

Chap. 5. Diffusional Transf. in Solids.

- The most of phase transf. occurs by thermally activated atomic movement

- types of phase transf.

a) ppt'n reaction



metastable supersat'd solid sol'n.

more stable than α' , w/ the same Xtal struc as α'
or a stable or metastable.

b) Eutectoid transf. $\gamma \rightarrow \alpha + \beta$

(w.r.t Temp.)

the replacement of a meta. phase (γ) w/ a more stable mixture of two ($\alpha + \beta$) phase.

(a), (b) involves the formation of phases w/ a diff. comp. to the matrix:
requires long-range diff.

c) Ordering rxn

(disordered)



d) massive transf.



(stable or meta.)

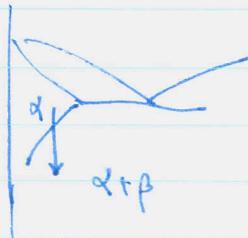
no change in comp. but in Xtal
→ cooling rate dependent !!

e) polymorphic



(c), (d), (e) proceed w/o any comp. change or l-r diffusion

1. Homo Nuclein in Solids.



proceeds : i) B in α diffuse to form a small cluster of β comp.
then, ii) the cluster rearrange in to β Xtal struc.
→ α/β interface created. → needs activation.

$$\text{In solidification of pure metals} \quad N_{\text{hom}} = f_0 C \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (4.12)$$

p19) \hookrightarrow depends on vib. freq. \Rightarrow act. energy for diffusion in liquid
 ③ the surface area of the crit. nuclei.

(2)

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surface F. increase ($\sum A_i Y_i$) :: varying value for coh. incoh. etc.

$$(5.5) \quad \therefore \Delta G = -V \Delta G_v + A\gamma + V \Delta G_s$$

$\xrightarrow{G \rightarrow \alpha + \beta}$ vol. free E reduction.

\downarrow misfit strain E.

(a vol. of β)

ΔG_s / unit vol. of β .

similar to that for the formation of a solid nucleus in liquid.

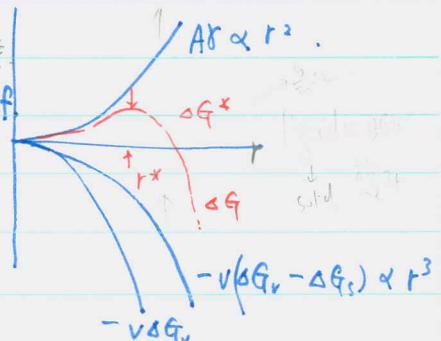
Assuming that γ is const. & nucleus is spherical.

$$(5.6) \quad \Delta G = -\frac{4}{3}\pi r^3 (\Delta G_v - \Delta G_s) + 4\pi r^2 \gamma$$

\hookrightarrow reduce the effective d.f.

differentiate (5.6)

$$\frac{d\Delta G}{dr} = -4\pi r^2 (\Delta G_v - \Delta G_s) + 8\pi r \gamma = 0$$



$$(5.7) \quad \therefore r^* = \frac{2\gamma}{(\Delta G_v - \Delta G_s)}$$

$$(5.8) \quad (5.6)(5.7) \quad \therefore \Delta G^*_{\alpha \beta} = \frac{16\pi r^* \gamma^2}{3(\Delta G_v - \Delta G_s)}$$

similar to the case for solidification

the conc. of crit.-sized nuclei C^*

$$(5.9) \quad C^* = C_0 \exp(-\Delta G^*/kT) \quad \text{where } C_0 = \# \text{ of atoms / unit vol.}$$

the nucleation rate for hom.

(receive an atom from α)

each nucleus become supercritical at

$$(5.10) \quad N_{\text{hom}} = f C^*$$

where f nuclei / second

f depends on the surface area of the

vib. freq. for the nucleus and the rate at which "diffusion" occurs
 + the area of crit nucleus

$$f = w \exp(-\Delta G_m/kT)$$

determining factor.

$$(5.11) \quad \therefore N_{\text{hom}} = w C_0 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{for this is } \Delta G_v$$

$$\begin{aligned} \Delta G^* &= \Delta f \\ \Delta f &\approx \Delta G^* \text{ (unit)} \end{aligned}$$

Compare w/ (4.12)

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$$w, G_m = \text{const.}$$

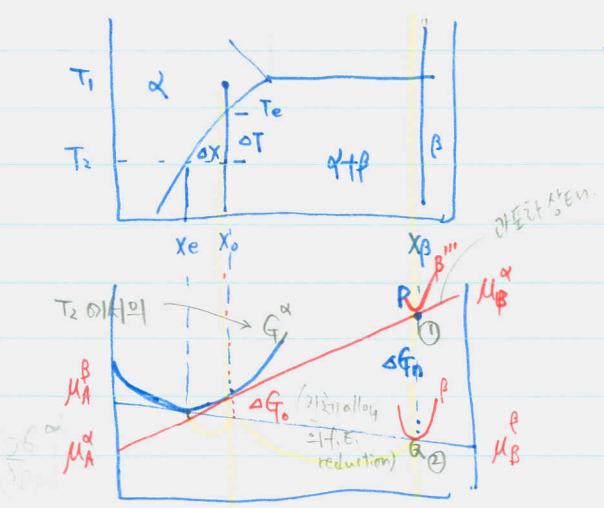
activation for nuclear growth

* $\Delta G_{\text{f.v.}}$: for nucleation.



(3)

Alloy X_0 (solutn treated at T_1) cooled to T_2
 \rightarrow supersaturated w/ B \rightarrow ppt β .



After the completion of transf. $\alpha \rightarrow \alpha + \beta$

f.E. of the alloy will be reduced by $\Delta G_0/\text{mol}$.
but ΔG_0 is not d.f. for nucleation.
 \because the composition of the first nuclei did not
change = composition from X_0 .
 $\rightarrow \Delta G^*$ is the total d.f. for the transformation.

* the f.e. released / mole of nuclei can be calculated as below.

taken out of

① if X_B^β of β (the nucleus comp.) formed from α , then the reduction in f.e. (P pt.)

$$(5.12) \quad \Delta G_1 = \mu_A^\alpha X_A^\alpha + \mu_B^\alpha X_B^\alpha \quad (X_A^\alpha + X_B^\alpha = 1) \quad \text{"(per mol } \beta \text{ removed)"}$$

② if these atoms are now rearranged into the β xtal stuc.

the total f.e. will increase by (Q pt.)

$$(5.13) \quad \Delta G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta \quad \text{"(per mole } \beta \text{ formed)."} \quad \text{d. 2}$$

$$(5.14) \quad \therefore \Delta G_n = \Delta G_2 - \Delta G_1 \quad (\text{PQ}).$$

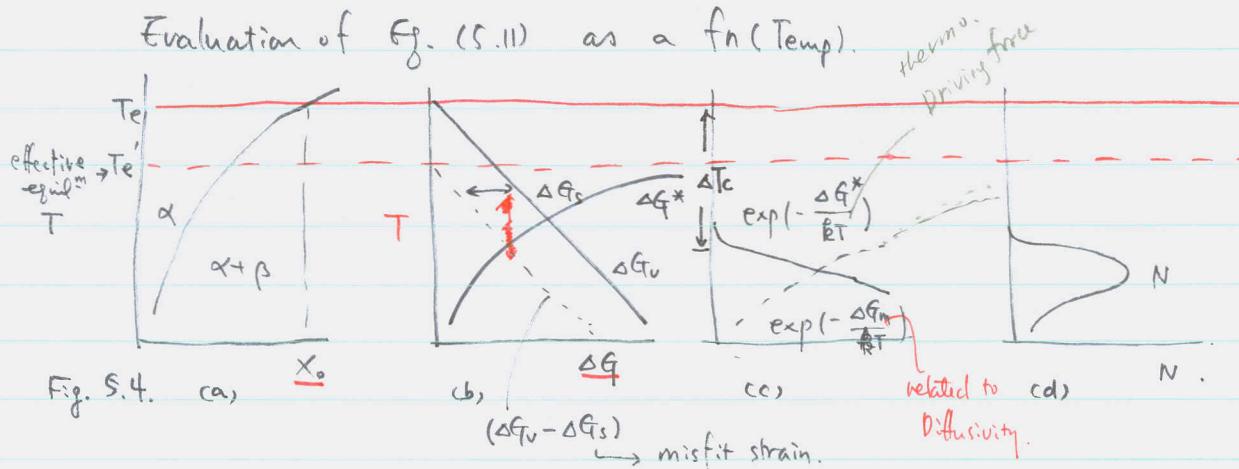
$$(5.15) \quad \boxed{\Delta G_{\text{f.v.}} = \frac{\Delta G_n}{V_m}} \quad / \text{unit vol. of } \beta.$$

(5.16) for dilute soln $\underline{\Delta G_{\text{f.v.}}} \propto \underline{\Delta X} (= X_0 - X_e)$, or from Fig. 5.3 (a)

$$= \frac{L_v \alpha T}{T_m} \quad \left. \right\} \alpha \Delta T$$

* Then N_{homo} ?

Evaluation of Eq. (5.11) as a fn(Temp).



w/ Known $(\Delta G_v - \Delta G_s)$, $\Delta G^* = \frac{16\pi r^2}{3(\Delta G_v - \Delta G_s)^2}$ (5.8) Can be obtained.

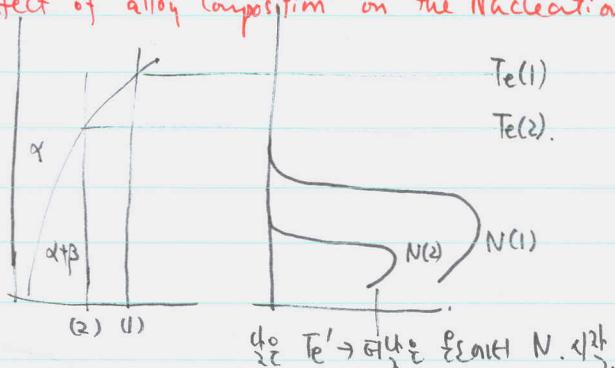
- i) $\exp(-\frac{\Delta G^*}{kT})$ is the potential/conc. of nuclei. $\exp() \rightarrow 0$ until T_e' .
- ii) $\exp(-\frac{\Delta f_m}{kT})$ is essentially the atomic mobility. $\Delta f_m \text{ const} \Rightarrow \exp() \downarrow$ as $T \downarrow$
- iii) homo. nucleation rate.

if $\Delta T < \Delta T_c$, N negligible ($\because \Delta G_v$ too small) \rightarrow max. N \rightarrow from intermet temp.

if $\Delta T \gg \Delta T_c$, N again " (\because diffusim too slow).

⇒ * The effect of alloy Composition on the Nucleation rate

Fig. 5.5.



reduction in
w/o considering the
conc. of B solute.

Assumptions for the discussion above i) N rate const. but \nearrow

ii) spherical w/ equl comp. but \nearrow dominant.

Homo.
Nucleation will be done by nucleus w/

\therefore incoh. homo. nucl. impossible \because incoh. nucl. \rightarrow high T

the min. ΔG^* coh. interface $\rightarrow \Delta G^* \text{ small} \rightarrow$ coh. homo nucleation feasible

↳ increase ΔG_s decrease in γ →
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↑ effects more compensating for the increase in ΔG_s .

$$\Delta G^* = \frac{16\pi r^2}{3(\Delta G_v - \Delta G_s)^2}$$

In most systems α, β have diff. xtal struc. \therefore incoh. interface

\rightarrow homo. nucle. of β impossible.

Thus, if starts w/ $\beta' \rightarrow$ coherent nucleus. \rightarrow then β .

used to check
the theories of
homonucle.

$$\Delta T_c = 40^\circ\text{C}$$

- Homo. nucleation sys.

Cu - 1-3% Co size diff. $< 2\%$. small coh. strain $\gamma = 200 \text{ mJ/m}^2$

Ni - Al. ppt. Ni_3Al (δ phase) in Ni " $\gamma = 30 \text{ mJ/m}^2$

$$\Delta T_c = 10-20^\circ\text{C}$$

5.2. Hetero. Nucl.

almost always. - Nucl. in solids.

nucleation sites - defects (vac. disl. g.b. stacky faults, inclusions free surfaces).

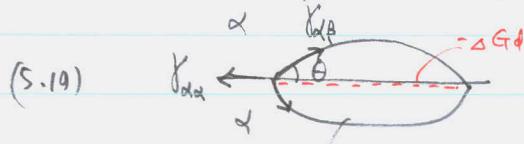
If the creation of a nucleus results in the destruction of a defect ΔG_d will be released \rightarrow reducig ΔG^*

$$\Delta G_{\text{het}} = -V(\Delta G_v - \Delta G_s) + A\gamma - \Delta G_d$$

A. Nucl. on G.B.

the optimum embryo shape to min. $\sum A_i \gamma_i$. (total int-f. E).

ex. the optimum shape for an incoh. g.b. nucleus - spherical cap.



$$\cos \theta = r_{\text{dd}} / 2r_{\text{gb}}$$

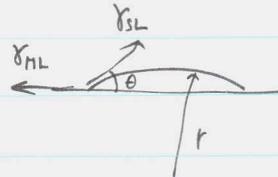
assume γ_{gb} isotropic.

$$(5.20) \quad \Delta G = -V \Delta G_v + A_{\text{dd}} \gamma_{\text{gb}} - A_{\text{dd}} r_{\text{dd}} \quad \Delta G_d$$

(

g.b. nucleation analogous to solid'n on a substrate.

$$(4.18) \quad r^* = \frac{2\gamma_{SL}}{\Delta G^*}$$



Similary

$$(5.21) \quad r^* = \frac{2\gamma_{\alpha\beta}}{\Delta G^*}$$

the activation E. barrier for hetero. nucl.

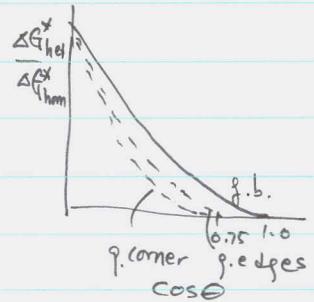
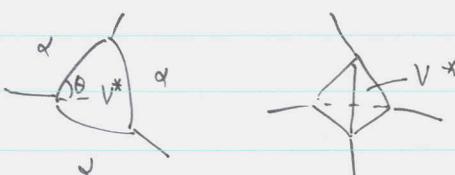
$$(5.22) \quad \frac{\Delta G_{het}^*}{\Delta G_{hom}^*} = \frac{V_{het}^*}{V_{hom}^*} = s(\theta) \quad \text{where } s(\theta) = \frac{1}{2} (2 + \cos\theta)(1 - \cos\theta)^2$$

To lower ΔG_{het}^* . "cosθ" plays the main role $\cos\theta = \frac{\gamma_{\alpha\alpha}}{2\gamma_{\alpha\beta}}$

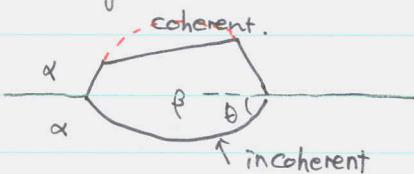
V^* , ΔG^* can come down further by nucleating on a grain edge or grain corner

- Dependence of $\frac{\Delta G_{het}^*}{\Delta G_{hom}^*}$ on $\cos\theta$.

Fig. 5.7.



- h-a g.b. : effective nucl. sites for incoh. ppt w/ high $\gamma_{\alpha\beta}$.



if it can form low. E. facets at g.b.

then V^* , ΔG_{het}^* further reduced.

→ the nucleus will have an orientat'l relationship w/ one of the grains. → easy to form

- In similar way to g.b. defects such as inclusion/matrix interfaces stacking faults, free surface behave.

less potent "lower E. faults Compared h-a g.b."

B. Dislocations

- lattice distortion near Is . help nucleation by reducing ΔG_s to ΔG^*
 $(\alpha_p < \alpha_d)$

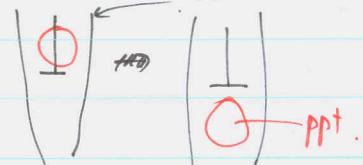
coh. nucleus w/ a neg. misfit,

→ smaller volume than the matrix, can reduce ΔG^* , form here

coh. nucleus w/ a pos. misfit

form under the extra plane.

$$\downarrow \Delta G^* = \frac{16\pi r^2}{3(\Delta G_v - \Delta G_s)} \uparrow$$



- Is : not effective for reducing γ contribution to ΔG^* w/ neg. w/ pos. misfit ppt.

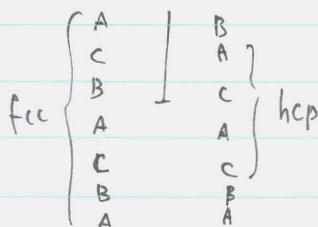
this means that nucl. on Is usually requires a good matching btwn

ppt & matrix at least one plane, so that $\text{bwE}(\gamma)$ coh. or semcoh. interface can form.

- If ignore the strain effect. the min. ΔG^* obtained from the equil^n shape of γ -plot.

C. S.F.

- In fcc a dislocation split. $\frac{a}{2} [110] \rightarrow \frac{a}{8} [121] + \frac{a}{8} [211]$



giving stacking fault on $(1\bar{1}\bar{1})$ separated by Schottley. partials.

S.F.: 4 hcp layer. (close-packed)

∴ becomes potent sites for an hcp ppt.

ex. γ' (hcp) in Al-Ag on S.F.

Nucleation: by the diffusion of Ag to the S.F.

$\therefore (0001)_\gamma // (\bar{1}\bar{1}\bar{1})_\gamma$

$[\bar{1}\bar{2}\bar{0}]_{\gamma'} // [\bar{1}\bar{1}\bar{0}]_\gamma$. good matching i.e. interface.

ex. in annealed sample: \downarrow p (density) sometimes high.

\therefore ppt'n Nb(CN) on Is in α -Fe.

D. Excess Vacancies

- quenched samples (age-h alloys) from h. temp. → retains excess vac.
→ assists nucleation by ↑ diffusion speed. or by relieving misfit E.
- They work individually or collectively by grouping into small clusters
 - ΔG_d is relatively small.
the combination of conditions (low. lat. E, small vol. S.E. high d.f.)
can make nucleation possible. ~ similar to homo cond.
 - evidence for the role of vac. indirect

I. Rate of Hetero Nucl.

- in order of increasing ΔG_d (i.e. $\Delta G^* \downarrow$)

1. homo sites. 2. vac. 3. ls 4. S.F. 5. 9.b./int. b. 6. free surface.

order in the list & conc. of defects will determine

- If. the conc. of hetero nucl. sites = C_1 /unit vol.

$$(5.24) \quad N_{\text{het}} = w C_1 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \text{nuclei/m}^3 \cdot \text{s.}$$

rel. mag. of the hetero / homo. vol. nucl. rate

$$(5.25) \quad \frac{N_{\text{het}}}{N_{\text{hom}}} = \underbrace{\frac{C_1}{C_0} \exp\left(\frac{\Delta G_{\text{hom}}^* - \Delta G_{\text{het}}^*}{kT}\right)}_{\substack{\text{also important} \\ \text{big factor.}}} \quad \begin{array}{l} \text{small} \\ \text{true.} \end{array}$$

w , ΔG_m assumed the same

Unless a kernel of wheat falls to the ground and dies, it remains only a single seed. But if it dies, it produces many seeds. (9)

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$$(5.26) \text{ for g.b. nucl. } \frac{C_1}{C_0} = \frac{\delta}{D} \quad \delta: \text{b. thickness} \quad D: \text{g.s.}$$

nucl. on g.edges and corners $\frac{C_1}{C_0} = \left(\frac{\delta}{D}\right)^2$ and corners $\frac{C_1}{C_0} = \left(\frac{\delta}{D}\right)^3$

ex. 50 μm grain size w/ δ 0.5 nm $\frac{\delta}{D} = 10^{-5}$. if exp. temp exceeds 10^5 , Nhet T.
i.e.,

- At very small d. forces (if σ_{eff}^* is high) the highest nucl. rate will be from g. corner nucl.

as very the d. forces increases, g.edge. & boundary will dominate.
At high d. forces C/C_0 might dominate

$$\frac{\gamma_{\text{ad}}}{2\gamma_{\text{exp}}} = \cos\theta$$

$\cos(\theta)$ ↘ $\sin(\theta)$ ↘

- If $\gamma_{\text{ad}} / \gamma_{\text{exp}}$ is high, noticeable transf. will begin at g. corners
" smaller (g.b. is less potent) hetero nucl. less import." ↪

5.3. Ppt. Growth.

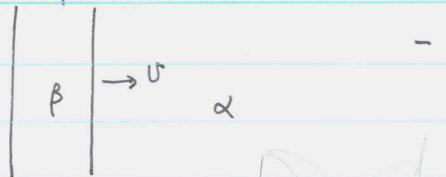
In the absence of S.E. effect, the shape of ppt determined to have min γ .
∴ resultant ppt. & growth rate (edge)

ledge mechanism. (coh. or semi-coh.) incoh → grow fast. (mobile)
(smoothly curved)

5.3.1. Growth behind Planar Incoh. Interfaces.

Normally, planar interface - semi- or coh. interface. in a matrix. (homo) hetero.
but after g.b. nucleation, planar incoh. interface possible. (i.e. ppt' n on g.b.)
(the formation of incoherent nuclei: a slab of β ppt. on a g.b.)

* the growth of Incoh. ppt on q.b (Planar).

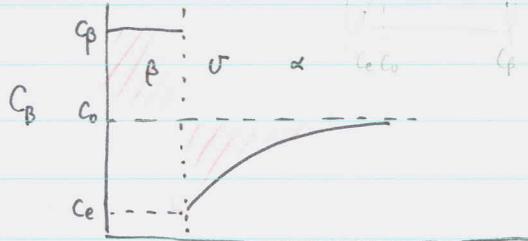


- a slab of solute-rich ppt.

Since incoh. diff-controlled growth. local equl^{ln} assumed.

(C_e, C_p)

$$v = f \left(\frac{dc}{dx} \right). \quad (j = cv = M \frac{\partial u}{\partial x} = -D \frac{\delta c}{\delta x})$$



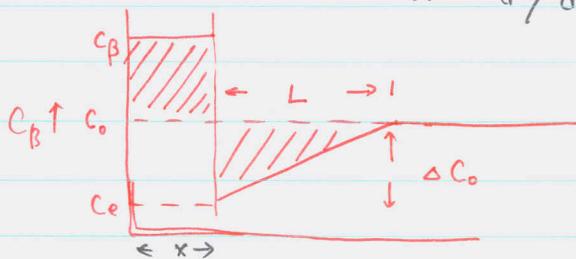
- For unit area of interface to advance dx .

$$v = \frac{dx}{dt} = \frac{\tilde{D}}{C_p - C_e} \cdot \frac{dc}{dx} \quad (5.27)$$

Fig 5.4 Diff.-controlled thickening of a ppt plate. $\{ \because (C_p - C_e) \cdot dx \cdot 1 = \tilde{D} (dc/dx) \cdot dt \cdot 1 \}$

As β grow, β has to come from a larger α region

$\therefore dc/dx$ decreases w/ time.



simplified conc. profile. $\Delta X_0 \approx x_e - x$

$$\frac{dc}{dx} = \frac{\Delta C_0}{L} \quad \Delta C_0 = C_0 - C_e. \quad (C_p - C_e)x = L \Delta C_0 / 2.$$

$$(5.28) \quad \frac{dx}{dt} = v = \frac{\tilde{D} (\Delta C_0)^2}{2 (C_p - C_e) (C_p - C_e) x} \quad \rightarrow \quad \frac{dx}{dt} = \frac{\tilde{D} (\Delta X_0)^2}{2 (X_p - X_e)^2 x}$$

if V_m is const. the $X = CV_m$.

w/ $C_p - C_e \approx C_p - C_e$ or $\frac{\partial C_p}{\partial t} / \frac{\partial C_e}{\partial t}$ (negl.)

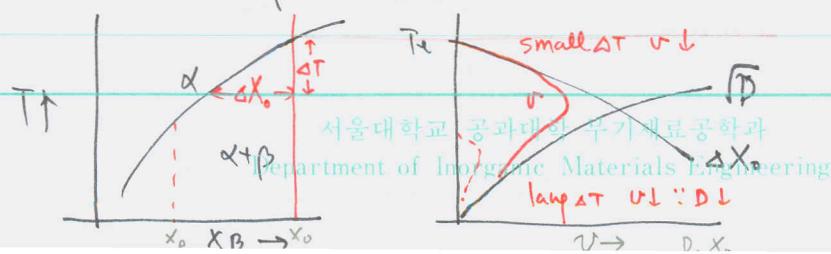
$$\int X dx = \int \frac{\tilde{D} (\Delta X_0)^2}{2 (X_p - X_e)^2} dt$$

$$\int X^2 = \frac{\Delta X_0^2}{X(X_p - X_e)^2} \tilde{D} t$$

$$(5.29) \quad X = \frac{\Delta X_0}{(X_p - X_e)} \sqrt{\tilde{D} t}$$

$$(5.30) \quad v = \frac{\Delta X_0}{2 (X_p - X_e)} \sqrt{\frac{\tilde{D}}{t}}$$

$\Delta X_0 = X_0 - X_e$ mole fraction.



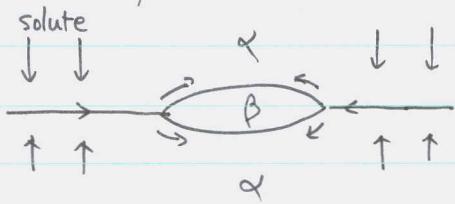
pts to note.

1. $X \propto \sqrt{\tilde{D} t}$. parabolic growth rate

2. $v \propto \Delta X_0$ supersaturation

3. $v \propto \sqrt{\tilde{D}/t}$.

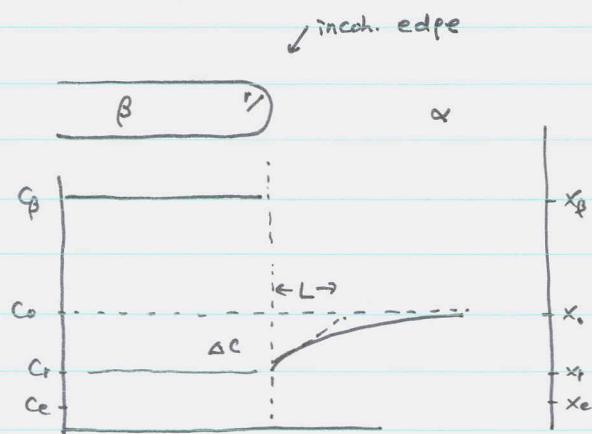
- When diff. fields of separate ppt overlap, eg (5.30) no valid. growth decelerate & and finally cease when ^{the} matrix conc. becomes X_e . (Fig. 5.17)
- The approach for planar interface : applicable to curved interfaces
 \therefore any linear dimension of a spheroidal ppt \uparrow as \sqrt{Dt}
provided all interfaces migrate under vol. diff. control.



the q.b. ppt in the form of particle grows faster than allowed by vol. diff.
 \therefore p.b. fast diffusion path.

- Growth of q.b. allotrope-morph.
 - 3 steps
 - 1) vol. diff. of solute to the q.b.
 - 2) diff thru q.b.
 - 3) diff along the α/β interface., allowing accelerated thickening.

5.3.2. Diffusion - Controlled "Lengthening" of Plates or Needles.



a plate of const. thickness w/ cylindrical curved incoh. edge of radius r .

Due to G-T effect, the equiv[≈] conc. in the matrix adj. to the edge,
 C_r
 \therefore the conc. grad. = $\frac{\Delta C}{L} = \frac{C_o - C_r}{L}$

const. char. dist.

$L = kr$ after the soln of the proper eq.

$$k^* = \sim 1$$

$$L = (D/V)$$

$$\therefore (5.27) \quad v = \frac{dx}{dt} = \frac{D}{\text{서울대학교-공대화 무기재료공학과}} \cdot \frac{\Delta C}{L}$$

characteristic dist

(5.31) Similarity \leftrightarrow

$$v = \frac{D}{C_o - C_r} \cdot \frac{\Delta C}{kr}$$

(12)

Date $r^* \rightarrow$ (level rule)
 $\beta \frac{2\sigma\delta}{kT} \frac{1}{r}$

Note $\Delta C = f(\text{radius}) \quad \therefore \Delta C = -(C_0 - C_r) \text{ where } C_r = C_e(1 + \frac{2\sigma\delta}{kT r})$.

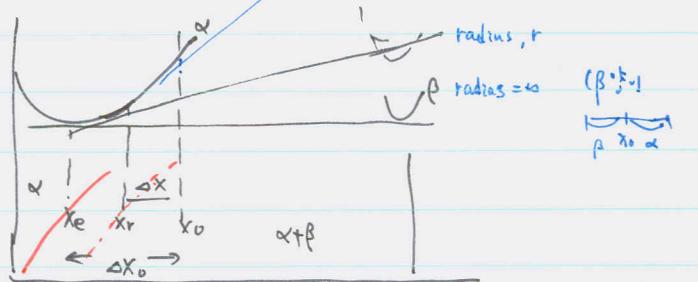
w/ some assumptions

$$(5.32) \quad \Delta x = \Delta X_0 \left(1 - \frac{r^*}{r}\right)$$

$$\text{where } \Delta x = X_0 - X_r$$

$$\Delta X_0 = X_0 - X_e$$

r^* the crit. nucleus radius = the value of r to make $\Delta x = 0$.



$$(5.33) \quad \frac{dx}{dt} = U = -\frac{\Delta X_0}{k(X_B - X_r)} \cdot \frac{1}{r} \left(1 - \frac{r^*}{r}\right)$$

this is good if there is no decrease in supersaturation due to
other ppts.

linear

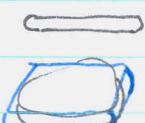
- diff. bet'n plate and edge growth



linear plate $v \rightarrow x \propto \sqrt{t}$ (parabolic)

cylindrical $v \rightarrow x \propto t$. (linear growth)

- lengthening of a needle under diffusion controlled growth.



needle tip spherical

cylindrical edge \leftarrow plate

$$C_r = C_e \left(1 + \frac{2\sigma\delta}{kT r}\right)$$

$$C_r = C_e \left(1 + \frac{\sigma\delta}{kT r}\right)$$

$$\Delta G = \frac{2\sigma\delta}{r}$$

$$\Delta G = \frac{\sigma\delta}{r}$$

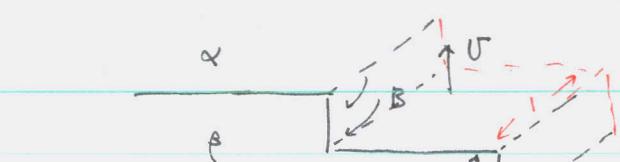
$\therefore r^*$ in (5.33) will be different.

- faceted edge by ledge mechanism
 - short-circuited diffusion
- } may change the description above

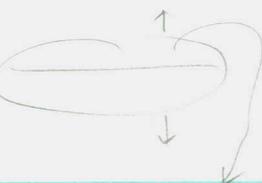
5.3. 3. "Thickening" of Plate-like ppts.

Previous: 5.2.1 planar incoh. interface w/ high accommodation factors

Now: Semicoh. broad face of plate-like ppt. \rightarrow lateral movement of ledges.



(5.34)



Date _____

for the half-thickness of the plate

$$V = \frac{uh \cdot 1}{\lambda \cdot 1} \quad (= \frac{\text{Vol / sec}}{\text{Area}} \text{ unit length})$$

linear ledge of const. spacing

a lateral growth rate (speed).

- long range diffusion to and from the ledge required.

- In a similar way as in (5.33) \rightarrow (plate lengthening) \rightarrow $V = \frac{D \Delta X_0}{k(x_p - x_r)} \cdot \frac{1}{r} (1 - \frac{r^*}{r})$.

 \uparrow lengthening of a plate

$$(5.35) \quad u = \frac{D \Delta X_0}{k(x_p - x_e) h}$$

$$\leftarrow w/h \approx r, \quad x_r = x_e, \quad (n.o. G.T.)$$

 $r \rightarrow \infty$ (ledge radius) \therefore thickening rate (5.34) (5.35)

$$(5.36) \quad V = \frac{D \Delta X_0}{k(x_p - x_e) \lambda} \quad \rightarrow$$

$$\boxed{V \propto \frac{1}{\lambda}} \quad \text{if the diff. field of diff ppt. don't overlap.}$$

valid if the ledges can be continuously provided.

 $\hookrightarrow \frac{1}{\lambda}$.

- ledges can be generated by repeated surface nucle. "spiral growth" nucle. at the ppt. edges. or from intersections w/ other ppt.

5.4 TTT-Diagrams.