생성 속도에 dominant하게 영향을 미치는 site 변화

Grain boundary	Grain edge	Grain corner	Dislocations		Excess vacancies
$D = 50\ \mu m$	$D = 50\ \mu m$	$D = 50\ \mu m$	$10^5\ mm^{-2}$	$10^8\ mm^{-2}$	$X_v = 10^{-6}$
10^{-5}	10^{-10}	10^{-15}	10^{-8}	10^{-5}	10^{-6}

In order to make nucleation occur exclusively on the grain corner, how should the alloy be cooled?

1) At very small driving forces (ΔG_v), when activation energy barriers for nucleation are high, the highest nucleation rates will be produced by grain-corner nucleation.

핵생성 구동력 ΔG_v ↓ increase

2) dominant nucleation sites: grain edges → grain boundaries

3) At very high driving forces it may be possible for the (C_1/C_0) term to dominate and then homogeneous nucleation provides the highest nucleation rates.

* The above comments concerned nucleation during isothermal transformations (driving force for nucleation: [isothermal] constant ↔ [continuous cooling] increase with time)

- ## Precipitate growth

1) Growth behind Planar Incoherent Interfaces

Diffusion-Controlled Thickening: $x \propto \sqrt{(Dt)}$ **Parabolic growth**

$$v = \frac{D(\Delta C_0)^2}{2(C_\beta - C_e)(C_\beta - C_0)x}$$

$$v \propto \Delta X_0 \propto \sqrt{(D/t)}$$

Supersaturation

2) Diffusion Controlled lengthening of Plates or Needles

Diffusion Controlled lengthening:

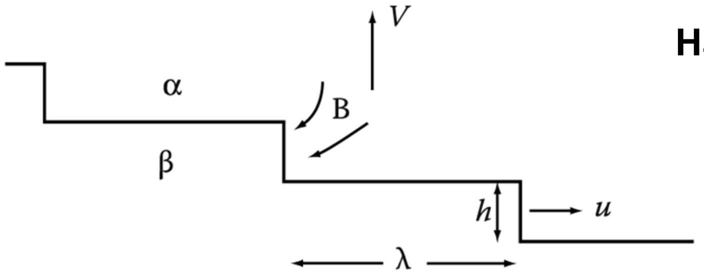
$$v = \frac{D\boxed{\Delta X_0}}{k(X_\beta - X_r)} \cdot \frac{1}{r}\boxed{\left(1 - \frac{r^*}{r}\right)}$$

$v \rightarrow$ **constant** $\rightarrow$ $x \propto t$

Linear growth

3) Thickening of Plate-like Precipitates

Thickening of Plate-like Precipitates by Ledge Mechanism



Half Thickness Increase

$$v = \frac{uh}{\lambda} \longrightarrow v = \frac{D\Delta X_0}{k(X_\beta - X_e)\lambda}$$

u : rate of lateral migration