

**2018 Fall**

# **“Phase Transformation *in* Materials”**

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# Chapter 3 Crystal Interfaces and Microstructure

- 1) Interfacial Free Energy
- 2) Solid/Vapor Interfaces
- 3) Boundaries in Single-Phase Solids
- 4) Interphase Interfaces in Solid ( $\alpha/\beta$ )
- 5) Interface migration

## Surface energy for high or irrational {hkl} index

$(\cos\theta/a)(1/a)$  : broken bonds from the atoms on the steps

$(\sin|\theta|/a)(1/a)$  : additional broken bonds from the atoms on the steps

Attributing  $\varepsilon/2$  energy to each broken bond,

$$E_{sv} = \frac{1}{1 \times a} \frac{\varepsilon}{2} \left( \frac{\cos\theta}{a} + \frac{\sin|\theta|}{a} \right)$$

$$= \frac{\varepsilon(\cos\theta + \sin(|\theta|))}{2a^2}$$

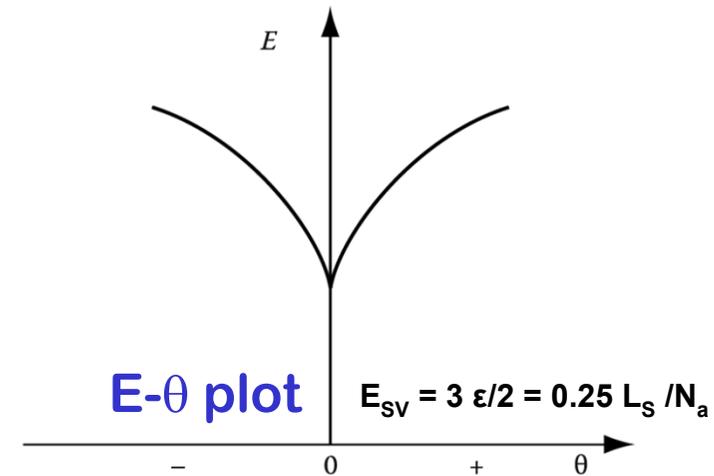


Fig. 3.4 Variation of surface energy as a function of  $\theta$

- **The close-packed orientation ( $\theta = 0$ ) lies at a cusped minimum in the E plot.**
- Similar arguments can be applied to any crystal structure for rotations about any axis from any reasonably close-packed plane.
- **All low-index planes should therefore be located at low-energy cusps.**
- If  $\gamma$  is plotted versus  $\theta$  similar cusps are found ( $\gamma$ - $\theta$  plot), but as a result of **entropy effects** they are **less prominent than in the E- $\theta$  plot**, and for the higher index planes they can even disappear.

# Equilibrium shape: Wulff surface

\* A convenient method for plotting the variation of  $\gamma$  with surface orientation in 3 dimensions

\* **Distance from center** :  $\gamma_{sv}$

→ Construct the surface using  $\gamma_{sv}$  value as a distance between the surface and the origin when measured along the normal to the plane

Several plane  $A_1, A_2$  etc. with energy  $\gamma_1, \gamma_2$

Total surface energy :  $A_1\gamma_1 + A_2\gamma_2 \dots$

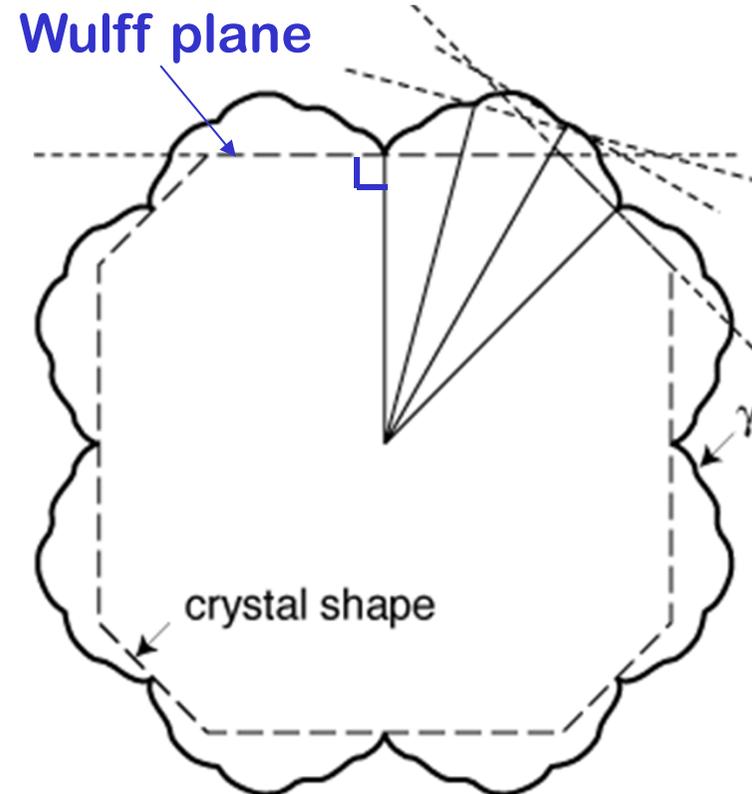
=  $\sum A_i \gamma_i \rightarrow$  minimum

→ equilibrium morphology

: can predict the equilibrium shape of  
an isolated single crystal

How is the equilibrium shape  
determined?

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



$\gamma$ - $\theta$  plot

Due to entropy effects the plot are less prominent than in the  $E_{sv}$ - $\theta$  plot, and for the higher index planes they can even disappear

# Contents for previous class

## 3) Boundaries in Single-Phase Solids

### (a) Low-Angle and High-Angle Boundaries

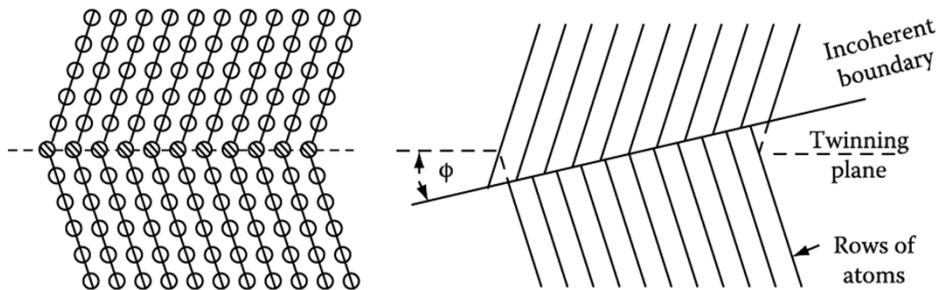
$\Theta < 15^\circ$  : total energy of the dislocations within unit area of boundary

$\Theta > 15^\circ$  : impossible to physically identify the individual dislocations  $\rightarrow$  strain field overlap  $\rightarrow$  cancel out

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

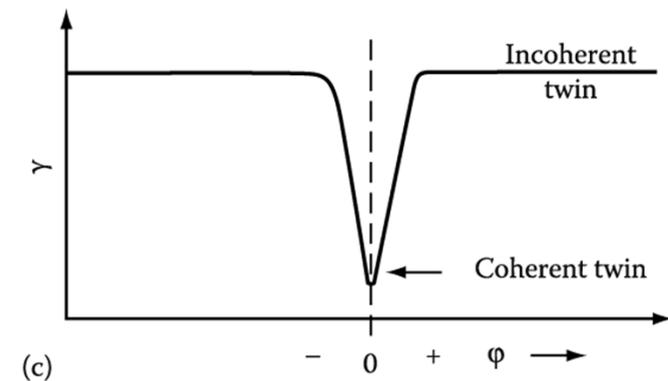
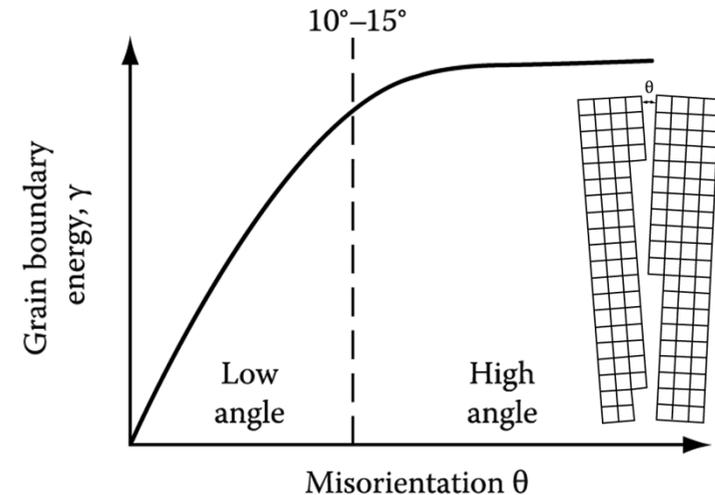
### (b) Special High-Angle Grain Boundaries

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



$\rightarrow$  twin boundary

Atoms in the boundary are essentially in undistorted positions  $\sim$  relatively little free volume



# Contents for today's class

< Boundaries in Single-Phase Solids >

## (c) Equilibrium in Polycrystalline Materials

### 1) GB intersection: Balance of 1) boundary E & 2) surface tension

GBs in a polycrystal can adjust themselves during annealing to produce a metastable equilibrium at the GB intersections.

### 2) Thermally Activated Migration of Grain Boundaries

- Grain coarsening at high T, annealing due to metastable equilibrium of GB

### 3) Kinetics of Grain Growth

- Grain boundary migration by thermally activated atomic jump

- Mobility of GB ~ GB structures and GB segregations

i.e Normal grain growth  $\longleftrightarrow$  Abnormal grain growth

### 4) Effect of second-phase particle on GB migration: Zener Pinning

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

# Q: Grain boundary ( $\alpha/\alpha$ interfaces)

= Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries

(b) Special High-Angle Grain Boundaries

(c) Equilibrium in Polycrystalline Materials

**1) GB intersection: Balance of 1) boundary E & 2) surface tension**

**GBs in a polycrystal can adjust themselves during annealing to produce a metastable equilibrium at the GB intersections.**

### (c) Equilibrium in Polycrystalline Materials

Microstructure → determined by how the different GBs join together in space

⇒ Examine how the possibility of different GB energies affects the microstructure of a poly crystalline material

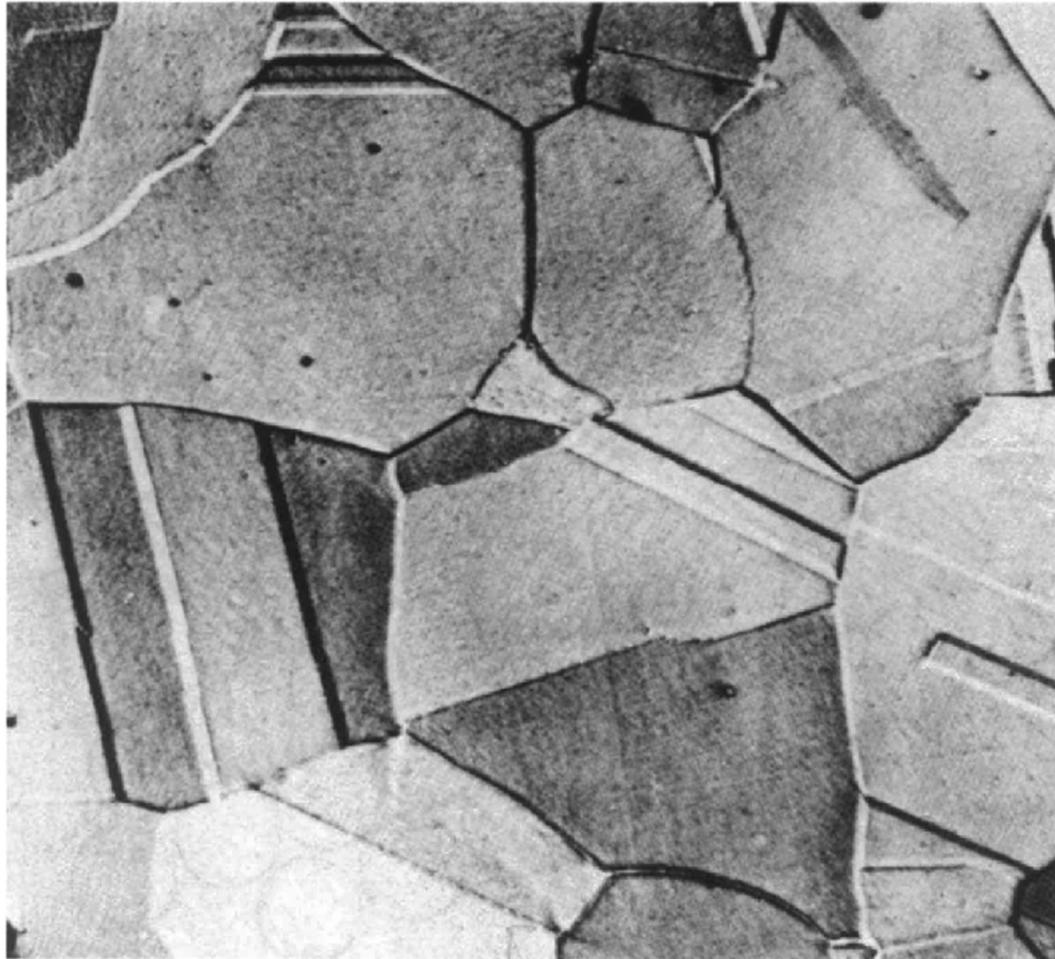


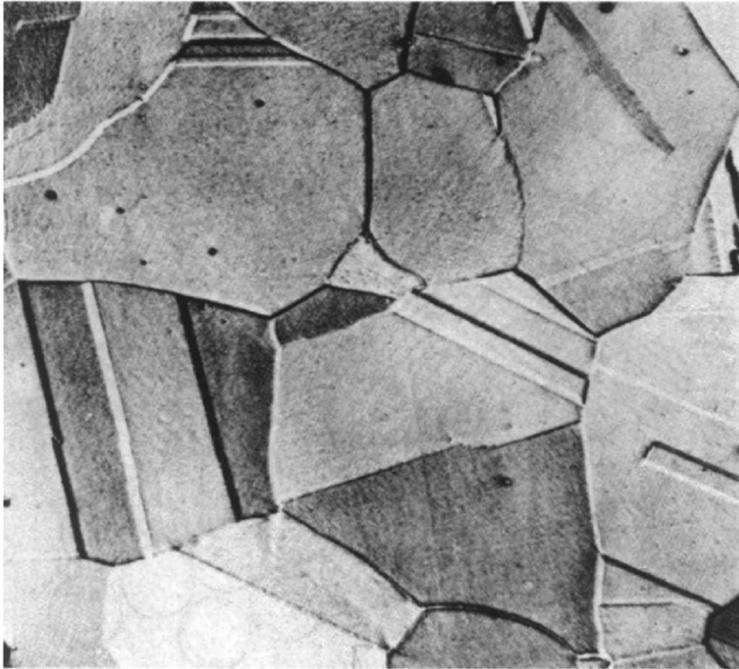
Fig. 3.15 Microstructure of an annealed crystal of austenitic stainless steel.

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: contains high-/low-angle GBs as well as (in-)coherent twin Bs with different GB energies

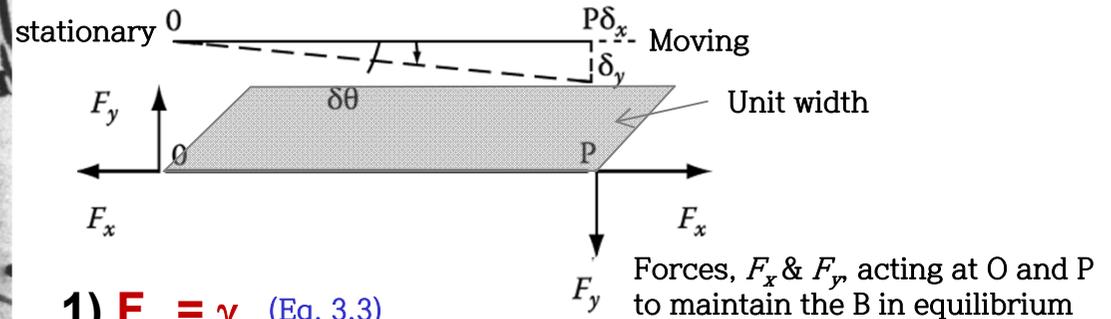
# Poly grain material: consider the factors that control the grain shapes!

Two grains: a plane (GB), three grains: a line (grain edge), four grains: at a point (grain corner)



## 2) Conditions for equilibrium at a GB junction

by considering the forces that each B exerts on the junction



1)  $F_x = \gamma$  (Eq. 3.3)

2)  $F_y$  ?

**P is moved at a small distance ( $\delta_y$ )**

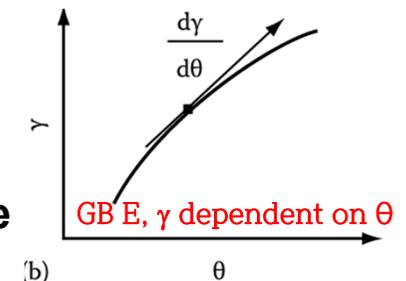
A. work done by :  $F_y \delta_y$

B. increase boundary energy caused

by the change in orientation  $\delta\theta \sim l (d\gamma/d\theta) \delta\theta$

$F_y \delta_y = l (d\gamma/d\theta) \delta\theta$  ( $\because \delta_y \sim l d\theta$ )

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



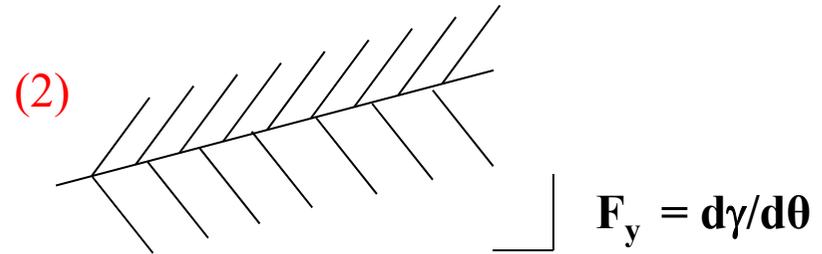
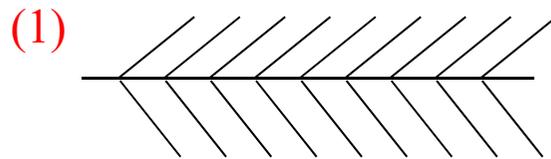
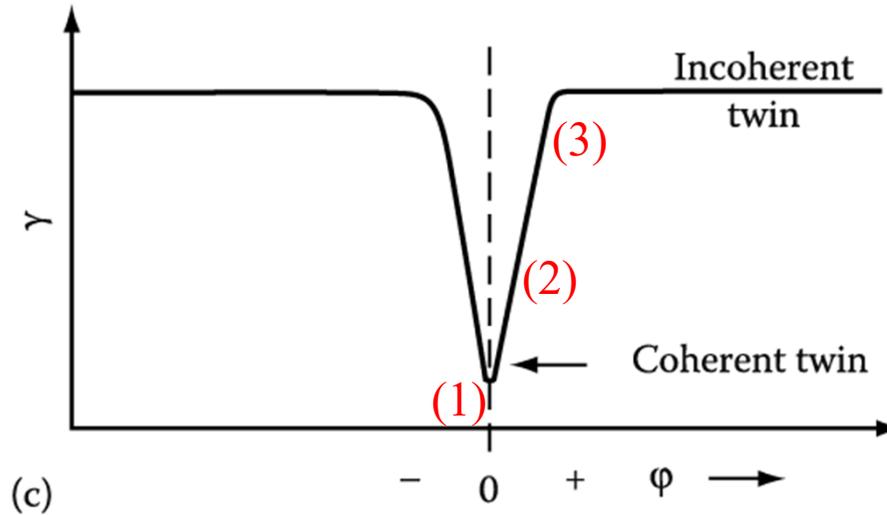
1) Why GBs exist at all in annealed materials?

Equilibrium ~ Mater. with no GB

$\because$  G.B.=high-E regions  $\rightarrow G \uparrow$

: never a true equilibrium structure

$\rightarrow$  GBs in a polycrystal can adjust themselves during annealing to produce a metastable equilibrium at the GB intersections.

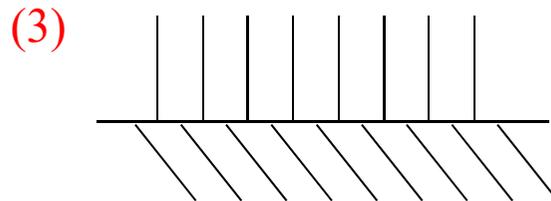


Minimum  $\gamma \sim \text{torque} = 0$  No rotation!

$F_y = d\gamma/d\theta \sim \text{torque} > 0$

If Pulling force,  $F_y > (d\gamma/d\theta)_{\text{cusp}} \rightarrow \text{Rotating}$

If the GB E is dependent on the orientation of the B, a force  $d\gamma/d\theta (>0)$  must be applied to the ends of the boundary to prevent it rotating into a lower energy orientation.



torque = 0

입계 E가 입계 방위에 의존한다면, 회전하지 않고 유지하기 위해 입계에 cusp까지 끌어당기는 힘에 대응하는 힘 작용

$\rightarrow$  There is little effect of orientation

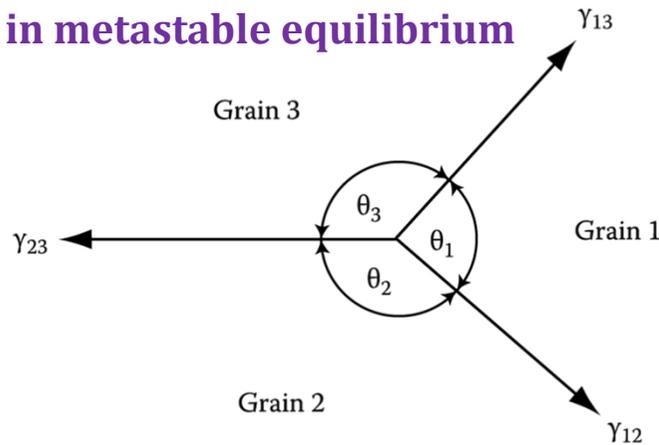
$\Rightarrow$  How metastable equilibrium?  $\rightarrow$  force (torque)

If the boundary E is independent of orientation,

\* **General high angle boundary** :  $d\gamma/d\theta \approx 0$  (GB behaves like a soap film)

→ Under these conditions the requirements for metastable equilibrium at junction between three grains is that the boundary tensions  $\gamma_{13}, \gamma_{23}, \gamma_{12}$  must balance.

**3) The balance of GB tensions for a GB intersection in metastable equilibrium**



$$\frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{31}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3} \quad (\text{Eq. 3.13})$$

if all GBs have same GB energy independent of boundary orientation

$$\rightarrow \theta = 120^\circ$$

Eq. 3.13 applies to any three boundaries i.e. grain 1 ~ different phase to grain 2 & 3.

**Ex) If the solid-vapor energy ( $\gamma_{sv}$ ) is the same for both grains,**

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

(Here, presence of any torque terms ~ neglected)

**One method of measuring GB energy:**

: anneal a specimen at a high temp. and then measure the angle at the intersection of the surface with B.

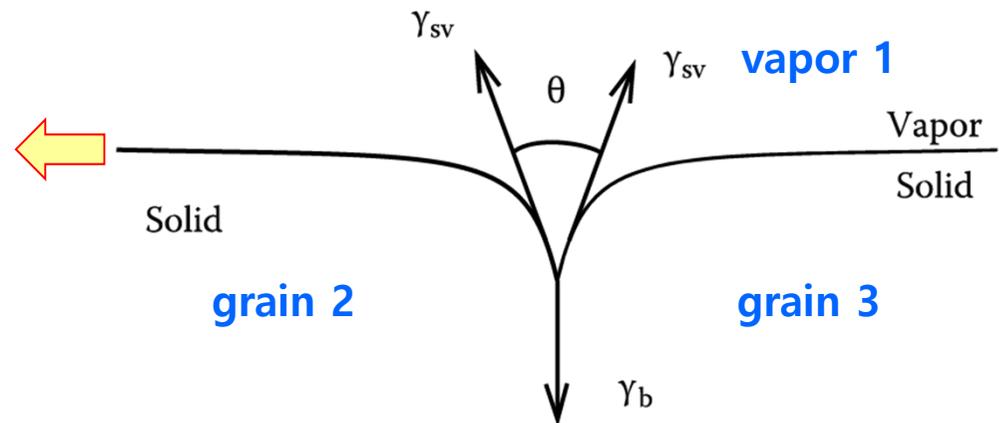


Fig. 3. 18 The balance of surface and grain boundary tensions at the intersection of a grain boundary with a free surface.

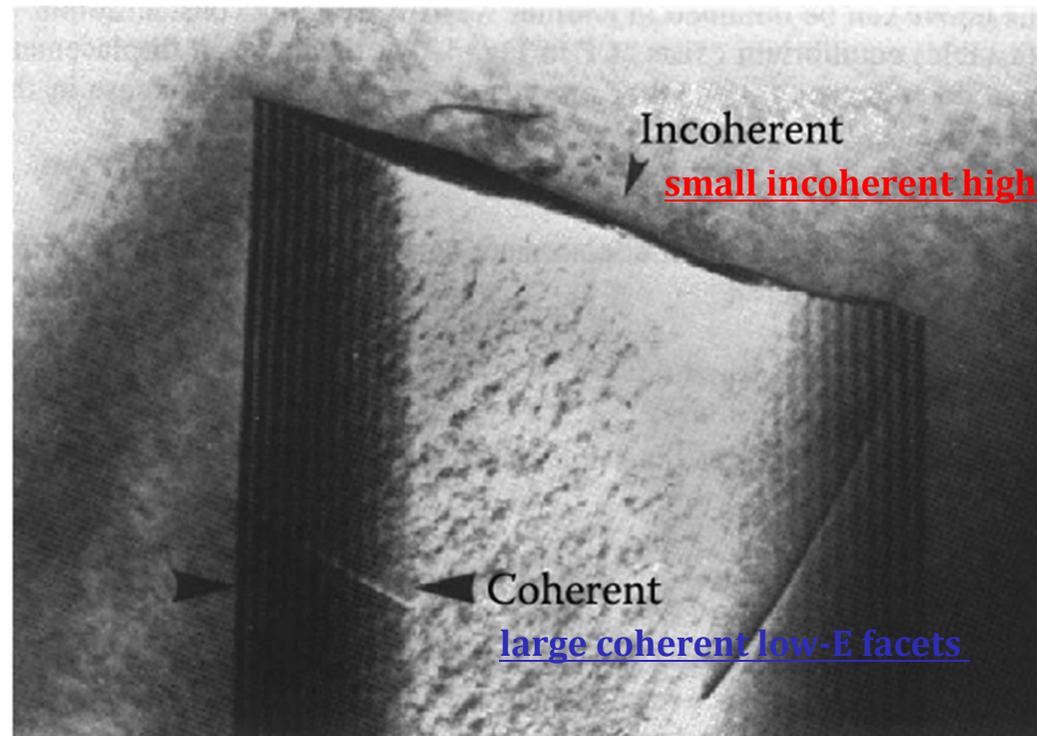
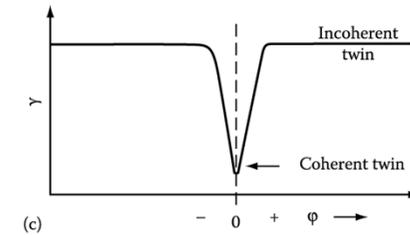
\* **Junction between coherent and incoherent twin boundary segments showing the importance of torque effects**

: the orientation dependence of twin boundary E, Fig. 3.13b

→ It is energetically favorable for twin boundaries to align themselves parallel to the twinning plane.

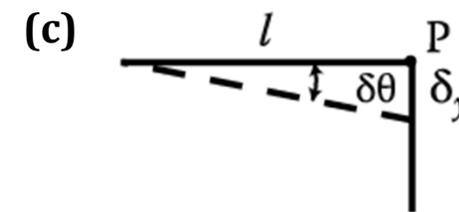
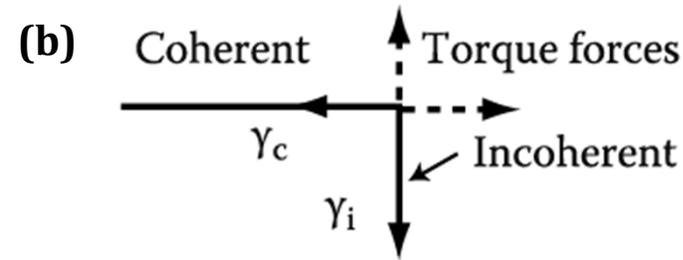
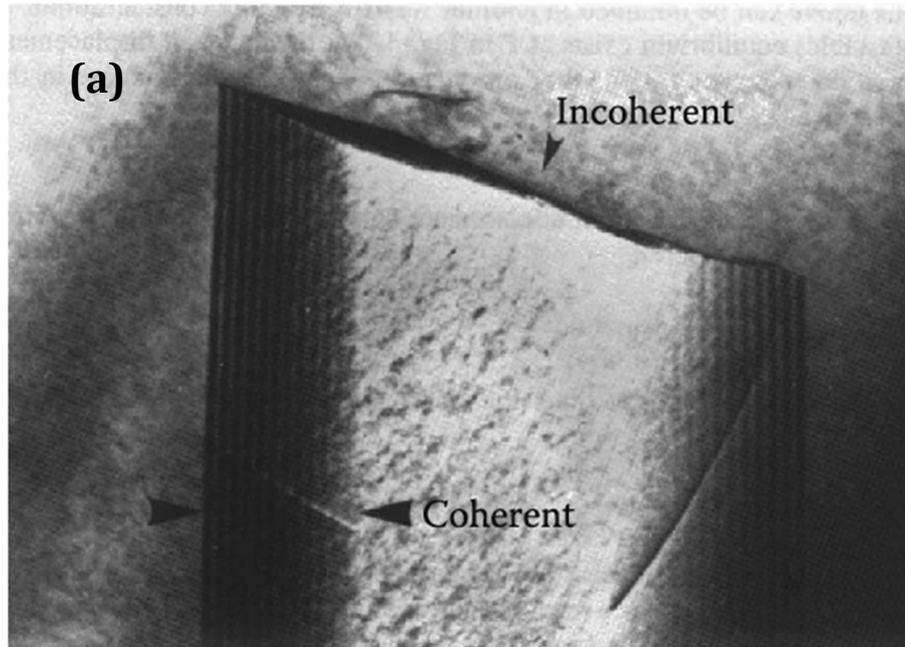
→ If the boundary is constrained to follow a macroscopic plane that is near but not exactly parallel to the twinning plane the boundary will usually develop a stepped appearance with large coherent low-E facets and small incoherent high-E risers.

→ does not minimize the total twin boundary E but minimize the total free E



(a) twin boundary in a thin foil specimen as imaged in the TEM

**\* Junction between coherent and incoherent twin boundary segments showing the importance of torque effects**



(a) twin B in a thin foil specimen as imaged in the TEM, (b) & (c), the coherent and incoherent segments of the twin B.

At the coherent/incoherent twin junction as shown in (b),

incoherent twin B tension,  $\gamma_i$  must be balanced by a torque term

$$\gamma_i \leq d\gamma_c/d\theta$$

Likewise, coherent twin B tension,  $\gamma_c$  must be balanced by a torque term

$$\gamma_c \leq d\gamma_i/d\theta$$

However, since  $\gamma_c$  is usually very small, the incoherent interface need only lie in a rather shallow energy cusp.

From energy consideration,

if (metastable) equilibrium exists at P in Fig. (c), then a small displacement such as that shown should either produce no change or an increase in the total free energy of the system, i.e.  $dG > 0$

considering unit depth a small displacement  $\delta y$  at P will increase the total free E by an amount

$$dG = l (d\gamma_c/d\theta) \delta\theta - \gamma_i \delta y > 0 \quad (\because \delta y \sim l d\theta) \quad \Rightarrow \quad \gamma_i \leq d\gamma_c/d\theta$$

# Q: Grain boundary ( $\alpha/\alpha$ interfaces)

= Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries

(b) Special High-Angle Grain Boundaries

(c) Equilibrium in Polycrystalline Materials

## 2) Thermally Activated Migration of Grain Boundaries

: Grain coarsening at high T, annealing due to metastable equilibrium of GB

## Considering factors of G.B. growth

**(a) Pinning particle**

**(b) 2<sup>nd</sup> phases**

**(c) Anisotropic  $\sigma$ , M**

**(d) Impurity (solute) drag**

**(e) Strain energy**

**(f) Free surface**

## GB intersection: Balance of 1) boundary E & 2) surface tension

### 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  $\gamma/r$  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

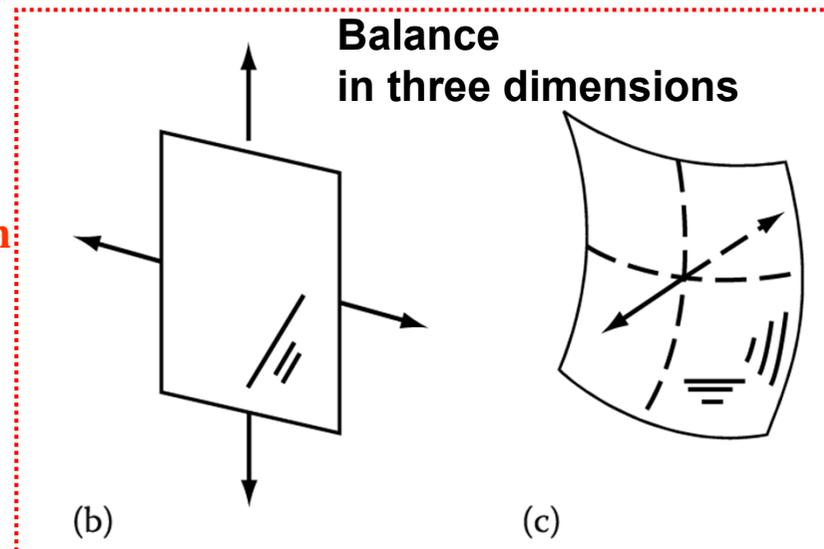
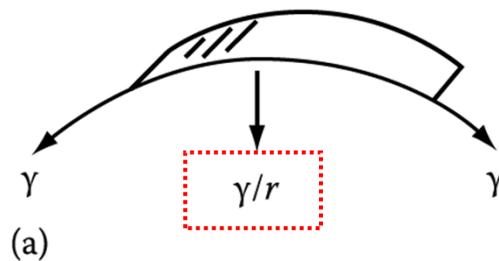


Fig. 3. 20 (a) A cylindrical boundary with a radius of curvature  $r$  is acted on by a force  $\gamma/r$ . (b) A planar boundary with no net force. (c) A doubly curved boundary with no net force.

A random grain structure is inherently unstable and, on annealing at high temperatures, the unbalanced forces will cause the boundaries to migrate towards their centers of curvature.

## a) Direction of Grain Boundary Migration during Grain Growth

For isotropic grain boundary energy in **two dimensions**,

Equilibrium angle at each boundary junction? → **120°** **3 boundaries intersections**

Equilibrium angle at each boundary junction in 3D? → **109°28'** **A corner formed by 4 grains**

**Morphology of metastable equilibrium state** → **Migration during annealing**

Effect of different boundary curvatures in two dimensions

**Boundaries** around Grain  $< 6$   
; **grain shrink, disappear**

**Boundaries** around Grain  $= 6$   
; **equilibrium**

**Boundaries** around Grain  $> 6$   
; **grain growth**

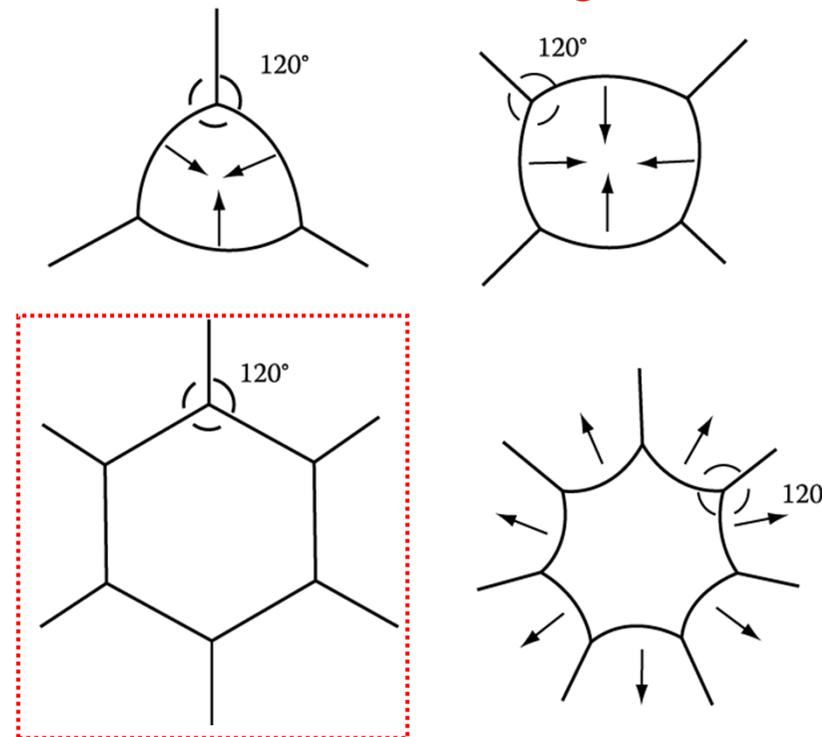


Fig. 3. 21 Two-dimensional GB configurations, The arrows indicate the directions boundaries will migrate during grain growth.

⇒ **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)

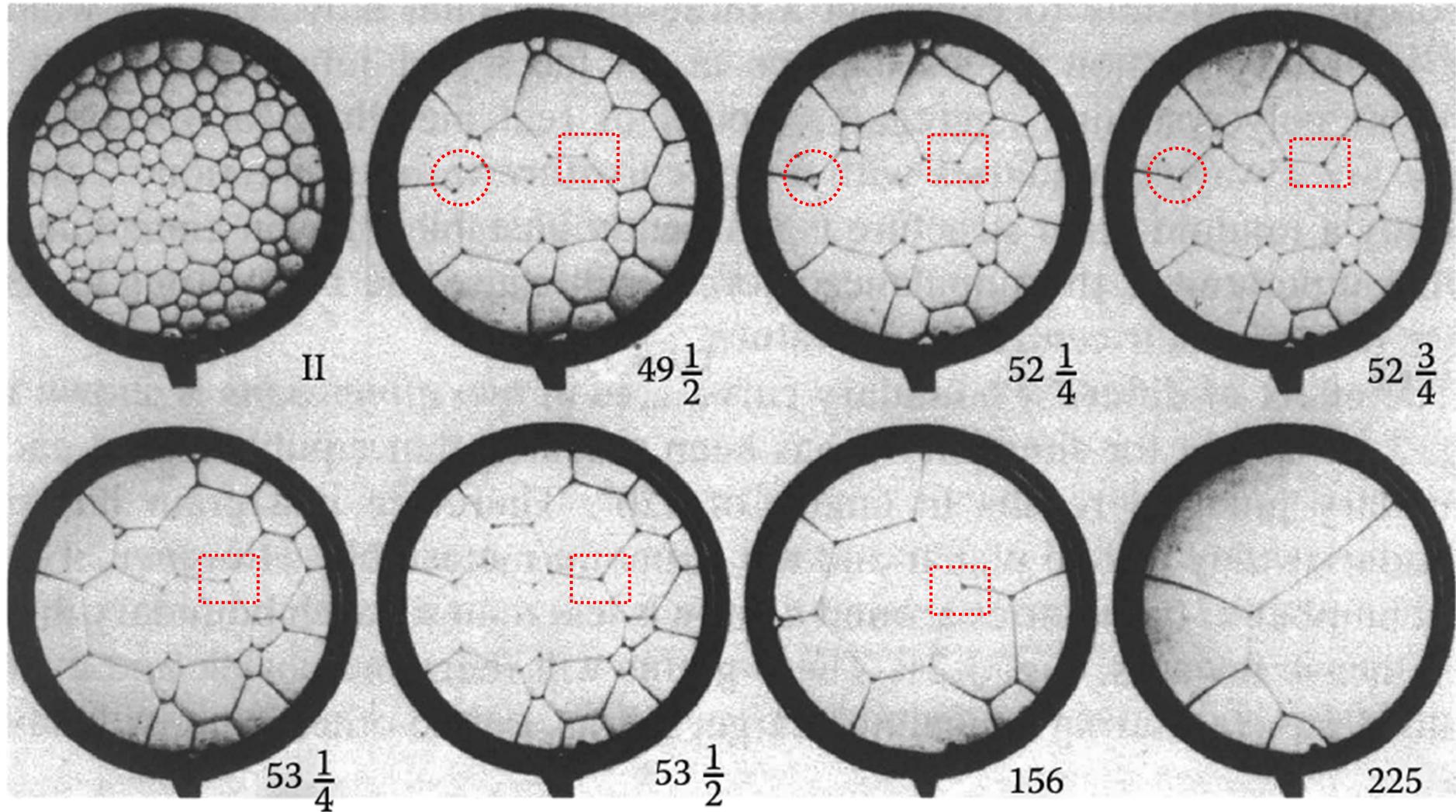
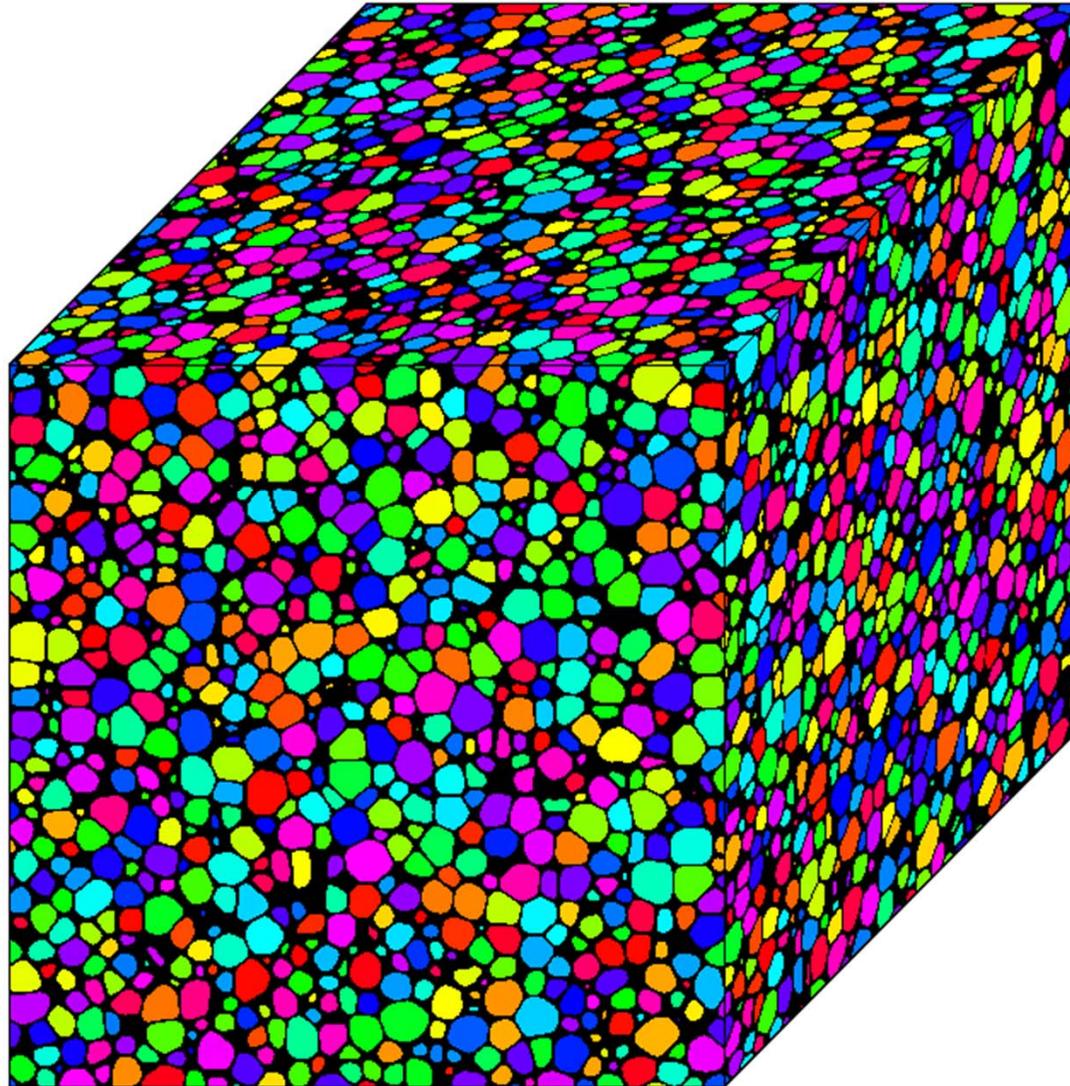


Fig. 3.22 Two-dimensional cells of a soap solution illustration the process of grain growth. Numbers are time in minutes.

## Example of Grain Growth simulation in 3D



**b) Grain Coarsening at High Temp. annealing (above about  $0.5 T_m$ ):**

The atoms in the shrinking grain detach themselves from the lattice on the high pressure side of the boundary and relocate themselves on a lattice site of the growing grain.

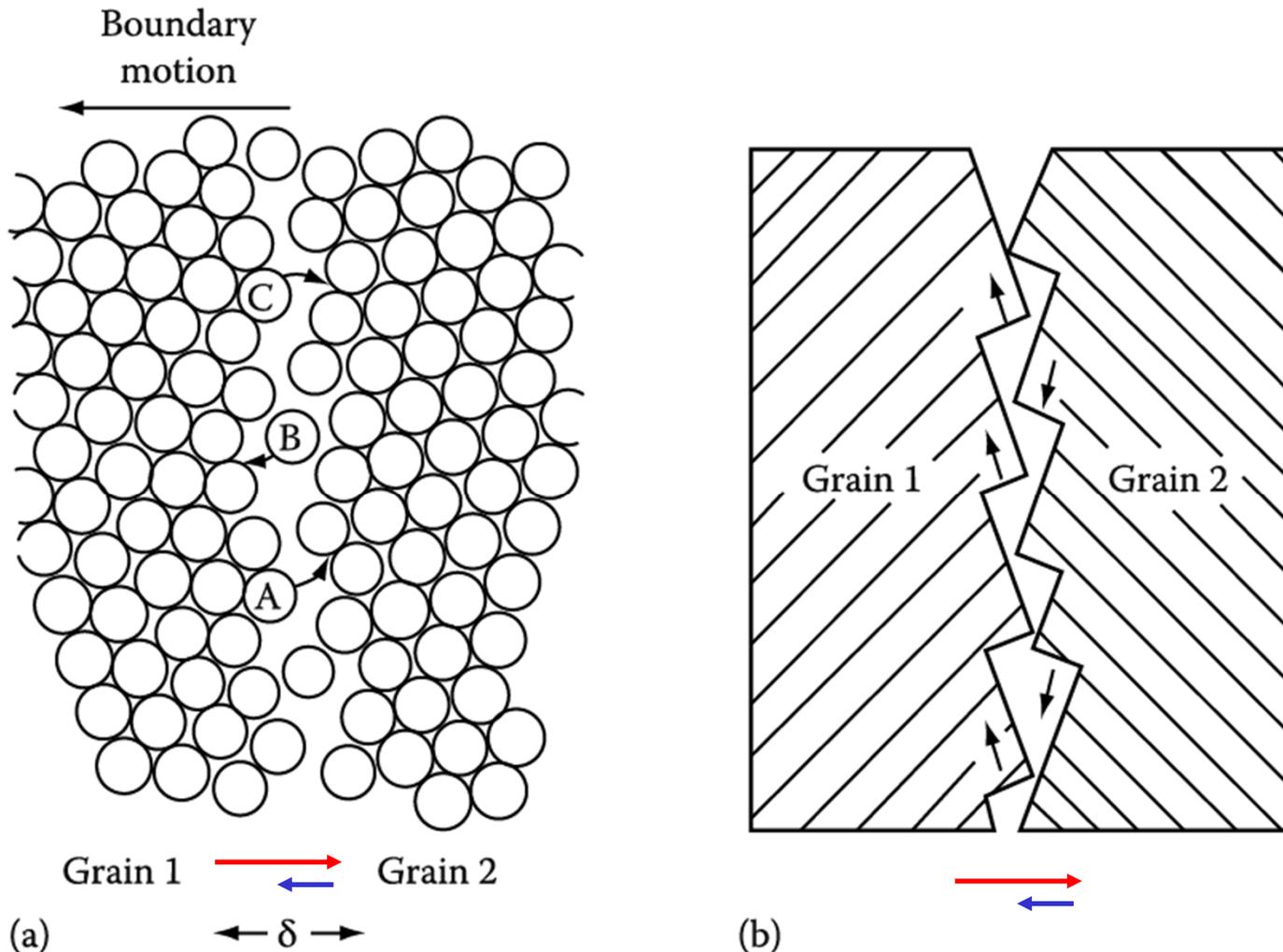


Fig. 3. 23 (a) The atomic mechanism of boundary migration. The boundary migrates to the left if the jump rate from grain 1  $\rightarrow$  2 is greater than 2  $\rightarrow$  1. Note that the free volume within the boundary has been exaggerated for clarity. (b) Step-like structure (돌출맥 구조) where close-packed planes protrude into the boundary.

\* Grain coarsening at high T annealing curvature  $\sim \Delta P \sim \Delta\mu$

→ metastable equilibrium state

: # ↓ , size ↑

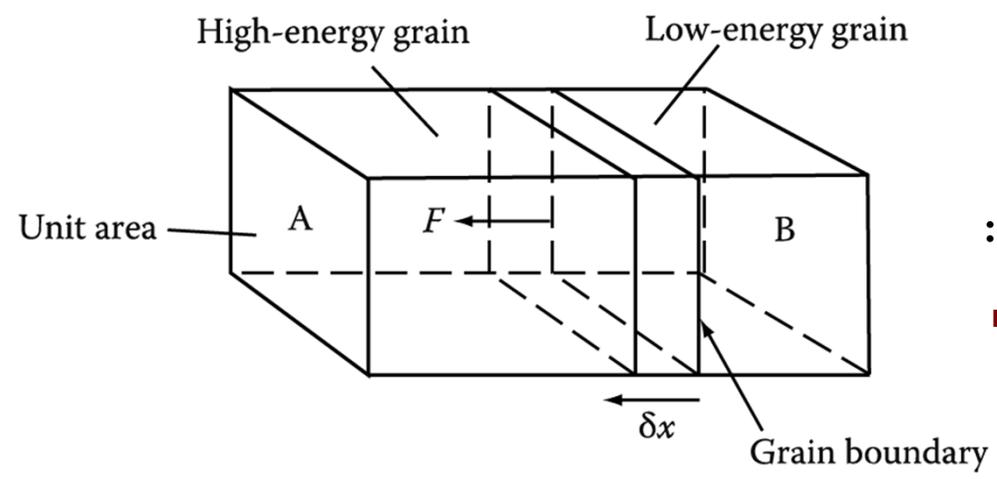
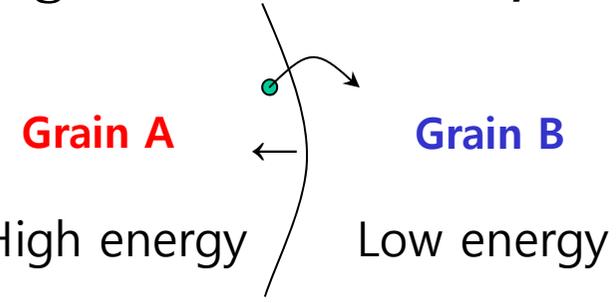


Fig. 3.25 A boundary separating grains with different free energies is subjected to a pulling force  $F$ .



$\Delta G = 2\gamma V_m / r \sim \Delta\mu$  **Gibbs-Thomson Eq.**  
 : effect of pressure difference by curved boundary

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

If unit area of GB advances a distance  $\delta x$ , # of moles of material that enter **grain B**

$$\delta x \cdot (1/V_m)$$

**Work :  $F dx = (2\gamma V_m / r) (\delta x / V_m)$**

→  $F = 2\gamma / r = \Delta G / V_m$  (by curvature)

**1) Pulling force per unit area of boundary :  $F = \frac{\Delta G}{V_m}$  ( $N m^{-2}$ ) (Eq. 3.18)**

Applies equally to any boundary whose migration causes a decrease in free energy, i.e. during recrystallization, the boundaries btw the new strain-free grains and the original deformed grains

Free energy difference per unit volume

# Q: Grain boundary ( $\alpha/\alpha$ interfaces)

(a) Low-Angle and High-Angle Boundaries

(b) Special High-Angle Grain Boundaries

(c) Equilibrium in Polycrystalline Materials

## 3) Kinetics of grain growth

- Grain boundary migration ( $v$ ) by thermally activated atomic jump

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

$v \sim \Delta G/V_m$  driving force  
 $\rightarrow F = \Delta G/V_m$

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

rate of grain growth  $dD/dt \sim 1/D$ , exponentially increase with  $T$

$\rightarrow \underline{D} = k't^n$  ( Experimental:  $n \ll 1/2$ ,  $1/2$  at pure metals or high Temp.)

- Mobility of GB  $\sim$  affected by both type of boundaries and GB segregation or 2<sup>nd</sup> phase precipitation

i.e Normal grain growth  $\longleftrightarrow$  Abnormal grain growth

## 2) How fast boundary moves? : Grain Growth Kinetics

Effect of the driving force on the kinetics of boundary migration

### Grain boundary migration by thermally activated atomic jump

\* (1) → (2) : Flux

(1) atoms in probable site :  $n_1$

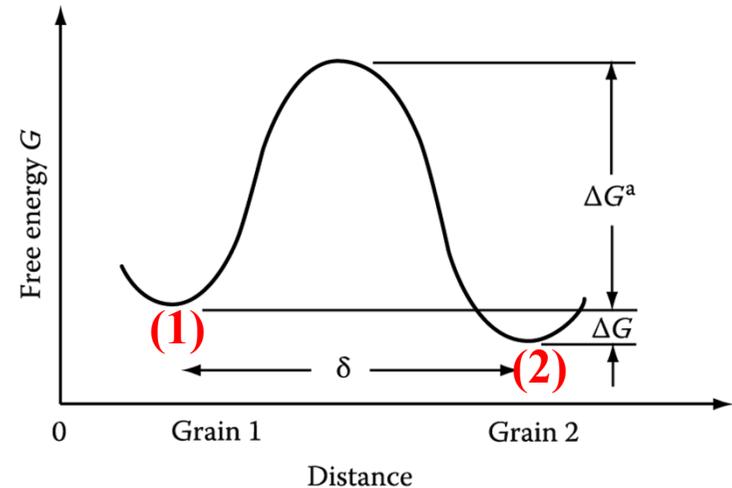
Vibration frequency :  $\nu_1$

$A_2$  : probability of being accommodated in grain (2)

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

\* (2) → (1) : Flux

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



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. (For a high-angle GB,  $A_1 \approx A_2 \approx 1$ )

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

$$J_{\text{net}} = J_{1 \rightarrow 2} - J_{2 \rightarrow 1} = An\nu \exp(-\Delta G^a/RT) [1 - \exp(-\Delta G/RT)] \quad 23$$

$$J_{1 \rightarrow 2} - J_{2 \rightarrow 1} = A n v \exp(-\Delta G^a/RT) [1 - \exp(-\Delta G/RT)]$$

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

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

Diffusion flux

If  $\Delta G$  is small [ $\Delta G \ll RT$ ]  $\rightarrow$  Apply Taylor expansion to  $\exp(-\Delta G/RT)$  term

$$J_{\text{net}} = A_2 n_1 v_1 \exp(-\Delta G^a/RT) [\Delta G/RT] \text{ (atom/m}^2\text{s)} = v / (V_m / N_a)$$

Boundary velocity  $v = \frac{A_2 n_1 v_1 V_m^2}{N_a R T} \exp\left(-\frac{\Delta G^a}{RT}\right) \frac{\Delta G}{V_m}$   $v \sim \Delta G / V_m$  driving force  $\rightarrow F = \Delta G / V_m$

or  $v = M \cdot \Delta G / V_m$   $M$ : mobility of boundary, i.e., the velocity under unit driving force

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

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

exponentially increase with temp

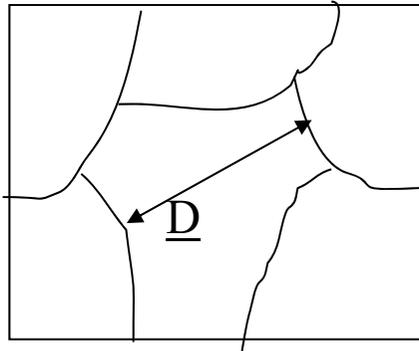
$\Rightarrow$  The boundary migration is a thermally activated process.

(입계 이동은 확산처럼 열활성화 과정)

## \* Kinetic of grain growth

1) driving force  $F = \Delta G/V_m$  →  $v = M (\Delta G/V_m)$  **Boundary velocity**  
**Pulling force** M : exponentially increase with temp.

$v$  : relation to grain coarsening



Mean grain size (diameter) :  $\underline{D}$

Mean radius of curvature of boundary :  $r$

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

$$\begin{aligned} \text{Mean velocity : } \underline{v} &= \alpha M (\Delta G/V_m) = d\underline{D}/dt \quad (\Delta G = 2\gamma V_m/r) \\ &= \alpha M(2\gamma/\underline{D}) = d\underline{D}/dt \quad (\alpha = \text{proportional constant} \sim 1) \end{aligned}$$

$\underline{v}$  (rate of grain growth)  $\sim 1/\underline{D}$ , exponentially increase with  $T$

Mean velocity :  $\underline{v} = \alpha M (\Delta G/V_m) = d\underline{D}/dt$  ( $\Delta G = 2\gamma V_m/r$ )  
 $= \alpha M(2\gamma/\underline{D}) = d\underline{D}/dt$  ( $\alpha = \text{proportional constant} \sim 1$ )

Integration of previous eq. from  $D_0$  to  $\underline{D}$ ,

$$\rightarrow \int_{D_0}^{\underline{D}} \frac{d\underline{D}}{\underline{D}} = \int 2\alpha M \gamma dt$$

$$\rightarrow \frac{1}{2} (\underline{D}^2 - D_0^2) = 2\alpha M \gamma t$$

$$\rightarrow (\underline{D}^2 - D_0^2) = 4\alpha M \gamma t = kt$$

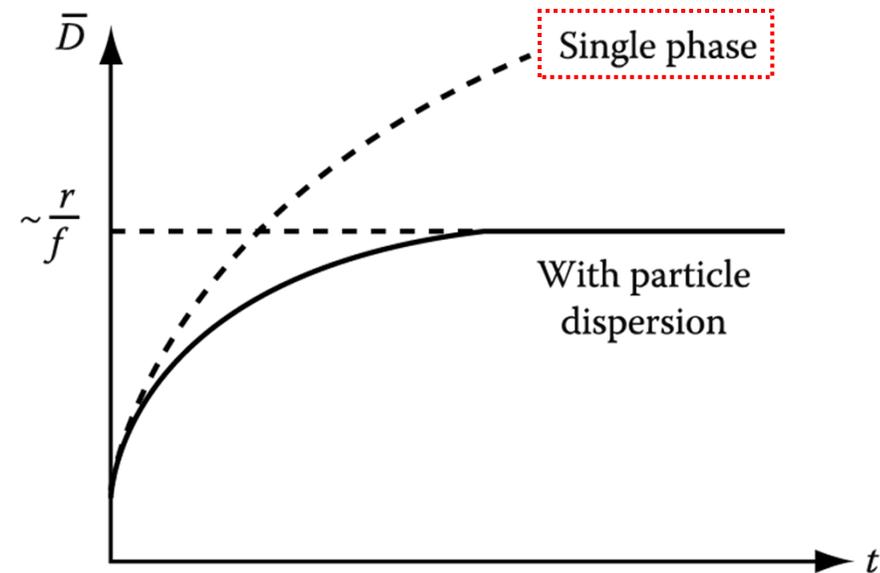
$$\rightarrow \underline{D}^2 = D_0^2 + kt$$

if  $D_0 \approx 0 \rightarrow \underline{D} = k't^{1/2}$

$\rightarrow \underline{D} = k't^n$  (experimental :  $n \ll 1/2$ ,  $1/2$  in very pure metals or only high temp.)

Single phase

- $\because$  the velocity of GB migration,  $v$  is not linear function of  $\Delta G$ .
- $\rightarrow M$  is not a const. but varies with  $\Delta G$  and thus also with  $D$ .
- $\rightarrow$  Variation of  $M$  in alloys could arise from solute drag effects. (M in alloy is relatively slower than that of pure metal)



$r = \text{average radius of particles}$   
 $f_v = \text{volume fraction of particles}$

# Whose mobility would be high between special and random boundaries?

By considering grain boundary structure,

(Mobility depending on GB structures)

High energy G.B. → relatively open G.B. structure → High mobility

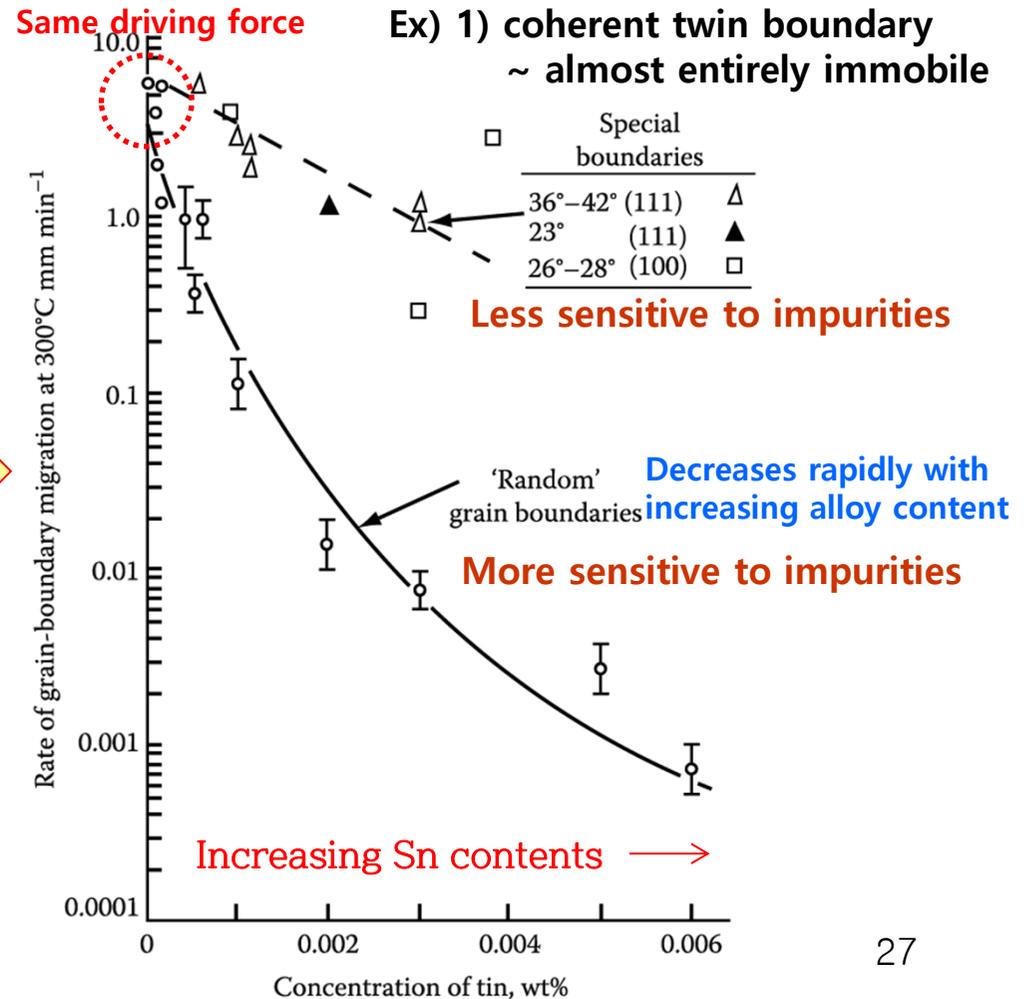
Low energy G.B. → closed (or denser) G.B. structure → Low mobility

But, **Ideal** ↔ **Real**

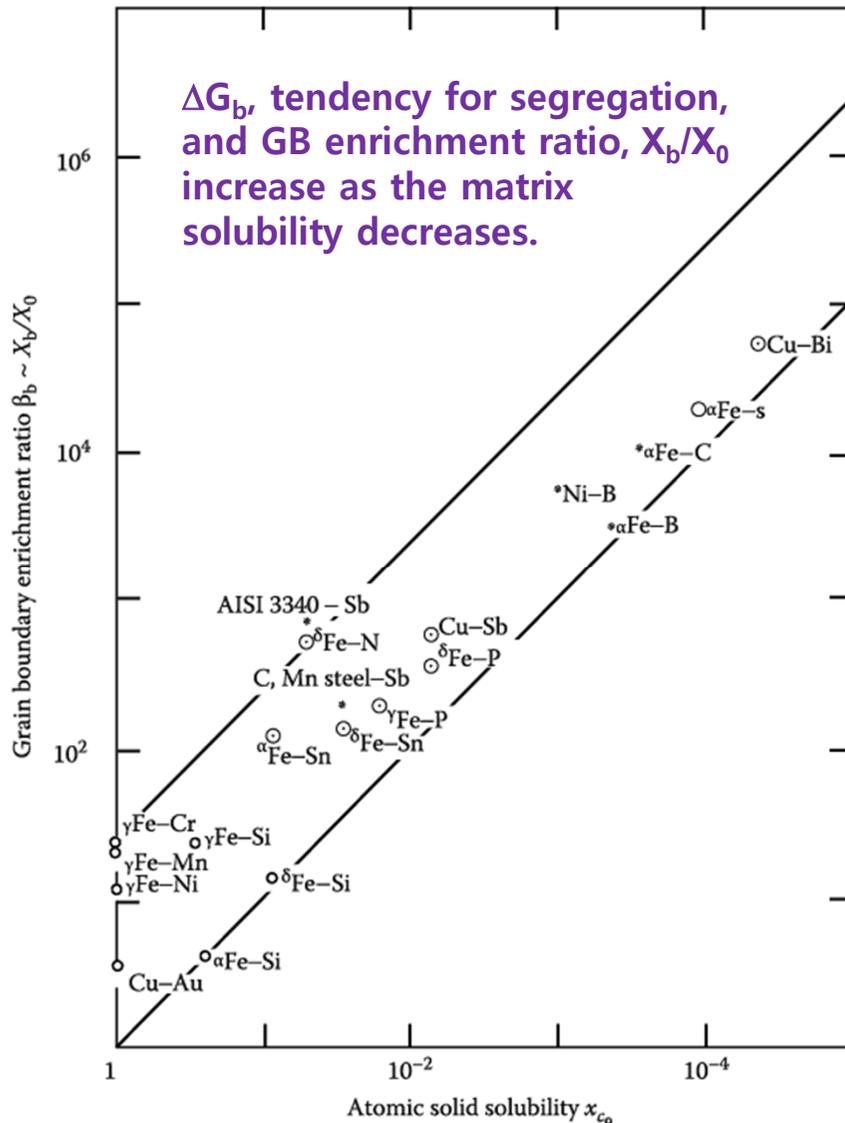
2) The other special boundaries are usually more mobile than random high-angle boundary. Why?

If the metal were “perfectly” pure the random boundaries would have the higher mobility.

⇒ Due to differences in the interactions of alloy elements or impurities with different boundaries



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



<Increasing GB enrichment with decreasing solid solubility in a range of system>

$X_0$  : matrix solute concentration/  $X_b$  : boundary solute concentration

$\Delta G_b$  : free energy reduced when one mole of solute is moved to GB from matrix.

( $\Delta G_b$ ) → The high mobility of special boundaries can possibly be attributed to a low solute drag on account of the relatively more close-packed structure of the special boundaries.

\* Solute drag effect

In general,  $G_b$  (grain boundary E) and mobility of pure metal decreases on alloying.

~Impurities tend to stay at the GB.

Generally,  $\Delta G_b$ , tendency of segregation, increases as the matrix solubility decreases.

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

$X_b/X_0$ : GB enrichment ratio

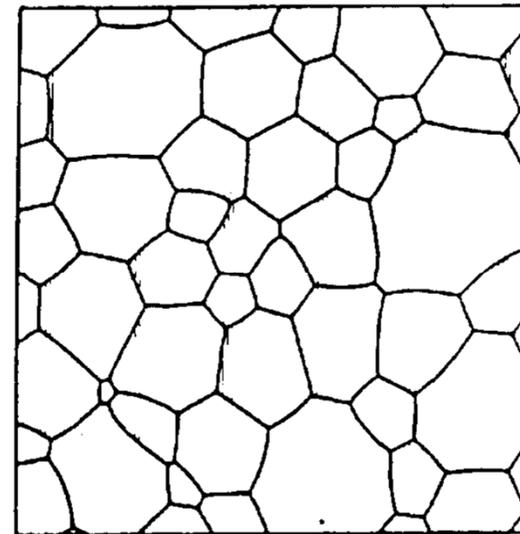
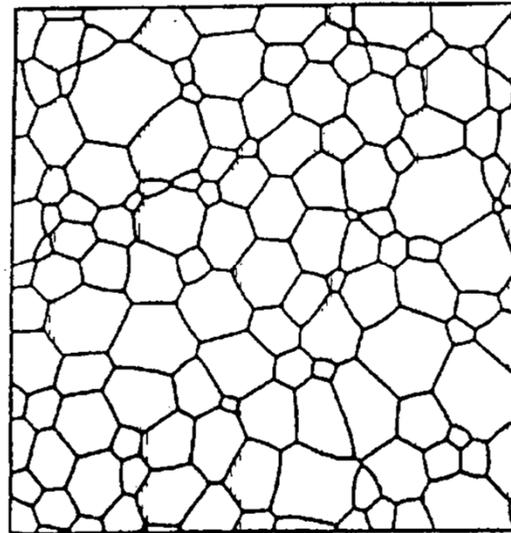
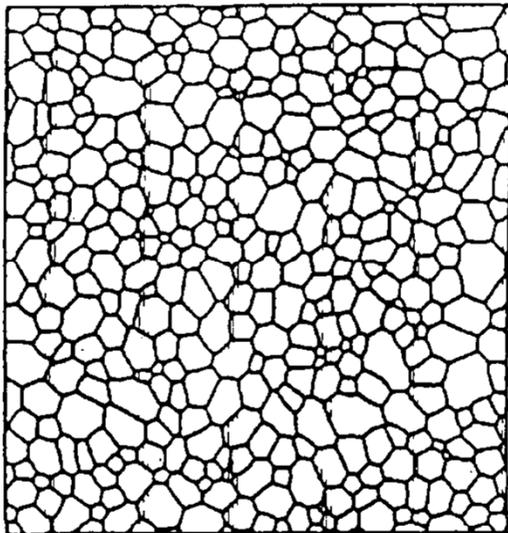
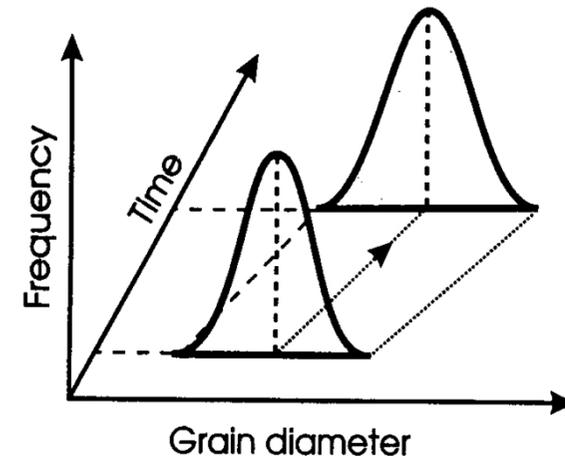
- Decreases as temp. increases, i.e., the solute "evaporates" into the matrix

Low T or  $\Delta G_b$  ↑  $X_b$  ↑ Mobility of G.B. ↓

→ Alloying elements affects mobility of G.B.

# 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

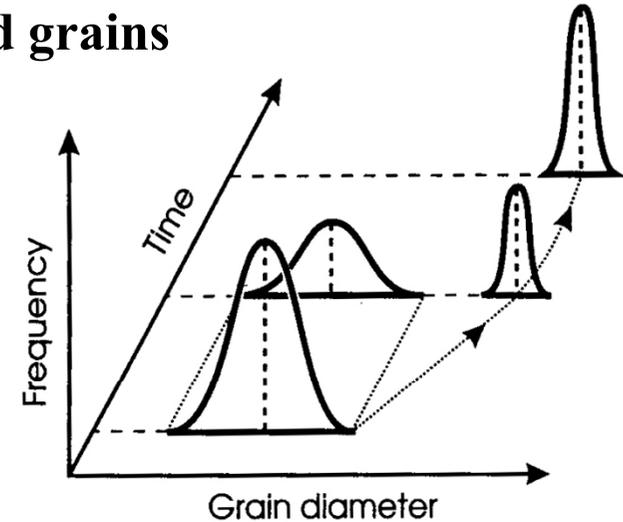


# Abnormal Grain Growth

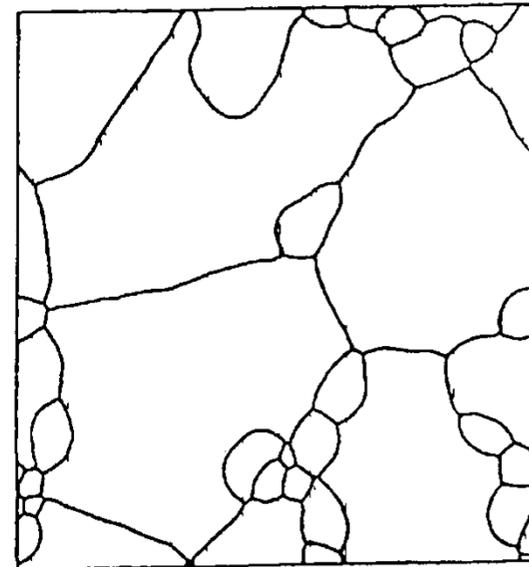
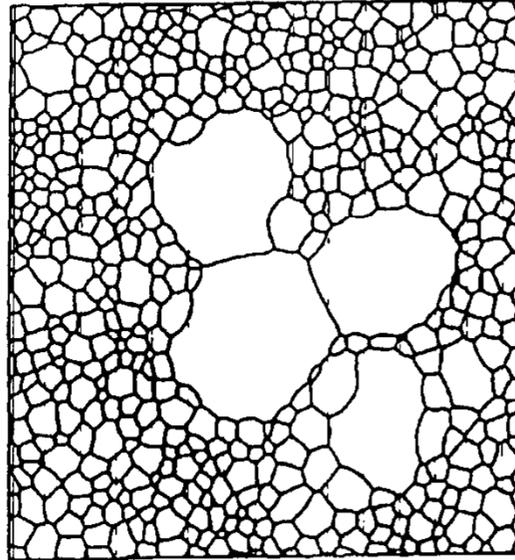
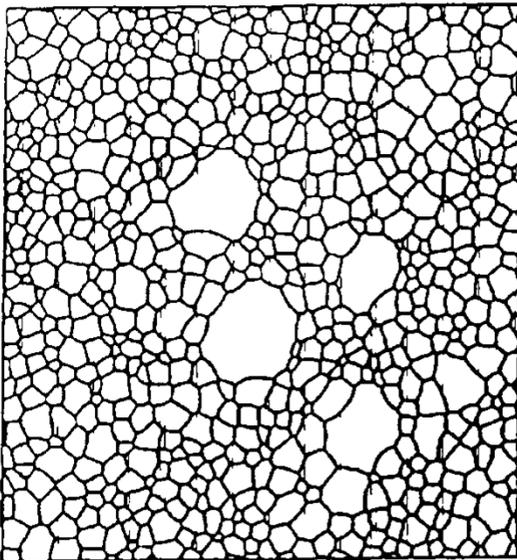
(high mobility of special GBs → development of recrystallization textures)

## ❑ 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

ex) Si steel → improvement of “soft magnetic property”  
= discontinuous grain growth or secondary recrystallization

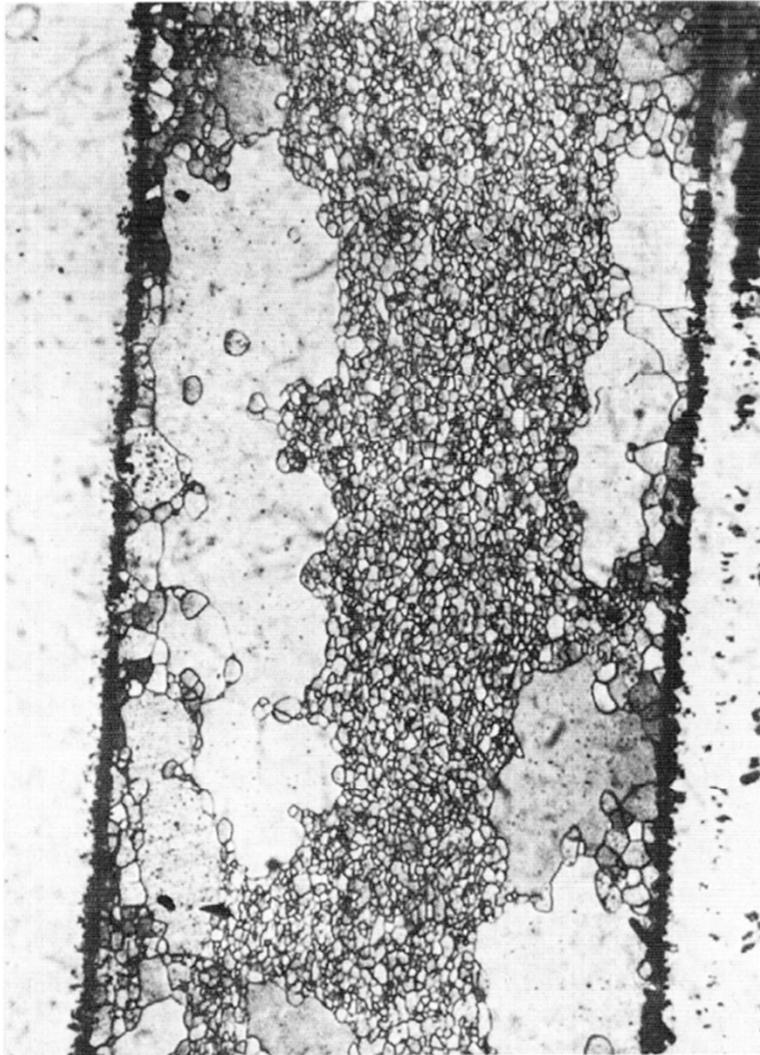


Figure 5.87 Optical micrograph showing abnormal grain growth in a fine grain steel containing 0.4 wt% carbon. The matrix grains are prevented from growing by a fine dispersion of carbide particles that are not revealed. Magnification  $\times 135$ . (After Gawne and Higgins 1971. Courtesy of the Metals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

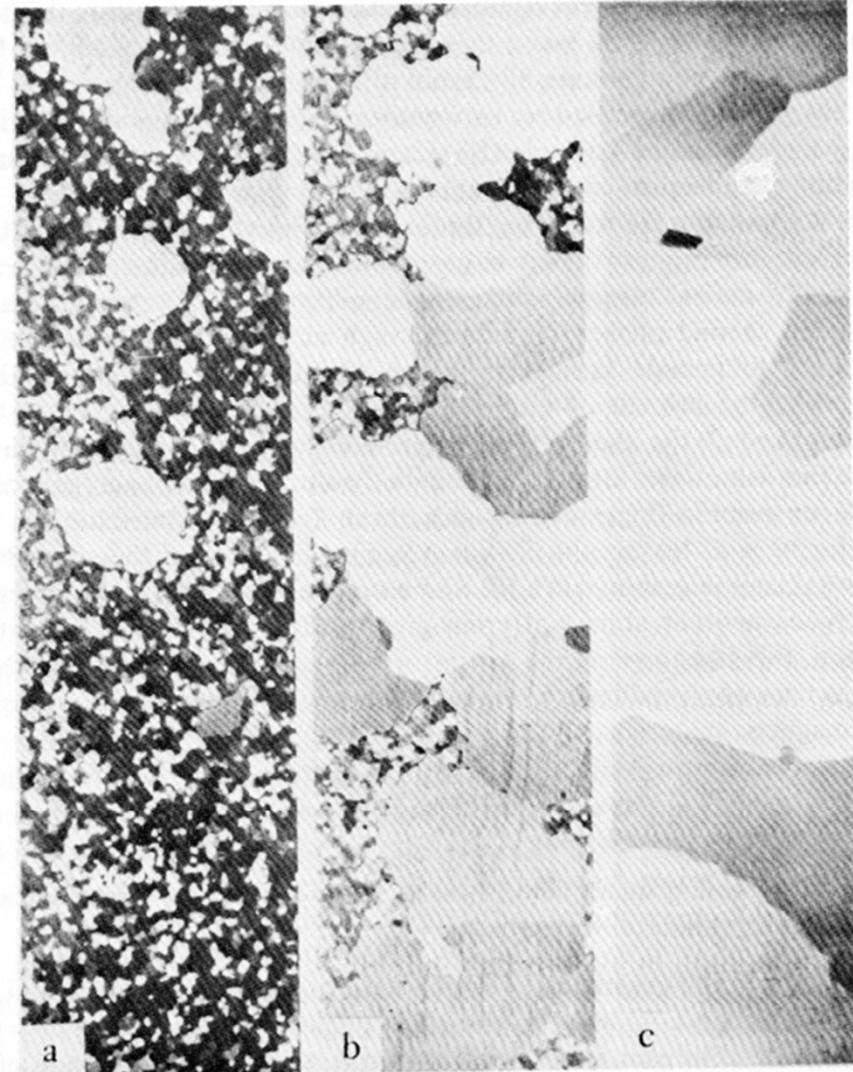


Fig. 5.48. Evidence for the preferential formation of (110)[001]-oriented grains by secondary recrystallization in 5% Si-Fe (Graham [1969]).

# Q: Grain boundary ( $\alpha/\alpha$ interfaces) = Boundaries in Single-Phase Solids

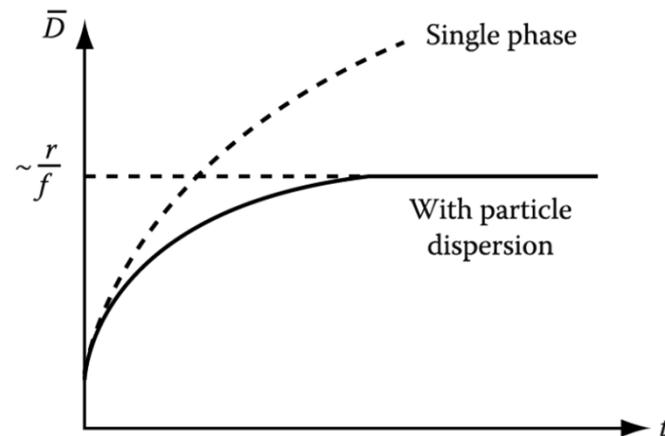
(a) Low-Angle and High-Angle Boundaries

(b) Special High-Angle Grain Boundaries

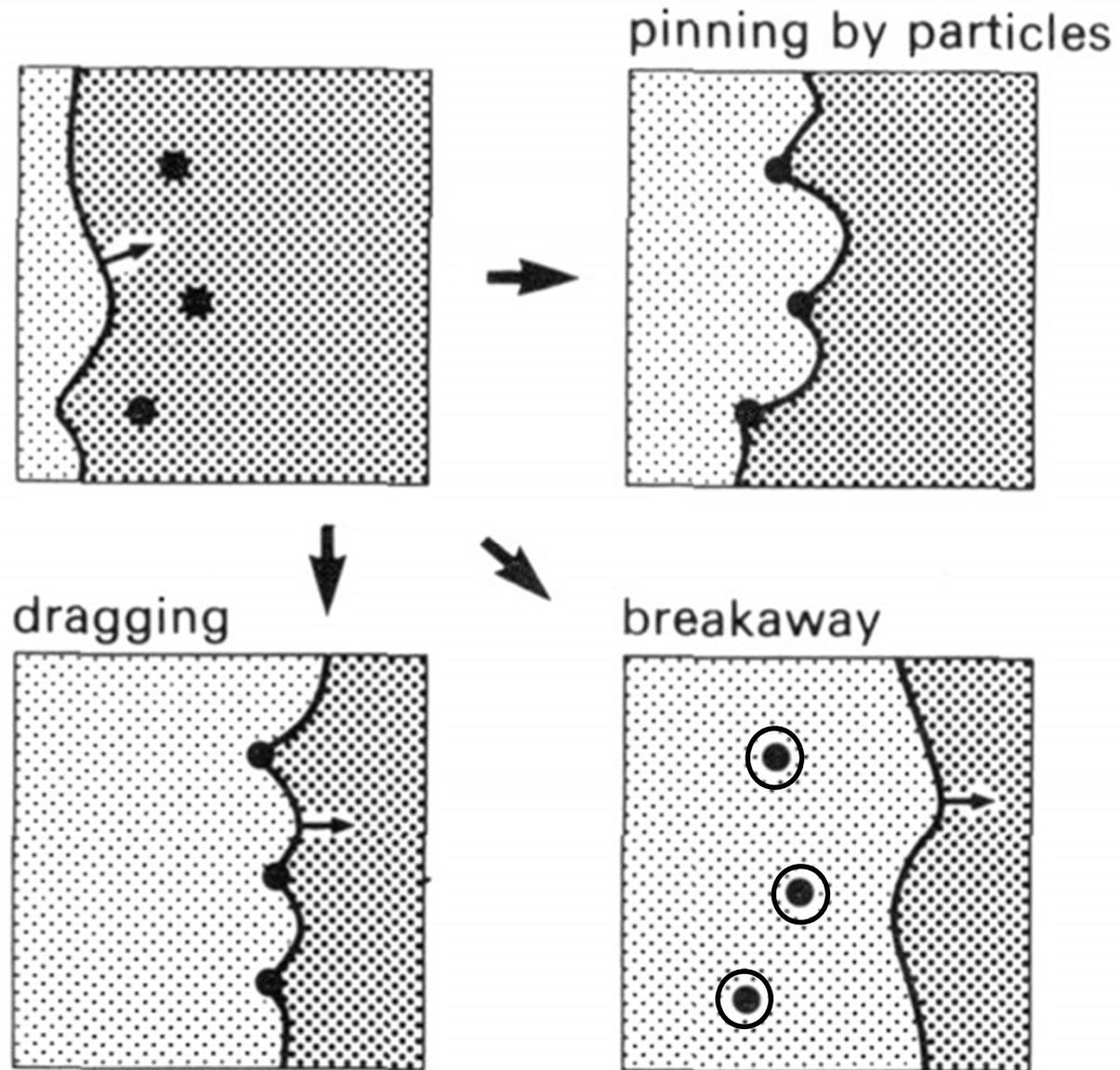
(c) Equilibrium in Polycrystalline Materials

## 4) Effect of second-phase particle on GB migration : Zener Pinning

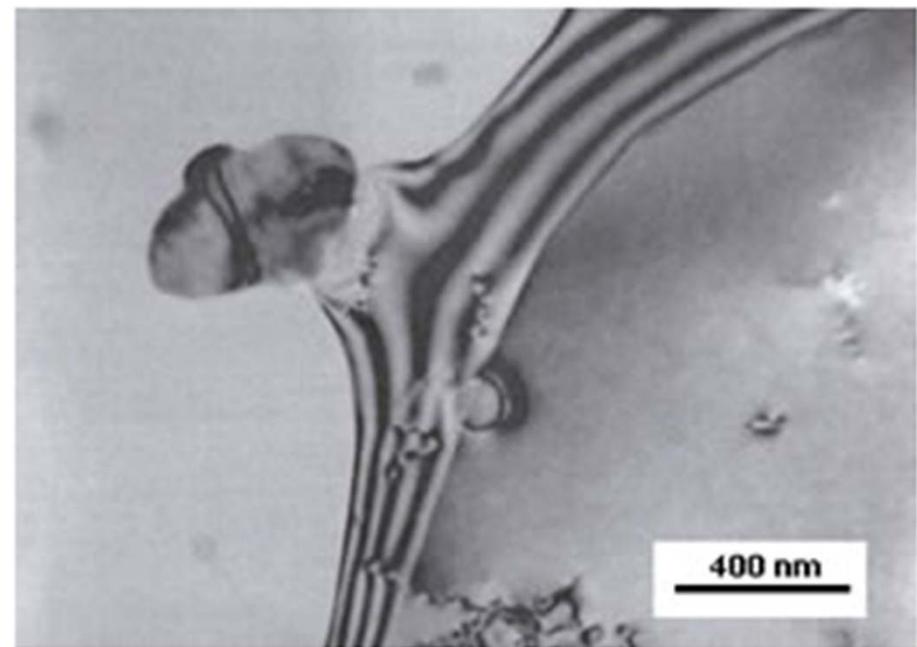
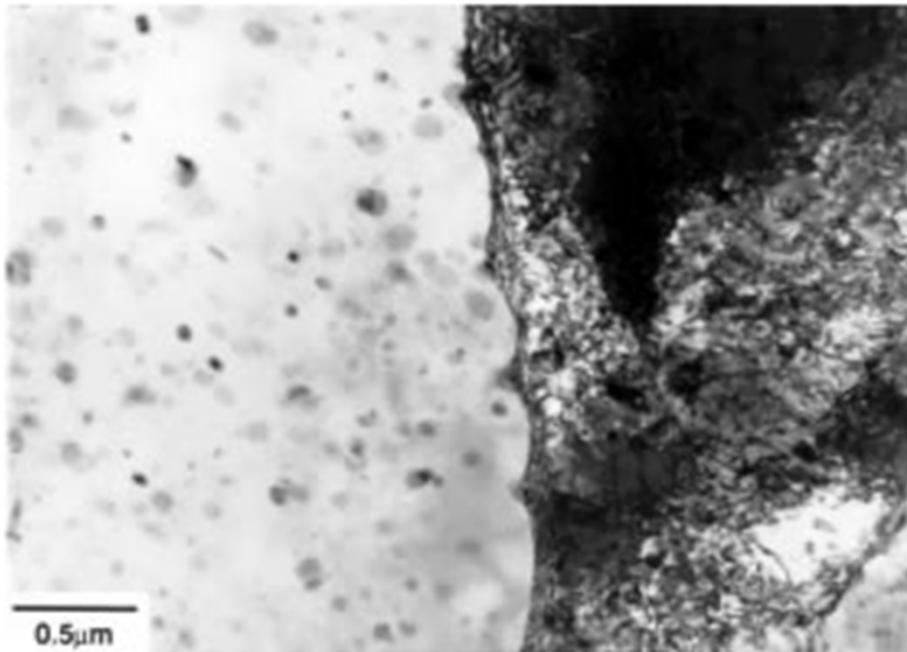
$$\bar{D}_{\max} = \frac{4r}{3f_v}$$



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



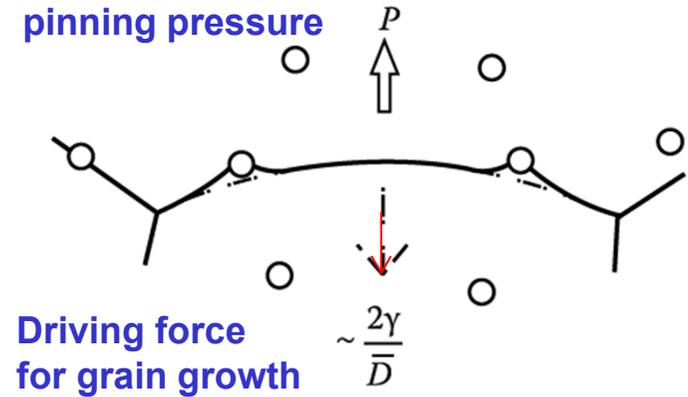
## Pinning by particle



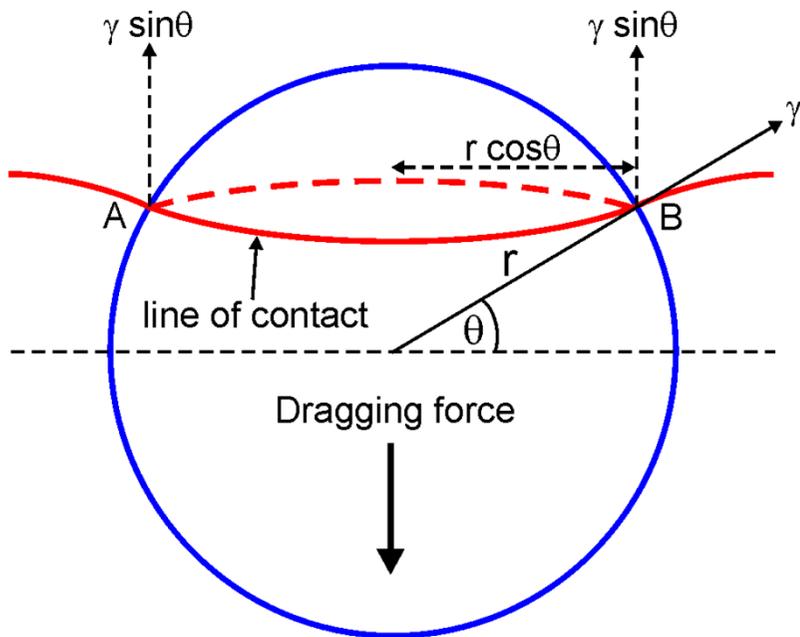
제 2 상이 존재할 때 결정립의 성장

# Effect of Second-Phase Particles on GB migration

## Interaction with particles **Zener Pinning**



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



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

$$F = \gamma \sin\{\theta\} \times \underbrace{2\pi r \cos\{\theta\}}_{\text{circumference}} = AB$$

so that at  $\theta = 45^\circ$

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

Maximum force exerted by a single particle

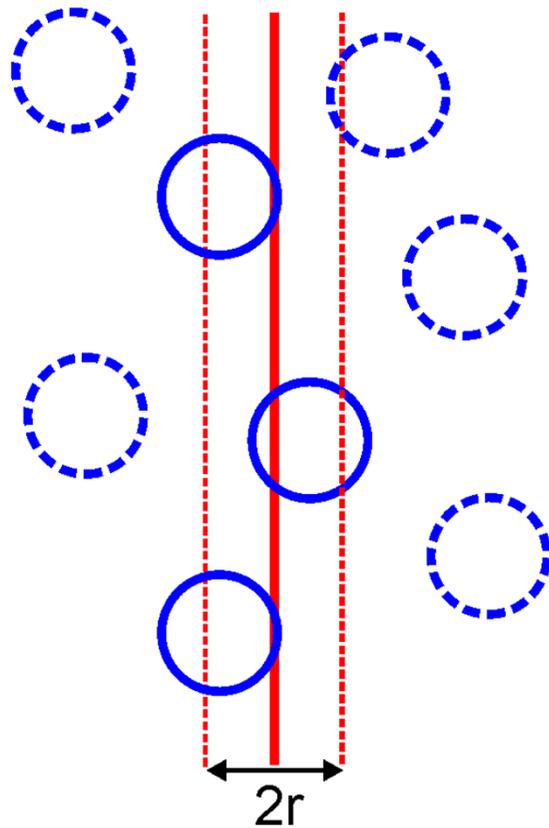
## Interaction with particles

## Zener Pinning

$f_v$  = volume fraction of randomly distributed particles of radius  $r$

$N_{\text{total}}$  = 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,

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

Mean # of particles intersecting unit area of a random plane

Given the assumption that

**all particles apply the maximum pinning force,**

the total pinning pressure

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

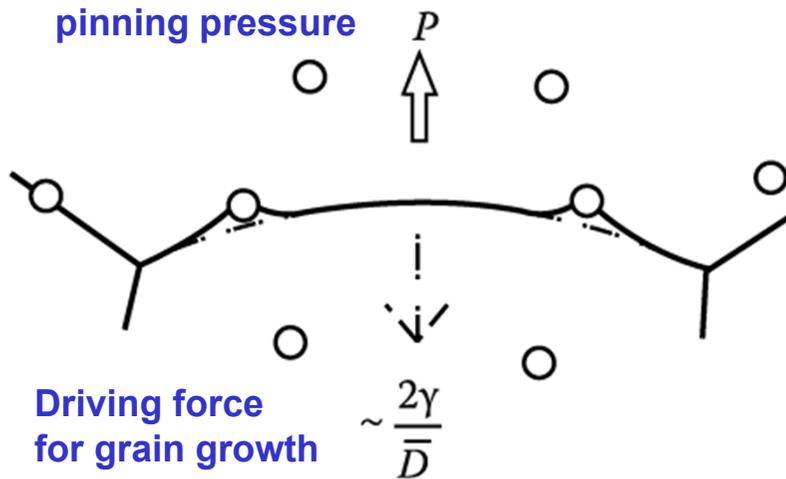
This force will oppose the driving force for grain growth,  $\frac{2\gamma}{\bar{D}}$ .

## 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,  $2\gamma/\bar{D}$ .



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

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

Driving force will be insufficient to overcome the drag of the particles and grain growth stagnates.

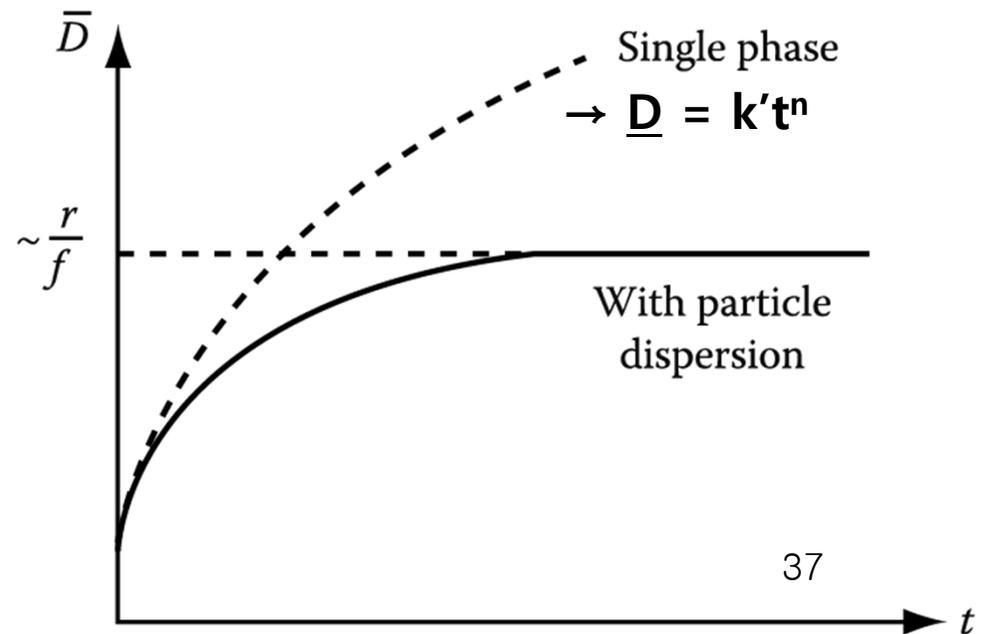
**For fine grain size**  
 **$\rightarrow$  a large volume fraction of very small particles**

## \* Effect of second-phase particles on grain growth

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

**: Stabilization of a fine grain size during heating at high temp.  $\rightarrow$  large volume fraction ( $f \uparrow$ ) of very small particles ( $r \downarrow$ ).**

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



## Summary for today's class

- **Thermally Activated Migration of Grain Boundaries:**

Metastable equilibrium of grain boundary (Balances of 1) boundary E + 2) surface tension)

→ real curvature ( $\Delta P \rightarrow \Delta G$ : Gibbs Thomson Eq.) →  $F = 2\gamma/r = \Delta G/V_m$  (by curvature)

(Pulling force per unit area of boundary)

→ Grain coarsening at high T annealing

- **Kinetics of Grain Growth**

- Grain boundary migration ( $v$ ) by thermally activated atomic jump

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

$v \sim \Delta G/V_m$  driving force  
→  $F = \Delta G/V_m$

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

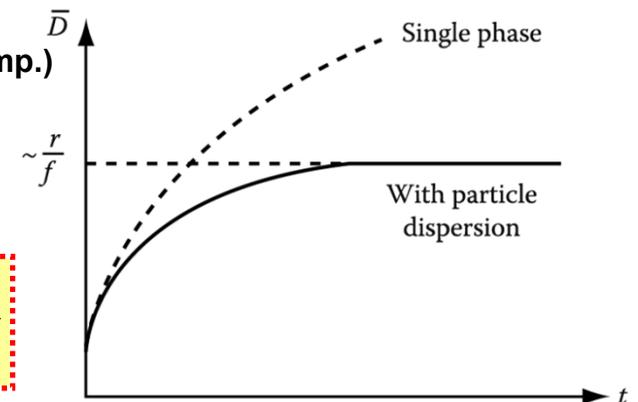
rate of grain growth  $d\bar{D}/dt \sim 1/\bar{D}$ , exponentially increase with T

→  $\bar{D} = k't^n$  (Experimental:  $n \ll 1/2$ ,  $1/2$  at pure metals or high Temp.)

- Mobility of GB ~ affected by both type of boundaries and GB segregation or 2<sup>nd</sup> phase precipitation

Ex) Effect of second-phase particle - Zener Pinning

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



# Summary for today's class

- Grain Growth**

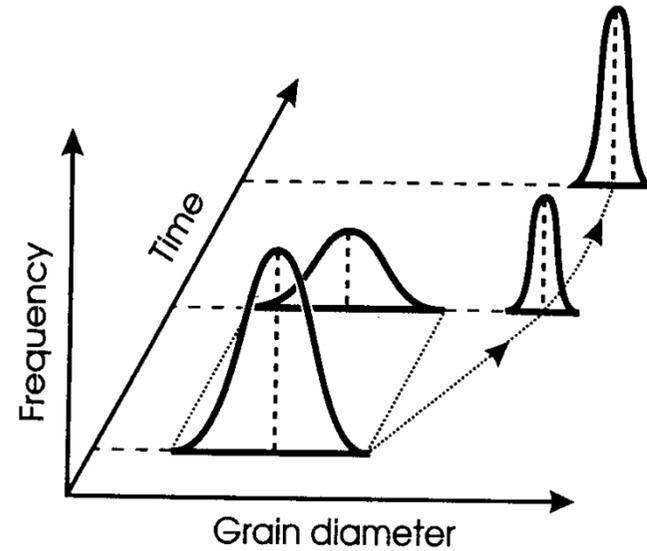
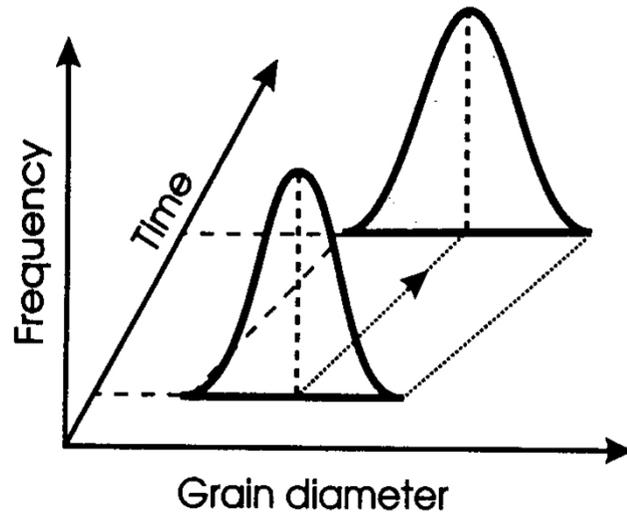
- Normal grain growth



**Abnormal grain growth**

(high mobility of special GBs

→ development of recrystallization textures)



< Bimodal Size distribution >

