2009 fall

Phase Transformation of Materials

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Contents for previous class

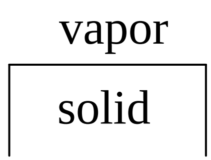
Chapter 3 Crystal Interfaces and Microstructure

계면의 단순한 형태를 사용하여 계면 자유에너지의 근원을 알아보고 계면에너지를 구할 수 있는 몇 가지 방법을 보여줌.

- **Interfacial Free Energy** (γ : J/m^2)

→ The Gibbs free energy of a system containing an interface of area A

→ $G_{bulk} + G_{interface}$



→ $\boxed{G = G_0 + \gamma A}$

* Interfacial energy (γ) vs. surface tension (F) → $F = \gamma + A\, d\gamma / dA$

* Origin of the surface free energy? → **Broken Bonds**

- **Solid/Vapor Interfaces** $\boxed{high\ T_m \rightarrow high\ L_s \rightarrow high\ \gamma_{sv}}$

* γ interfacial energy = free energy (J/m^2)

→ $\gamma = G = H - TS$

$= E + PV - TS$ (: PV is ignored)

→ $\boxed{\gamma = E_{sv} - TS_{sv}}$ (S_{sv} thermal entropy, configurational entropy)

→ $\partial\gamma / \partial T = -S$: surface energy decreases with increasing T

γ-θ plot

Equilibrium shape: Wulff surface

$$\sum_{i=1}^{n} A_i \gamma_j = Minimum$$

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- **Boundaries in Single-Phase Solids**

(a) Low-Angle and High-Angle Boundaries

symmetric tilt or twist boundary
non-symmetric tilt or twist boundary

Θ < 15° : 단위 면적 안에 있는 전위의 총 에너지

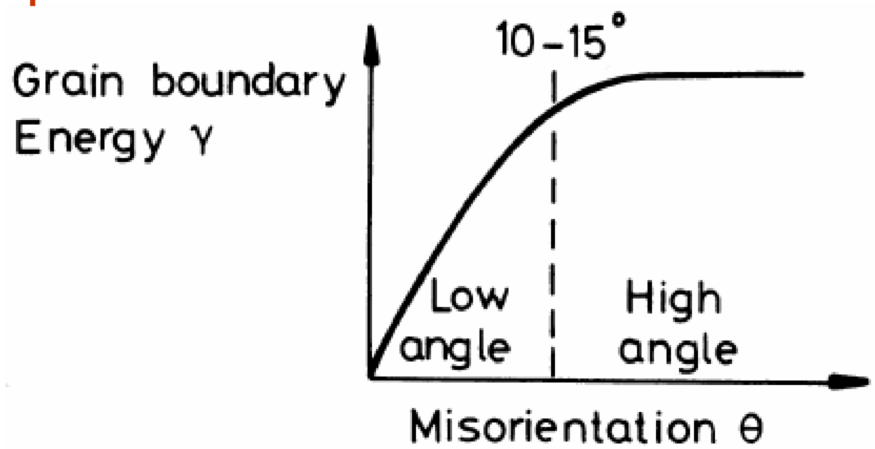
- Relation between D and γ ?

$\sin\Theta = b/D$, at low angle

→ $D=b/\Theta$ → $\gamma_{g.b.}$ is proportional to 1/D

→ low angle tilt boundary

→ Density of edge dis.



Θ > 15° : 전위 간격이 너무 작아 전위중심은 중복되고 각각의 전위 물리적 구별이 어려움.

high angle $\gamma_{g.b.} \approx 1/3\ \gamma_{S/V.}$ → Broken Bonds

Contents for today's class

Chapter 3 Crystal Interfaces and Microstructure

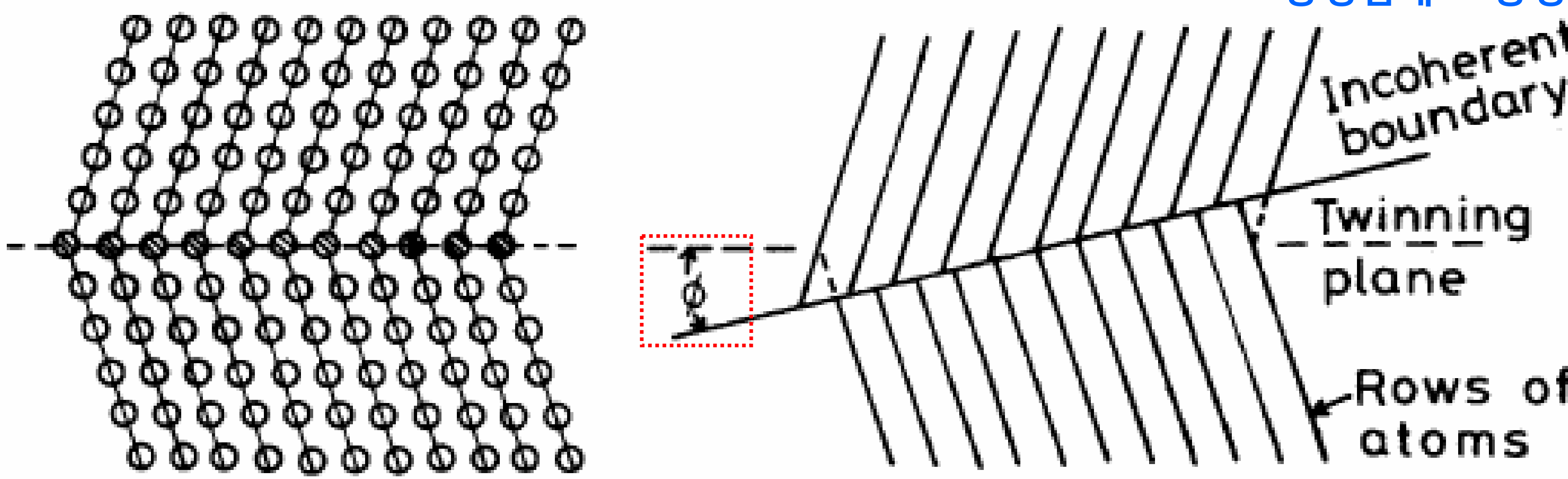
계면의 단순한 형태를 사용하여 계면 자유에너지의 근원을 알아보고 계면에너지를 구할 수 있는 몇 가지 방법을 보여줌.

- Interfacial Free Energy
- Solid/Vapor Interfaces
- Boundaries in Single-Phase Solids
  - (a) Low-Angle and High-Angle Boundaries
  - **(b) Special High-Angle Grain Boundaries**
  - **(c) Equilibrium in Polycrystalline Materials**
- **Thermally Activated Migration of Grain Boundaries**
- **The Kinetics of Grain Growth**
- **Interphase Interfaces in Solid**

Special High-Angle Grain Boundaries

: high angle boundary but with low $\gamma_{g.b.}$.

쌍정립계 ≠ 쌍정면



(a) **Coherent twin boundary**

symmetric twin boundary

→ **low $\gamma_{g.b.}$.**

입계의 원자들이 변형되지 않은 위치에 존재

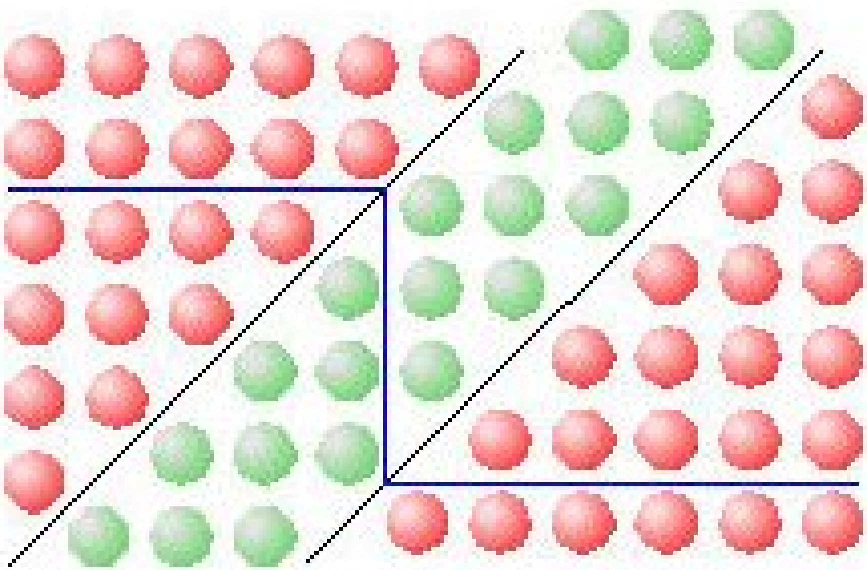
(b) **Incoherent twin boundary**

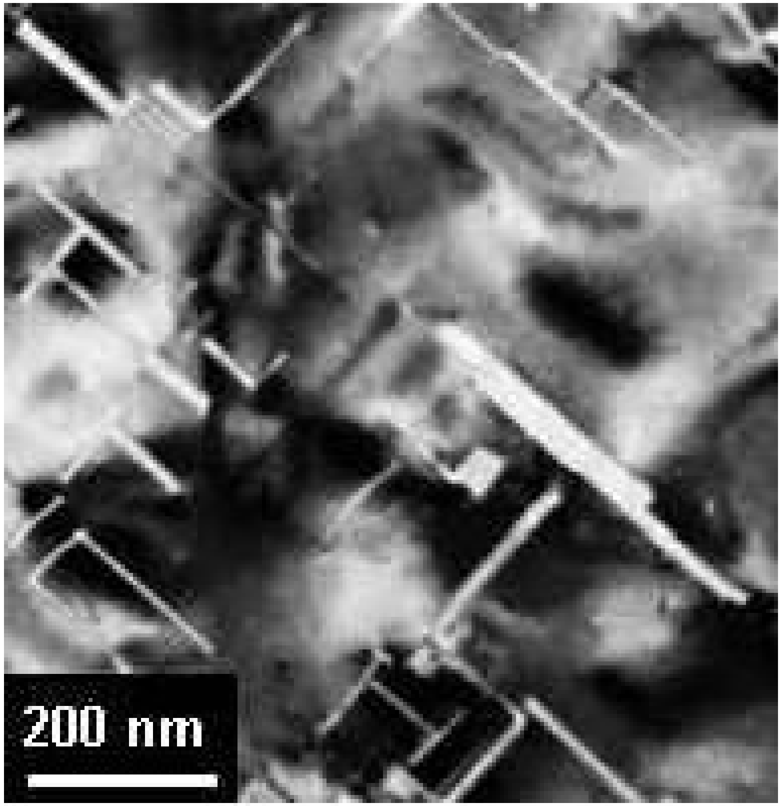
asymmetric twin boundary

→ **low $\gamma_{g.b.}$.**

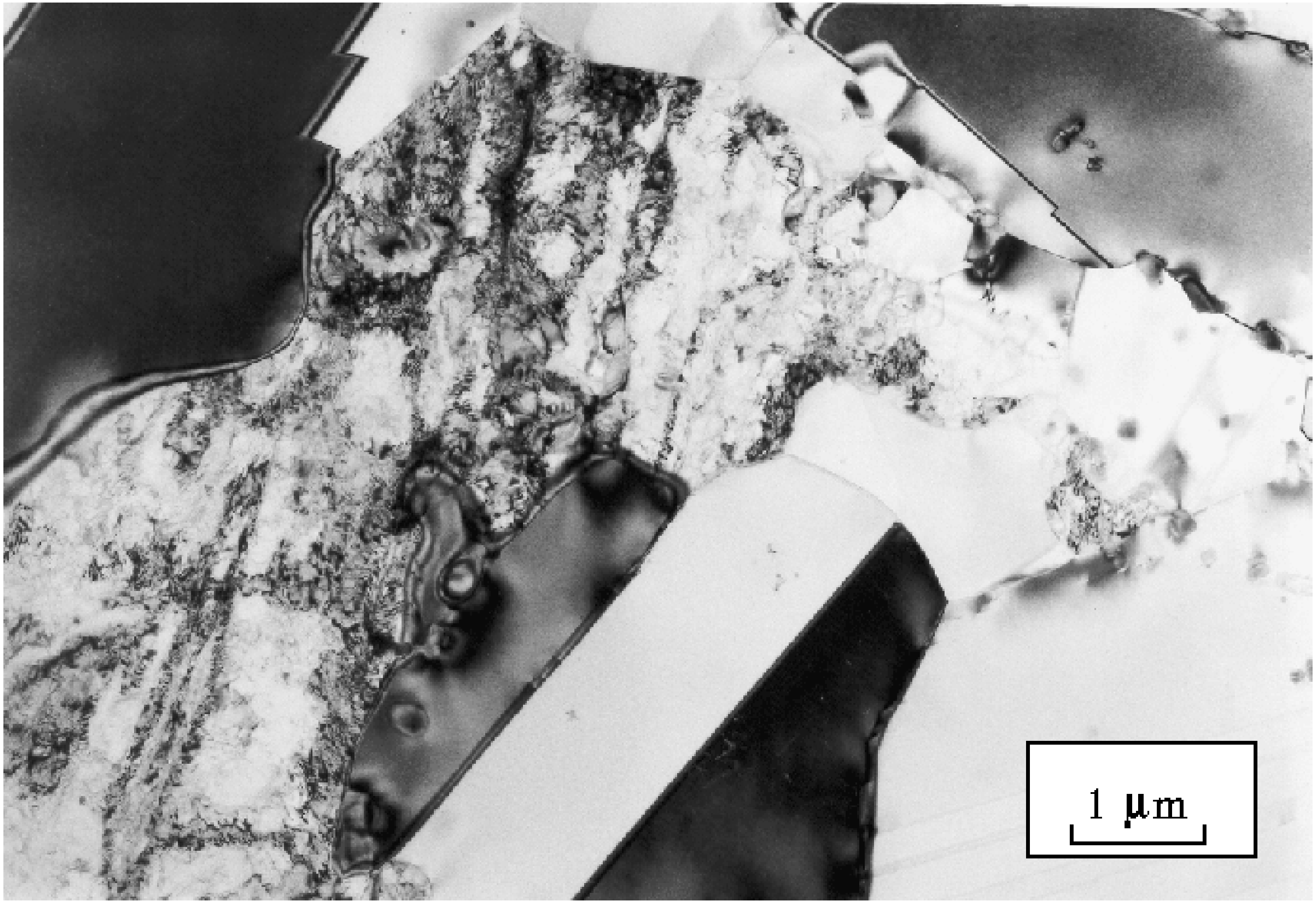
쌍정립계 E 입계면의 방위에 따라 민감하게 변화

Twin boundary

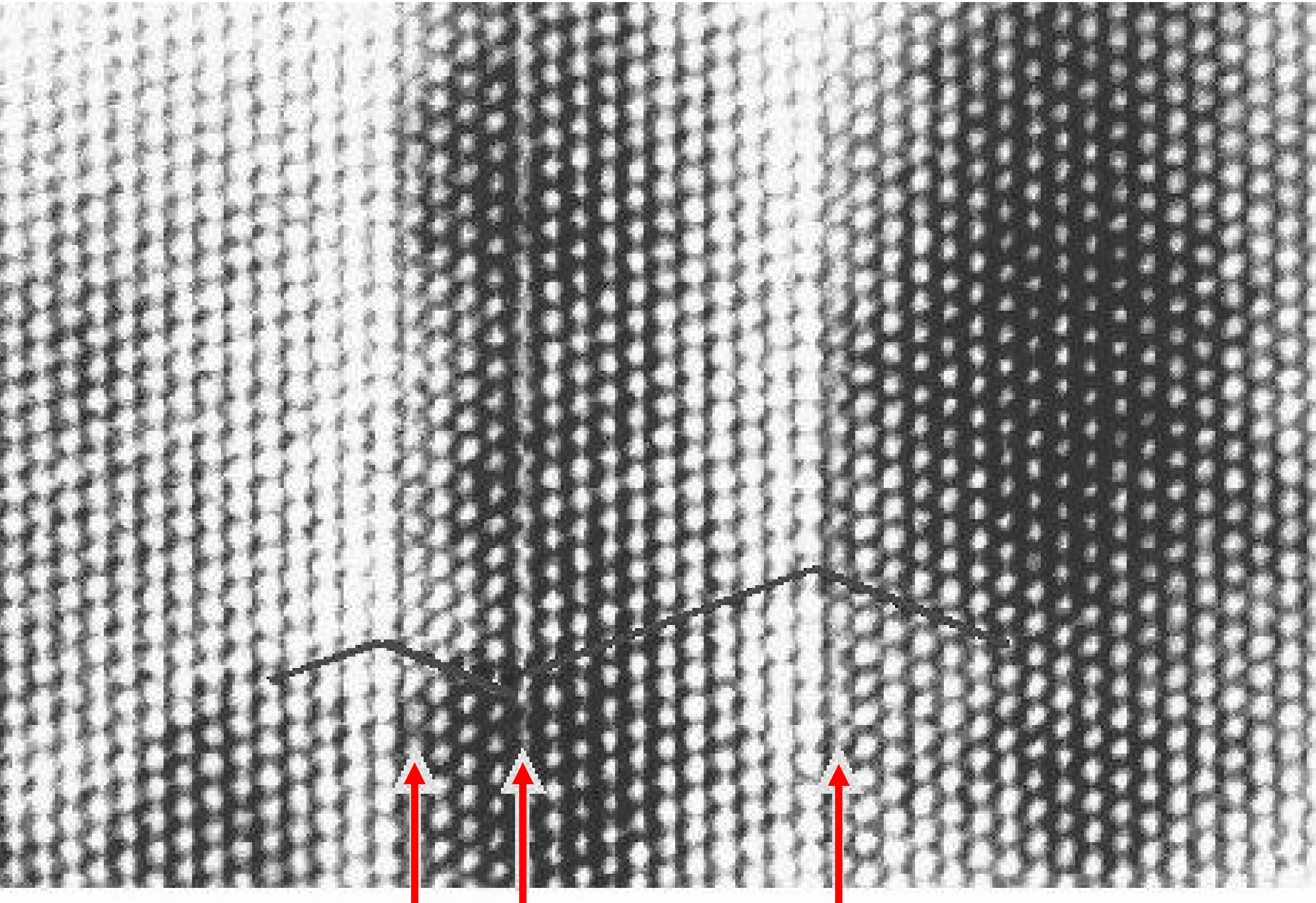




Twin boundary



Twin boundary



Special High-Angle Grain Boundaries

(c) Twin boundary energy as a function of the grain boundary orientation

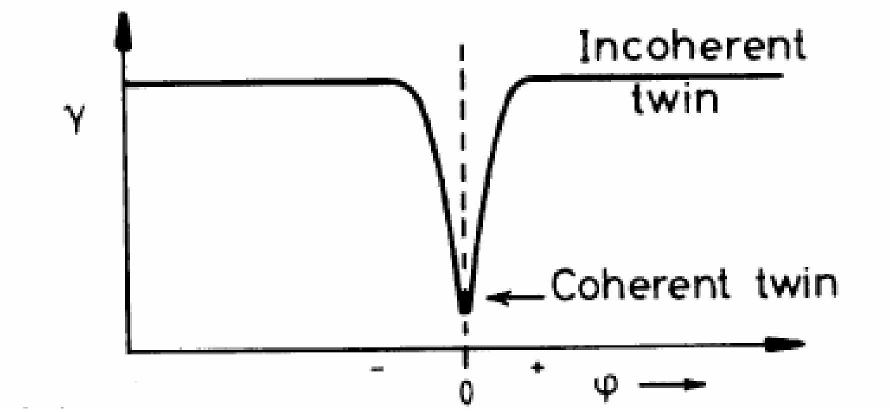


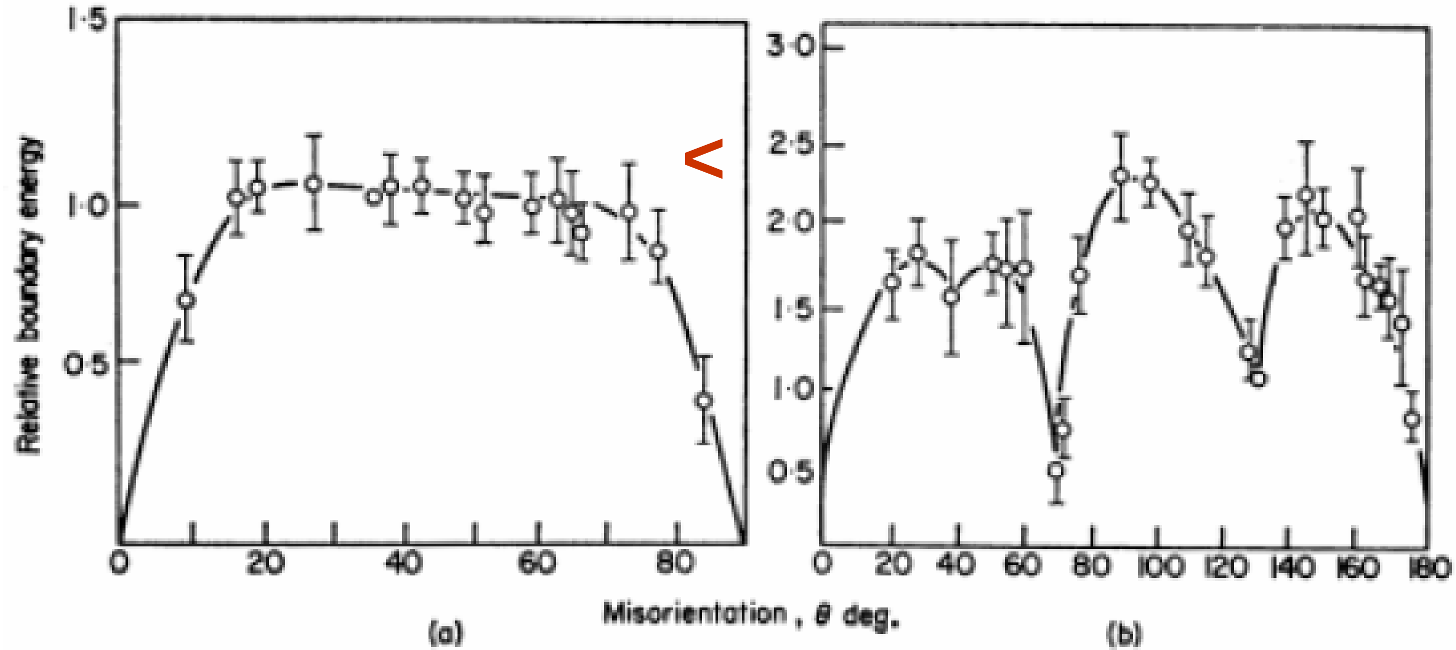
Table 3.3 Measured Boundary Free Energies for Crystals in Twin Relationships

(Units mJ/m²)

Crystal	Coherent twin boundary energy		Incoherent twin boundary energy		Grain boundary energy
Cu	21		498		623
Ag	8	<<	126	<	377
Fe-Cr-Ni (stainless steel type 304)	19		209		835

Special High-Angle Grain Boundaries

2개의 결정립이 <100> 축을 중심으로 회전 2개의 결정립이 <110> 축을 중심으로 회전



고경각 경계~대략 같은 E 가짐

Fig. 3.13 Measured grain boundary energies for symmetric tilt boundaries in Al (a) When the rotation axis is parallel to <100>, (b) when the rotation axis is parallel to <110>. (After G. Hasson and C. Goux, Scripta Metallurgica, 5 (1971) 889.)

Why are there cusps in Fig. 3.13 (b)?

FCC 금속에서 쌍정립계 양쪽 결정의 <110> 축은 서로 70.5° 이룸: 정합 쌍정립계

• 대칭적 경각입계

• 소규모 집단의 반복

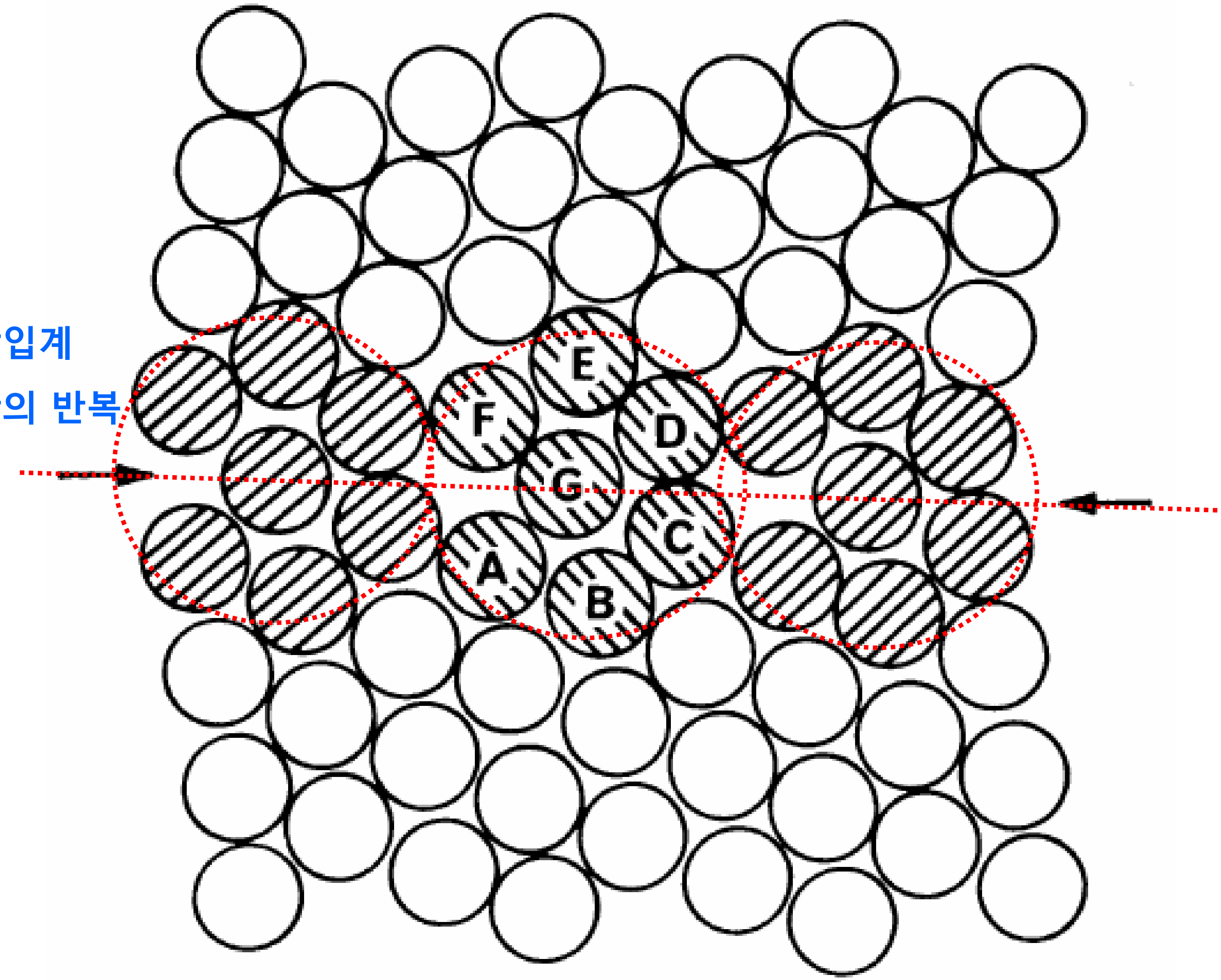


Fig. 3. 14 Special grain boundary. (After H. Gleiter, Physica Status Solidi (b) 45 (1971) 9.)

Equilibrium in Polycrystalline Materials

현미경 조직 → 서로 다른 입계들이 공간에서 어떻게 연결되는가에 따라 결정

⇨ 서로 다른 E 갖고 있는 입계 때문에 다결정체 재료의 미세구조가 어떻게 영향을 받는지 고려

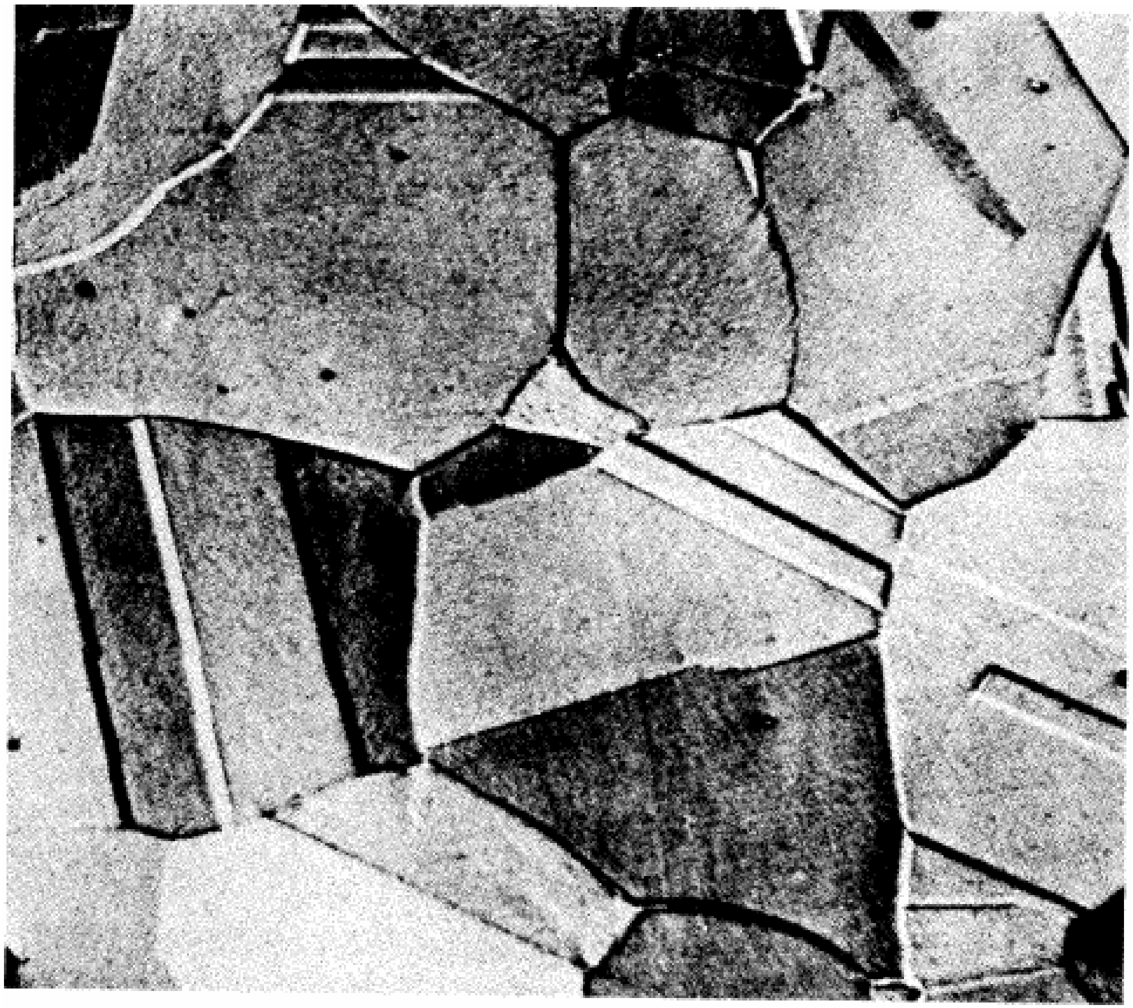


Fig. 3.15 Microstructure of an annealed crystal of austenitic stainless steel. (After P.G. Shewmon, Transformations in Metals, McGraw-Hill, New York, 1969)

Poly grain material

두 결정립은 면(입계), 세 결정립은 선 (결정 모서리),
네 결정립은 점(결정립 모퉁이) 에서 만남.

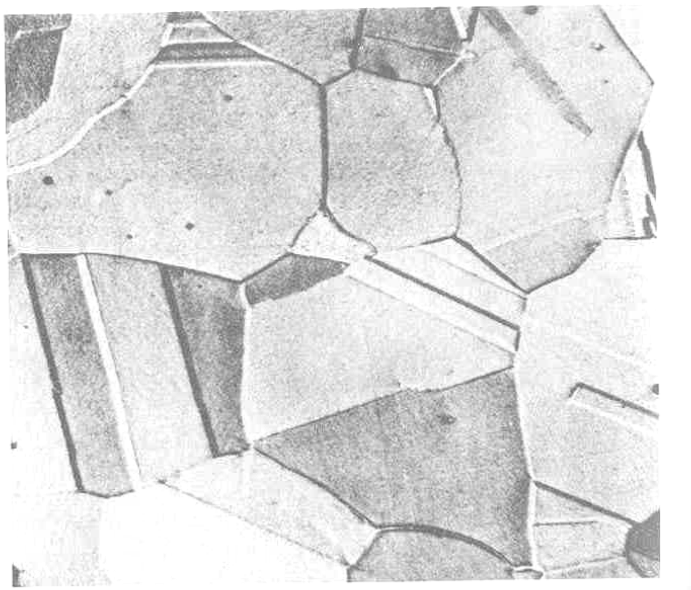
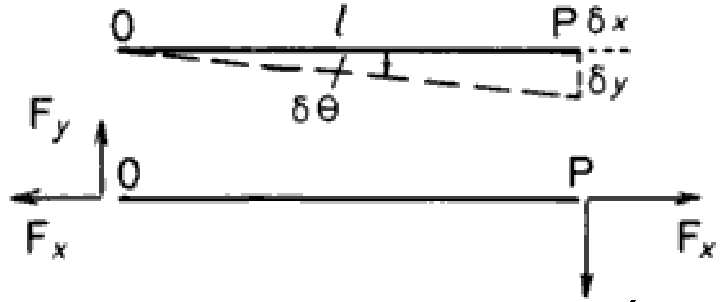


Fig. 3.15 Microstructure of an annealed crystal of austenitic stainless steel. (After P.G. Shewmon, *Transformations in Metals*, McGraw-Hill, New York, 1969.)

입계 교차점에서 평형조건



1) $F_x = \gamma$

2) F_y ?

P is moved at a small distance(δy)

A. work done by : $F_y\,\delta y$

B. increase boundary energy caused by the change in orientation $\delta\theta \sim l\,(d\gamma/d\theta)\,\delta\theta$

G.B.는 고 에너지 영역

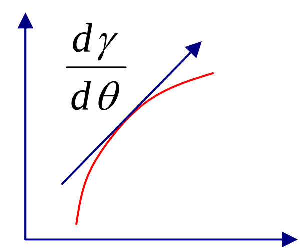
Equil. ~ no grain boundary

→ 다결정재료 실제 평형조직 아님

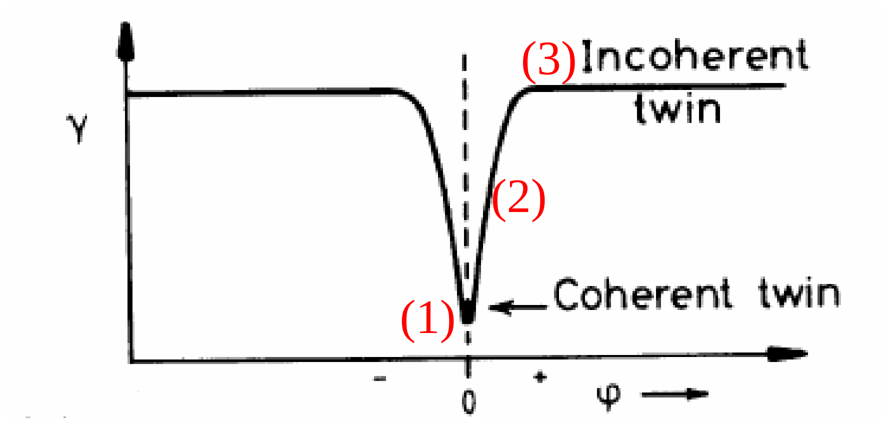
→ 어닐링시 다결정체 내의 입계는 이동하거나 회전하여 입계의 교차점에서 준안정 평형상태 유지

$F_y\,\delta y = l\,(d\gamma/d\theta)\,\delta\theta$

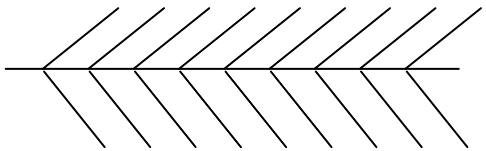
→ $F_y = d\gamma/d\theta$ torque force



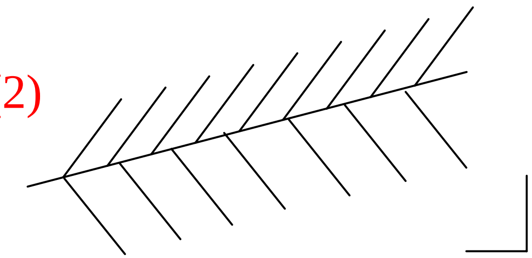
→ segment of g.b. moves to low energy position



(1)



(2)

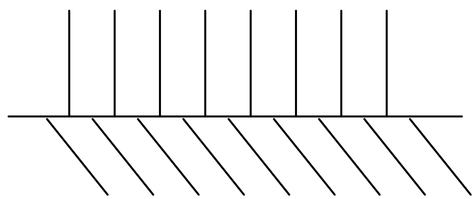


$F_y = d\gamma/d\theta$

입계에너지 최소~torque = 0

회전하지 않고 유지하기 위해 입계에 cusp 까지 끌어당기는 힘에 대응하는 힘 작용

(3)



→ **There is little effect of orientation**

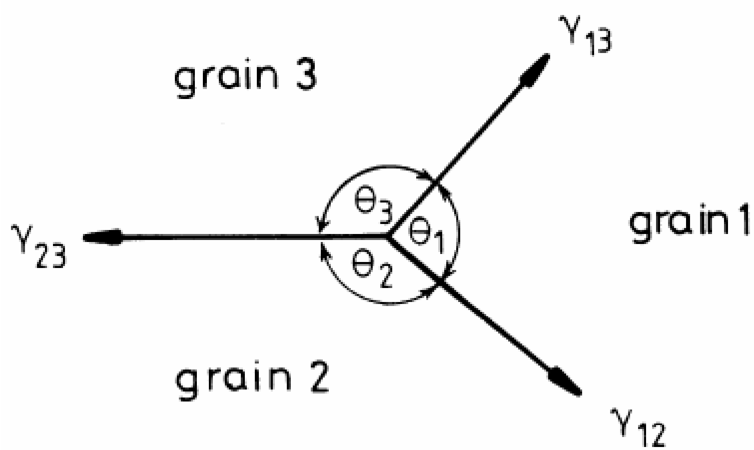
⇨ **How metastable equil. ? → force (torque)**

* general high angle boundary : $d\gamma/d\theta \approx 0$

동일한 입계에너지/방위와 무관

→ **consider more simply**

→ **3 grain 사이의 연결점에서 준안정 평형에 필요한 요구조건**



$$\frac{\gamma_{23}}{\sin\theta_1} = \frac{\gamma_{31}}{\sin\theta_2} = \frac{\gamma_{12}}{\sin\theta_3}$$

→ **θ = 120°**

결정상 2, 3이 1 과 다른 경우도 성립

If the solid-vapor energy ($\gamma_{S/V}$) is the same for both grains,

$$2\gamma_{SV}\cos\frac{\theta}{2} = \gamma_b$$

(단, torque 효과 무시)

입계에너지 측정하는 한 방법:

높은 온도에서 시편 어닐링 후

입계와 표면 교차점의 각도 측정

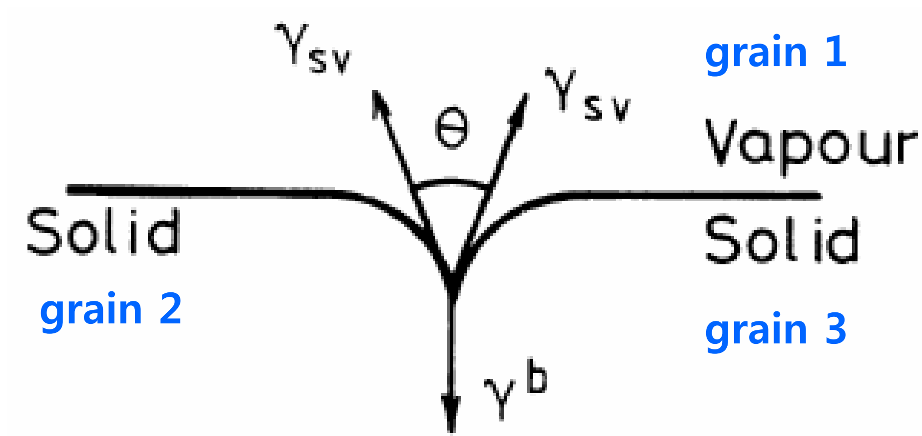


Fig. 3. 18 The balance of surface and grain boundary tensions at the intersection of a grain boundary with a free surface.

G.B 만날 때 1) 입계 E 균형 + 2) 표면 장력 균형

3.3.4. Thermally Activated Migration of Grain Boundaries

If the boundary is curved in the shape of cylinder, Fig. 3.20a, it is acted on by a force of magnitude γ/r towards its center of curvature.

Therefore, the only way the boundary tension forces can balance in three dimensions is if the boundary is planar ($r = \infty$) or if it is curved with equal radii in opposite directions, Fig. 3.20b and c.

Net Force due to Surface Tension

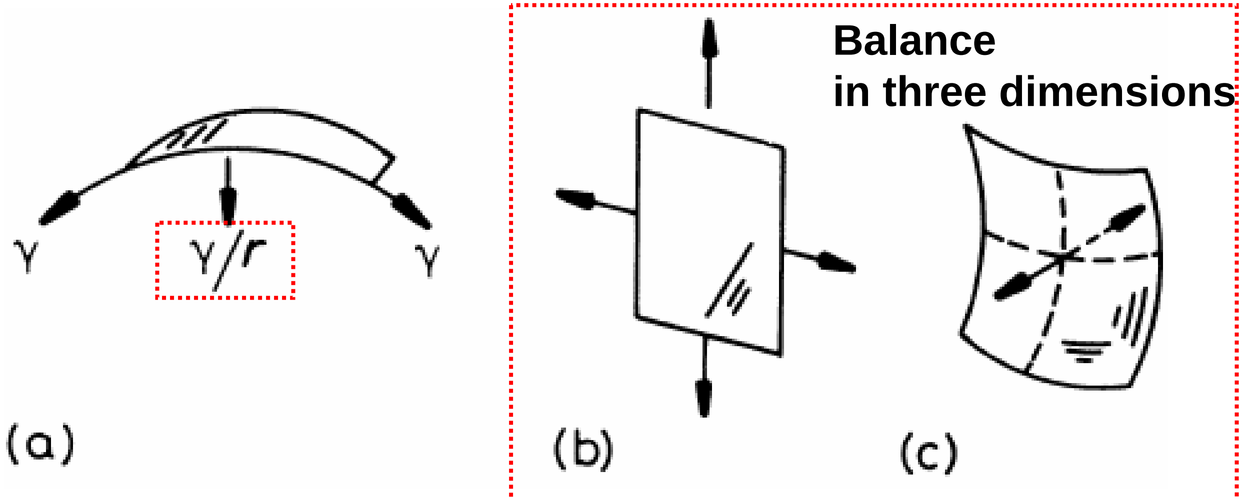


Fig. 3.20 (a) A cylindrical boundary with a radius of curvature r is acted on by a force γ/r. (b) A planar boundary with no net force. (c) A doubly curved boundary with no net force.

Direction of Grain Boundary Migration during Grain Growth

For isotropic grain boundary energy in two dimensions,

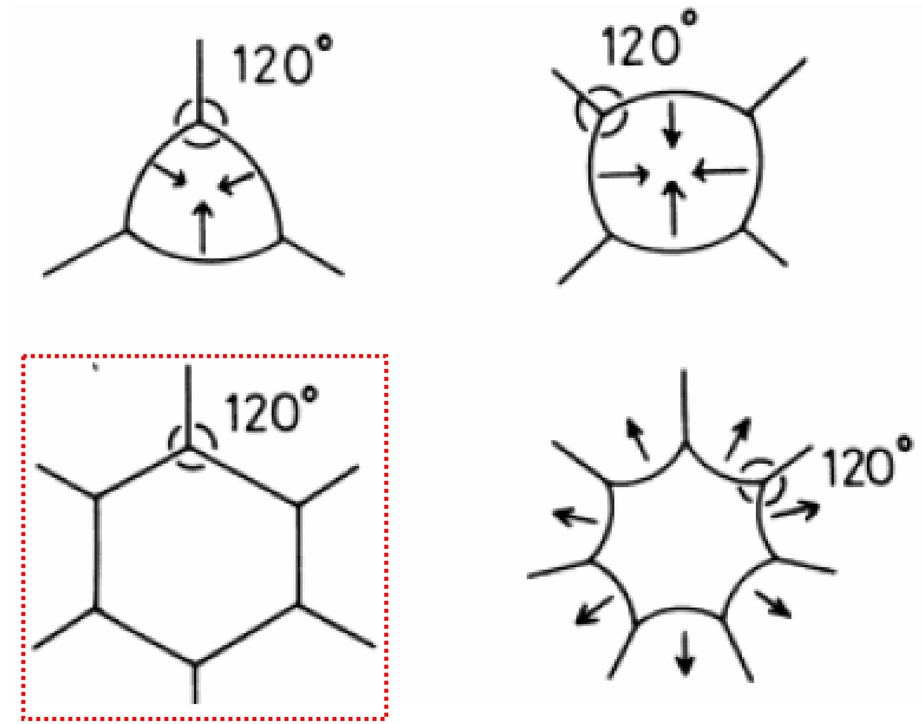
Equilibrium angle at each boundary junction? **→120°**

Equilibrium angle at each boundary junction in 3D? **→109°28'**

Morphology of metastable equilibrium state → 고온 어닐링시 이동

Boundaries around Grain < 6

; grain shrink, disappear



Boundaries around Grain = 6

; equilibrium

Boundaries around Grain > 6

; grain growth

Reduce the # of grains, increase the mean grain size, reducing the total G.B. energy

called grain growth (or grain coarsening): at high temperature above about 0.5 T_m

Grain Growth (Soap Bubble Model)

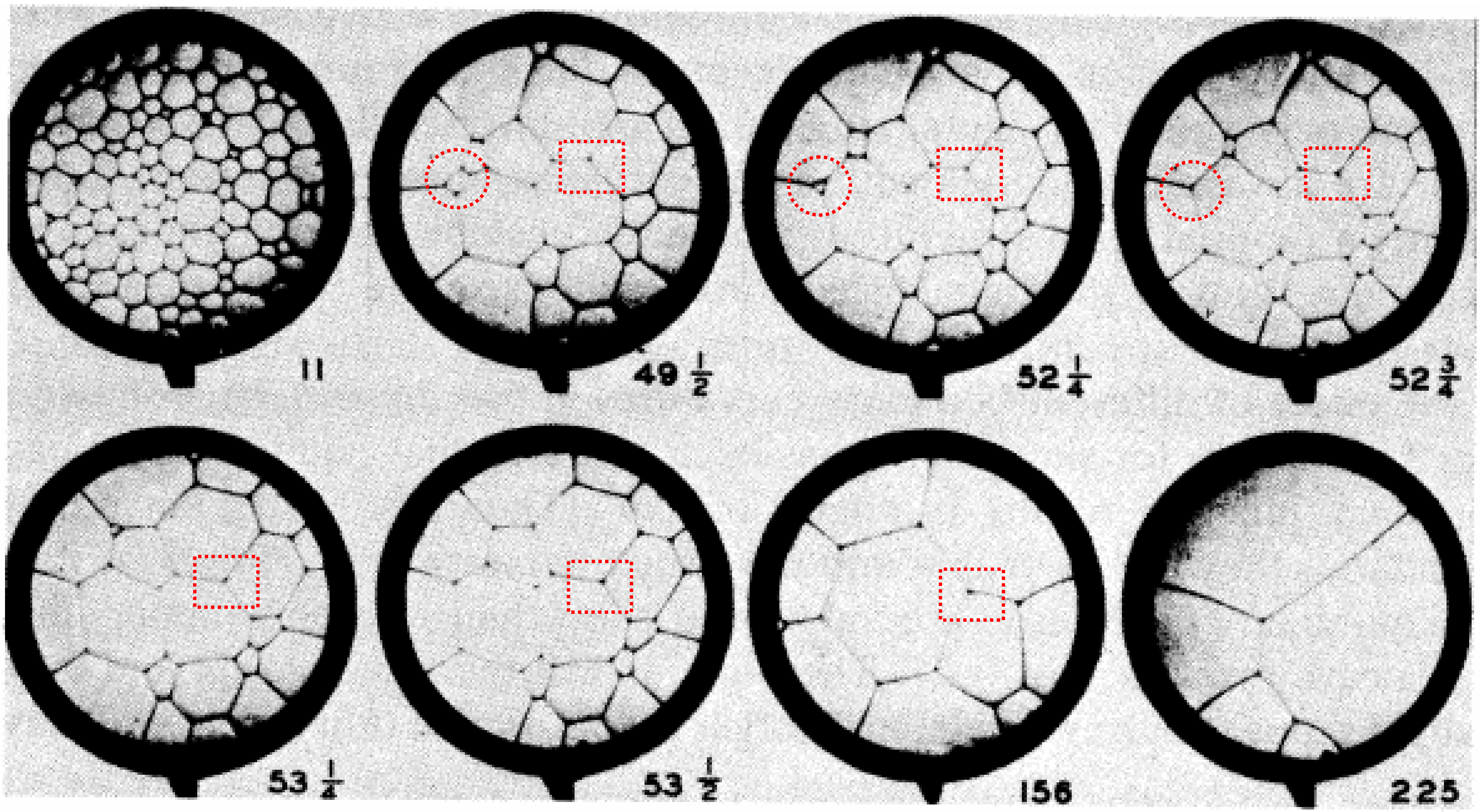
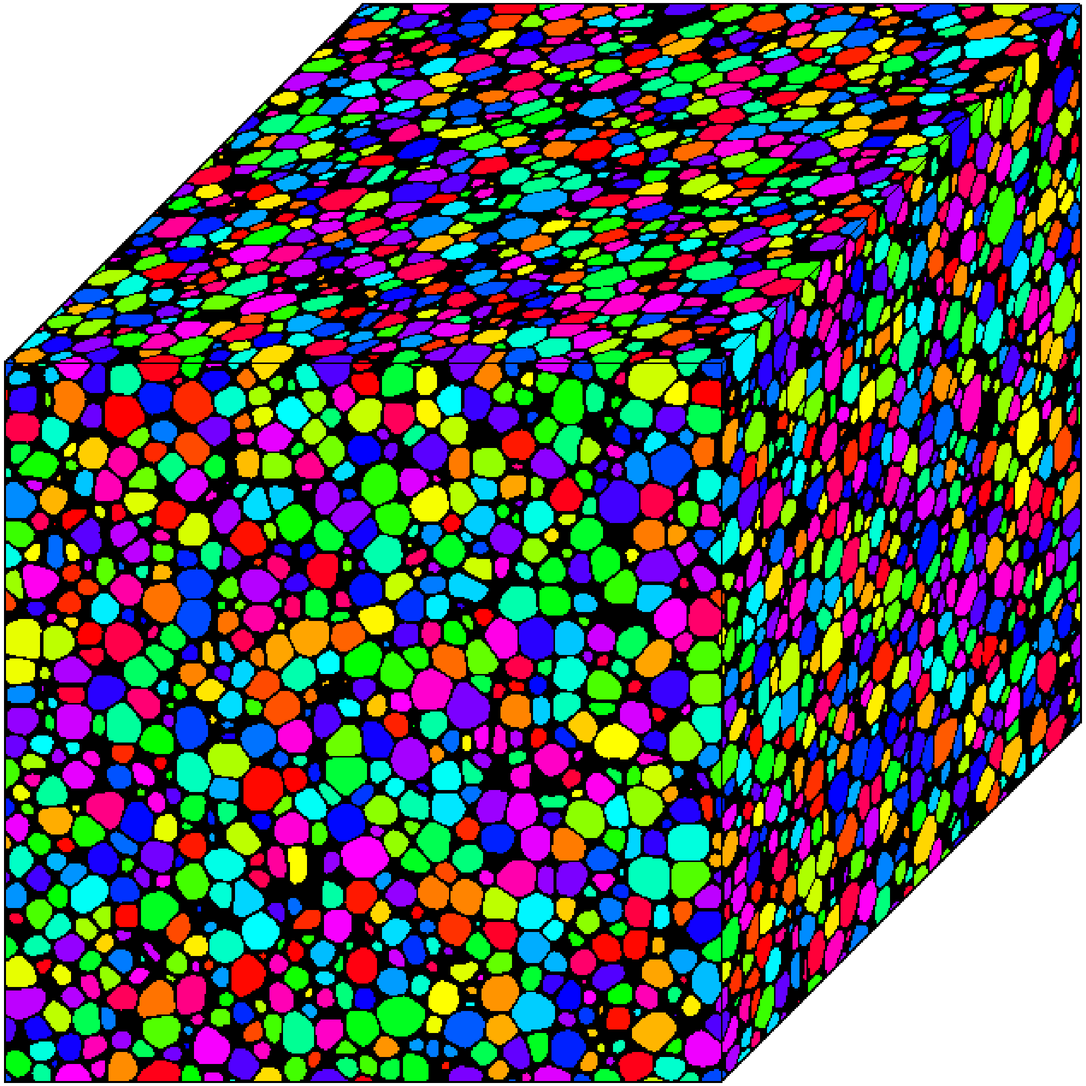


Fig. 3.22 Two-dimensional cells of a soap solution illustration the process of grain growth. Numbers are time in minutes. (After C.S. Smith, Metal Interfaces, American Society for Metals, 1952, p. 81.)

Example of Grain Growth simulation in 3D



Grain Coarsening at High Temp. annealing:

줄어드는 결정립에 있는 원자들 입계 에너지에 의해 높은 압력을 받음.
격자로부터 떨어져 나가서 성장하는 결정립의 격자 자리에 다시 붙음.

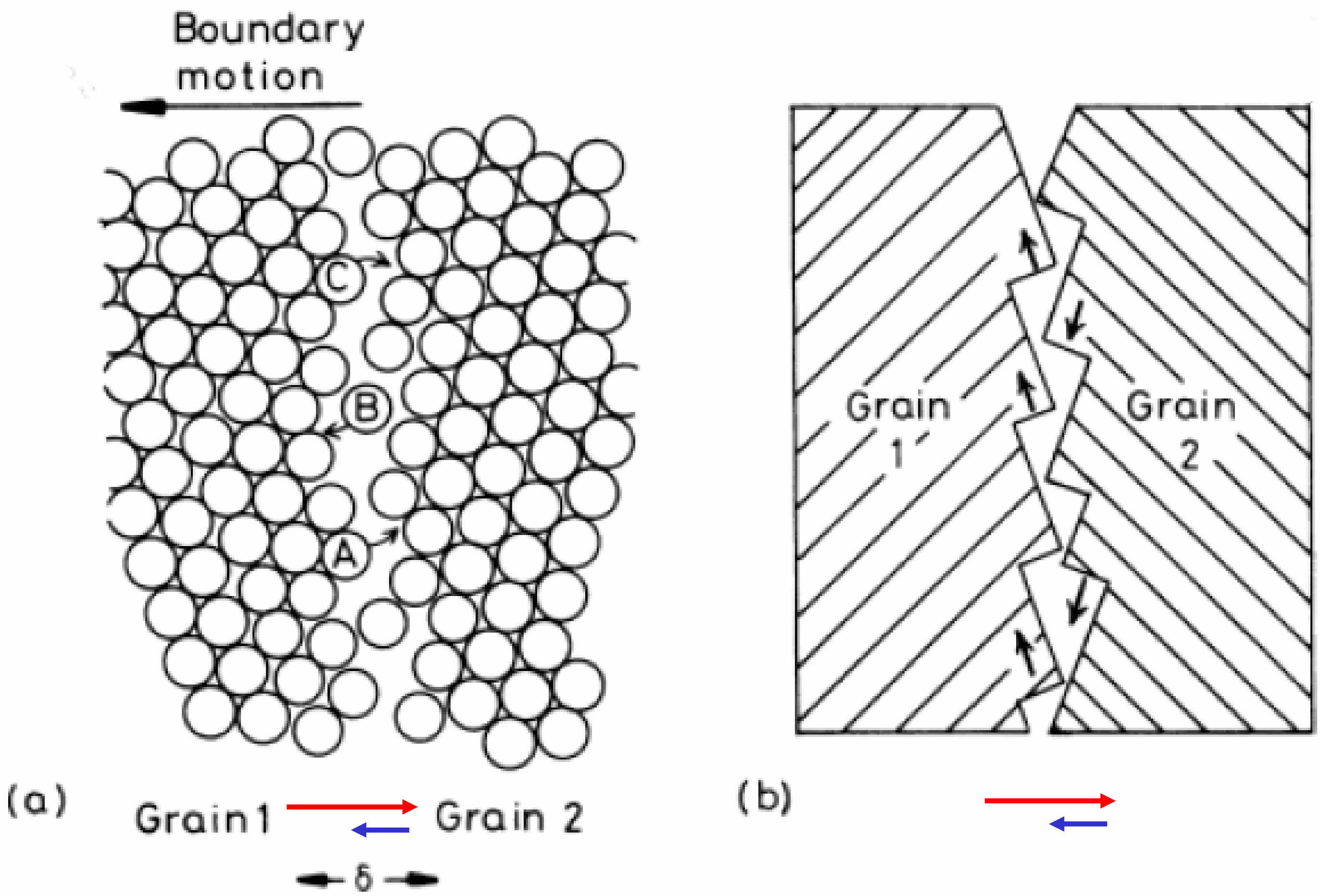


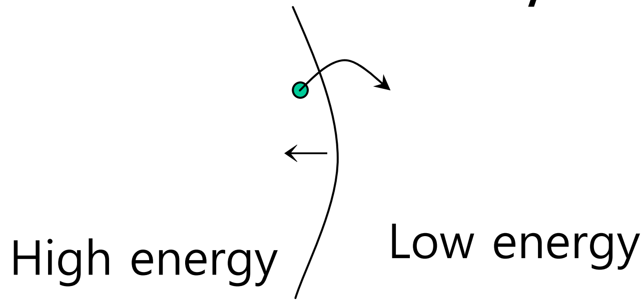
Fig. 3.23 (a) The atomic mechanism of boundary migration. The boundary migrates to the left if the jump rate from grain 1→ 2 is greater than 2 → 1. Note that the free volume within the boundary has been exaggerated for clarity. (b) Step –like structure where close-packed planes protrude into the boundary.

Grain coarsening at high T, annealing

→ metastable equil. state

: # ↓ , size ↑

curvature ~ Δ*P* ~Δ*μ*



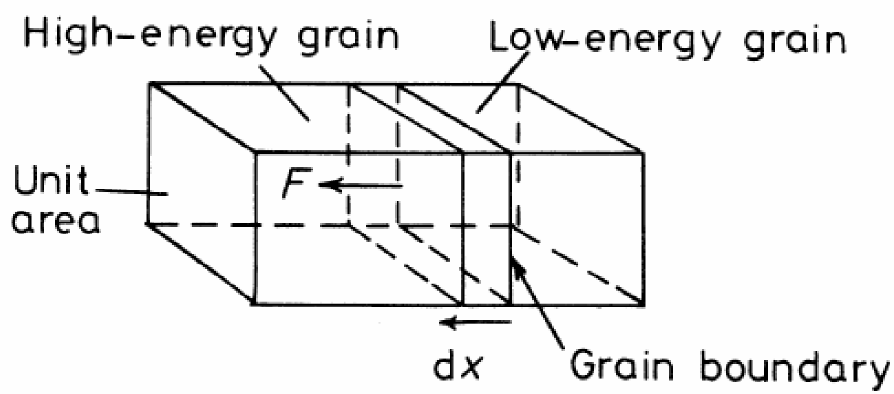


Fig. 3.25 A boundary separating grains with different free energies is subjected to a pulling force *F*.

$\boxed{\Delta G = 2\gamma V_m / r = \Delta\mu}$ Gibbs-Thomson Eq.

: effect of pressure difference by curved boundary

➡ **Driving force for grain growth : F**

결정립 B로 들어가는 물질의 몰수:

1 (dx/V_m)

Work : $F\,dx = (2\gamma V_m/r)\,(dx/V_m)$

$\rightarrow \boxed{F = 2\gamma/r = \Delta G/V_m \text{ (by curvature)}}$

Pulling force per unit area of boundary : $F = \dfrac{\Delta G}{V_m} \quad (N\,m^{-2})$

물질의 단위체적당 자유에너지 차이

Gibbs-Thompson Equation

ΔG of a spherical particle of radius, r

$$\Delta G_{r(s)} = 4\pi r^2 \gamma$$

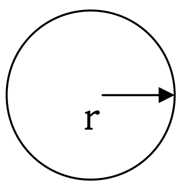
ΔG of a supersaturated solute in liquid in equilibrium with a particle of radius, r

$$\Delta G_{r(l)} = \frac{4\pi r^3}{3} \times \Delta G_V$$

Equil. condition for open system

$\longrightarrow$ $\Delta\mu$ should be the same.

$$\Delta\mu = 8\pi r\gamma = 4\pi r^2 \Delta G_V$$



$\dfrac{2\gamma V_m}{r}$ /mole or $\dfrac{2\gamma}{r}$ / per unit volume

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

r*: in (unstable) equilibrium with surrounding liquid

$$\boxed{r^* = \frac{2\gamma_{SL}}{\Delta G_V}}$$

* How fast boundary moves ? : Grain Growth Kinetics

Grain boundary migration by thermally activated atomic jump

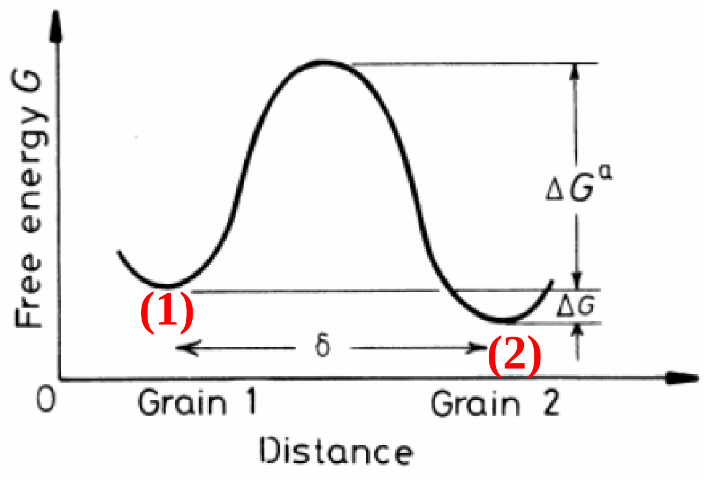
*** (1) → (2) : Flux**

(1) atoms in probable site : n_1

Vibration frequency : ν_1

A_2 : probability of being accommodated in grain (2)

→ $A_2\, n_1\, \nu_1\, \exp(-\Delta G^a/RT)$ atom/m^{2}s $= J_{1\rightarrow 2}$



*** (2) →(1) : Flux**

→ $A_1\, n_2\, \nu_2\, \exp[-(\Delta G^a + \Delta G)/RT] = J_{2\rightarrow 1}$

When **$\Delta G=0$**, there is no net boundary movement.

$$A_2\, n_1\, \nu_1 \approx A_1\, n_2\, \nu_2 = An\nu$$

When **$\Delta G > 0$**, there will be a net flux from grain 1 to 2. **(고경각 경계 A1≈A2≈1)**

($A_2\, n_1\, \nu_1 \approx A_1\, n_2\, \nu_2 = An\nu$)

$$J_{1\rightarrow 2} - J_{2\rightarrow 1} = An\nu \exp(-\Delta G^a/RT)\,[1-\exp(-\Delta G/RT)]$$

- If the boundary is moving with a velocity v, the above flux must also be equal to ?

$$J = c \cdot v \;\rightarrow\; v/(V_m/N_a) \quad (V_m/N_a : \text{atomic volume})$$

If ΔG is small [ΔG <<RT] → exp (- ΔG/RT)항을 Tayler 전개

$$J_{net} = A_2 n_1 \nu_1 \exp(-\Delta G^a/RT)\,[\Delta G/RT]\ \boxed{(\text{atom/m}^2\text{s})} = v(V_m/N_a)$$

입계 이동 속도

$$\boxed{v = \frac{A_2 n_1 v_1 V_m^{\ 2}}{N_a R T}\exp\left(-\frac{\Delta G^a}{RT}\right)\frac{\Delta G}{V_m}}$$

$\boxed{v \sim \Delta G/V_m \text{ driving force}}$

$\rightarrow F = \Delta G/V_m$

$$or \quad v = M \cdot \Delta G / V_m$$

M: 입계 이동도
단위 구동력하에서의 속도

$$where\ M = \left\{\frac{A_2 n_1 v_1 V_m^{\ 2}}{N_a R T}\exp\left(\frac{\Delta S^a}{R}\right)\right\}\exp\left(\frac{-\Delta H^a}{RT}\right)$$

M : mobility = velocity under unit driving force ~ exp (-1/T)

⇨ The boundary migration is a thermally activated process.

Whose mobility would be high between special and random boundaries?

입계구조의 고찰을 통해

High energy G.B. => Open G.B. structure => High mobility

Low energy G.B. => closed (or dense) G.B. structure => Low mobility

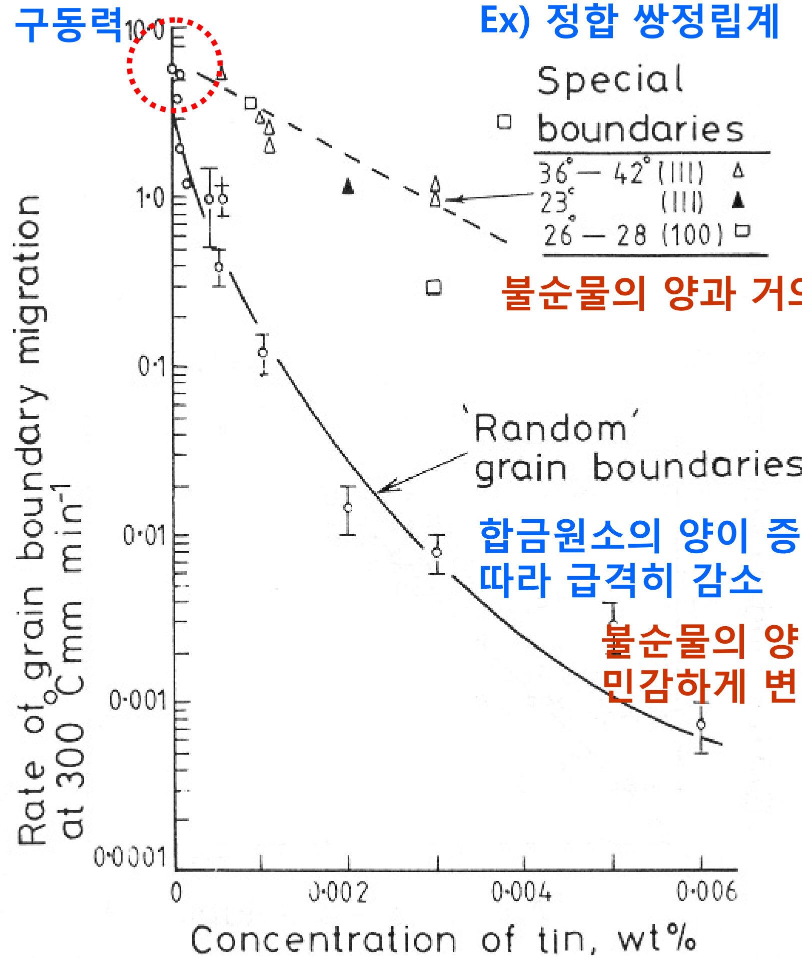
But, **Ideal** ⟺ **Real**

다른 특수 입계의 경우, 무질서한
고경각 입계보다 이동도가 크다. Why?

⇨ 불순물과 입계의 상호작용이
입계의 종류에 따라 변화

같은 구동력

Ex) 정합 쌍정립계



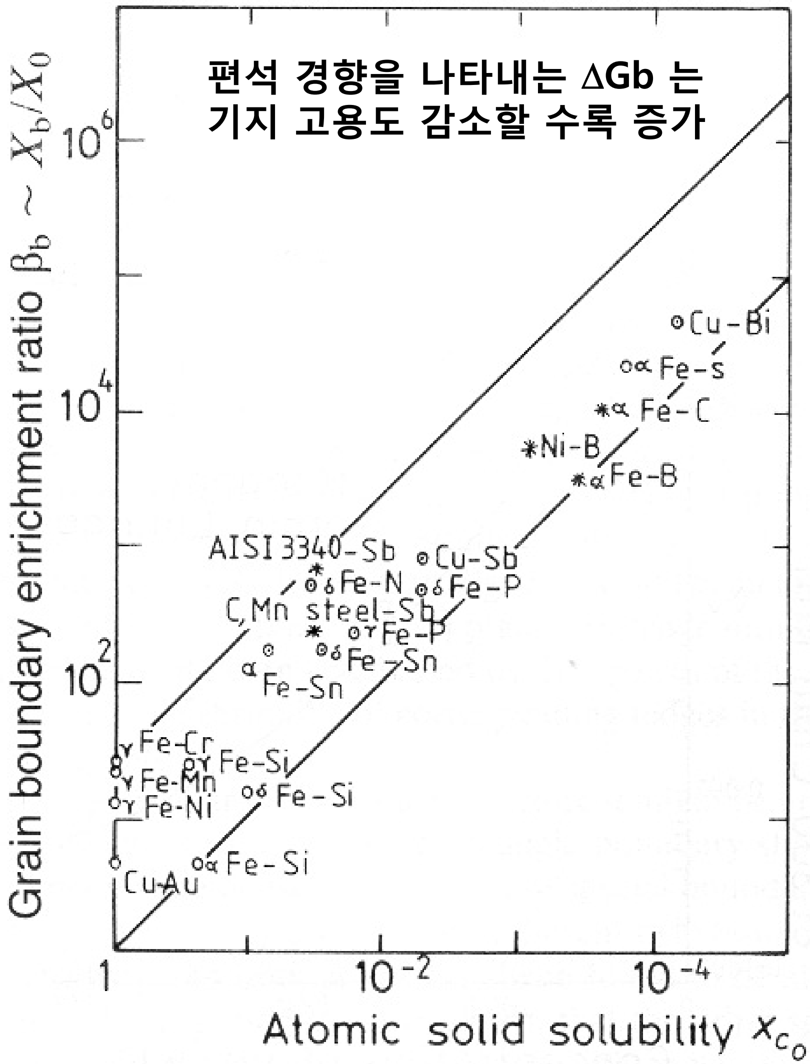
불순물의 양과 거의 무관

합금원소의 양이 증가함에
따라 급격히 감소

불순물의 양에 따라
민감하게 변함

Migration rate of special and random boundaries at 300 °C
in zone-refined lead alloyed with tin under equal driving forces

Solute drag effect



In general,
G_b and mobility of Pure metal decreases on alloying.

~Impurities tend to stay at the GB.

Generally, ΔG_b, tendency of seg-regation, increases as the matrix solubility decreases.

$$X_b = X_0 \exp\frac{\Delta G_b}{RT}$$

X_b/X_0: GB enrichment ratio

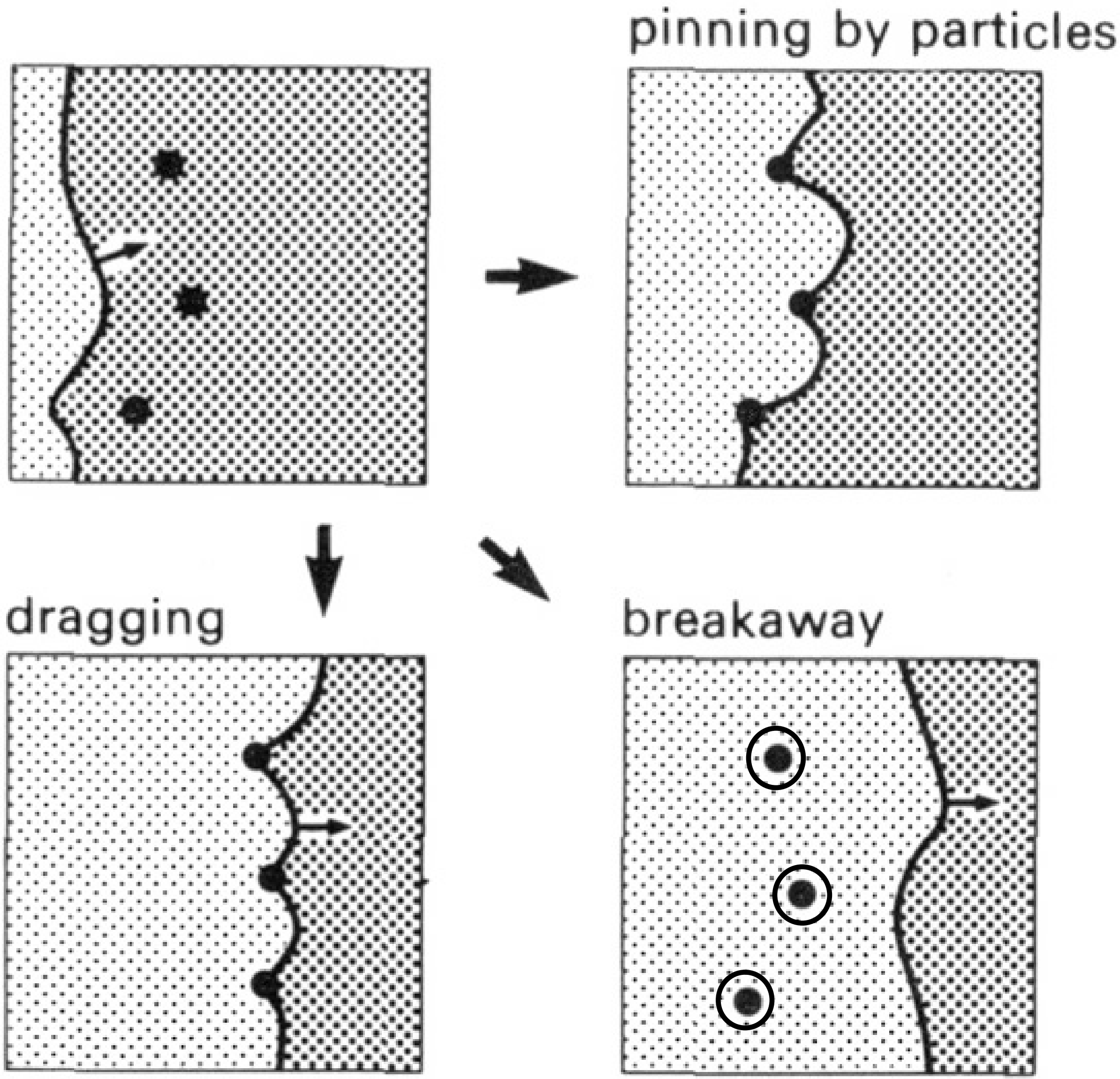
- 온도 증가시 입계 편석 감소

G_b ⇧ X_b ⇧ Mobility of G.B. ⇩

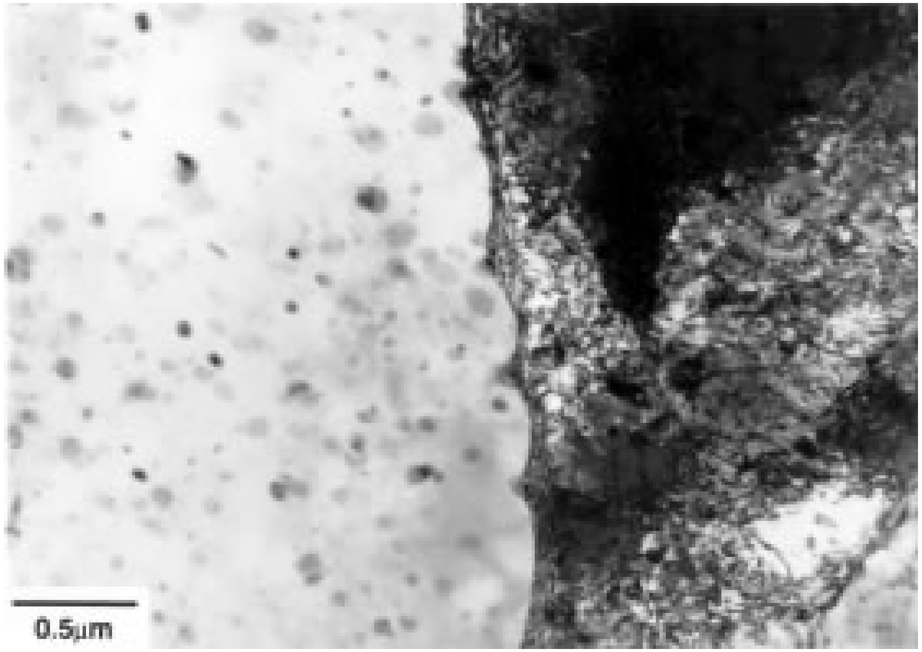
Alloying elements affects mobility of G.B.

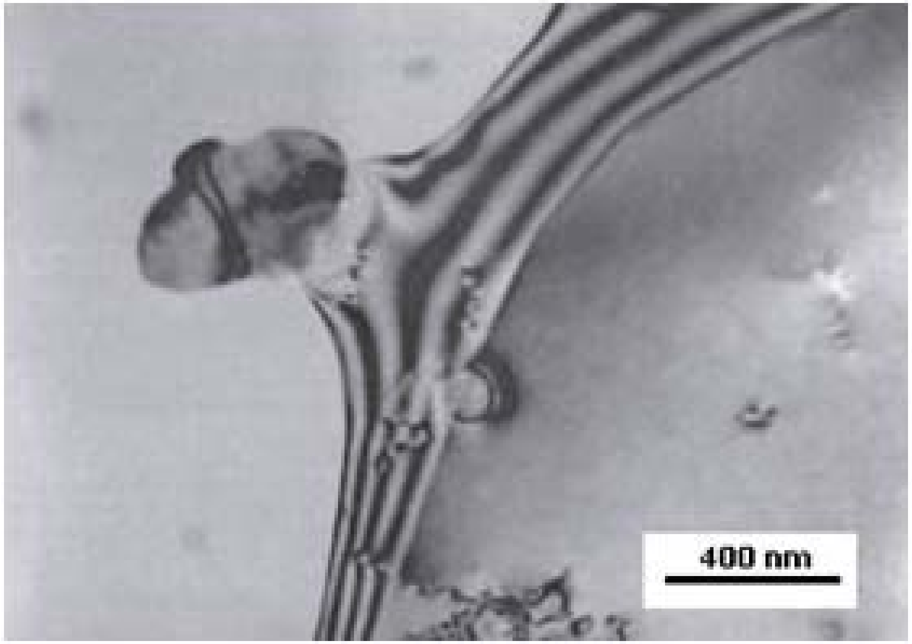
X_0 : matrix solute concentration/ X_b : boundary solute concentration
ΔG_b : free energy reduced when a solute is moved to GB from matrix.
양수, 용질원자와 기지원자와의 원자크기차 클수록 증가, 용질원자간 결합력 감소하면 증가

Schematic diagram illustrating the possible interactions of second phase particles and migrating grain boundaries.



Pinning by particle



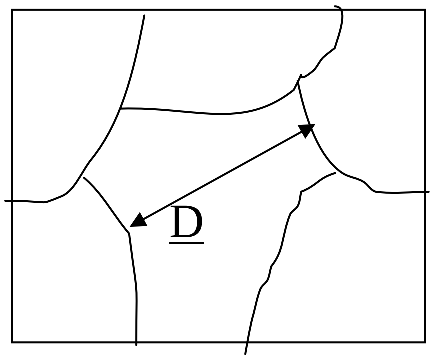


The kinetic of grain growth

* driving force $F = \Delta G/V_m$ → $\boldsymbol{v} = M(\Delta G/V_m)$ 입계 성장속도

M : exponentially increase with temp.

$\boldsymbol{v}$: relation to grain coarsening



Mean grain size : $\underline{D}$

Mean radius of curvature of boundary : r

if $\underline{D} \propto r$,

Mean velocity : $\underline{\boldsymbol{v}} = \alpha M(\Delta G/V_m) = d\underline{D}/dt$ $(\Delta G = 2\gamma V_m/r)$

$\alpha M(2\gamma/\underline{D}) = d\underline{D}/dt$ (α = proportionality const ~1)

$d\underline{D}/dt$ **(rate of grain growth)** ~ ***$1/\underline{D}$*** **, exponentially increase with *T***

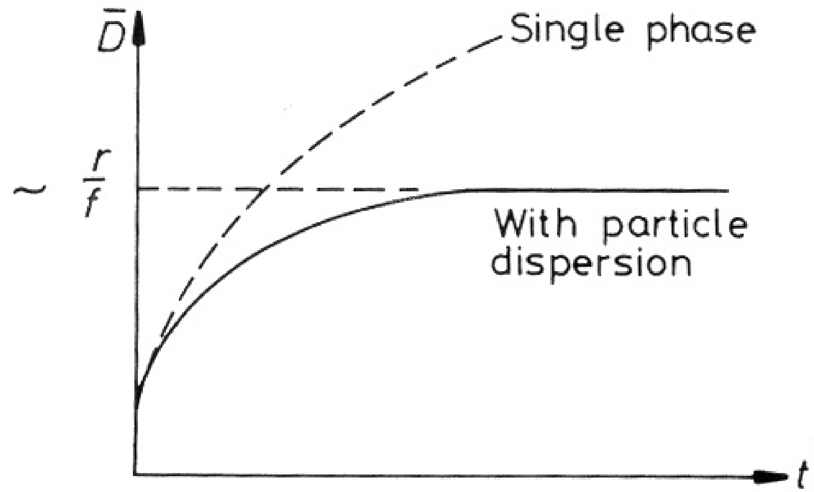
앞의 식을 D_0, $\underline{D}$ 구간에서 적분,

$$\rightarrow \int_{D_o}^{D} \underline{D}\, d\underline{D} = \int 2\alpha M\gamma dt$$

$$\rightarrow \tfrac{1}{2}(\underline{D}^2 - D_o^2) = 2\alpha M\gamma t$$

$$\rightarrow (\underline{D}^2 - D_o^2) = \boxed{4\alpha M\gamma}t = kt$$

$$\rightarrow \underline{D}^2 = D_o^2 + kt$$



r = average radius of particles

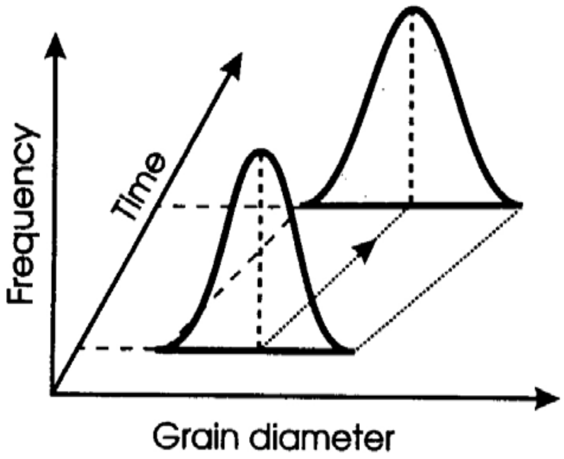
f_v = volume fraction of particles

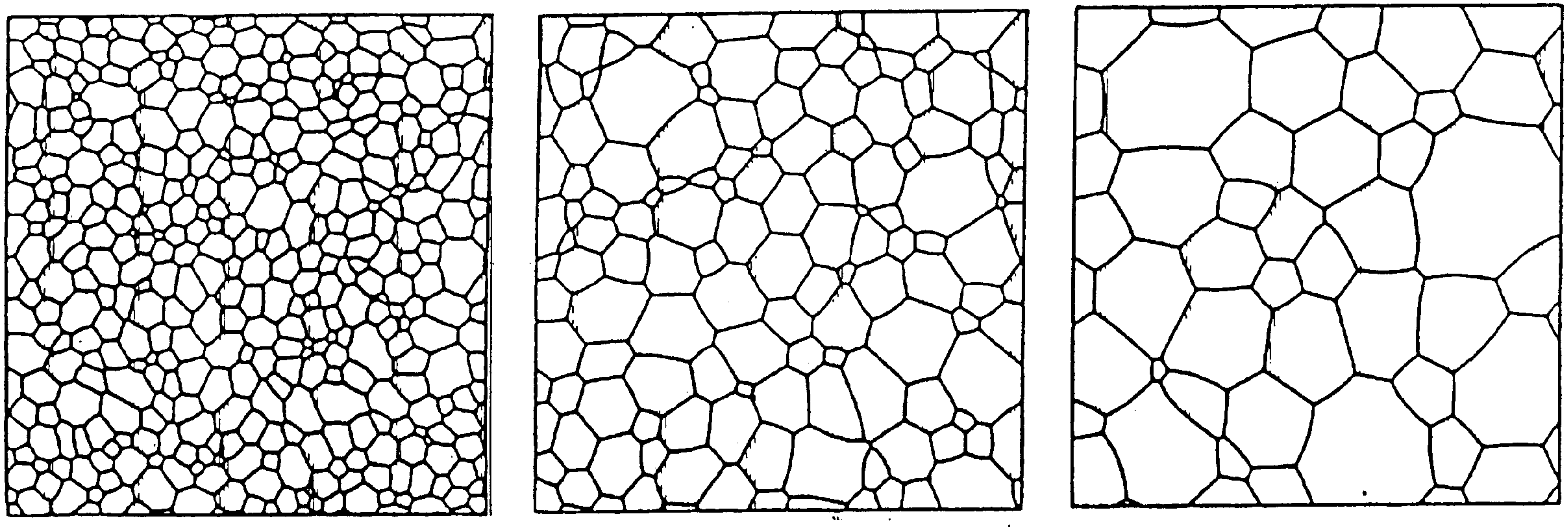
if $D_o \approx 0 \rightarrow \underline{D} = k' t^{1/2}$

$\rightarrow \underline{D} = k' t^n$ (experimental : n << ½, ½ at only high temp.)

Normal Grain Growth

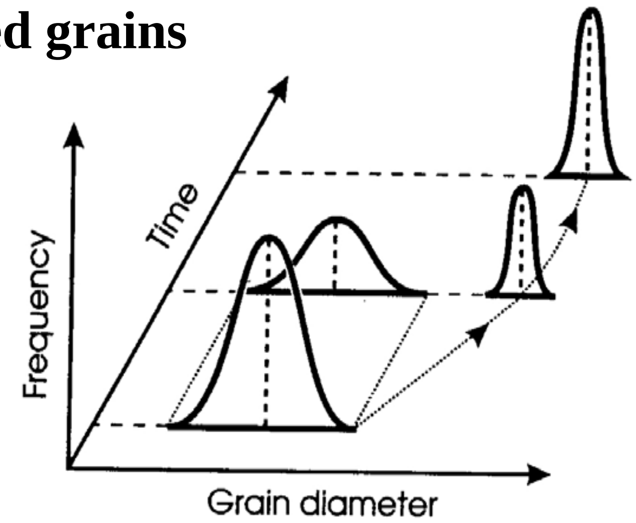
- Grain boundary moves to reduce area and total energy
- Large grain grow, small grains shrink
- Average grain size increases
- Little change of size distribution



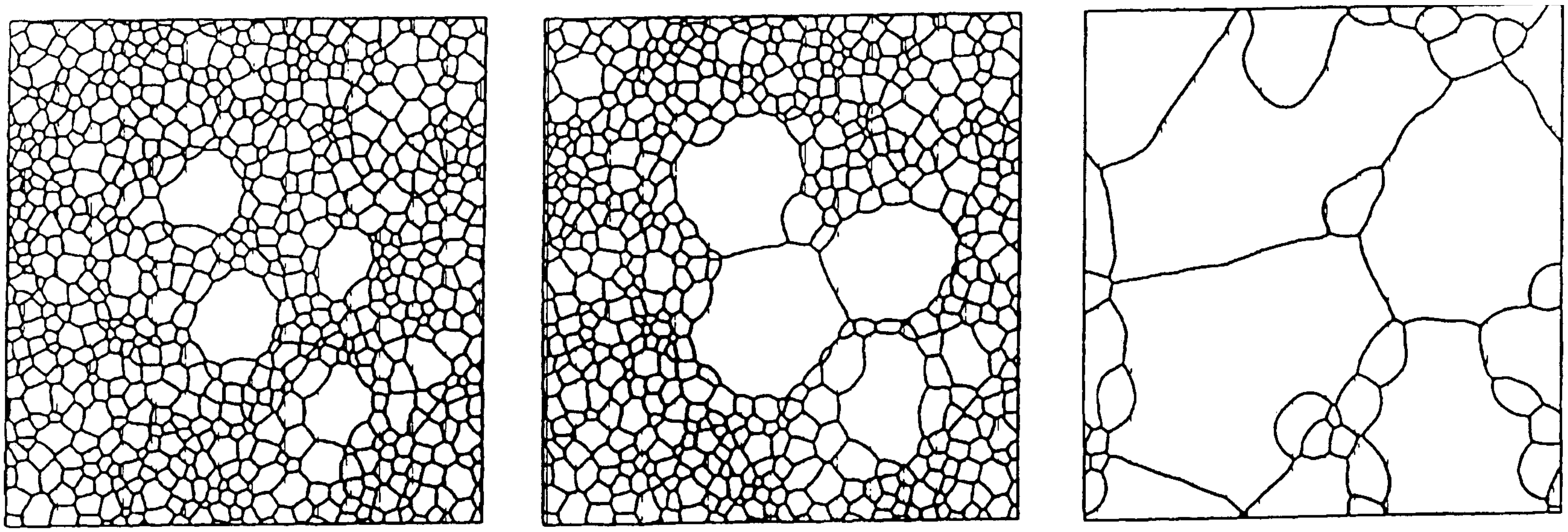


Abnormal Grain Growth

- **Discontinuous grain growth of a few selected grains**
  - Local breaking of pinning by precipitates
  - Anisotropy of grain boundary mobility
  - Anisotropy of surface & grain boundary energy
  - Selective segregation of impurity atoms
  - Inhomogeneity of strain energy



- **Bimodal Size distribution**



Abnormal Grain Growth
= discontinuous grain growth or secondary recrystallization

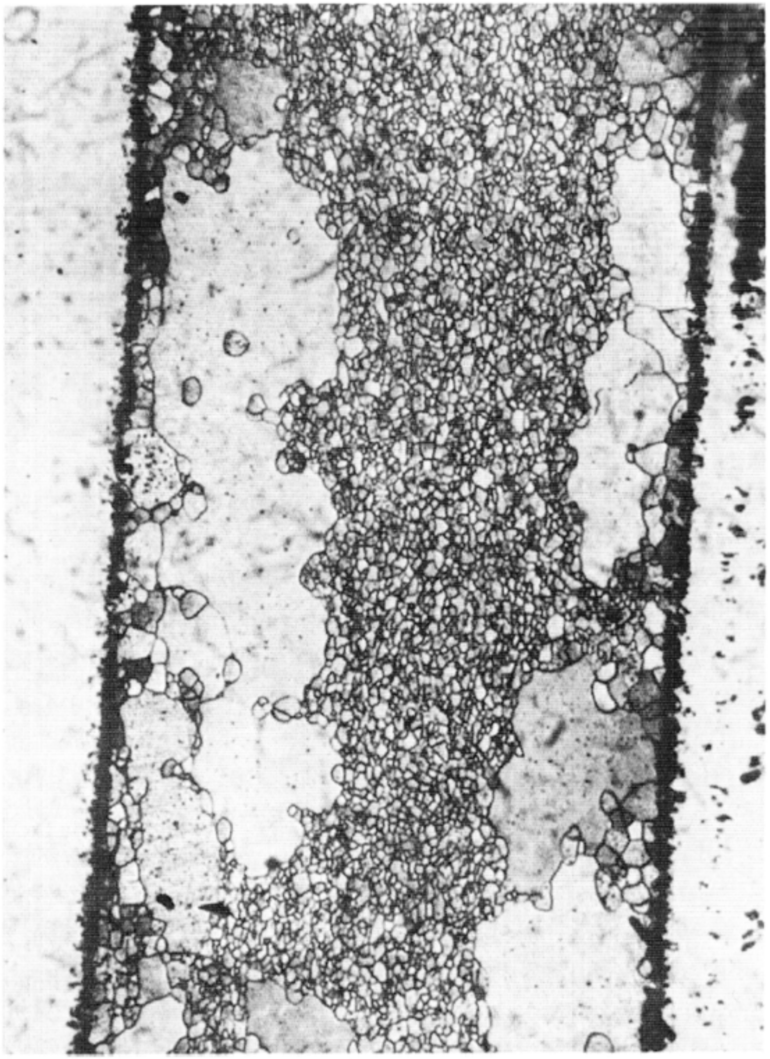


Figure 5.87 Optical micrograph showing abnormal grain growth in a fine grain steel containing 0.4 wt% carbon. The matrix grains are prevented from growing by a fine dispersion of carbide particles that are not revealed. Magnification ×135. (After Gawne and Higgins 1971. Courtesy of the Metals Society.)

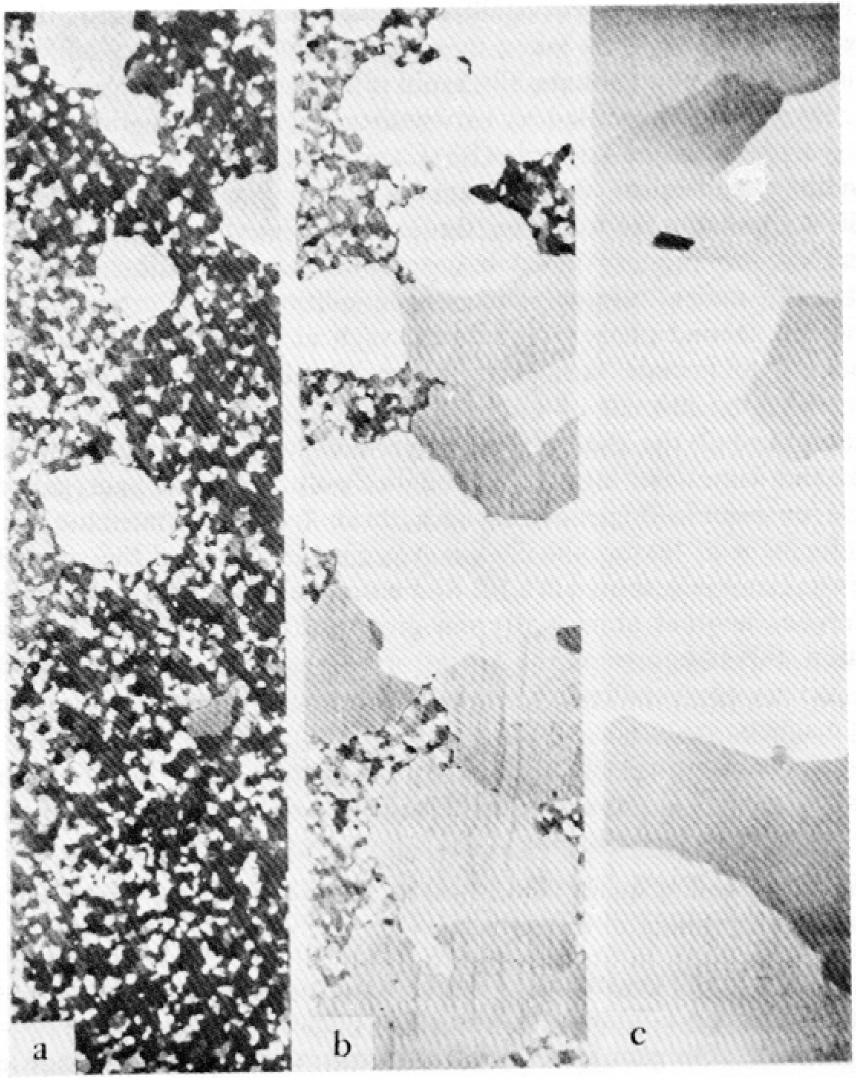
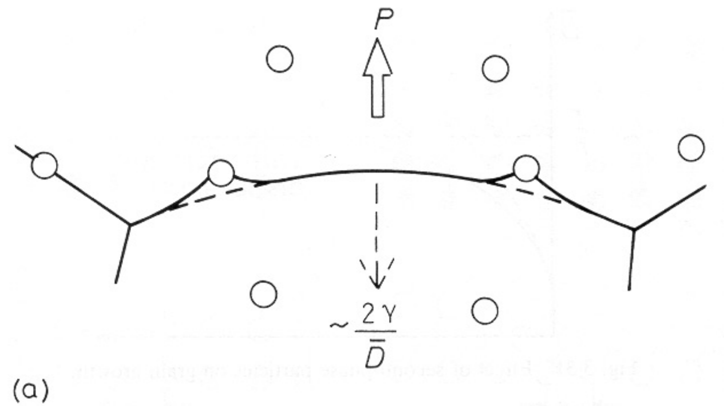


Fig. 5.48. Evidence for the preferential formation of (110)[001]-oriented grains by secondary recrystallization in 5% Si–Fe (Graham [1969]).

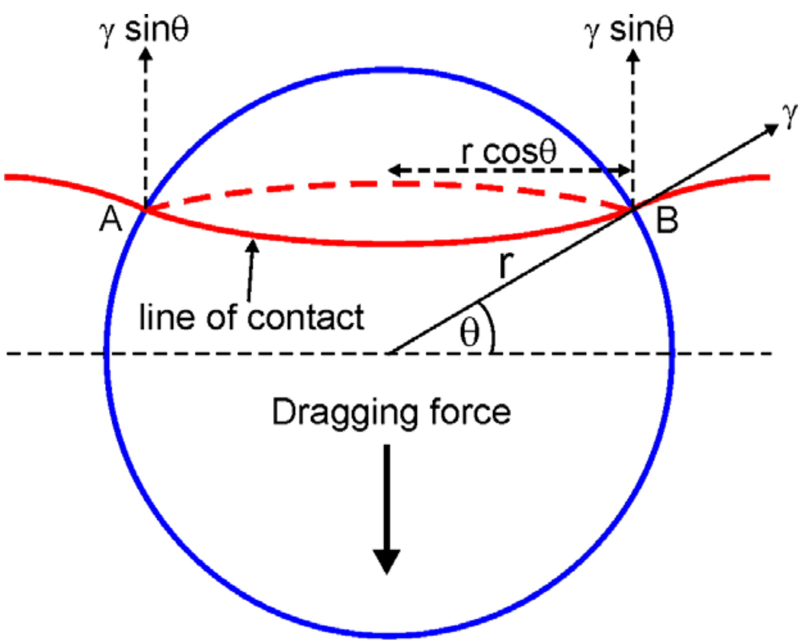
Effect of Second-Phase Particles



Interaction with particles

Zener Pinning

Derive the expression for the pinning effect of grain boundary migration by precipitates.



$$\text{since} \;\; \gamma \sin\{\theta\} = \text{force per unit length}$$

$$F = \gamma \sin\{\theta\} \times \boxed{2\pi r \cos\{\theta\}} = AB$$

원의 둘레

$$\text{so that at} \;\; \theta = 45°$$

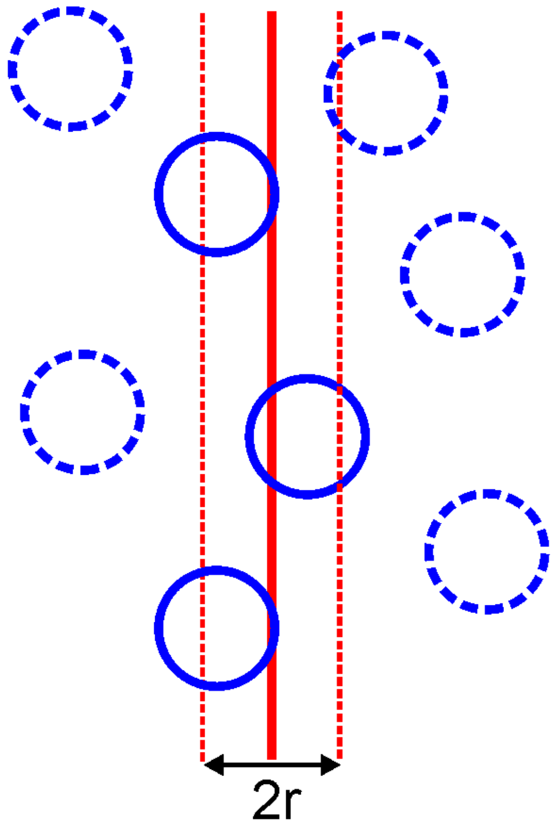
$$F_{max} = \gamma \pi r$$

단일 입자로 인해 생긴 힘의 최대값

Interaction with particles **Zener Pinning**

f_v = volume fraction of randomly distributed particles of radius r

N_{total} = number of particles per unit volume $$N = \frac{f_v}{\frac{4}{3}\pi r^3}$$



Only particles within one radius (solid circles) can intersect a planar boundary

If the boundary is essentially planar,

$$N_{interact} = 2rN_{total} = 3f_v/2\pi r^2$$

Given the assumption that

all particles apply the maximum pinning force,

the total pinning pressure

$$\boxed{P = \frac{3f_v}{2\pi r^2}\cdot \pi r \gamma = \frac{3f_v\gamma}{2r}}$$

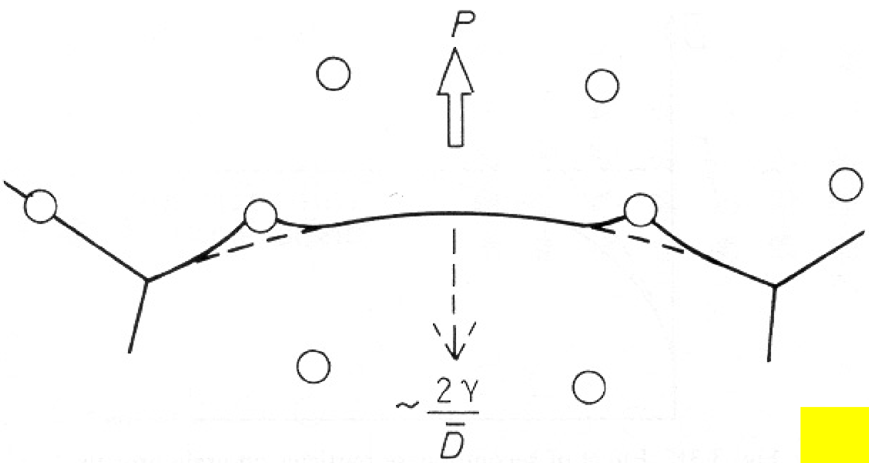
This force will oppose the driving force for grain growth, $\boxed{2\gamma/\bar{D}}$

Interaction with particles

Zener Pinning

$$P = \frac{3f_v}{2\pi r^2} \cdot \pi r \gamma = \frac{3f_v \gamma}{2r}$$

This force will oppose the driving force for grain growth, $2\gamma / \bar{D}$



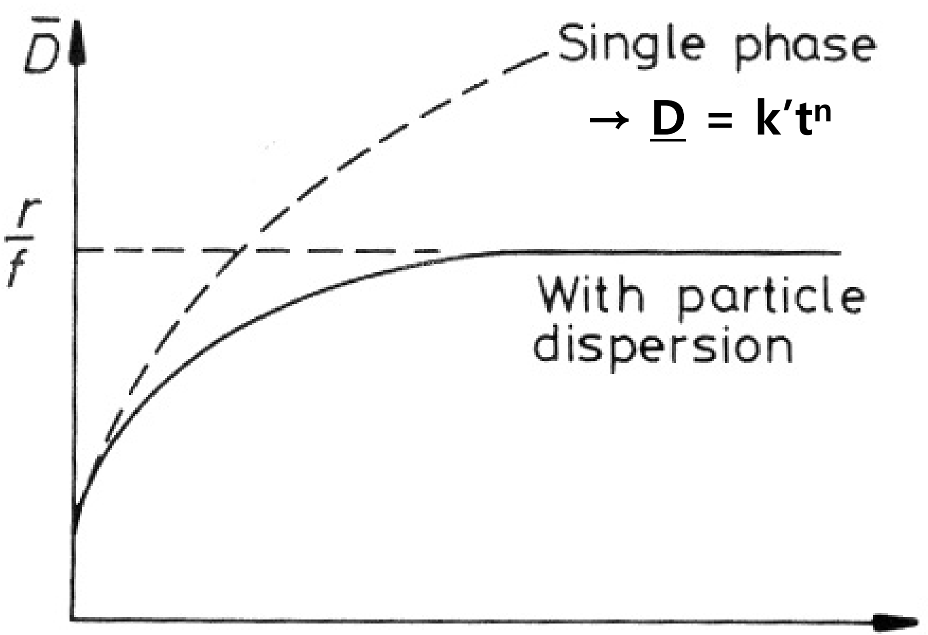
→ F = 2γ/r = ΔG/V_m (by curvature)

$$\frac{2\gamma}{\bar{D}} = \frac{3f_v \gamma}{2r} \Rightarrow \boxed{\bar{D}_{max} = \frac{4r}{3f_v}}$$

For fine grain size
→ a large volume fraction of very small particles

* Effect of second-phase particles on grain growth

$$\boxed{\bar{D}_{max} = \frac{4r}{3f_v}} \sim$$



→ **D = k′t^n**

: 미세한 결정립이 안정화되려면
매우 작은 입자 (r ↓)가 많아야 한다 (f ↑).

$$\boxed{\bar{D}_{max} = \frac{4r}{3f_v}} \downarrow$$