2018 Fall

"Phase Transformation *in* Materials"

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Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

3.4 Interphase Interfaces in Solids

Interphase boundary - different two phases : different crystal structure
different composition

coherent,   **Perfect atomic matching at interface**
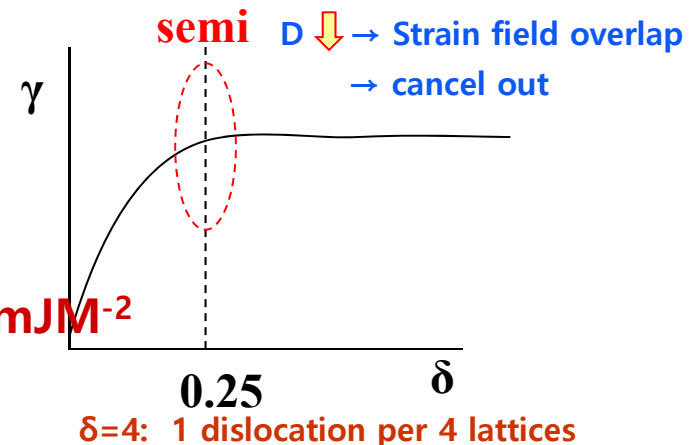
γ **(coherent) = γ_{ch}** γ **(coherent) ~ 200 mJM^{-2}**

semicoherent $\gamma(semicoherent) = \gamma_{ch} + \gamma_{st}$ γ

semi D ⬇ → **Strain field overlap**
→ **cancel out**

γ_{st} → **due to structural distortions**
caused by the misfit dislocations

γ**(semicoherent) ~ 200~500 mJM^{-2}**

0.25   **δ**

δ=4: 1 dislocation per 4 lattices

incoherent   **1) δ > 0.25** No possibility of good matching across the interface

2) different crystal structure (in general)

γ **(incoherent) ~ 500~1000 mJM^{-2}**

Complex Semicoherent Interfaces
Nishiyama-Wasserman (N-W) Relationship   **Kurdjumov-Sachs (K-S) Relationships**   2

**(The only difference between these two is a rotation in the closest-packed planes of 5.26°.)**
The degree of coherency can, however, be greatly increased if a macroscopically irrational interface is formed.

3.4 Interphase Interfaces in Solids

$$\sum A_i \gamma_i + \Delta G_S = minimum$$

Lowest total interfacial free energy
by optimizing the shape of the precipitate and its orientation relationship

Fully coherent precipitates

γ_{ch}

different composition

0.1 μ
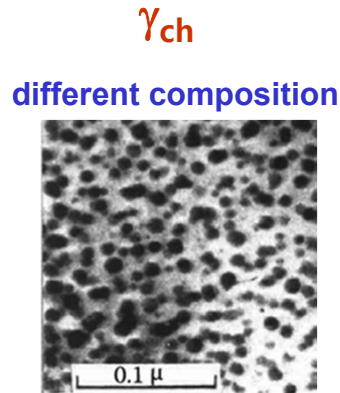
$\Rightarrow$ γ_{ch} + *Lattice misfit* $\Rightarrow$ γ_{ch} + $\boxed{Volume\ Misfit\quad \Delta = \dfrac{\Delta V}{V}}$

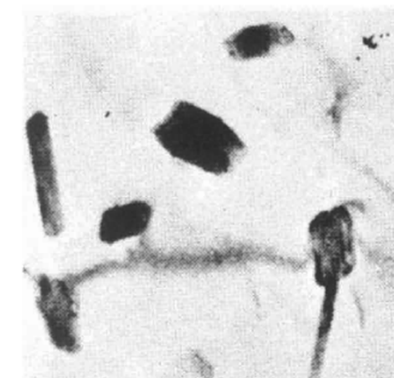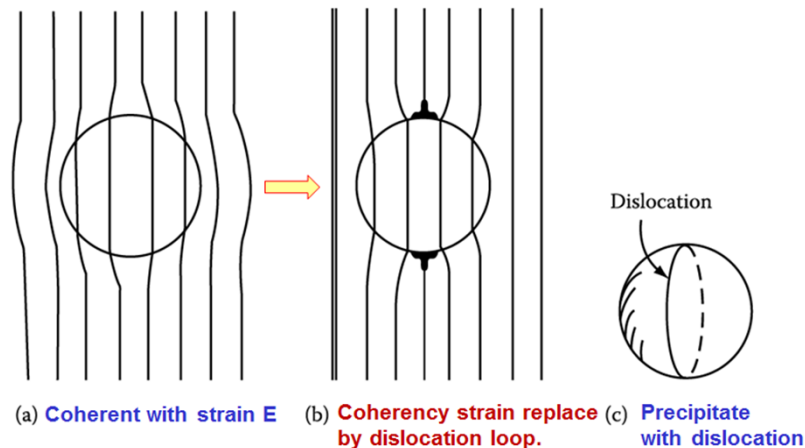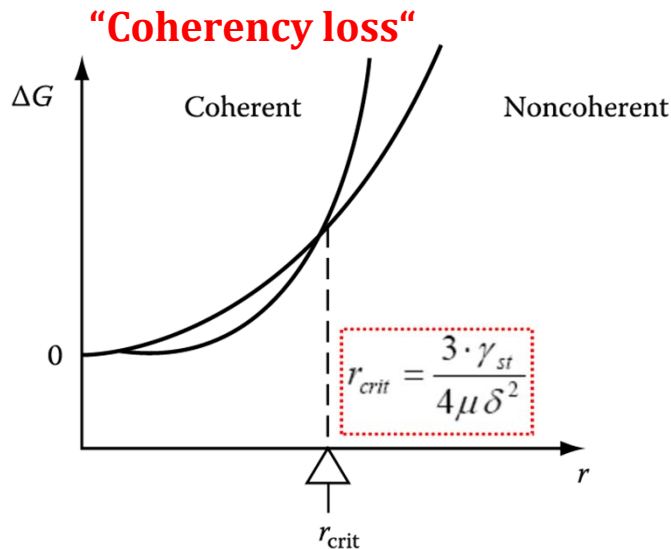**Coherency strain energy**   **Chemical and structural interfacial E**

$$\Delta G_S = 4\mu\delta^2 \cdot V \quad \text{(If v=1/3)} \quad \Longleftrightarrow \quad \Delta G_S = \frac{2}{3}\mu\Delta^2 \cdot V \cdot \boxed{f(c/a)}$$

Fully coherent precipitates   **Incoherent inclusions**

$$\Delta G(coherent) = 4\mu\delta^2 \cdot \frac{4}{3}\pi r^3 + 4\pi r^2 \cdot \gamma_{ch}$$

$$\Delta G(non-coherent) = 4\pi r^2 \cdot (\gamma_{ch} + \gamma_{st})$$

$\Rightarrow$ **Incoherent inclusions**

"Coherency loss"

ΔG

Coherent   Noncoherent

$$r_{crit} = \frac{3 \cdot \gamma_{st}}{4\mu\delta^2}$$

0

r_{crit}

Dislocation

(a) **Coherent with strain E**   (b) **Coherency strain replace** (c) **Precipitate**
                                    by dislocation loop.   **with dislocation**

3

Q: What is Glissile interface?

Glissile interface → coordinated glide of the interfacial disl. → (α→β) phase transformation

Interphase Interfaces in Solid (α/β)

1) Glissile Interfaces (평활 이동 계면)
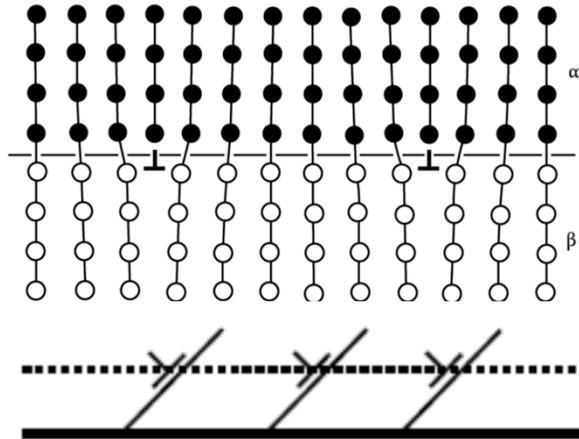
: epitaxial; Can't move forward or backward

(interface//burgers vector) ⟶ **Non-glissile interface**

: Glide of the interfacial disl. cannot cause the interface to advance

: Glissile; Boundary moves toward α or β

: semi-coherent interfaces which can advance
 by the coordinated glide of the interfacial disl.

Interfacial dislocations

Macroscopic plane of interface

Corresponding slip planes
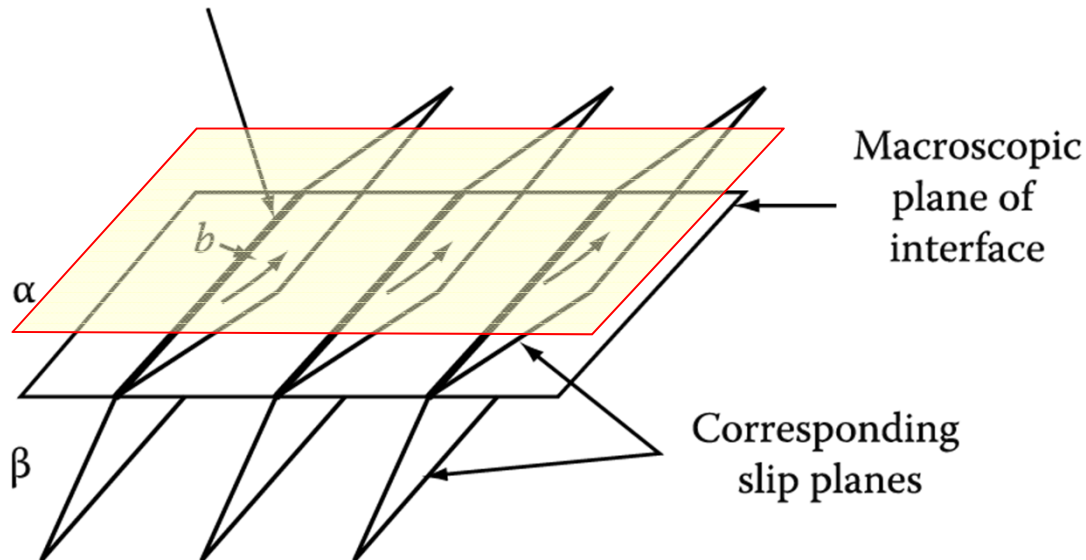
The dislocations have a Burgers vector that can glide on matching planes in the adjacent lattices.

Slip planes : continuous across the interface

Gliding of the dislocation :
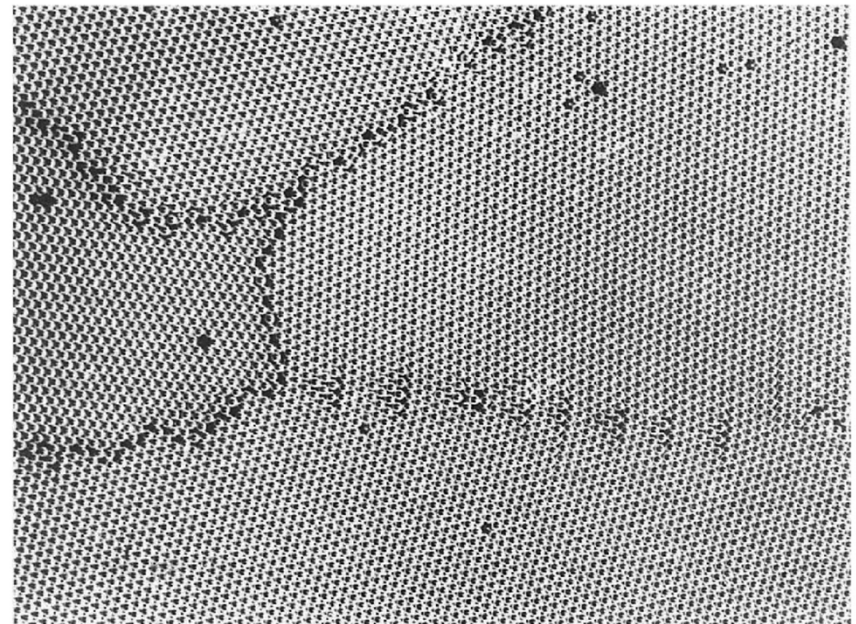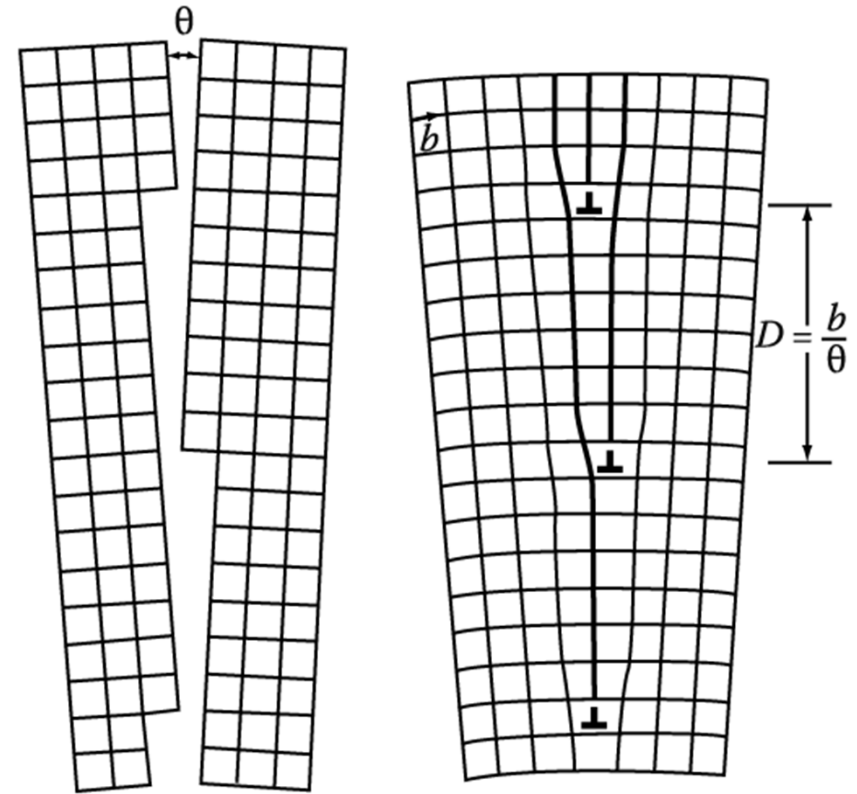α is sheared into the β structure.

Fig. 3. 55 The nature of a glissile interface.

Low-Angle tilt Boundaries

Bugers vector = edge dislocation

But, this is not interphase interface.

∵ crystal structure is same,
  only lattice rotation

$$D = \frac{b}{\theta}$$

* As disl. glide at low-angle grain boundary

  : no change in crystal structure,
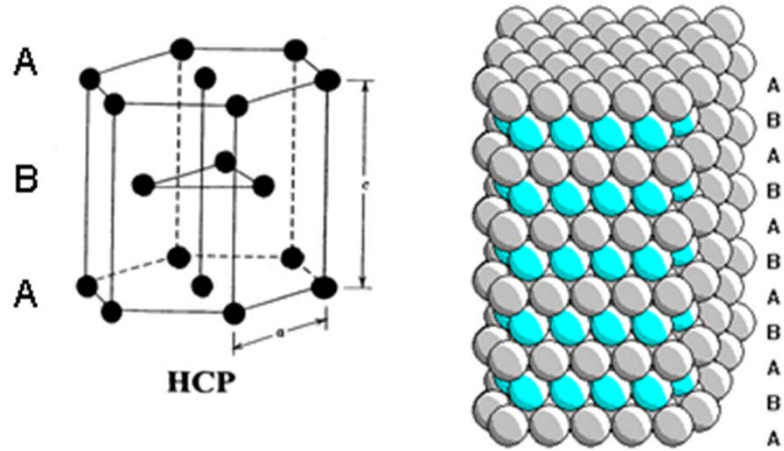
   just rotation of the lattice into the other grain

Glissile Interfaces between two lattices

Shockley partial dislocation
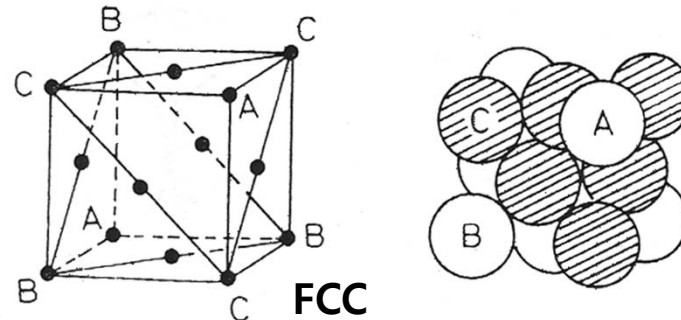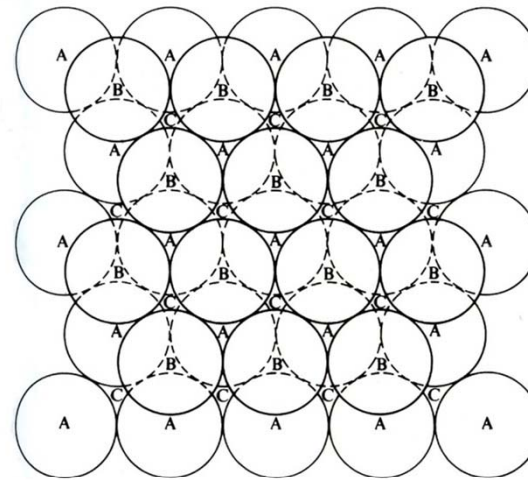
HCP: ABABABAB…

close packed plane: (0001)

close packed directions: $<11\bar{2}0>$

FCC: ABCABCAB…

close packed planes: {111}

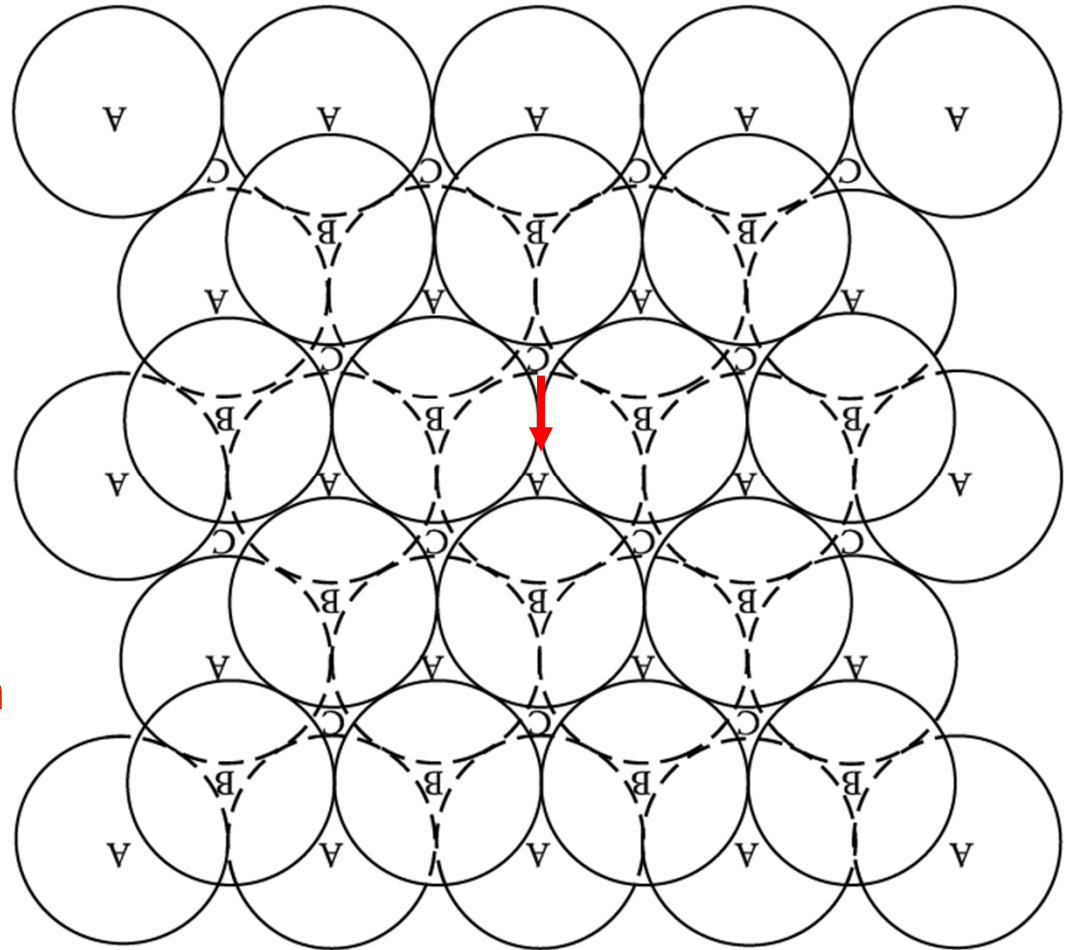close packed directions: $<110>$

HCP

FCC

1) Perfect dislocation

$$\vec{b} = \frac{a}{2}[10\bar{1}]$$

In C layer, atoms move
C' → C''

: remain a cubic close-packed
arrangement with a fcc unit cell

< FCC → FCC >

2) Shockley partial dislocation

when atoms move: C' → C''
possible to move C' → A → C''

$$\frac{a}{2}[10\bar{1}] = \frac{a}{6}[11\bar{2}] + \frac{a}{6}[2\bar{1}\bar{1}]$$

This burgers vector of partial disl.
is not located at lattice point.

(can't connect lattice points in the FCC structure)

C'

$$\vec{b} = \frac{a}{2}[10\bar{1}] \qquad \frac{a}{6}[11\bar{2}]$$

A

$$\frac{a}{6}[2\bar{1}\bar{1}]$$

C''

8
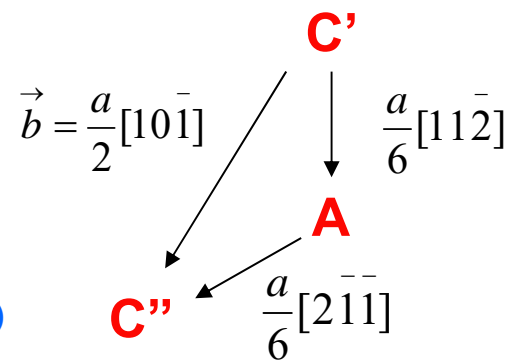
< FCC → HCP: phase transformation by stacking fault over the area of glide plane swept by the disl.>

Gliding of Shockley partial dislocations ⟹ Stacking fault region
적층결함

In thermodynamically <u>stable FCC lattices</u>, the stacking fault is a region of high free energy. →gliding of partial dislocations : difficult

Dislocation sliding
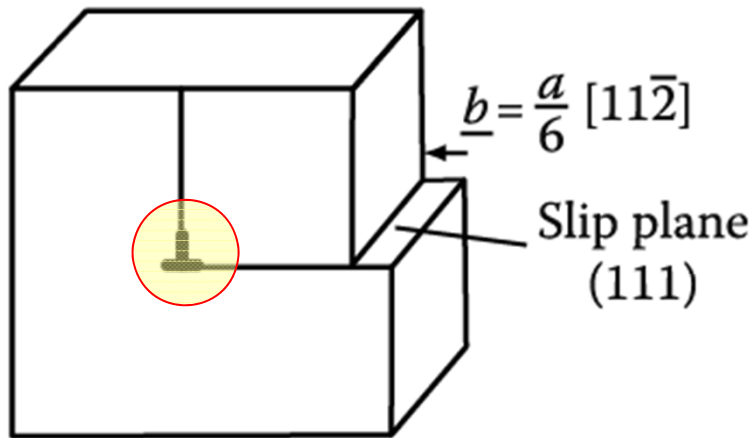
(a)
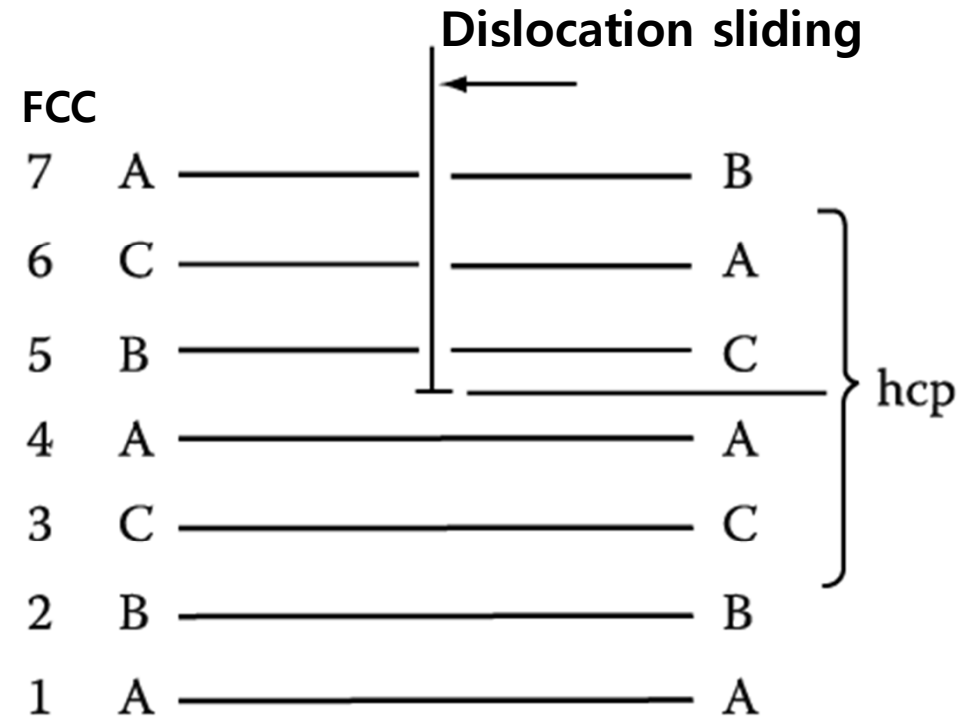
(b)

Fig. 3. 59 (a) An edge dislocation with a Burgers vector b = $\frac{a}{6}$[11$\overline{2}$] on (11$\overline{1}$). (shockley partial dislocation.)
(b) The same dislocation <u>locally changes the stacking sequence from fcc to hcp.</u>

If FCC lattice is <u>only metastable with respect to the HCP structure</u> → stacking fault E ~ effectively negative → gliding of partial dislocation: easy due to decrease the free energy of system

Glissile Interfaces between two lattices

Stacking Faults misfit → hcp

ABCABCABC → ABCA|CABC..........

Sequence of Shorkley partial dislocations between every other (111) plane

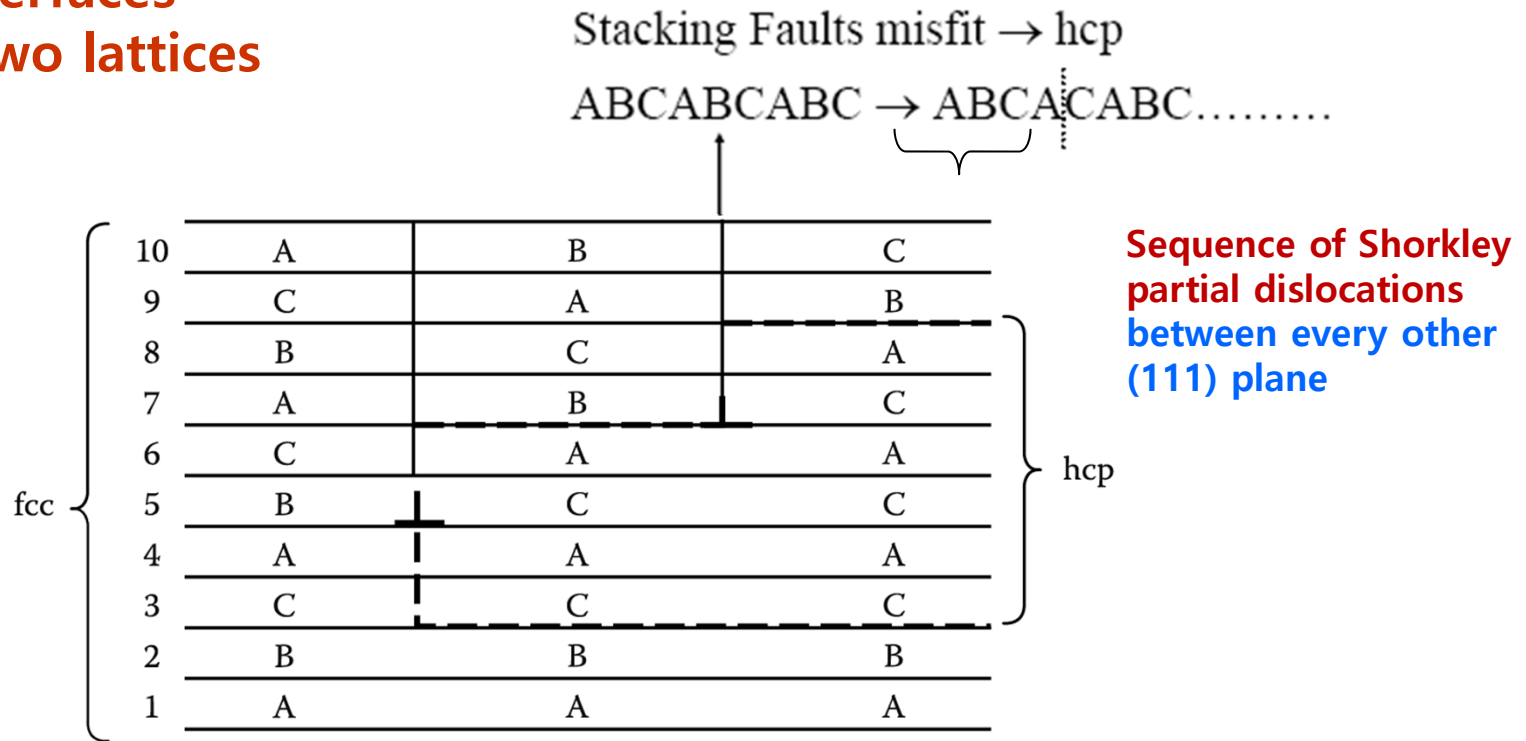|			
10	A	B	C
9	C	A	B
8	B	C	A
7	A	B	C
6	C	A	A
5	B	C	C
4	A	A	A
3	C	C	C
2	B	B	B
1	A	A	A

fcc

hcp

Fig. 3. 60 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

FCC {111} plane

Macroscopic interface plane

C
B   fcc
A
C
B
A
C
B
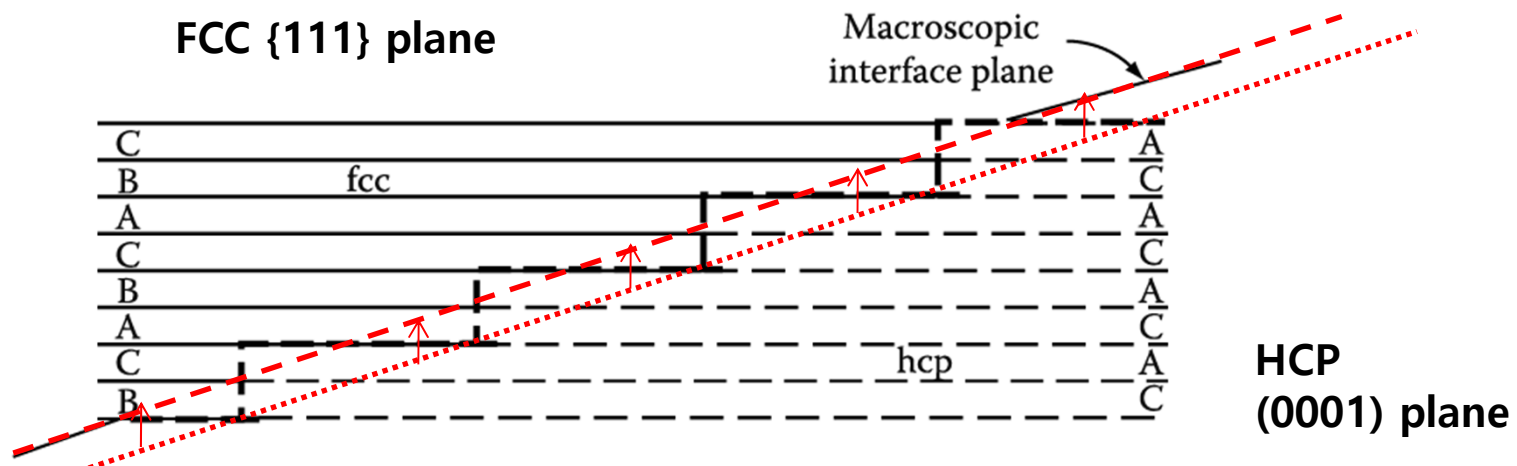
A
C
A
C
A
C
A
C

hcp

HCP (0001) plane

Fig. 3. 61 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

An important characteristic of glissile dislocation interfaces
  → **they can produce a macroscopic shape change in the crystal.**

1) Sequence of same Shorkley partial dislocations between every other (111) plane

  → **Pure shear deformation**
  → **Fcc → Hcp**
  → **shape change**
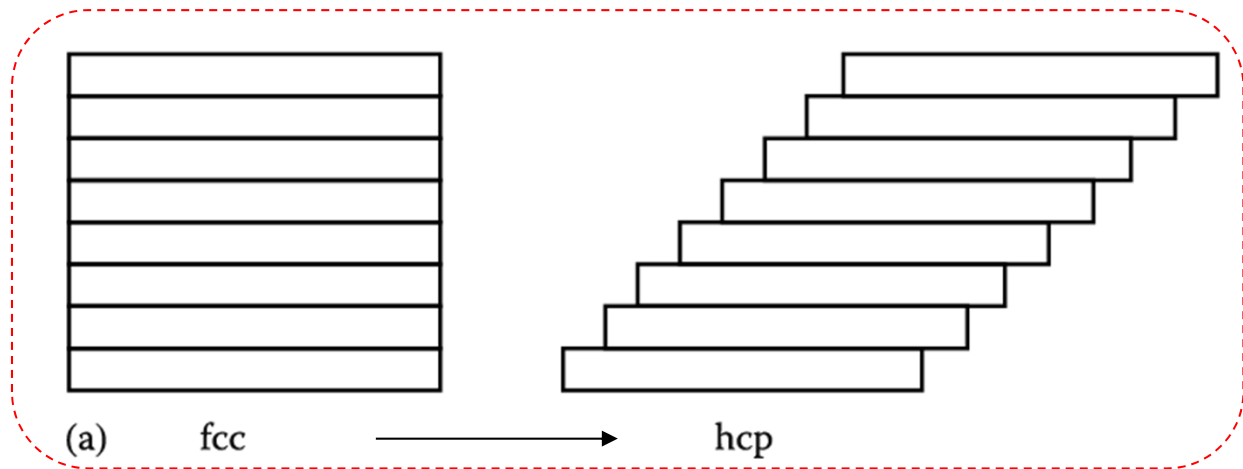
2) If transformation is achieved using all three partials in equal #s,

C'

$$\vec{b} = \frac{a}{2}[10\bar{1}] \qquad \frac{a}{6}[11\bar{2}]$$

A

C" $\frac{a}{6}[2\bar{1}\bar{1}]$
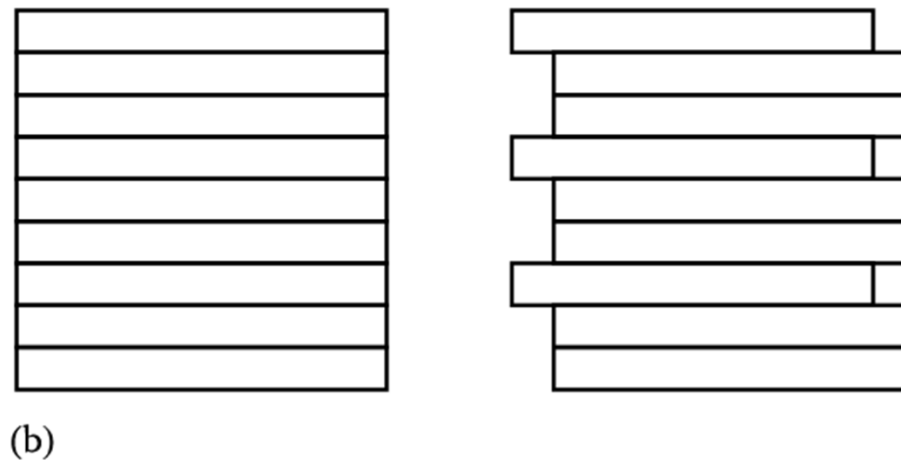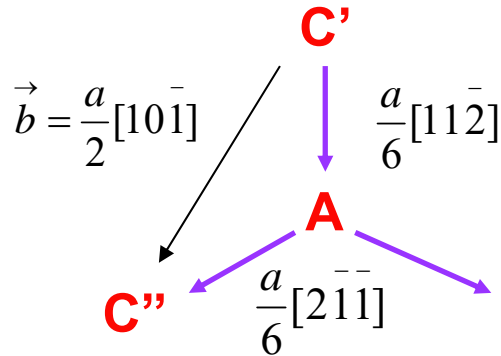
→ **No overall shape change**

Fig. 3. 62 Schematic representation of the different ways of shearing cubic close-packed planes into hexagonal close-packed (a) Using only one Shockley partial, (b) using equal numbers of all three Shockley partials.

* Formation of martensite in steel and other alloys: Motion of Glissile-dislocation interface
  : macroscopic shape change & no change in composition
  → **more complex interface but same principles (chapter 6)**

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Q: What is the role of interface migration on phase transformation ?

Interface controlled growth ⟺ **Diffusion controlled growth**

3.5. Interface Migration

Phase transformation = Interface creation & Migration

Heterogeneous Transformation (general): parent and product phases during trans.

Nucleation (interface creation) + **Growth** (interface migration)

Nucleation barrier   Ex. Precipitation

- at certain sites within metastable alpha phase → new beta phase = Nucleation
- <u>most of transformation product</u> is formed during the growth stage
  by the transfer of atoms across the moving parent/product interface.

Homogeneous Transformation: PT occurs homogeneously throughout the parent phase.

Growth-interface control

No Nucleation barrier   Ex. Spinodal decomposition (Chapter 5)

Order-disorder transformation

* **Types of Interface** ⟶ **Types of transformation**

- **Glissile Interface: Athermal, Shape change** ⟶ **Military transformation**
  Dislocation gliding

- **Non-Glissile Interface: Thermal,** ⟶ **Civilian transformation**
  Random jump of individual atoms: extremely sensitive to temp.
  ~ **similar way to the migration of a random high angle GB**

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Classification of Nucleation and Growth Transformation

Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent. Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different compositions		
Nature of diffusion process	No diffusion	Short-range diffusion (across interface)	Long-range diffusion (through lattice)		
Interface, diffusion or mixed control?	Interface control	Interface control	Mainly interface control	Mainly diffusion control	Mixed control
Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Soldification and melting	Precipitation dissolution Eutectoid Cellular precipitation

Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface

(need to additional research)

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3.5. Interface Migration

* Civilian Transformation

Composition (vertical axis)

Distance (horizontal axis)
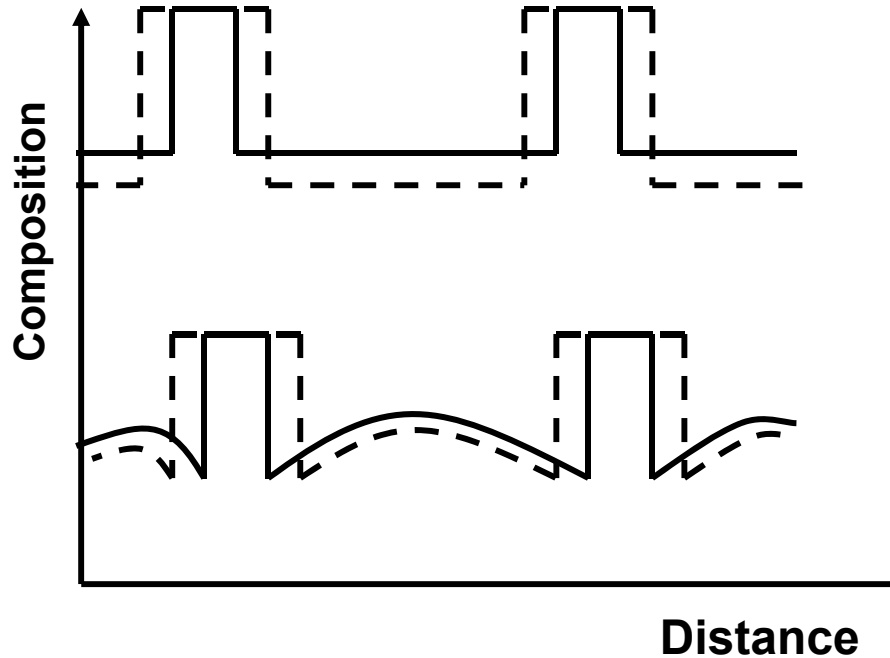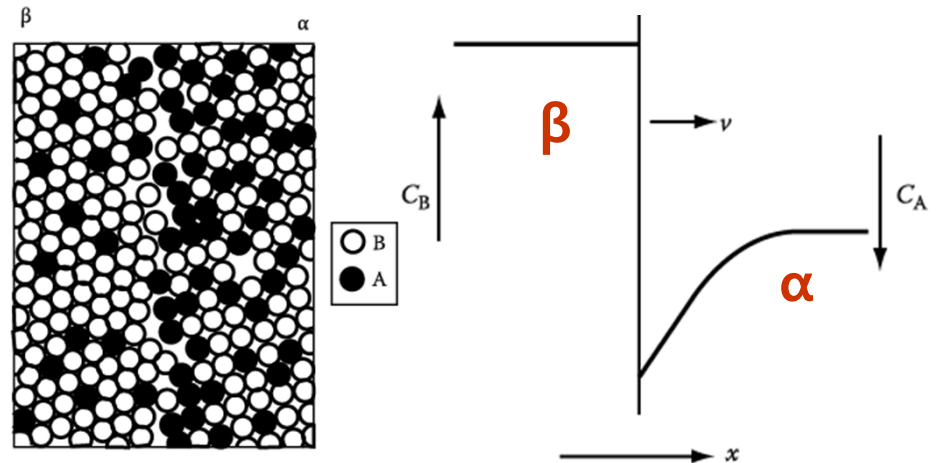
1) Interface control

Same composition between parent and product
(Ex. $\alpha \rightarrow \gamma$ transformation in pure iron)

The new phase will be able to grow as fast as the atoms can cross the interface. : <u>interfacial reaction velocity dominant</u>

2) Diffusion control

Different composition between parent and product
(Ex. The growth of the B-rich phase into the A-rich α-phase)

Growth of the new phase will require long-range diffusion
Growth rate: governed by the rate at which lattice diffusion can remove the excess atoms from ahead of the interface.
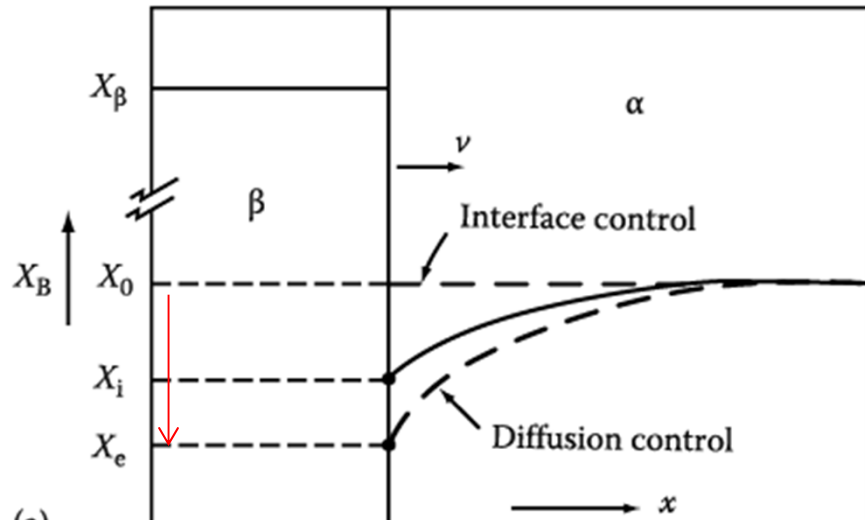

β

α

C_B

○ B
● A

C_A

ν

x

15

3) Mixed control: interface reaction = diffusion process

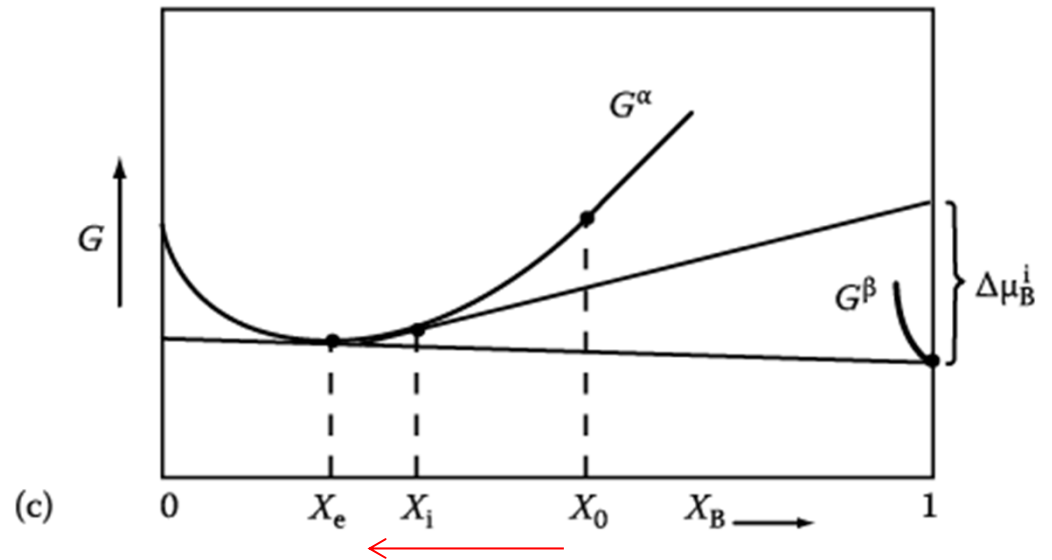# 3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion

; the migration of interface separating two phases of different composition

(a) Composition profile across the interface

(c) A schematic molar free energy diagram showing the relationship between $\Delta\mu_B^i$, X_i, X_0

(a)

(b)

(b) The origin of the driving force for boundary migration into the α-phase $\Delta\mu_B^i$

(c)

1) Initial composition of A-rich α phase X_0

2) Concentration B in the α phase adjacent to the inteface X_i
   → B concentration in α : $X_0 \rightarrow X_i$

3) For growth to occur the interface, composition must be greater than the equilibrium concentration X_e.

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Total Free Energy Decrease per Mole of Nuclei ΔG_0

: Driving force for phase transformation of system

$\Updownarrow$

Driving Force for Precipitate Nucleation $\boxed{\alpha \rightarrow \alpha + \beta}$ ΔG_V
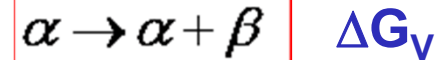
$$\Delta G_1 = \mu_A^\alpha X_A^\beta + \mu_B^\alpha X_B^\beta$$

: **Decrease of total free E of system**
  by removing a small amount of material
  with the nucleus composition (X_B^β) (P point)

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

: **Increase of total free E of system**
  by forming β phase with composition X_B^β
  (Q point)

$$\boxed{\Delta G_n = \Delta G_2 - \Delta G_1}\text{ (length PQ)}$$

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

: **driving force for β precipitation**

For dilute solutions,

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

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

∝**undercooling below T_e**

(a)

(b)

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3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion

; the migration of interface separating two phases of different composition

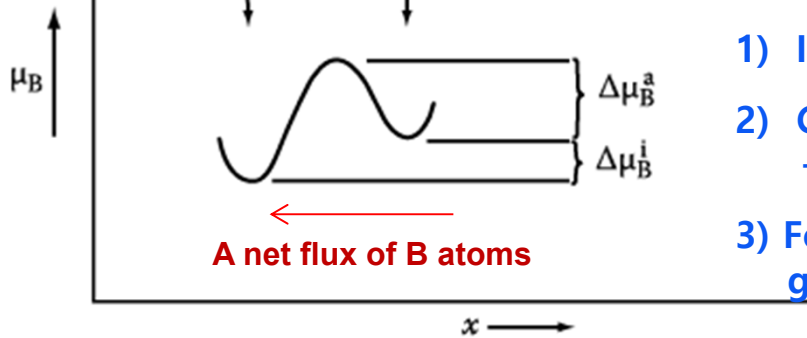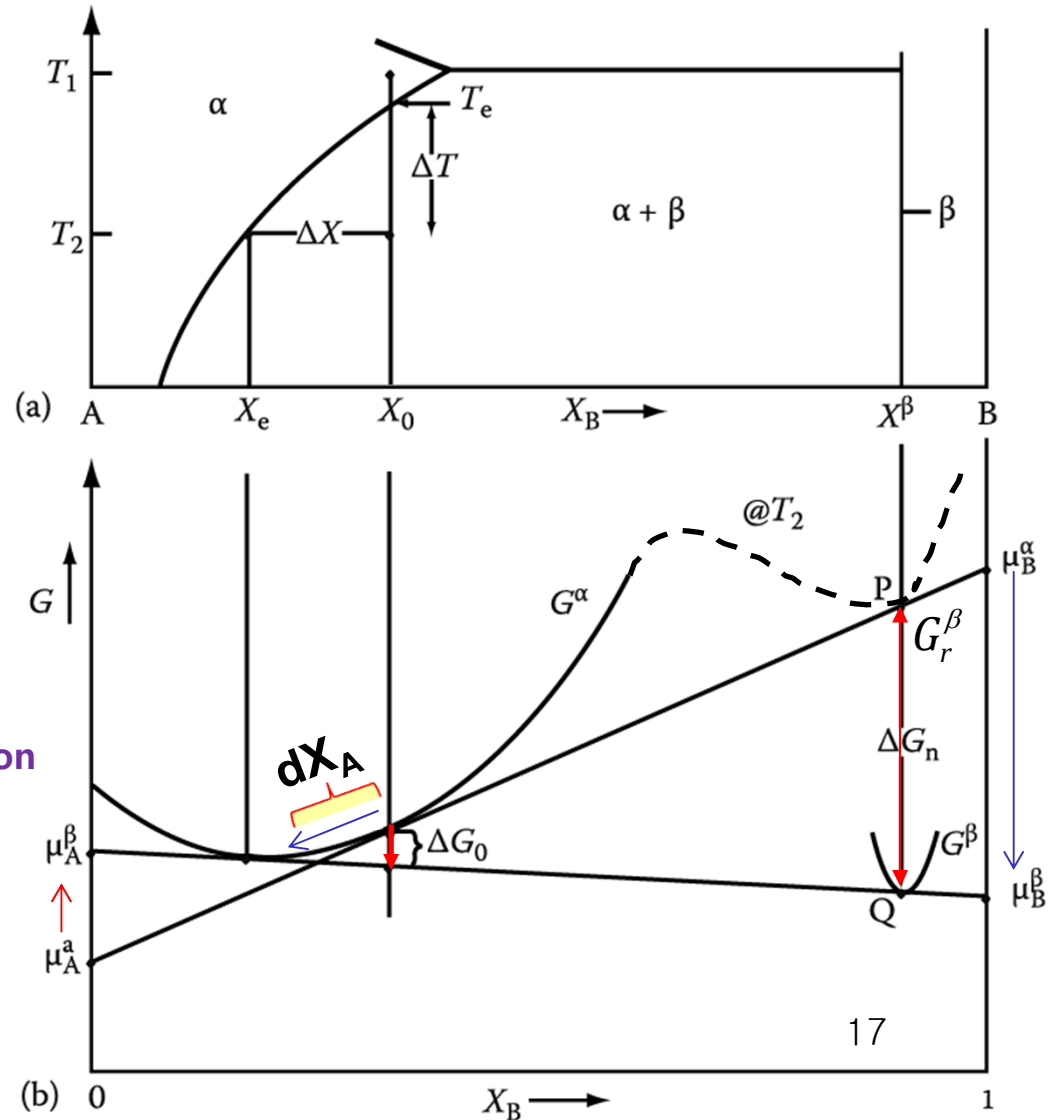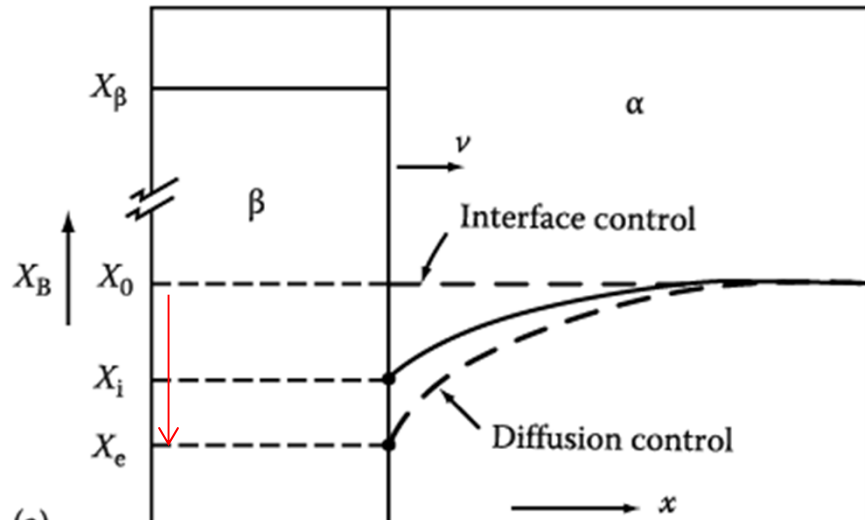(a) Composition profile across the interface

(c) A schematic molar free energy diagram showing the relationship between $\Delta\mu_B^i$, X_i, X_0

(a)

(b)

(b) The origin of the driving force for boundary migration into the α-phase $\Delta\mu_B^i$

A net flux of B atoms

(c)

1) Initial composition of A-rich α phase X_0

2) Concentration B in the α phase adjacent to the inteface X_i
   → B concentration in α : $X_0 \rightarrow X_i$

3) For growth to occur the interface, composition must be greater than the equilibrium concentration X_e.

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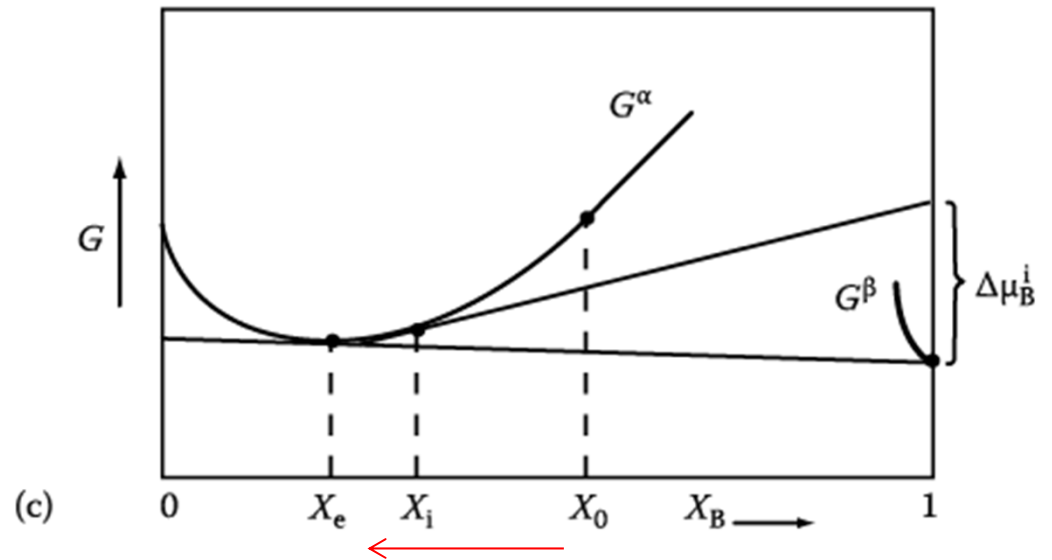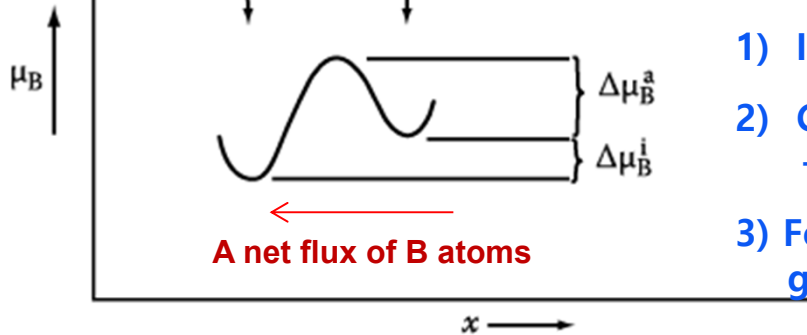
By analogy with the migration of a high-angle GB (section 3.3.4), **the net flux B across the interface will produce an interface velocity** *v* **given by**

- **(section 3.3.4) 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

$\to F = \Delta G/V_m$

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

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

- Interface velocity of precipitate
$$v = M\Delta\mu_B^i / V_m$$

M = interface mobility,
V_m = molar volume of the β phase

- **Corresponding flux across the interface (negative sign_negative direction of flux along the x-axis)**

β ⟵ α

$$J_B^i = -C_B^i v_B$$

$$= -\frac{1}{V_m}\left(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}\right)$$

$$= J_B^\alpha = -D\left(\frac{\partial C_B}{\partial X}\right)_{interface}$$

$$\Delta\mu_B^i \frac{1}{V_m} = \frac{Jmol^{-1}}{m^3 mol^{-1}}$$

Steady state at interface,

$$J_B^i = J_B^\alpha$$

A flux of B atoms toward the interface by the concentration gradient in the α phase

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Corresponding flux across the interface (negative sign_negative direction of flux along the x-axis)

$$J_B^i = -C_B^i v_B$$

$$= -\frac{1}{V_m}(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m})$$

$$= J_B^\alpha = -D(\frac{\partial C_B}{\partial X})_{\text{interface}}$$

$$\Delta\mu_B^i \frac{1}{V_m} = \frac{Jmol^{-1}}{m^3 mol^{-1}}$$

Steady state at interface,

$$J_B^i = J_B^\alpha$$

A flux of B atoms toward the interface by the concentration gradient in the α phase

1) If the interface mobility is very high, e.g. an incoherent interface,

High Mobility: $\Delta\mu_B^i$ small, $X_i \approx X_e$, Diffusion-Control
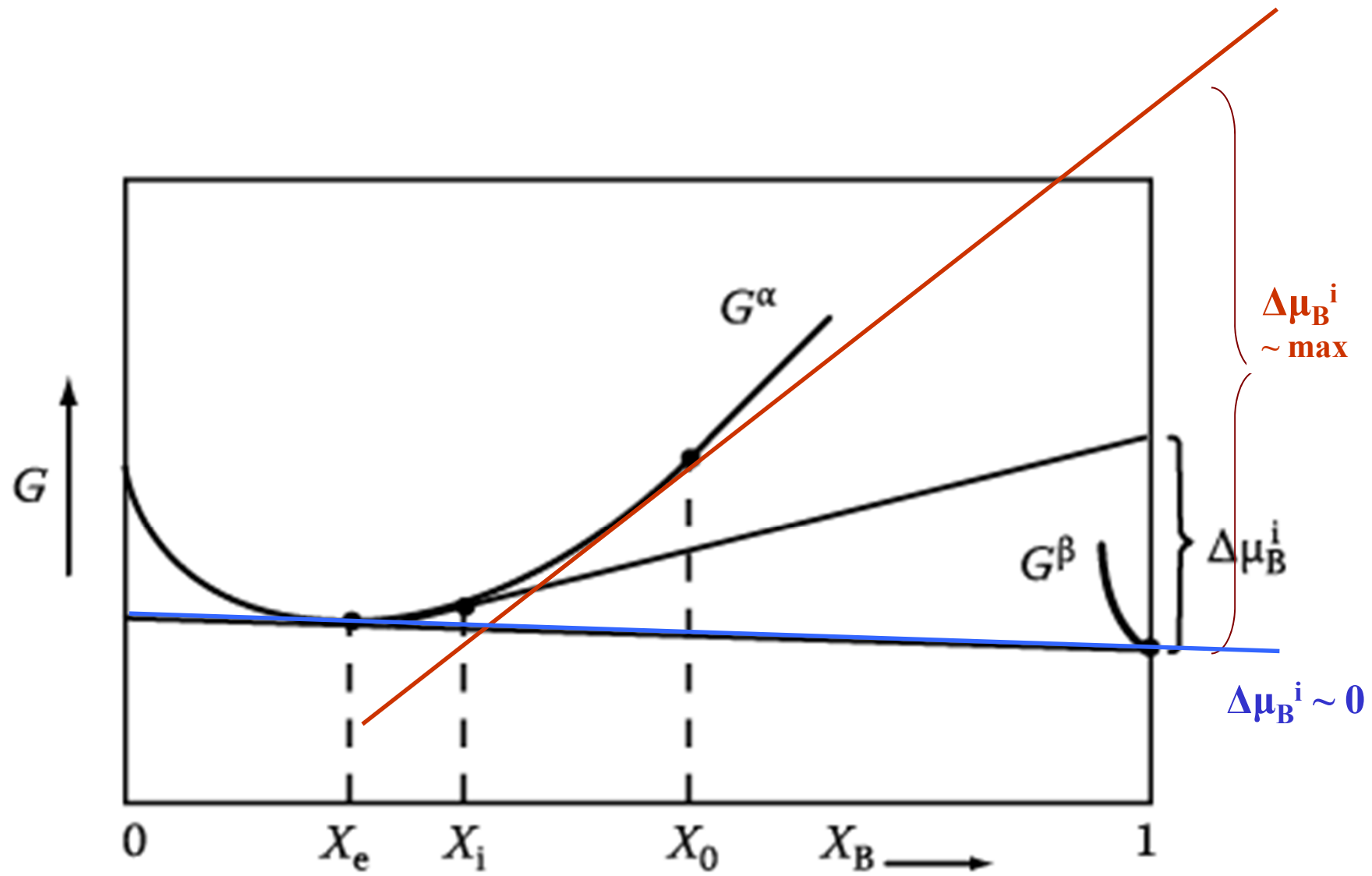
2) When the interface has a low mobility,

Low Mobility: $\Delta\mu_B^i$ must be large, Mixed-Control

3) In the limit of a very low mobility,

Very low Mobility: $Xi \approx X_o$, $\left(\dfrac{\partial C}{\partial X}\right)_{\text{intrface}} \approx 0$, Interface-Control

$\Delta\mu_B^i$ 는 최대

When two phases have a different composition,

In general,

the necessary long-range diffusion involves a great many atom jumps

while interface reaction essentially involves only one jump.

All interface reactions should be very rapid in comparison to lattice diffusion, i.e.,

all growth should be diffusion controlled. (next page)

Ex) Diffusion control

Al-Cu ppt structures

If two phases with different compositions, but the same crystal structure are separated by a coherent interface

Interface can advance by normal lattice diffusion involving vacancies.

No need for a separated interface reaction

Ex) GP zones/ semicoherent interface with misfit dislocation (vacancy creation and annihilation)

○ Al   ● Cu

(a) Bright-field TEM image showing G.P. zones, and (b) HRTEM image of a G.P. zone formed on a single $(0\ 0\ 0\ 1)_\alpha$ plane. Electron beam is parallel to in both (a) and (b).

When two phases have a different composition,

In general,

the necessary long-range diffusion involves a great many atom jumps

while interface reaction essentially involves only one jump.

All interface reactions should be very rapid in comparison to lattice diffusion, i.e.,

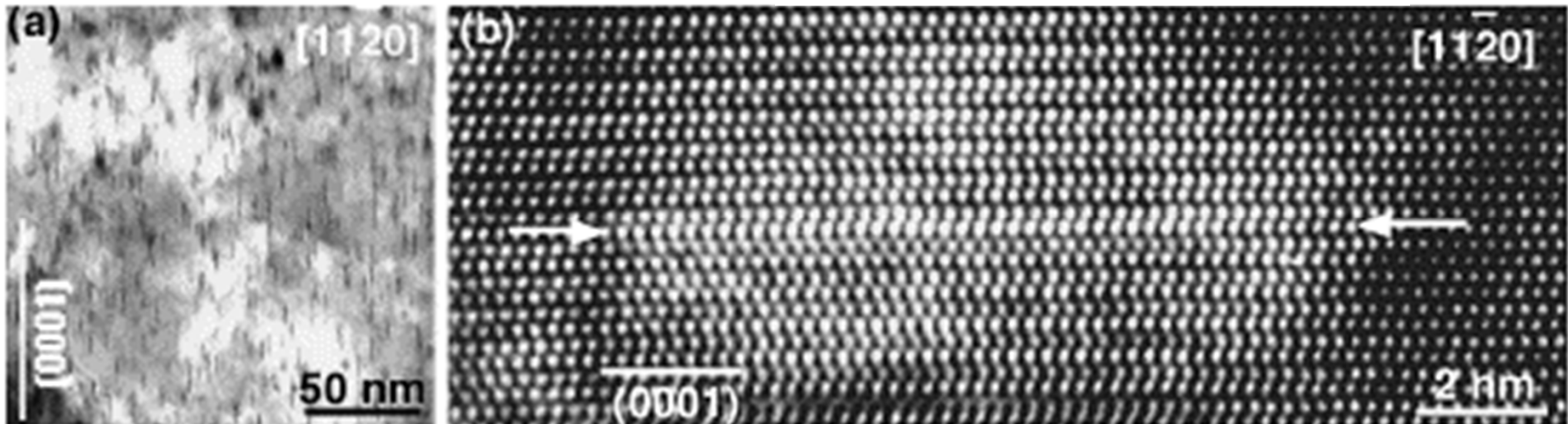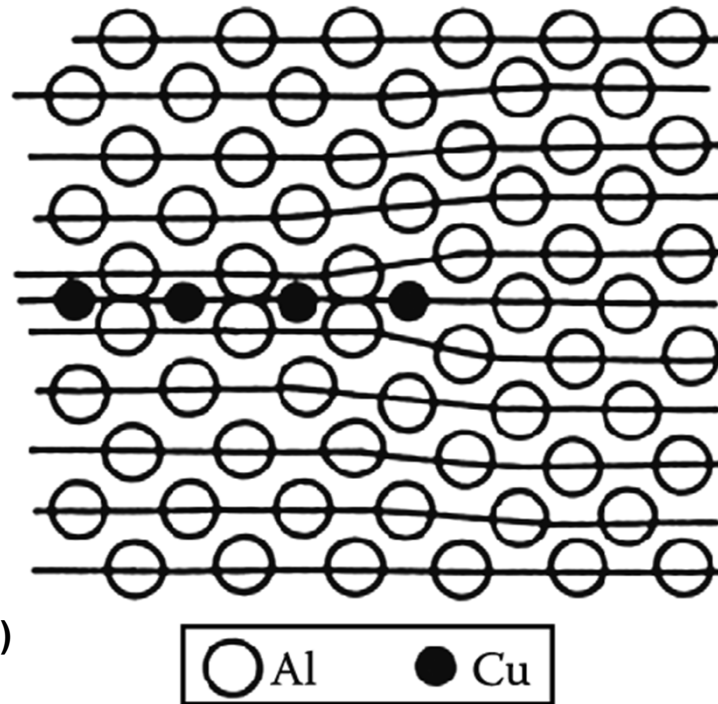**all growth should be diffusion controlled.** (next page)

➡ **In many cases ~ valid, but under certain conditions ~ insufficient**

Accommodation factor (A_수용인자)
Probability that an atom crossing the boundary will accommodated on arrival at the new phase

**Incoherent interfaces and diffuse interface solid/liquid interfaces,
as high-angle grain boundaries = value of A close to unity ➡ "diffusion control"**

**Coherent or semicoherent interfaces as well as
smooth solid/liquid interfaces = low values of A ➡ "Some degree of interface control"**

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Ex) Interface control

1) When two phases forming a coherent or semicoherent interface have different crystal structures.

$$A \quad A \quad A \quad A \quad A \quad A$$

fcc   B   B   B   B   B   B

Coherent close-packed interface between fcc and hcp crystals

C   C   C   C   B   C   **A loop of Shorkley partial disl.**

A   A   A   A   A   A   **~ high E/ unstable configuration → force back to its original position**

hcp   B   B   B   B   B   B

A   A   A   A   A   A
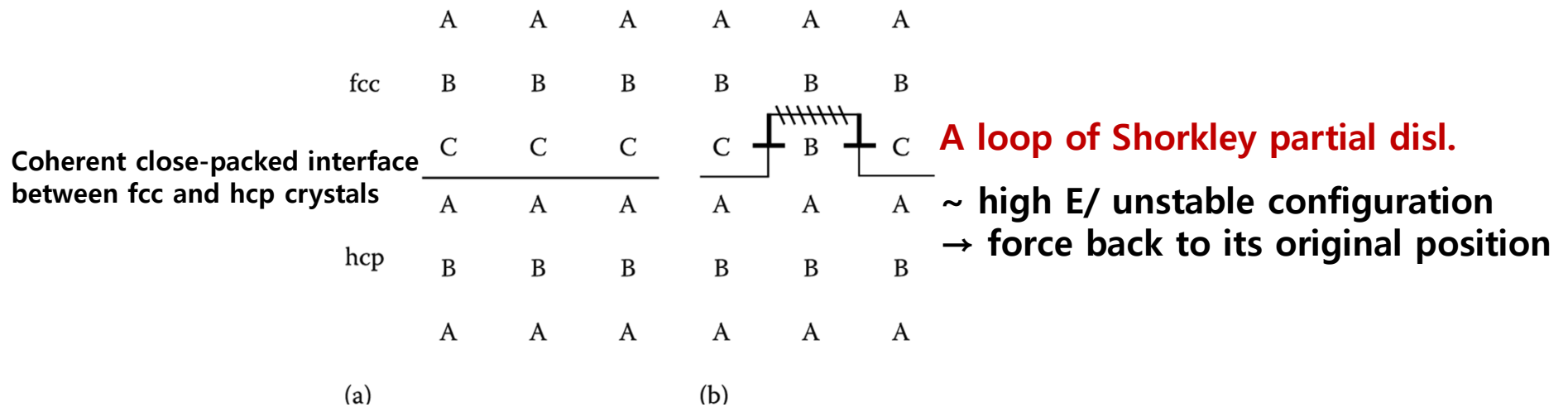
(a)   (b)

Fig. 3. 68 Problems associated with the continuous growth of coherent interfaces between phases with different crystal structures.

hcp phase growth by individual atomic jumps (i.e., so-called continuous growth) ~ very difficult (very low accommodation factors and low mobility)

2) Solid/vapor as well as smooth solid/liquid interfaces ~ similar manner

* A way of avoiding the difficulties of continuous growth

"Growth by ledge mechanism"

Facets: AB, CD, EF
Ledge: BC, DE

Nucleating new ledges: Interface control - heterogeneous nucleation

A ——————— B

Growth direction: diffusion control
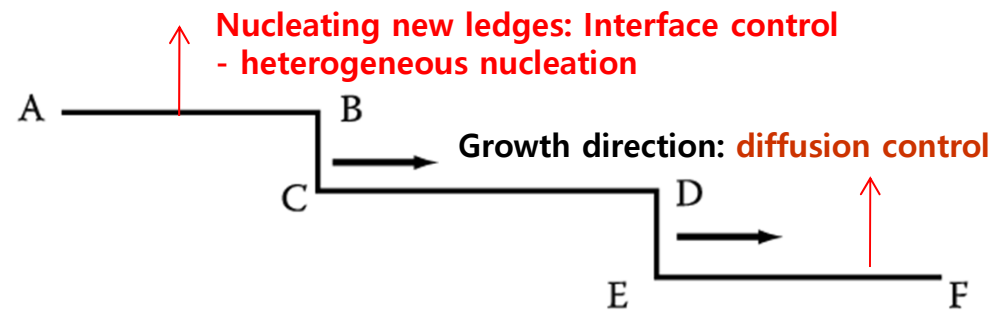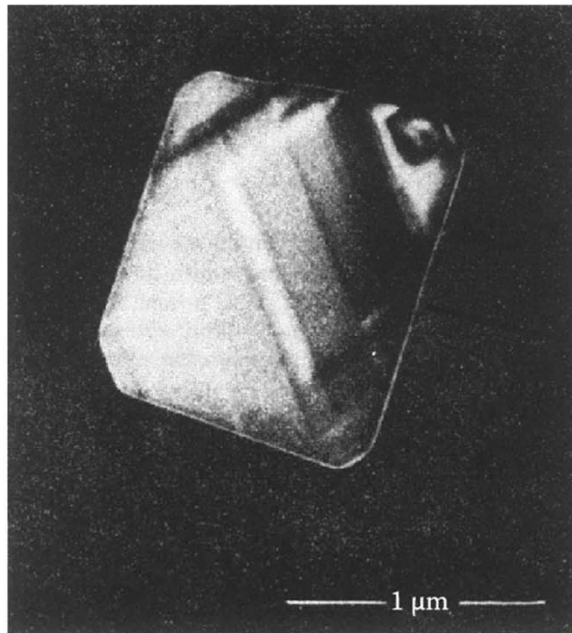
C ———————————— D

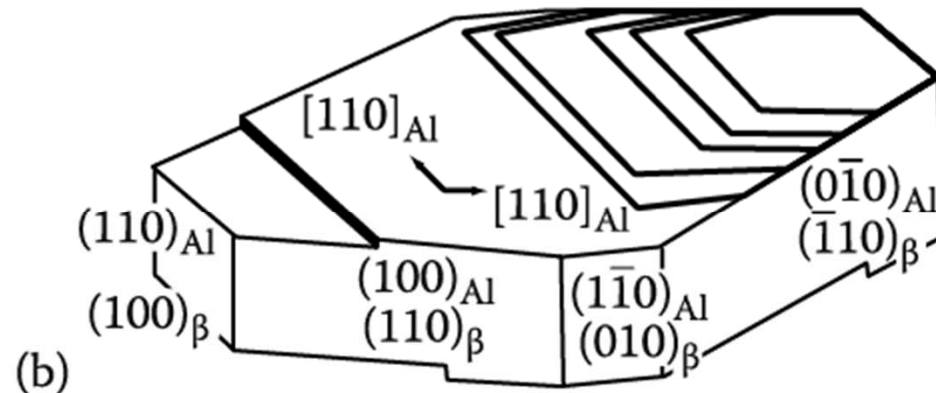E ———————————— F

Fig. 3. 69 The ledge mechanism.   25

→ **Problem of nucleation new ledges may often lead to a degree of interface control on the overall rate.**

Fig. 3. 70 (a) Growth ledges at an Mg$_2$Si plate in Al-1.5 wt% Mg$_2$Si, solution treated
             and aged 2h at 350 ℃. Dark field micrograph.

     (b) Schematic diagram of (a) showing ledges on Mg$_2$Si plate.

(a)

Note that growth ledges are usually hundreds of atoms layers high.
성장 돌출맥의 층 두께는 보통 수백 원자층 두께

**The mechanism of interface migration can have important effects on
the shape of second-phase inclusions. (section 3.4.2)**

- **if absence of strain E effect, equilibrium shape of a precipitate should be determined by**
  a) **the relative energies of the bounding interfaces (dominant)** γ-plot 계면 E의 상대적 비
     ex) a partially coherent precipitate~disk or plate shape with an aspect ratio of γi / γc
  b) **(in practice) "relative rates" at which the coherent and incoherent interface can migrate**
       정합/ 부정합 계면의 상대적인 이동속도 차에 의해 형상 변화

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Classification of Heterogeneous (Nucleation and Growth) Transformation

Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent. Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different compositions		
Nature of diffusion process	No diffusion	Short-range diffusion (across interface)	Long-range diffusion (through lattice)		
Interface, diffusion or mixed control?	Interface control	Interface control	Mainly interface control	Mainly diffusion control	Mixed control
Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Soldification and melting	Precipitation dissolution Eutectoid Cellular precipitation

Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface

(need to additional research)

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* Homework 3 : Exercises 3 (pages 186-188)

until 4th November (before midterm)

Good Luck!!

MIDTERM (4th November, 1 PM-4 PM)

Scopes: Text ~ end of Chapter 3/

Teaching notes: 1~15/

and Homework

Places: 33-225

Good Luck!!