재 료 상 변 태

Phase Transformation of Materials

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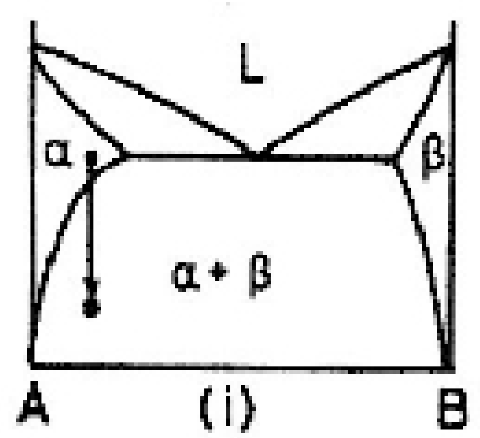
Contents for previous class

< 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**

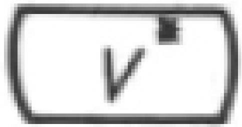
  - Growth behind Planar Incoherent Interfaces
  - Diffusion Controlled lengthening of Plates or Needles
  - Thickening of Plate-like Precipitates

- **Overall Transformation Kinetics – TTT Diagram**

  - Johnson-Mehl-Avrami Equation

- **Precipitation in Age-Hardening Alloys**

5.3 Precipitate Growth



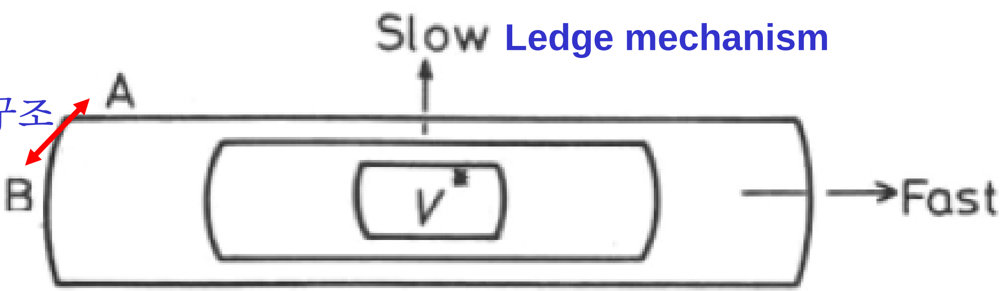
석출물 모양

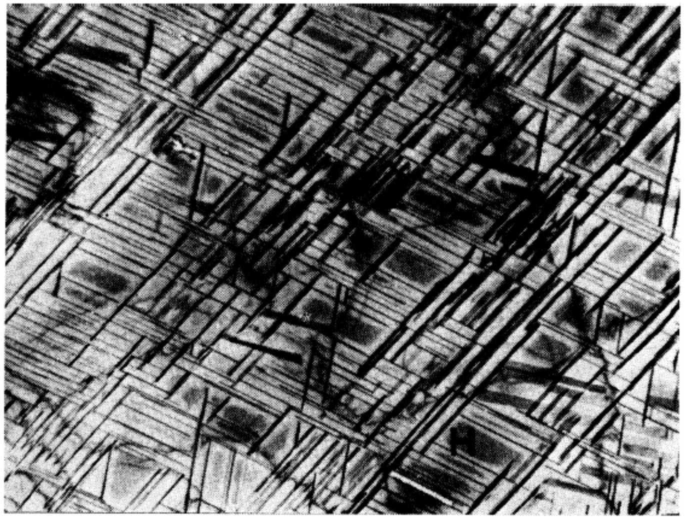
계면 자유에너지를 최소로 하는 모양

석출물 성장 → 계면의 이동

: 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

Growth behind Planar Incoherent Interfaces

Incoherent interface → **similar to rough interface**

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

Diffusion-Controlled Thickening: 석출물 성장 속도

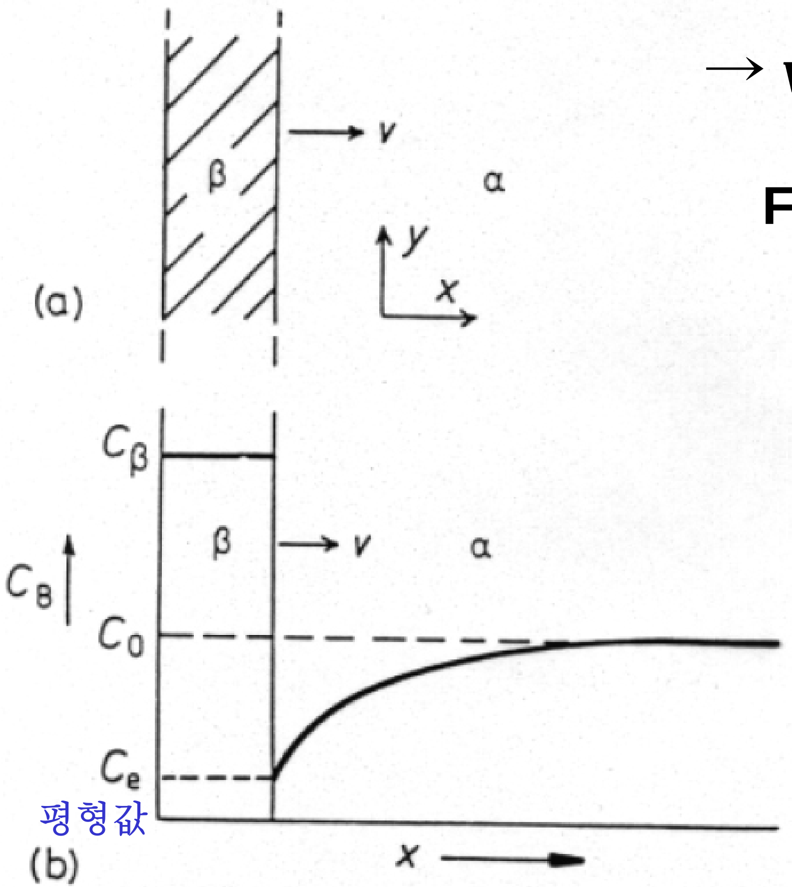


Fig. 5.14 Diffusion-controlled thickening of a precipitate plate.

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

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

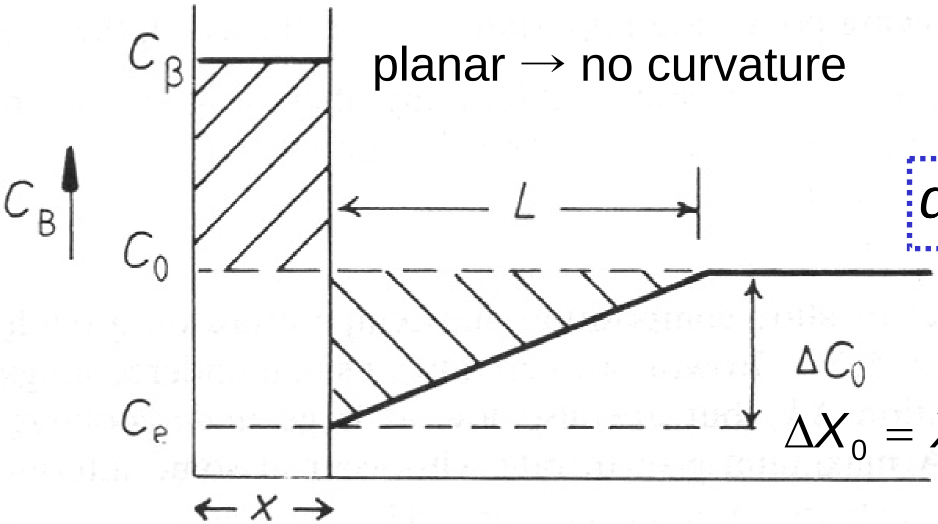
or interstitial diffusion coeff.

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

Growth behind Planar Incoherent Interfaces

Simplification of concentration profile

planar → no curvature



정량적 계산 (Zener)

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

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

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

$$\Delta X_0 = X_0 - X_e$$

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

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

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

적분 →

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

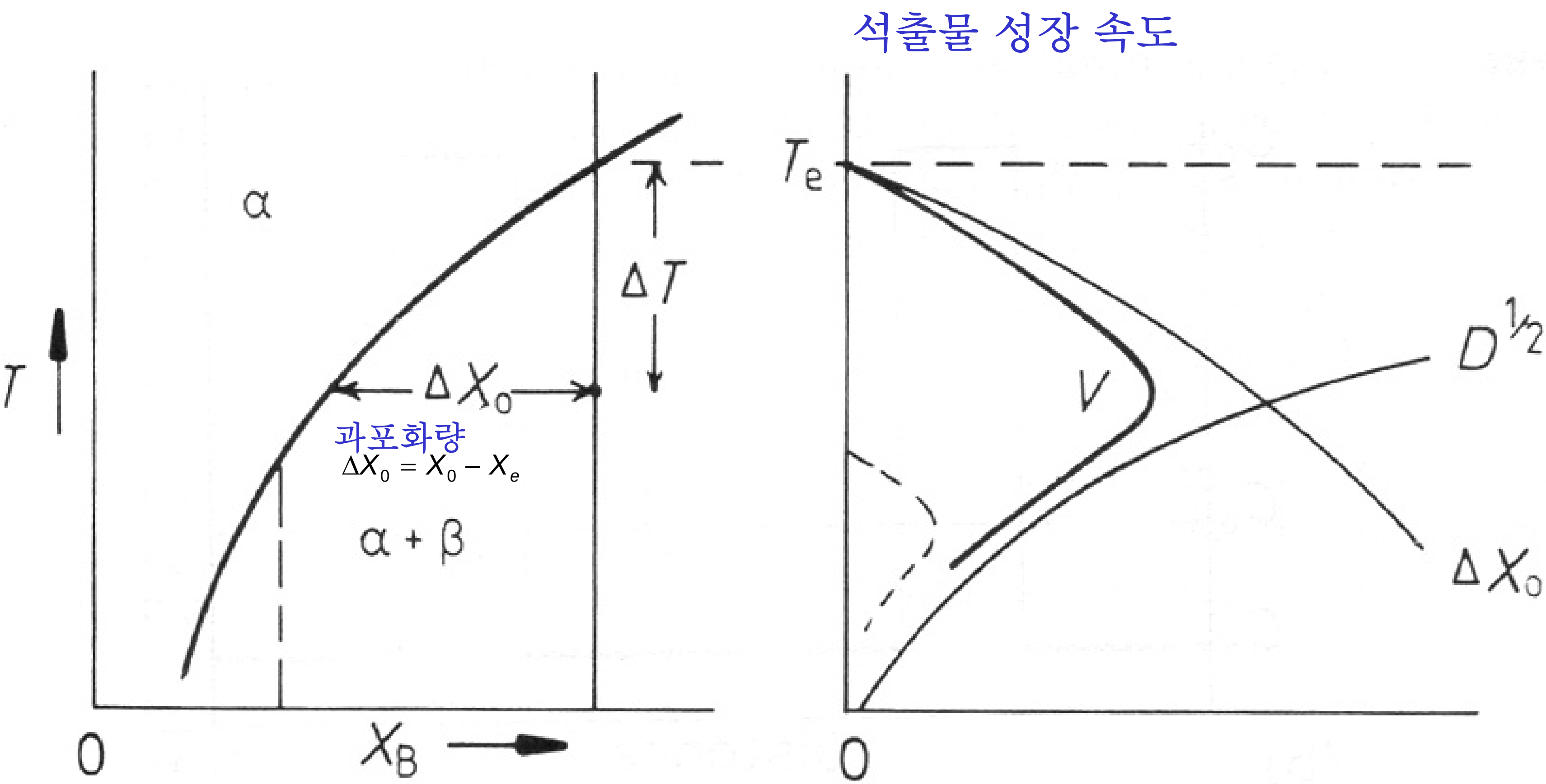
$$x \propto \sqrt{(Dt)}$$

포물선 성장

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

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

Growth behind Planar Incoherent Interfaces

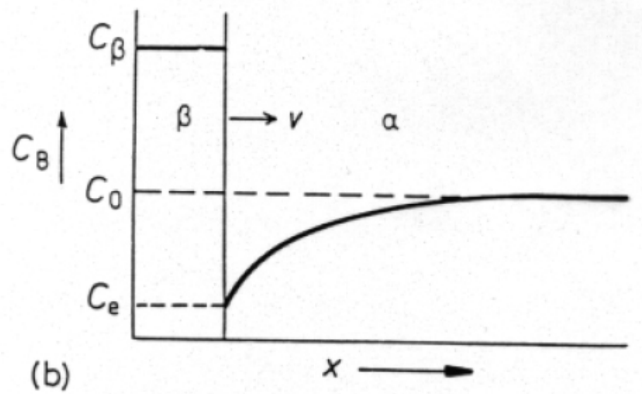


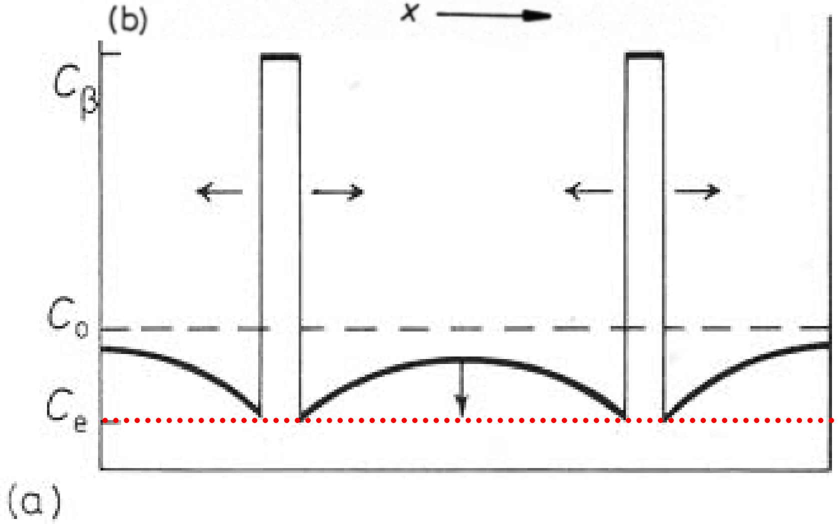
$$v \propto \Delta X_0 \propto \Delta T \qquad v \propto \sqrt{(D/t)}$$

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

Growth behind Planar Incoherent Interfaces

Effect of Overlap of Separate Precipitates





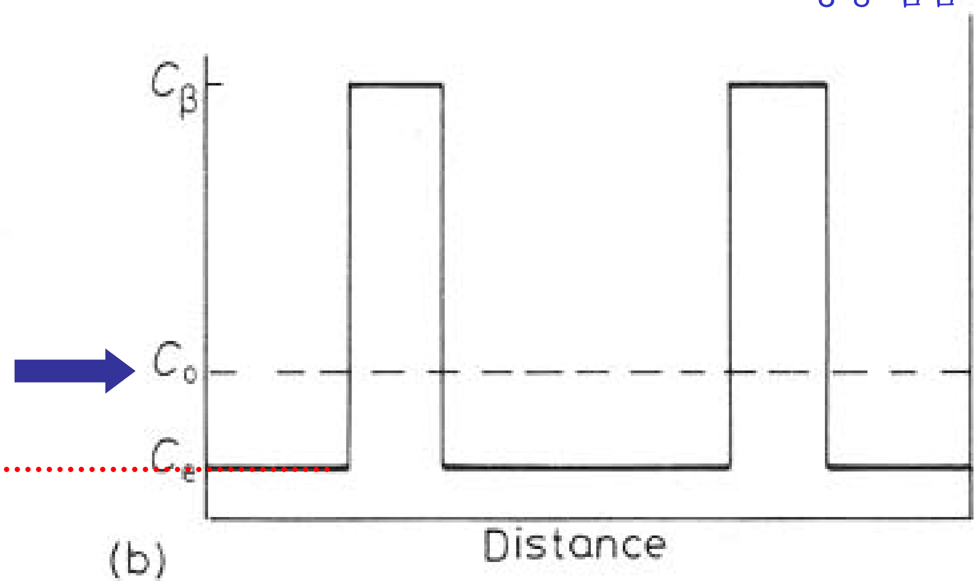
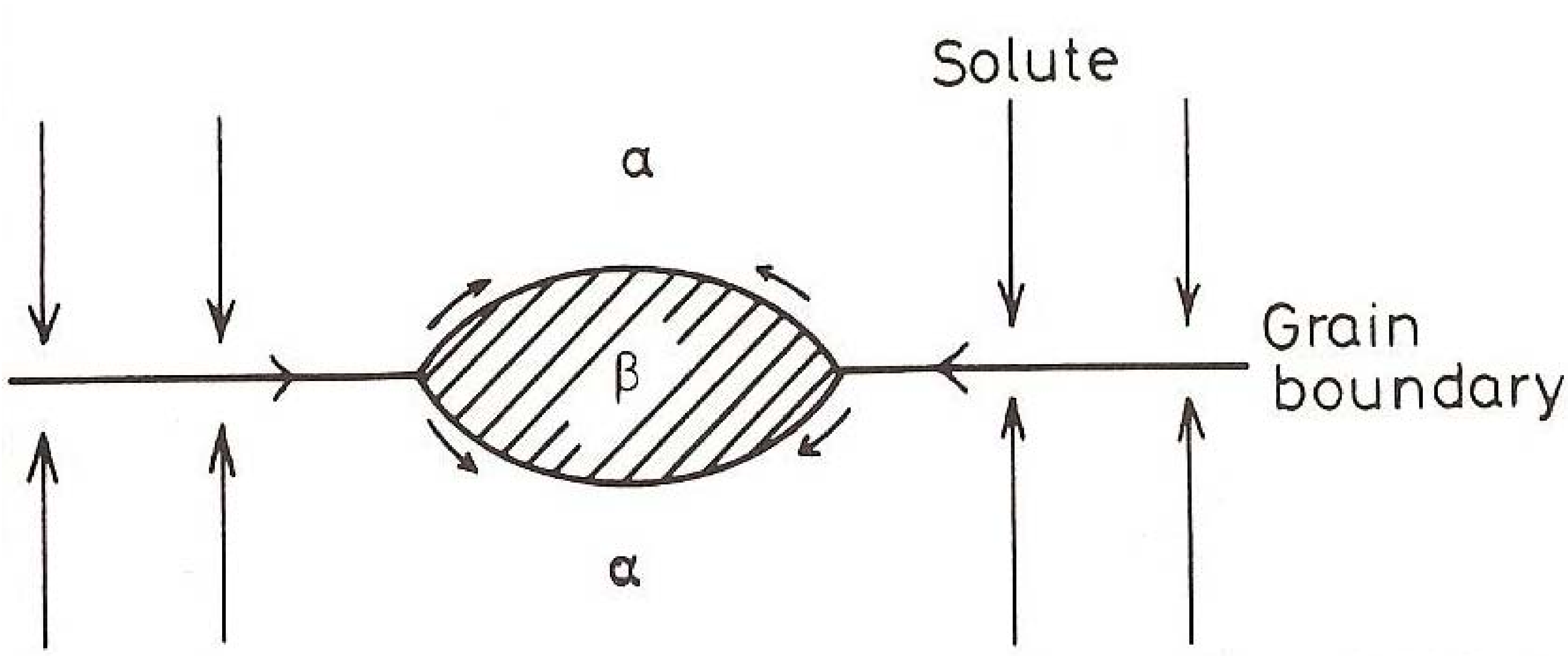


Fig. 5.17 (a) Interference of growing precipitates due to overlapping diffusion fields at later stage of growth. (b) Precipitate has stopped growing.

Growth behind Planar Incoherent Interfaces

Grain boundary precipitation ➡ 빠른 속도로 성장



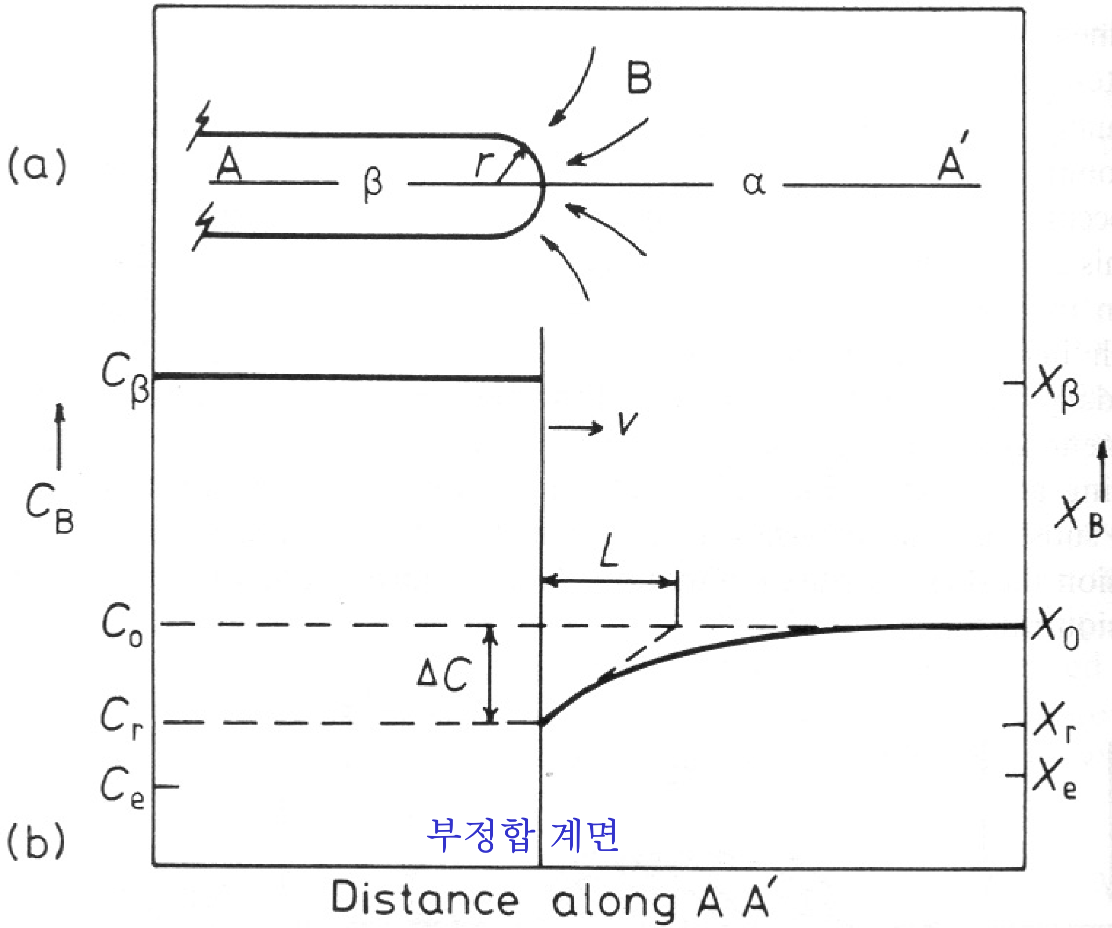
Grain boundary allotrioboundary

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

치환형 확산이 필요한 경우 상대적으로 중요

Diffusion Controlled lengthening of Plates or Needles

Plate Precipitate of constant thickness



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

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

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

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

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

V → constant

$x \propto t$

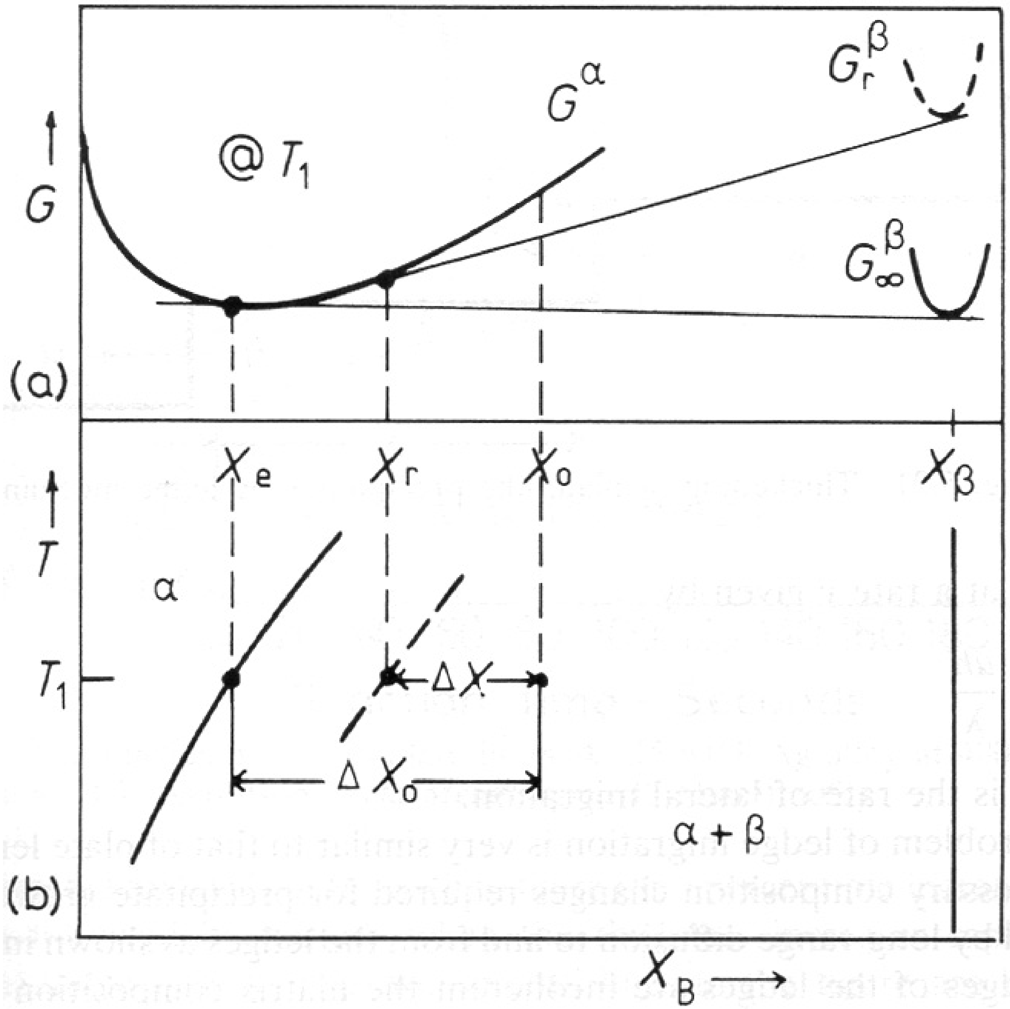
선형 성장

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

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

Diffusion Controlled lengthening of Plates or Needles

The Gobs-Thomson Effect : 계면에너지로 인해 자유에너지 증가하는 현상



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

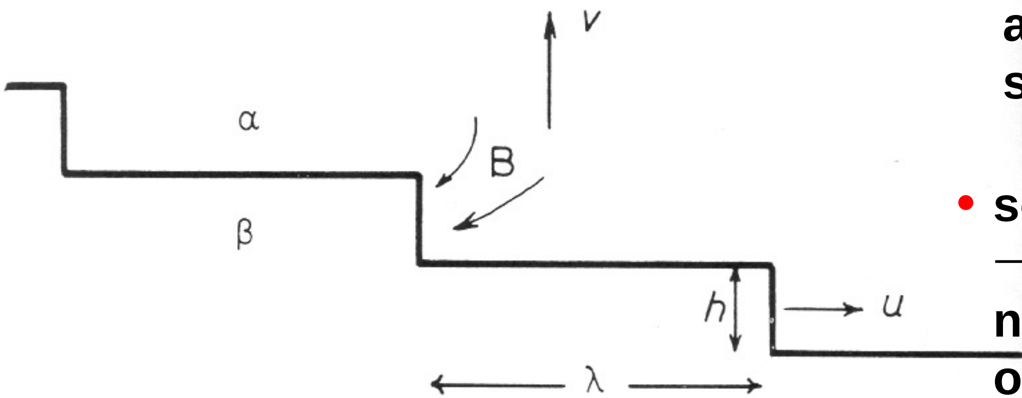
$$\Delta X = X_0 - X_r$$

$$\Delta X_0 = X_0 - X_e$$

r^*: 임계핵의 반지름

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

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

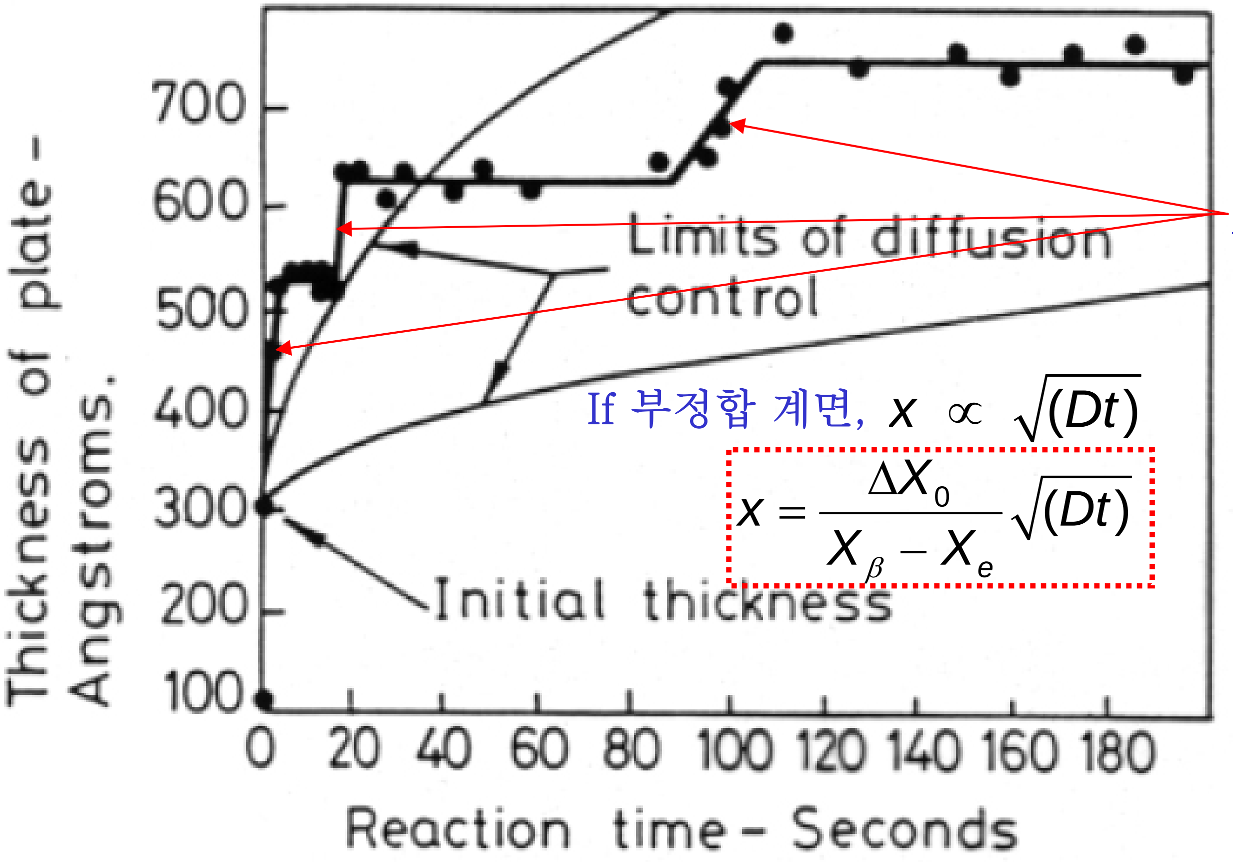
u : rate of lateral migration

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

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

Thickening of Plate-like Precipitates

Thickening of γ Plate in the Al-Ag system



If 부정합 계면, $x \propto \sqrt{(Dt)}$

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

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.

5.4 Overall Transformation Kinetics – TTT Diagram

The fraction of Transformation as a function of Time and Temperature

→ f **(t,T)**

Plot f vs log t.

- isothermal transformation
- f ~ β 의 체적분율

Plot the fraction of transformation (1%, 99%) in T-log t coordinate.

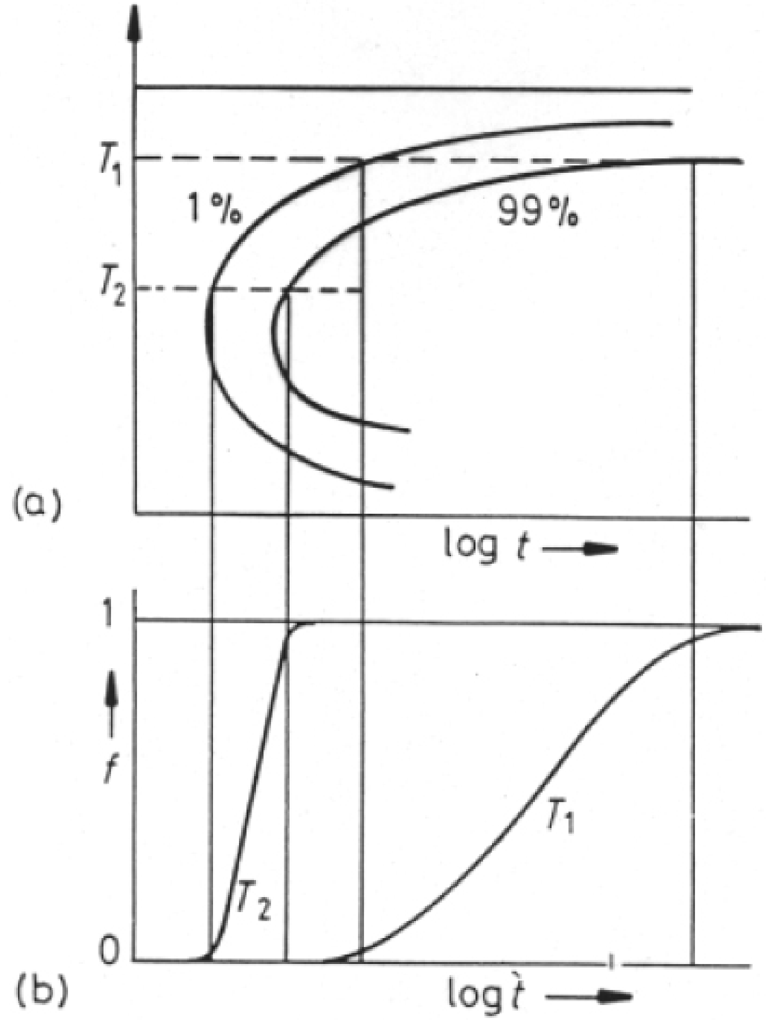


Fig. 5.23 The percentage transformation versus time for different transformation temperatures.

5.4 Overall Transformation Kinetics – TTT Diagram

Three Transformation Types

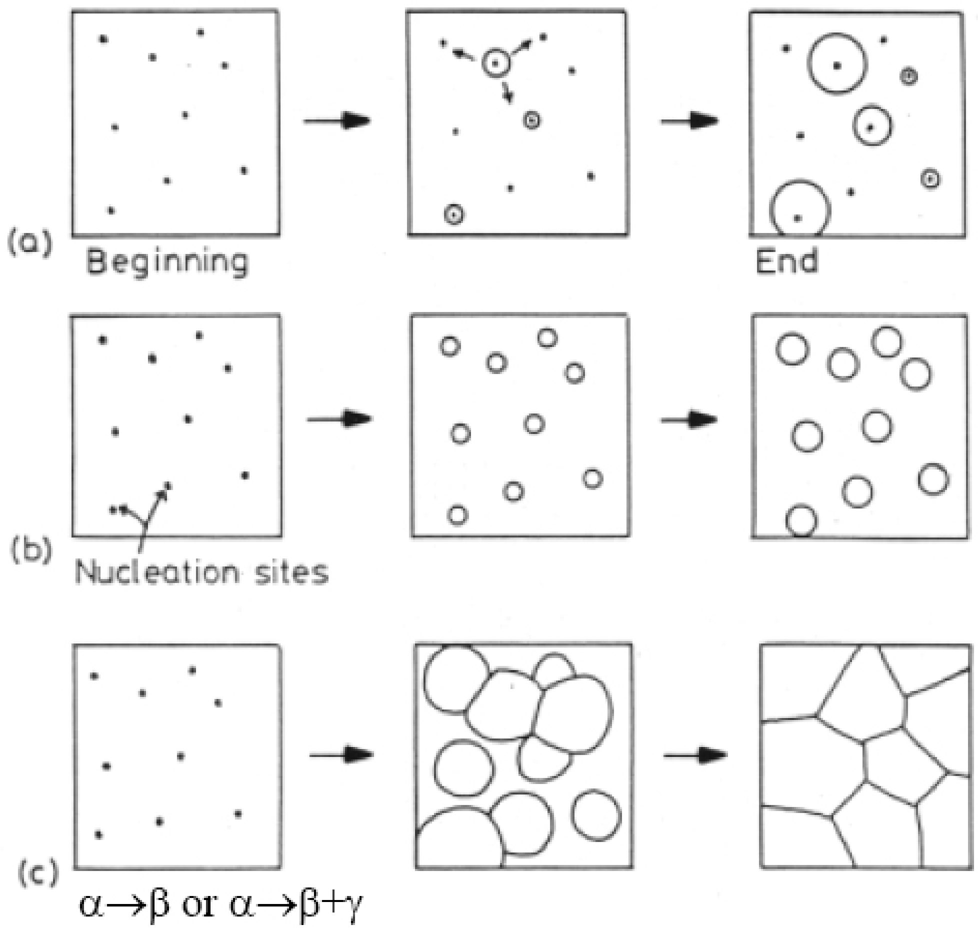


Fig. 5.24 (a) Nucleation at a constant rate during the whole transformation.
(b) Site saturation − all nucleation occurs at the beginning of transformation.
(c) A cellular transformation.

(a) continuous nucleation
→ *f* depends on the nucleation rate and the growth rate.

(b) all nuclei present at t = 0
→ *f* depends on the number of nucleation sites and the growth rate.

(c) All of the parent phase is consumed by the transformation product.
→ pearlite, cellular ppt, massive transformation, recrystallization

일정한 속도로 성장, 생성상이 서로 만나 충돌

5.4 Overall Transformation Kinetics – TTT Diagram

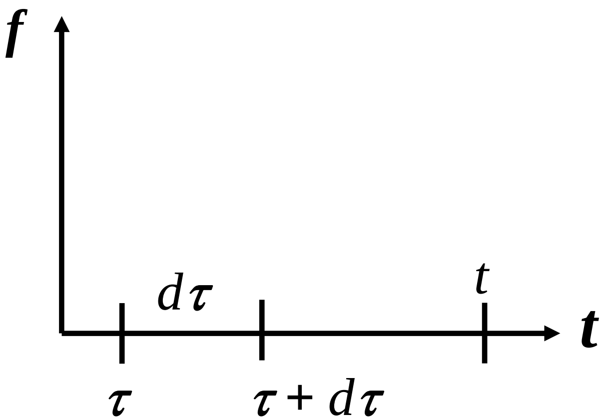
Johnson-Mehl-Avrami Equation : 변태속도 비교

Assumption:

- **reaction produces by N + G**
- **nucleation occurs randomly throughout specimen**
- **reaction product grows radially until impingement**

define volume fraction transformed $f = \dfrac{Vol.\ of\ new\ phase}{Vol.\ of\ specimen}$

How much transformation occurred on time interval $d\tau$



$$df = \frac{\begin{pmatrix} vol.\ of\ one\ particle\ nucleated \\ during\ d\tau\ measured\ at\ time\ t \end{pmatrix} \times \begin{pmatrix} number\ of\ nuclei \\ formed\ during\ d\tau \end{pmatrix}}{volume\ of\ specimen}$$

$$df = \frac{\frac{4}{3}\pi[v(t-\tau)]^3 \times (NV_0 d\tau)}{V_0}$$

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\ (vt)^3$$

$$V' = \frac{4}{3}\pi v^3 (t-\tau)^3$$

v : cell growth rate (assumed const.)

N : nucleation rate (const.)

5.4 Overall Transformation Kinetics – TTT Diagram

$$f = \int_0^x d\hat{f} = \frac{4}{3}\pi N v^3 \int_0^t (t-\tau)^3 \, d\tau$$

$$f = \frac{\pi}{3} N v^3 t^4$$

→ **do not consider impingement & repeated nucleation**

→ **only true for $f \ll 1$**

$$df = (1-f)\ df_e$$

$$1 - f = \frac{df}{df_e}$$

f_e : extended volume fraction

ignored impingement + repeated nucleation

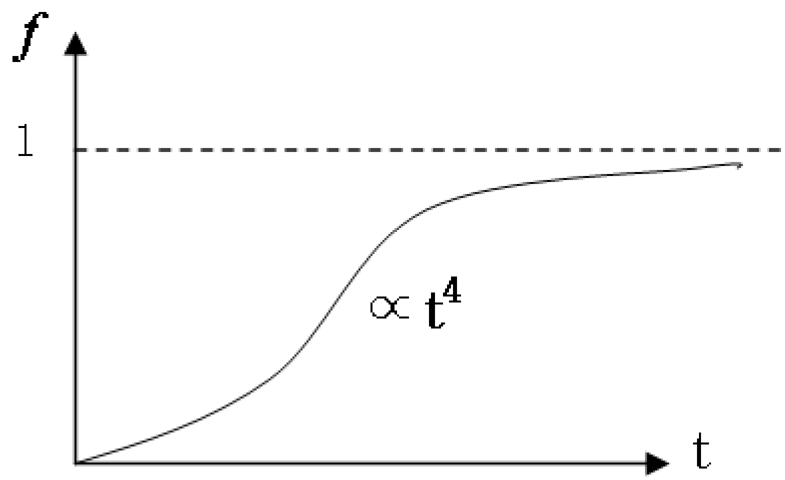
J-M-A Eq.

$$f = 1 - \exp\left(-\frac{\pi}{3} N v^3 t^4\right)$$

$$f = 1 - \exp\ (-kt^n)$$

k **: sensitive to temp. (N, *v*)**

n **: 1 ~ 4**



Example above.

i.e. 50% transform

Exp (-0.7) = 0.5

$$kt_{0.5}^n = 0.7 \qquad t_{0.5} = \frac{0.7}{k^{1/n}} \qquad t_{0.5} = \frac{0.9}{N^{1/4} v^{3/4}}$$

5.5 Precipitation in Age-Hardening Alloys

Precipitation in Aluminum-Copper Alloys

Al-4 wt%Cu (1.7 at %)

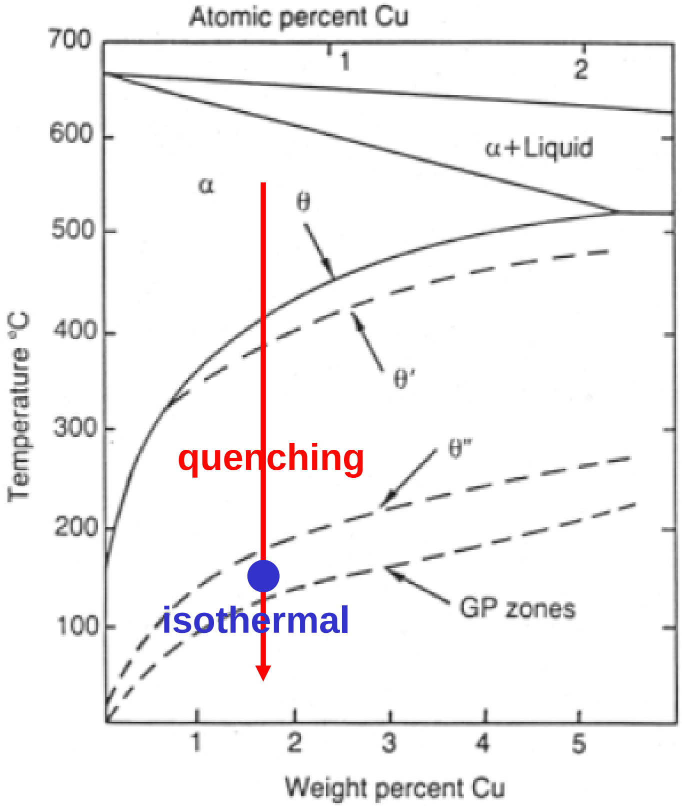


Fig. 5.25 Al-Cu phase diagram showing the metastable GP zone, Θ″ and Θ′ solvuses. (Reproduced from G. Lorimer, *Precipitation Processes in Solids*, K.C. Russell and H.I. Aaronson (Eds.), The Metallurgical Society of AMIE, 1978, p. 87.)

α_0

$\rightarrow \alpha_1$+GP zones

$\rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta$

($CuAl_2$)

5.5.1 GP Zones

$$\Delta G_{\theta}^{*} > (\Delta G_V - \Delta G_s) >> \Delta G_{zone}^{*}$$

The zones minimize their strain energy by choosing a disc-shape perpendicular to the elastically soft <100> directions in the fcc matrix.

두께: **1~2** 개의 원자층, 지름은 대략 **25**개의 원자 직경거리

정합상태의 **Cu** 농축지역

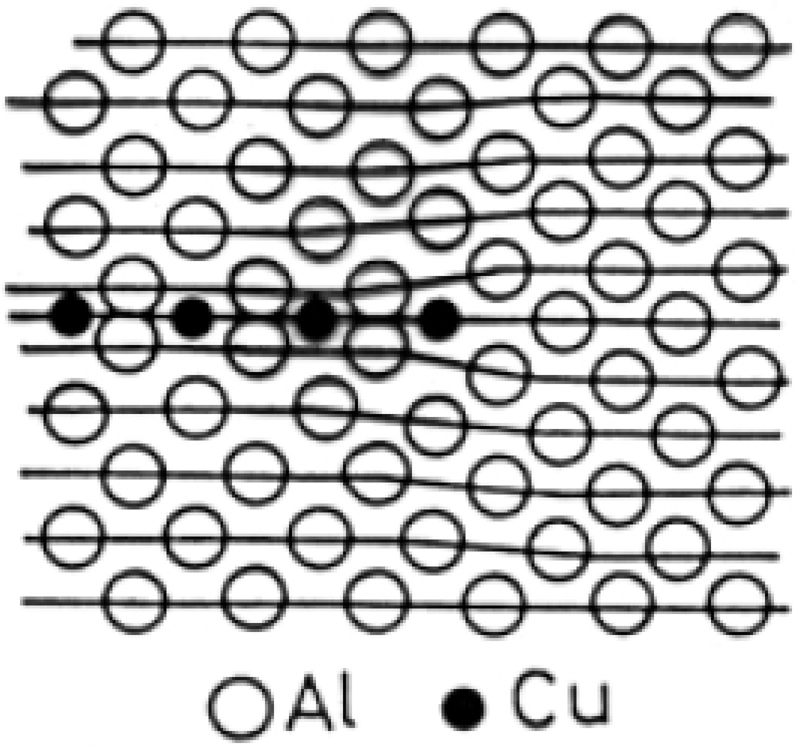
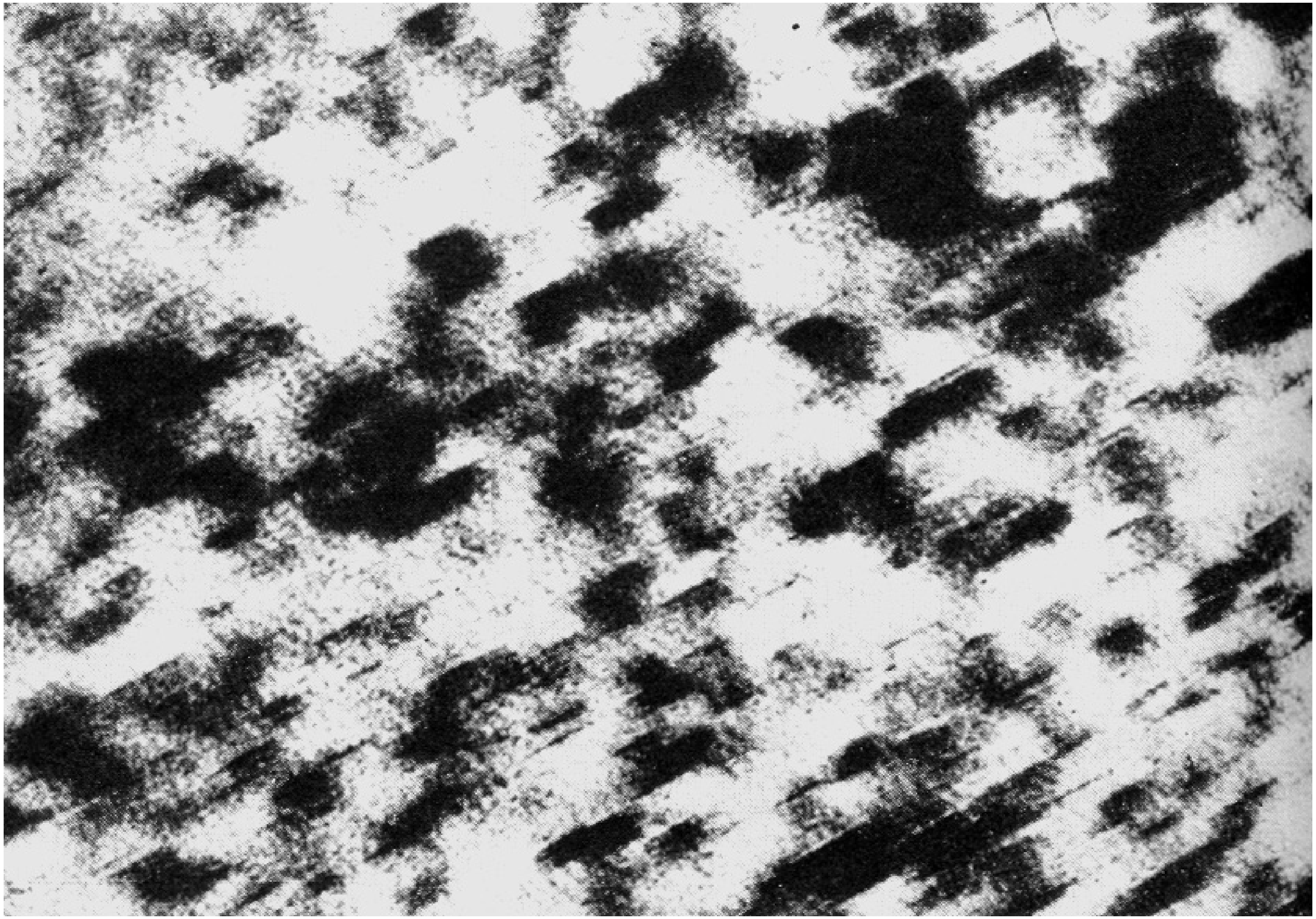


Fig. 5.26 Section through a GP zone parallel to the (200) plane. (Based on the work of V. Gerold: *Zeitschrift für Metallkunde* **45** (1954) 599.)

: 이러한 응집체는 완전한 석출 입자로 볼 수 없으며, 때때로 석출대 **(zone)**로 명명함.

GP zones of Al-Cu alloys x 720,000



Fully coherent, about 2 atomic layers thick and
10 nm in diameter with a spacing of ~ 10 nm

Transition phases

$\alpha_0 \rightarrow \alpha_1$+GP zone$\rightarrow \alpha_2+\theta'' \rightarrow \alpha_3+\theta' \rightarrow \alpha_4+\theta$ (**$CuAl_2$**)

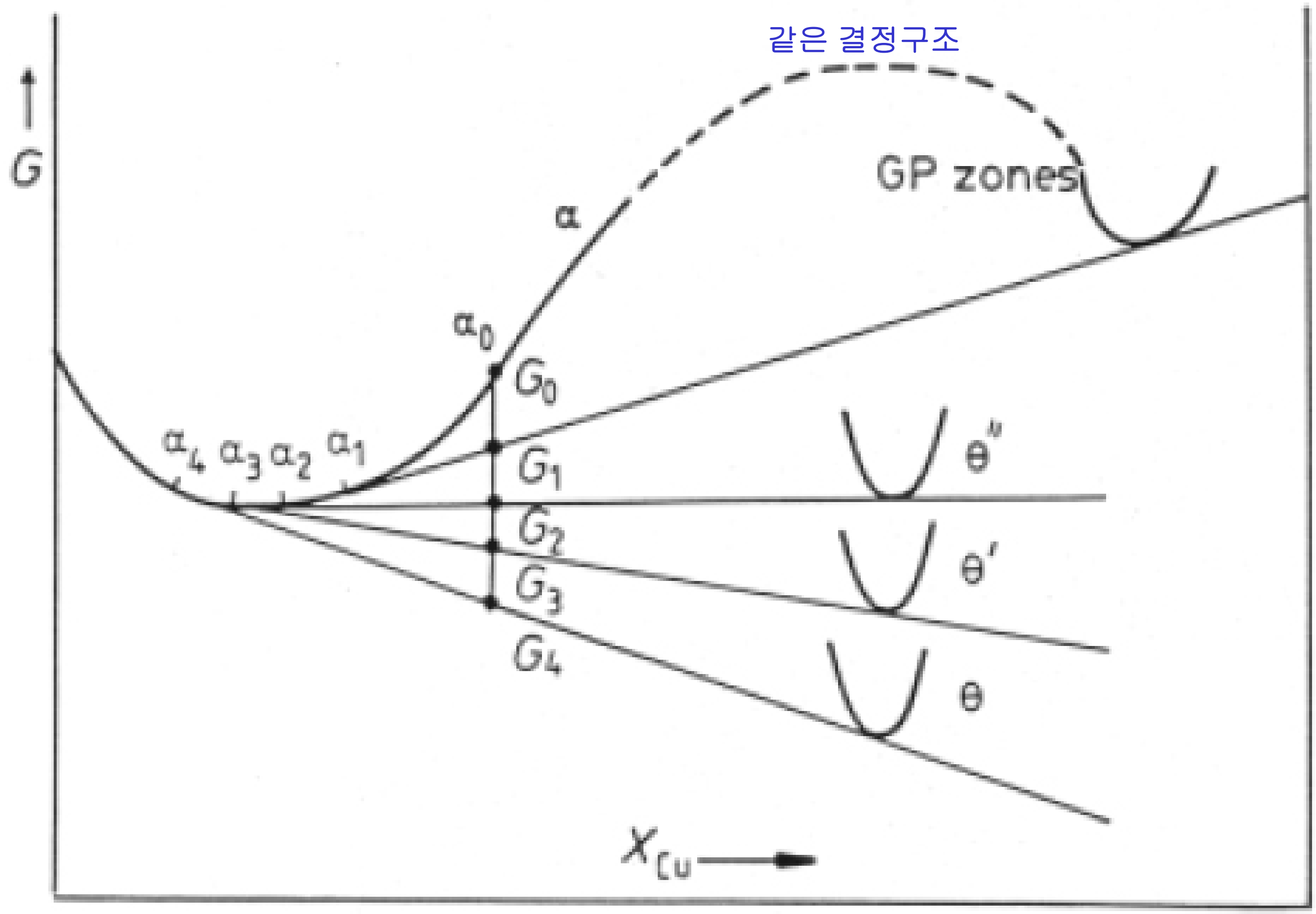
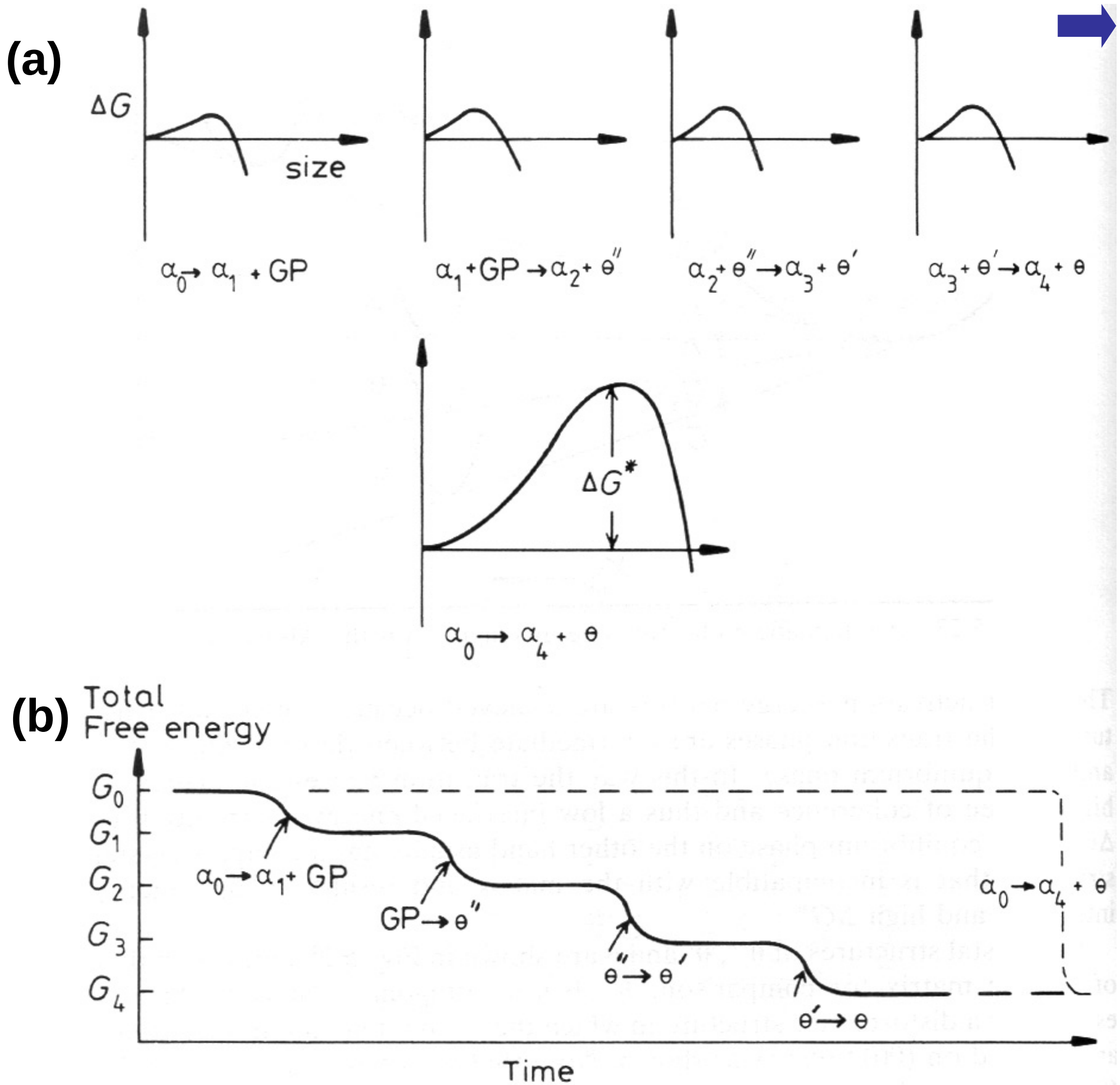


Fig. 5.27 A schematic molar free energy diagram for the Al-Cu system.

$\alpha_0 \rightarrow \alpha_1$+GP zone$\rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta$ (**$CuAl_2$**)

Low Activation Energy of Transition Phases

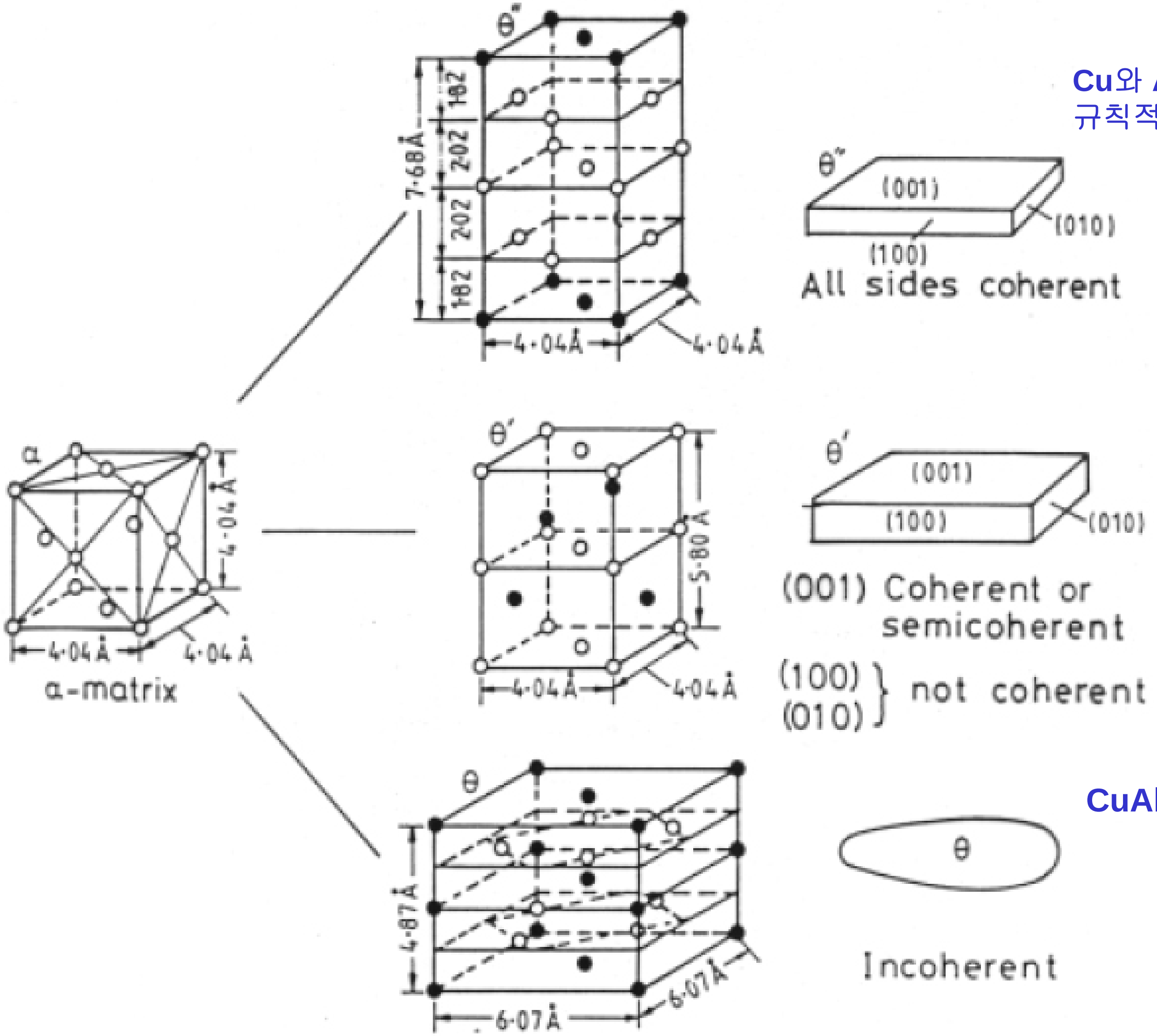


천이상의 결정구조가 모상과 평형상의 중간상태를 갖기 때문

천이상 : 정합 정도가 높고 ΔG*에 기여하는 계면에너지는 작은 값 가짐.

평형상: 기지와 격자를 잘 일치시킬 수 없는 복잡한 결정구조= 고 계면 E

The Crystal Structures of θ″, θ′ and θ

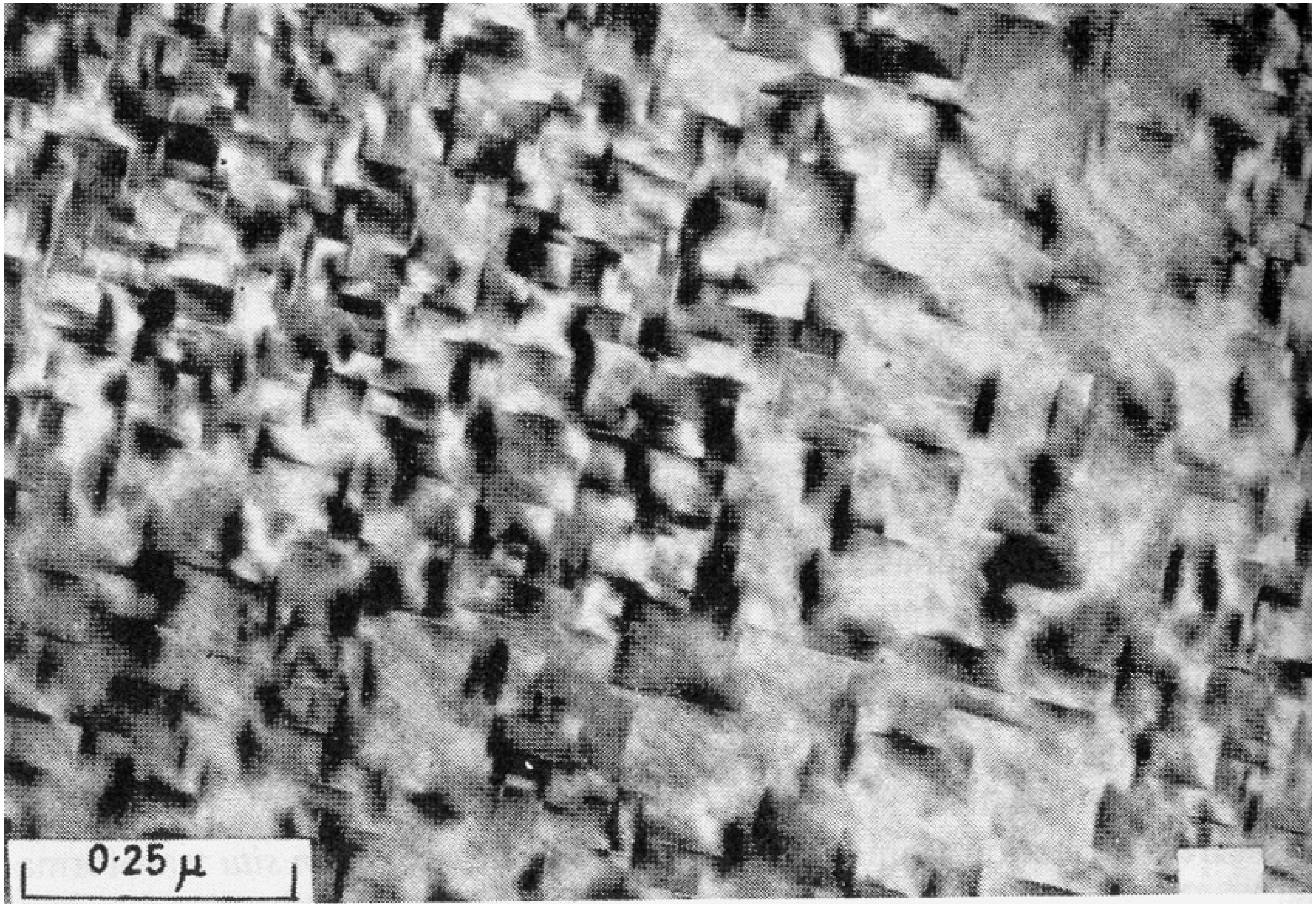


Cu와 **Al** 원자가 **(001)** 면에 규칙적으로 놓여있는 변형된 **fcc** 구조

$CuAl_2$ 조성**,** 복잡한 **bct** 구조

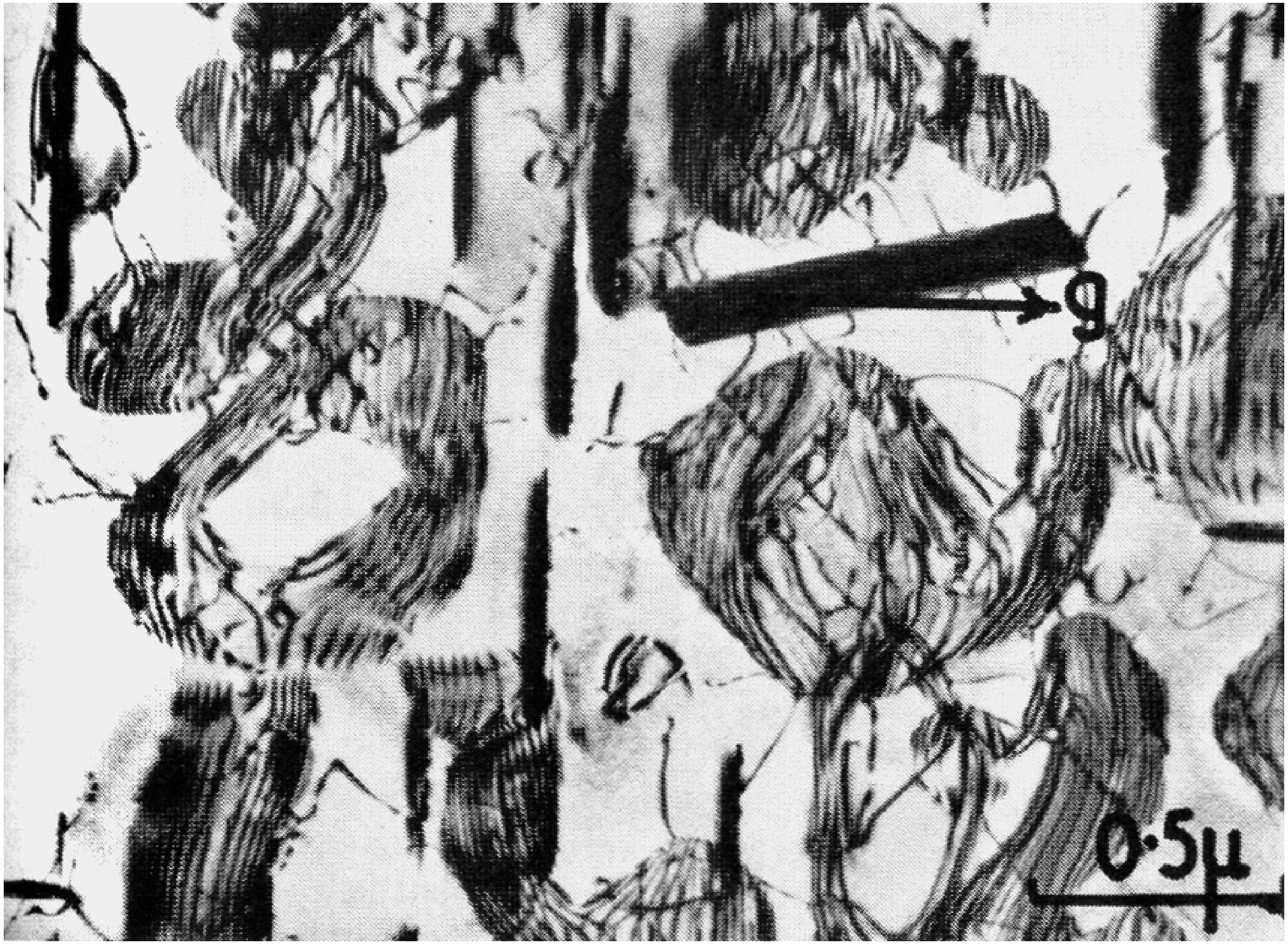
Fig. 5.29 Structure and morphology of Θ″, Θ′ and Θ in Al-Cu (○ Al, ● Cu).

θ'' of Al-Cu alloys x 63,000



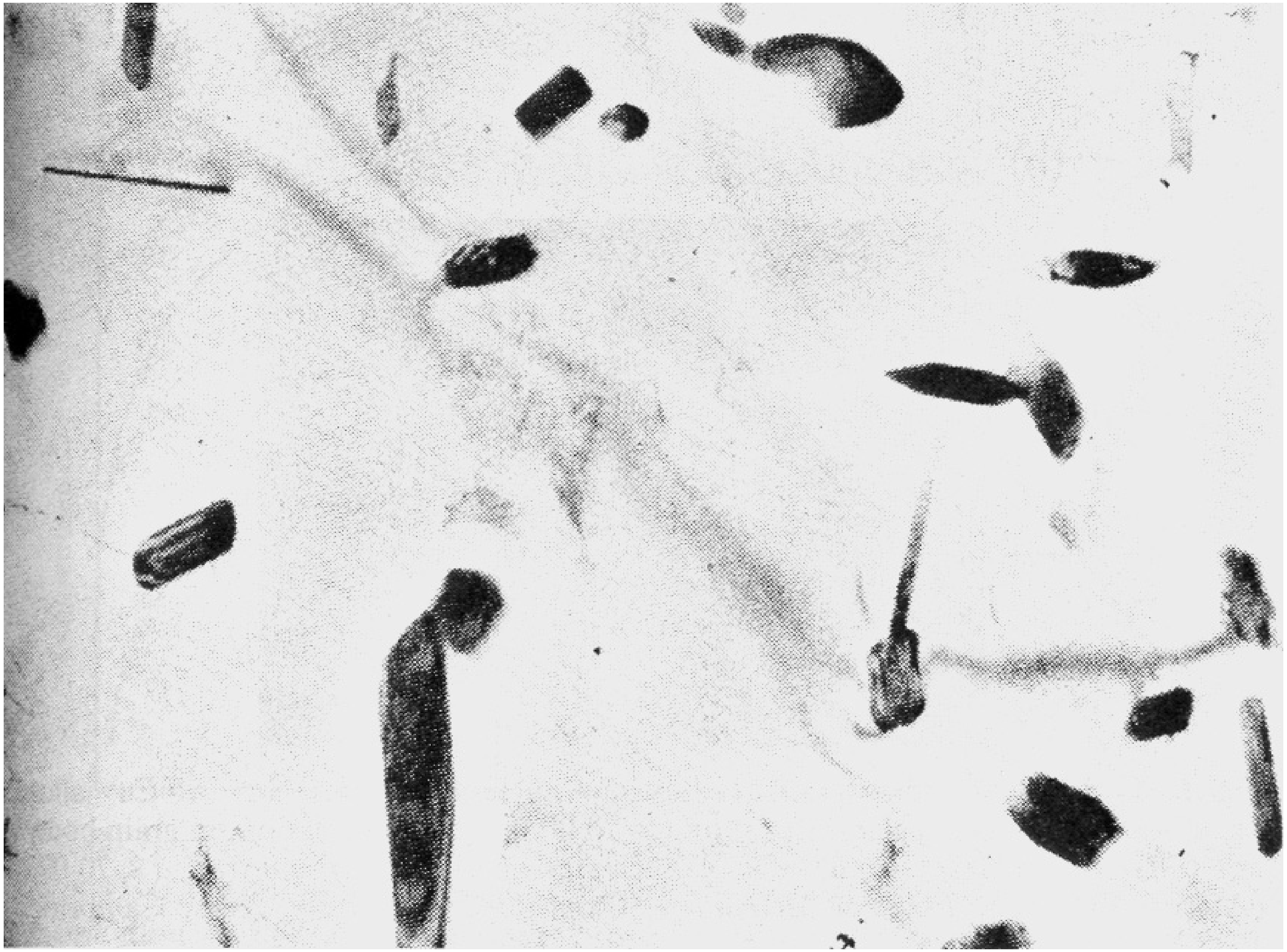
Tetragonal unit cell, essentially a distorted fcc in which Cu and Al atoms are ordered on (001) planes, fully-coherent plate-like ppt with $\{001\}_{\alpha}$ habit plane. ~ 10 nm thick and 100 nm in diameter.

θ′ of Al-Cu alloys x 18,000



θ′ has (001) planes that are identical with $\{001\}_\alpha$ and forms as plates on $\{001\}_\alpha$ with the same orientation relationship as θ″. (100), (010) → incoherent , ~ 1 μm in diameter.

θ of Al-Cu alloys x 8,000



$CuAl_2$: complex body centered tetragonal, incoherent or complex semicoherent

Nucleation sites in Al-Cu alloys

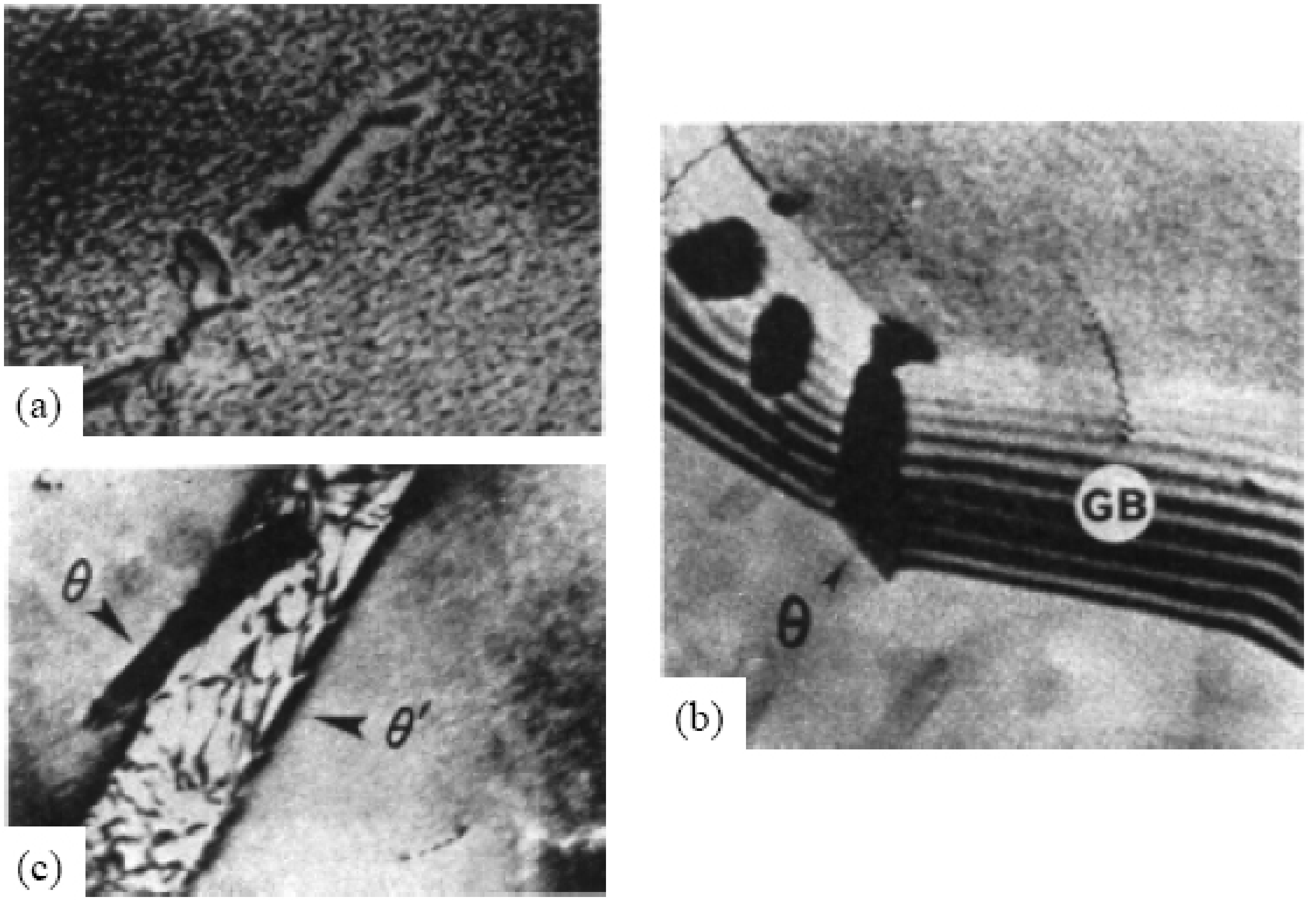


Fig. 5.31 Electron micrographs showing nucleation sites in Al-Cu alloys. (a) $\Theta'' \rightarrow \Theta'$. Θ' nucleates at dislocation (x 70,000). (b) Θ nucleation on grain boundary (GB) (x 56,000). (c) $\Theta' \rightarrow \Theta$. Θ nucleates at Θ'/matrix interface (x 70,000). (After P. Haasen, *Physical Metallurgy*, Cambridge University Press, Cambridge, 1978.)

The Effect of Ageing Temperature on the Sequence of Precipitates

석출순서에 따라 미세조직 조대화 됨.

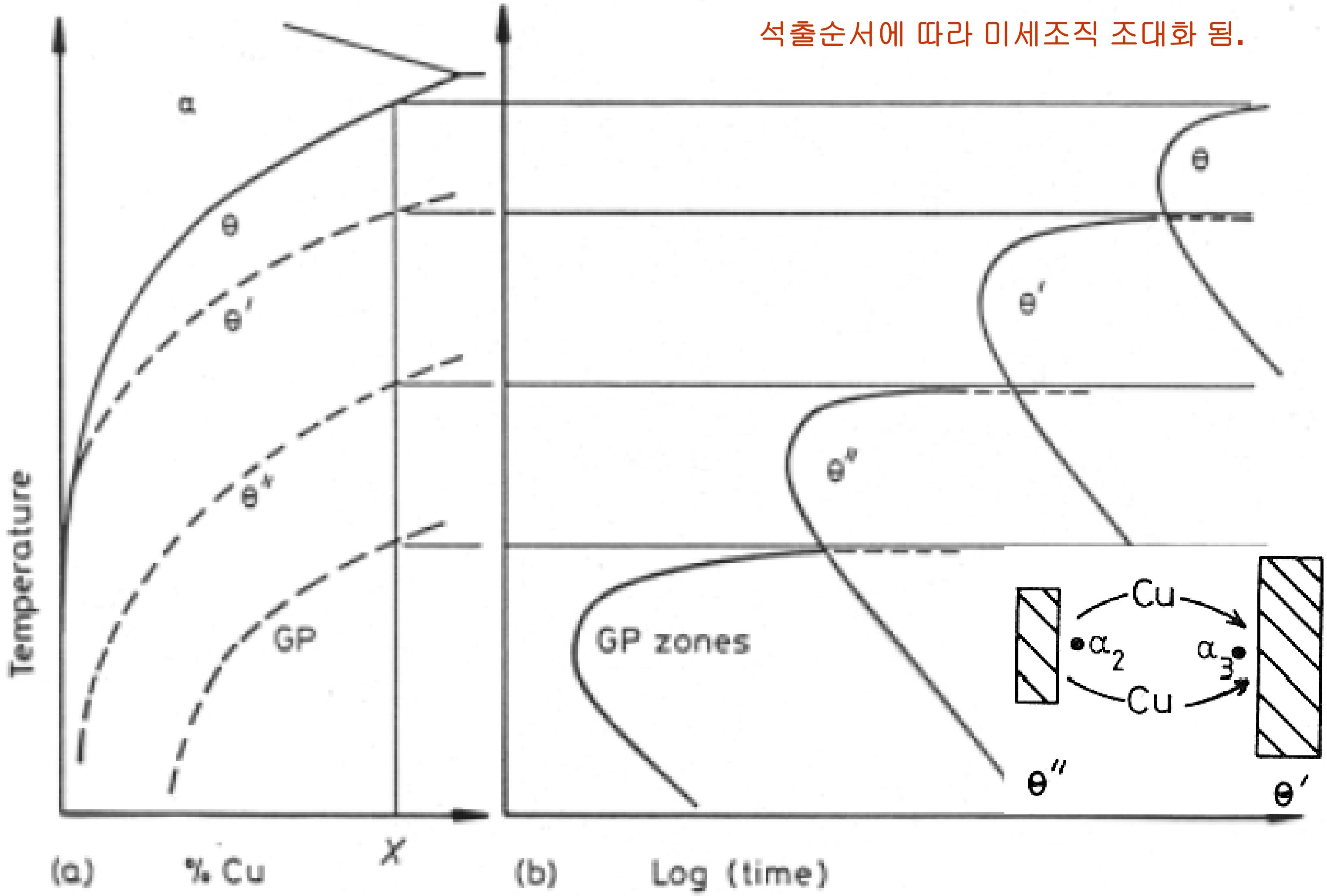
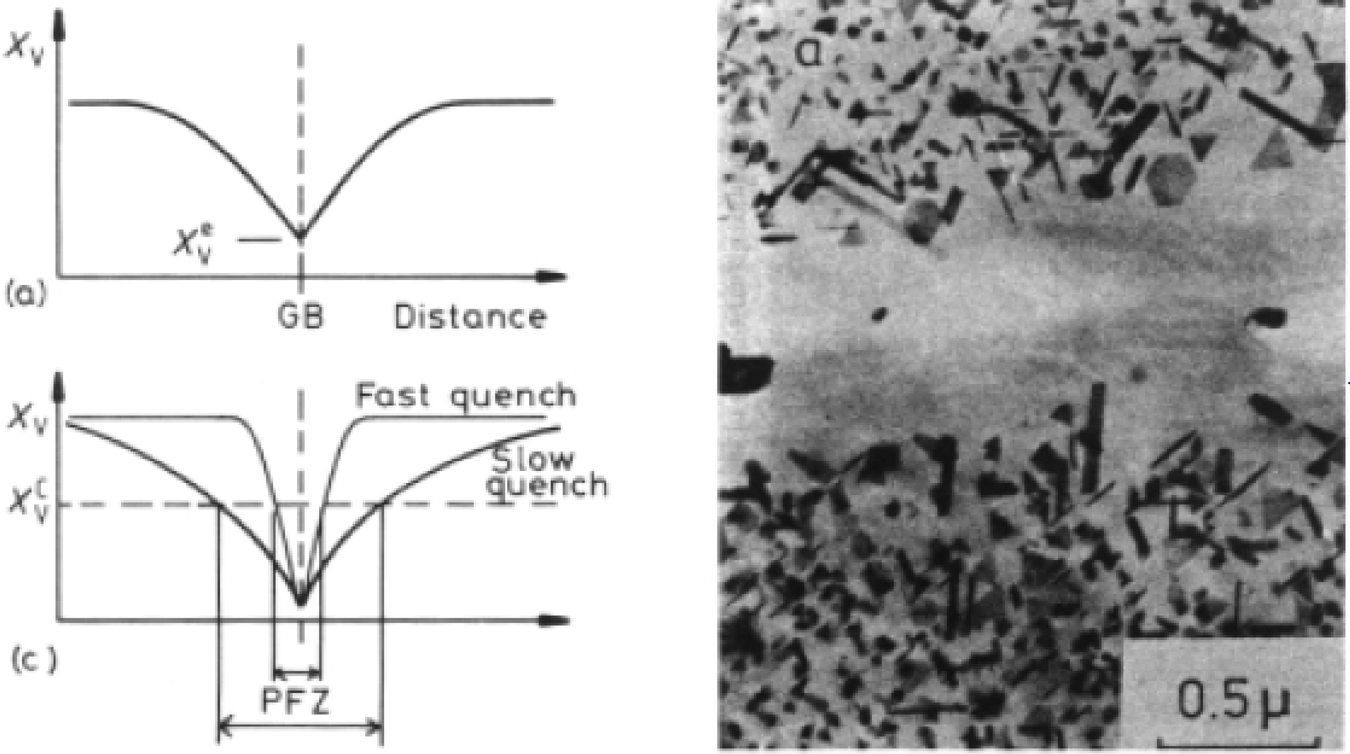


Fig. 5.32 (a) Metastable solvus lines in Al-Cu (schematic). (b) Time for start of precipitation at different temperatures for alloy *X* in (a).

5.5.3. Quenched-in Vacancies

Precipitate-Free Zone(PFZ) due to Vacancy Diffusion during quenching



GB 농도 결정립 내부 농도와 거의 유사**,** 하지만 핵이 형성되려면 공공농도가 임계 과포화 공공농도를 초과해야만 하기 때문**.**

Fig. 5.35 A PFZ due to vacancy diffusion to a grain boundary during quenching. (a) Vacancy concentration profile. (b) A PFZ in an Al-Ge alloy (x 20,000). (c) Dependence of PFZ width on critical vacancy concentration X_v^c and rate of quenching. [(b) After G. Lorimer in *Precipitation in Solids*, K.C. Russell and H.I. Aaronson (Eds.), The Metallurgical Society of AIME, 1978.]

5.5.3. Quenched-in Vacancies

PFZs can also be induced by the nucleation and growth of grain boundary precipitates during cooling from the solution treatment temperature

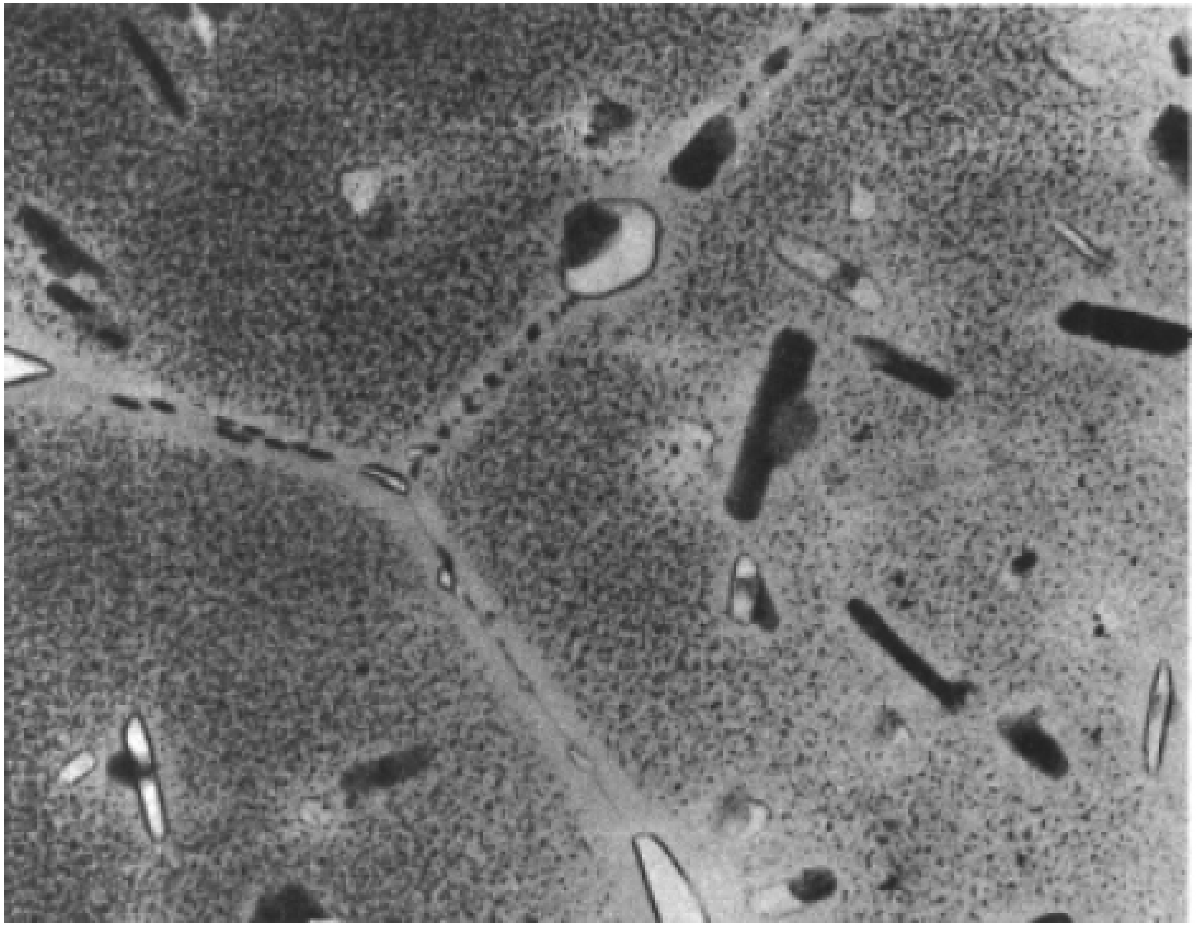


Fig. 5.36 PFZs around grain boundaries in a high-strength commercial Al-Zn-Mg-Cu alloy. Precipitates on grain boundaries have extracted solute from surrounding matrix. (x 59,200)

5.5.4. Age Hardening

중간상 형성시 커다란 격자변형 수반하고, 소성 변형시 전위의 이동을 방해함

최대경도 θ″와 θ′ 공존할때

Hardness vs. Time by Ageing

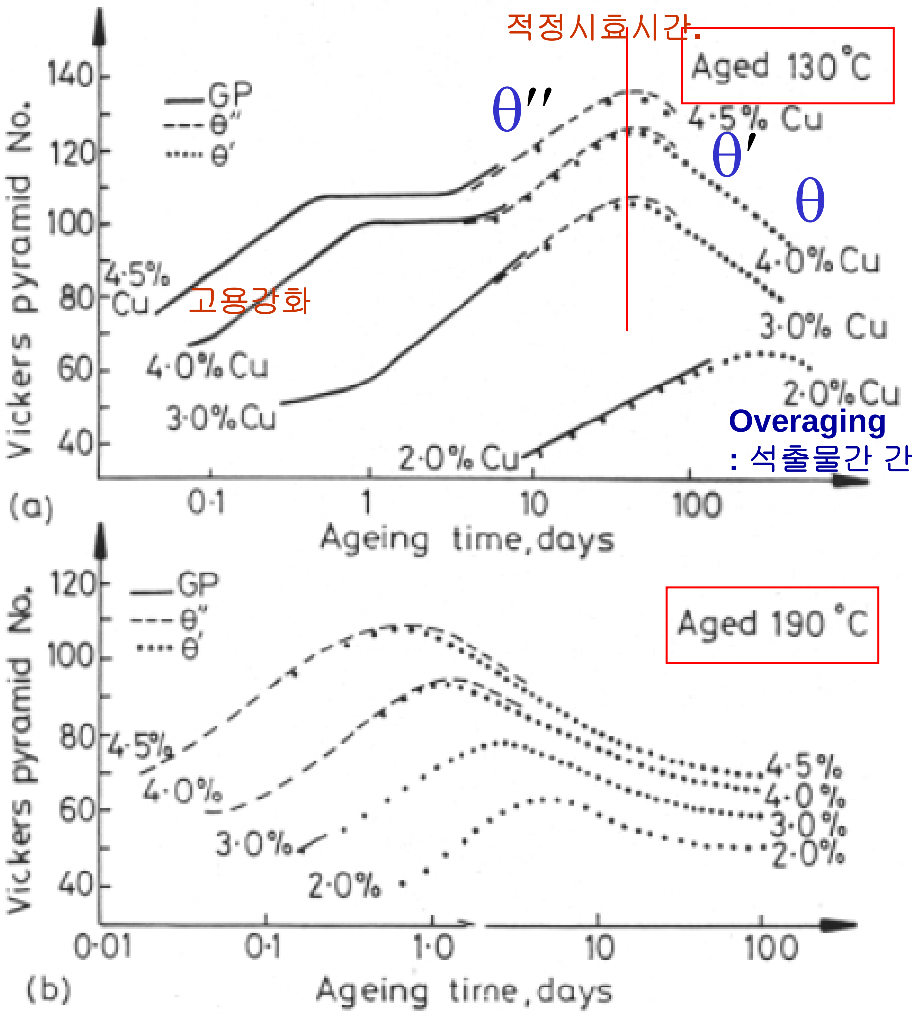


Fig. 5.37 Hardness vs. time for various Al-Cu alloys at (a) 130°C (b) 190°C. (After J.M. Silcock. T.J. Heal and H.K. Hardy, *Journal of the Institute of Metals* **82** (1953-1954) 239.

Ageing at 130°C produces higher maximum hardness than ageing at 190°C.

At 130°C, however, it takes too a long time.

How can you get the high hardness for the relatively short ageing time?

Double ageing treatment
first below the GP zone solvus
→ fine dispersion of GP zones
then ageing at higher T.

미세한 석출물의 분포