2009 fall

Phase Transformation of Materials

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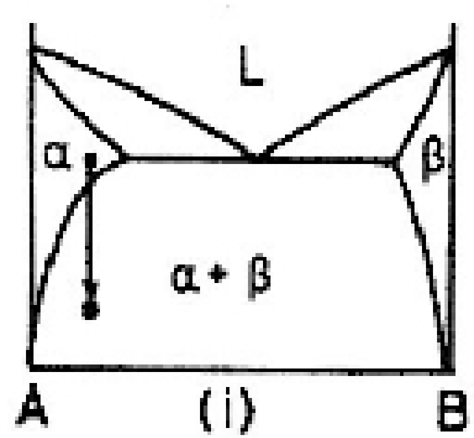
Contents for previous class

< Phase Transformation in Solids >

1) Diffusional Transformation

(a) Precipitation



Homogeneous Nucleation

→ Misfit strain energy의 영향

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

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

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

Heterogeneous Nucleation

→ 격자결함에 위치 (핵생성이 격자결함 제거 역할)

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

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

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

Contents for today's class

- **Precipitate growth**

  - Growth behind Planar Incoherent Interfaces

  - Diffusion Controlled lengthening of Plates or Needles

  - Thickening of Plate-like Precipitates

- **Overall Transformation Kinetics – TTT Diagram**

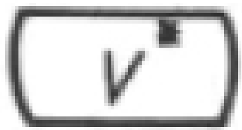
  - Johnson-Mehl-Avrami Equation

- **Precipitation in Age-Hardening Alloys**

  - GP Zones

  - Transition phases

5.3 Precipitate Growth



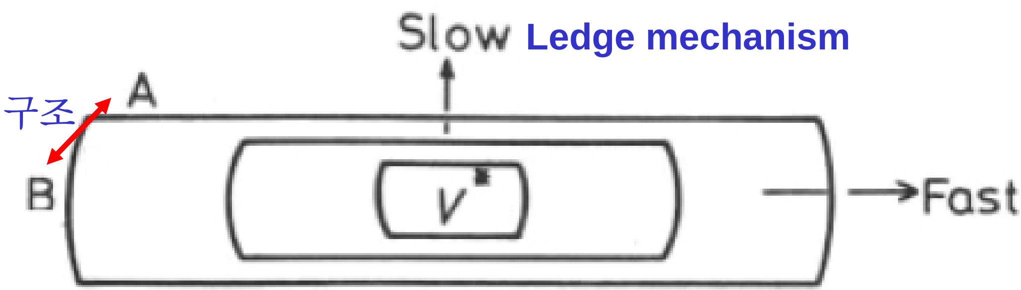
초기 석출물 모양

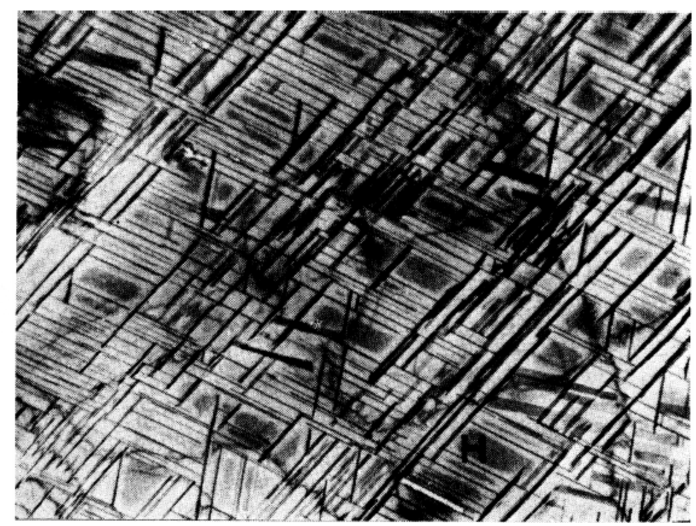
계면 자유에너지를 최소로 하는 모양

석출물 성장 → 계면의 이동

: 성장하는 동안 석출물 모양 각 계면의 상대적 이동 속도에 의해 좌우됨.

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





→ Origin of the Widmanstätten morphology

1) Growth behind Planar Incoherent Interfaces

Incoherent interface → **similar to rough interface**

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

Diffusion-Controlled Thickening: 석출물 성장 속도

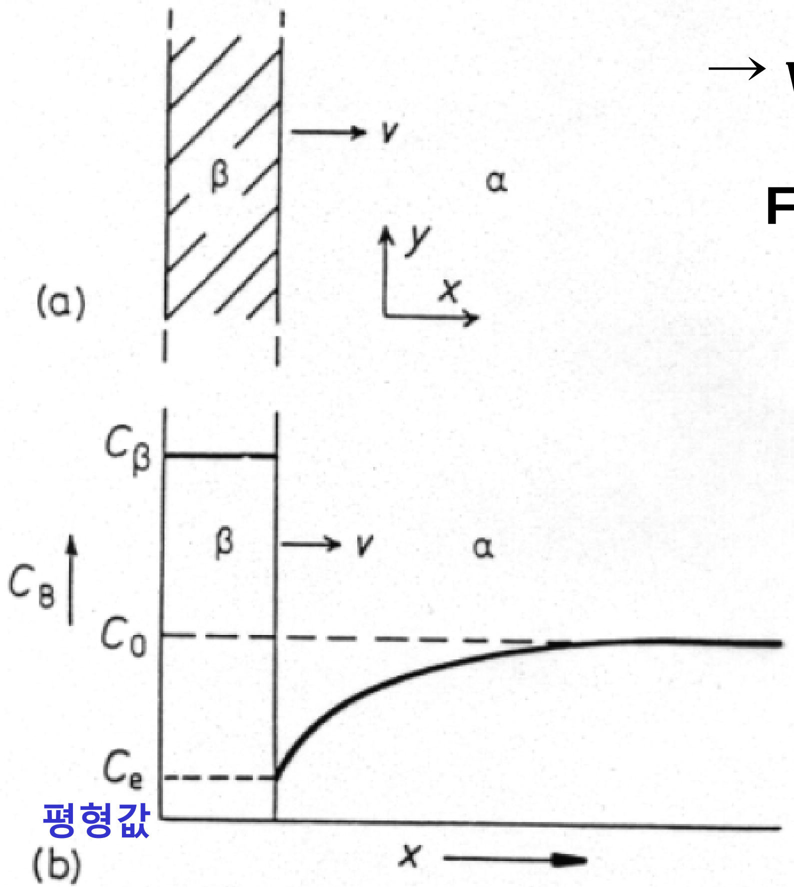


Fig. 5.14 Diffusion-controlled thickening of a precipitate plate.

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

From mass conservation,

β 형성시 용질 증가량

$$(C_\beta - C_e)dx \text{ mole of } B$$

$$= J_B = D(dC/dx)dt$$

B 원소의 총 이동양

D: interdiffusion coefficient

or interstitial diffusion coeff.

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

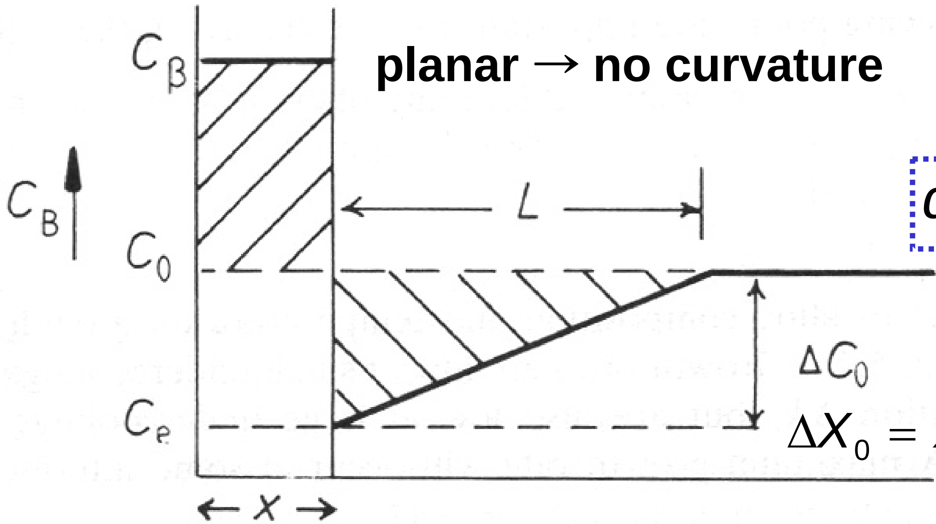
1) Growth behind Planar Incoherent Interfaces

Simplification of concentration profile

정량적 계산 (Zener)

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

planar → no curvature



석출물 판의 두께

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

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

$$\Delta X_0 = X_0 - X_e$$

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

if $C_\beta - C_0 \cong C_\beta - C_e$ **and** $X = CV_m$ **,**

$$xdx = \frac{D\left(\Delta X_0\right)^2}{2\left(X_\beta - X_e\right)^2} dt$$

적분 →

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

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

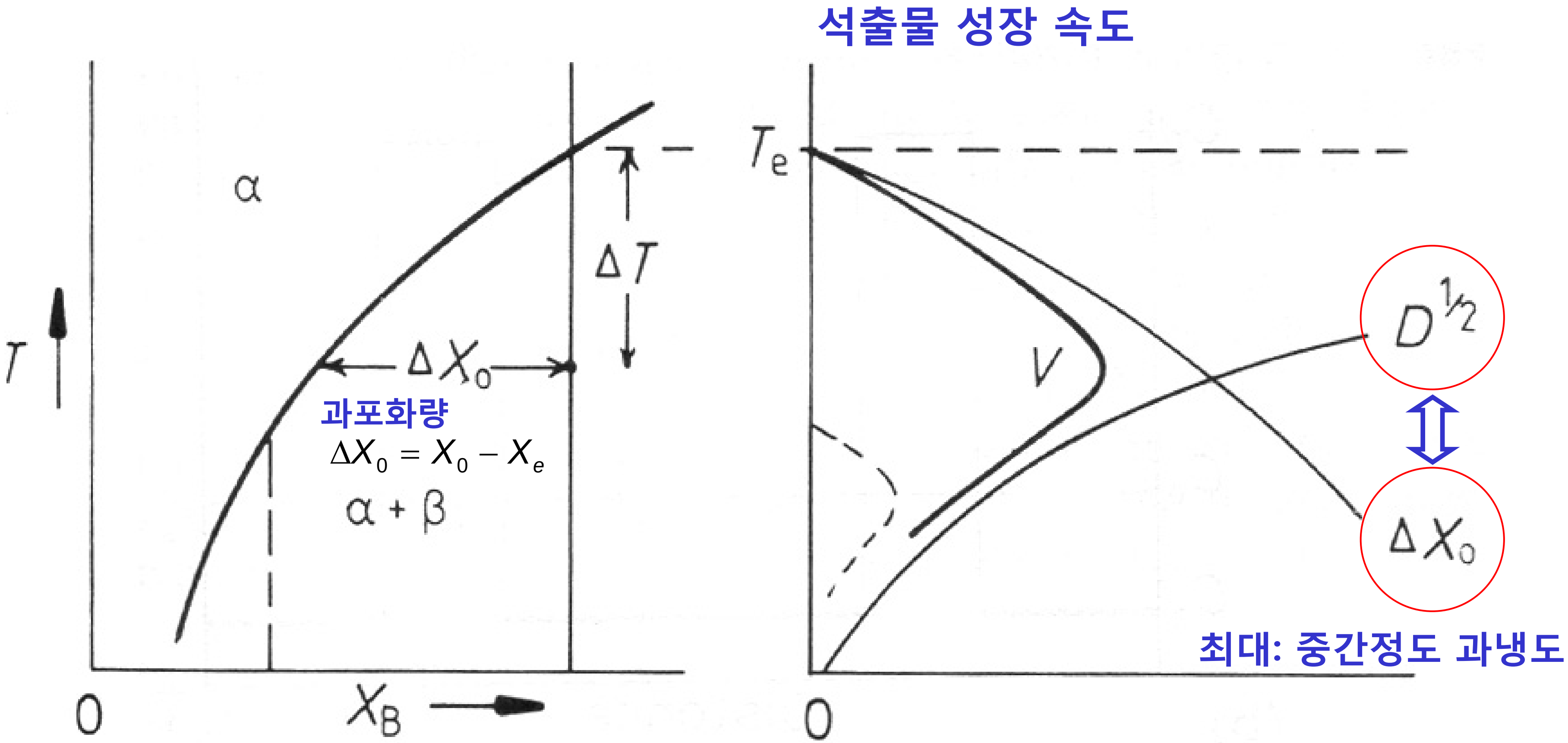
포물선 성장

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

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

과포화도

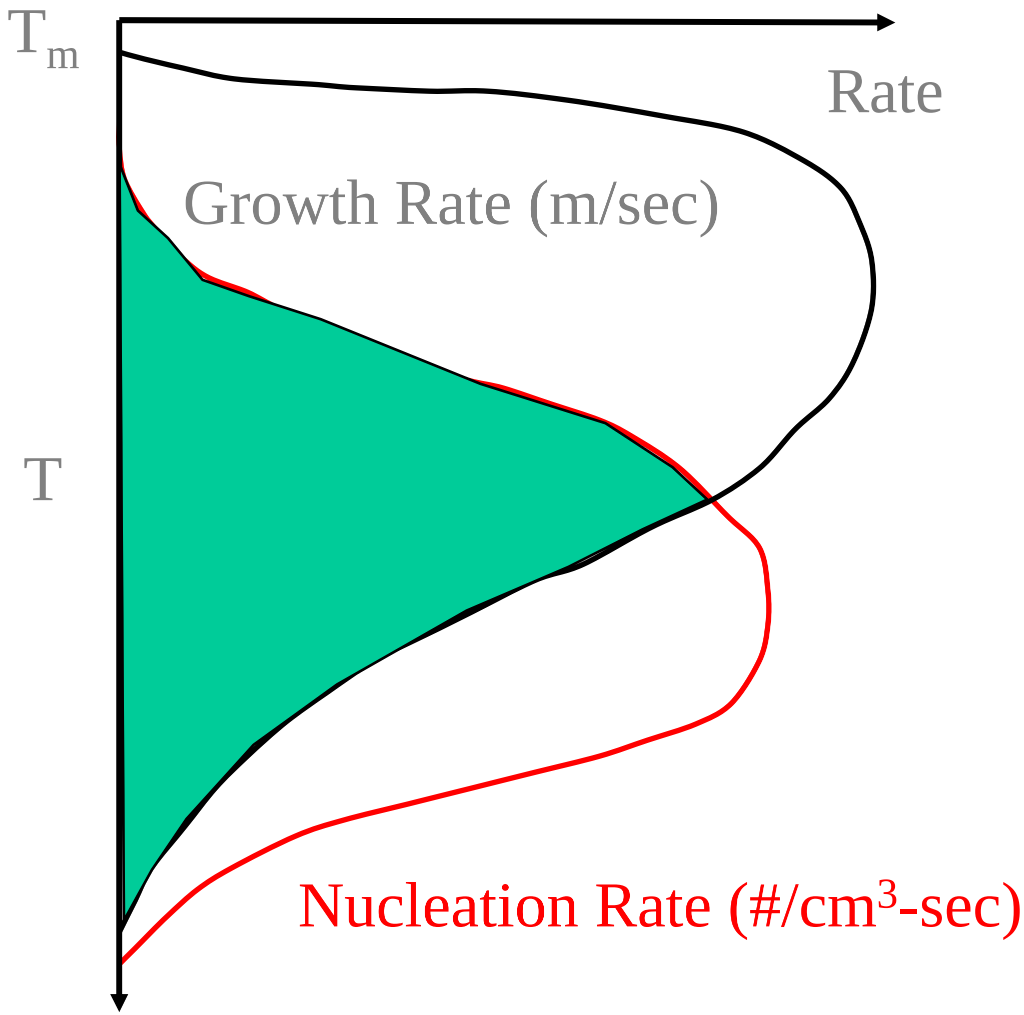
1) Growth behind Planar Incoherent Interfaces



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

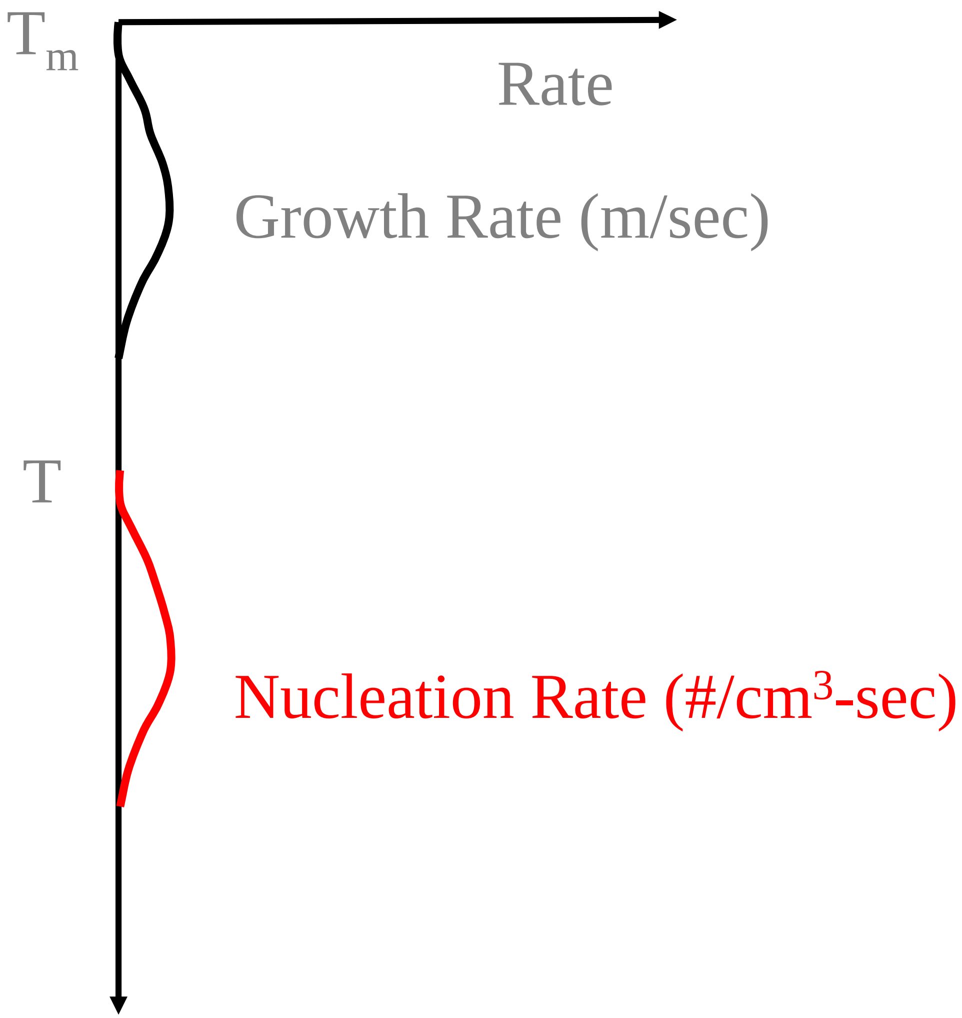
Fig. 5.16 The effect of temperature and position on growth rate, v.

Nucleation and Growth Rates – Poor Glass Formers



- **Strong overlap of growth and nucleation rates**
- **Nucleation rate is high**
- **Growth rate is high**
- **Both are high at the same temperature**

Nucleation and Growth Rates – Good Glass Formers



- **No overlap of growth and nucleation rates**
- **Nucleation rate is small**
- **Growth rate is small**
- **At any one temperature one of the two is zero**

1) Growth behind Planar Incoherent Interfaces

Effect of Overlap of Separate Precipitates

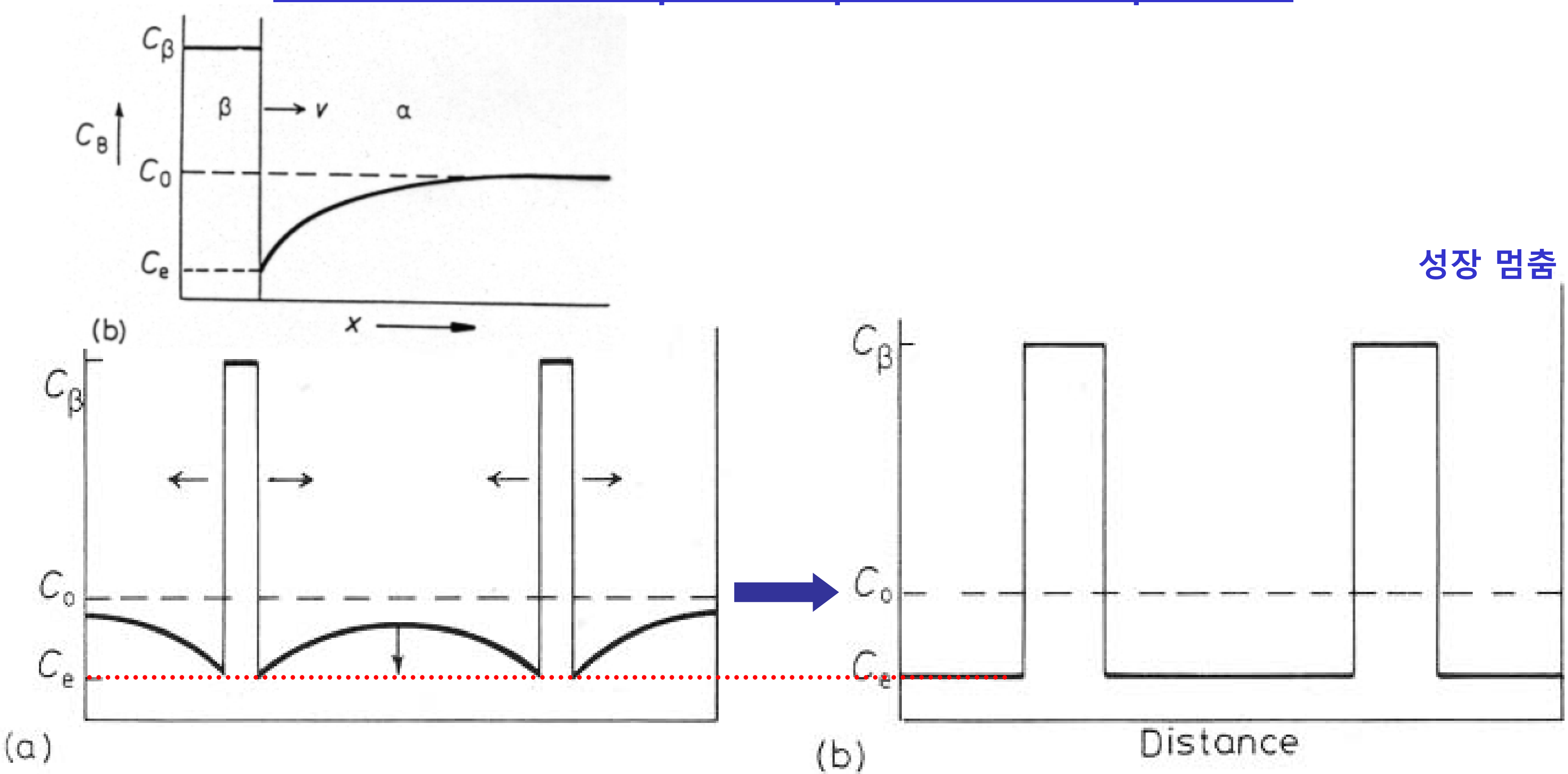
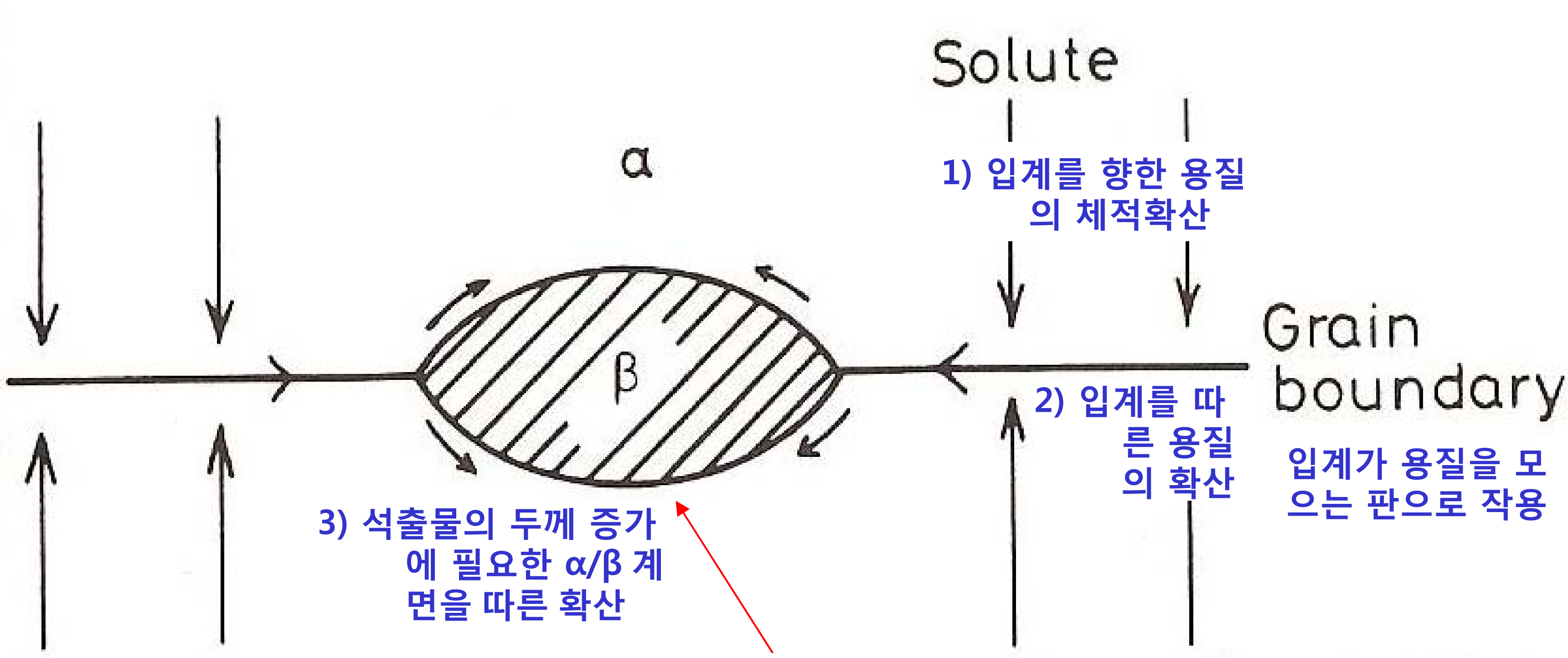


Fig. 5.17 (a) Interference of growing precipitates due to overlapping diffusion fields at later stage of growth. (b) Precipitate has stopped growing.

1) Growth behind Planar Incoherent Interfaces

Grain boundary precipitation ➡ 빠른 속도로 성장



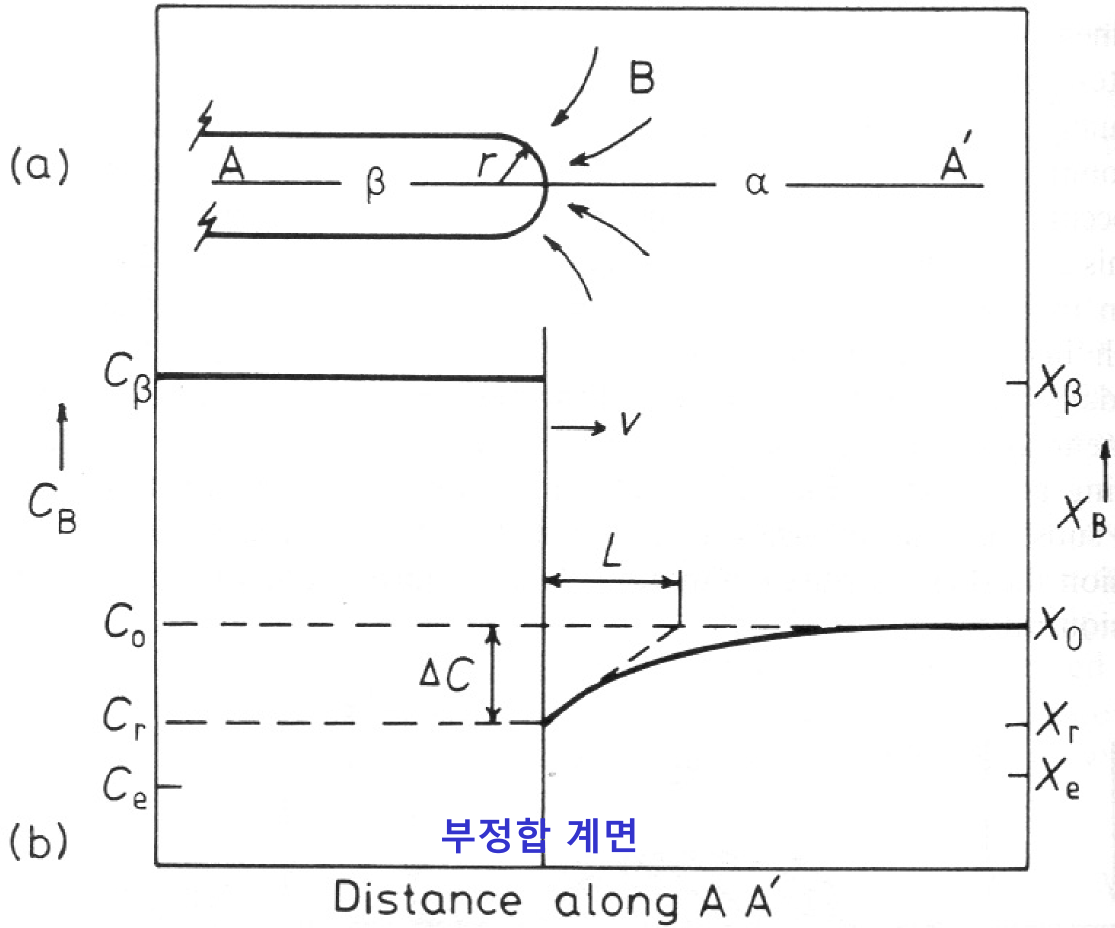
Grain boundary allotrioboundary

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

치환형 확산이 필요한 경우 상대적으로 중요

2) Diffusion Controlled lengthening of Plates or Needles

Plate Precipitate of constant thickness



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

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

k **(const)~1**

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

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

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

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

선형 성장

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

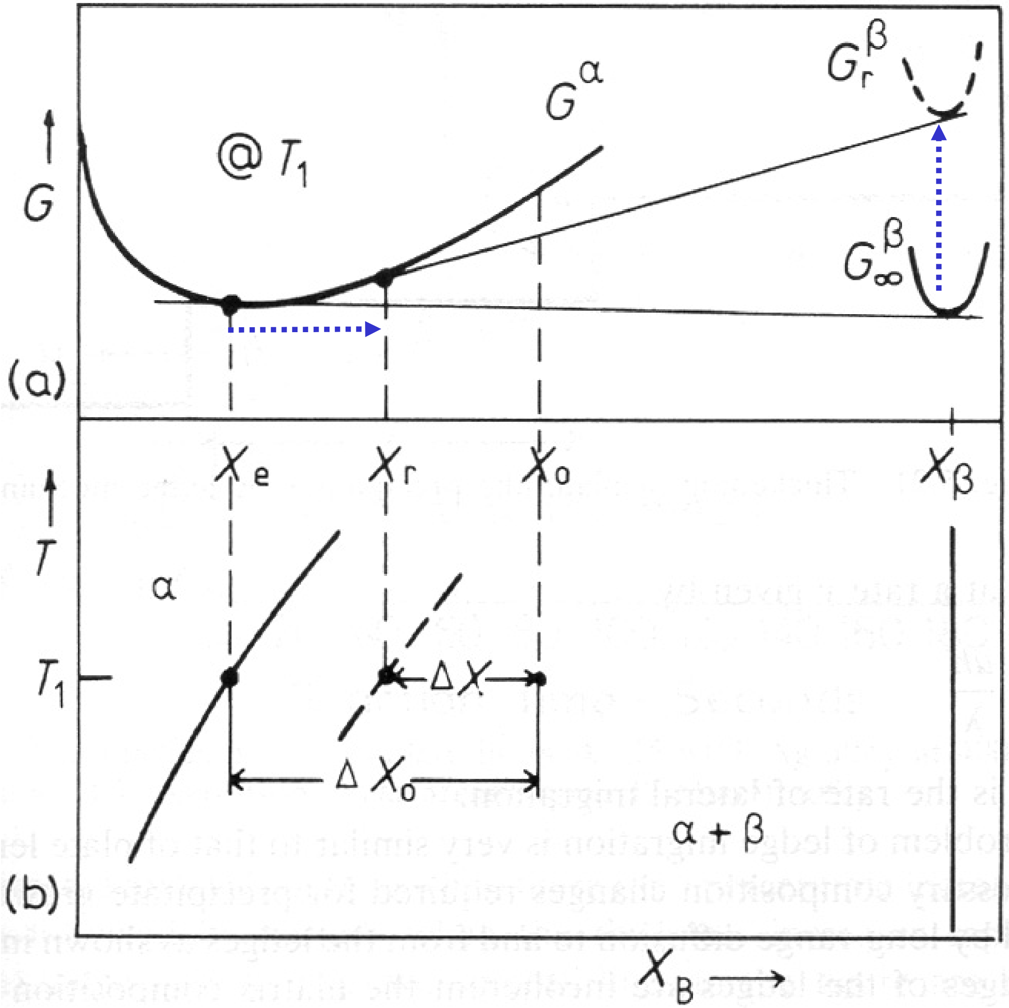
→ **the same equation but the different value of r^***

2) Diffusion Controlled lengthening of Plates or Needles

The Gobs-Thomson Effect : α/β 계면의 곡률로 인해 여분의 압력 $\Delta P=2\gamma/r$

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

계면 에너지로 인한 자유 E 증가



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

$$\Delta X = X_0 - X_r$$

$$\Delta X_0 = X_0 - X_e$$

r^*: 임계핵의 반지름

r ↑ ⟶ ΔX ↓

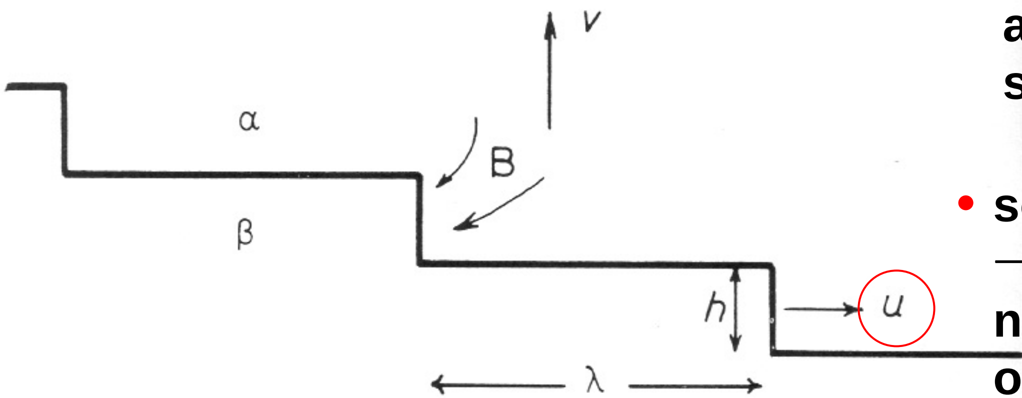
* 모서리 구형인 경우, 위 식 적용

실제의 경우 facets 면 많음

Ledge mechanism에 의한 성장

3) Thickening of Plate-like Precipitates

Thickening of Plate-like Precipitates by Ledge Mechanism



- **For the diffusion-controlled growth, a monatomic-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

Assuming the diffusion-controlled growth, $v = \frac{D}{C_\beta - C_r} \cdot \frac{\Delta C}{kr}$

돌출맥 모서리가 부정합인 경우

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

3) Thickening of Plate-like Precipitates

Thickening of γ Plate in the Al-Ag system

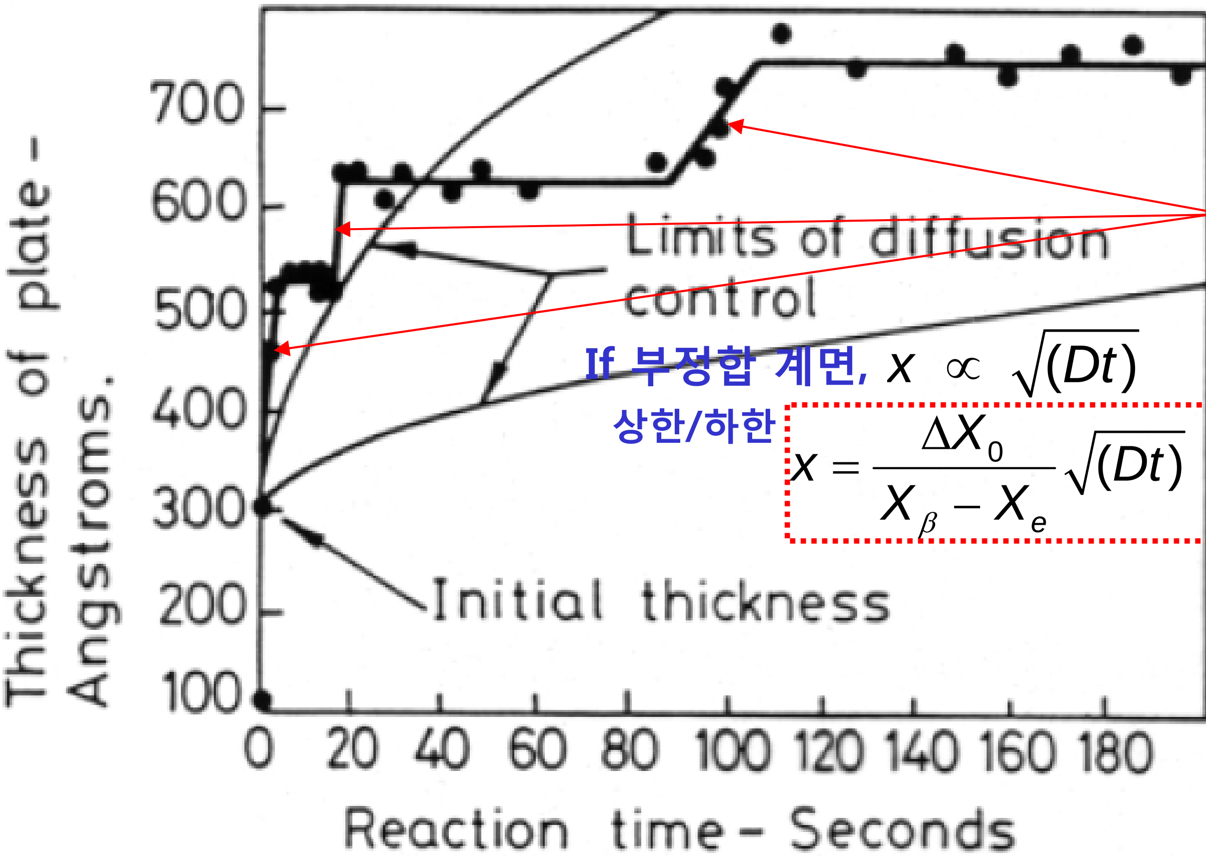


Fig. 5.22 The thickening of a g plate in an Al-15 wt% Ag alloy at 400°C. (From C. Laird and H.I. Aaronson, *Acta Metallurgica* **17** (1969) 505.)

What does this data mean?

돌출맥이 통과할 때를 제외하고는 두께의 증가가 거의 일어나지 않음

⬇

반정합계면의 이동도 매우 낮다.

⬇

Ledge nucleation is rate controlling.