

We all like sheep, have gone astray; each of us has turned to his own way. (14)

Date \_\_\_\_\_

5) s. The Kinetics of G. Growth.

- at H.T. the g. b. migrate to reduce p. b area (high  $\bar{\epsilon}$  imperfection) causing tharp. g. diameter increase.

① the growth rate (Avg.  $\frac{d\bar{D}}{dt}$ ) = f (g. b. mobility &  $\Delta G_m$ )

If the avg. radius of curvature  $\propto \bar{D}$ ,  $\Delta G_{\text{for migration}} \propto \frac{2\gamma}{\bar{D}} = f$  (Eq. 3.17)

(3.24)  $\bar{D} = \alpha M \frac{2\gamma}{\bar{D}} = \frac{d\bar{D}}{dt} \rightarrow \text{growth rate} \propto \frac{1}{\bar{D}}$

Integrate (3.24)  $\int_{D_0}^{\bar{D}} \bar{D} d\bar{D} = \int_0^t \alpha M 2\gamma dt$   
 "  $\uparrow$  w/ Temp. ( $\because M \uparrow$ )

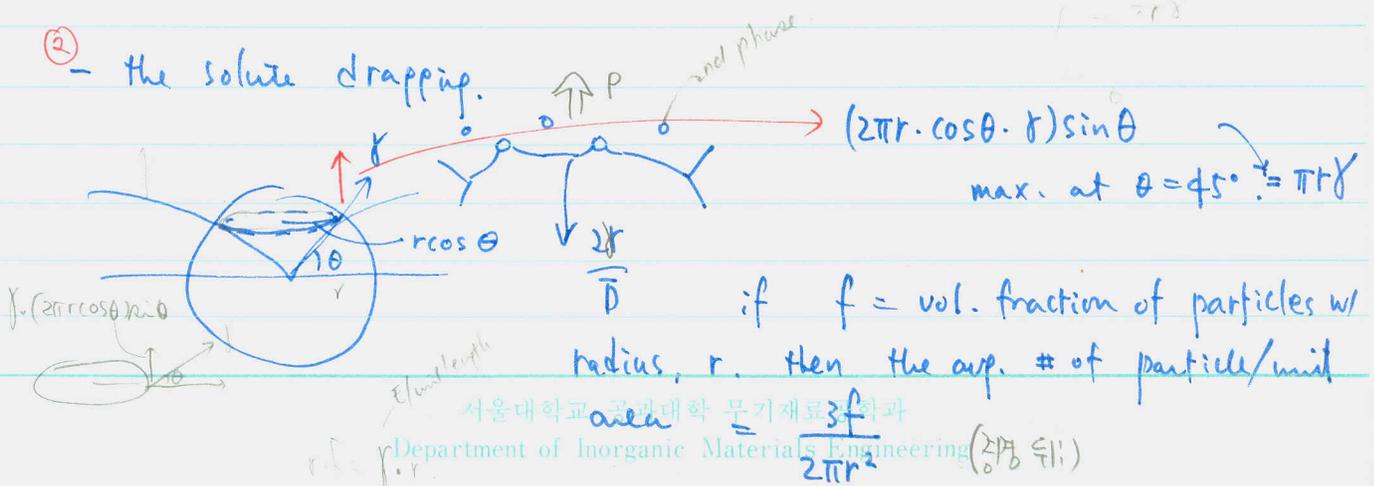
(3.25)  $\bar{D}^2 = D_0^2 + kt$ ,  $k = 4\alpha M \gamma$

(3.26) Experimentally  $\bar{D} = k' t^n$  —  $n < 0.5$  usually H.T.  
 $n \approx 0.5$  pure metal or at

why? ①  $v$  is not a linear fn of  $\Delta G$  i.e.  $M$  in (3.21)  $\neq$  const  
 ② solute dragging effect.  $= e < D \left( - \frac{H_a}{RT} \right)$

B. Abnormal p. growth few grains  $\rightarrow$  to very large dia. consuming the surrounding grains — known as discontinuous p. growth, coarsening or secondary recrystall'n.

② — the solute dragging.



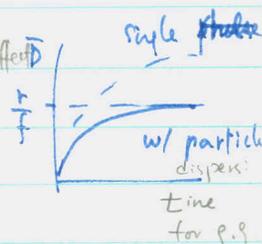
*drapping force*

$$(3.27) \quad P = \frac{3f}{2\pi r^2} \cdot \pi r r \gamma = \frac{3f\gamma}{2r} : P \text{ opposes the driving force for p.p.} \\ \left( = \frac{2r}{D} \right)$$

When  $\bar{D}$  is small,  $P$  insignificant effect.

as  $\bar{D} \uparrow$ , the driving force  $\left( \frac{2r}{D} \right) \downarrow$ ,  $P$  significant effect

$$(3.28) \quad \text{equil.}^m \text{ force } \frac{2r}{D} = \frac{3f\gamma}{2r} \rightarrow \boxed{\bar{D} = \frac{4r}{3f}}$$



$\therefore$  the fine <sup>(microstructure)</sup> p. size can be stabilized by the existence of a large vol. fraction of small particles.

At very high temp. the particles coarsen or dissolve.  $\rightarrow$  p. growth occurs

ex. aluminum-filled steel

Al-Ni  $\rightarrow$  AlN ppt. Keep the p. size of  $\gamma$ -steel at below 1000°C.

at 1000°C AlN dissolves.

### 3.4. Interphase Interfaces in Solids.

- So far the struc. & prop. of boundaries were dealt with.  
In this section: dealing w/ boundaries bet'n diff solids.  
(diff. xtal struc. & comp.) ( $\alpha/\beta$ )

- Three diff. interphase boundaries: coherent, semi-co, incoherent.

#### 3.4.1. Interface Coherence.

##### A. Fully Coherent Interface.

" " when two xtals match perfectly.  
at the interface - continuous across the interface.



(a) chemically diff. but the same Xtal struc (b) diff. lattice.

- Full coherency : achieved if the interfacial plane has the same atomic configuration in both phase. (lattice para. equal).

- Ex. In Cu-Si the Si-rich  $\kappa$  & Cu-rich  $\alpha$  phases.

hcp.

fcc

+ orientational relationship  $(111)_\alpha \parallel (0001)_\kappa$  interatomic dist. equal  
 $[\bar{1}10]_\alpha \parallel [11\bar{2}0]_\kappa$  joined along C-packed pl

+ optimum arrangement of nearest neighbors - produces a low  $E$ .

+ Structurally O.K but chemical effect :

wrong (diff.) neighbors  $\rightarrow$  causes the  $E$ . of interfacial atoms  $\rightarrow$  chemical contribution to  $\gamma$



(3.29)

$$\therefore \gamma_{coh} = \gamma_{chemical}$$

+ In the case of the  $\alpha$ - $\kappa$  interface  $\gamma_{coh} \approx 1 \text{ mJ/m}^2$  !!  
 normal  $\gamma_{coh} \approx 200 \text{ mJ/m}^2$ .

hcp/fcc fully coh. interface - only one plane possible.

fcc/fcc, hcp/hcp etc. (the same Xtal struc)  $\rightarrow$  very many.

+ Still possible to have full coh. by straining one or both lattices

(lattice distortion)  $\rightarrow$  strain coherency strain.  
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 (Fig. 3.34).

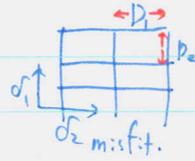
when lattice para. interatomic spacing is close.

## B. Semicohesive Interfaces

- for sufficiently large atomic misfit : energetically more favorable to replace the coh. int. w/ a semi c. int. - periodical placement of misfit dislocations (Fig. 3.35)
- $d_\alpha, d_\beta$  : unstressed interplanar spacings of matching planes.

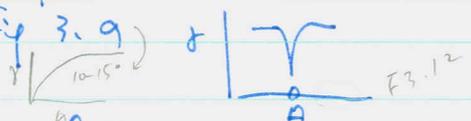
misfit (disregistry)  $\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$

(3.31)(3.32) the spacing bet'n misfit disl. ( $\perp$  disl.)  $D = \frac{d_\beta}{\delta} \approx \frac{b}{\delta} = \frac{d_\alpha + d_\beta}{2}$  "Burger's vector" for small  $\delta$ .

- In practice misfits are in 2-D non parallel sets of  $\pm s$  w/  $D_1 = \frac{b_1}{\delta_1}$  &  $D_2 = \frac{b_2}{\delta_2}$    $\rightarrow$  strain field completely relieved (!).

(3.33)  $\gamma(\text{semi-coh}) = \gamma_{\text{coh}} + \gamma_{\text{strain}}$  i) chemical effect, ii) structural distortion around  $\pm s$ .

(3.34) • (3.32) as  $\delta \uparrow$ ,  $D \downarrow$ . (lattice para 2014 2015 10이각후 2014 2015)  
for small  $\delta$   $\gamma_{\text{st}} \propto \delta$

$\gamma_{\text{st}} \uparrow$  less rapidly as  $\delta$  becomes larger : levels out when  $\delta \approx 0.25$   
as q.b.E in Fig 3.9)  F3.12

$\therefore$  as  $D \downarrow$  ( $\delta \uparrow$ ), the assoc'd strain field overlaps & annul each other.

- $\gamma_{\text{semicoh}} \approx 200 - 500 \text{ mJ/m}^2$ .
- if  $\delta > 0.25 \rightarrow$  called "incoherent"

### C. Incoherent Interfaces

- very diff. atomic configuration. - no possibility of good matching across the interface ( $\delta > 0.25 = 25\%$ )
- $\gamma_{\text{incoh}} \sim 500 - 1000 \text{ mJ/m}^2$  <sup>①</sup> insensitive to the orientation of the interface: <sup>②</sup> no long range periodicity of coh. & semcoh. interface.

### D. Complex Semicoh. Int.

- Semicoh. int. - observed at boundaries formed by low-index planes (atom pattern & spacing are almost equal).
- Even if good lattice matching is not initially obvious, the semi. int. can form.

ex. fcc & bcc Fe Xtds w/ the closest-packed planes.

$(110)_{\text{bcc}} \parallel (111)_{\text{fcc}}$ ,  $[001]_{\text{bcc}} \parallel [\bar{1}01]_{\text{fcc}}$  Nishiyama-Wasserman relationship (N-W)  
 0.26° rotation of c-packed planes.  
 " ,  $[\bar{1}\bar{1}1]_{\text{bcc}} \parallel [011]_{\text{fcc}}$  Kurdjumov-Sachs relationship

Fig 3.38 fit 8% of interfacial atoms. in  $\diamond$  shape.  
 (N-W)  $\rightarrow$  coh. & semicoh. impossible.  $\rightarrow$  incoherent.

$\rightarrow$  The degree of coherency can be increased greatly by having irrational interface (high index planes).

### 3.4.2. Second-Phase Shape: Int. E. Effects ( $\gamma$ )

- embedded phase in the matrix seeks a min. free E. (strain free).

#### A. Fully coherent Ppt's

- if  $\alpha, \beta$  have the same struc. (xtal)  $\rightarrow$  coherency <sup>two lattices</sup> // orientation.
- This happens during early stages of many ppt'n hardening  $\beta$  phase is then called 'fully coh. ppt.' or GP (Guinier Preston) zone

Shape factor

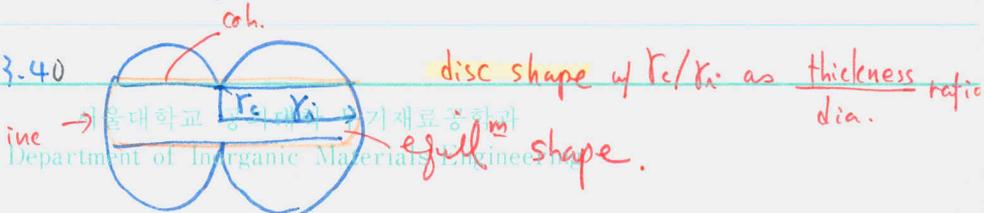
- Since the two xtal struc. match well  $\rightarrow$  can have any shape - coherent  $\gamma$ -plot of  $\alpha/\beta$  int. E.  $\rightarrow$  spherical  $\rightarrow$  shape: spherical  
no strain E. effect. (reduced chemical)

- Fig 3.39 GP zones  $\sim 100\text{Å}$  ppt's in Al-4% Ag Ag-rich ppt (fcc) in Al. size diff. bet'n Al & Ag atoms = 0.7%.  $\therefore$  coherency strain = negligible  
In Al-Cu size diff. larger, the coh. E becomes important than  $\gamma$  in finalizing the shape.

#### B. Partially Coh. PPTs

- coh. int. preferred (low. E) from int. E. standpoint.
- But when  $\alpha, \beta$  have diff xtal struc. there may be 'one plane' which provide (identical) close match.
- w/ a proper orient'n relationship  $\rightarrow$  coh. or semicoh. int. possible. and no other plane of good matching  $\rightarrow$  bounded by high E. incoh. int.

- $\gamma$ -plot. Fig 3.40

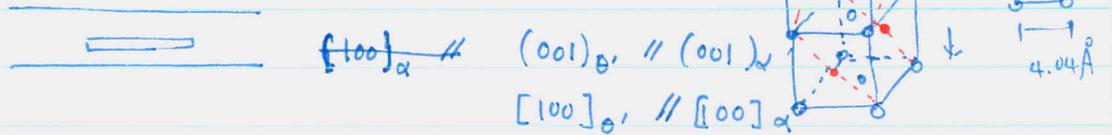


The ppt shapes in practice may deviate from this shape

- ∴ i)  $\delta$ -plot predicts the equil<sup>m</sup> shape w/ misfit  $\epsilon$ . E. effect ignored
  - ii) due to growth constraints
- ex. hep  $\delta'$  in aged Al-4wt% Ag.  grow fast.  equil shape  $\rightarrow$  due to kinetic res.



ex. tetragonal  $\theta'$  in aged Al-4w/o Cu.



$\rightarrow$  ppted on  $\{100\}_{\alpha} \rightarrow$  Widmanstätten morphology.

plate-like, lath-shape, needle shapes are also possible.

$\left. \begin{array}{l} \text{S phase in Al-Cu-Mg (laths)} \\ \beta' \quad \quad \quad \text{Al-Mg-Si (needle)} \end{array} \right\} \text{produce W. struc}$   
 due to ppt'n on the habit plane.

### 9. Incoherent Ppt's.

- when two phases completely diff. struc.  $\&$  in a random orientation.  
 $\rightarrow$  incoherent int.

- Int. E. should be high for all int. planes. the  $\delta$ -plot  $\sim$  shape  $\sim$  sphere<sup>roughly</sup>
- polyhedral shapes also possible  $\rightarrow \therefore$  faceting not necessarily mean the existence of coh. or semicoh. int.

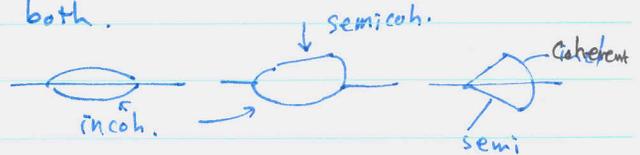
• The  $\theta$  (CuAl<sub>2</sub>) ppt incoh. in Al-Cu.  $\theta$  maintains the orient'l relationship w/ Al as  $\theta'$ . but not coherent.  $\rightarrow$  means that  $\theta$  formed was from  $\theta'$ .

D. ppts on G. B.

- the formation of interfaces w/ two diff. ly oriented grains.

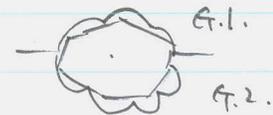
- possibility i) i) incoh to both grains.
- in interface. ii) incoh to one grain, semi, or coh. to ~~the~~ other grain
- formation iii) coh. or semi to both.

i), ii) common.



- the min. of Int. E. + int. tensions and torque balance.

the shape: superimposing the r-plots. of both grains



3.4.3. Second-Phase Shape: Strain Effects.

A. Fully coh. ppt.

- equil<sup>m</sup> shape of a coh. ppt → r-plot. when δ is small. (misfit)
- when δ exists, coh. int ↑ ΔG due to ε. (= ΔG<sub>strain</sub>) elastic strain.

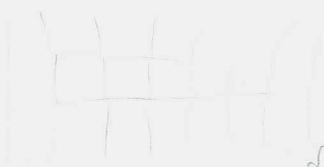
(3.35) for equil<sup>m</sup>  $\sum A_i \gamma_i + \Delta G_{strain} = \min.$

-  $a_\beta, a_\alpha$ : lattice para. of the unstrained ppt.

(3.36) unconstrained misfit  $\delta = \frac{a_\beta - a_\alpha}{a_\alpha}$

- In order to maintain coherency, the stresses at the int. distort the ppt if ppt in the form of sphere. the distortion purely hydrostatic.

(3.37)  $\epsilon = \frac{a_\beta' - a_\alpha}{a_\alpha}$   
 insitu constrained misfit

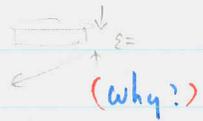


$$\begin{pmatrix} da \\ d\beta \end{pmatrix} \rightarrow \begin{pmatrix} da' \\ \alpha\beta \end{pmatrix} \quad \text{Date} \quad \text{②②}$$

$$\delta = \frac{a_\beta - a_\alpha}{a_\alpha}$$

- if the elastic moduli of the matrix & ppt are equal &  $\nu$  (poisson's ratio)  $\frac{1}{3}$

then



$$\epsilon_y = \epsilon_z = -\nu \epsilon_x = -\frac{\nu \sigma_x}{E}$$

(3.38)  $\frac{\epsilon}{\delta} = \frac{a_\beta - a_\alpha}{a_\beta - a_\alpha} = \frac{2}{3}$

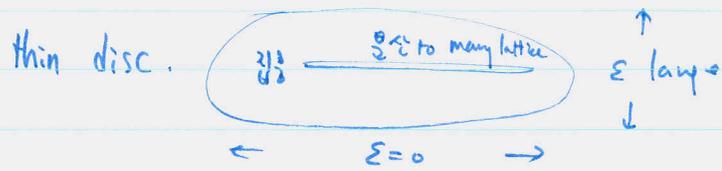
$$\epsilon = \frac{2}{3} \delta = 2\nu \delta$$

By superposition of the components of  $\epsilon_x, \epsilon_y, \epsilon_z$

$$\epsilon_x = \frac{1}{E} [\sigma_x - \nu(\sigma_y + \sigma_z)]$$

But in reality  $E_{ppt} \neq E_{mat} \therefore 0.5\delta < \epsilon < \delta$

$$\nu = -\frac{\epsilon_y}{\epsilon_x} = -\frac{\epsilon_z}{\epsilon_x}$$



- the total elastic E. = f (shape, elastic prop. of matrix & ppt.)

if the matrix is "isotropic" &  $E_{ppt} = E_{matrix}$

①  $\Delta G_s \neq f(\text{shape of ppt})$

$$\mu = \frac{\tau_{xy}}{\gamma_{xy}} = \frac{E}{2(1+\nu)}$$

(3.39) w/  $\nu = \frac{1}{3}$

$$\Delta G_s = 4\mu \delta^2 \cdot V$$

(why?)

shear modulus vol. of unconstrained hole in the matrix.

$\therefore \Delta G_s \propto \text{vol. of ppt.}$ ,  $\Delta G_s \uparrow$  as  $\delta^2 \uparrow$ .

② if " $E_{ppt} \neq E_{matrix}$ " but isotropic

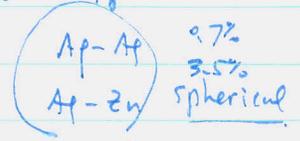
③  $\Delta G_s$  min for a sphere if ppt is hard for a disc. " soft

④ if anisotropic. (ex. most metal are soft in  $\langle 100 \rangle$  direction hard in  $\langle 111 \rangle$ )

Then the shape w/ a min  $\Delta G_s$  is a disc.  $\{100\}$  matrix most of the misfit is then accommodated in the soft dir

- when  $\delta < 5\%$   $\Delta G_{strain}$  effect less important than  $\Delta G_s$

spherical zones minimize the  $\Delta G_{total}$



when  $\delta > 5\%$ , Al-Cu (10.5%), the small increase in  $\delta$  caused

by choosing a disc shape is more compensated by the reduction

in coh. strain E. ( $\Delta G_s$ ).

### B. Incoherent Inclusions.

① no coherency strain for matching two lattices.  $\therefore$  no bonding.  
 But Still misfit strain can arise if the inclusion is the wrong size for the hole.

-  $\delta$  has no meaning here, vol misfit  $\Delta$  was considered.

(3.40)  $\Delta = \frac{\Delta V}{V}$   $v$ : vol. of unconstrained hole  
 $\Delta V$ :  $V$  - unconstrained inclusion.

- For a coh. spherical inclusion  $\Delta = 3\delta$   
 for non-coh. sphere the # of lattice sites within hole not preserved and  $\Delta \neq 3\delta$



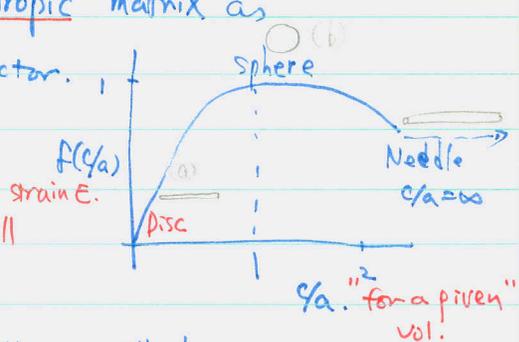
$\Delta = \frac{d_2 - d_1}{d_1}$   
 $d_2 = d(1 + \delta)$   
 $\Delta = \frac{(nd)^2(1 + \delta)^3 - \frac{4}{3}\pi(d_1 n)^3}{\frac{4}{3}\pi(d_1 n)^3}$   
 $= 3\delta + 3\delta^2 + \delta^3$

② this elastic prob. solved for spheroidal inclusions.

(3.41)  $\frac{x^2}{a^2} + \frac{y^2}{a^2} + \frac{z^2}{c^2} = 1$

- Nabarro gives the elastic strain  $\epsilon$  for a homogeneous incompressible inclusion in an isotropic matrix as

$\Delta G_s = \frac{2}{3}\mu \Delta^2 \cdot V \cdot f(\frac{c}{a})$  shape factor,  $\epsilon$  in the matrix



- For elastic anisotropy is included  $\rightarrow$  still valid w/ small changes in values.

① the equil<sup>m</sup> shape of an incoh. inclusion will be a disc (oblate spheroid) w/  $c/a$  value balanced w/ the opposing effects of  $\gamma$  and  $\epsilon \cdot E$ .

② when "(strain)  $\Delta$  is small",  $\gamma$  effects dominate and the inclusion will be roughly spherical.

C. Plate-like PPTs.



- Fig 3.51 coh. broad faces and incoh. or semicoh. edges.  
misfit across the broad faces → coh. strains // to the plate  
no coh. strain across the edges.
- In-situ misfit ↑ as the plate thickness ↑. → cause greater strain to the matrix & higher shear  $\sigma$  at the corner of the plates.
- Eventually, the broad faces tend to be semicoh. & the ppt. behaves as an incoh. inclusion w/ little misfit  $\epsilon, E$ .  
ex.  $\theta'$  in Al-Cu. (coh or <sup>Semi</sup>semicoh.)

3.4.4. Coherency Loss.

Coh. PPTs → low  $\gamma$  but in the presence of misfit → assisted w/ a coh.  $\epsilon, E$ .  
incoh. ppt → high  $\gamma$  but no coh.  $\epsilon, E$ . ( $\Delta G_{\epsilon}$ ).

-  $\Delta G$  of a xtal containing a fully coh. spherical ppt.

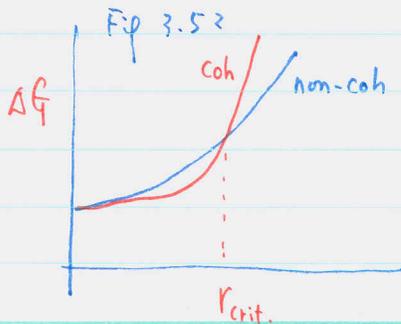
two contributors i) the coh.  $\epsilon, E$  ( $= \Delta G_{\epsilon}$ ) (3.39)

ii)  $\gamma_{ch}$ . ( $= \Delta G_{\gamma}$ )

(3.43)  $\Delta G_{coh} = 4\mu\delta^2 \cdot \left( \frac{4}{3}\pi r^3 + 4\pi r^2 \cdot \gamma_{ch} \right)$  ( $= \Delta G_{\epsilon}$ )



(3.44)  $\Delta G_{incoh} = 0 + 4\pi r^2 (\gamma_{ch} + \gamma_{struc})$  if no constrained vol.  $\Delta \epsilon = 0$



coherency loss misfit  $\epsilon, E = 0$  but  $\perp$  generation

$\Delta G_{coh} = \Delta G_{incoh}$

due to misfit  $I_s$  (distortions)

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

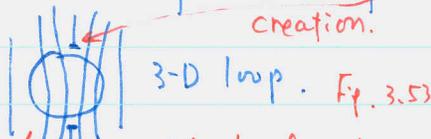
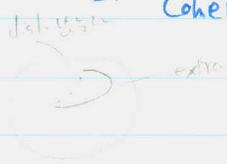
If  $\delta$  is small, semicoh interface will be formed

← coh → ← incoh → 서울대학교 공과대학 무기재료공학과 w/  $\gamma_{st} \propto \delta$   
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for a given  $\delta$  ( $\frac{d\Delta G}{dr}$ )

(3.46)  $\therefore r_{crit} \propto \frac{1}{\sigma}$

- If a coh ppt grows  $\rightarrow$  lose coherency when  $r > r_{crit}$ .  
this requires the intro. of  $\perp$  loops around the ppts.  $\rightarrow$  difficult to have  $\therefore r_{observed}$  for coh. ppt  $\gg r_{crit}$ .

- Coherency loss (a) for a  $\perp$  loop to be punched out at the interface creation. in Fig 3.54



$\rightarrow$  should exceed the  $\sigma_{th}$  of matrix (Peir's force)

(3.47) -  $P_s = 3\mu\epsilon$  the constrained misfit  $\epsilon$ . in-situ.  $\neq f$  (ppt size) (why?)

(3.48)  $\epsilon_{crit} = 0.05$  estimation of  $\epsilon_{crit}$  which cause the  $\sigma_{th}$  of matrix to be exceeded

$\rightarrow$  ppt가 일정한  $r_{crit}$  보다 클수록 가능.

coherency loss (b) Matrix  $\perp$  wraps around the ppt. (HRing slip) release the strain



can happen by mech. deformation.



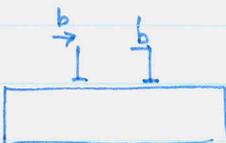
(c) disc type ppt. high  $\sigma$  at the edge to generate  $\perp$ s by exceeding  $\sigma_{th}$  of the matrix requires

(d)  $\perp$  loop created inside ppt. (disc type ppt.)  
 $\therefore$  vac. condensation - forcing a prismatic  $\perp$  loop

### 3.4.5. Glissile Interface.

- Semicoh. interface.

i)



$\vec{b}$  of misfit  $\perp$ s  $\parallel$  to the interfacial plane epitaxial misfit.

Glide of the int.  $\perp$ s don't cause the interface to advance.

is non-glissile.

total strain  $\gamma$   $\frac{2b}{a}$  extra plane (Simple case)

① - plissite semicoch. interfaces which can advance by the glide of  $\perp$ s. if the  $\perp$ s have a  $\vec{b}$  that can glide on matching planes in the adjacent lattice.

interface.

slip plane  $\beta$

slip plane  $\alpha$

extra plane

- slip plane must be continuous across the interface  
don't have to be  $\parallel$ .  
cause  $\alpha$  to be sheared into  $\beta$ .

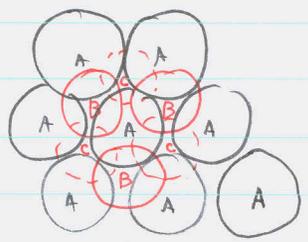
② - Shockley partial  $\perp$ s. complex  
total strain  $\gamma$   $\frac{2b}{a}$  extra plane  $(\frac{2b}{a})$

- stacking of fcc & hcp

fcc ABCABC (111)  $\frac{a}{6} \langle 11\bar{2} \rangle$

hcp ABAB (0001)  $\frac{a}{6} \langle 11\bar{2} \rangle$  close-packed direct

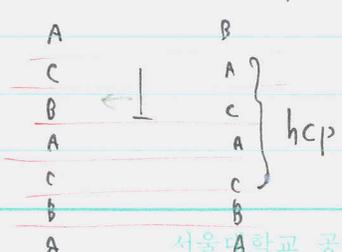
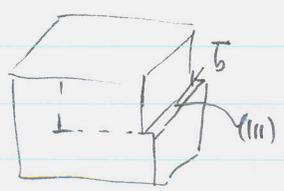
for fcc the distance bet'n B & C sites corresponds to  $\frac{a}{6} \langle 11\bar{2} \rangle$



$$a_0 [10\bar{1}] \rightarrow \frac{a_0}{6} [2\bar{1}1] + \frac{a_0}{6} [11\bar{2}]$$

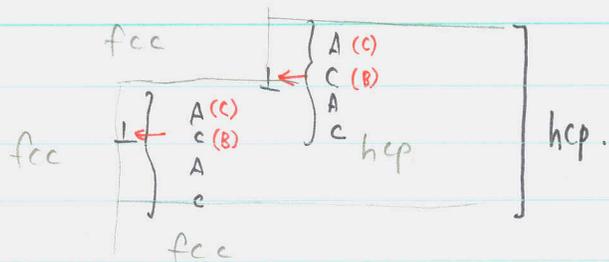
on (111) all atoms in  $\beta$ -sites are moved to C-sites & " in A-sites move to B-sites by  $\vec{b} = \frac{a}{6} \langle 11\bar{2} \rangle$  called Shockley partial  $\perp$ .

→ This causes disruption the crystal lattice, resulting in a S.F. (stacking fault) over the area of glide plane swept by the dislocation.

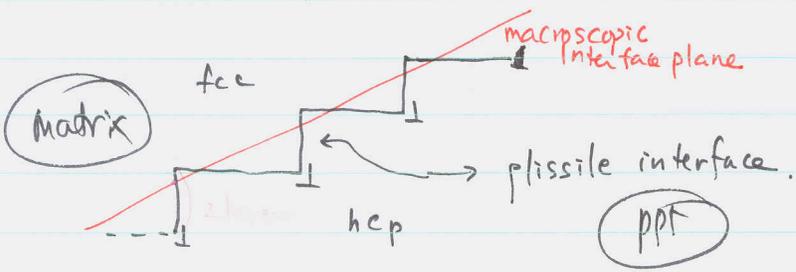


∴ compared to thermally stable fcc, hcp is a region of high f.e.

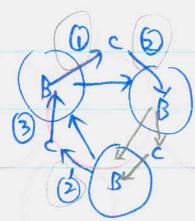
Fig. 3.60



If another partial passes hcp. s.f is now extended by a further two layers.



- If the  $\perp$  network slides into the fcc klat it results in a transf. of fcc  $\rightarrow$  hcp. The reverse motion hcp  $\rightarrow$  fcc. transf.
- Macroscopically the interfacial plane lies at an angle to (000 $\bar{1}$ ) or (111) if can be irrational.
- Microscopically, stepped into "planar coh. facets" parallel to (111)<sub>fcc</sub> and (0001)<sub>hcp</sub> with a step height the thickness of two closed-packed layers.
- plissile disl. interfaces can change the shape of the klat.
- if three shockley partials. all work in equal #, no overall shape change

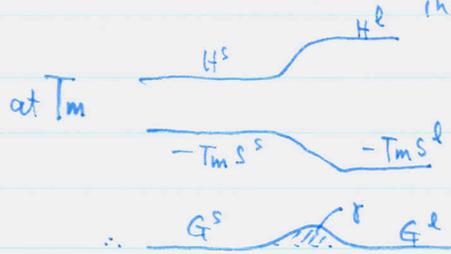


### 3.4.6. Solid / Liquid Interfaces

s/v interface - similar to s/l interface in interpretation & ideas  
 ↓ low p                      ↓ high p → make differences.

① two basic type of s/l interfaces.

- i) atomically flat c-p interfaces. : s-l transition occurs over a  
 (narrow trans. zone) atom layer thick. → faceted atom, smooth, sharp interface.
- ii) atomically diffuse interface. → s-l transition over a several  
 atom layers. - ∴ gradual weakening of the interatomic bonds.  
 increasing disorder across the interface.



rough, nonfaceted : spherical

- thermo terms changes across the interf.  
 at  $T_m$ .

Since s/l equil<sup>m</sup>  $G^s = G^l$ .

$$G^{xs} = \gamma_{SL}$$

② Choice of the interface : to minimize the  $\gamma$

i) Jackson's <sup>theory</sup> ~~experimental~~ approach.

idea : opt. atomic arrangement =  $f(L_f/T_m)$ .

critical value

$$L_f/T_m \approx 4R.$$

if  $L_f/T_m > 4R$  interface flat.

if  $L_f/T_m < 4R$  " diffuse - most metal's  $L_f/T_m \approx R$  (diffuse)

- some intermetallic compounds & Si, Ge, S.

+ non-metals

$L_f/T_m \gg R$  (flat)

this model  
 if extended to s/v =  $f(L_s/T_m)$

(i) the broken-bond model.

the atoms in the interface - roughly half bonded to the solid  
and half to the liquid

$\therefore$  interface enthalpy  $\sim 0.5 L_f/N_A$  /atom. (cf. surface E  $E_{sv} = 0.25 L_s/N_A$ )

$\leftarrow$  this: experimentally o.k. since  $\gamma_{SL}$  (measured)  $\sim 0.45 L_f/N_A$   
accidental (fortuitous)  $\leftarrow$  for most metals.  
 $\therefore$  entropy effects should be taken into account.

- Table 3.4.  $\rightarrow \gamma_{SL}$ : determined by indirect method. for homo. nucleation

Table 3.2 & 3.3  $\rightarrow \gamma_{SL} \approx 0.30 \gamma_b \sim 0.45 \gamma_b$

$\leftarrow$  (3.6)  $\gamma_{sv} = 0.15 L_s/N_A$ .

$\rightarrow \gamma_{SL} \approx 0.15 \gamma_{sv} \leftarrow \gamma_{sv}$

-  $\gamma_{sv} > \gamma_{SL} + \gamma_{LV}$  empirical relationship.

$\rightarrow$  meaning: energetically favorable for the surface to melt & have s/L & L/V interfaces instead of s/V interface.

### 3.5. Interface Migration

- phase transf. occurs by nucl. & growth process

i.e.  $\beta$  forms at a certain sites within  $\alpha$  (parent) during nucleation (interface created) then the  $\alpha/\beta$  interface "migrate" into the parent phase during growth.

- two type of interfaces ( $\alpha/\beta$ ): glissile and non-glissile.

① glissile: ① by  $\perp$  glide  $\rightarrow$  results in the shearing of the parent lattice into the product ( $\beta$ ).

② motion (glide) insensitive to temp.  $\therefore$  athermal migration

- non-glissile (most of the case): migration by random jump of individual atoms across the interface (similar to h-angle p.b. migration)
  - thermal activation  $E$  needed.  $\therefore$  sensitive to temp.

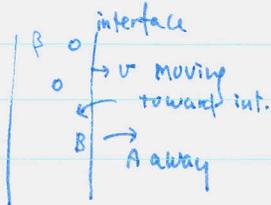
A. Hetero Transf.

- Classifying nucleation and growth transformation. (=hetero. transf.)
  - Transf. by the migration of a glissile interface - military transf.
  - the uncoordinated transfer of atoms across non-glissile inter- civilian transf.

\* military transf.: the nearest neighbors of any atom are unchanged  
 $\therefore$  the parent & product phases - the same comp., no diffusion involved (Martensitic transf. mech twins).

\* Civilian transf.: diff comp. bet'n parent & product  
 i) if no comp. change ( $\alpha \rightarrow \gamma$  transf. in Fe) the new phase grows as fast as the atoms can cross the interface  $\rightarrow$  called interface controlled: a very small conc. grad. sufficient to have flux  
 ii) if diff. comp. growth will need l-range diffusion.

Fig 3.66



if interfacial rxn is fast (easy transfer across the interface), the growth of product ( $\beta$ ) is controlled by diffusion of B & A  $\rightarrow$  called diffusion controlled.  
 (ex. solid'n & melting)

- if both process (diff. & interfacial rxn rate): a similar rate  
 - mixed control.

- Table 3.5  
Summary.

- "non-glissile" int. includes s/e & s/v, s/s interfaces (coh. incoh. semicoh).

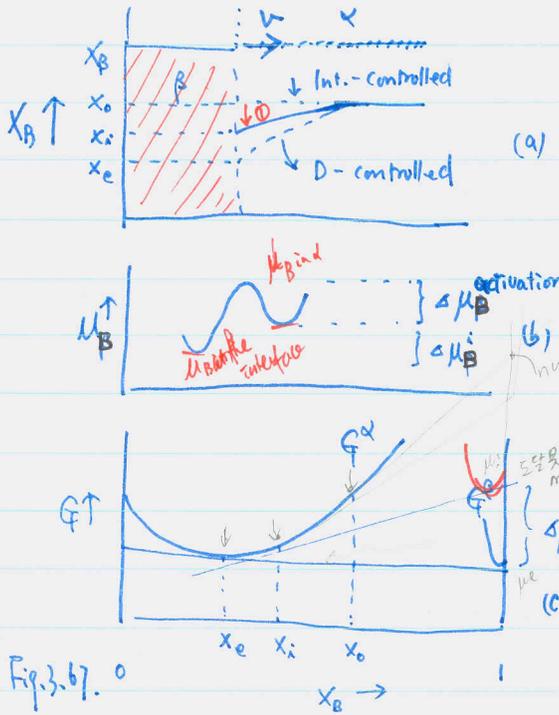
Heterogeneous Transf.

← don't occur by the creation and migration of interface (Spinodal decomp., Ordering Transf.) - Chap. 5.

Come to me, all you who are weary and burdened, and I'll give you <sup>rest</sup> 31  
 Take my yoke upon you and learn from me, for I am gentle and humble in heart,  
 and you will find rest for your souls. For my yoke is easy and my burden is light.

### 3.5.1. Diff-controlled and Int-controlled Growth.

(11:28-30)



-  $\beta$  ppt (almost pure B) grows behind a planar interface into A-rich  $\alpha$  of  $x_0$  composition.

- $\alpha$  near interface: B depletes  $x_i \rightarrow x_i < x_0$  (bulk conc.)
- $\beta$  growth requires  $\Delta\mu_B^i$  driving force.

the origin of the d.f. (Eq 3.67C)  
 for growth:  $x_i$  must be greater than  $x_e$ .

w/ net flux of B (Section 3.3.4). (3.21)  
 the interface vel.  $v$ .  $v = M \cdot \frac{dG}{V_m}$

(3.49)

$$v_i = M \cdot \frac{\Delta\mu_B^i}{V_m} \quad \text{where } M \text{ is interface mobility.}$$

The corresponding flux across the interface.  $V_m$  is molar vol. of  $\beta$ .

$$(3.50) \quad C_B = \frac{x_B}{V_m} \quad J_B^i = G_B v_i = -M \Delta\mu_B^i x_B / V_m^2 \quad [\text{moles of B} / \text{m}^2 \cdot \text{sec.}]$$

Based on the conc. grad. in the  $\alpha$  phase.

a flux of B atoms towards the interface =  $J_B^\alpha$

$$(3.51) \quad J_B^\alpha = -D \left( \frac{\partial C_B}{\partial x} \right)_{\text{interface}}$$

at a s. state (3.50) · (3.51) must be balanced.

$$(3.52) \quad J_B^i = J_B^\alpha$$

(interface mobility)

① If  $M$  is  $\uparrow$  (very high), e.g. an incoherent interface,  $\Delta\mu_B^i \ll kT$   
 $x_i \approx x_e$  local equil.

the interface moves as fast as diffusion allows,  $\therefore$  diffusion control.

- the growth rate can be expressed as a fn of time

by solving (3.50)(3.51) w/ b.c.  $x_i = x_e, x_B(\infty) = x_0$ .

Mobility (M)

② If the ~~col.~~ mobility of the interface is low, it need a chem. grad. ( $\Delta\mu_B^i$ ) and there will be a departure from local equilibrium at the interface

$X_i$  will satisfy eg. (3.52)  $J_B^i = J_B^v$

then the interface will migrate under mixed control.

③ In the limit of a very low mobility  $X_i \approx X_0$ ,  $(\frac{\partial C}{\partial x})_{int.} = 0$  : interface control

By ✓

- In a dilute or ideal solution, the d.f.  $\Delta\mu_B^i$  exp(-x) ≈ 1-x

$\mu_B^i - \mu_B^e = RT \ln \frac{X_i}{X_e}$  (Comp. vs.  $\Delta\mu_B$  chap. 2).  
 $\Delta\mu_B^i = RT \ln \frac{X_i}{X_e} = \frac{RT}{X_e} (X_i - X_e)$  when  $(X_i - X_e) \ll X_e$ .  
 $\ln(1 + \frac{X_i - X_e}{X_e})$

∴ the rate (v.) of the interface <sup>that</sup> moves under interface control  $\propto (X_i - X_e)$

∴ (3.49)  $v_i = M \cdot \Delta\mu_B^i / V_m \propto (X_i - X_e)$  ∴  $J = C (X_i - X_e)$

and  $X_i \approx X_0$   $\approx C(X_0 - X_e)$

④ - Why interface control should occur when  $\alpha, \beta$  have a diff. comp.

① diffusion control: long-range diffusion involving many atom jumps  
interface rxn involves only one jump

Activation E for Diffusion across the interface <sup>is not likely greater than</sup> A.E. thru lattice.

∴ interface rxn rapid. → ∴ diffusion controlled

Interface control:

② Eg. (3.22)' for an interphase interface w/  $\Delta\mu_B^i$  replacing  $\Delta G$ .

(3.22)  $M = \left( \frac{A_2 N_A V_m^2}{N_A R T} \exp\left(\frac{\Delta S_i^a}{R}\right) \right) \exp\left(-\frac{\Delta H_i^a}{RT}\right)$  → g.b. <sup>is not likely greater than</sup>

① "neglect the accommodation factor". A: prob. that an atom crossing the boundary will be accommodated on arrival at the new phase

$A \approx 1$  for incoh. interfaces, diffuse s/l interfaces

$\neq$  h-a g.b. - diffusion control.

$A \neq 1$  for certain types of "coh, semicoh"

### 3.5.2. Effect of Phase Struc. On the Interface Migration.

Date \_\_\_\_\_

- ① - two phase w/ diff. comp but w/ the same Xtal struc. (coh. interface. (semicoh. " )

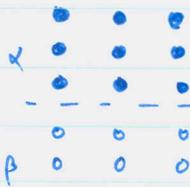


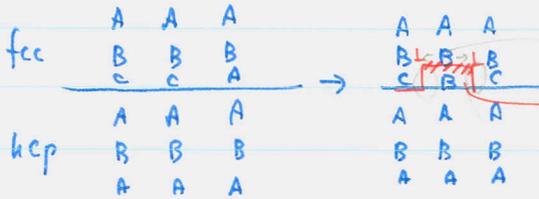
Fig 3.32a

the interface advances by the replacement of  $\alpha$  atoms w/  $\beta$  atoms

- no need for a separate int. rxn.

migration - diff. controlled. (ex. G.P zones)

- ② - " w/ two diff. Xtal struc.



of B/C split

migration by individual jump cause instability

Ch. energy, unstable conf.

B/C split

low accommodation factor  
low mobility.

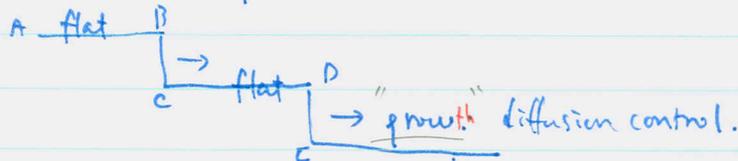
- B on B. a loop of Schockley partial  $\perp$  around the B  
 $\therefore$  forced back to its original positions.

Effect of Surface Smoothness

this happens to ① s/v or ② smooth s/l interfaces  
③ coherence of semi-coh. interface w/ diff. struc. (Xtal) but w/ less change. (less extent)

+ possibility for a single atom to attach itself to a flat close-packed interface is low. ( $\because$  increase surface E.) very low A, M.

- way to do : ledge mechanism. (s/s, s/v interface)



- the source of new ledges is considered to be heterogeneous nucleation "at the point of contact w/ another ppt."

- nucleating "new ledges"  $\rightarrow$  interface control.  $equil^m$

\* The mechanism of interface migration influences the shape of 2nd phase

inclusions (①  $D_i/D_c$  of bounding interfaces (semicoh.)

+ ② the relative rates at which the coh. & incoh. interface migrates. (ex. if problems of ledge nucleation  $\rightarrow$  easy growth of ledge)

controls  $equil^m$  shape

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