2015 Fall

"Phase Transformation in Materials"

11.04.2015

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Contents for today's class 3.4 Interphase Interfaces in Solids

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Interphase boundary - different two phases : different crystal structure different composition
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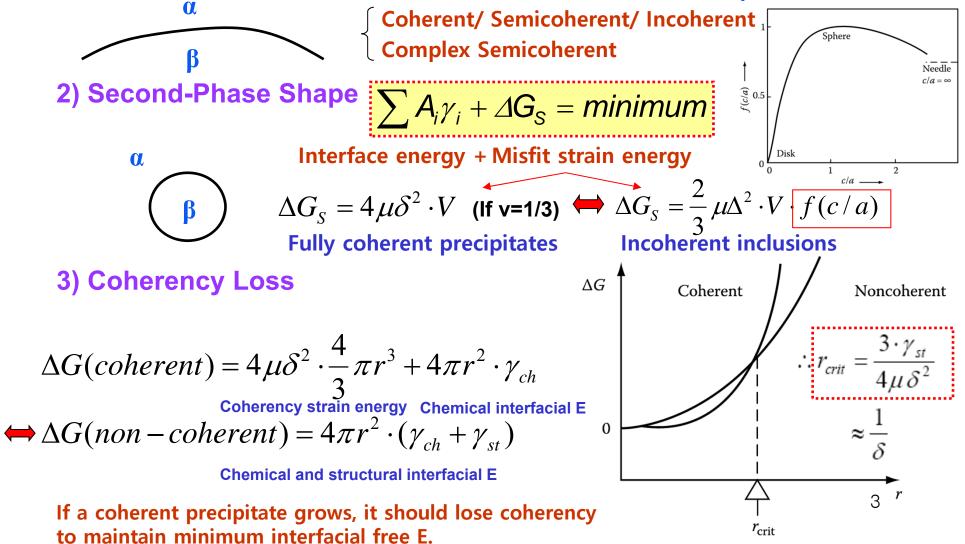
Perfect atomic matching at interface coherent, γ (coherent) = γ_{ch} γ (coherent) ~ 200 mJM⁻² **semi** $D \downarrow \rightarrow$ Strain field overlap semicoherent γ (semicoherent) = $\gamma_{ch} + \gamma_{st}$ \rightarrow cancel out γ $\gamma_{st} \rightarrow$ due to structural distortions caused by the misfit dislocations γ (semicoherent) ~ 200~500 mJM⁻² δ 0.25 δ =4: 1 dislocation per 4 lattices incoherent 1) $\delta > 0.25$ 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.

Contents for today's class

3.4 Interphase Interfaces in Solids (α/β)

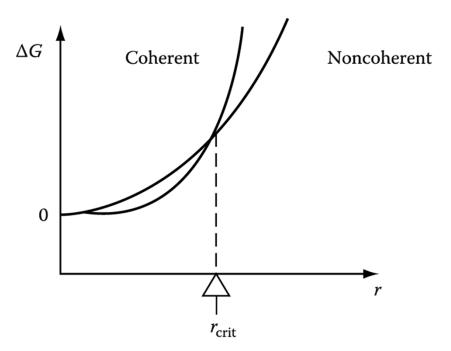
1) Interphase boundary - different two phases : different crystal structure different composition



Q: Which state produces the lowest total E for a spherical precipitate?

"Coherency loss"

If a coherent precipitate grows, during aging for example, It should lose coherency when it exceeds r_{crit} .



Coherency Loss Precipitates with coherent interfaces=low interfacial E + coherency strain E Precipitates with non-coherent interfaces=higher interfacial E

If a coherent precipitate grows, it should lose coherency to maintain minimum interfacial free E.

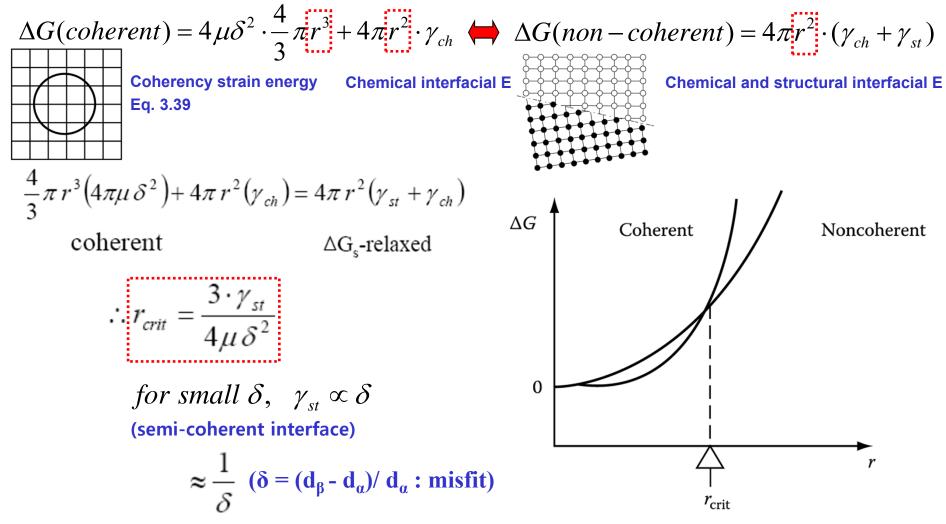


Fig. 3. 52 The total energy of matrix + precipitate vs. precipitate radius for spherical coherent and <u>non-coherent (semicoherent of incoherent)</u> precipitates.

If a coherent precipitate grows, during aging for example, It should lose coherency when it exceeds r_{crit} .

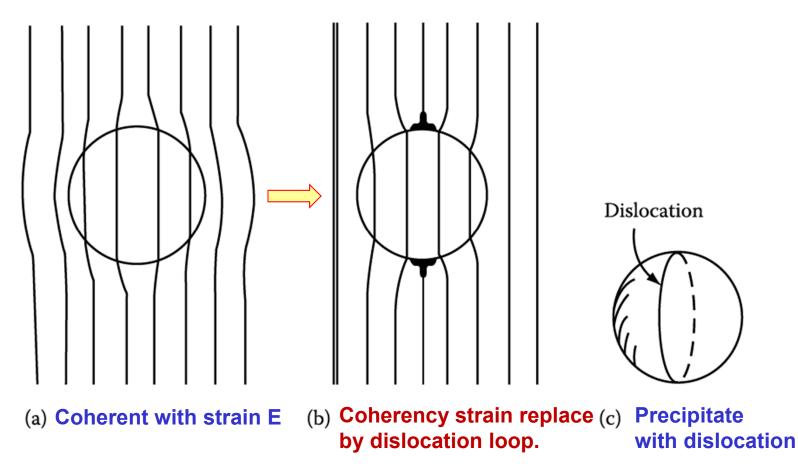


Fig. 3.53. <u>Coherency loss</u> for a spherical precipitate

In practice, this phenomena can be rather difficult to achieve. — Coherent precipitates are often found with sizes much larger than r_{crit}.

Dislocation * Punching stress (P_s) ~ independent of size, 1) spherical precipitate but $P_{\rm s} \propto \text{constrained misfit}$, $\varepsilon \ (> \epsilon_{\rm crit} \sim 0.05)$, "precipitates with a smaller ε cannot lose coherency by (a), no matter how large." Matrix dislocation wraps around the precipitate with a Precipitate suitable Burgers vector Punched-out **Dislocation** loop punching from requires the stresses at the interface interface to exceed the theoretical strength of the matrix assisted by mechanical deformation Interfacial (a) dislocation (b) Capture of matrix dislocation 2) Plate precipitate **Prismatic dislocation loop** High stress at the edges Misfit New dislocation Nucleation of D loops within the precipitate dislocation as plate **Constant inter D spacing** (d) Vacancies can be attracted to coherent (c) lengthens interfaces and 'condense' to form a

"Mechanisms for coherency loss": all require the precipitate to reach a larger size than r_{crit}

Nucleation of dislocation at the edge \rightarrow maintain a roughly prismatic dislocation loop which can constant inter-dislocation spacing during plate lengthening

expand across the precipitate

Contents for today's class

- Interphase Interfaces in Solid (α/β)
 - Types of interphase interfaces in solid (α/β)
 - Second-Phase Shape (Interface Energy Effects) $\sum_{i=1}^{n} A_{i}\gamma_{i} + \Delta G_{s} = minimum$ Coherent / Semi-coherent / Inco

Coherent / Semi-coherent / incoherent

- Coherency Loss
- Glissil Interfaces 👄 Solid/Liquid Interfaces
- **Interface migration**

Q: What is Glissile interface?

Glissile interface \rightarrow coordinated glide of the interfacial disl. $\rightarrow (\alpha \rightarrow \beta)$ 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

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

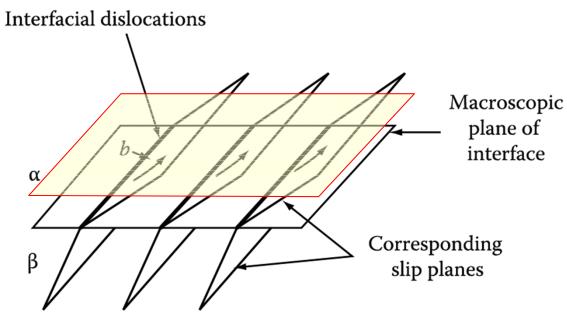


Fig. 3. 55 The nature of a glissile interface.

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

Slip planes : continuous across the interface

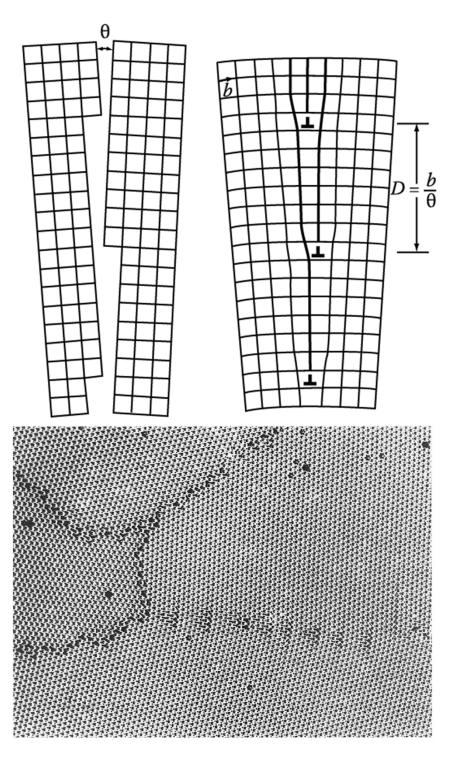
Gliding of the dislocation : α is sheared into the β structure.

Low-Angle tilt Boundaries

Bugers vector = edge dislocation

But, this is not interphase interface.

∵ crystal structure is same, only lattice rotation

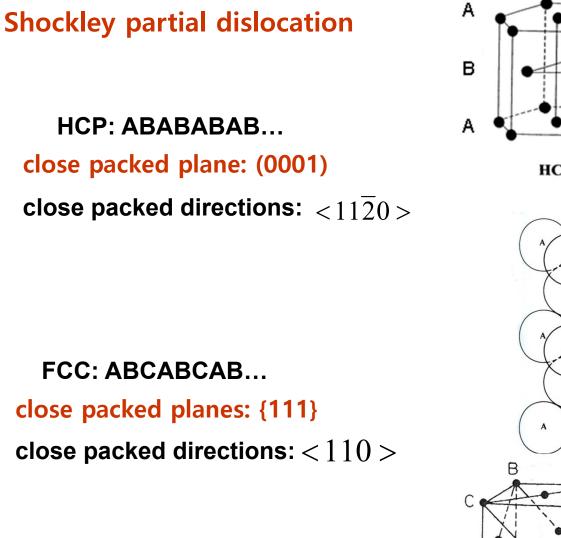


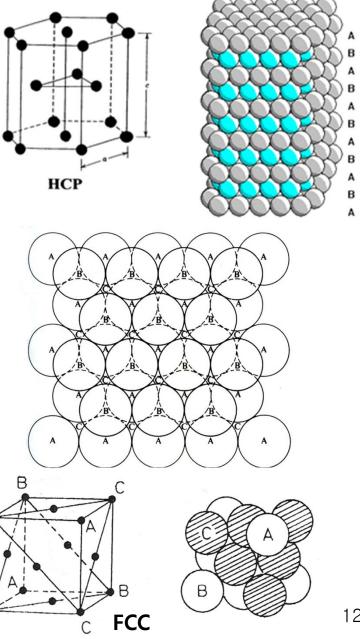
* As disl. glide at low-angle grain boundary

: no change in crystal structure,

just rotation of the lattice into the other grain

Glissile Interfaces between two lattices





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1) Perfect dislocation

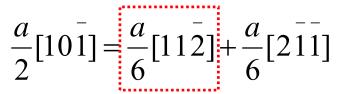
$$\vec{b} = \frac{a}{2}[10\overline{1}]$$

In C layer, atoms move $C' \rightarrow C''$

: remain a cubic close-packed arrangement with a fcc unit cell < FCC → FCC >

2) Shockley partial dislocation

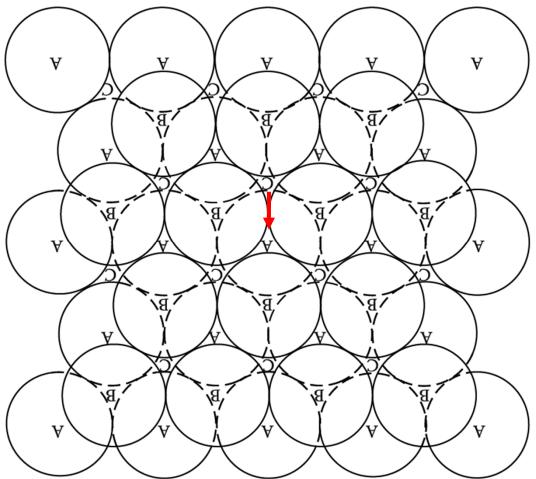
when atoms move: $C' \rightarrow C''$ possible to move $C' \rightarrow A \rightarrow C''$

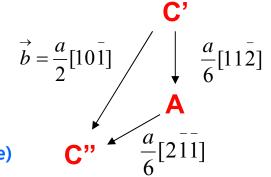


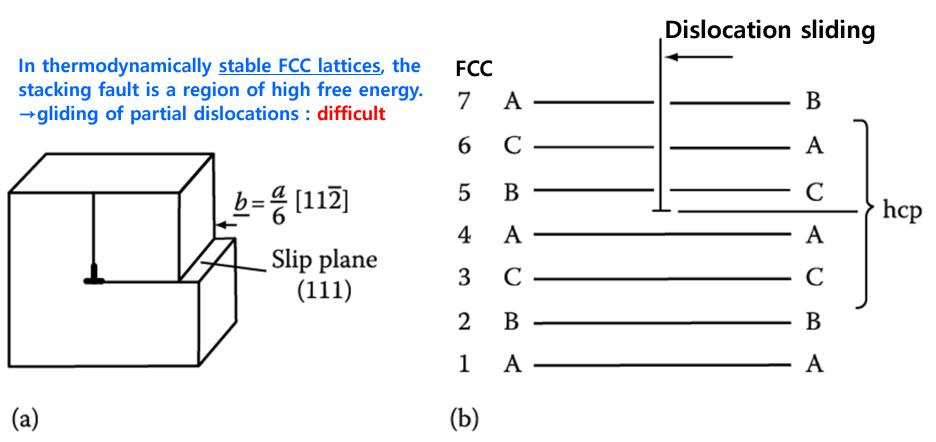
This burgers vector of partial disl. is not located at lattice point.

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

< FCC \rightarrow 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

Fig. 3. 59 (a) An edge dislocation with a Burgers vector $b = \frac{a}{6} [112]$ on $(11\overline{1})$. (shockley partial dislocation.) (b) The same dislocation locally changes the stacking sequence from fcc to hcp.

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

Glissile Interfaces between two lattices

fcc

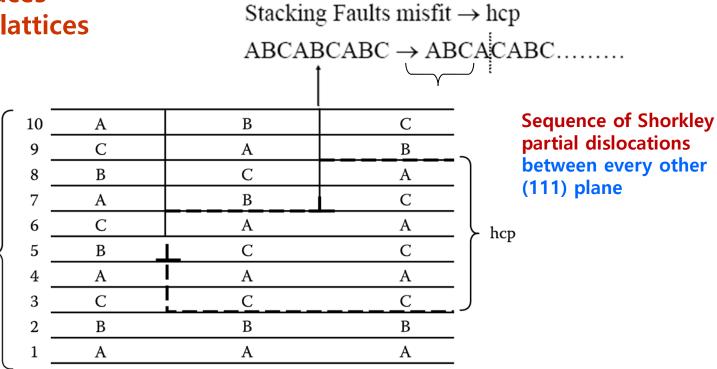


Fig. 3. 60 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

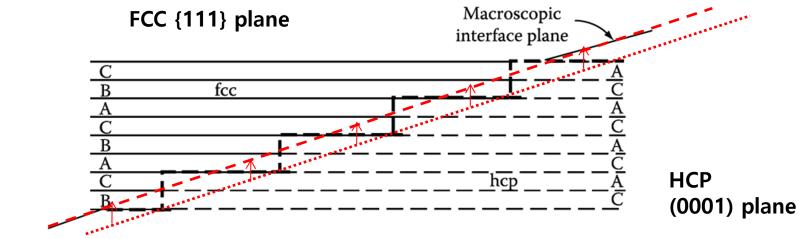
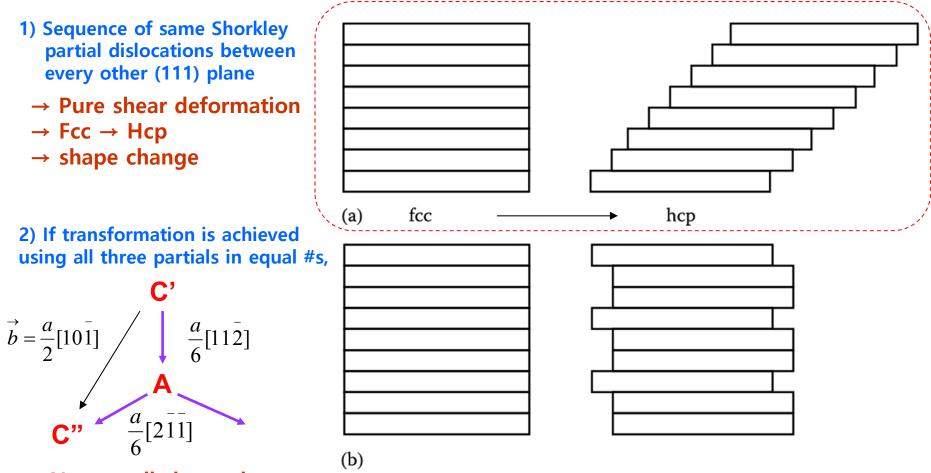


Fig. 3. 61 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

An important characteristic of glissile dislocation interfaces

→ they can produce a macroscopic shape change in the crystal.



→ 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)

Q: What is the structure of interface between liquids and crystals?

Interphase Interfaces in Solid (α/β)

2) Solid /Liquid Interfaces: consequences for the structure and energy of the interface

Faceted interface Rather narrow transition zone approximately one atom layer thick ~ same as solid/vapor interfaces, i.e., atomically flat close-packed interface

: some intermetallic compounds, elements such as Si, Ge, Sb, and most nonmetals

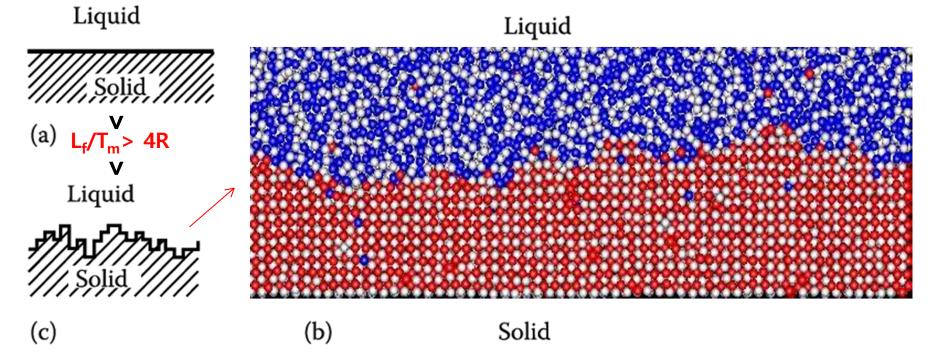
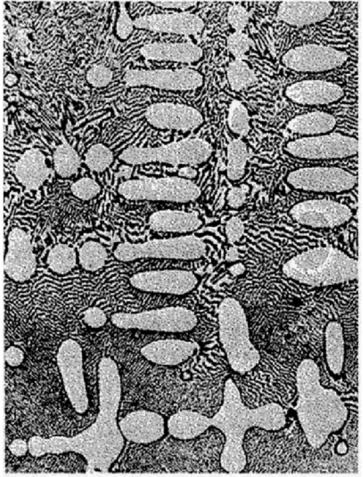


Fig. 3. 63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces.

Diffusion interface (non-faceted) Rather wide transition zone over several atom layers : most metals, L_f/T_m ~ R (gas constant) ~automatically rough & diffuse interface 18

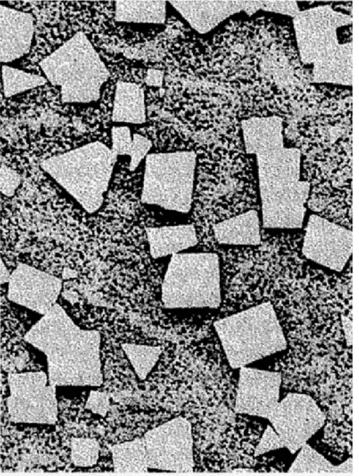
Primary Ag dendrite in Cu-Ag eutectic matrix



(a) Non-faceted

- Free E ~do not vary with crystallographic orientation
- γ-plot ~ spherical

β'-SnSb intermetallic compound in Sn(Sb) solid solution

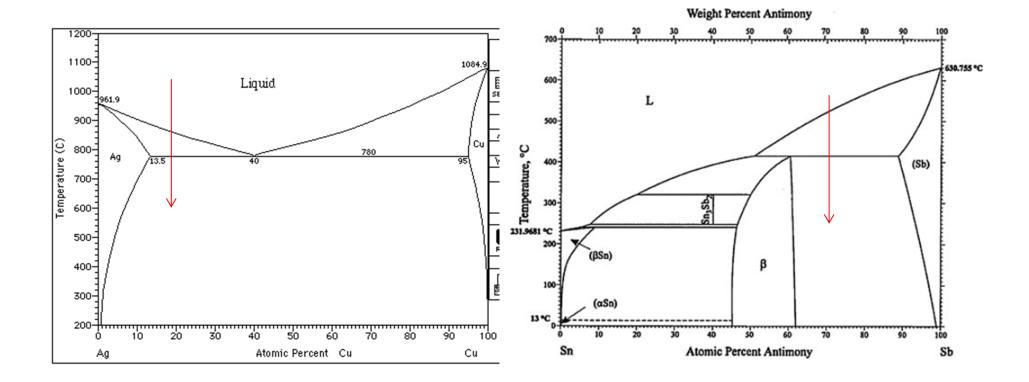


(b) Faceted

- Strong crystallographic effects
- Solidify with low-index close-packed facets

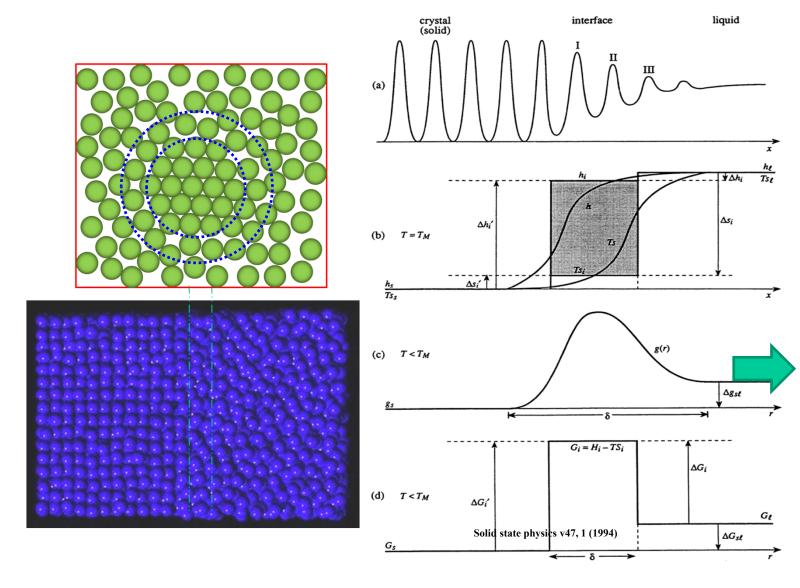
Primary Ag dendrite in Cu-Ag eutectic matrix

β'-SnSb intermetallic compound in Sn(Sb) solid solution



What is the structure of interface between liquids and crystals? Turnbull's solid-liquid interface

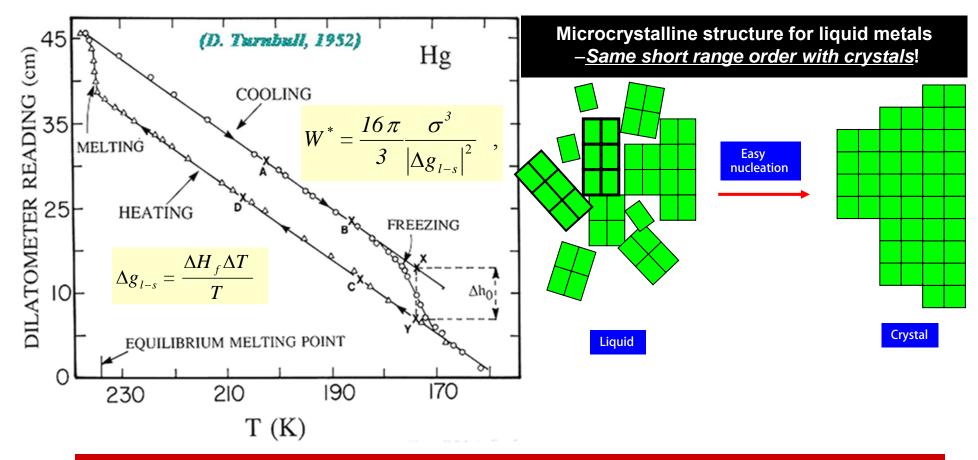
<u>Turnbull's insight:</u> Liquid orders substantially near a crystal surface due to entropy decreasing caused by the crystal-melt interfacial tension



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Supercooling

Turnbull's Insight for Supercooling



How does the liquid metals resist on the crystallization?
 What the origin of high nucleation barrier against the crystallization?

* Broken bond model \rightarrow calculation of the E of solid/ liquid interface

 $0.5L_f/N_a \rightarrow 0.45L_f/N_a$ (엔트로피 효과로 감소)

 Table 3.1.
 Relationship between Maximum Supercooling,

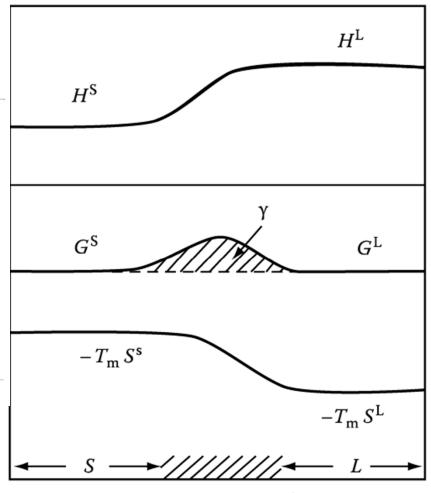
 Solid-Liquid Interfacial Energy and Heat of Fusion^a

	Interfacial Energy σ	-		ΔT_{MAX}	
Metal	$(ergs/cm^2)$	σ_g (cal/mole)	σ_g/L	(deg)	
Mercury	24.4	296	0.53	77	
Gallium	55.9	581	0.44	76	
Tin	54.5	720	0.42	118	
Bismuth	54.4	825	0.33	90	
Lead	33.3	479	0.39	80	
Antimony	101	1430	0.30	135	
Germanium	181	2120	0.35	227	
Silver	126	1240	0.46	227	
Gold	132	1320	0.44	230	
Copper	177	1360	0.44	236	
Manganese	206	1660	0.48	308	
Nickel	255	1860	0.44	319	
Cobalt	234	1800	0.49	330	
Iron	204	1580	0.45	295	
Palladium	209	1850	0.45	332	
Platinum	240	2140	0.45	370	

^a Data from D. Turnbull, J. Appl. Phys., 21, 1022 (1950) and Ref. 3.

 $\gamma_{SL} \approx 0.45 \gamma_b$ (= 0.15 γ_{SV}) for the most metals

at equilibrium melting temp.



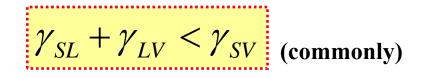
Distance across interface

Showing the origin of the solid/ liquid $_{23}$ interfacial energy, γ

4.1.4. Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

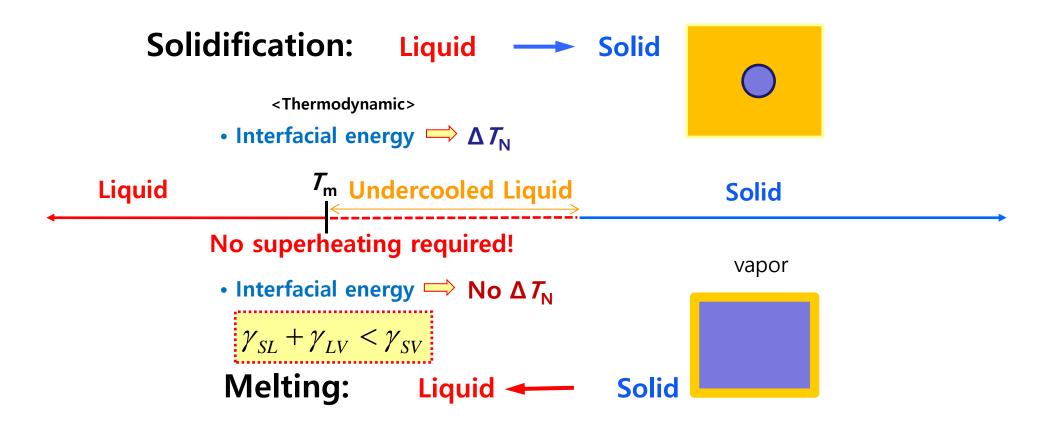
Why?





In general, wetting angle = 0 > No superheating required!

Melting and Crystallization are Thermodynamic Transitions



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 \rightarrow 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 \longrightarrow 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

Classification of Nucleation and Growth Transformation

Туре	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	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Soldification and melting	Precipitation dissolution Eutectoid Cellular precipitation	
		Condensation Evaporation				

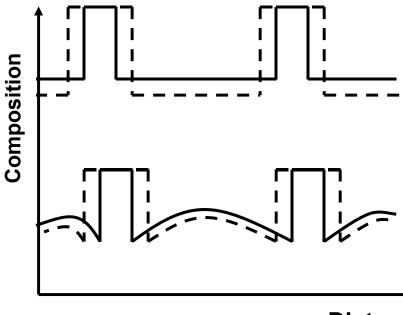
Source: Adapted from Christian, J.W., in Phase Transformations, Vol. 1, Institute of Metallurgists, 1979, p. 1.

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

(need to additional research)

3.5. Interface Migration

* Civilian Transformation



Distance



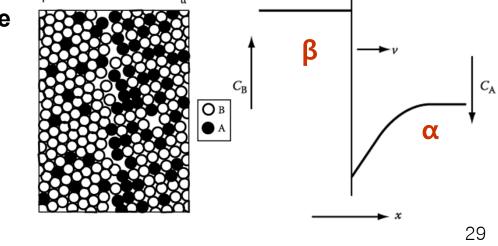
Same composition between parent and product (Ex. $\alpha \rightarrow \gamma$ transformation in pure iron)

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.

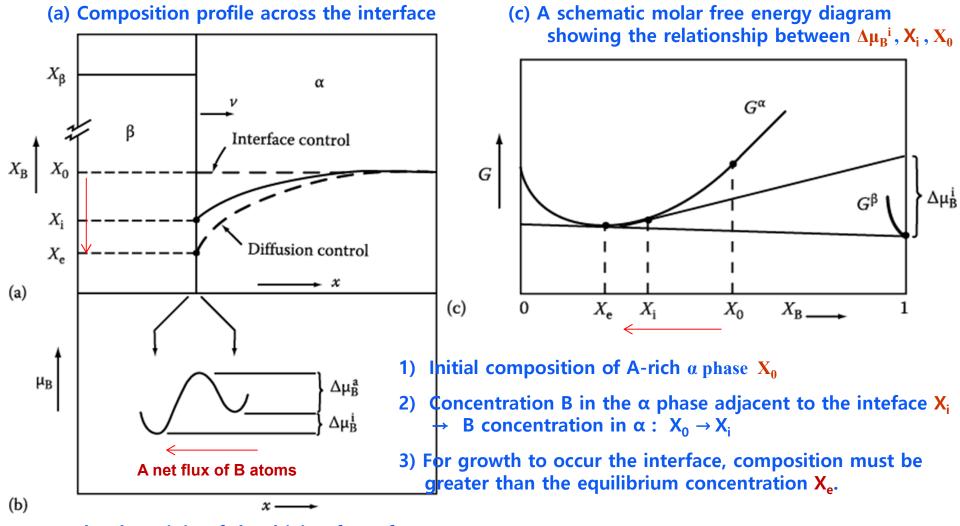


3) Mixed control: interface reaction = diffusion process

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



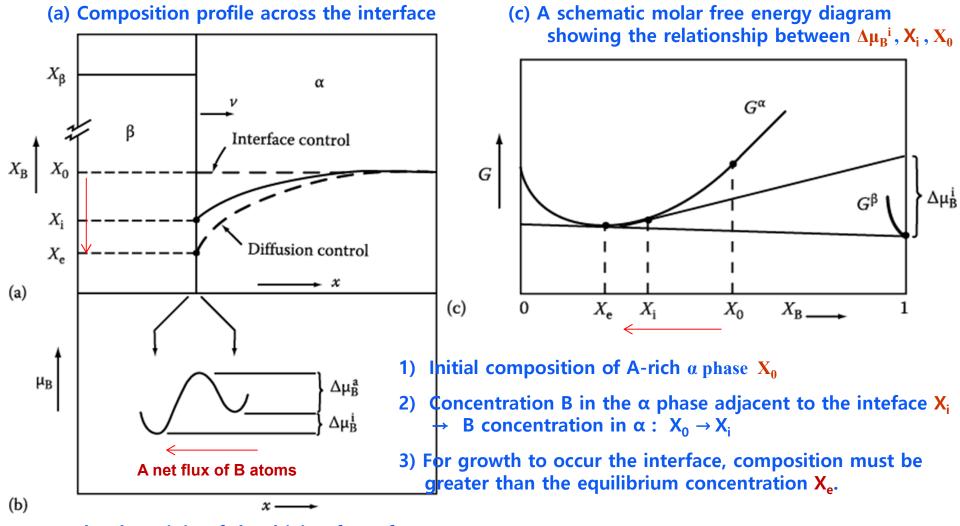
(b) The origin of the driving force for boundary migration into the α -phase $\Delta \mu_{B}{}^{i}$

Total Free Energy Decrease per Mole of Nuclei ΔG_{n} : Driving force for phase transformation of system **Driving Force for Precipitate Nucleation** $\alpha \rightarrow \alpha + \beta$ $\Delta \mathbf{G}_{\mathbf{V}}$ $\Delta G_1 = \mu_A^{\alpha} X_A^{\beta} + \mu_B^{\alpha} X_B^{\beta}$ α : Decrease of total free E of system by removing a small amount of material $\alpha + \beta$ **-** B with the nucleus composition (X_{B}^{β}) (P point) T_2 $\Delta G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta$: Increase of total free E of system (a) A Xe X_0 X^{β} by forming β phase with composition X_{R}^{β} $X_{\rm B} \longrightarrow$ B (Q point) $@T_2$ $\Delta G_n = \Delta G_2 - \Delta G_1$ (length PQ) $\mu_{\rm B}^{\alpha}$ G G^{α} G_r^{β} $\Delta G_{V} = \frac{\Delta G_{n}}{V}$ per unit volume of β : driving force for β precipitation ΔG_n dXA For dilute solutions, ΔG_0 IG^β μβ μβ $\Delta G_{V} \propto \Delta X$ where $\Delta X = X_{0} - X_{e}$ ↑ μ^a_A $\Delta G_{V} \propto \Delta X \propto (\Delta T)$ 31 \propto undercooling below T_a (b) 0 $X_{\rm R}$ – 1

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



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

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

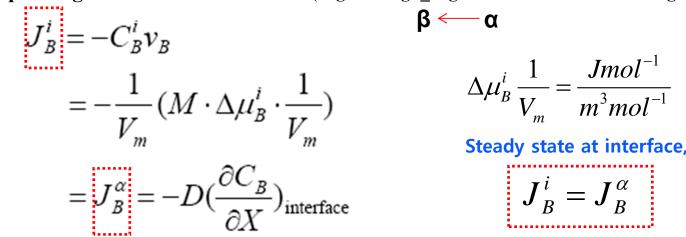
- Grain boundary migration (v) by thermally activated atomic jump

Boundary velocity $\boldsymbol{v} = \frac{A_2 n_1 v_1 V_m^2}{N_a RT} \exp\left(-\frac{\Delta G^a}{RT}\right) \frac{\Delta G}{V_m} \qquad \qquad \boldsymbol{v} \sim \Delta G/V_m \text{ driving force} \\ \rightarrow \mathbf{F} = \Delta G/V_m$ M^{-1} : mobility = velocity under unit driving force ~ exp (-1/T)

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

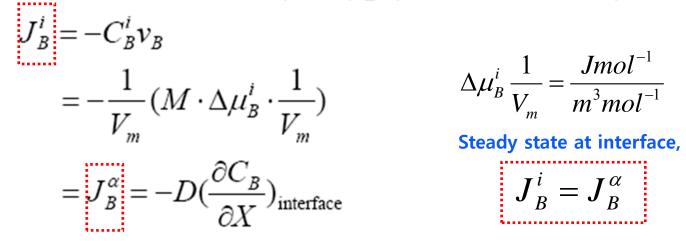
Interface velocity of precipitate $v = M \Delta \mu_B^i / V_m$ M = interface mobility, $V_m = \text{molar volume of the }\beta \text{ phase}$ 0

Corresponding flux across the interface (negative sign_negative direction of flux along the x-axis) 0



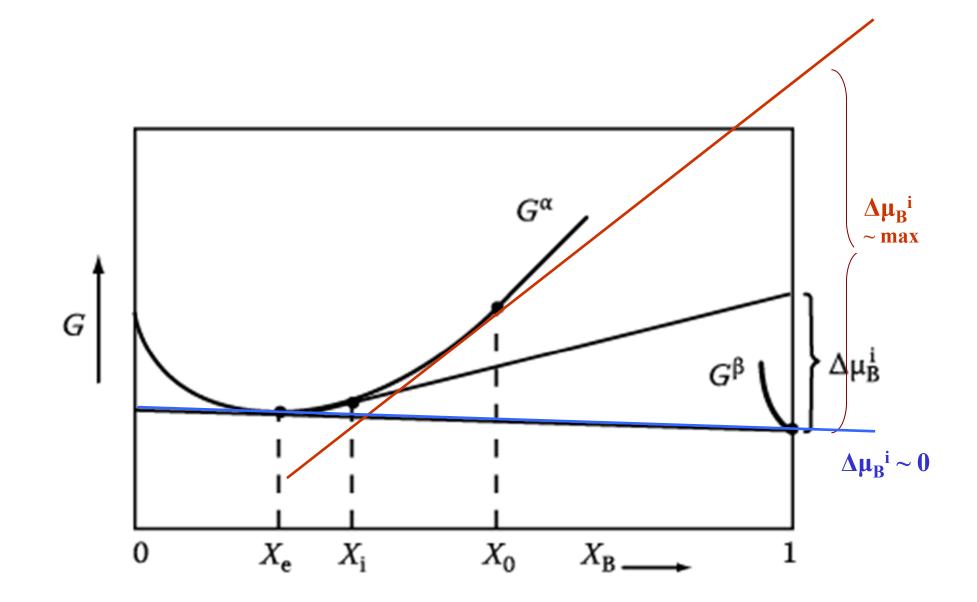
A flux of B atoms toward the interface by the concentration gradient in the α phase

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



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



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

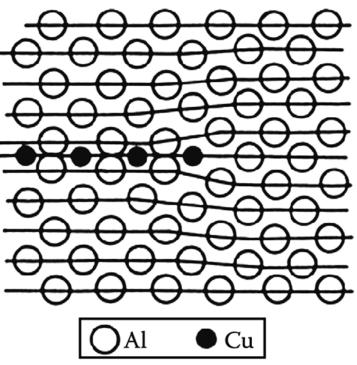
Al-Cu ppt structures

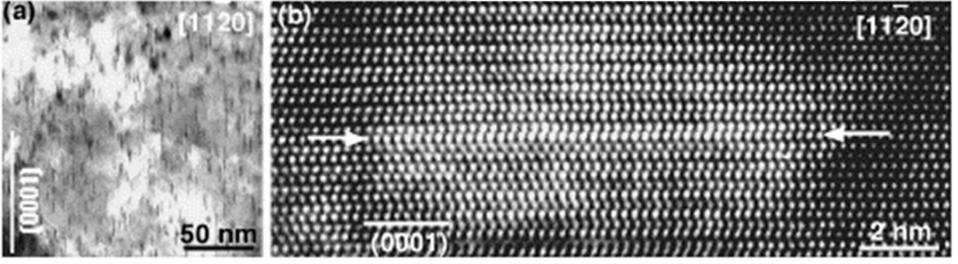
If two phases with different compositions, but the same crystal structure are separated by a coherent interface

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)





(a) Bright-field TEM image showing G.P. zones, and (b) HRTEM image of a G.P. zone 37 formed on a single (0 0 0 1)_a 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 \implies "diffusion control"

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

Ex) Interface control

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

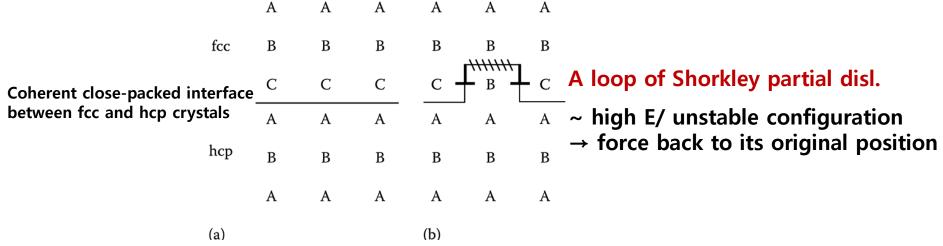
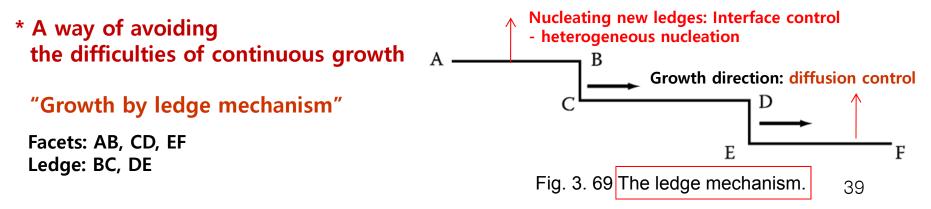


Fig. 3. 68 Problems associated with the continuous growth of coherent interfaces between phases with different crystal structures.

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

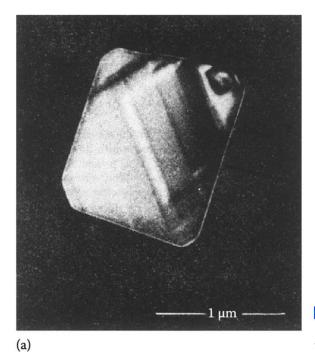
2) Solid/vapor as well as smooth solid/liquid interfaces ~ similar manner

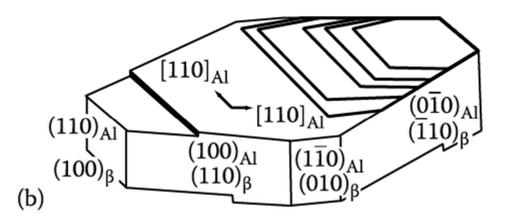


→ Problem of nucleation new ledges may often lead to a degree of interface control on the overall rate.

Fig. 3. 70 (a) Growth ledges at an Mg_2Si plate in Al-1.5 wt% Mg_2Si , solution treated and aged 2h at 350 °C. Dark field micrograph.

(b) Schematic diagram of (a) showing ledges on Mg_2Si plate.





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

The <u>mechanism of interface migration</u> can have <u>important effects on</u> <u>the shape of second-phase inclusions.</u> (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 $\gamma i / \gamma c$
- b) (in practice) "relative rates" at which the coherent and incoherent interface can migrate

정합/ 부정합 계면의 상대적인 이동속도 차에 의해 형상 변화

* Homework 3 : Exercises 3 (pages 186-188) until 13st November (before class)

Good Luck!!

Contents in Phase Transformation

Background to understand phase transformation

(Ch1) Thermodynamics and Phase Diagrams (Ch2) Diffusion: Kinetics

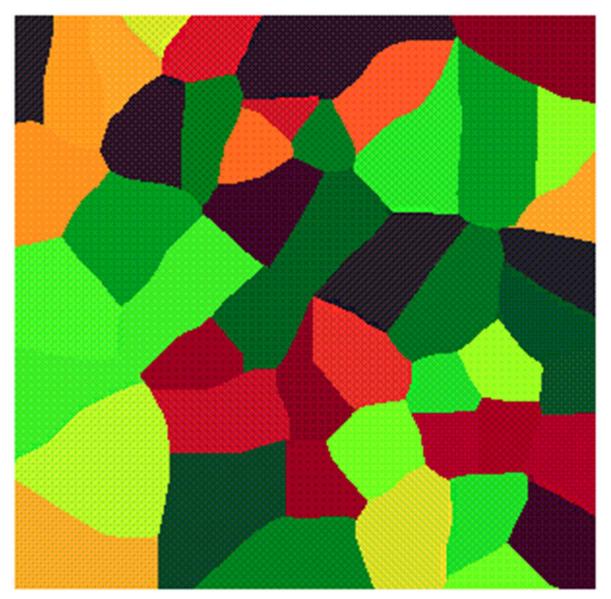
(Ch3) Crystal Interface and Microstructure

(Ch4) Solidification: Liquid \rightarrow Solid

Representative Phase transformation

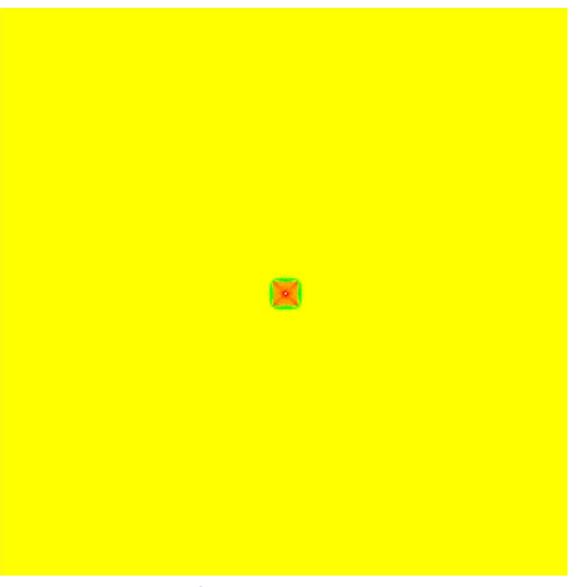
(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid



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

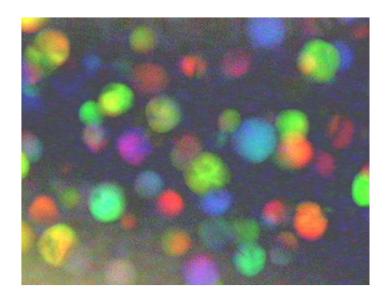
43



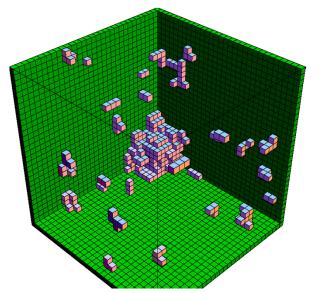
4 Fold Symmetric Dendrite Array

Solidification: Liquid ----- Solid

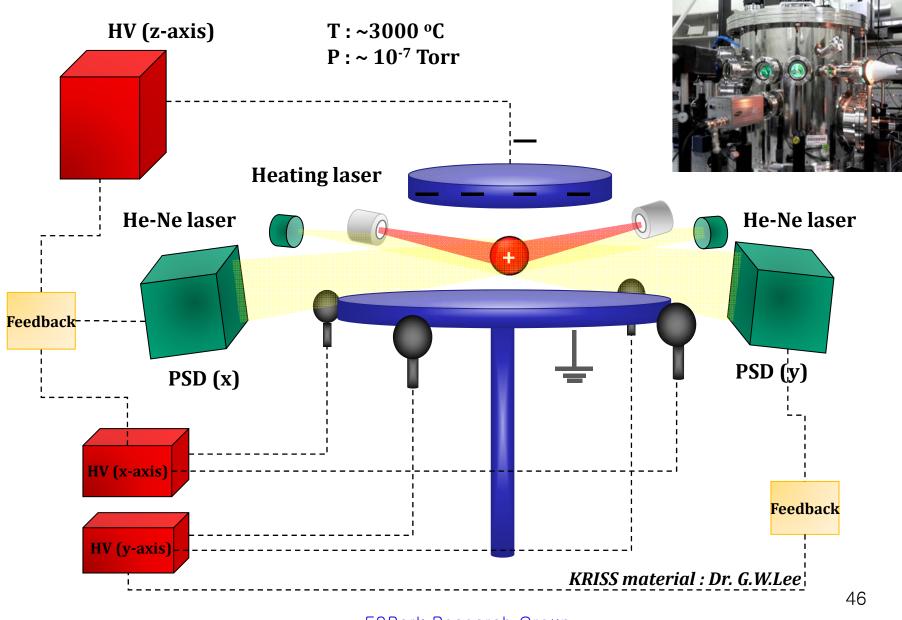
- casting & welding
- single crystal growth
- directional solidification
- rapid solidification
- 4.1. Nucleation in Pure Metals
 - $T_{\rm m}$: $G_{\rm L}$ = $G_{\rm S}$
 - Undercooling (supercooling) for nucleation: 250 K ~ 1 K
 - <Types of nucleation>



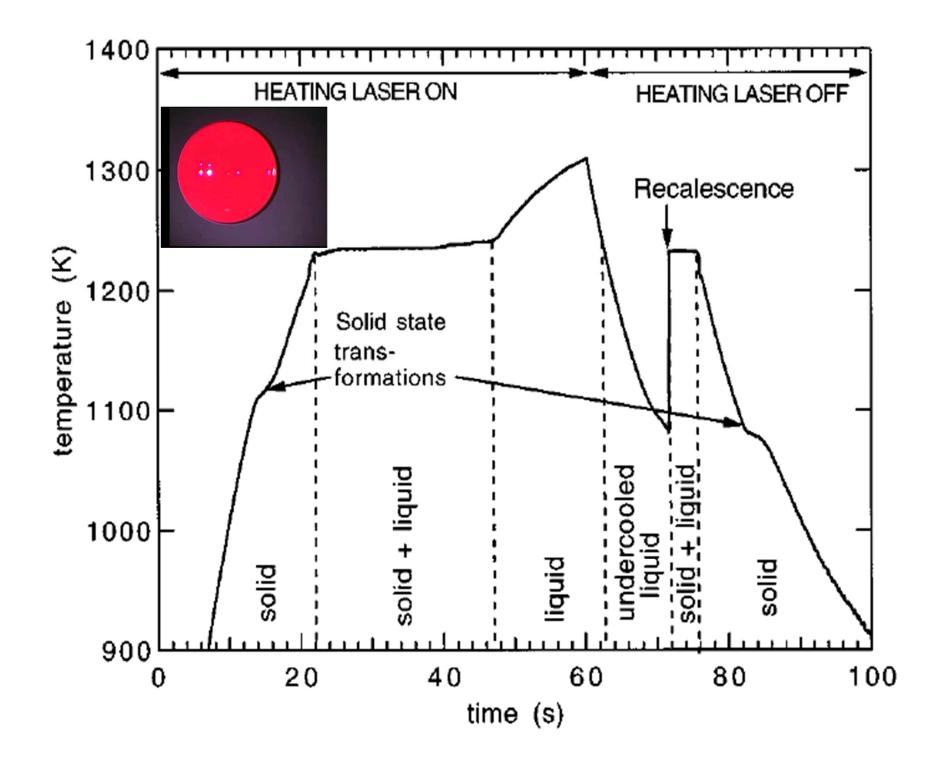
- Homogeneous nucleation - Heterogeneous nucleation



Electrostatic levitation in KRISS



ESPark Research Group



Electrostatic Levitation: cooling curve of Vitreloy 1 system

