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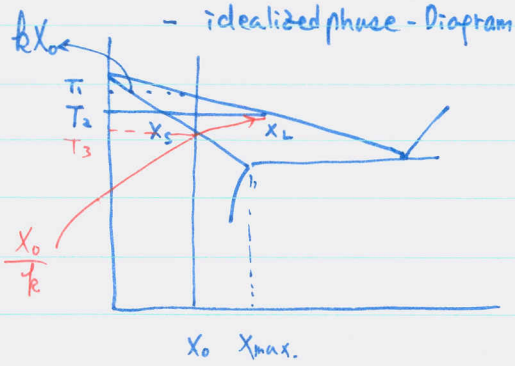
4.3 Alloy Solid'n.

a single-phase binary, eutectic, peritectic.

1. Solid'n of Single-Phase Alloys.

- idealized phase-Diagram



k (partition coef.) $= \frac{X_S}{X_L}$ – mole frac. < 1

Assume $k \neq f$ (ccomp.)

- a planar S-l interface assumed file in a zone-melting. (simple)

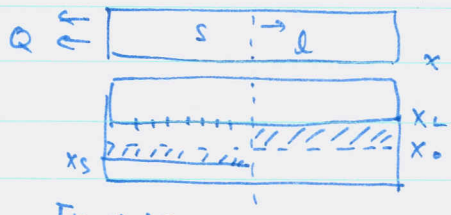
- Three limiting cases.
  1. slow (equil^m) solidif'n (full diff. in solid)
  2. Solid'n w/o diffusion in the solid perfect mixing in the liquid.
  3. Solid'n w/o diffusion in the solid diffusional mixing in the liquid.

All one directional Solid'n

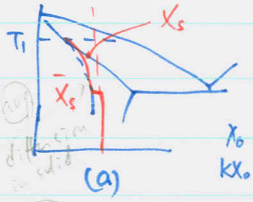
i) * Equil^m solid'n.

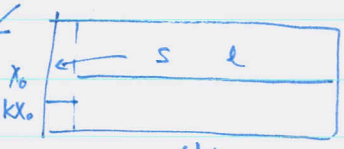
*) slow cooling sufficient time for diffusion in solid & liquid : ∴ kX_0, X_0
- the rel. amount of solid and liquid – lever rule.

slow enough from $T_1 \to T_3$



shaded area equal

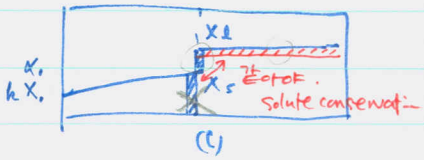




(b)

Fig. 4.20.

ii) * No diff. in solid, perfect mixing in Liquid.
↳ cooling too rapid.



(c)

Final

Fig. 4.21 (d)

$C_s f_s + C_L f_L = C_0$

weight fraction

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- no diffusion in the solid, the separate layers of solid retain their original compositions. → avg. comp. of the solid ($\bar{X}_s$) < X_s (after compl diffusion & equil^m)

diff comp : ≠ X_s

kX_0

- The rel. amount of s. & l. determined by the <u>lever rule</u> using "$\bar{X}_s$ and X_L"

- Liquid become richer than X_0/k → X_E !! final eutectic struc ($\alpha+\beta$)
  → Fig 4.21(d) $\bar{X}_s = X_0$

- The variation of X_s : solute rejected to the liquid
  mass balance $(X_L - X_s)\, df_s = (1-f_s)\, dX_L$
  - Integrate this n.s. B.C $X_s = kX_0$ when $f_s = 0$.

$$\int_0^{f_s} \frac{df_s}{1-f_s} = \int_{X_0}^{X_L} \frac{dX_L}{X_L - X_s} = \int \frac{dX_L}{X_L(1-k)}$$

$$\therefore \int_0^{f_s} (1-k)(-1)\, d\ln(1-f_s) = \int_{X_0}^{X_L} d\ln X_L$$

(4.33) → $\ln\frac{X_L}{X_0} = (k-1)\ln\underbrace{(1-f_s)}_{f_L}$ $\boxed{\therefore X_L = X_0 f_L^{(k-1)}}$

non-equil^m lever rule.
(Scheil Eq.).

Scheil eq → $k<1$ ∴ $k-1<0$ → predicts that if no diff. in the solid some eutetic always exist to solidify. $X_L = \frac{X_0}{f_L^{1-k}}$ ← 작다 ↑ X_E 근처.

iii) * No Diffusion in Solid, Diffusional Mixing in Liquid

no stirring convection (대류)

Solute rejected from solid → diffuse into liquid. w/ limitation.
∴ rapid build up of solute in front of the solid
→ ∴ rapid increase in the comp. of solid forming.

↓ X_0

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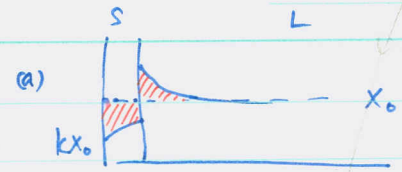


- initial transient
- If it solidifies at a const (speed) rate, v, then a steady state is finally obtained at T_3 in Fig 4.19 (reference 6)

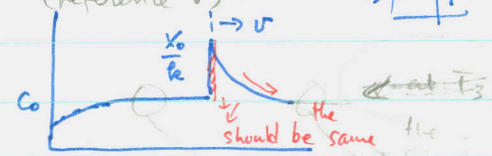


Fig 4.22 at T_3

- Liquid $\frac{X_0}{k}$, solid X_0.

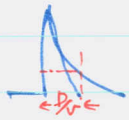
- Duly s. state growth.

mass balance $\quad -D\frac{dX_L'}{dx} = v(C_L - C_s)$. $\quad$ -(4.34)

more precisely $\quad D_L\frac{d^2X_L}{dx^2} + v\frac{dX_L}{dx} = 0$.

(4.35) - Solution of this $\quad X_L = X_0\left[1 + \frac{1-k}{k}\exp\left(-\frac{x}{(D/v)}\right)\right]$ how ~~why~~? 식!

- Characteristic width $\quad x = D/v \rightarrow \exp(-1) \rightarrow \frac{1}{e}$



$X_L - X_0 = \left[\frac{1-k}{k}X_0\right]e^{-1}$ $\quad$ max의 30%로 떨어지는 거리

- If the s-l interface is within ~D/v of the end of the bar ⊥ → compressed to ∫ final transient (eutectic comp

→ In practice, have features from all three of the cases. i), ii), iii)

yes, stirring (pouring, convection current) but not sufficient

yes, some liq. diffusion $\quad$ betin Fig 4.21 d (ii) and 4.22 c (iii)

yes, diffusion in solid too, especially when interstitial atoms (solute) and bcc (open struc) solvent → solute diffuse into liquid and solid, either way.

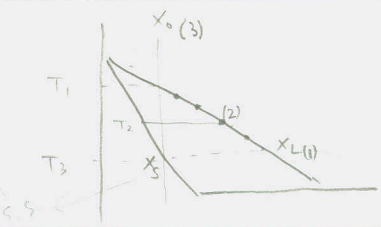
iv) Cellular and Dendritic Solidification.

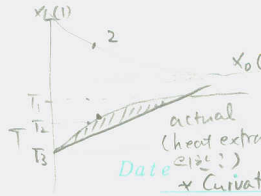
Solute diffusion in alloy similar to the conduction of latent heat in pure metal

possible to break up the planar front into dendrites.

→ complicated by the possible temp. grad. in the liquid

(mixed problem pure (T) + alloy (solute) instability)





← planar 상태에서

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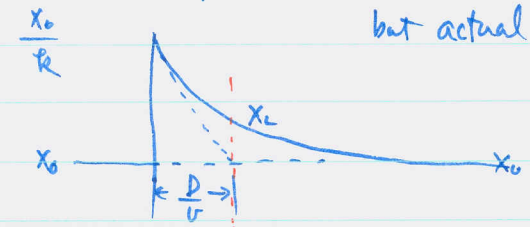
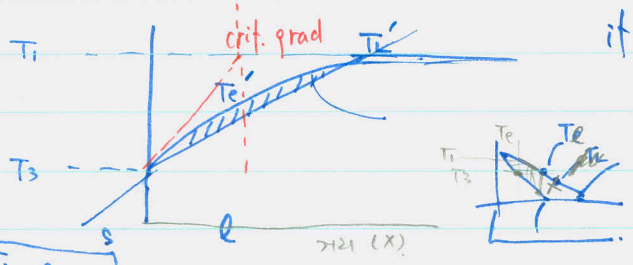
* Curvature effect 로 티상이 생길 수 있다 when dend form

- Varying solute conc. ahead of solid'n front. → correspondg variatn of equil^m Solid'n temp. T^e but actual temp. grad is T_L.



At the interface $T_3 = T_e = T_L$.



if the slope of crit. grad > that of T_L.
if is supercooled. → Constitutional Supercoolg
(due to comp.)

Fig 4.23

- A necessary condition for stable protrusions on a planar interface
→ ∃ a region of constitutional supercooling

i.e., If $T_L' < T_e'$, temp at the tip of any protrusion ~~even if this is true~~ > that of surroundg ~~develop.~~ Protrusion develops. (dendritic or columnar)
if c.s 클때 작을때

If $T_L' > T_e'$ " melts.
to dilute the liquid.

(why? back!)

- S. state planar growth : the critical grad $= \frac{T_1 - T_3}{(D/v)}$ T_1: liquidus, T_3: solidus.

① planar

$\therefore T_L' = \frac{dT_L}{dx} \geq \frac{T_1 - T_3}{D/v}$ stable planar interface.

(4.36) Rearrange $T_L'/v \geq (T_1 - T_3)/D$ for planar.
known as equil^m freezing range

- Planar Solid'n difficult w/ large " & high v.

- $\frac{dT}{dx}$, v controlled by heat conduction.

② dendrite

- If $\frac{dT}{dx}$ (T_L') in front of planar interface < the crit. grad. (T_e') → break down of the planar → forming a cellula stru. (supercooled)

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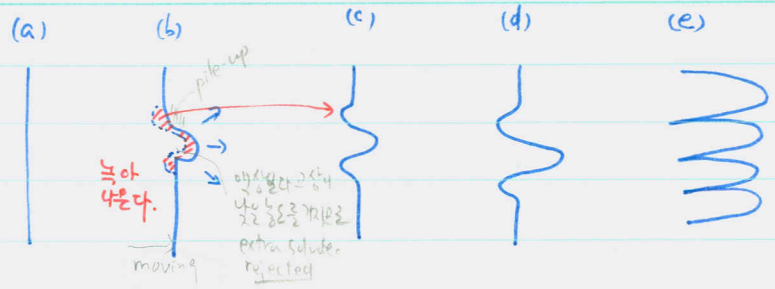
Fig. 4.24.



(b) the solutes rejected laterally piles up at the root of the protrusion.

(c) ↳ lowers T_e and but $T_L > T_d$ (to dilute the liquid) ∴ results in recesses to form.

higher solute conc of liquid

i.e. solute conc. ↑ T_e ↓ but real temp. is higher than T_e

to be isothermal, need more "solvent" to dilute → melting.

(d) this cause other protrusion.

(e) the same situation repeated (b) – (c) – (d) → cellular struc.

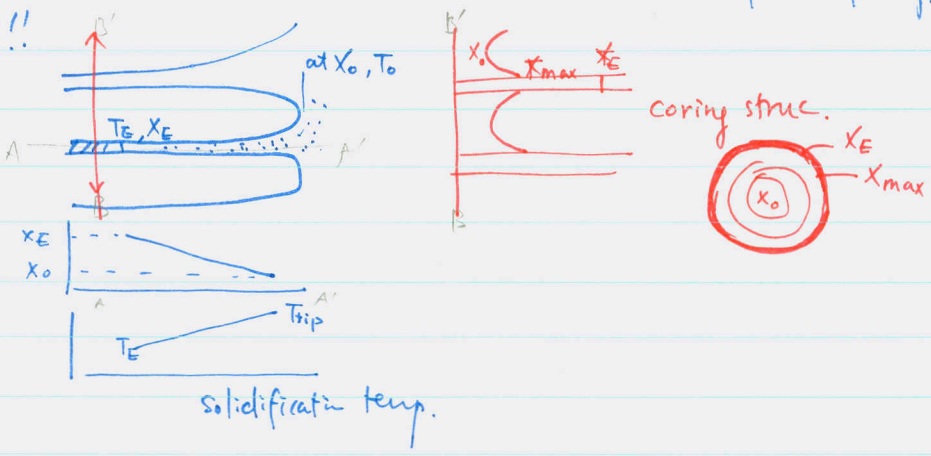
as the s-l interface advances.

→ The solute rejected from the solidifying liquid remain bet'n cell walls. solidifies last at T_E.

→ The tips of cellular struc. grow into the hottest liquid at X_0

have to solidify at high temp ← (lowest conc)

Fig 4.25 !!



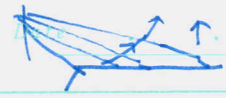
- Cellular struc. → develops 2ndary arms → tertiary arms

↓ dendritic struc ↓ ↓

stable only for a certain range of pradient. | at sufficiently low temp. grad. | at still lower temp grad.

- the direction of primary arm → determined by the direc. of heat flow or preferred direct Xtallograp

c. supercool 이 많을수록 columnar.
" 클 " dendritic growth



- tendency to form dendritic struc ↑ as the solid'n range ↑
  ∵ small partition ($k = \frac{X_S}{X_L}$) → dendritic conc.
  large " ($k \simeq 1$) → cellular effect of 2nd solutes
  possibly related to the constitutional supercooling → interface instability in the transverse dir
- Directional Solid'n (DS) : no temp. grad. perpendicular to the growth direct'n
  high temp. grad. parallel to "
- why dendrites develop from cell? no clear.
  Maybe in DS : that which reduces the const'l supercooling to a very low level.
- observation consistent d. spacing ↓ as cooling rate ↑
  higher cooling rate → less chance for lateral diffusion of solute
  → required smaller cell. d.a. spacing to avoid c. supercooling

2. Eutectic Solid'n.

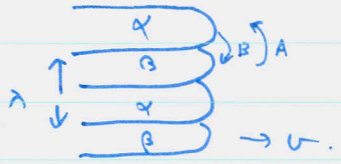
Quiz #2

- rxn $L \rightarrow \alpha + \beta$, classified - normal, anomalous eutectic rxns.

→ ① normal struc: two phases in the form of alternating lamellae
~~for~~ focus on this struc.
↳ grow simultaneously behind an planar s-l interf
↳ obtained when both phases have low ΔS_m
rod or lamellae

② Anomalous struc: occurs when one of the two phases is capable of faceting. high ΔS_m ($= \frac{\Delta H_m}{T_m}$) → flaky struc. in Al-Si

i) Growth of Lamellar Eutectic.



the rate of growth depends on the diffusion of A, B. → to α, β.

- small spacing (λ) → rapid growth.
- But small λ → increases the interfacial E, $\gamma_{\alpha\beta}$.
  should be balanced !!

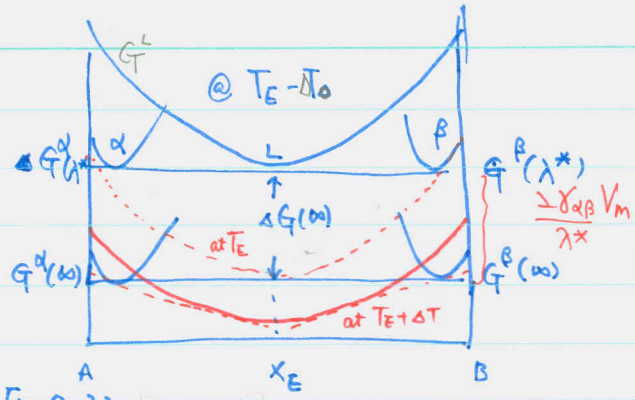


Fig 4.32

for λ, total area of α/β interface/m^3 $= \left(\frac{2}{\lambda}\right) m^2/m^3$.

(4.37) $\Delta G(\lambda) = -\Delta G(\infty)_{l\to s} + \frac{2}{\lambda}\gamma_{\alpha\beta}V_m$

large

for the solid'n of 1 mole liquid. molar Vol.

(4.38) w/ ΔT_0 undercooling below T_E $\quad \Delta G(\infty)_{l\to s} \simeq \frac{\Delta H \cdot \Delta T_0}{T_E}$

$\therefore$ min. $\lambda \to \lambda^*$ obtained when $\Delta G(\lambda^*) = 0$

(4.39) $\lambda^* = \frac{2\gamma_{\alpha\beta}V_m T_E}{\Delta H \cdot \Delta T_0}$ and eutectic, liq. at equil$^{\underline{m}}$ at λ^*

- α/β interface raises the $G^\alpha(\lambda)$, $G^\beta(\lambda)$
  $\because$ balance interfacial tension $\alpha/\beta/L$ triple pt.

* Mechanism of Growth.

- for solid'n to occur, need a flux of atoms bet'n tips of α & β.
  $\xleftarrow{l\to s}$ B : conc. of B higher at the tip of α than those of β.

- If $\lambda = \lambda^*$ growth will be very slow. $\because$ the liq. comp in contact w/ α, β is the same. $(= X_E)$

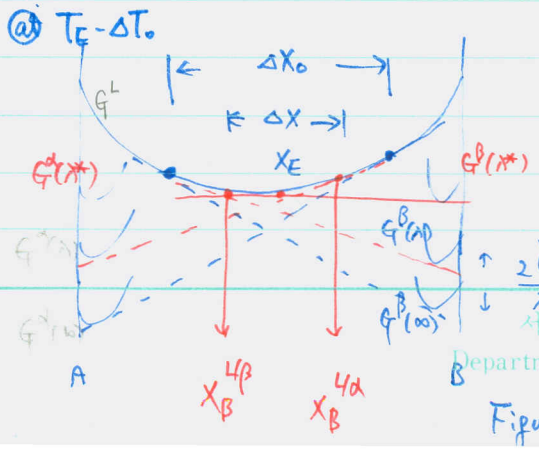


Figure 4.33

If $\lambda > \lambda^*$ less free E. is locked in the interfaces and G^α, G^β are reduced.

$\therefore$ the liquid in front of α $= X_B^{L/\alpha}$ (B-richer than $X_B^{L/\beta}$ $\to$ diffusion $\to$ prm

* Mobility of the Interface

growth rate

- the mobile interface (diffusion controlled). $v \propto J$ of solute $= -D \frac{dc}{dl}$: $\propto \frac{\Delta X}{\lambda}$

  l measured along the direction of diffusion. $\therefore \frac{dc}{dl}$ is not a simple value

(4.40) $\boxed{\therefore v = k_1 D \frac{\Delta X}{\lambda}}$ (const) when $\Delta X = X_B^{L/\alpha} - X_B^{L/\beta} = f(\lambda)$

$\Delta G(\lambda) = 0$. equil^m $\rightarrow v = 0. \rightarrow \Delta X = 0.$

- $\Delta X = 0$ when $\lambda = \lambda^*$, as $\lambda \uparrow$ $\Delta X \rightarrow \Delta X_0$. max. value.

  $\alpha \beta . L \rightarrow$ all at X_B

roughly this is true

(4.41) $\boxed{\Delta X = \Delta X_0 \left(1 - \frac{\lambda^*}{\lambda}\right)}$

ΔX_0 can be obtained by extrapolating the equil^m liquidus line of the phase diagram ($\lambda = \infty$)

See Fig 4.33 !!

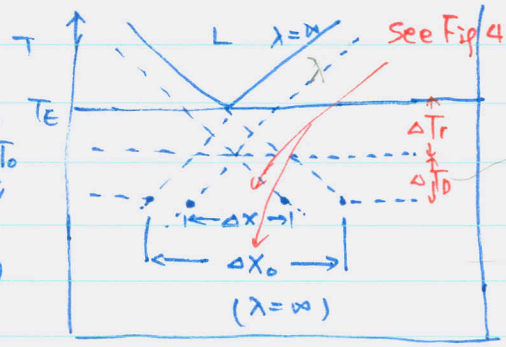


Fig 4.34

diffusion이 일어나기 위한 중요한 ΔX를 가지기 위한 supercooling

For small undercoolings

(4.42) $\Delta X_0 \propto \Delta T_0$

from (4.40)

(4.43) $\boxed{\therefore v = k_2 D \Delta T_0 \frac{1}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)}$

- (4.43) shows. by varying ΔT_0 $\xrightarrow{\text{can}}$ vary v. λ. independently.

  Experiments shows a λ (always is) ass'ted w/ a v

- From (4.43) if $\lambda = 2\lambda^*$ ① v is max. (find thru $\frac{dv}{d\lambda} = 0$)

  at a given ΔT_0. or ~~min~~ ③ ΔT_0 is. min required for a given growth rate ~~undercooling~~.

- If growth occurs under the optimum conditions

  the spacing (λ_0) and growth rate (v_0) will be

  $\lambda_0 = 2\lambda^*$, $v_0 = k_2 D \Delta T_0 / 4\lambda^*$ (why not $4\lambda^*$?)

(4.44) (4.39) $\rightarrow \Delta T_0 \propto \frac{1}{\lambda^*}$ $v_0 \lambda_0^2 = k_3$ (const.) and

(4.45) $\frac{v_0}{(\Delta T_0)^2} = k_4$ (const.)) exptly observed.

- The total undercooling at the eutectic front (ΔT_0) has two components

(4.46) $$\Delta T_0 = \Delta T_r + \Delta T_D. \quad (+\Delta T_k)$$

① undercooling required to overcome the interfacial curvature ② to have a suff. composition diff. to drive diffusion.

$(+\Delta T_k)$ to move the atom across the interface, negligible for high mobility interface

- Theoretically ΔT_D varies from α tip to β tip. ∵ diff composition varies

Since the interface is isothermal (ΔT_0 const)

the variation of T_D causes ΔT_r to change correspondingly.

→ i.e., the interface curvature change across the interface.

- Interface instability w/ planar interface : caused by impurities

- Changing direction., fanning out to.

can be stabilized by a high temp. grad. (DS).

3. Off-Eutectic Alloys.

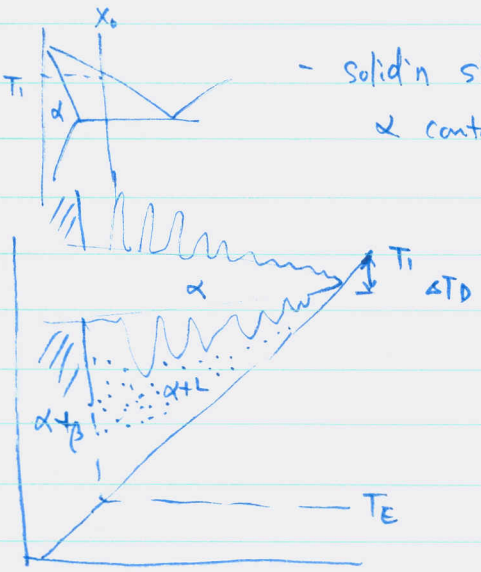


Fig. 4.37

- solid'n starts at T_1, forming α (primary dendrites)

α contains less B → rejecting into liquid & make $l \to T_E$

- w/ less solid-state diffusion, the centers of the dendrites have less solute than the outer layer.

→ results in coring in the final struc.

- The eutectic in lamellae as two-phase mixture or divorced eutectic : isolated islands of minor phase when vol. fraction of one phase is very small.

- In DS. $\frac{dT}{dx} \gg 0$ high ↑↑ or v high ↑↑ then, the dendrite tip are overgrown by eutectic and it solidifies 100% eutectic (overall comp. X_0) instead of X_E

planar, no α dendrites

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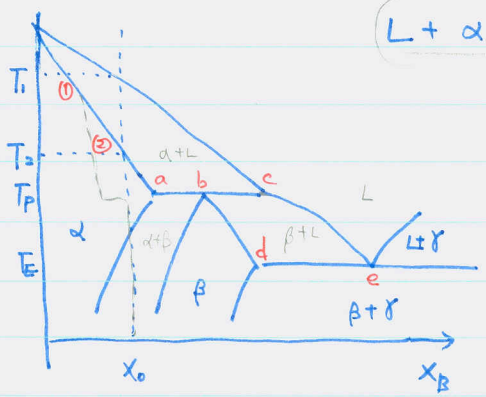
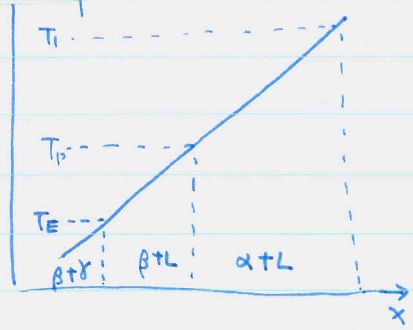
4. Peritectic Solid'n.

$L + \alpha \rightarrow \beta$



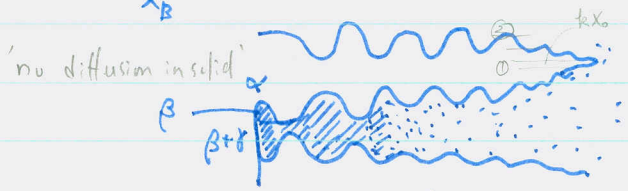


'a' & 'c' make 'b' at T_p

1) α : $\sim kX_0$ $\sim T_1$

2) α grow with layer of comps along solidus (①-②) limited diff. in solid

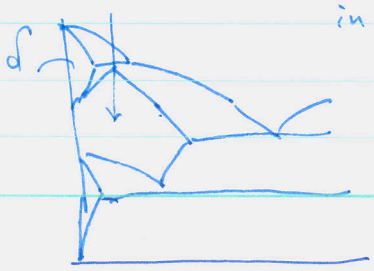
3) If diffusion in dendrites is slow, the liquid will be at C comp.



4) Further cooling $\alpha + L \xrightarrow{\text{start producing}} \beta$ layer (along b-d)

5) The Remaining liquid, if there's no diffusion in the solid, will reach e and produce $\beta+\gamma$

- If alloy X_0 were DSed at $(T_L'/v)\uparrow$, tip temp of dendrites fall from T_1 to T_2. & last liquid temp → T_2
- Planar-front can be obtained for alloys beyond 'a' if T_L'/v ↑↑ high.
  - alloys bet'n a & b - eutectic like $\alpha+\beta$ called composite.
  - " b & d - β single phase.
  - beyond d - $\beta+\gamma$
- Fe-C. due to high diffusivity of C.
  in peritectic rxn primary δ dendrites converts into γ stable form.



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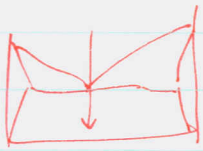
1. ① α.β.L 의 free E diagram 을 (T_E, $T_E-\Delta T$, $T_E+\Delta T$ 에 관한) 그려라.
(G vs. Comp).



② ΔG 를 expression (λ, 층간두께로 표시하고) 그림에 해당 quantity 를 표시하라

③ lamellar 가 최대 속도가 되는 λ 를 구하라!