2009 fall

Advanced Physical Metallurgy

“Phase Equilibria in Materials”

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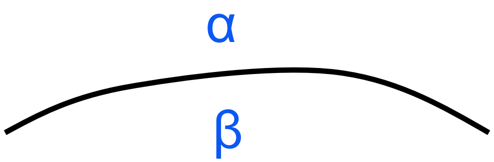
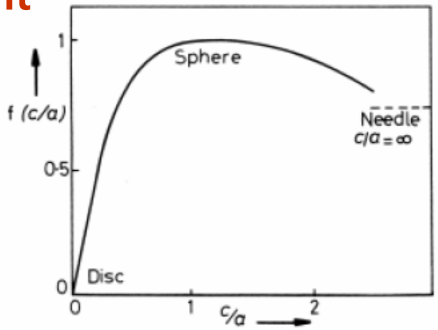
Contents for previous class

3.4 Interphase Interfaces in Solids (α/β)

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

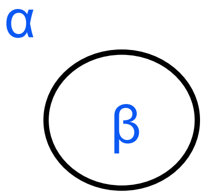


Coherent/ Semicoherent/ Incoherent
Complex Semicoherent



2) Second-Phase Shape

$$\boxed{\sum A_i \gamma_i + \Delta G_S = minimum}$$



Interface energy + Misfit strain energy

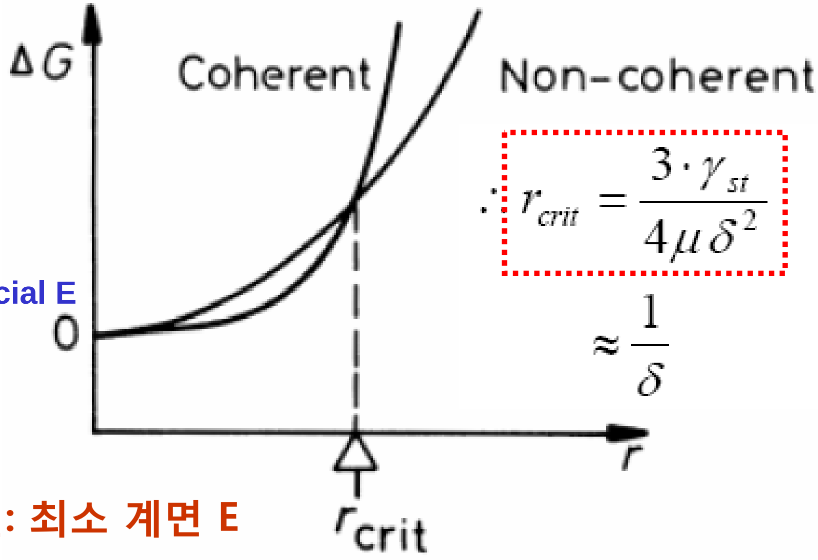
$$\Delta G_S = 4\mu\delta^2 \cdot V$$ **(If ν=1/3)** ⬄ $$\Delta G_S = \frac{2}{3}\mu\Delta^2 \cdot V \cdot f(c/a)$$

Fully coherent precipitates Incoherent inclusions

3) Coherency Loss

$$\Delta G(coherent) = \underbrace{4\mu\delta^2 \cdot \frac{4}{3}\pi r^3}_{\text{Coherency strain energy}} + \underbrace{4\pi r^2 \cdot \gamma_{ch}}_{\text{Chemical interfacial E}}$$

⬄ $$\Delta G(non-coherent) = \underbrace{4\pi r^2 \cdot (\gamma_{ch} + \gamma_{st})}_{\text{Chemical and structural interfacial E}}$$



$$\boxed{\therefore r_{crit} = \frac{3 \cdot \gamma_{st}}{4\mu\delta^2}} \approx \frac{1}{\delta}$$

정합석출물 성장시 전위 루프 도입을 통해 정합성 상실: 최소 계면 E

Contents for today's class

- **Interphase Interfaces in Solid (α/β)**

  - Interphase boundary

  - Second-Phase Shape

    Interface Energy Effects/ Misfit Strain Effects

  - Coherency Loss

  - **Glissil Interfaces**

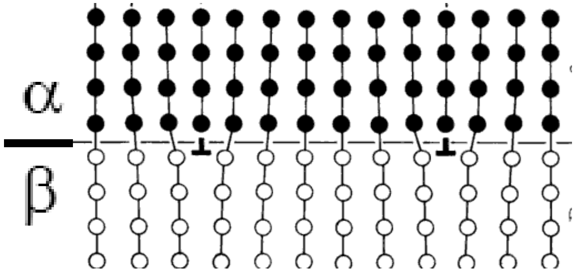
  - **Solid/Liquid Interfaces**

- **Interphase migration**

  - **Diffusion controlled and Interface controlled growth**

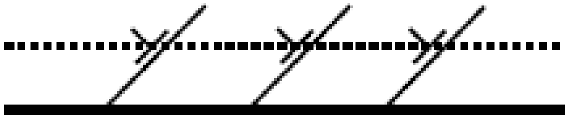
Interphase Interfaces in Solid (α/β)

1) Glissile Interfaces (평활 이동 계면)



: epitaxial; Can't move forward or backward

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



: Glissile; Boundary moves toward α or β

: 전위의 이동에 의해 전진할 수 있는 반정합계면

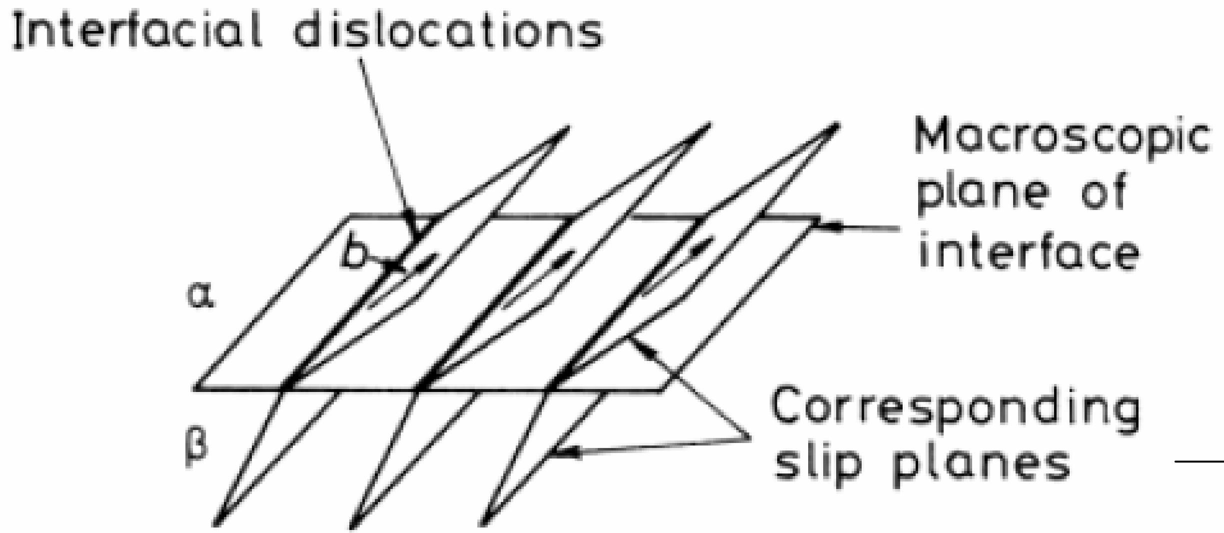


Fig. 3.55 The nature of a glissile interface.

전위의 버거스벡터 만큼

→ **Dislocations sliding**

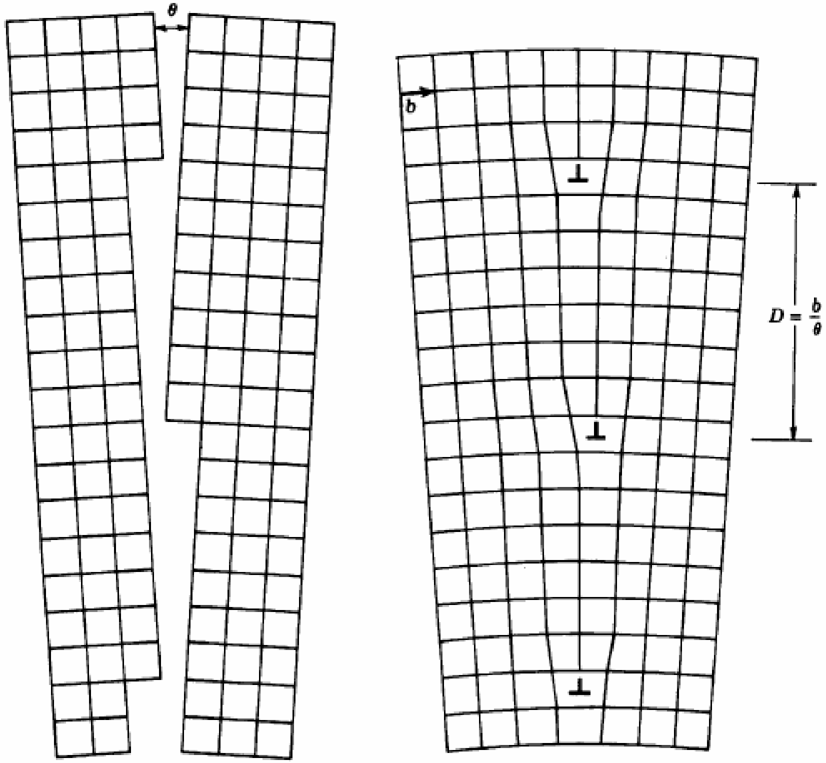
→ **Shear deformation**

Low-Angle tilt Boundaries

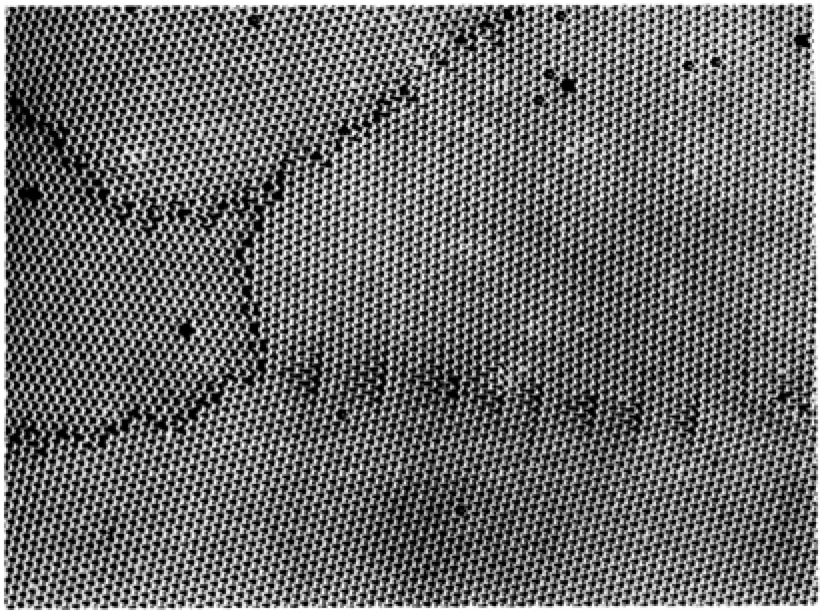
Bugers vector = edge dislocation

But, this is not interphase interface.

∵ crystal structure is same,
only lattice rotation



(a)



Glissile Interfaces between two lattices

Shockley partial dislocation

HCP: ABABABAB…

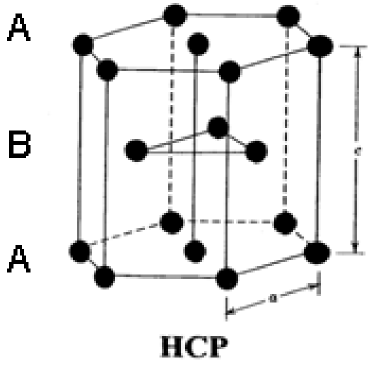
close packed plane: (0001)

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

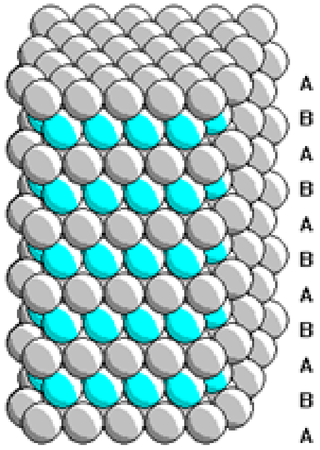
FCC: ABCABCAB…

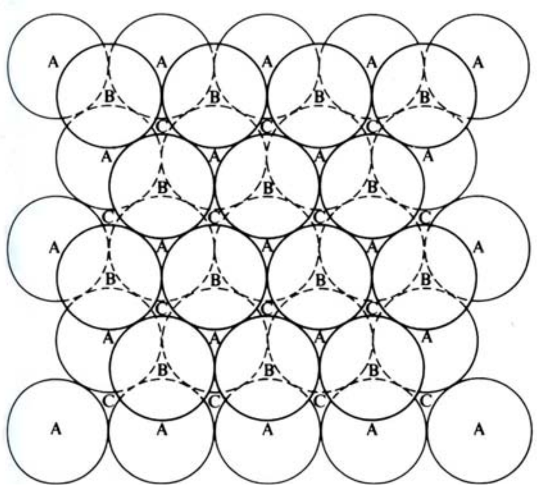
close packed planes: {111}

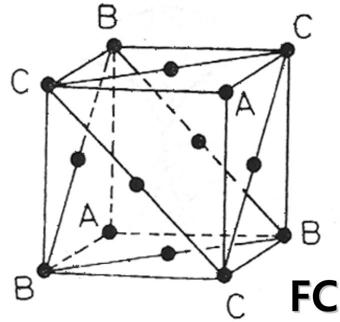
close packed directions: $<110>$



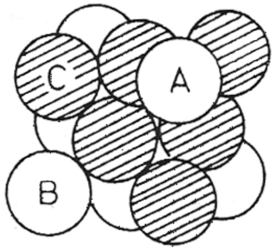
HCP







FCC



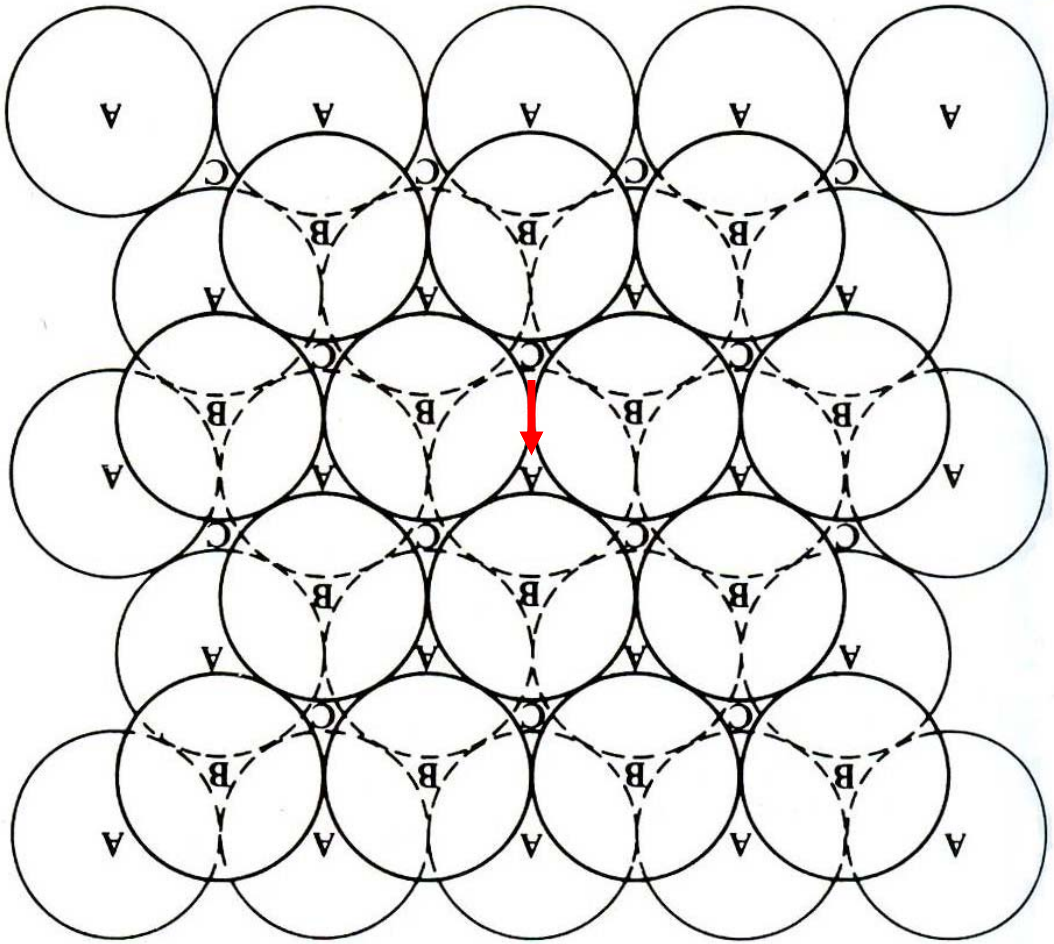
1) Perfect dislocation

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

C layer에서 보면

C’ → C”

: perfect crystal을 그대로 유지



2) Shockley partial dislocation

C’ → C”로 갈 때

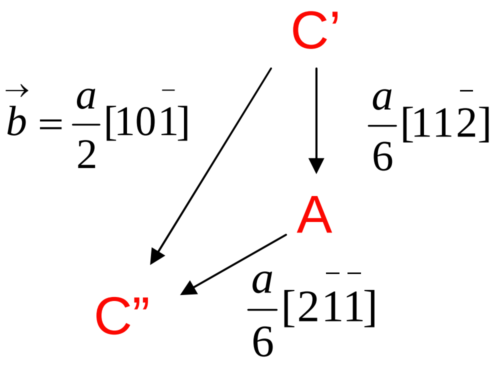
C’ → A → C” 일수 있음

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

이 burgers vector는

lattice point에 있지 않다.

(격자점과 격자점을 연결하지 못함)



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

$\frac{a}{6}[11\bar{2}]$

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

Shockley partial dislocation sliding → Stacking fault region

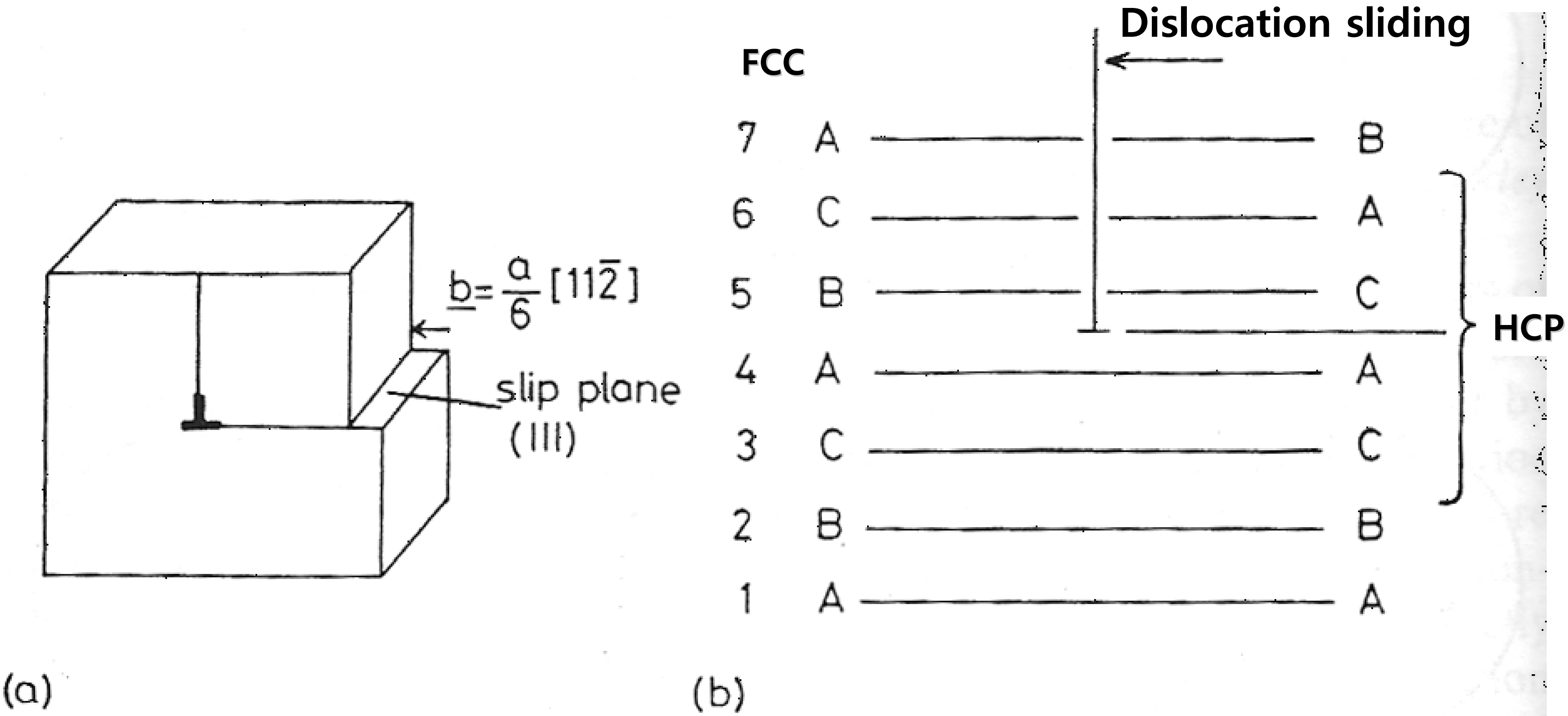


Fig. 3.59 (a) An edge dislocation with a Burgers vector b = $\frac{a}{6}[11\bar{2}]$ on (111). (Shockley partial dislocation.) (b) The same dislocation locally changes the stacking sequence from fcc to hcp.

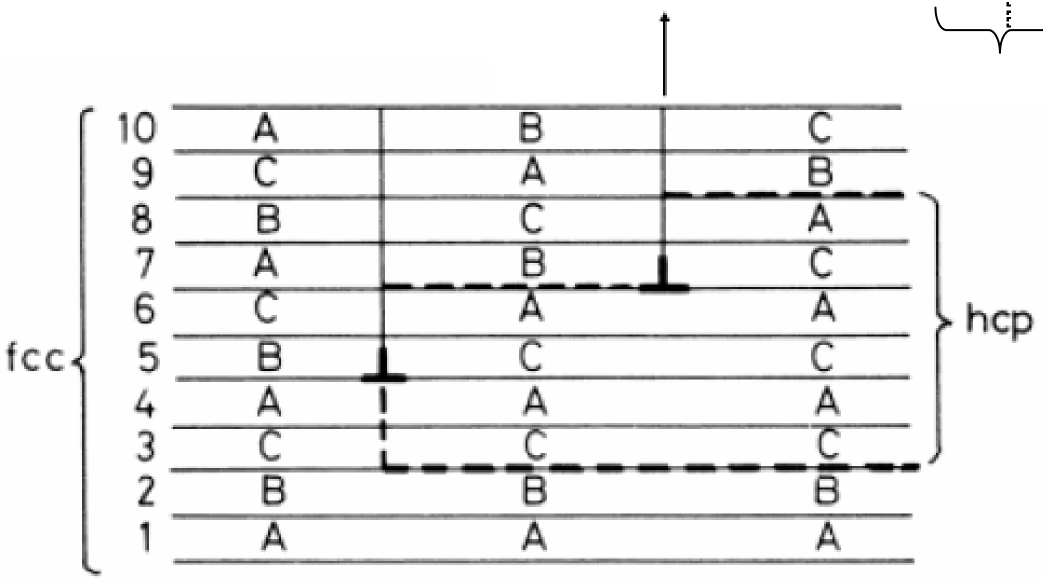
1) 안정한 FCC의 경우, Stacking fault 영역은 높은 자유에너지를 가짐-부분전위 이동 어려움

2) Fcc 격자가 HCP 구조에 대해 준안정상태라면 적층 결함에너지 (-)/ 부분전위 이동 용이

Glissile Interfaces between two lattices

Stacking Faults misfit → hcp

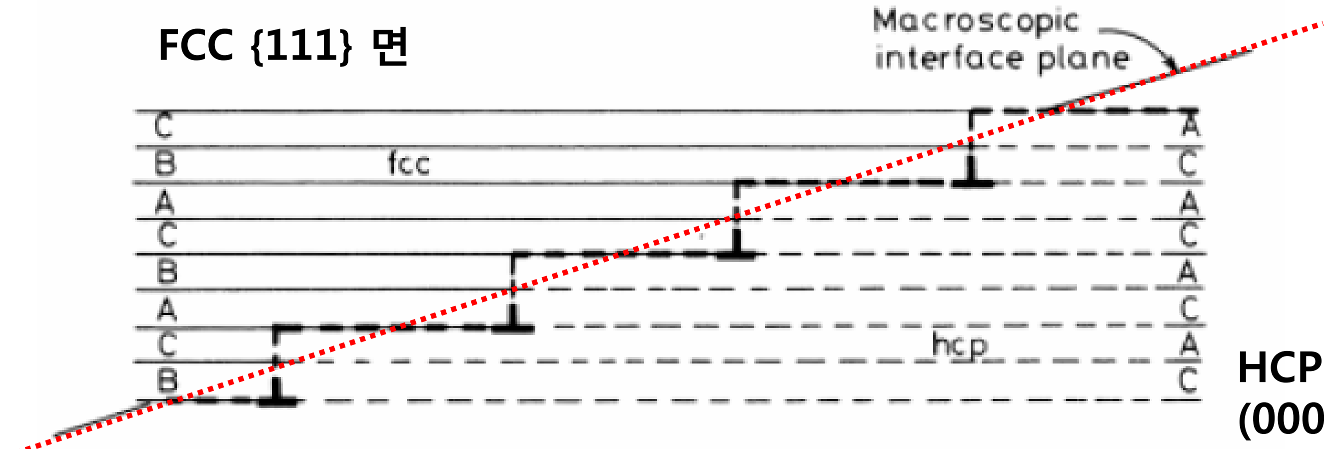
$$ABCABCABC \rightarrow AB\underbrace{CA\vdots CA}BC\ldots\ldots$$



두개의 (111) 면마다 하나씩 Shorkley partial dislocation 있음.

Fig. 3.60 Two Shockley partial dislocations on alternate (111) planes create six layers of hcp stacking.

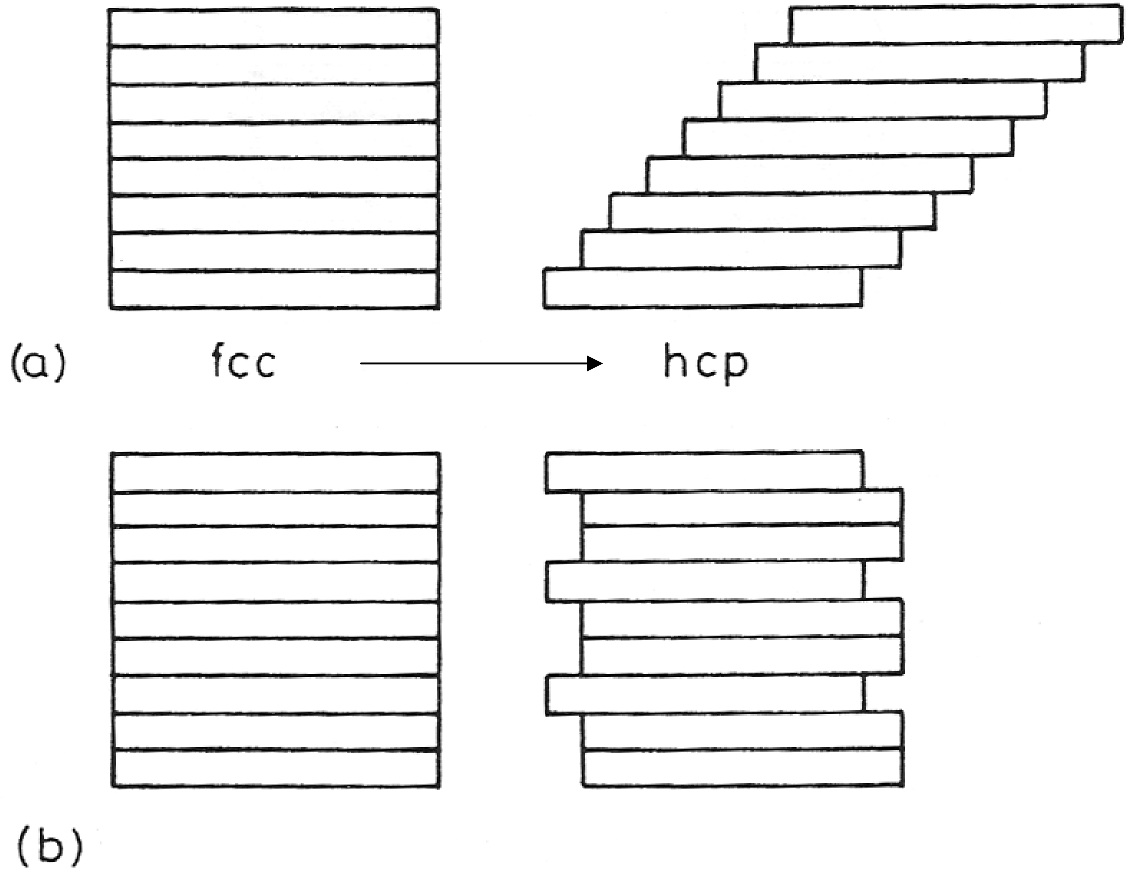
FCC {111} 면



HCP (0001) 면

Fig. 3.61 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

평활 이동 전위가 있는 계면의 중요한 특징: 그 면들이 결정의 모양을 변화시킬 수 있다는 것.



두 개의 (111) 면마다
동일한 Shorkley partial
dislocation 있음.

Pure shear deformation

같은 수를 갖는 3종류의
부분전위에 의한 변태

모양 변화 없음

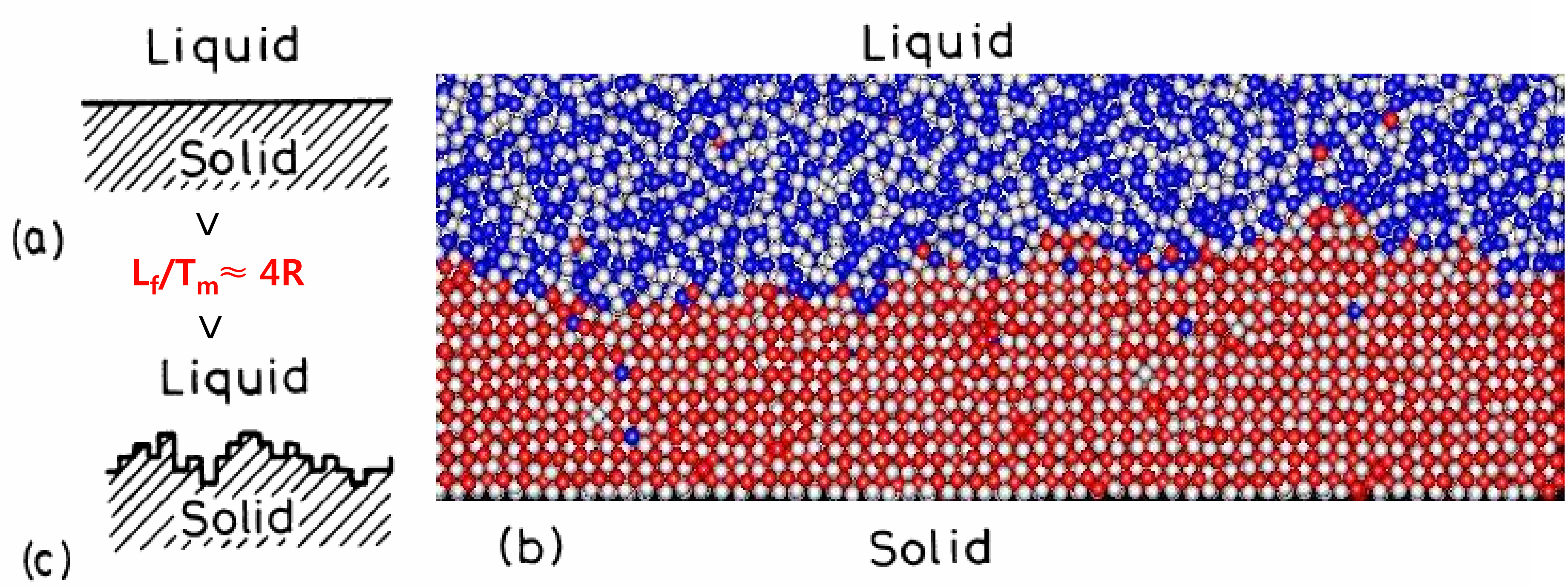
Fig. 3.62 Schematic representation of the different ways of shearing cubic close-packed planes into hexagonal close-packed (a) using only one Shockley partial, (b) using equal numbers of all three Shockley partials.

평활이동전위가 있는 계면의 이동 ⟶ Cu 나 다른 합금에서 마텐사이트 의 형성

2) Solid / Liquid Interfaces

Faceted interface 1 원자층 두께의 매우 좁은 천이대

: 일부 금속간 화합물, 대부분의 비금속의 고상/액상, Si, Ge, Sb 같은 원소



V

$L_f/T_m \approx 4R$

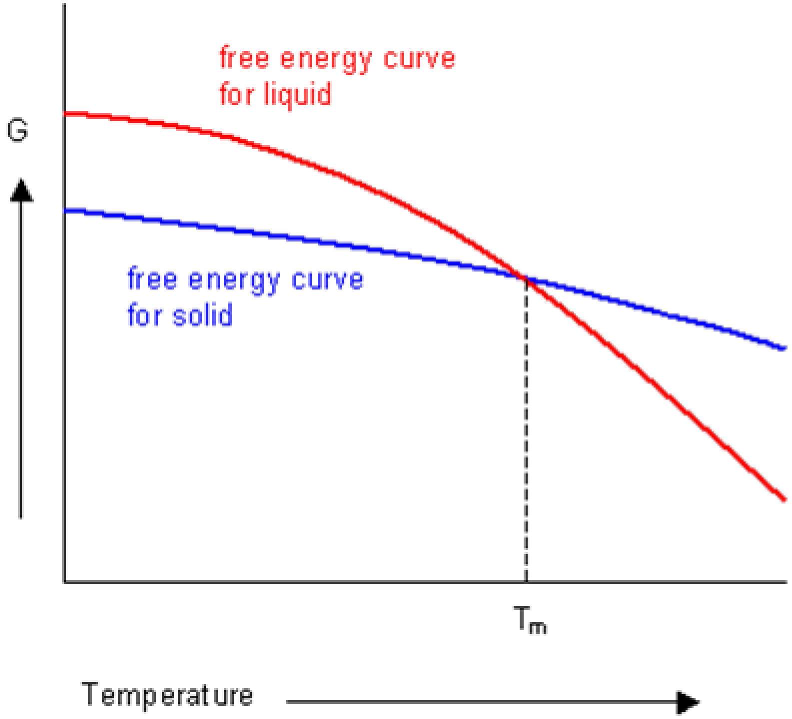
V

Fig. 3.63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces. (After M.C. Flemings, *Solidification Processing*, McGraw-Hill, New York, 1974.)

Diffusion interface 몇 개의 원자층에 걸쳐서 천이가 일어남

: 대부분의 금속 ~ R (기체상수)

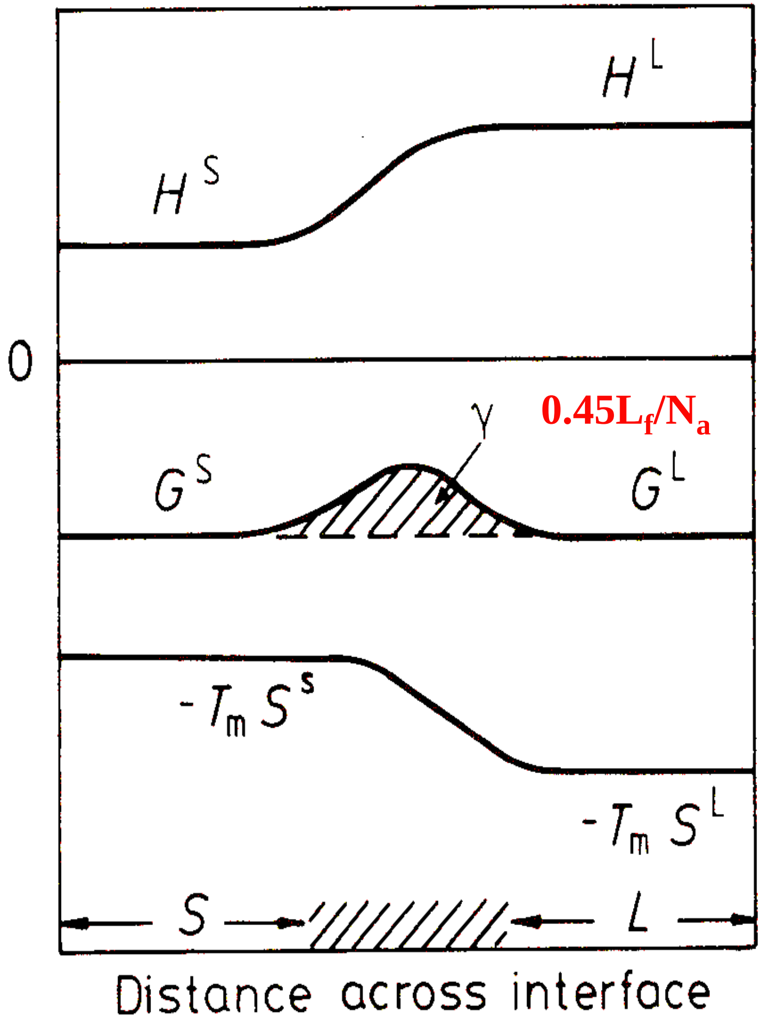
Solid / Liquid Interfaces



$$\boxed{\gamma_{SV} > \gamma_{SL} + \gamma_{LV}}$$

$\gamma_{SL} \approx 0.45\ \gamma_b$ (결정립계) ($\approx 0.15\gamma_{SV}$)

at melting point



$0.45L_f/N_a$

고상/액상 계면 양쪽에서 거리에 따른 H, $-T_m S$ 및 G의 변화로서 계면에너지의 생성

Interface Migration

Heterogeneous Transformation :

Nucleation (계면 형성) + Growth (계면 이동)

Nucleation barrier   Eg. Precipitation

Homogeneous Transformation :

Growth-Interface control

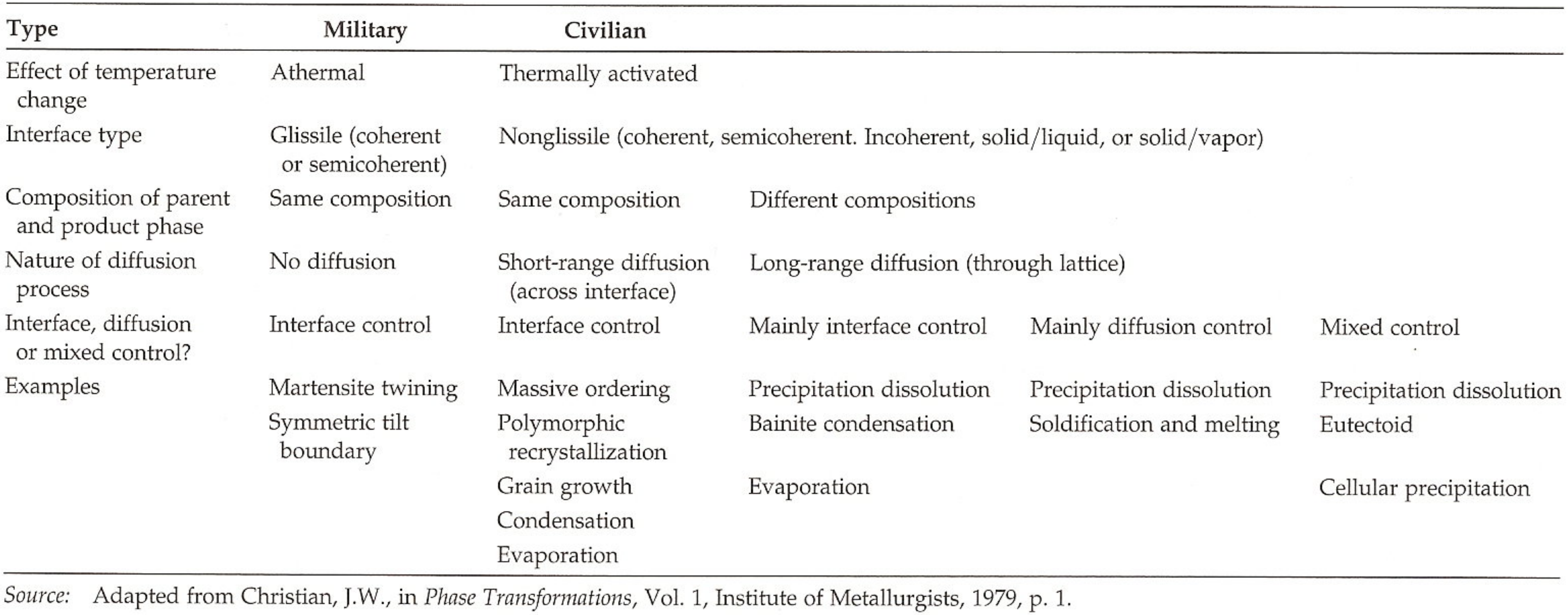
No Nucleation barrier   Eg. Spinodal decomposition (Chapter 5)

Types of Interface

- **Glissile Interface: Athermal, Shape change → Military transformation**
- **Non-Glissile Interface: Thermal, 원자들의 불규칙 도약 → Civilian transformation**

예외) bainite 변태: 열활성화에 의해 일어남/ 평활 이동 계면의 이동에 의한 것과 비슷한 모양 변화 등

Classification of Nucleation and Growth Transformation

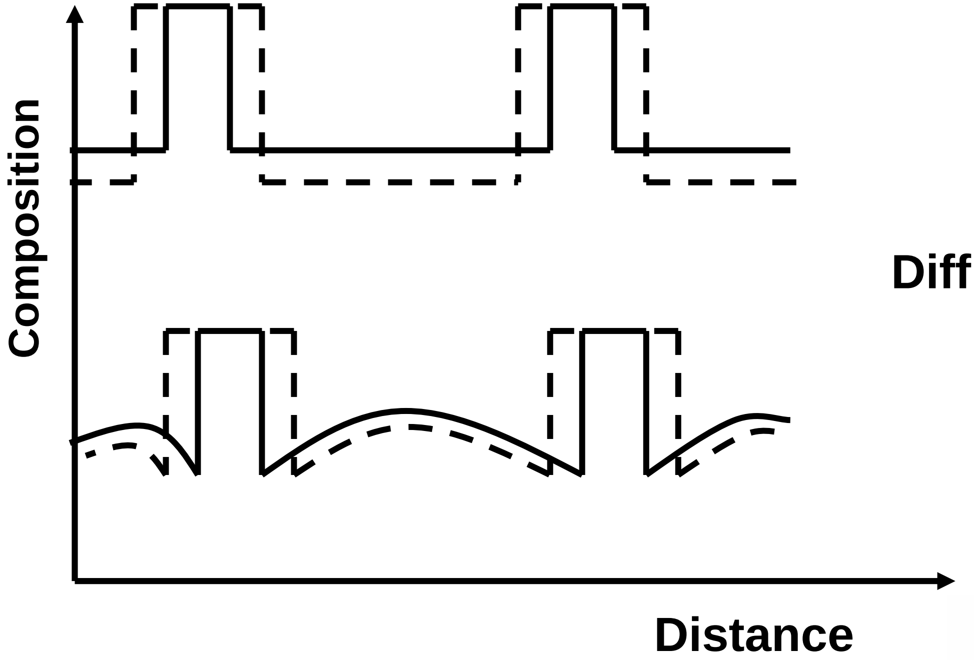


Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent. Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different 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	Massive ordering	Precipitation dissolution	Precipitation dissolution	Precipitation dissolution
	Symmetric tilt boundary	Polymorphic recrystallization	Bainite condensation	Soldification and melting	Eutectoid
		Grain growth	Evaporation		Cellular precipitation
		Condensation			
		Evaporation			

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

Interface Migration

Civilian Transformation



Interface control

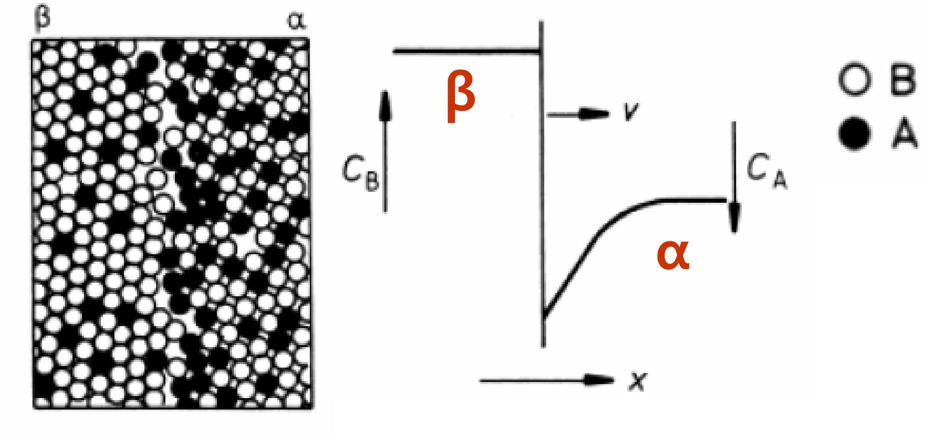
모상과 생성상이 조성변화 없는 경우
(Ex. 순철에서의 α→γ 변태)

계면은 원자가 계면을 가로질러 가는 속도로 성장함
계면의 반응이 느려서 계면 반응 속도가 dominant 함

Diffusion control

모상과 생성상이 다른 조성을 가지는 경우
(생성상의 성장을 위해 장범위 확산이 필요)

생성상의 성장속도는 격자내 확산에 의해 계면 전방의
과잉 원자들이 제거되는 속도에 의해 제어

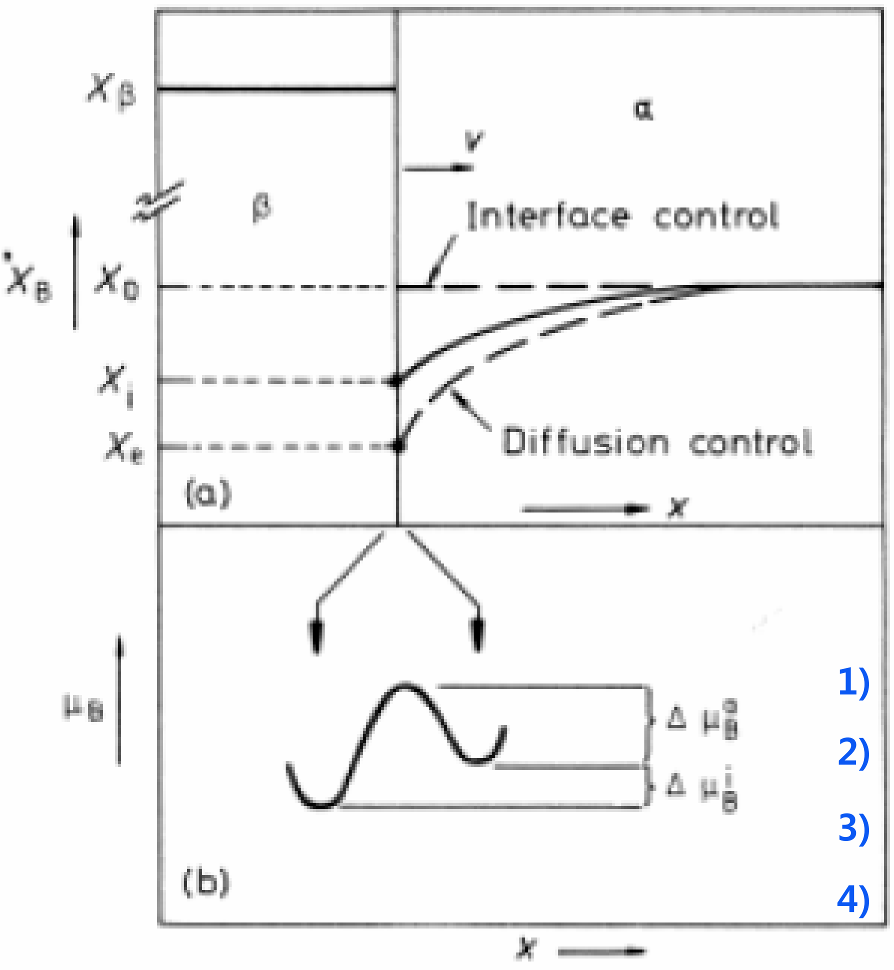


Mixed control

Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion

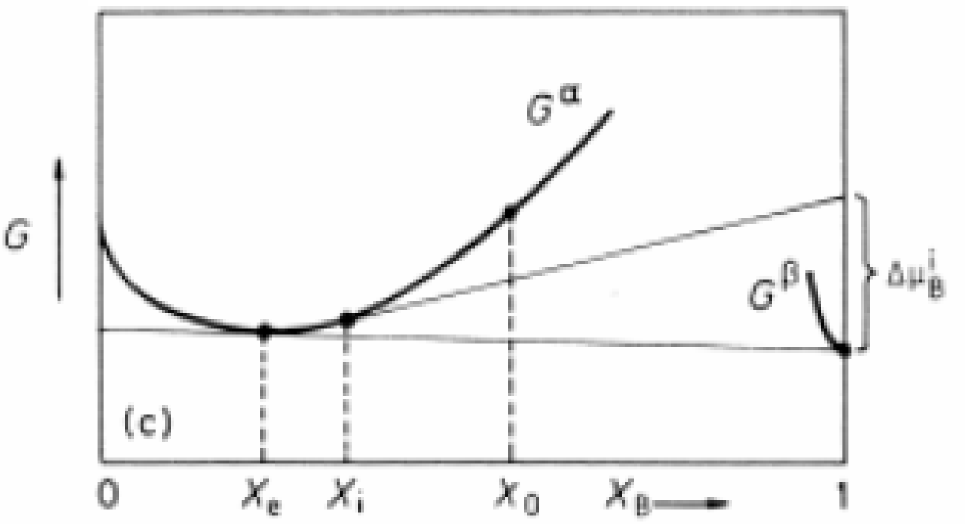
(a) 계면 양쪽의 농도 분포



(b) α 상으로 계면이 이동할 때의 구동력

(c) 각 상의 조성에 따른 자유에너지 변화

α/β 계면에 $\Delta\mu_B^i$ 가 생기는 원인



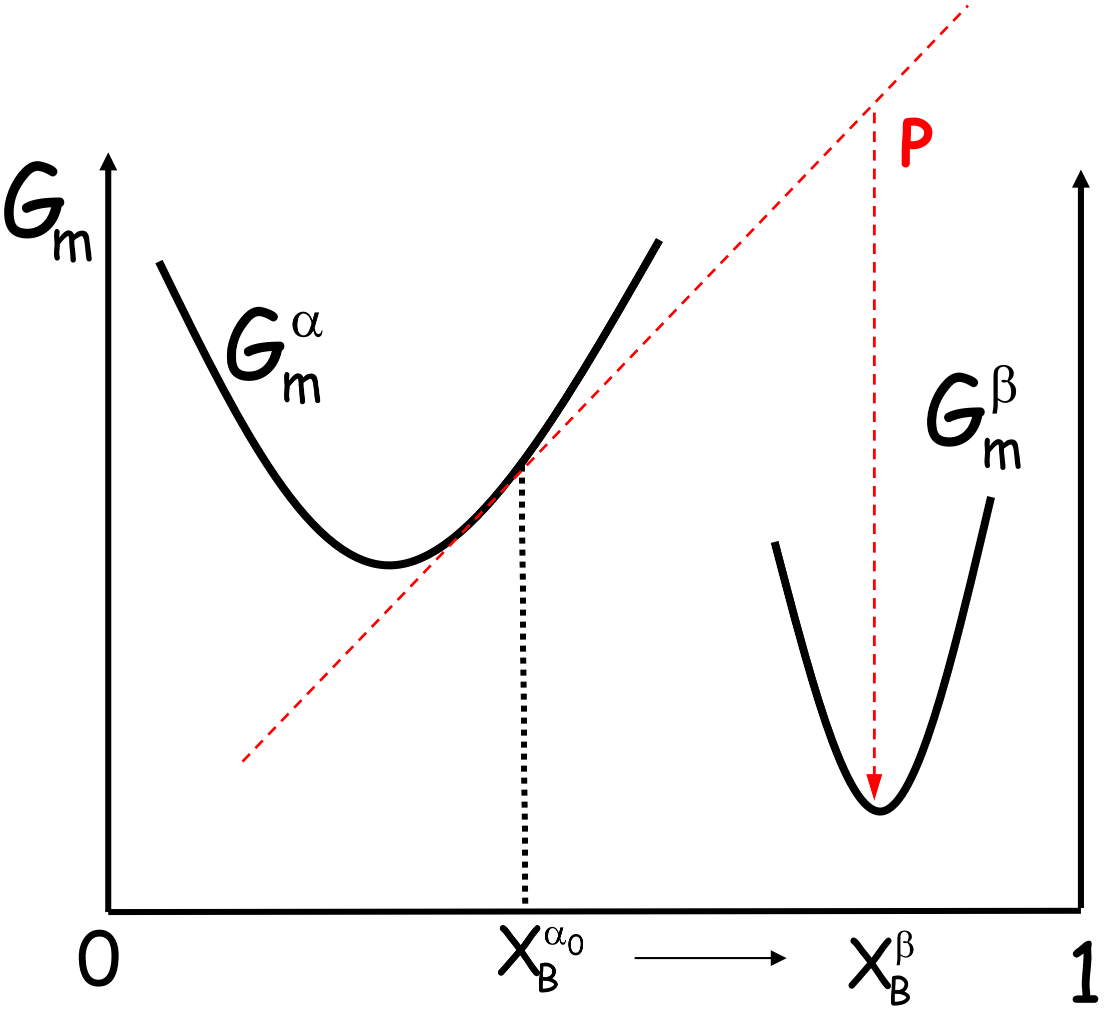
1) 초기 α상의 조성 X_0

2) α상 계면에 B 성분 고갈: B 농도 X_0 이하로 감소 X_i

3) 석출물 성장을 위해선 α상→β상으로 B 원자 이동 필요 $\Delta\mu_B^i$

4) 석출물 성장을 위해선 계면조성이 평형농도 X_e보다 커야함.

What is the driving force for precipitation of β from α?



$$\Delta G = \bar{G}_A X_A^\beta + \bar{G}_B X_B^\beta - G_m^\beta(X_B^\beta)$$

Driving force: precipitation

* Consider the chemical potential of component *B* in phase *alpha* compared to *B* in *beta*. This difference, labeled as ΔG_n on the right of the lower diagram is the driving force (expressed as energy per mole, in this case).

* To convert to *energy/volume*, divide by the molar volume for *beta*: $\Delta G_V = \Delta G_n / V_m$.

Driving force for the reaction : ΔG_0

Driving force for nucleation : ΔG_n

Because the first nuclei of beta to appear do not ignificantly change the composition of the parent material

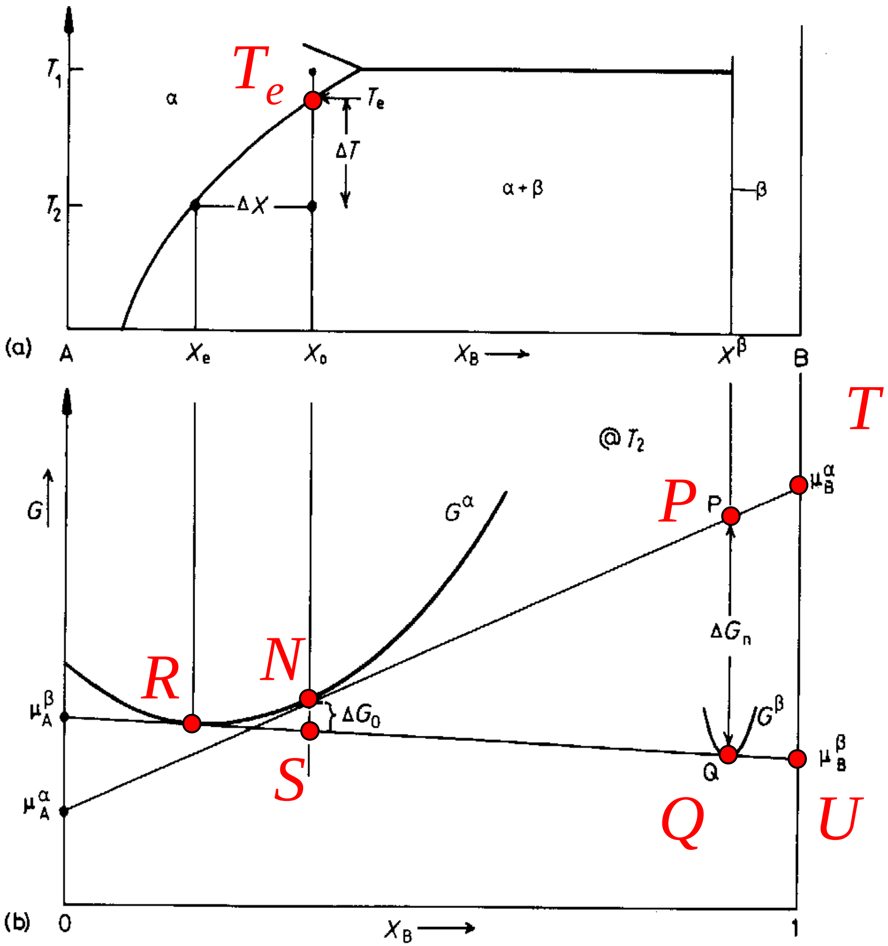


Fig. 5.3 Free energy changes during precipitation. The driving force for the first precipitates to nucleate is $\Delta G_n = \Delta G_v V_m$. ΔG_0 is the total decrease in free energy when precipitation is complete and equilibrium has been reached.

고경각 입계의 이동과 유사하게 계면을 가로지르는 B의 실유속으로 인하여 계면 속도 v 생김.

$$v = M\Delta\mu_B^i / V_m$$

M= 계면 이동도, V_m = β상의 몰당 체적

$$\begin{aligned} J_B^i &= -C_B^i v_B \\ &= -\frac{1}{V_m}\left(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}\right) \\ &= J_B^\alpha = -D\left(\frac{\partial C_B}{\partial X}\right)_{\text{interface}} \end{aligned}$$

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

계면에서 정상상태인 경우,

$$\boxed{J_B^i = J_B^\alpha}$$

1) 부정합 계면처럼 계면 이동도가 매우 높다면,

High Mobility: $\Delta\mu_B^i$ small, $X_i \approx X_e$; Diffusion-Control

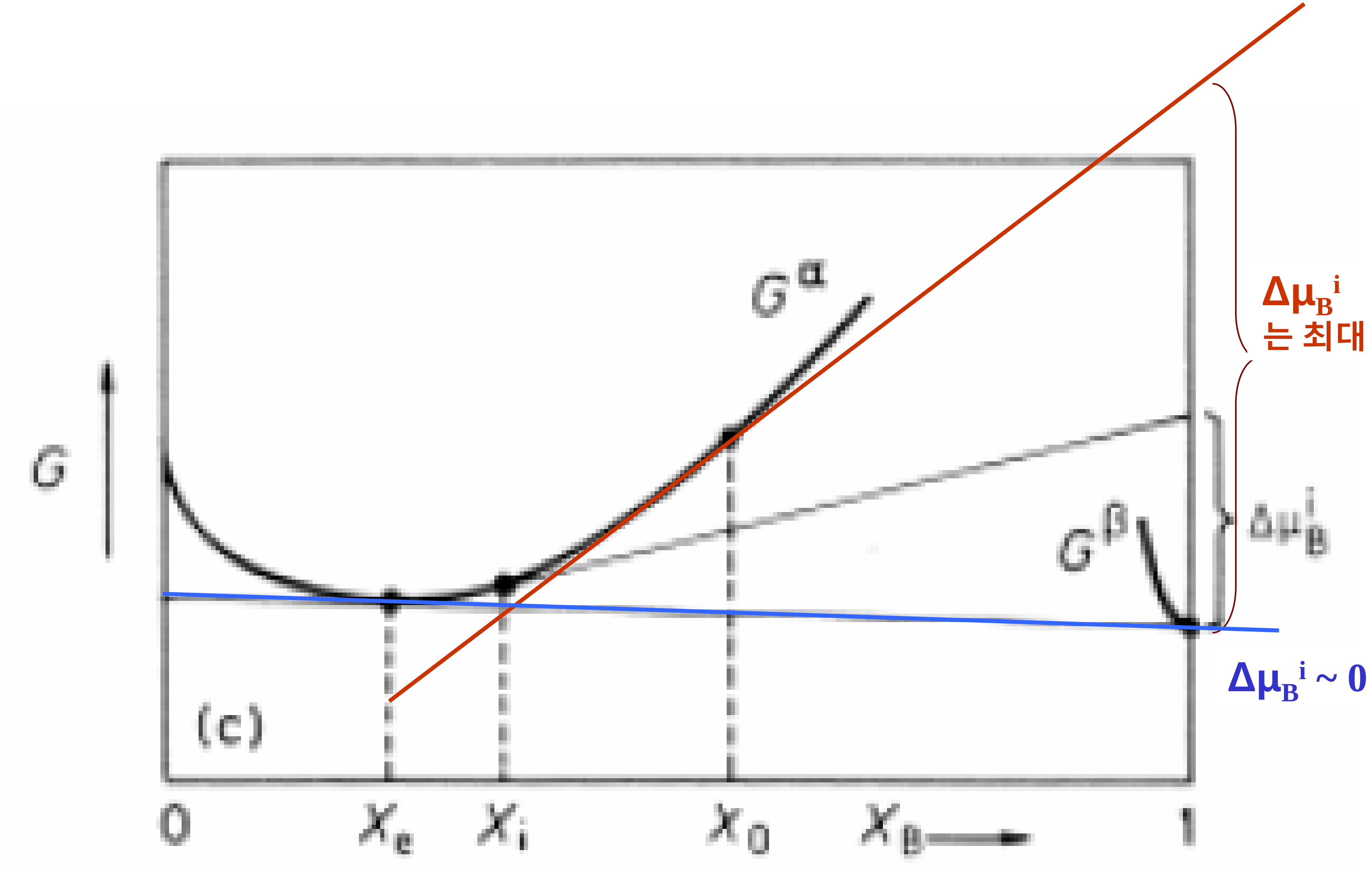
2) 계면 이동도가 낮은 경우,

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

3) 계면 이동도가 매우 낮은 경우,

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

$\Delta\mu_B^i$ 는 최대



$\Delta\mu_B{}^i$ 는 최대

$\Delta\mu_B{}^i \sim 0$

두상이 다른 조성을 갖는 경우,

일반적으로,

장범위 확산은 원자도약 수 천 번 일어나야 함

계면 반응은 단번의 도약에 의해서 일어남/
계면을 가로지르는 확산의 활성화 E < 격자를 통한 확산의 활성화 E

➡ 확산은 확산제어를 통해 일어남 : 대부분의 경우 해당

예외를 유발하는 요인,

생성상에 도달한 원자들이 수용되는 확률: 수용인자(A) 에 대한 고려 필요

고경각 입계, 부정합 계면, 고/액 확산 계면 = 수용인자 1에 가까운 값 ➡ 확산 제어

정합/반정합 계면, 평활한 고/액 계면 = 작은 수용인자 값 ➡ 계면 제어 가능

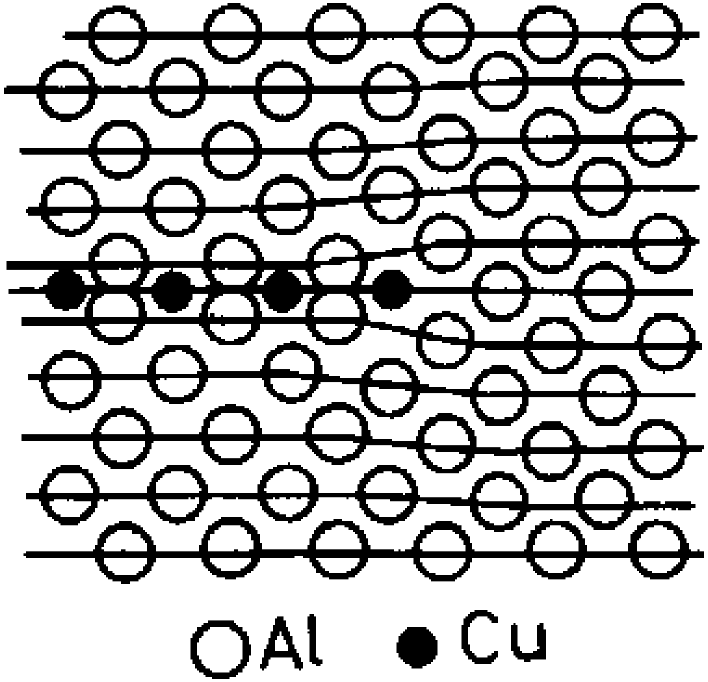
Al-Cu ppt structures

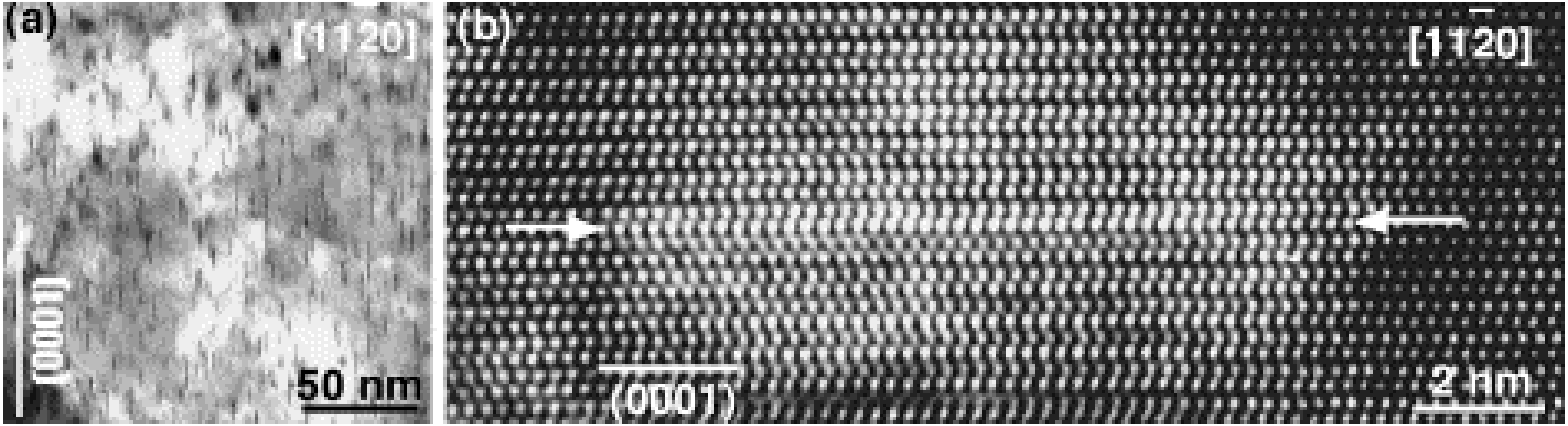
조성은 다르지만 같은 결정구조를 갖는 두상이
정합계면에 의해 분리되어 있는 경우,

공공의 이동에 의한 격자확산에 의해 계면 전진

별도의 계면 반응이 필요 없음

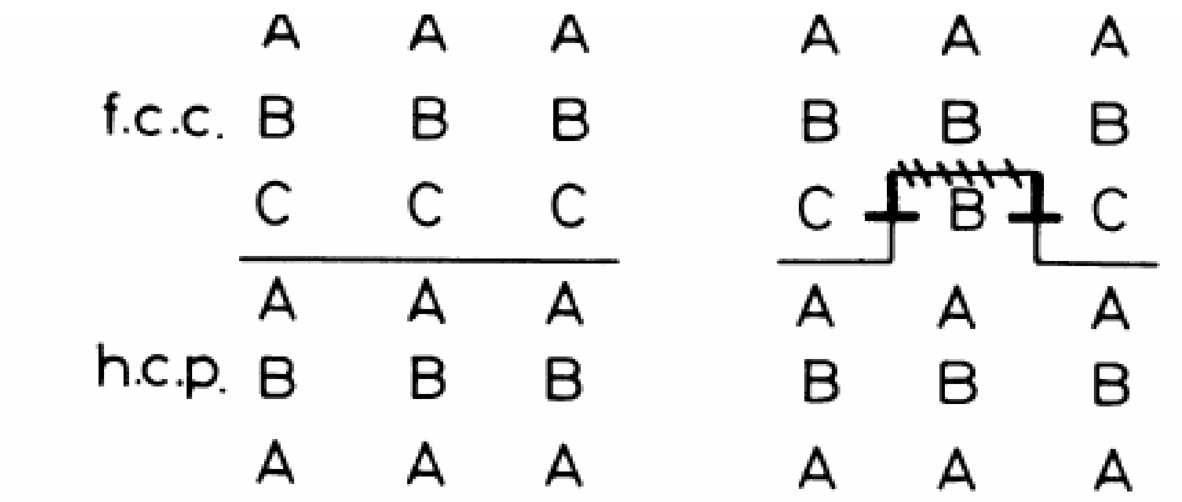
GP zone structure **확산 제어**





(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).

정합 또는 반정합 계면을 형성하는 두상이 다른 결정구조를 가질 경우,



Shorkley 전위 loop 형성

매우 불안정한 E 상태

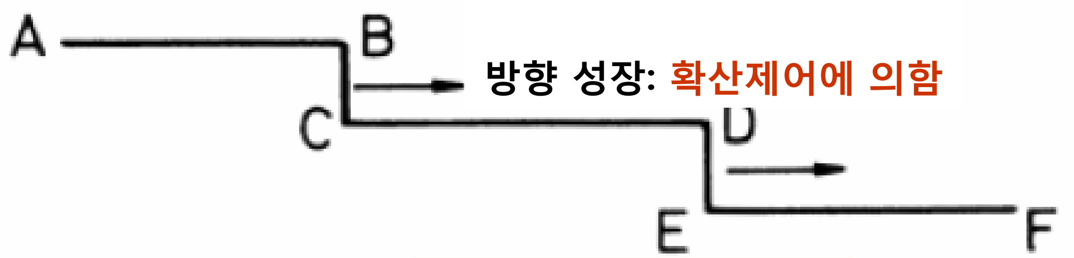
HCP의 성장이 개개의 원자도약 (Continuous growth)에 의해 일어나기 어려움.
(낮은 수용인자와 낮은 이동도를 가질 것으로 예측됨)

Fig. 3.68 Problems associated with the continuous growth of coherent interfaces between phases with different crystal structures. (After J.W. Martin and R.D. Doherty, *Stability of Microstructure in Metallic Systems*, Cambridge University Press, Cambridge, 1976.)

평평한 고/액 계면과 고/기 계면도 정도는 다르지만 비슷하게 거동

연속 성장의 어려움 피하는 법

돌출맥 기구에 의한 성장



방향 성장: 확산제어에 의함

Fig. 3.69 The ledge mechanism.

새로운 돌출맥 발생이 어려우면 정합/반정합 계면이 그면에 수직하게 성장하는 속도는 계면제어에 의함.

계면 이동 기구는 제 2 상의 개재물의 모양에 큰 영향을 미침.

- 변형에너지 효과가 없는 경우, 개재물을 둘러싸고 있는 계면에너지의 상대적인 비에 의해 평형 모양 결정

- 때로 정합 계면과 부정합 계면의 상대적 이동속도 차 영향 있음.

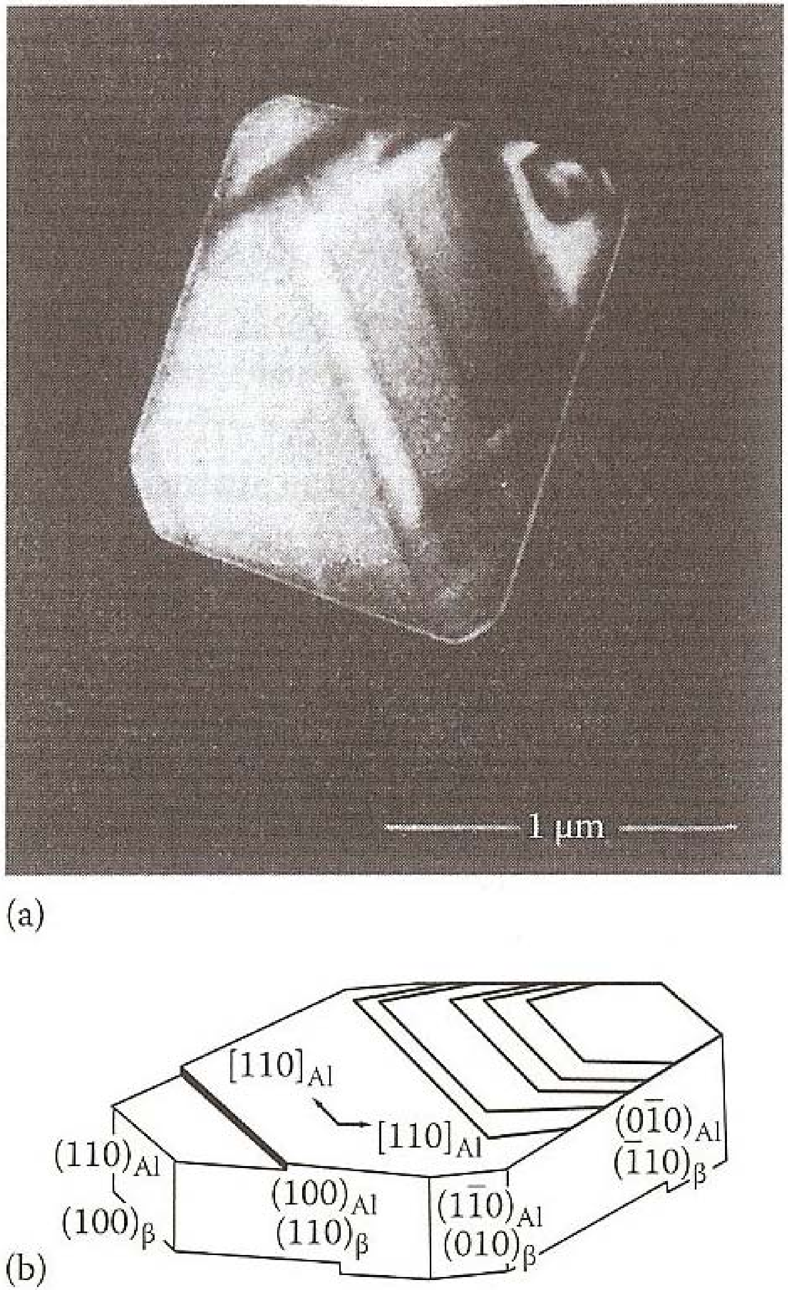


FIGURE 3.70
(a) Growth ledges at an Mg_2 Si plate in Al–1.5 wt% Mg_2Si, solution treated and aged 2 h at 350°C. Dark field micrograph. (b) Schematic diagram of (a) showing ledges on Mg_2Si plate. (After Weatherly, G.C., *Acta Metall.*, 19, 181, 1971.)

성장하는 돌출맥 두께는 수백개의 원자층 높이

Contents in Phase Transformation

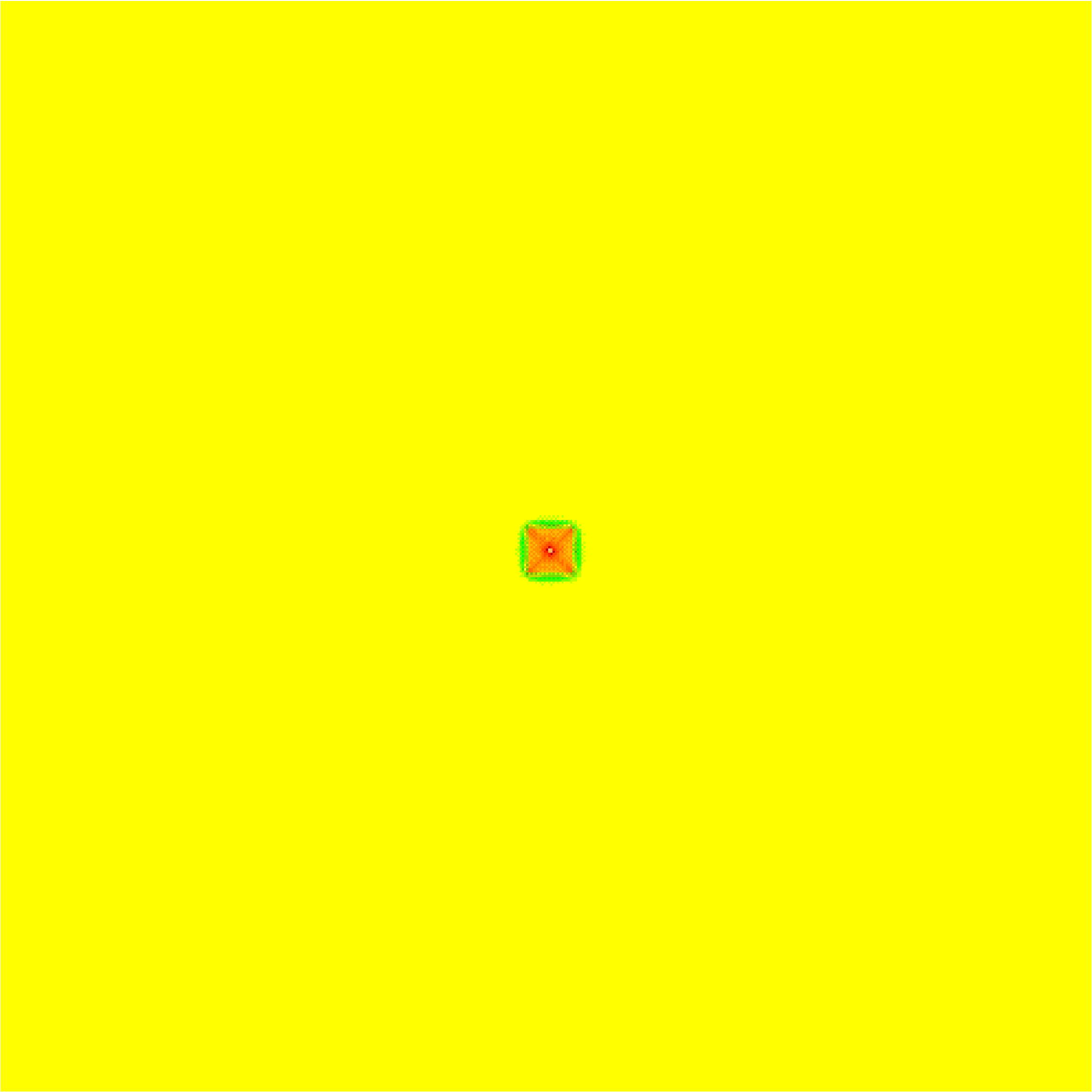
상변태를
이해하는데
필요한 배경

- (Ch1) 열역학과 상태도: **Thermodynamics**
- (Ch2) 확산론: **Kinetics**
- (Ch3) 결정계면과 미세조직

대표적인 상변태

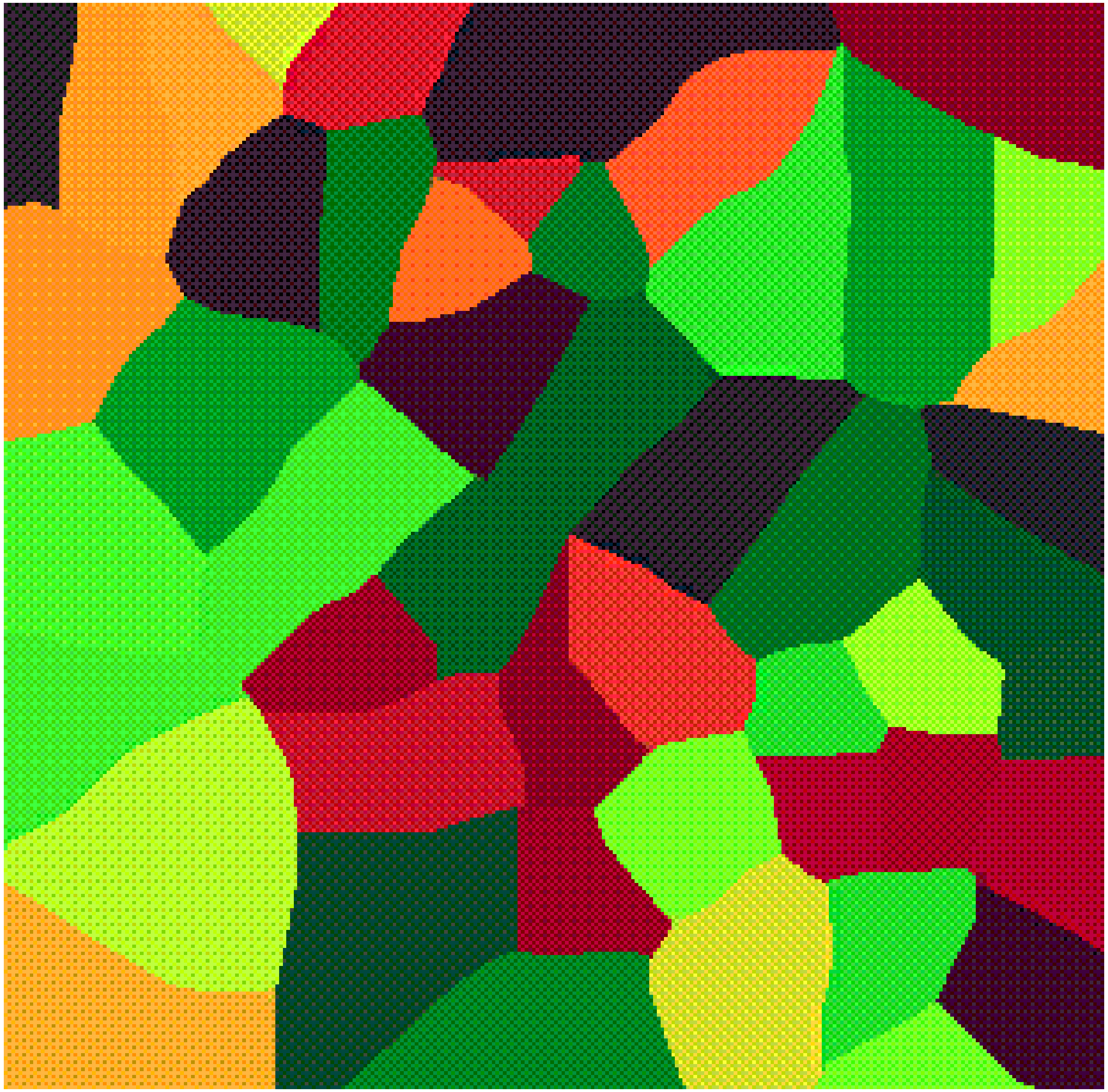
- (Ch4) 응고: **Liquid → Solid**
- (Ch5) 고체에서의 확산 변태: **Solid → Solid (Diffusional)**
- (Ch6)고체에서의 무확산 변태: **Solid → Solid (Diffusionless)**

Solidification: Liquid → Solid



4 Fold Symmetric Dendrite Array

Solidification: Liquid ⟶ Solid



4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds