Chap. 3. Xtal Interface and Microstructure.

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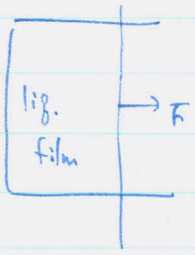
- three basic types of interfaces.
  1. Solid / Vapor interf. (surface) evaporation, condensation.
  2. g.b. interface (α/α) — diff. orientation. recrystallization.
  3. Interphase interface. (α/β) — " , Xtal struc. comp.
     (s/ℓ)

- major phase transf : growth of a new β within the parent α
  ∴ α/β interface important

3.1. Interfacial free E. γ.

(3.1) $G = G^\circ + A\gamma$ — excess f.E. by the fact that some mat'l sits close to the interface : the work done at const T.P. to creat the unit area of interface.

f.E. ↳ bulk prop. of the system.



from (3.1) $dG = A\,d\gamma + \gamma\,dA$. $G = H - TS$

force/unit length $= F\,dA$ = force · dx. $H = U + PV$

(3.2) ∴ $F = \gamma + A \cdot \frac{d\gamma}{dA}$ $dq - dw$.

If surface E $\neq f(A) \rightarrow \frac{d\gamma}{dA} = 0$. valid for liquid, x solid at Tm 0.k

(3.3) ∴ $F = \gamma$ J/mol.

3.2. Solid / Vapor interface

- Surface struc. : hard ball model
  assume that the surface is parallel to a low-index Xtal plane.
  (small change in lattice para. of surface arrangement.)
  otherwise the same as those in the bulk
  - surface adsorption of impurities to reduce the S.E.

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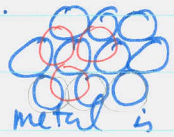
- Assume fcc metal (111) (200) (220). the higher the index, the less pac
- the origin of the surface f.E from the atoms in the layers nearest the surface w/o their neighbors.

1) Quantification of surface ε, γ_{sv}

- Consider the neighbor nearest. of fcc. ← this case



let's think, ① the bond strength of the metal is ε, ② & the bond lowers the internal energy of each atom by $\varepsilon/2$ (∵ ε betw 2 atoms)

fcc case each atom on the surface loses 3 neighboring atoms on the top
(12 nearest neighbors : 3 each : top & bottom. 6 around the)

∴ 3 broken bond $= 3 \cdot \frac{\varepsilon}{2}$ excess energy/atom. (사진참고) → (1)

- the heat of sublimation, L_s, $(= L_m + L_v)$
when 1 mole of solid is vaporized → $12 N_a$ broken bonds

∴ $L_s = 12 N_a \cdot \frac{3\varepsilon}{2} = 6\varepsilon \cdot N_a$. ∴ $\varepsilon = \frac{L_s}{6 N_a}$ —(2)

from (1), (2)

(3.4) ∴ $\boxed{E_{sv} = \frac{3}{2} \cdot \frac{L_s}{6 N_a} = 0.25 \frac{L_s}{N_a}}$ J/surface atom. on (111)

(ignored the effect of 2nd nearest neighbors)
& assumed the strength of other bonds of surface atoms unchanged!

$G_r = U$ on the surface

(3.5) the surface f.E. $\gamma = E + pV - TS$

Could be ignored. important.

positive excess S.
→ reduces γ

(surface atoms have more freedom to move ∴ higher thermal S. than atoms in the bulk)
& extra S_{conf} due to vac. formation

(3.6) $\boxed{\gamma_{sv} = 0.15\, L_s / N_a}$ for pure metal near T_m.

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- Due to $-ST$ term in γ. γ is a weak fn of Temp.

(3.7) $\left(\frac{\partial G}{\partial T}\right)_p = \left(\frac{\partial \gamma}{\partial T}\right)_p = -S \qquad 3 > S > 0.\ mJ/m^2K.$

$G = G^\circ + A\gamma = H - TS$

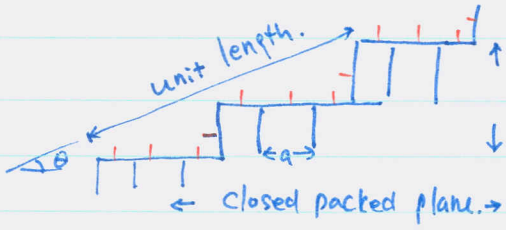
Table 3.1. high L_s, t_{sv} for high Tm metal.

- ∴ diff. Xtal struc → diff. E_{sv}. depending on the # of broken bonds

# of broken bonds ↑ thru {111} {200} {220}. ∴ γ_{sv} increase.

3/atm 4 8.

- high or irrational {hkl} index → appears as a stepped layer struc.



↑ $\left(\frac{\sin\theta}{a}\right)\left(\frac{1}{a}\right)$

↓ # of broken bonds.

consisty of c-p plane.

energy/bond = $\frac{\varepsilon}{2}$

∴ unit area

(3.8) $\left(\frac{\cos\theta}{a}\right)\left(\frac{1\ \text{bond}}{a\ \text{dist}}\right)$

$$\therefore E_{sv} = (\cos\theta + \sin|\theta|)\cdot\frac{\varepsilon}{2a^2}$$

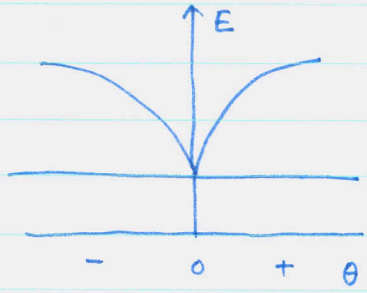


Fig. 3.4.

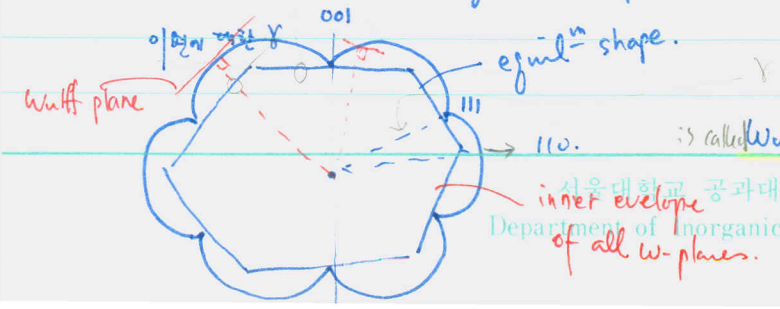
- Variation of surface E. as a fn of θ.

θ = 0. min. with the Closed-packed orientation

All low-index planes be located at low E. Cusps.

- In γ-θ plot (entropy effect) : less prominent than E-θ plot due to entropy effect.

- Prediction of an equilm shape of an isolated single Xtal.



when $\Sigma A_k\gamma_k = A_1\gamma_1 + A_2\gamma_2 + \cdots$ is min.

γ of any plane is equal to the dist. bet'n the surface and the origin

is called Wulff construction

Equilm shape : polyhedron. w/ largest facets having the lowest γ.

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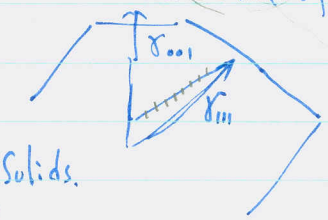
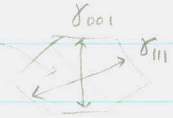
- Experiments to prove this
  ① by annealing single Xtals at h.t. in an inert atmosp.
  ② " small voids inside a crystal.
- if γ is isotropic, equil^{m} shapes are spheres
  if equil^{m} shape is known, we can have relative γ of the observed facet planes.

the widths of the Xtal = ratio of $\gamma_{111} : \gamma_{100}$





3.3. Boundaries in Single-Phase Solids. (α/α).

- two special types of simple boundary
  i) pure tile boundary when the axis of rotation parallel to the plane of b. boundary
  ii) pure twist boundary. " is ⊥ "

1. Low-Angle & High-Angle Boundaries.

i) type

- the boundary : an array of ⊥s

low-angle tilt boundary : array of // edge ⊥s. Fig 3.7(a)

low-angle twist " : a cross-grid of "two" sets of screw ⊥s. Fig. 3-7(b)

- In general, boundaries : a mixture of the tilt & twist b. (Fig 3.8)

ii) Energy

the Energy of l-angle b. = total energy of ⊥s within unit area of boundary.

(3.9) unit ⊥ $D = \frac{b}{\sin\theta}$ ⊥ unit

$\therefore D = \frac{b}{\sin\theta} \simeq \frac{b}{\theta}$

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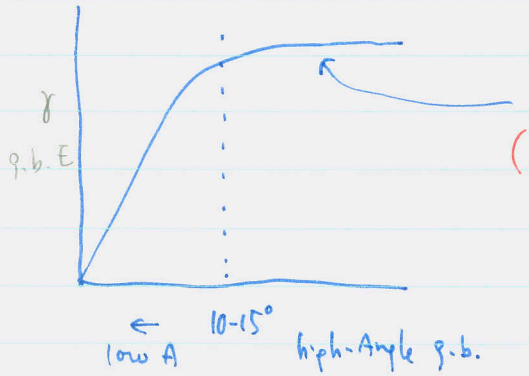
- At very small values of θ : D ↑↑ & then g.b. energy, γ, ↓

(3.10) $\gamma \propto \frac{1}{D}$ (disl. density) → $\gamma \propto \theta$



As θ ↑, the strain field of the ⊥s ↓ (비중이 커짐에 영향을 cancel out.)
thus γ increases at a decreasing rate.
(As θ↓, D↑) → θ↑, D↓
If θ exceeds 10-15°, D ↓↓ so small that ⊥ cores overlap, impossible to identify the individual ⊥s. (Fig 3.10)

- Difference bet'n low & high Angle g.b.

	high	~~low~~ low
1. misfit area	poor, rel. open struc.	well fitted, little free vol.
2. bonds bet'n atoms	broken or highly distorted	slightly distorted → poor fit only in
3. boundary E.	high	low.

only high → ⊥ cores.
here as high A.g.b

- Experimental

(3.11) $\gamma_b \simeq \frac{1}{3}\gamma_{sv}$ (Table 3.2)

2. Special H-Angle G.B.

Normally h-angle g.b. → open disordered struc.
Some special " → have significantly lower E than ordinary b.
occurs at a special misorientation
& boundary plane.
→ the boundary bet'n twins.

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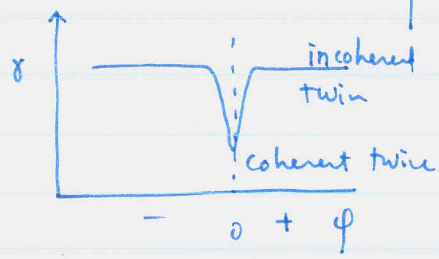
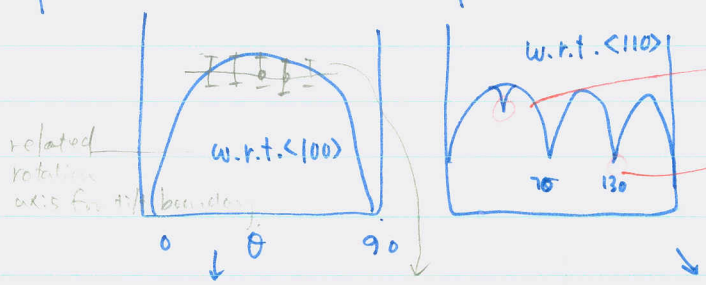
- twin boundaries | coherent / incoherent. → Fig. 3.12. → high E.



If the twin b is // to the twinning plan
the atoms in the b. fit perfect!!
→ undistorted positions → coherent
→ extremely low E.

- In fcc twin → misorientation of 70.5° about a <110> axis
→ special high-Angle b.
if it's coherent, a symmetrical tilt.

- Fig 3.13 : measured g.b. E. w.r.t axis for symmetric tilt.



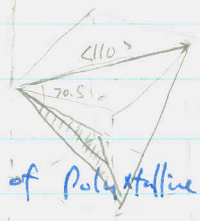
→ Fig 3.14. rather well fit w/o much free vol.

not understood well
→ expected to have a good fitted area

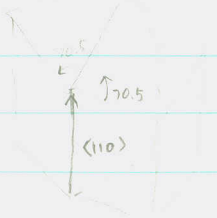
most h-angle b. → the same E.
→ implies disordered struc. of random b.

several (3) large-angle b. w/ noticeable low E. θ = 70.5 : coherent twin.

3. Equil^m in Polyxtalline Mat'ls.



- the effect of diff. g.b. E. on the micro. of Polyxtalline mat'ls.
Fig. 3.15 γ-S.S. (fcc) annealed.



- 2-D g. struc. (from 3-D)
two grains → meets in a plane. (g.b)
three grains → " line (g. edge)
foure grain → a line or pt. (g. corner)

* Factors controlling g. shapes in a rextallized polyxtal.

why g.b. exist which are high E areas (regions). : even in annealed mat'l
metastable equil^m boundaries

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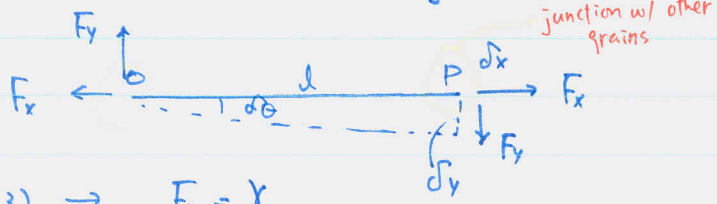
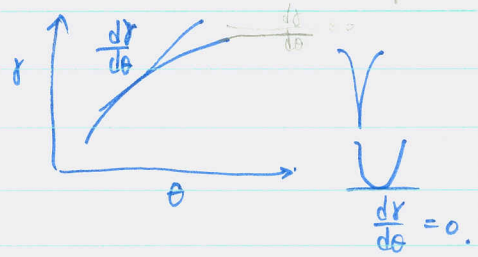
polyxtalline mat'l — never be in a true equil^{m}
→ but moves toward the metastable (semi-) equil^{m}
→ final equil^{m} will be w/ single xtal. but ...

① Conditions for equil^{m} at a g.b. junction. can be determined
by ① considering forces of boundary on the junction.
or by ② considering total p.b. E.

Fig. 3.16. if the boundary is mobile. F_x, F_y must act on at o. p. to maintain the boundary in equil





(3.3) → $F_x = \gamma$

* for F_y? if P moves by δy while O is fixed

surface or line E. force/unit length

$$\delta W \text{ (work)} = F_y \delta y = l \cdot \left(\frac{d\gamma}{d\theta}\right) \cdot \delta\theta \qquad \text{and since } \delta y = l \cdot \delta\theta$$

work (E. change) to surface E.

(3.12) $\therefore F_y = \frac{d\gamma}{d\theta}$

this means if the g.b. E $\equiv f$ (boundary orientation)
$\frac{d\gamma}{d\theta}$ should exist at the ends of the boundary to prevent rotating
otherwise it will rotate to a lower E. position (orientation)
the boundary

known as a torque term

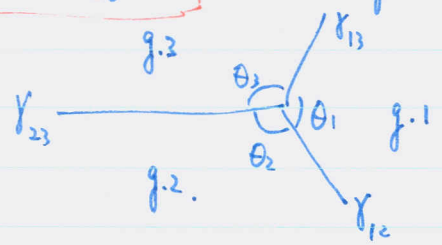
* If the boundary is at the min. E. position (cusp orientation).
$\frac{d\gamma}{d\theta} = 0$ (see above the figure above)
no torque acting.

If the boundary E is indep. of orientation. $\frac{d\gamma}{d\theta} = 0$ (isotropic γ) torque term.

g.b behave like a soap film!

$\boxed{\text{When } \frac{d\gamma}{d\theta} = 0.}$ the requirement for metastable equil^{m}

(3.13)



$$\frac{\gamma_{23}}{\sin\theta_1} = \frac{\gamma_{13}}{\sin\theta_2} = \frac{\gamma_{12}}{\sin\theta_3}$$

- grains could be diff. phases. i.e, vapor, solid etc.

② Method of measuring g.b. E.

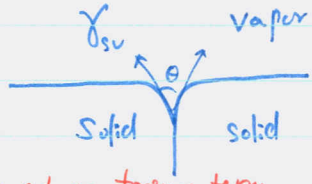
① anneal it at h.temp.

② measure the angle at the intersection.

if γ_{sv} known

$$\therefore 2\gamma_{sv}\cos\frac{\theta}{2} = \gamma_b$$

↑ calculate!



true when $\frac{d\gamma}{d\theta} \cong 0$ assumed no torque term.

no torque term otherwise it will generate a huge error in E.

③ - the effect of $\frac{d\gamma}{d\theta}$ (consider coherent, incoherent twin boundary)

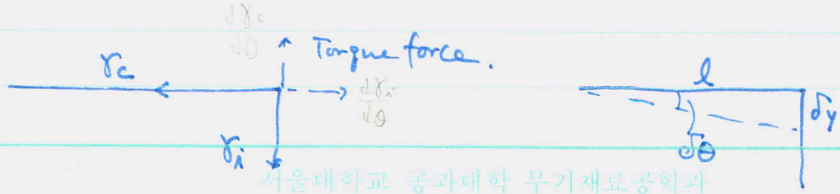
$= f$(orientation)

for twin b.: tend to align // to the twinning plane.

if the boundary is restricted to follow a macroscopic plane, which is near but not exactly // to the plane, the boundary will have a stepped appearance. w/ large coherent low-E facets. and small incoherent high-energy risers

→ not min. E. ~~but~~ for twin b. but reduces total f.E.

Fig 3.19.



at the coh/incoh twin junction γ_i must be balanced by $\frac{d\gamma}{d\theta}$ (torque ten

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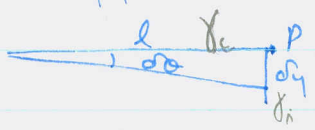
(3.15) when
if $\gamma_i \le \frac{d\gamma_{coh.}}{d\theta}$ the step is stable.
(F_γ)
if $\gamma_c \le \frac{d\gamma_i}{d\theta}$ incoherent facet become a special boundary w/ good fit.

↳ Since this is very small, $\frac{d\gamma_i}{d\theta}$ does not have to be large.

③' From Energy considerations



at P. equil^m ∴ a small displacement increases G total.

i.e. $dG \geq 0$ for this motion

$$dG = l \cdot \frac{d\gamma_c}{d\theta} d\theta - \gamma_i \delta y \geq 0 \qquad \text{since } l\,d\theta = \delta y.$$

(bond) (initial) → strained 되지 않은 incoherent

strained 된 coherent interface 를 만들기 위한 Energy

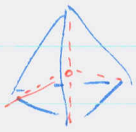
$$\therefore \frac{d\gamma_c}{d\theta} \geq \gamma_i.$$

→ 그러면 step이 안정화

4. Thermally activated migration of G.B.

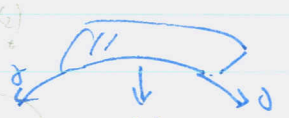
① - At a triple point. if $\gamma_{12} = \gamma_{23} = \gamma_{31} = \text{const} \neq f(\text{orientation})$
then $\theta_1 = \theta_2 = \theta_3 = 120°$ ← Eq. (3.13)

At a quariple pt. $\theta = 109° 28'$

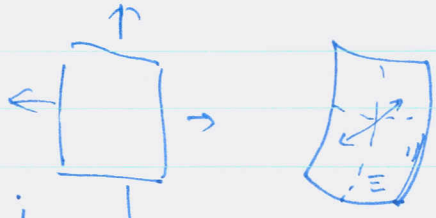


"metastable" g.b junct.
→ no g.b equil^m.

② - In a complete metastable equil^m the surface tension must balance over all the boundary faces



∴ $r \to \infty$ for $\frac{\gamma}{r}$ to be 0.
or curved w/ equal radii in opposite direct.



planar boundary — doubly curved boundary

no net force

- theoretically surface tension be in balance

g.b migrat

drip annealing at H.T.

In reality - w/a net curvature in one direction → the unbalance removed by

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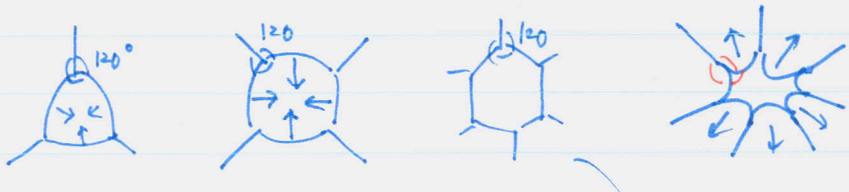
- the effect of diff. boundary curvature in 2-D



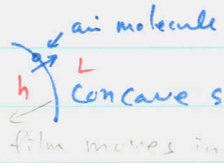
- junction angle → 120° ∴ if a grain has 6 boundaries they will be planar & the struc. metastable

if # of boundary > 6 → this grain will grow.

if the # of g.b. is less than 6, must be concave inwards. & shrink, disappear.

these result of boundary migration is to reduce the # of grains.
→ increasing mean grain size, reducing the total g.b. E.
⇒ This phenom called grain growth, grain coarsening.
→ occurs > 0.5 Tm.

- Soap froth. as an example. high pressure

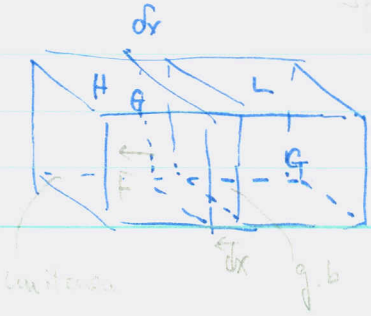


In metal the atoms in the shrinking grain detach themselves from the lattice on the high pressure side of the boundary & relocate to growing g. (Fig. 3.23 example).

③ the effect of the pressure diff. by a curved boundary (변곡점 factor for g.b. migration)

(3.17) ⇒ $\Delta G = \frac{2\gamma V_m}{r} = \Delta\mu$.

pulling the g.b towards the grain w/ higher ΔG.



if unit area of g.b. advances δx

the # of moles $= \frac{\delta x \cdot 1}{V_m}$

$\therefore \Delta G' = \Delta G \cdot \frac{\delta x}{V_m} =$ work done by $F \cdot \delta x$

(3.18) $\therefore F = \frac{\Delta G}{V_m}$ N/m² pulling force / unit area of boundary.

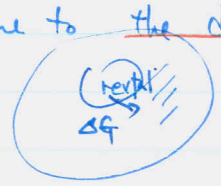
↳ free Energy diff / unit vol.

ex.① In g. growth. ΔG is from the boundary curvature

(3.18) applicable to any boundary.

ex.② During rextall'n. the boundaries bet'n the new strain-free & the original deformed grain are mobilized by $\frac{\Delta G}{V_m}$

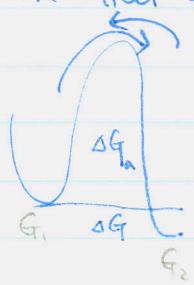
ΔG is due to the diff in dis'l. strain E. bet'n grains.



rextallized grain grow → total g.b. area increases but $\Delta G\downarrow$ for rextall'n is higher than $\Delta G\uparrow$ due to increase in g.b. area.

- ΔG is the greatest when the new grain is small.

④ the effect of ΔG on the kinetics (velocity) of b. migration. (kinetic factor for g.b. migration)



freq. ν_1 # of vib. / sec.

$\nu_1 \exp(-\Delta G^a/RT)$. atoms of this energy

n_1 = atoms in favorable position. in Grain 1

$n_1 \nu_1 \exp(-\Delta G^a/RT)$

A_2 = prob. of being accomodated in G 2.

the effective flux of atoms from grain 1 to grain 2.

$J_{1\to2} = A_2 n_1 \nu_1 \exp(-\Delta G^a/RT)$.

- Reverse direction. $J_{2\to1} = A_1 n_2 \nu_2 \exp\left[-\frac{(\Delta G^a + \Delta G)}{RT}\right]$

(가정) $\Delta G = \Delta G^\circ + RT \ln K_p$

(가정) $\Delta G = \Delta G^\circ + RT \ln \frac{C_C C_D}{C_A C_B}$

i) At equil^m $\Delta G = 0$ $\therefore A_1 n_2 \nu_2 = A_2 n_1 \nu_1$

no net flux.

ii) For a h-angle g.b. $A_1 \simeq A_2 \simeq 1$ little problem w/ accomodation.

$(A_1 n_2 v_2 = A_2 n_1 v_1)$

Assume that the equality holds for small non-zero driving forces w/ $\Delta G > 0$ ∴ net flux from grain 1 to 2.

(3.19) $$J_{net} = A_2 n_1 \nu_1 \exp\left(-\frac{\Delta G^a}{RT}\right)\left\{1 - \exp\left(-\frac{\Delta G}{RT}\right)\right\} \quad \text{— (1)}$$

if the boundary vel. is v.

$$\text{net flux} = v / \underbrace{(V_m / N_a)}_{\text{the atomic vol.}} = v C_B \left(= \frac{X_B}{V_m}\right) \quad \text{— (2)}$$

atoms / cm² · sec ← grain migration might

$$\therefore \exp\left(-\frac{\Delta G}{RT}\right) \simeq 1 - \frac{\Delta G}{RT} \quad \text{if } \frac{\Delta G}{RT} \ll 1. \quad \text{— (3)}$$

(1)(2)(3)에서

(3.20) $$\therefore v = \underbrace{\frac{A_2 n_1 \nu_1 V_m^2}{N_a RT} \exp\left(-\frac{\Delta G^a}{RT}\right)}_{M} \frac{\Delta G}{V_m} \rightarrow v \propto \frac{\Delta G}{V_m} \text{ d.force}$$

(3.21) $v_B \propto M_B \frac{\partial \mu}{\partial x}$ (diffusion) $\quad v = M \cdot \frac{\Delta G}{V_m}$ M is the mobility of the boundary vel. under unit d.f.

(3.22) $M = f(T) \sim \exp\left(-\frac{\Delta H^a}{RT}\right)$ → an exponential increase in mobility w/ Temp.

$D_B = M_B RT = \frac{1}{2} a^2 \cdot 2\nu \exp\left\{\frac{-(\Delta G_m + \Delta G_v)}{RT}\right\}$

!! ∴ the boundary migration - thermally activated process like diffusion.

- In reality some atoms ~~may~~ will jump more easily than others. atoms in "ledge" or "step" ends. A, B, C in Fig. 23a. Boundary migration effected by the growth of the ledges in one grain w/ the shrinking of corresponding ledges in the other grain (F 3.23)

- the open struc. of h-angle g.b - high mobility (coherent : special bond
  the dense pack'g of l-angle g.b - low " (twin b. - immobile.)
  perfect fit of atoms.

- Some special boundary w/ higher mobility than h-a g.b. ~~less~~ small amount
  ∵ different impurity-bond → interaction associated w/ impurities. (alloying solute)

Date . .

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- the impurity effect on the boundary mobility Fig 3.27.
  the vel. of random b. ↓ w/ increasing alloying content.

Random b: a small quantity of impurities ~~reduces~~ s the vel. by orders of mg.

Special b: less sensitive to impurities ∴ perfectly pure Random b moves fast

→ g.b: preferred area for solutes (impurities) if no impurities.

- the g.b energy of a pure metal changes on alloying : lowering E.

- In g.b. segregation

low mole fraction of solute in the Matrix!

(3.23) g.b. solute conc. $X_b = X_0 \exp \frac{\Delta G_b}{RT}$ ⑦ free E. released / mole when a solute is moved from the matrix to b.

$X_b = 1$ one monolayer - complete single closed-packed layer of atoms in the boundary.

ΔG_b ↑ as ① the size misfit bet'n solute & matrix ↑

② the solute - solute bond strength ↓

③ the matrix solubility ↓ (Fig 3.28)

(Eq. 3.23) → g.b segregation ↓ as T ↑. → solutes moves into the matrix

$X_b \to 1$ at low T or at high ΔG_b.

!! Solutes drapping Effect onto the boundary !!

the magnitude of the drag ∝ f (binding energy, conc in the boundary)

ex. a "low solute" drag - high mobility of special boundary

conc. insensitive to conc. of solute ∵ more close packed str

- the high mobility of special g.b. → important in rextall'n.

heavily deformed metal → deformed texture (like deformed single xtal) $\xrightarrow{\text{on heating to h.t.}}$ new grains nucleate & grow: Some grains w/ special orientation w.r.t. the matrix → higher mobility. then overgrow the random boundaries. $\xrightarrow[\text{causes}]{}$ rextall'n texture

low carbon steel - deep drawing possible due to