2009 fall

Phase Transformation of Materials

11. 26. 2009

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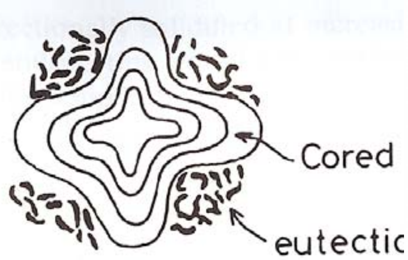
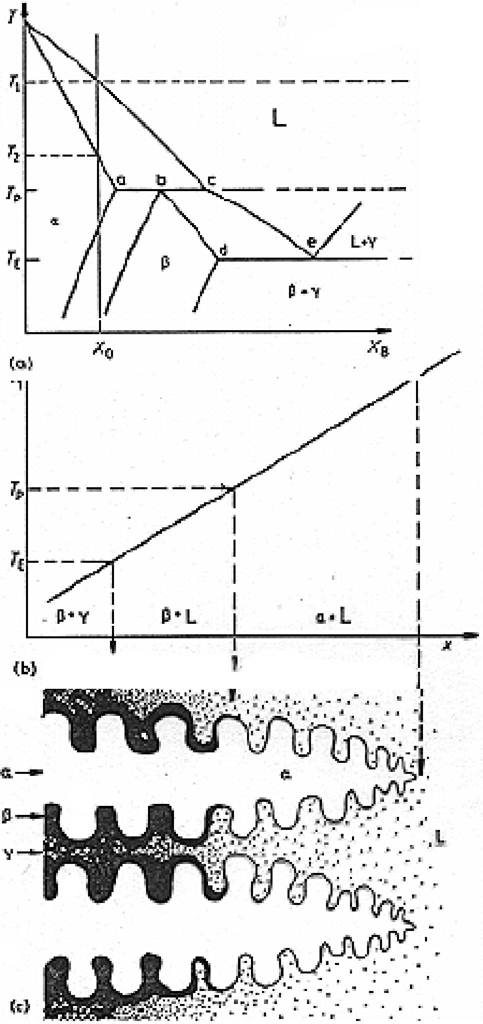
Contents for previous class

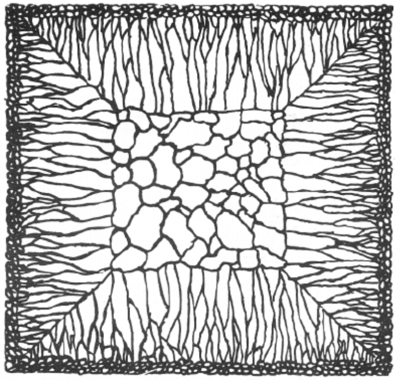
4.3 Alloy solidification





- Solidification of single-phase alloys
- Eutectic solidification
- Off-eutectic alloys   primary α (coring) + eutectic lamellar
- Peritectic solidification- $L + \alpha \rightarrow \beta$, difficult to complete.

4.4 Solidification of ingots and castings



- Ingot structure

  Chill Zone, Columnar Zone, Equiaxed Zone

- Segregation in ingot and castings

  Composition changes over distances

- Continuous casting

  Vertical, Curved, Horizontal contiuous casting/ Strip casting

4.6 Solidification during quenching from the melt

** T_g depends on thermal history.- Kinetic nature of the glass transition*

** Glass formation: Liquid stability + Formation of crystalline phase ➡ BMG*

** Are amorphous matal useful? ➡ At the Cutting Edge of Metals Research*

Contents in Phase Transformation

상변태를
이해하는데
필요한 배경

- **(Ch1)** 열역학과 상태도**: Thermodynamics**
- **(Ch2)** 확산론**: Kinetics**
- **(Ch3)** 결정계면과 미세조직

대표적인 상변태

- **(Ch4)** 응고**: Liquid → Solid**
- **(Ch5)** 고체에서의 확산 변태**: Solid → Solid** (Diffusional)
- **(Ch6)**고체에서의 무확산 변태**: Solid → Solid (Diffusionless)**

< Phase Transformation in Solids >

1) Diffusional Transformation

2) Non-diffusional Transformation (Athermal Transformation)

From what we've learned, what can we say roughly about diffusional transformation in solid?

1) Thermally-activated process: rate $\propto$ exp $(-\Delta G^{*}/kT)$

2) Misfit strain energy ⬅ lattice distortion

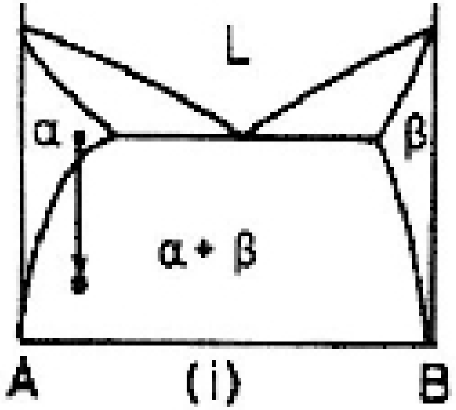
3) Kinetic path for low nucleation barrier
→ coherent or semi-coherent interfaces
→ heterogeneous nucleation

4) Local equilibrium for incoherent (rough) interfaces
→ diffusion-controlled growth

5. Diffusion Transformations in solid

(a) Precipitation

$$\alpha' \rightarrow \alpha + \beta$$



Homogeneous Nucleation

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

Heterogeneous Nucleation

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

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

➡ 적합한 위치는 격자결함

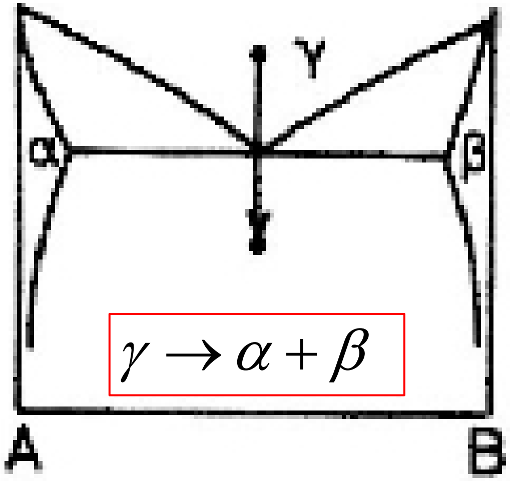
(핵생성이 격자결함 제거 역할)

(b) Eutectoid Transformation

Composition of product phases differs from that of a parent phase.

→ **long-range diffusion**

Which transformation proceeds by short-range diffusion?

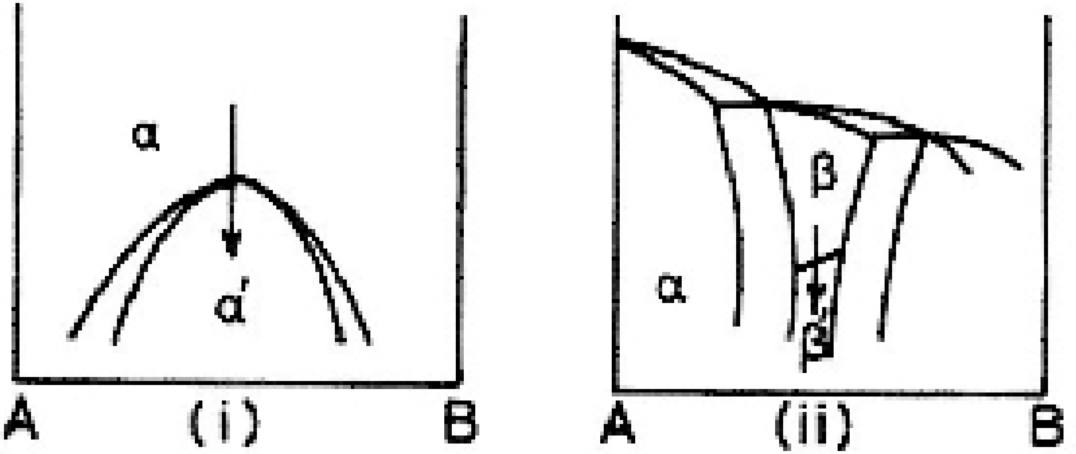


$$\gamma \rightarrow \alpha + \beta$$

5. Diffusion Transformations in solid

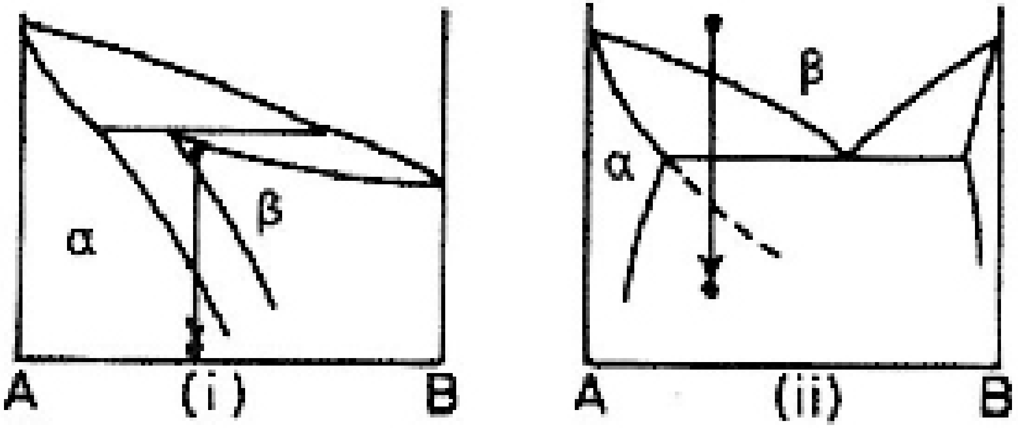
(c) Order-Disorder Transformation

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



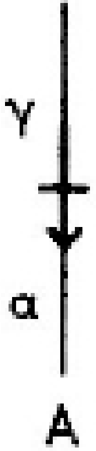
(d) Massive Transformation

: 조성 변화 없이 결정구조가 다른 당상 또는 다상으로 분해



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

(e) Polymorphic Transformation



: 온도 범위에 따라 서로다른 결정구조가 안정

Homogeneous Nucleation in Solids

Free Energy Change Associated with the Nucleation

Negative and Positive Contributions to ΔG?

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

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

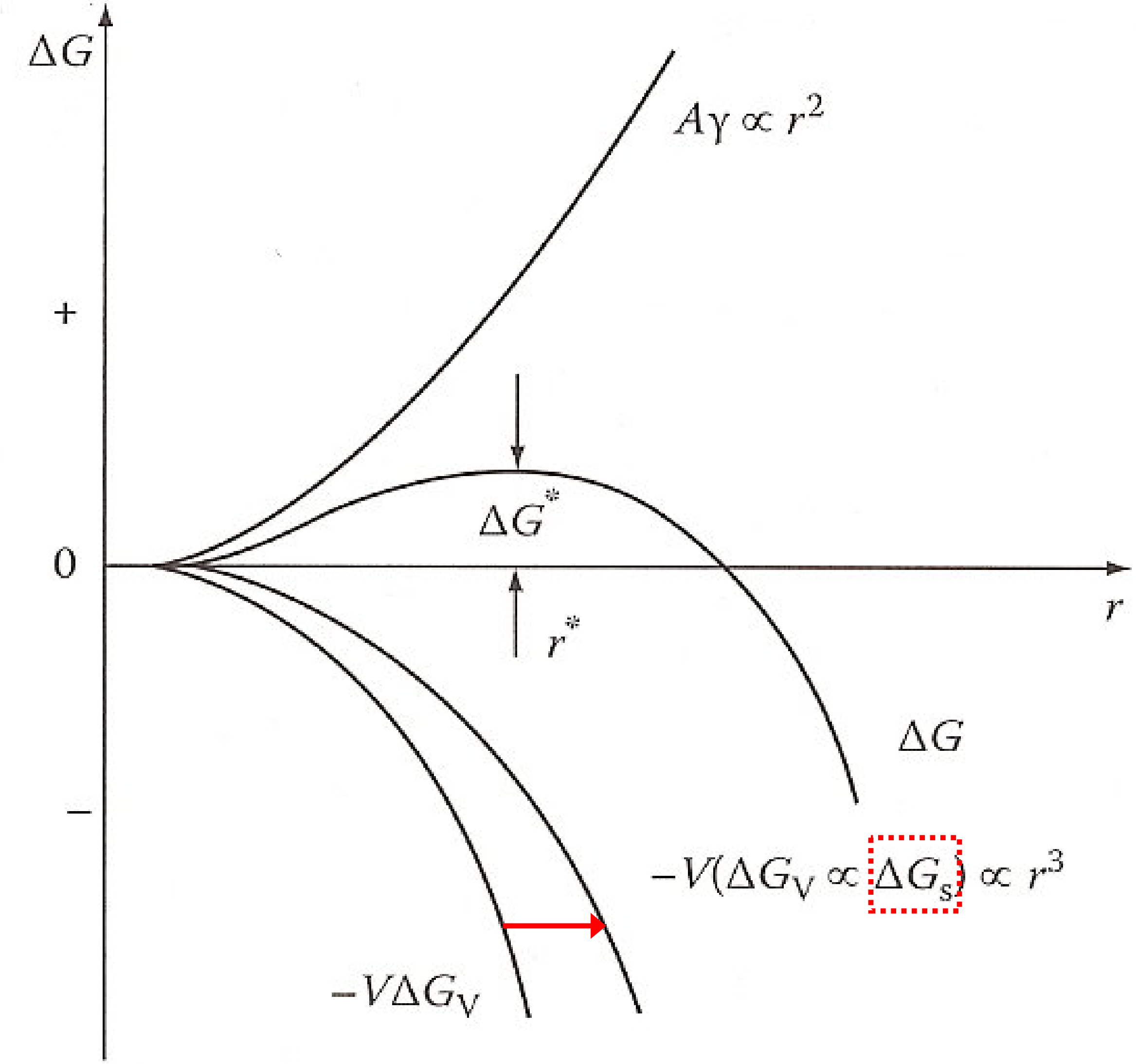
$$\Delta G = -\frac{4}{3}\pi r^3(\Delta G_V - \Delta G_S) + 4\pi r^2\gamma$$

Plot of ΔG vs r?

r* = ?

ΔG* = ?

Homogeneous Nucleation in Solids



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

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

: driving force for nucleation

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 : 단위체적당 임계 크기를 갖는 핵의 수

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

C_0 : number of atoms per unit volume in the phase

Nucleation Rate

: 각각의 핵이 단위 시간당 f의 빈도로 임계크기 값 보다 커진다면,

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

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

: f는 임계핵이 얼마나 빈번히 모상 α로부터 원자를 공급받는가에 따라 변하는 함수

$$\omega \propto \textit{vibration frequency, area of critical nucleus}$$

$$\Delta G_m : \textit{activation energy for atomic migration}$$

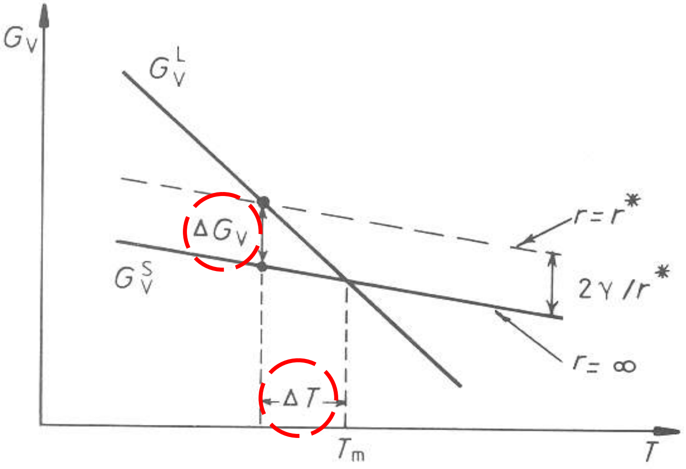
$$N_{\text{hom}} = \boxed{\omega} C_0 \exp\left(-\frac{\boxed{\Delta G_m}}{kT}\right) \exp\left(-\frac{\boxed{\Delta G^*}}{kT}\right)$$

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

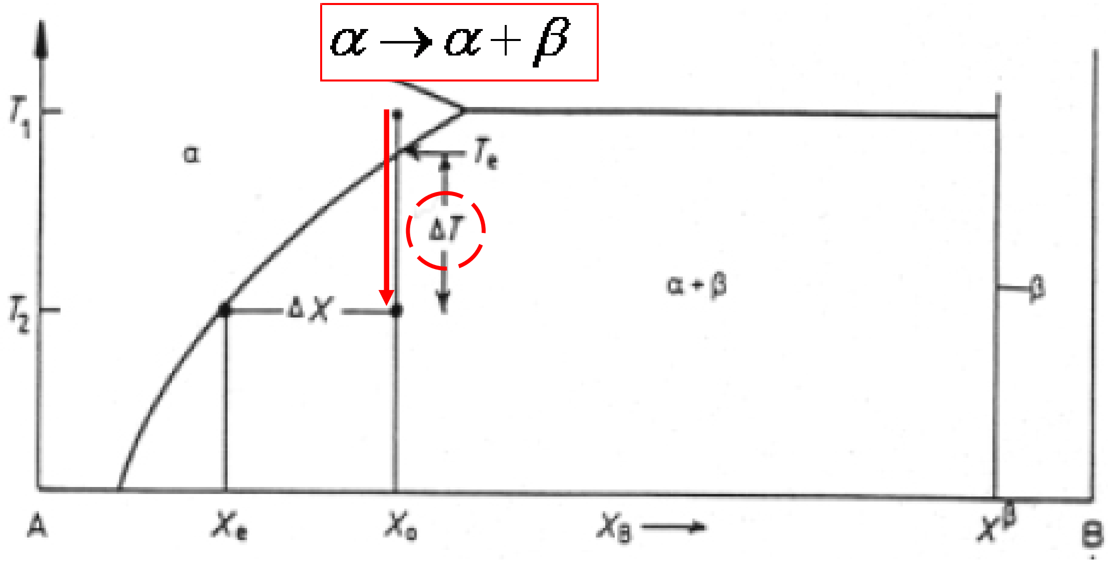
: T에 민감하게 변함

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

$\Delta G^* \propto \Delta G_V$ (화학적 구동력)



Liquid → Solid



1) For X_0, solution treatment at T_1

2) For X_0, quenching down to T_2

α → α + β : B 성분이 과포화되어 β 석출

ΔG_V (화학적 구동력)는 조성에 따라 변함

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: 변태를 위한 전체 구동력/핵생성을 위한 구동력은 아님

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$

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

: 핵의 조성(X_B^β)을 갖는 작은 양이 제거될 때 단위 몰당 자유E 변화 (P point)

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

: β상 생성시 단위 몰당 자유E 변화 (Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}$$

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

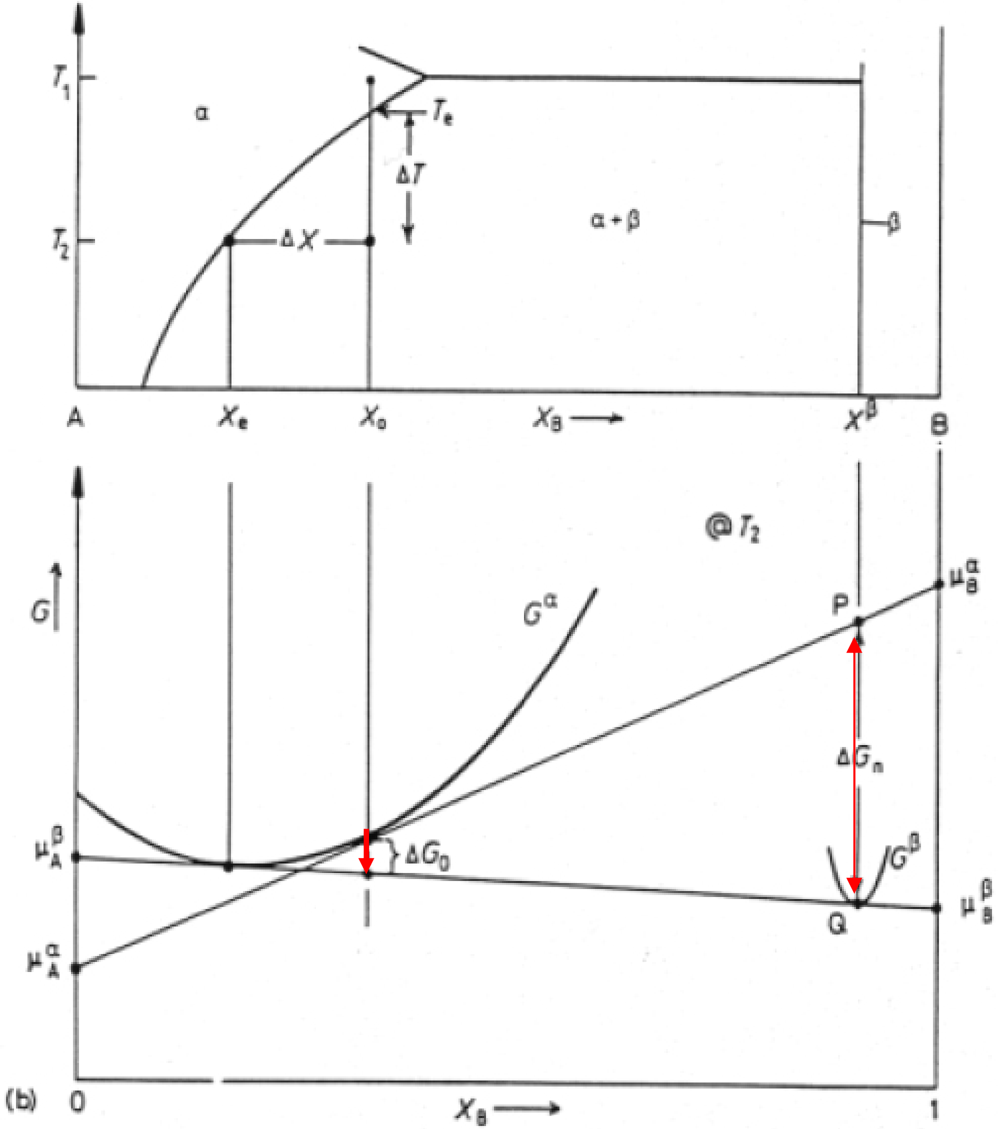
: driving force for nucleation

For dilute solutions,

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

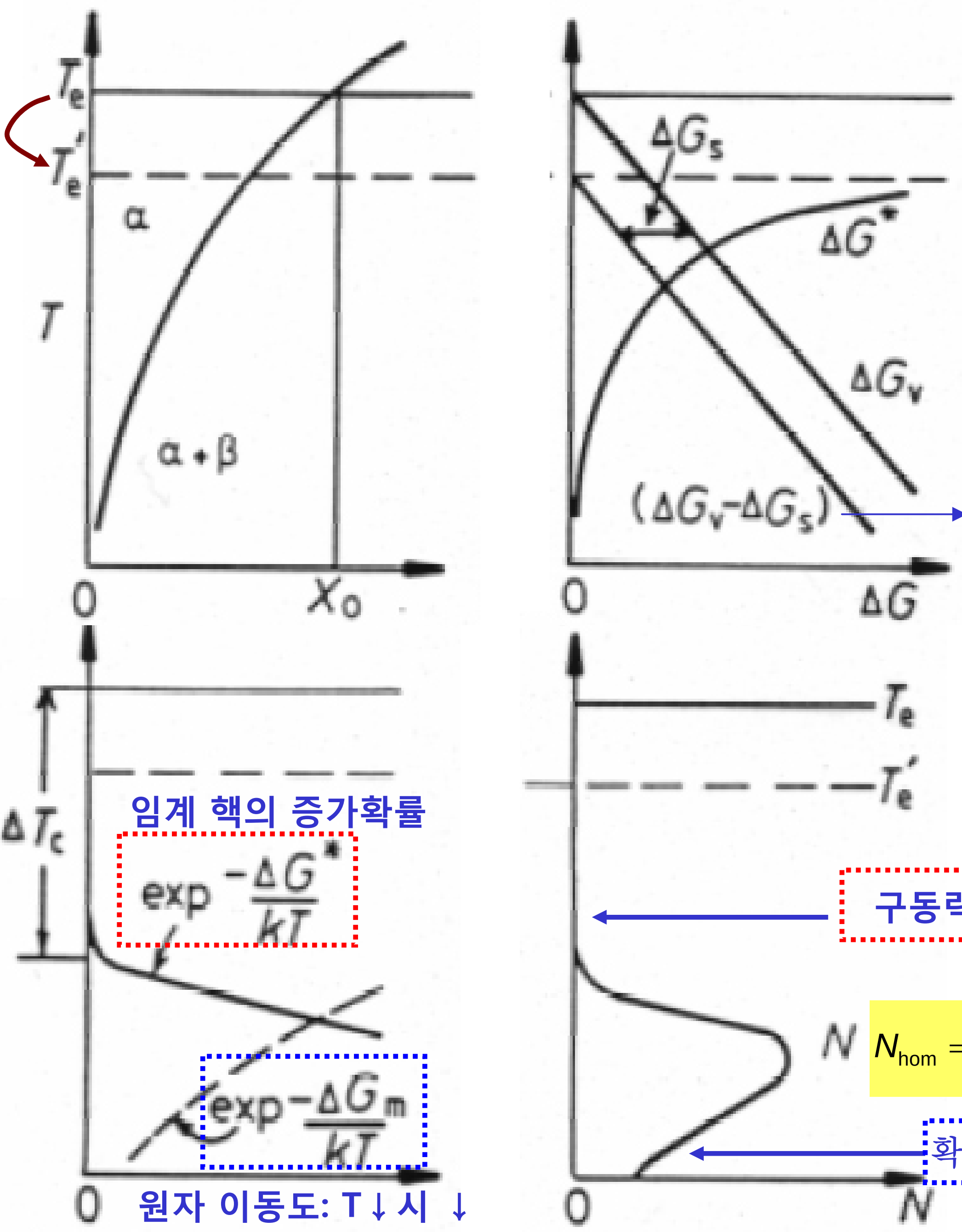
$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

: driving force for nucleation



Rate of Homogeneous Nucleation Varies with Undercooling

실제의 평형온도
ΔGs 에 의해 감소



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

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

임계 핵의 증가확률

구동력 ΔGv 너무 작으므로 N ↓

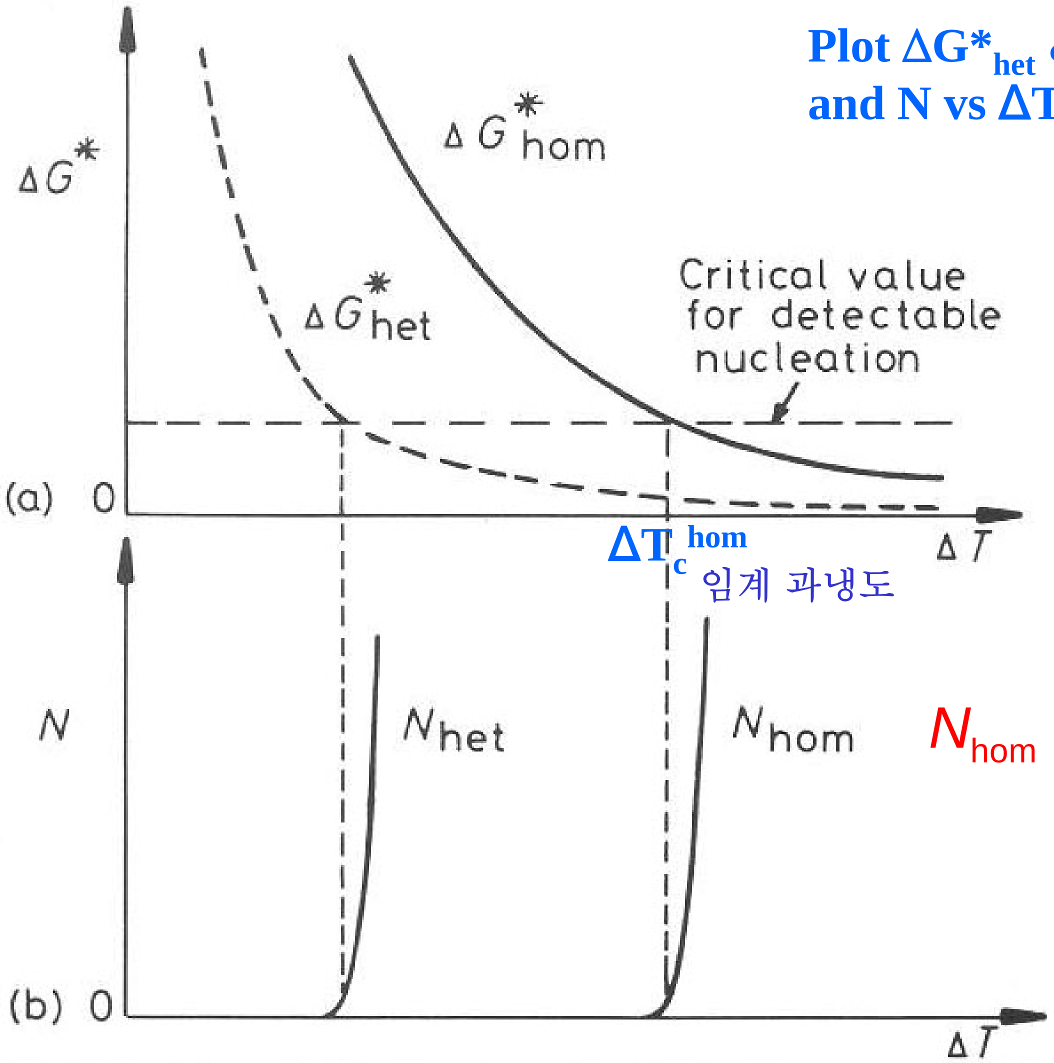
$$N_{hom} = \omega C_0 \exp\left(-\frac{\Delta G_m}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

확산이 너무 느리기 때문에 N ↓

원자 이동도: T↓시 ↓

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom}?

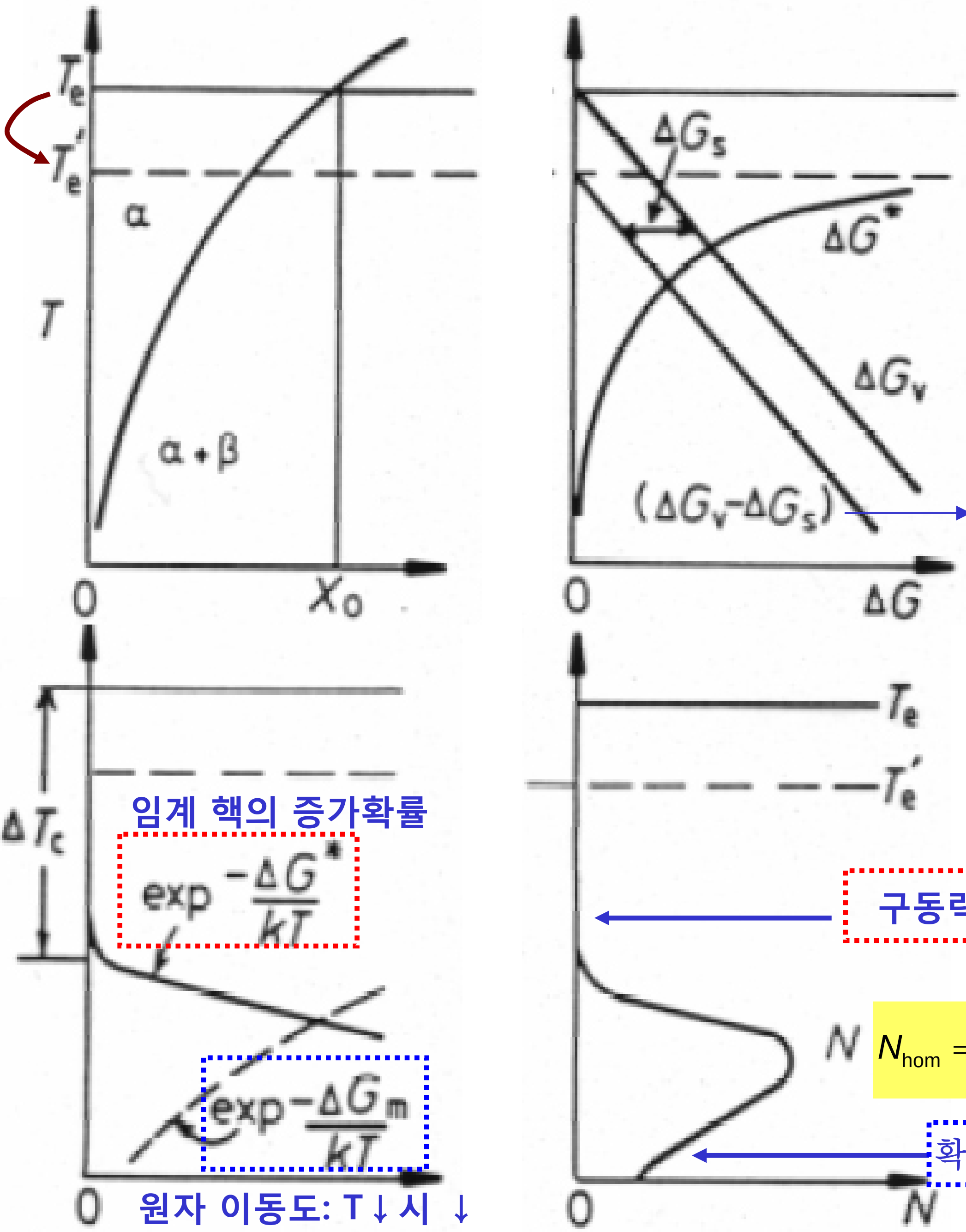
Plot ΔG^*_{het} & ΔG^*_{hom} vs ΔT and N vs ΔT.



$$N_{hom} \approx 1\ \mathrm{cm}^{-3} s^{-1}$$

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^*

Rate of Homogeneous Nucleation Varies with Undercooling



실제의 평형온도 ΔGs 에 의해 감소

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

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

임계 핵의 증가확률

원자 이동도: T↓ 시 ↓

중간정도 과냉에서 N 최대

구동력 ΔGv 너무 작으므로 N ↓

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

확산이 너무 느리기 때문에 N ↓

Homogeneous Nucleation in Solids

The Effect of Alloy Composition on the Nucleation Rate

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

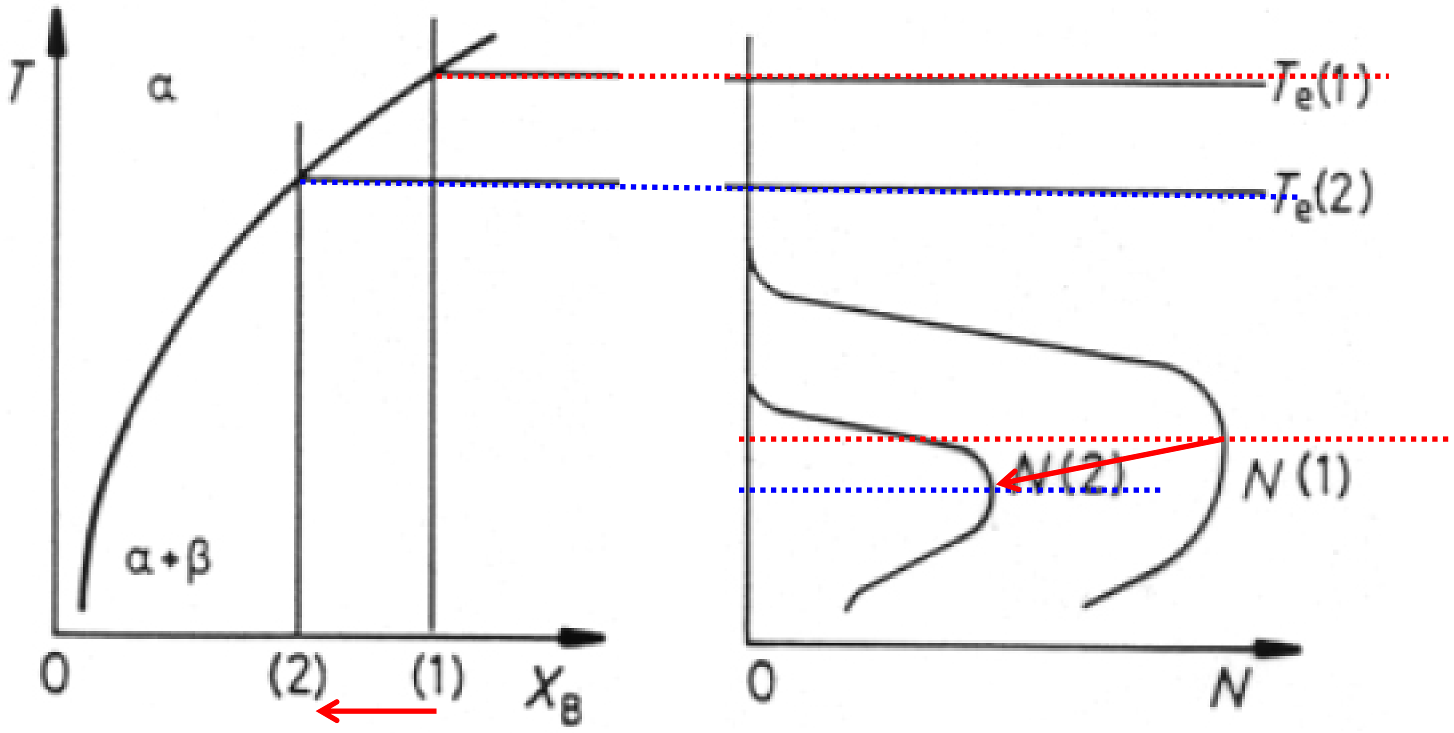


Fig. 5.5 The effect of alloy composition on the nucleation rate. The nucleation rate in alloy 2 is always less than in alloy 1.

Heterogeneous Nucleation in Solids

➡ 대부분의 핵생성이 해당, 적합한 위치는 격자결함 (핵생성이 격자결함 제거 역할)

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

Nucleation on Grain Boundaries

가정: ΔG_S (불일치 변형 에너지)= 0,

핵의 모양 전체 계면 자유에너지를 최소로 하는 상태

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

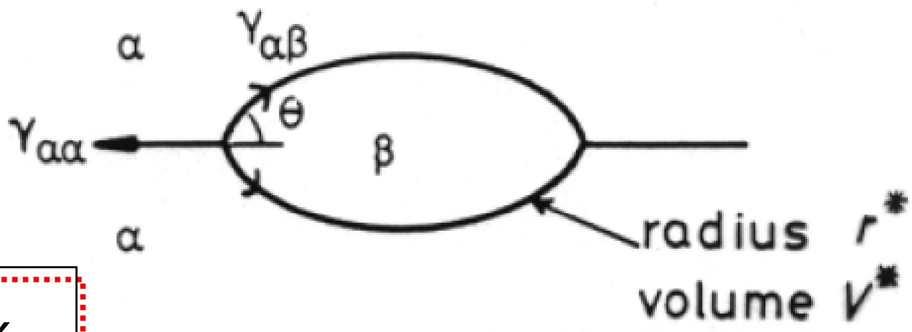
$$\boxed{\Delta G = -V\Delta G_V + A_{\alpha\beta}\gamma_{\alpha\beta} - \boxed{A_{\alpha\alpha}\gamma_{\alpha\alpha}}}$$

주형벽에서 불균일 핵생성에 의한 응고와 유사

구형 모자 형태 핵의 임계 반경

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

입계에서 핵생성이 일어날 때 입계에서 핵생성의 크기



불균일 핵생성에 필요한 활성화에너지 장벽

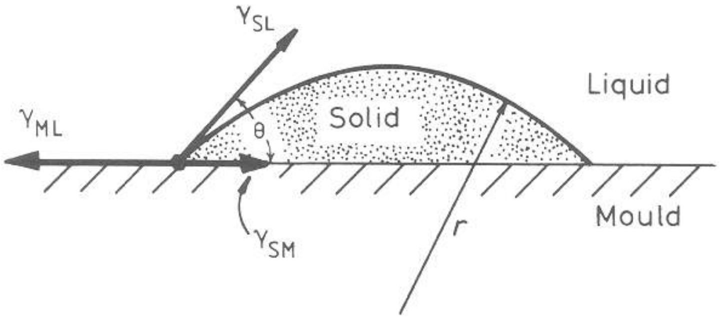
$$\frac{\Delta G^*_{het}}{\Delta G^*_{hom}} = \frac{V^*_{het}}{V^*_{hom}} = S(\theta)$$

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

Barrier of Heterogeneous Nucleation

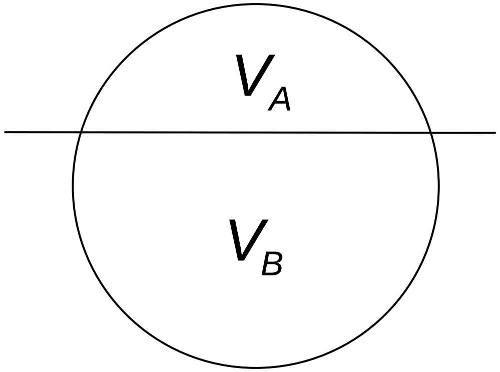
$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

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



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

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



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

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

Heterogeneous Nucleation in Solids

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

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

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

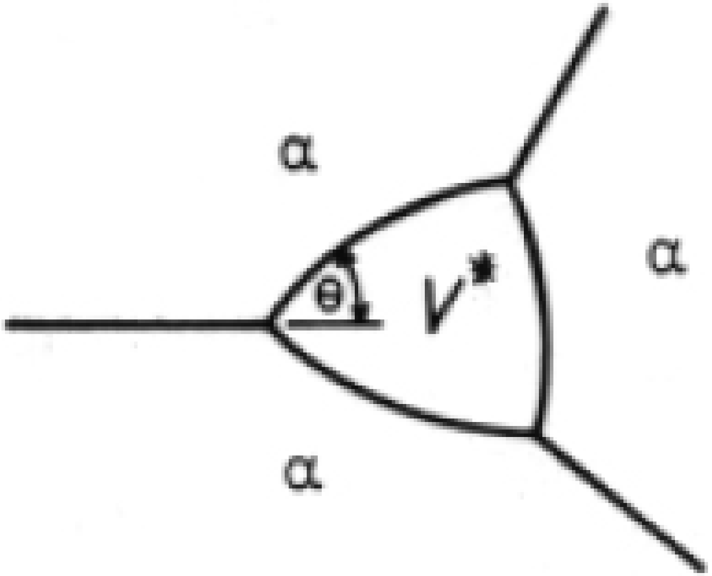


Fig. 5.7 Critical nucleus shape for nucleation on a grain edge.

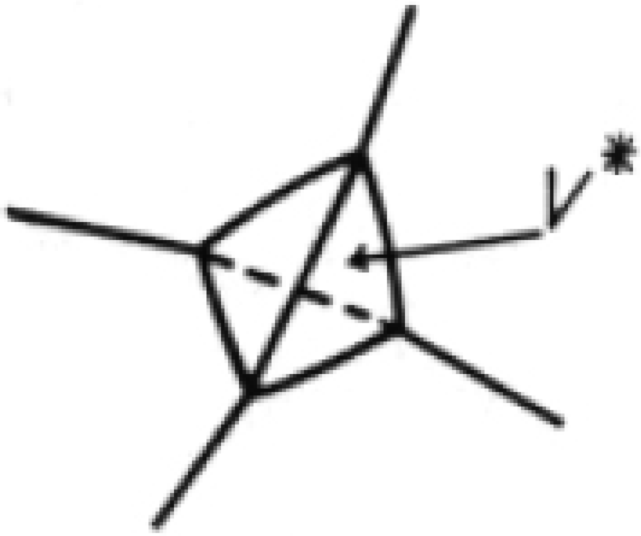


Fig. 5.8 Critical nucleus shape for nucleation on a grain corner.

Heterogeneous Nucleation in Solids

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

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

Activation Energy Barrier

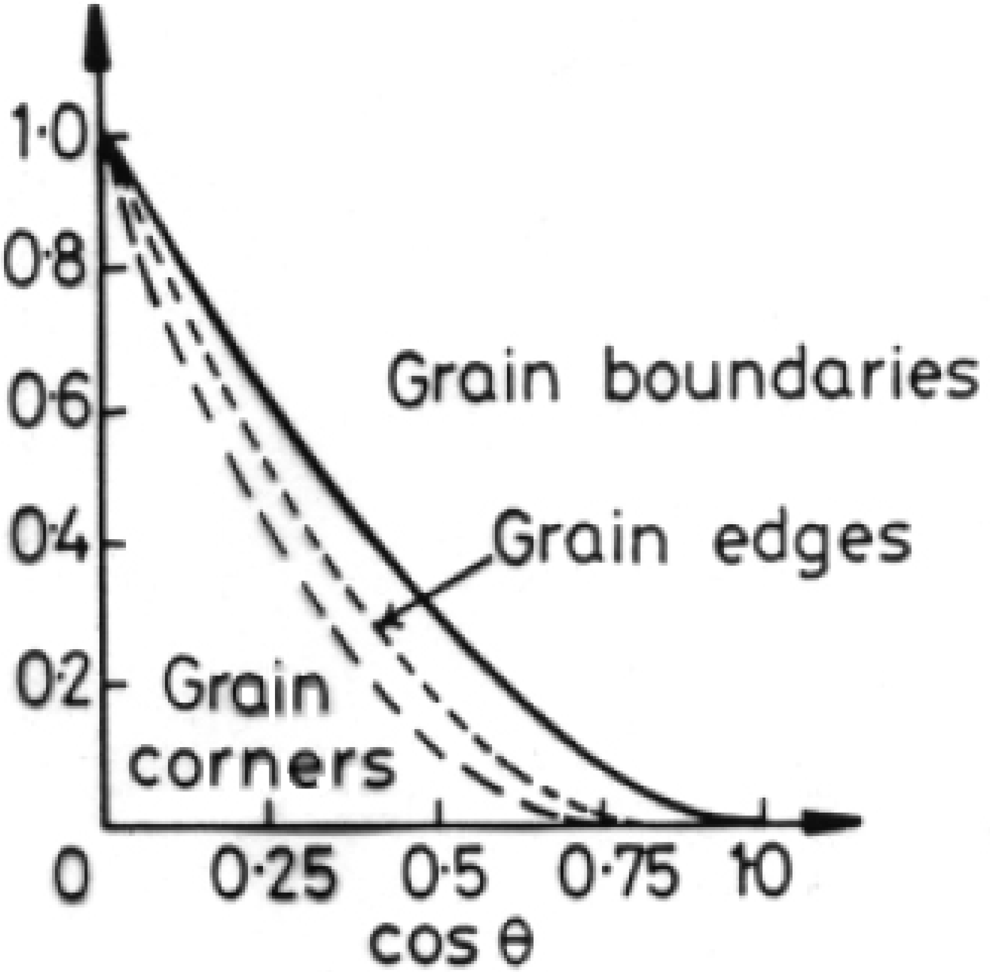


Fig. 5.9 The effect of θ on the activation energy for grain boundary nucleation relative to homogeneous nucleation. (After J.W. Cahn, *Acta Metallurgica* **4** (1956) 449.)

Heterogeneous Nucleation in Solids

High-angle grain boundaries 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.

< Nucleus with Coherent Interface >

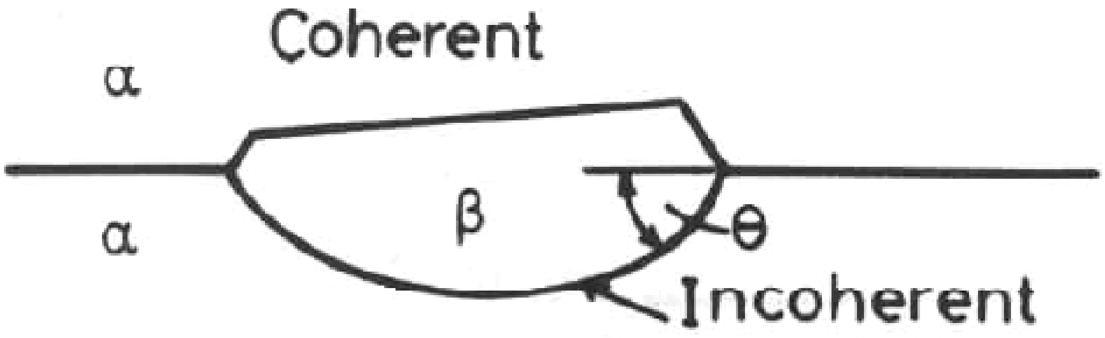


Fig. 5.10 The critical nucleus size can be reduced even further by forming a low-energy coherent interface with one grain.

- 전위 혹은 과잉공공은 핵생성시 불일치 변형에너지를 감소시킴으로써 핵생성을 도와준다.

Heterogeneous Nucleation in Solids

Rate of Heterogeneous Nucleation

Decreasing order of ΔG*(Activation Energy Barrier for nucleation)

: 아래로 갈수록 핵생성이 빨리 일어난다.

1) homogeneous sites
2) vacancies
3) dislocations
4) stacking faults
5) grain boundaries and interphase boundaries
6) free surfaces

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

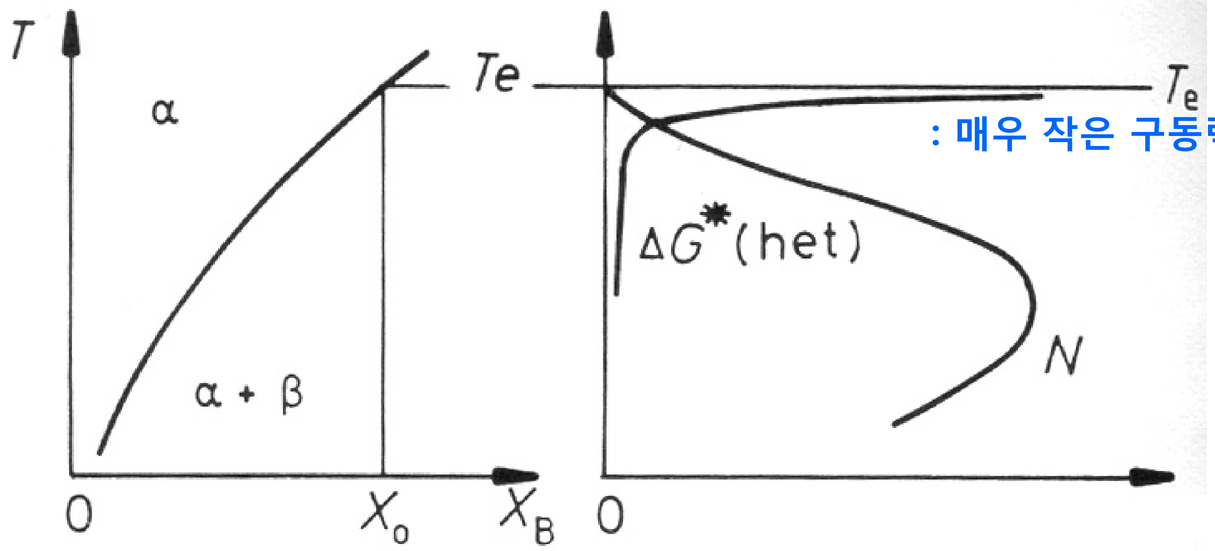
C_1 : concentration of heterogeneous nucleation sites per unit volume

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

: 단위체적당 임계 크기를 갖는 핵의 수

Heterogeneous Nucleation in Solids

The Rate of Heterogeneous Nucleation during Precipitation



: 매우 작은 구동력에서도 핵생성 발생

균일핵생성과 불균일 핵생성의 상대적인 크기

$$\boxed{\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0}\exp\left(\frac{\boxed{\Delta G^*_{hom} \overset{>}{-} \Delta G^*_{het}}}{kT}\right)} > 1$$

C_1/C_0 for GB nucleation?

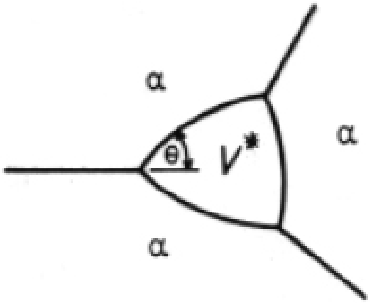
$$\frac{C_1}{C_0} = \frac{\delta(GB\ thickness)}{D(grain\ size)}$$

For D = 50 μm, δ = 0.5 nm

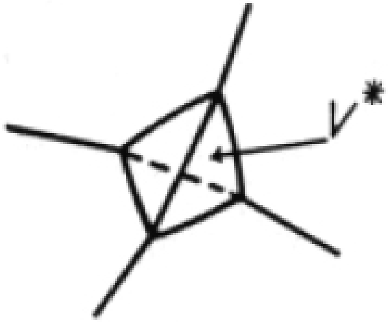
$$\frac{C_1}{C_0} = \frac{\delta}{D} \approx \boxed{10^{-5}}$$

Heterogeneous Nucleation in Solids

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



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



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}

불균일 핵생성이 상대적으로 우세해지려면 앞선 식에서 뒤의 exp 항의 영향이 위의 비보다 더 커져야만 함.

Heterogeneous Nucleation in Solids

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

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

2) Grain edge or Grain boundary

3) At very high cooling rate?

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.