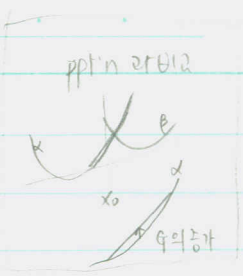
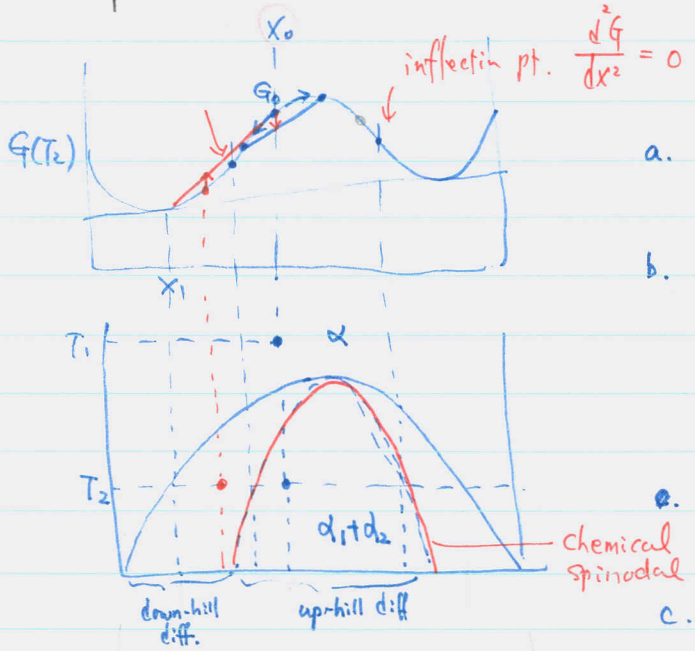
Date

5.5.5. Spinodal Decomposition.



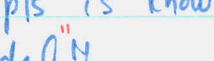
spinodal mode of transf : no barrier to nucleation. (no activation energy required)



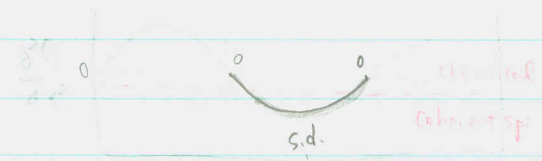
a. Quenched from $T_1 \rightarrow T_2$.
$G(T_2) = G_0$ initially.

b. but it feels unstable ∵ small changes in comp (A-, B-rich comp.) result in lower free E. → ∴ uphill diffusion starts (diffusion to higher conc. region) &

c. finishes when they reach X_1, X_2.

c. this process happens for any comp. where the f.e. curve has a neg. (Fig 5.39) curvature. $\frac{d^2G}{dX^2} < 0$. bet'n two inflection points!! why?  inflec. pt. energy ↑.

d. The locus of the inflection pts is known as the "chemical spinodal"!!



e. the alloys outside the chemical spinod. the changes in comp raise the free E.
∴ metastable - the f.E. can only be reduced only if nuclei are formed w/ a diff. comp. from matrix.

f. ∴ outside the spinodal the transf. must occur by nucl. & growth process. : down-hill diffusion.

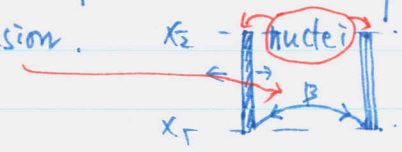


Fig. 5.39와 40 비교

g. Fig. 5.39 rate controlled by interdiffusion coeff. $\tilde{D}$ - comp. fluctuation $\propto \exp(-\frac{t}{\tau})$
where $\tau = -\frac{\lambda^2}{4\pi^2 D}$

→ transf. rate ↑↑ ∵ λ ↓↓ 시간이 훨씬 짧음 takes less time

but λ_{min} exists below which spinodal decomp. cannot be possible

Taylor's Series Formula

$$f(c) = f(c_0) + \frac{(c-c_0)}{1!}\left(\frac{\partial f}{\partial c}\right)_{c=c_0} + \frac{(c-c_0)^2}{2!}\left(\frac{\partial^2 f}{\partial c^2}\right)_{c=c_0} + \cdots$$

analytic fn

ΔG_c = f.e/unit vol of a homo matl

$f(z_1) = f(z_0) + \cdots$

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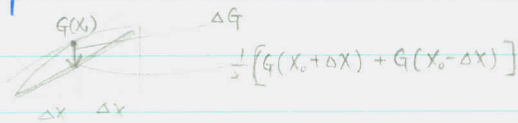
- For the wavelength, λ, of the comp. fluctuation.
  need to take care of (1) interfacial E. & (2) coh. strain energy effect as well as ΔG_c.

$\Delta G_{tr} = \Delta G_c + \Delta G_\gamma + \Delta G_\varepsilon$

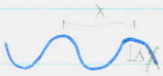
ΔG_c • when a homo. alloy of X_0 → decomposed into $X_0 + \Delta X$, $X_0 - \Delta X$.

$$\boxed{\Delta G_c = \frac{1}{2}\frac{d^2G}{dX^2}(\Delta X)^2}$$

$\ominus$ $\oplus$



ΔG_γ • If the two regions are finely dispersed & coh. w/ each other.
→ have to consider interfacial energy.
early stage: the interface bet'n A-, B-rich diffuse.
& $\gamma_{ch} = f\left(\frac{dc}{dx}\right)$ (conc. grad.). called "grad. energy".
the origin of grad. energy = the increased # of unlike nearest neighbor

• For  a sinusoidal comp. modulation. of λ & ΔX.
the max. comp. grad. $\propto \Delta X/\lambda$. ΔX could be $\oplus$ and $\ominus$

$$\therefore \boxed{\Delta G_\gamma = K\left(\frac{\Delta X}{\lambda}\right)^2}$$ ← to make this $\oplus$

ΔG_ε • If the sizes of the atoms for a solid sol'n - different
the formation of diff. comp. → coh. strain E., ΔG_s. w/ misfit δ.

(3.39) p157.
$\Delta G_s \simeq 4\mu\delta^2 \cdot V$
if incoh.

$$\Delta G_s \propto E\delta^2$$

$\frac{1}{a}\frac{da}{dx}\Delta X$ conc

• For a total comp. diff, ΔX, $\delta = \frac{da}{dx}\cdot\frac{\Delta X}{a}$. a: lattice para.

$$\boxed{\Delta G_s = \eta^2(\Delta X)^2 E' V_m}$$ where $\eta = \frac{1}{a}\left(\frac{da}{dx}\right)$. the fractional change in lattice para./unit comp.

$\neq f(\lambda)$

$$E' = \frac{E}{1-\nu}$$

Date . .

∴ total f.e. change.

(5.47) $$\Delta G = \left\{ \frac{d^2G}{dx^2} + \frac{2K}{\lambda^2} + 2\eta^2 E' V_m \right\} \frac{(\Delta x)^2}{2}$$

the cond. for a homo. s.s. to be unstable and spinodal decomp. starts

(5.48) $$\Delta G < 0. \rightarrow -\frac{d^2G}{dx^2} > \frac{2K}{\lambda^2} + 2\eta^2 E' V_m$$

Spinodal decomp starts w/ $\lambda = \infty$. first. surface $E \simeq 0$

(5.49) chem spinodal $$\frac{d^2G}{dx^2} = -2\eta^2 E' V_m.$$ strain E (ε) → this gives the line in the phase diagram known as "the Coherent spinodal"

coh. spinodal

the coh. spinodal $\frac{d^2G}{dx^2} < 0 \left(= -2\eta^2 E' V_m\right)$ is within the chemical spinodal $\left(\frac{d^2G}{dx^2} = 0\right)$

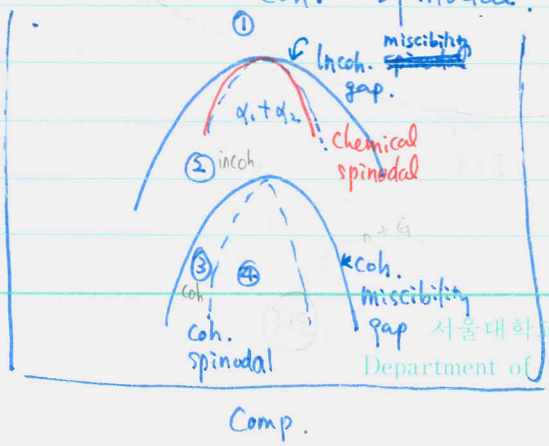
From (5.48) the wavelength of the comp. modulation that can develop inside the coh. spinodal must satisfy the cond.

$\Delta G_v = \Delta H \left(\frac{\Delta T}{T}\right)$ ↑

(5.50) $$\lambda^2 > -2K \Big/ \left(\frac{d^2G}{dx^2} + 2\eta^2 E' V_m\right)$$

$\Delta G_v \propto \Delta T$

∴ the min. possible wavelength decreases with ΔT ↑ below the coh. spinodal.



- coh. misc. gap : the line defining the equil^m composition of the coh. phases (X_1, X_2) from spinodal decomp. (X_1 & X_2 in Fig 5.39)
- Incoh. misc. gap : shown on an equil^m phase. dia. (absence of strain fields)
- Chem. spinodal: no practical use.

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- All sys. in which GP zones ~~also~~ forms — also contains metastable coh. miscibility gap : GP zone solvus. (Fig 5.34)

- at high saturation GP zones are able to form by S. decomp.
  ① if aging is carried out below the coh. solvus but outside the spinodal, GP zones can only form by nucl. & growth
  ② Bet'n incoh & coh. misc. gap. still $\Delta G_v - \Delta G_s < 0$.
  but ~~and~~ incoh. ε-free nuclei form.

- ΔT bet'n the coh. and incoh. misc. gap, or the ch. and coh. spinod : dependent of $|\eta|$ $\quad \eta = \frac{1}{a}\frac{da}{dx}$.

- large atomic size diff → η large. large ΔT required to overcome energy in <100> direction. comp. modulation // {100}.

5.5.6. Particle Coarsening

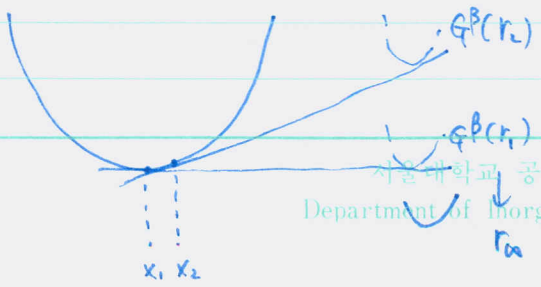
다음 관찰

①

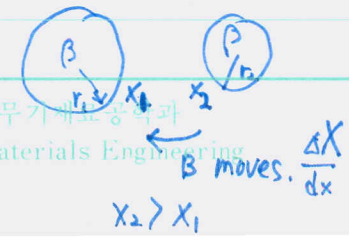
- microstruc. w/ small ppt tend to coarsen to min. total f. e. (then of smaller total interfacial area. ② 주위 conc.이 크기에 따라 다른 결 kinetic

- This accompanies undesirable degradation of prop: loss of strength, the disappearance of g.b. pinning.

- ∵ particle size difference ∴ difference in the time of nucl & rate of growth.



G-Thompson effect.



$$X_r = X_\infty \exp\frac{2\gamma V_m}{RTr} \cong X_\infty\left(1+\frac{2\gamma V_m}{RTr}\right)$$

small shrinks
large grows.
total # of particle
↓
$\bar{r}$ grows

Date

∴ Diffusion controlled sys. growth relationship

(5.51) $(\bar{r})^3 - r_0^3 = kt$. where $k \propto \frac{D\gamma X_e \Omega}{kT}$ atomic vol.

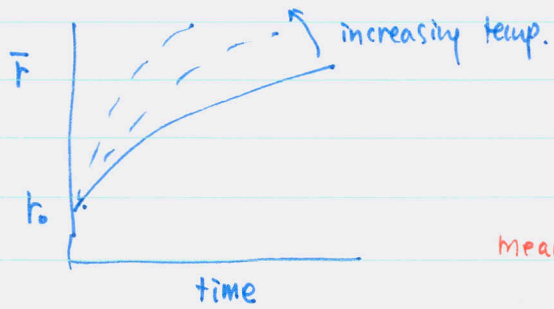
↳ mean. dia at $t=0$.

since D, X_e increases exponentially w/ temp.

$D = D_0 \exp(-Q/kT)$, $X_e = X_0 \exp(-\frac{Q}{kT})$.

∴ $\frac{d\bar{r}}{dt}$ ↑↑ rapidly w/ temp.

(5.52)



$\boxed{\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}}$ the rate of coarsening

meaning: distributions of small ppts coarsen most rapidly.

- a linear $r^3 - t$ relationship may not be kept.
  deviation from diff. short-circuits (⊥. g.b). $r^4 - t$ (g.b.)

  Interface controll $\bar{r}^2 - r_0^2 = kt$. $k \propto \frac{c\gamma X_e \Omega}{kT}$.
  c: Interface control. coeff.
- For low coarsen rate to achieve high strength.
  D, γ, X_e, must be low.

P326. ~~5.8.~~ E

a single particle $\frac{dr}{dt} = -D\frac{X_r - X_a}{r}$ (1) $X_r \cong X_e\left(1 + \frac{2\sigma\Omega}{kTr}\right)$ (2)

vol frac. of β const, mass conservation.

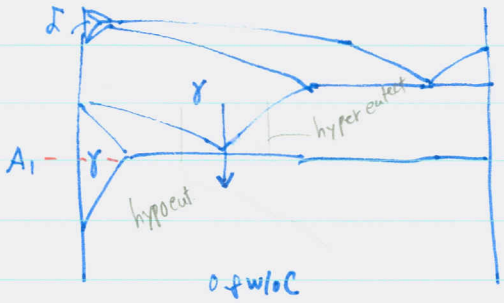
many particle $\frac{d}{dt}\sum \frac{4\pi r_i^3}{3} = 0$ (3) $D\text{-}C\frac{dr_i}{dt} = \frac{2\sigma D\Omega}{kT}\frac{X_e}{r}\left(\frac{1}{\bar{r}} - \frac{1}{r}\right)$

$\frac{dr_i}{dt}$ 제일 빠르게 작아지는 입자 크기는 $r = 2\bar{r}$

p326.

Date . .

5.8 Eutectoid Transf.



- eut. transf.
  $\gamma \rightarrow \alpha + Fe_3C$: lamellae or sheet of Fe_3C in ferrite
  → called pearlite.
- Both Fe_3C & α form directly in contact w/ γ.

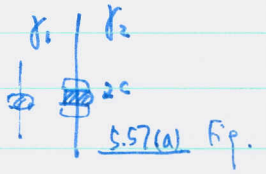
- Pearlite nodules. nucleat on g.b. → move into γ.
  at below A_1 : nodule in the form of hemisphere spheres.

At larger ΔT. the nucle. rate is high & site Saturation occurs. (F.5.56
at g.b. → pearlite forming
→ covered w/ nodule

Nucl. of Pearlite.

1. the nucl. of. Fe_3C or α "on γ g.b."
   which forms first (α or Fe_3C)
   · the order of nucl. (Fe_3C, or α) = f (g.b. struc & comp)
   · if Fe_3C nucl. first, Fe_3C will try to min. the act. E. barrier to nucl. by forming w/ an orientation rel. to γ_1. (Fig 5.57a)

Fe_3C (orthorhombic) $(100)_c // (1\bar{1}1)_\gamma$ $(010)_c // (110)_\gamma$.
$(001)_c // (\bar{1}12)_\gamma$



5.57(a) Fig.

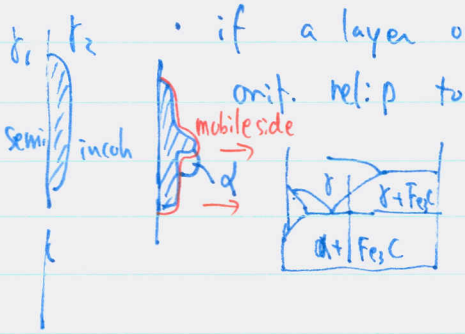
· Fe_3C nucleus : a semicoh. interface w/ γ_1 (starting) low mobility
incoh. mobile interface w/ γ_2

Surrounding : depleted of C. → increase d.f. for the pptn of α
∴ the nucleus of α forms. next to Fe_3C.
w/ an orif. relationship to γ_1 (K-S rel.ip).

p146

2. After nucl. the colony can grow edgewise by the movement of incoh. interfaces → pearlite grows into γ grain of no orientational relat with.

3. if proeutectoid comp. g.b. covered w/ a proeutectoid α or Fe_3C.



· if a layer of procementite (Fe_3C) exists on g.b., α will form w/ an orif. rel. p to Fe_3C on the mobile incoh. side of allotriomorphs (5.57b).

→ Branching of a single lamella into two lamellae !! → two interpenetrating (α & Fe_3C) single xtals

→ the nucl. of pearlite needs the establishment of cooperative growth of the two phase (α, Fe_3C) ∴ takes time

∴ the rate ↑ as time ↑.

→ if not cooperative (같은 속도로 성장하지 않으면) → α & Fe_3C grow in a non-lamellar manner called "degenerate pearlite".

Pearlite Growth

- Pearlite growth analogous to that of a lamellar eutectic

↓ C diffusion interstitially thru γ to the tips of Fe_3C (Sec. 4.3.2)

$\Delta H \frac{\Delta T_0}{T_E}$

(4.37) $\Delta G(\lambda) = -\Delta G(\infty) + \frac{2\gamma_{\alpha\beta} V_m}{\lambda}$ ∴ $\lambda^* = \frac{2\gamma V_m T_E}{\Delta H \Delta T_0}$

(5.53) - min. possible interlamellar spacing (S^*) $\propto (\Delta T)^{-1}$ below A_1 eutectoid temp.

observed spacing (S^0) $\propto S^*$

$U_0 = k_1 \frac{D}{2\lambda} \Delta T$

(5.54) - $\boxed{\text{Growth rate}}$ of pearlite colony (= const) $U = k D_C^{\gamma} (\Delta T)^2$

" controlled by D- const.

① carbon diffusion thru α/γ interface & Fe_3C/γ interface.

→ results in a higher growth rates

Fe-C interstitial

lattice diffusion → slow

- ② but → In alloys of subst'l s. sol'n → diffusion occurs thru the colony/matrix interface

$U = k D_B (\Delta T)^3$

boundary diff. coeff.

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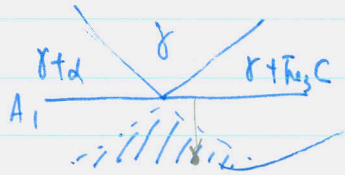
Pearlite in Off-Eutectoid Fe-C alloys

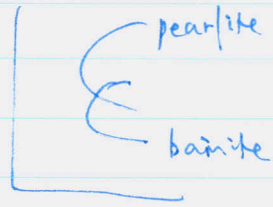
- the formation of pearlite is preceded by the ppt'n of proeutectoid α, Fe_3C.
- If ΔT is large and ΔX is small from eutectoid comp. (by suppressi of proeutectoid appearance) possible to have direct $\alpha + Fe_3C$ (pearlite)



the region that γ is sat'd w/ α & Fe_3C

5.8.2. The Bainite Transf.

TTT



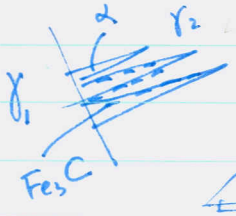
when γ is cooled to large supersaturation → bainite (mixture of α and Fe_3C)

fn (formation temp) microstructurally diff. from pearlite.

~ 500°C both forms competatively.

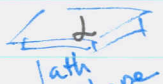
Upper Bainite.

- At 350 – 550°C bainite consists of needles or laths of α w/ Fe_3C inbet'n. : upper bainite.



- Growth : Widmanstätten side-plate

α: nucleated on a p.b w/ K-S rel. w/ one pri γ_2



lath shape.

Since ΔT is very large. the nucleus grows fast into γ_2 w/ α of low energy semicoh. interfa

Date . .

- As the α laths thicken, the C content ↑ in γ → Fe_3C nucleates
- upper bainite resembles finely spaced Widmanstätten plate.
  as the formation temp ↓, individual spacing ↓
- At the highest temp where pearlite & bainite grow competatively it can be difficult to distinguish the pearlite from the upper bainite.

- Diff. bet'n P and Bainite : Xtallography.
  In P Fe_3C and α have no special orient'n relationship to γ in which they are growing. (γ_2)
  In B they do have a relationship to γ "
  α - γ_2 (K-S relationship)

Lower Bainite.

- At sufficiently low temp. the microst. of bainite changes from laths into plates, carbide dispersion → finer like in tempered martensite.
- transf. temp. = f (carbon content)
  C < 0.5 wt %. T_{transf} ↑ with C ↑.
  C = 0.5 ~ 0.7 ↓ "
  0.7% < C " → const at 350°C w/ C ↑.

- Carbides ppt in the ferrite for low bainite.
  ↳ metastable transition carbide (ε-carbide) or Fe_3C aligned at the same angle to the plane of α plates

Transformation Shear.

- bainite plates form by a shear mechanism as in the growth of M.
- It's supposed that the Fe atoms are transferred across the α/γ interface in an ordered military manner.

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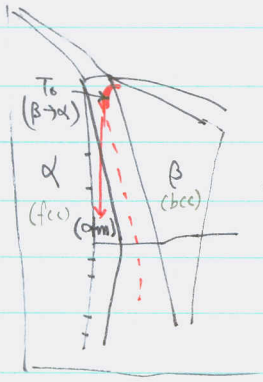
- but the growth rate of the bainite plate · controlled ① by carbon diffusion rate away from the interface or ② by the rate of carbide ppt'n behind the interface
  cf. martensite : no diffusion, grow fast as the plissile interface advance.
- Similar in phenomenological behavior.
  orientation relationships, habit planes.

p 338 - 349 (skip)

5.9 Massive Transf. (Cooling rate dep.)

- Cu-38 a/o Zn. the most stable state β (bcc) above ~500°C
  " α (fcc) below 500°C
  " $\alpha+\beta$ inbetween



- the type of transf occurring on cooling the β phase depends on the cooling rate.!!
  - slow to moderate cooling rates : α ppts like ppt. of α from γ in Fe-C
    α: g.b. ppt. of γ
  - slow cooling rates the formation of equiaxed α at small ΔT.
  - higher cooling rates: transf. at lower temp. & Widmanstätten a needles ppt.
- α richer in Cu than β requires the diffusion of Zn away from the α/β interface
  → slow process ∵ Cu-Zn forms substit. solid. sol'n.
  If this is quenched fast, there's no time for the α ppt'n
  β retained below 500°C $\beta \to \alpha$ w/ the same comp.

Mass. transform.
Massive α grains nucleate at g.b's → grow quickly into β.
∴ α/β boundary irregular

ppt'n	N+G mechanism	cooling rate	ppt'n site	
massive	diffusion of	slow	g.b & matrix	thermal
	" less	intermediate	g.b ppt'n	"
martensite	" less	rapid	g.b & matrix	a thermal

β → T → R

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by diffusionless

no comp. change / struc. change only.

- $\alpha_{massive}$ grows as fast as the Cu & Zn cross the α/β interface
  - → long-range diffusion not needed.
  - → only involves thermally activated jumps across the α/β int

- the massive transf. = diffusionless civilian transf.

Fig 5.75 TTT, CCT (continuous cooling transf.) curves for this.

TTT보다 냉각속도 (cooling rate)에 의한 phase transf 를 나타내는

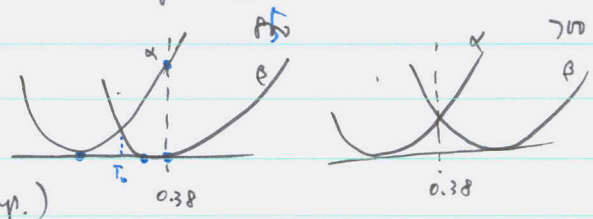
- the migration of the α/β interface ~ similar to that of g.b. during recrystallizn. of single-phase matl., but the driving force ~~of~~ the massive transf. ~orders of mag. greater than for recrystallizn
- It is not martensite!! mechanism different.
  - ↳ by the cooperative movement of atoms across a plissile interface
  - massive transf. → by thermally activated interface migration
    - → also transform martensitically if quench rate is high
    - : w/ some β retained at g.b. after quench.

- Transformation to α from β at higher temp. where α is not stable.
  - conditions ① the f.e. of new phase < that of parent phase (β)
  - ② both phase same composition.

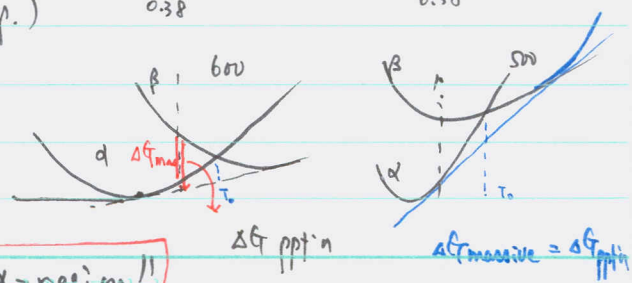
ex. Cu-38 a/o Zn Fig 5.77

at 700°C $G^\beta = G^\alpha$

T_0 ↑ (locus for diff. comp.) in phase diagram.



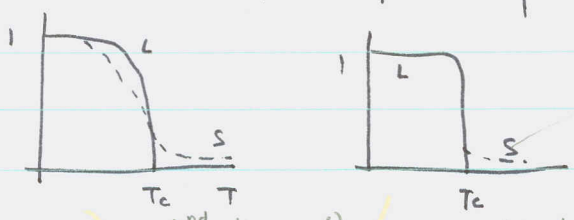
Anywhere below T_0, massive transf possible in two-phase region.



In practice, it occurs in only in α-region!!

Date

1 Fig. 5.81. the variation of l-range order (L)



$S = \frac{P_{AB} - P_{AB(random)}}{P_{AB(max)} - P_{AB(random)}}$

Fig. 1.21~22.

2nd order (continuous) 1st order nucl. growth

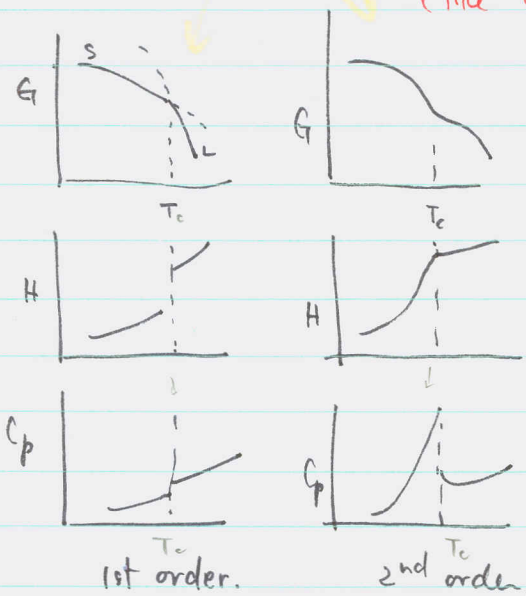
(a) Cu-Zn type. (b) Cu_3Au type.

($\beta' \to \beta$) continuous decrease L decreases near Tc. why different? due to atomic conf.

Above Tc, L=0 but since $\Omega < 0$ ($= Na^2 z \varepsilon^0$) some tendency of ordering (short range order)

2 the majority of phase transf. – 1st order transf. → means the 1st der. of the G.f.e. $\left(\frac{\partial G}{\partial T}\right)_p$ & $\left(\frac{\partial G}{\partial p}\right)_T$ are discontin (like in melting)
(=-S) (=V)

$dG = -SdT + Vdp$



1st order: S, V, H discontinuous

2nd order transf → mean the 2nd der. of G.f.e. $\frac{\partial^2 G}{\partial T^2}$, $\frac{\partial^2 G}{\partial p^2}$ discon

H. continuous. $\frac{C_p}{T}$ discon

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right) = \frac{C_p}{T}$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T = -V\beta$$ compressibility

3 (Cu-Zn)

Fig 5.81(a) gradual disordering ∴ U (int. E) & H. continuous across Tc

∴ Fig 5.82(b) a 2nd-order transf. $\beta' \to \beta$ (Cu-Zn)

diffusional process

Fig 5.81(b) abrupt change to disordered struc. at Tc.

(Cu-Zn) the disordered state will have a higher U & H. (=U+PV) than order

1st order ∴ greater # of like-like atoms – discontinuous H wrt T

∴ many like-like atom → needs H-like Ener-state

Date . .

ii) Disorder to Order

A. * two mechanisms (Disorder to Order)

equivalent to spinodal decomp & ppt'n as mechanisms for the formation of coherent zones in alloys w/ $\Delta H^M > 0$ ($\Omega > 0$) !!

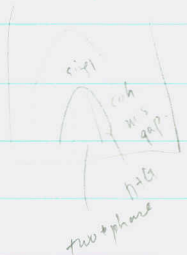
i) a continuous increase in short-range order by local rearrangement → to l-range order

ii) by nucleation & growth process if there is an energy barrier to the formation of ordered domains.

i) mechanisms operable in 2nd-order transf. (Fig. 5.81 (a) 정규반) or at very high supercooling below T_c.

ii) mech more common !!

Fig 5.83. nucl. & growth process.



2 Fig 5.83 the nucl & growth mech. (process) mechanism.

independently nucleated domains will often be out of phase.
→ grow and form APB (anti-phase domain boundary or APB)
high energy area !!

3 Nucleation process expected to be homogeneous, indep. of lattice defects & g.b.

∵ (1) Since nucleus & matrix have the same Xtal struc.
∴ ΔG^* for ordered domain (act. E. barrier) → small.
∴ coh interface w/ a low γ.

(2) if it is a stoich. composition, both have the same comp.
∴ small ΔG_ε.

例: Coft. nucl. & growth.

B. * Effect of degree of Undercooling.

$N = A \exp\left(-\frac{\Delta G^*}{kT}\right)$ f.o.o $\quad \Delta G^* = \left(\frac{16\pi \gamma^3 T_m^2}{3 L_v^2}\right) \Big/ (\Delta T)^2$ solid'n

low ΔT : nucleation rate small ∴ large domain size.

high ΔT " high ∴ small "

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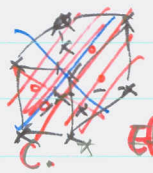
- Fig 5.81 → the degree of l-r order = f(T) : the degree of order ↑ as T↓ by homo. diffusive rearrangement with in a domain

~~Fig 1.20b~~ - the degree of l-r order (5.83) initially small → eventually l-r order established by the coarsening of APB.

a fn of (type of superlattice)



C. Effect of Struc on APB

Fig 1.22(a) - Cu_3Zn ($L2_0$) two different sublattices ∴ no metastable APB struc. (continuous) → easy to coarsen

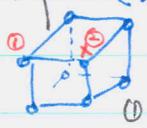


Fig 5.85

Cu_3Au ($L1_2$) (N+G) 〃 〃 ∴ diff. to 〃 go thru various metastable

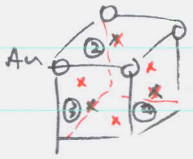


Fig 1.22(b) Fig 5.86 APBs tend to align // to {100} to minimize the # of high energy Au-Au bond.

- Cu_3Zn rapid continuous ordering ∵ the transformation is 2nd order

〃 can happen. by a rapid cont. ord

Cu_3Au slow even though atomic mobility ~ similar to Cu_3Zn

∴ ~~2nd order~~ 1st transf. ~~but~~ by nucl. & growth.

D. * Effect of Stoichiometry

cf. 1st order transf. always end up w/ a two-phase region at non-stoich. comp.

(disordered phase → ordered ppt. + disordered matrix

∴ Changes in comp. on ordering, l-r diffusion } must be involved

2nd order transf. a single phase. even at non-stoi. comp. (vacancy, wrong sites remained)

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- Massive transf. interface incoherent, migrate by ① continuous growth like a h-a g.b. ② sometimes by the lateral movement of ledges across faceted interfaces.

- System
  0. Cu-20at% Al
  1. Fe-C. $\gamma \rightarrow \alpha$ transformation provided that the quenching rate is bet'n that for ppt'n growth and that for martensitic transf.
  2. Metastable phase also form. massively.
  3. two phases, (one of them metastable) transf. product can be
     ↳ the same comp. as the parent phase.
     ↳ form simultaneously

not necessary a single phase ←

5.10. Ordering Transf.

Ω = N.Z.E

A system of $\Delta H^{m} < 0$ ($\Omega < 0$) prefer unlike nearest neighbors
→ tend to form ordered phases

- Two ways of forming ordered struc. of non-stoich. phases
  ① some atom sites can be left vacant
  ② " can be located on wrong sites

i) Order to Disorder.

- Completely ordered single Xtal (CuZn, Cu_3~~Al~~ Au)

long-range order para. $L = \dfrac{r_A - X_A}{1 - X_A}$ or $\dfrac{r_B - X_B}{1 - X_B}$

r_A: prob. that an A site is occupied by the right kind of atom

X_A: mole fraction of A.

$S = \dfrac{P_{AB(real)} - P_{AB(random)}}{P_{AB(max)} - P_{AB(random)}}$

at 0K $L = 1$. G_{min} (lowest Internal E)

at higher temp $L < 1$ w/ some disorder

($\Delta G = \Delta H - T\Delta S$ as $T\uparrow$, $\Delta S\uparrow$ needed to $\Delta G\downarrow$.)