2018 Fall

Advanced Solidification

11.23.2018

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Solidification of Pure Metal   : Thermal gradient dominant

⇕

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional Supercooling (C.S.)

Planar → Cellular growth → cellular dendritic growth → Free dendritic growth

Thin zone formation by C.S. at the sol. Interface **Dome type tip / (surrounding) hexagonal array**	**T↓ → Increase of C.S. zone** **Pyramid shape of cell tip / Square array of branches / Growth direction change toward Dendrite growth direction**	**formed by releasing the latent heat from the growing crystal toward the supercooled liquid** **Dendrite growth direction/ Branched rod-type dendrite**

→ "Nucleation of new crystal in liquid" **which is at a higher temp. than the interface at which growth is taking place.**

b) Segregation

: **normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inverse segregation, coring and intercrystalline segregation, gravity segregation**

: **undesiable ~ deleterious effects on mechanical properties**

→ **subsequent homogenization heat treatment, but diffusion in the solid far to slow**

→ **good control of the solidification process**

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5.10. Types of Segregation

* **Last discussion on "solute redistribution in single phase alloys"**

   → **"Various types of segregation"**

* **Segregation: result of rejection of solute at the interface during solidification**

   The difference depends on the "rejection direction / distance / solute motion".

* Segregation

(a) Macrosegregation : Large area
   <u>composition changes over distances </u>comparable to the
   size of the specimen.

    Four important factors that can lead to **macrosegregation**

    a) **Shrinkage** due to solidification and thermal contraction.
    b) **Density differences** in the interdendritic liquid.
    c) **Density differences** between the solid and liquid.
    d) **Convection currents** driven by temperature-induced density differences in the liquid.

(b) Microsegregation : in secondary dendritic arms
   occur <u>on the scale of the secondary dendrite arm spacing</u>.

Fig. Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).
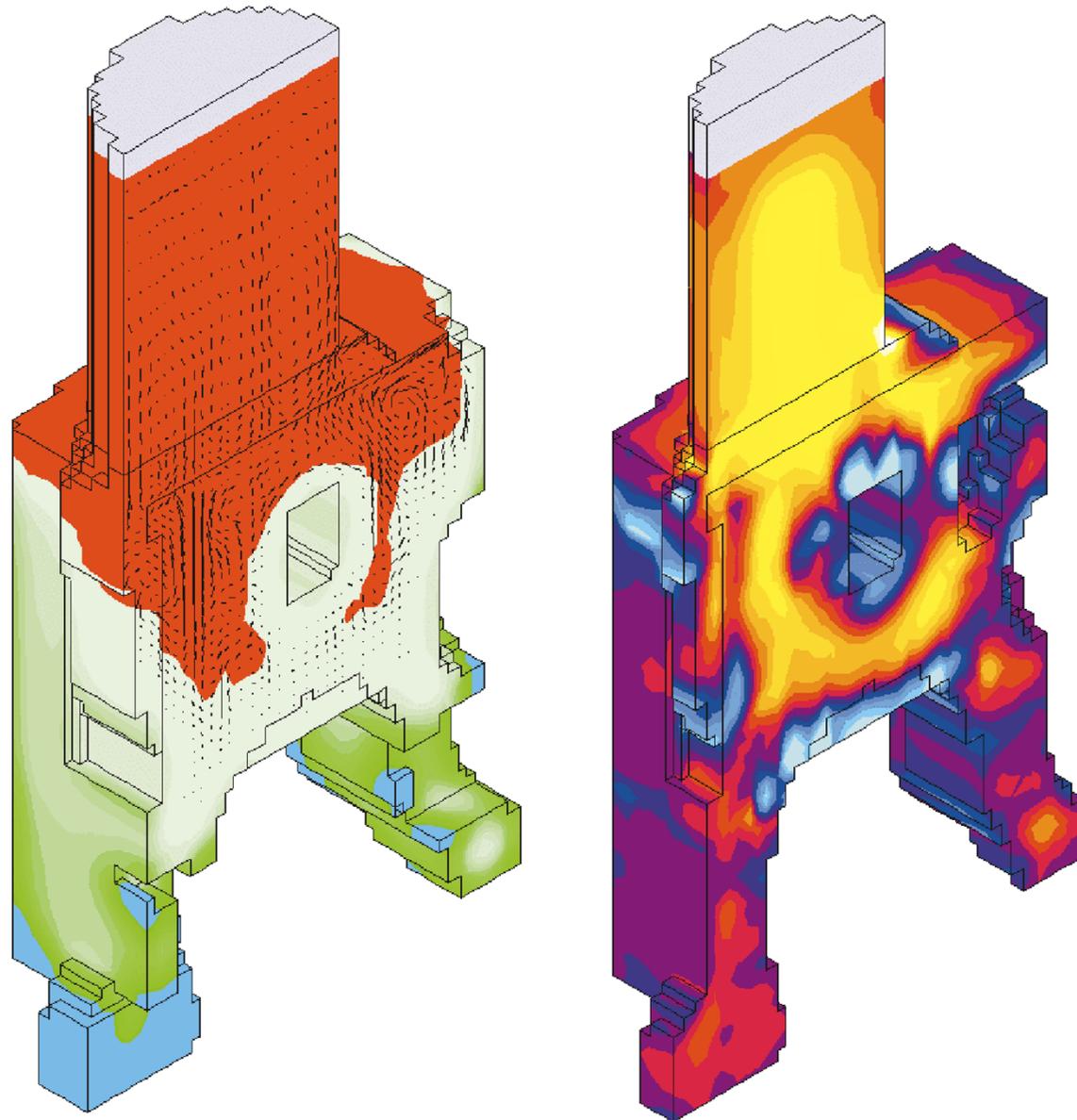
Fig.
Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a <u>single freckle </u>(right) (courtesy of A. F. Giamei, United Technologies Research Center).

Fig.
Sulfur print showing centerline segregation in a continuously cast steel slab (courtesy of IPSCO Inc.).

t, center

Boron

25 nm

130 nm

Z

$(10 \times 10 \times 20 \ nm^3)$

Si

C

B

Austenite   **G.B.**   **Austenite**   **G.B.**
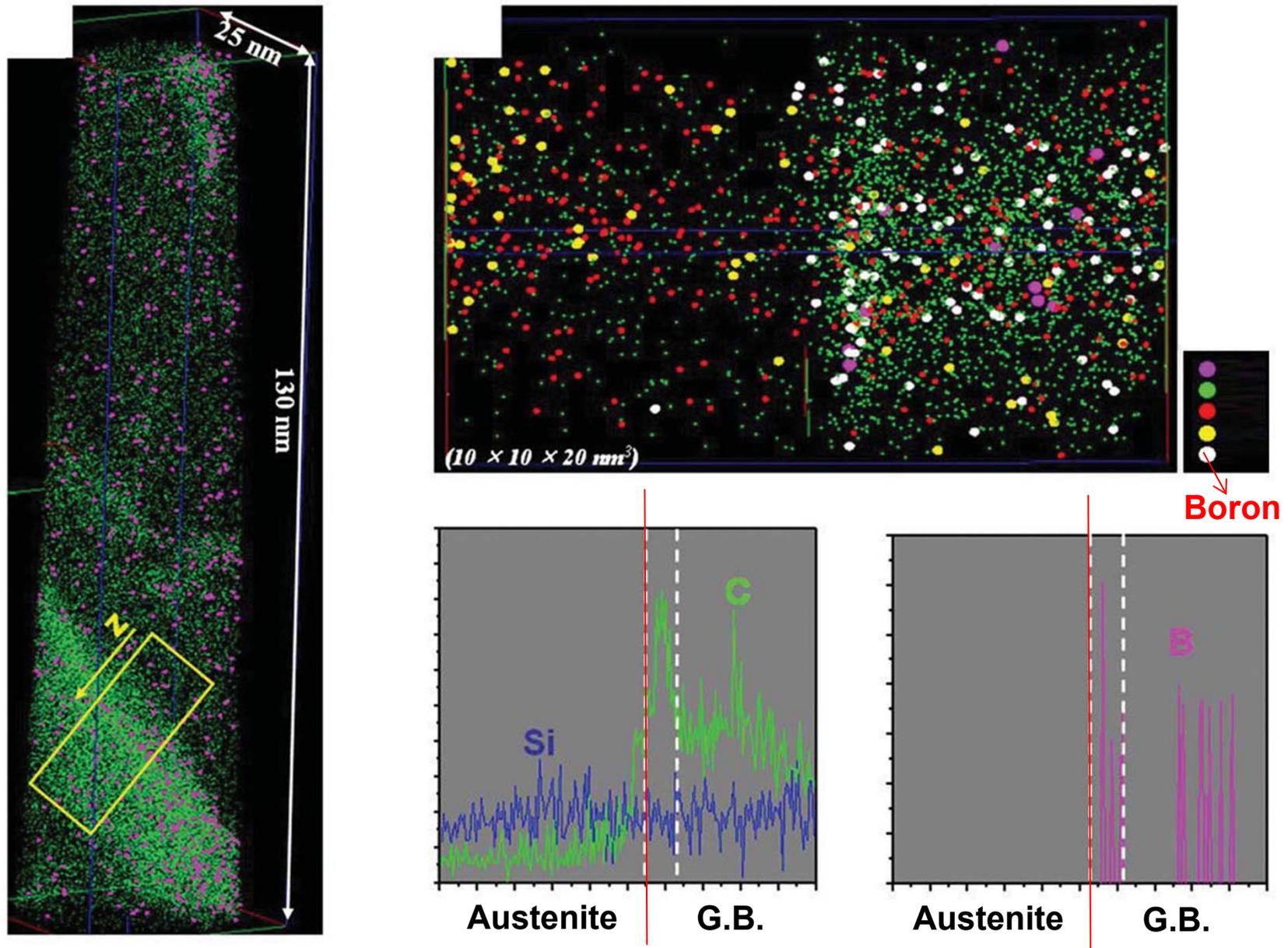
The result obtained by APT analysis. (a) 3D Atom map of **Boron steel containing 100 ppm Boron** and (b) composition profile showing **solute segregation within retained austenite and grain boundary**

1) Normal segregation

: motion of solute parallel to the direction of solidification

The form of curve depends on ① equilibrium distribution coefficient k_0, ② the rate of R of solidification (or the time-distance relationship if R is not constant), and ③ the amount of mixing by fluid motion.

→ **Actual segregation**: depends very much on **"sample geometry"**

influences **both** ① **solidification rate** ② **amount of convection**

→ **difficult to state general rule for predicting the result**
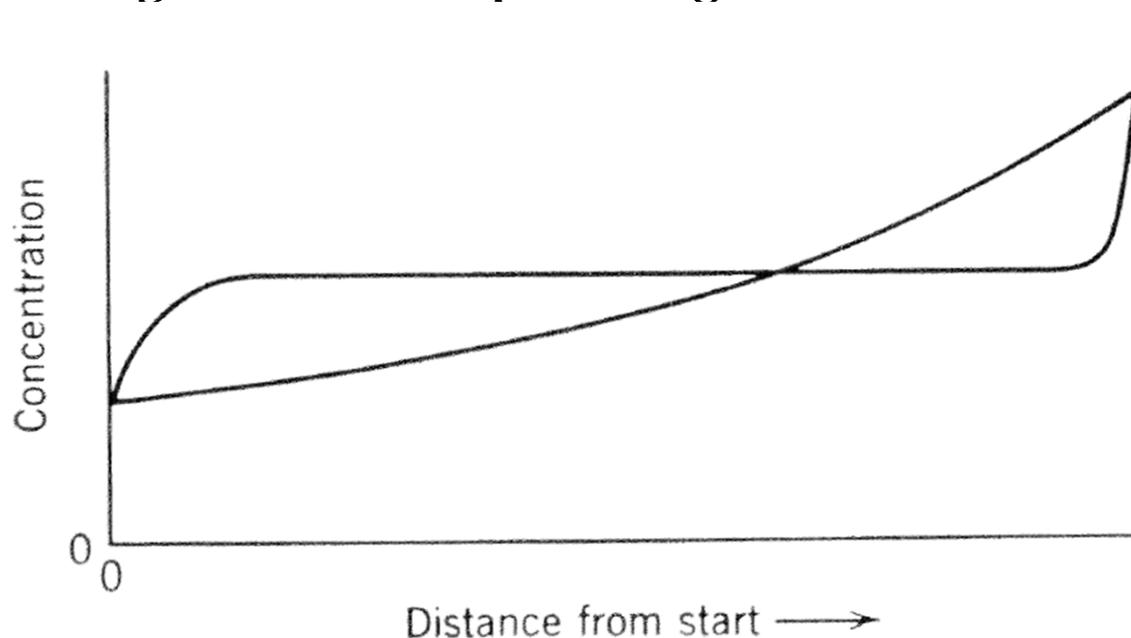
Fig. 5.42. Extreme cases of normal segregation

1) Normal segregation

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- **Variation of Segregation pattern**

  Solidification rate

  Below 2 cm/hr ⟷ Above 20 cm/hr

  Mixing dominant   Diffusion control

→ **Oversimplification, because <u>the form of the interface</u>, which depends on the extent of constitutional supercooling, has an important influence on the mixing process.**
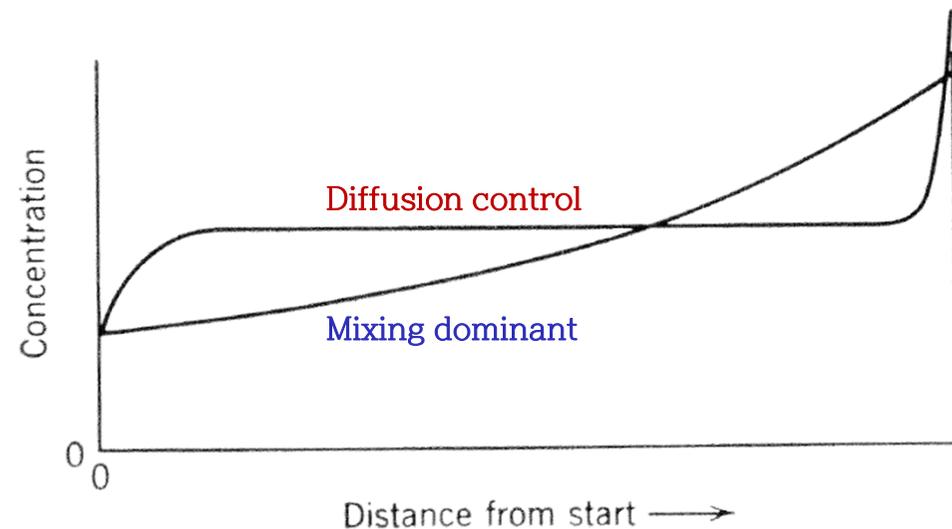

Fig. 5.42. Extreme cases of normal segregation

2) Grain boundary segregation during the process of solidification

: This is not to be confused with equilibrium segregation at GB.

A groove: there is no significant segregation to the boundary unless there is some constitutional supercooling, in which case cellular segregation would also occur.

→ Segregation to the low-angle boundaries that are the characteristic feature of macromosaic or lineage structure
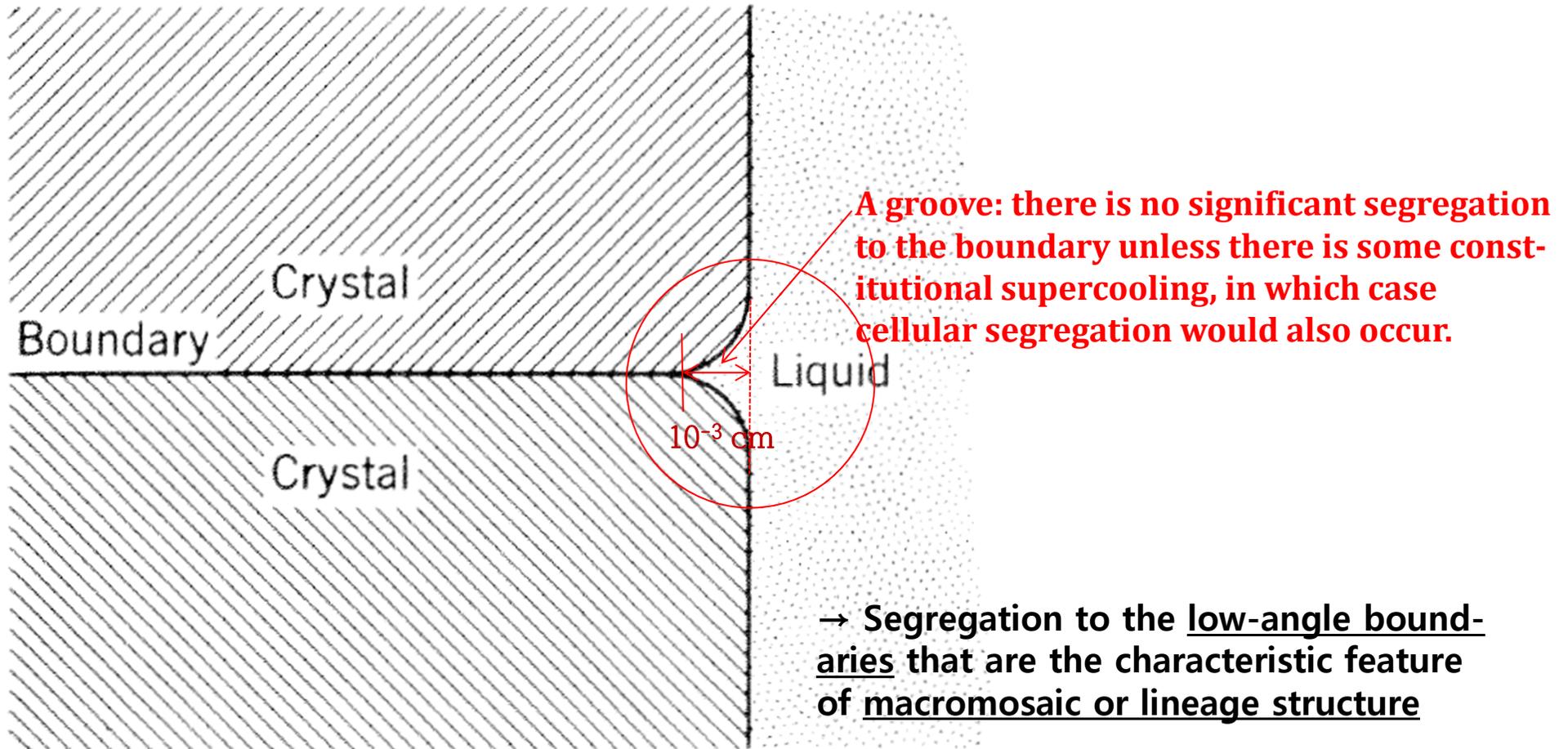
Fig. 5.43. Conditions for grain boundary segregation

Whose mobility would be high between special and random boundaries?

By considering grain boundary structure, (Mobility depending on GB structures)

High energy G.B. → relatively open G.B. structure → High mobility

Low energy G.B. → closed (or denser) G.B. structure → Low mobility

**But,**

Ideal ⟺ Real

2) The other special boundaries are usually more mobile than random high-angle boundary. Why?

If the metal were "perfectly" pure the random boundaries would have the higher mobility.

⇒ **Due to differences in the interactions of alloy elements or impurities with different boundaries**

Same driving force

Ex) 1) coherent twin boundary ~ almost entirely immobile

Special boundaries	
36°–42° (111)	△
23° (111)	▲
26°–28° (100)	□

Less sensitive to impurities

'Random' grain boundaries — **Decreases rapidly with increasing alloy content**

More sensitive to impurities

Increasing Sn contents ⟶

Rate of grain-boundary migration at 300°C mm min⁻¹

Concentration of tin, wt%
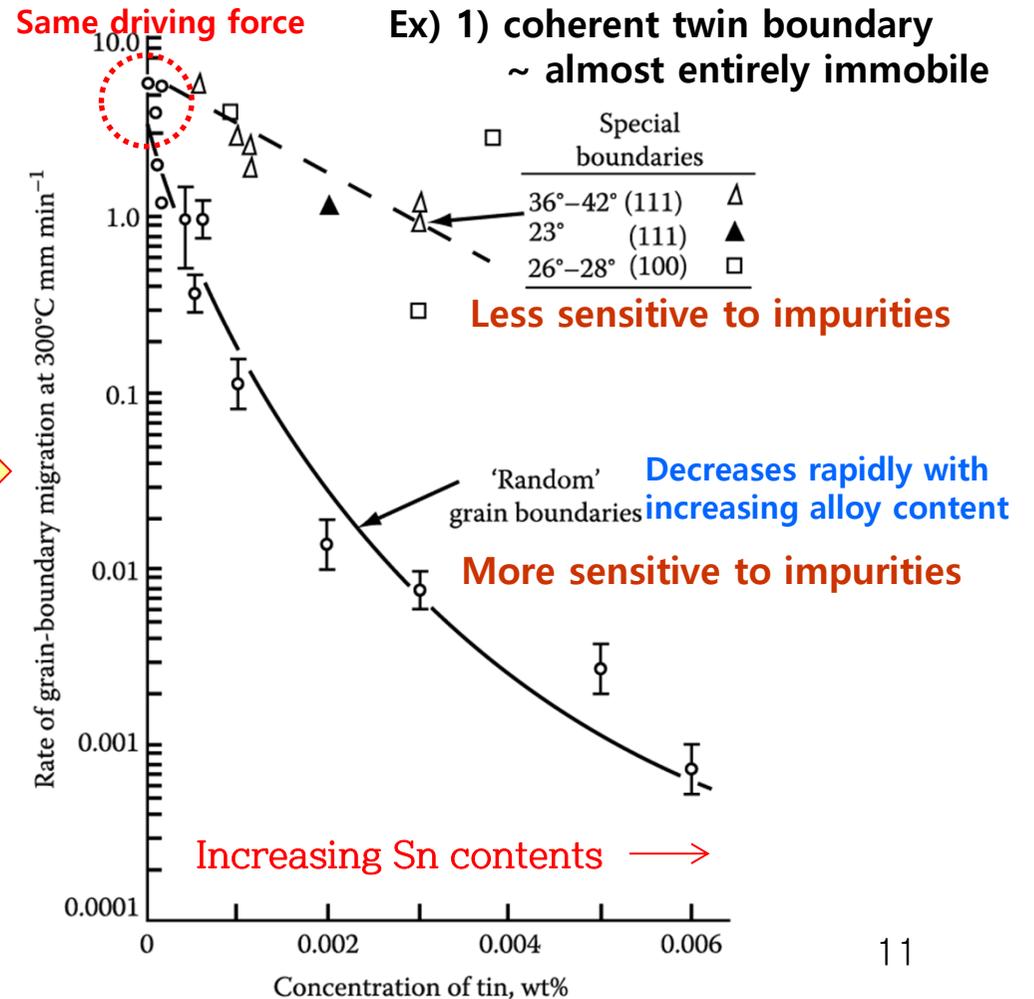
Migration rate of special and random boundaries at 300 ºC in zone-refined lead alloyed with tin under equal driving forces

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ΔG_b, tendency for segregation, and GB enrichment ratio, X_b/X_0 increase as the matrix solubility decreases.

Grain boundary enrichment ratio β_b ~ X_b/X_0

⊙Cu–Bi
○αFe–s
*αFe–C
*Ni–B
*αFe–B
AISI 3340 – Sb
⊙δFe–N
C, Mn steel–Sb
⊙Cu–Sb
⊙δFe–P
*⊙γFe–P
⊙αFe–Sn
⊙δFe–Sn
γFe–Cr ○γFe–Si
δγFe–Mn
○γFe–Ni   ○δFe–Si
○αFe–Si
Cu–Au

Atomic solid solubility x_{c_0}

<Increasing GB enrichment with decreasing solid solubility in a range of system>
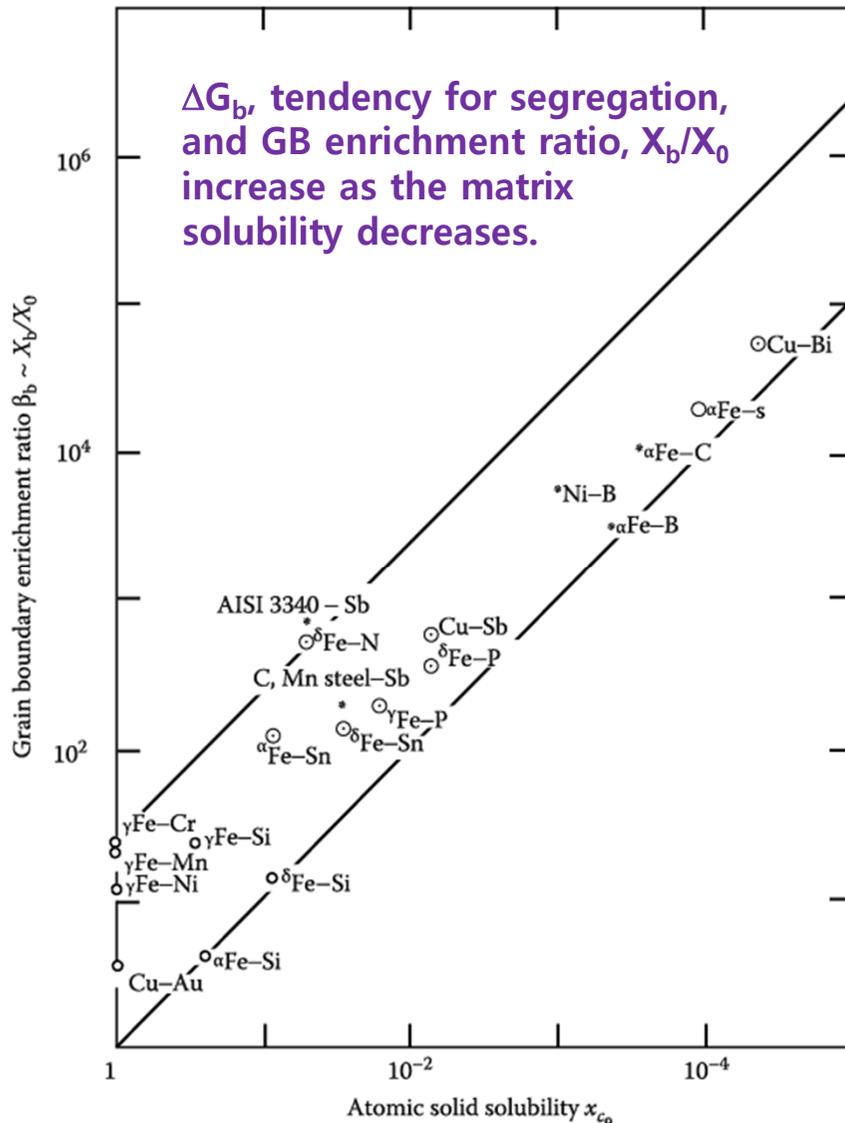
X_0 : matrix solute concentration/ X_b : boundary solute concentration
ΔG_b : free energy reduced when one mole of solute is moved to GB from matrix.

→ The high mobility of special boundaries can possibly be attributed to a low solute drag on account of the relatively more close-packed structure of the special boundaries.

* Solute drag effect

In general,
G_b (grain boundary E) and mobility of pure metal decreases on alloying.

~Impurities tend to stay at the GB.

Generally, ΔG_b, tendency of seg-regation, increases as the matrix solubility decreases.

$$X_b = X_0 \exp\frac{\Delta G_b}{RT}$$

X_b/X_0: GB enrichment ratio

- Decreases as temp. increases, i.e.,
  the solute "evaporates" into the matrix

Low T or Δ G_b ⇧   X_b ⇧   Mobility of G.B. ⇩

→ Alloying elements affects mobility of G.B.

3) Cellular segregation

: after cellular solidification, **at the "terminal transient" region**

* **Temp. and solute distributions associated with cellular solidification.**

1) Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.
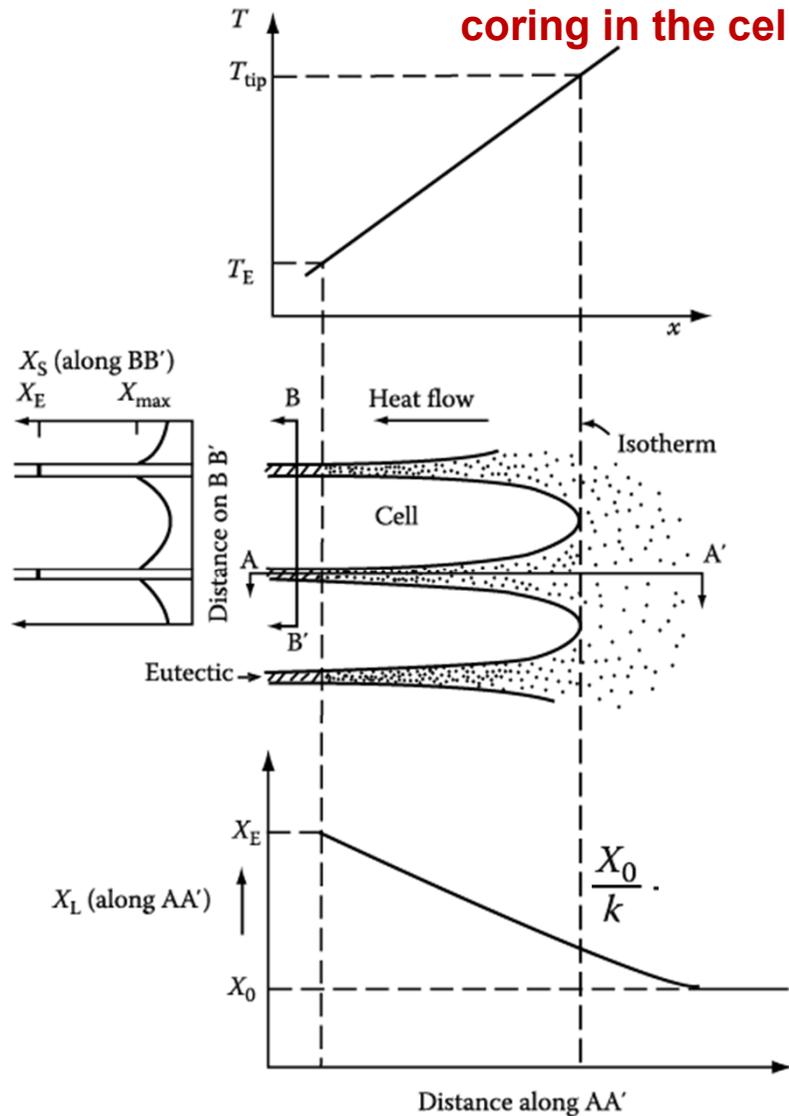
2) **Tips of the cells grow into the hottest liquid and therefore contain the least solute.**

3) **Even if $X_0 \ll X_{max}$**

Solute file up → eutectic solidification

→ formation of 2nd phases at the cell wall

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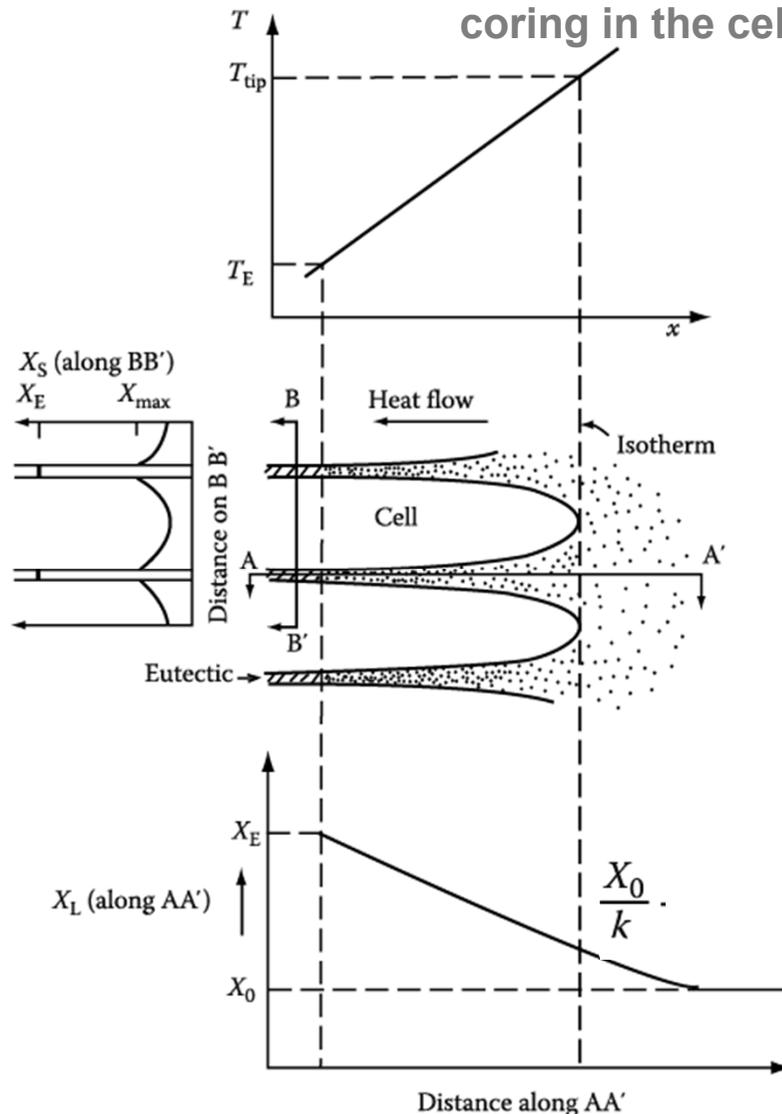
2) Tips of the cells grow into the hottest liquid and therefore contain the least solute.

3) Even if $X_0 << X_{max}$
   Solute file up $\rightarrow$ eutectic solidification
   $\rightarrow$ formation of 2nd phases at the cell wall

- **Segregation deceases as a result of diffusion**

  ① **during cooling down after solidification**

  ② **any subsequent annealing process**

$\rightarrow$ **but, "dislocation" associated with the solute at the cell walls may tend to stabilize it and limit the homogenizing effect of annealing.**

4) Dendritic segregation

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

Fig. 5.44. Distribution of Cu in an Al−4.5% Cu alloy

Fig. 5.45. Segregation in Al−Cu alloy

Cu segregation
: light contrast in microradiograph
  most concentrated close to the plates

used Biloni's epitaxial film technique

to show the segregation in Al−Cu alloys

4) Dendritic segregation

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

Quantitative work on the actual distribution of solute has been carried out using electron microprobe technique, with which they were able to establish solute "iso-concentration lines", it is apparent that the plate-like structure is in this case built up of a main stem and coalesced branches. → The extremely complicated geometry of the cellular structure makes it very difficult to form realistic theoretical predictions with which to compare the experimental results. → "Phase field modeling"
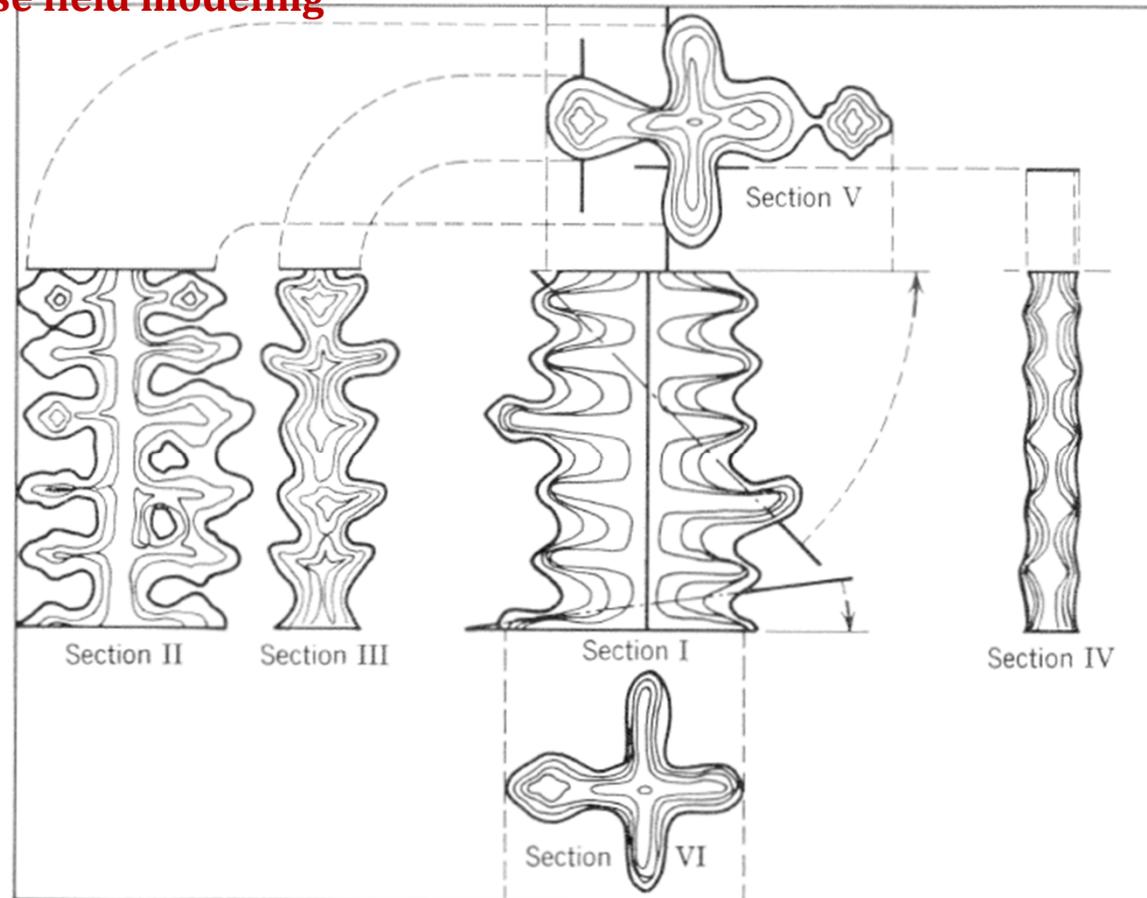
Fig. 5.46. Quantitative results on distribution of solute in columnar dendritic crystal

4) Dendritic segregation

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But, **Flemings and Brody** have shown that good agreement with the electron-probe results can be obtained from calculations based on a very simple model (solidification is regarded as taking place inward from two plane "walls" whose spacing is equal to that of the cell walls.

The calculated distribution using

$$C_s = k_E C_0 (1 - g)^{k_0 - 1}$$

is shown in Fig. 5.47 for some Al-Cu alloys.

- The speed of solidification does not appear explicitly in this solution, because the cell wall spacing depends upon speed.

- Thus, the distribution of solute is independent of speed if it is plotted in the dimensionless form of Fig.5.47.
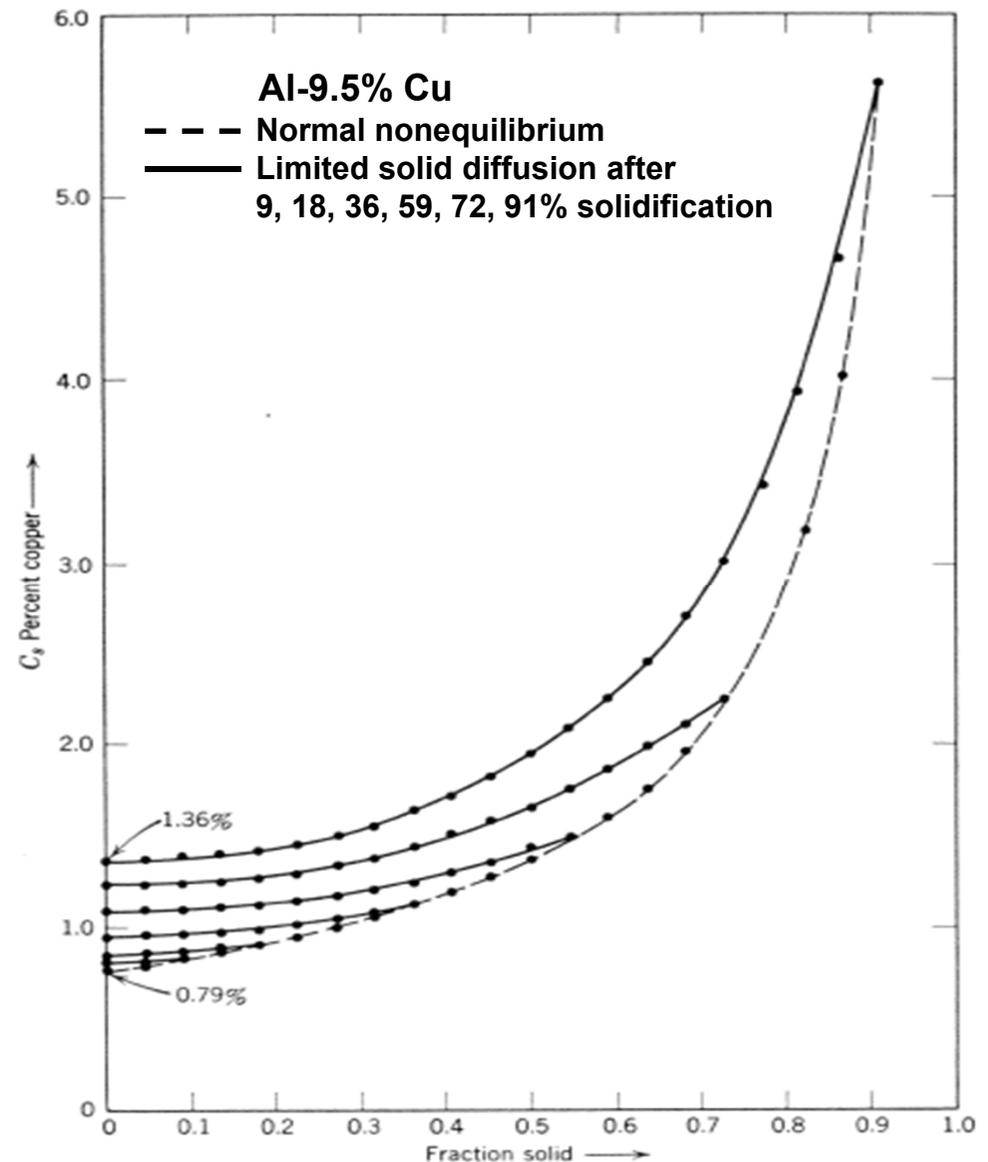
Fig. 5.47. Calculated distribution of solute between walls of cellular dendritic structure

4) Dendritic segregation

: Almost all work on micro-segregation in alloys has been on cellular-dendritic structure

* Maximum concentration (eutectic composition & independent of the rate of solidification)
  → compared experimental results with theoretical values based on various assumptions
  of the amount of diffusion that occurs in the solid during solidification

* Small scale cellular dendrite structure
  (= large difference in concentration btw
  initial and terminal transient regions)
  give rise to very steep concentration
  gradients in the alloy as it solidifies.
  → some homogenization should take
  place by diffusion while the alloy is
  cooling down after solidifying.

——— Calculated γ=1.2 x 10⁻⁹

⊗ — 12 hours total time of solidification
○ — 36 hours total time of solidification
□ — 60 hours total time of solidification
△ — 84 hours total time of solidification

Fig. 5.48. Comparison between calculated and experimental distributions of solute.

4) Dendritic segregation

: **Almost all work on micro-segregation in alloys has been on cellular-dendritic structure**

*** Flemings and Poirier have shown that the amount of homogenization during cooling can be predicted with reasonable accuracy if the initial distribution is calculated in the manner discussed above. → Fig. 5.49.**
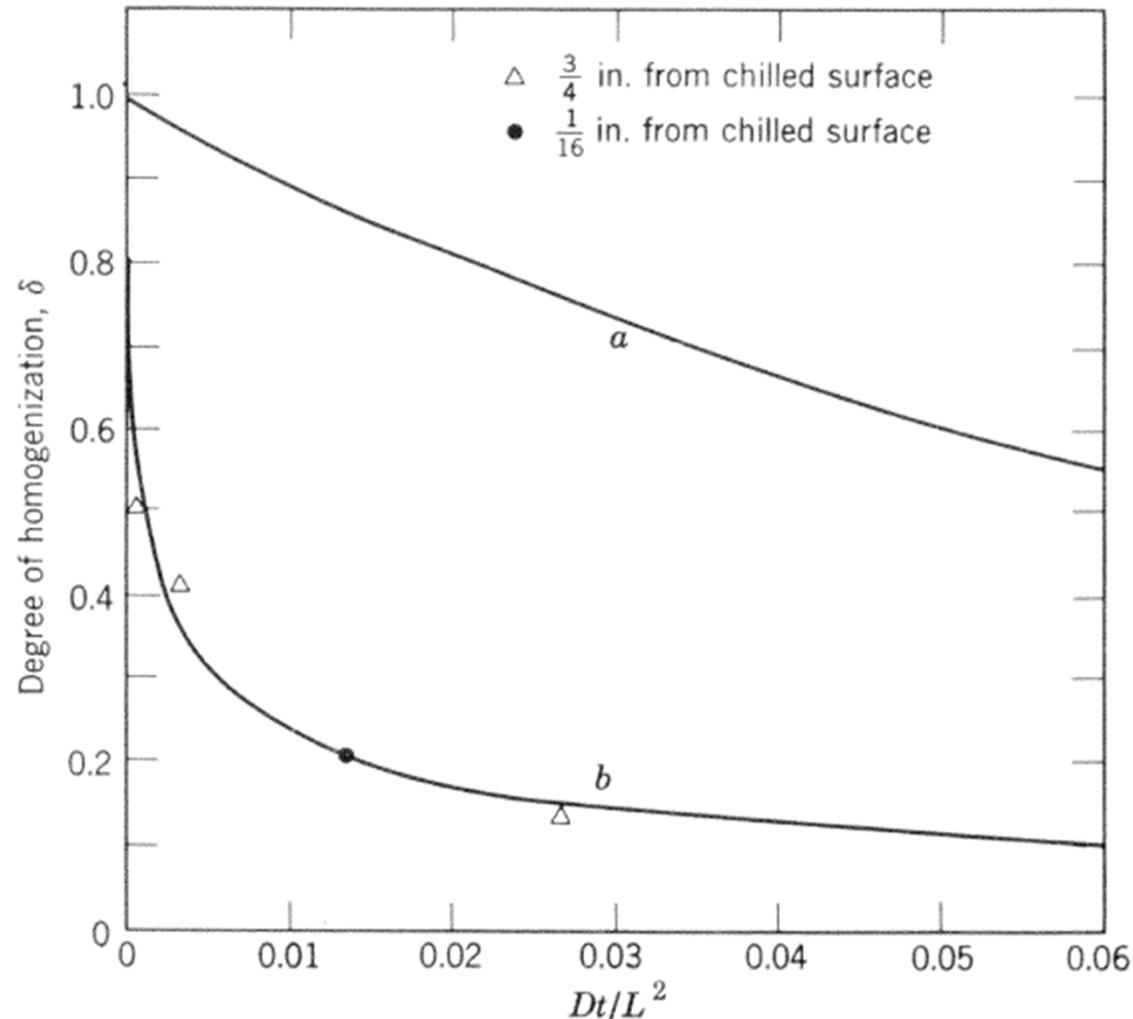

Fig. 5.49. Experimental and calculated results for homogenization during cooling.

5) Inverse segregation

：occurs when a solute that is rejected during solidification is present at a higher concentration in regions that solidified earlier than in those that solidified later. (=solute moves in the direction opposite to that of normal segregation)

→ **Formation mechanism originally proposed by Scheil.**

* Shrinkage that in most alloys accompanies solidification **may cause motion of the most "solute enriched" liquid in a direction opposite to that of the general solidification front.**
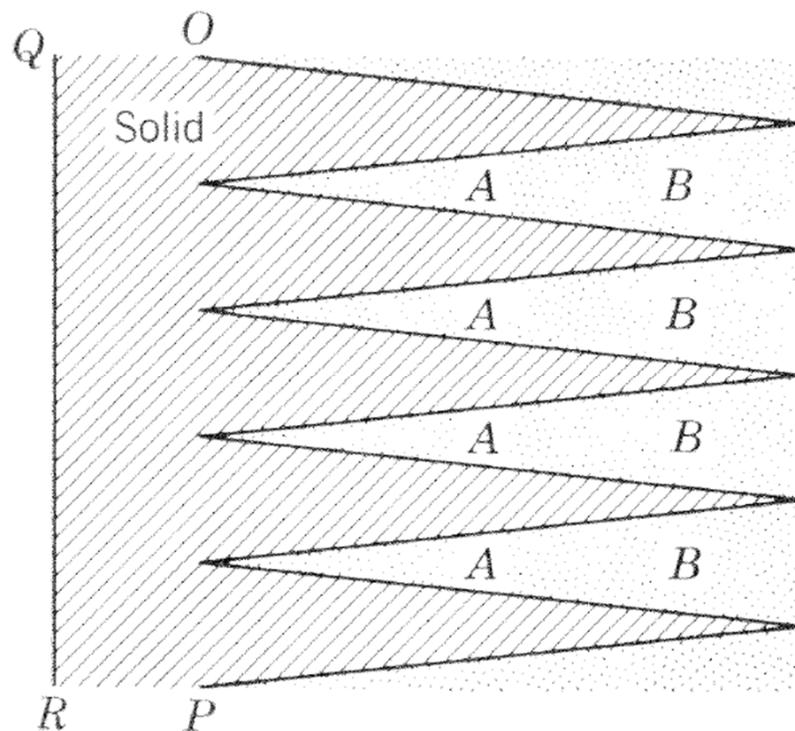
Fig. 5.50. mechanism of inverse segregation

* Left of OP line: completely solidified.

→ **As the region AA solidify, shrinkage takes place, causing the solute enriched liquid at BB to move toward the left.**

* The effect is larger than might be expected due to the highly enriched composition of the liquid in the terminal transient condition, i.e. when there is only a small amount remaining in a given region.

* General validity of this theory : inverse segregation does not occur in alloys that expand on solidification.

5) Inverse segregation

* Quantitative approach of inverse segregation (by Kirkaldy & Youdelis)

(Assumption1) No shrinkage void →liquid: compensate completely for the shrinkage

(Assumption2) Liquid in the interdendritic region is always of uniform composition.

& it is always in equilibrium with the solid that has just been deposited on dendrite.

However, the dendrites are not of uniform composition, since they formed from a liquid of continuously changing composition.

* This theory describes an alloy system in which enrichment of the liquid is limited by a eutectic composition; the case considered by Kirkaldy and Youdelis was that of the Al-Cu system, of which the relevant part of the diagram is shown in Fig. 5.51.
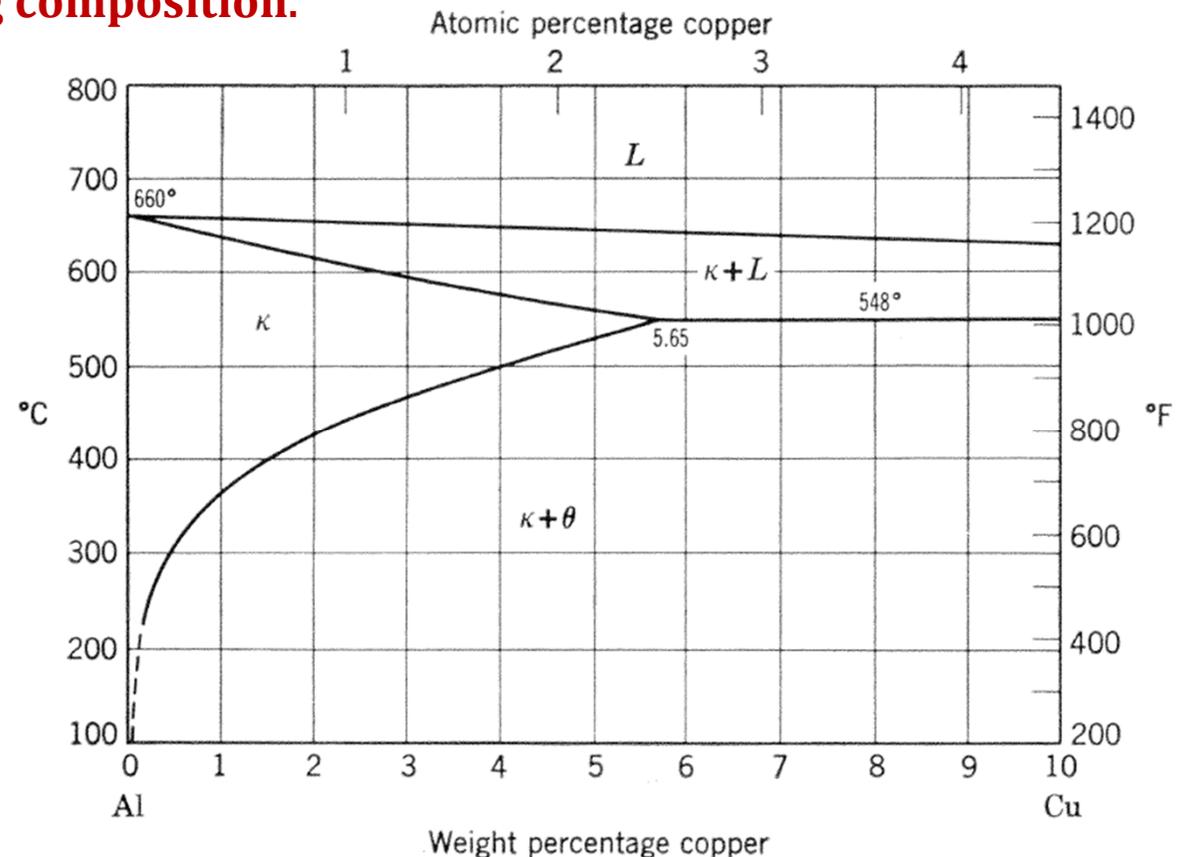
Fig. 5.51. Part of the phase diagram for the Cu–Al system.

* Good agreement btw theory and experiment in inverse segregation of Al-Cu alloy.
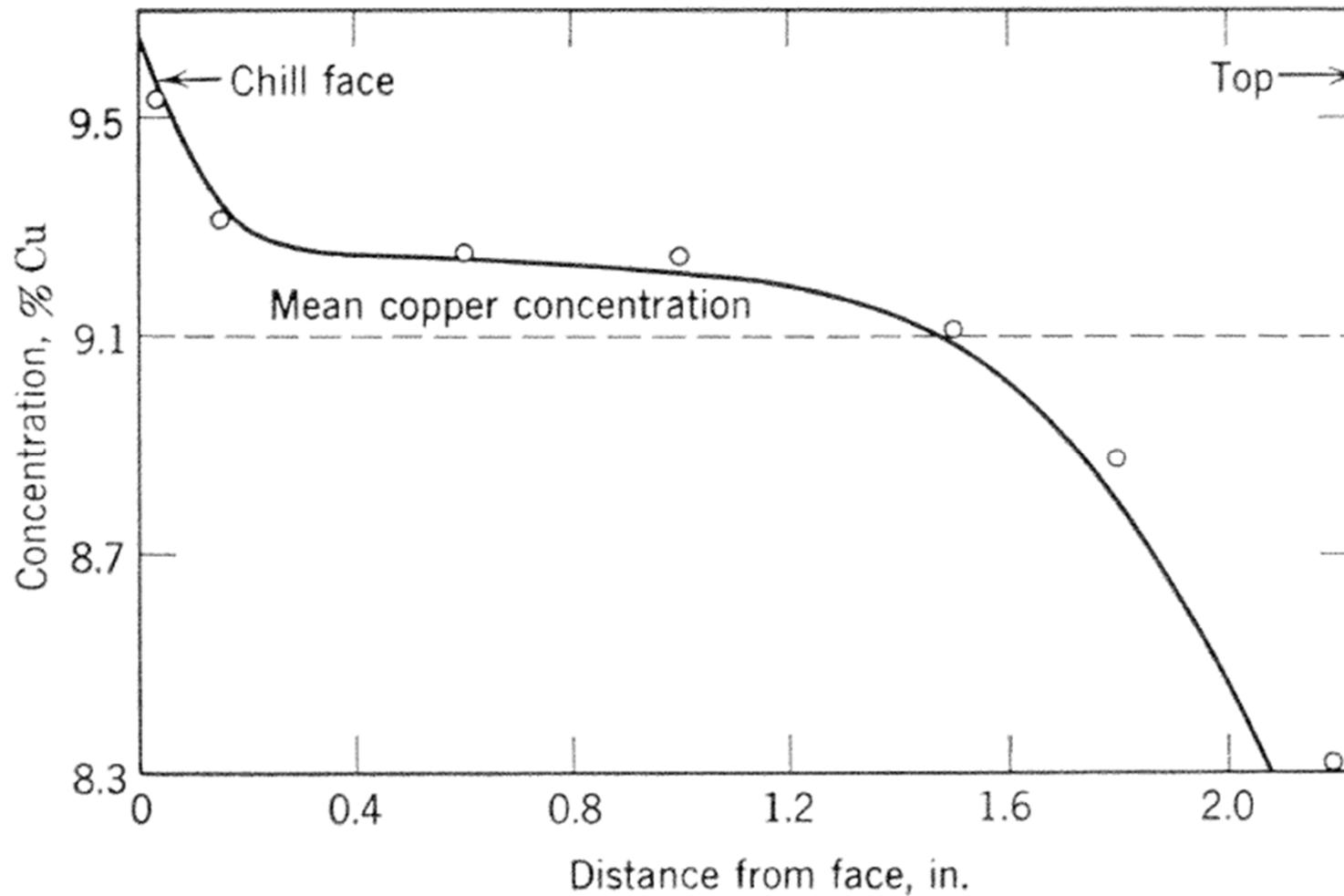
Fig. 5.52. Comparison between experimental and calculated inverse segregation in Al–Cu.

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* Case of Al-Zn system_studied by youdelis & Colton (Fig. 5.53)

: somewhat more complicated, because

a) Assumption of constant k_0 can no longer be regarded as correct,

b) stepwise integration is used.

However, Fig. 5.54 shows good agreement btw experimental and calculated inverse segregation.
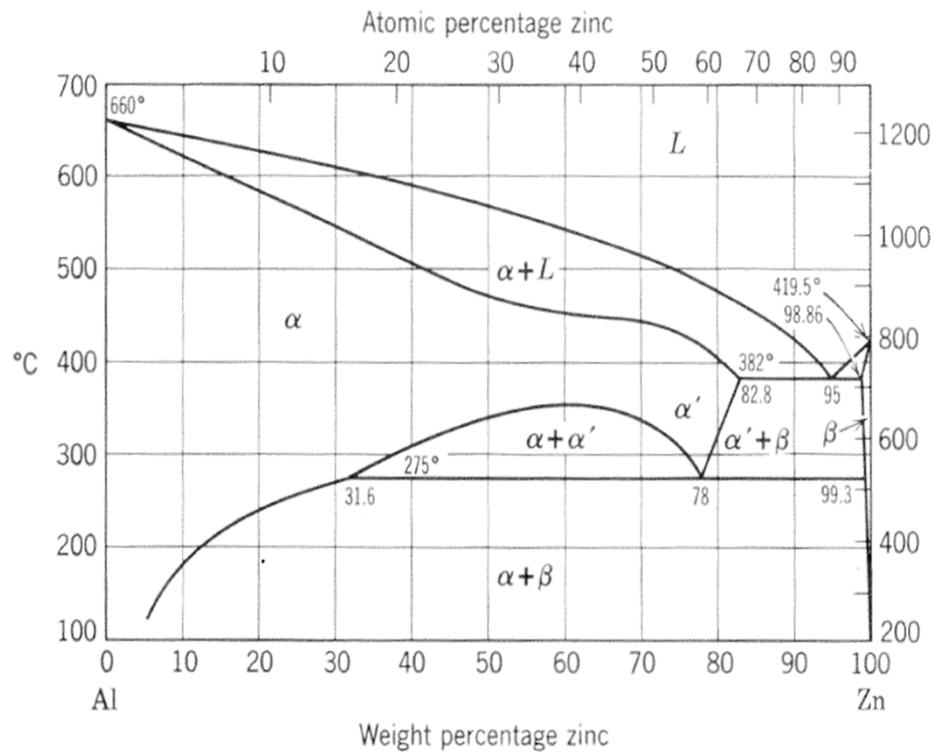
Fig. 5.53. Part of phase diagram for the Al-Zn system
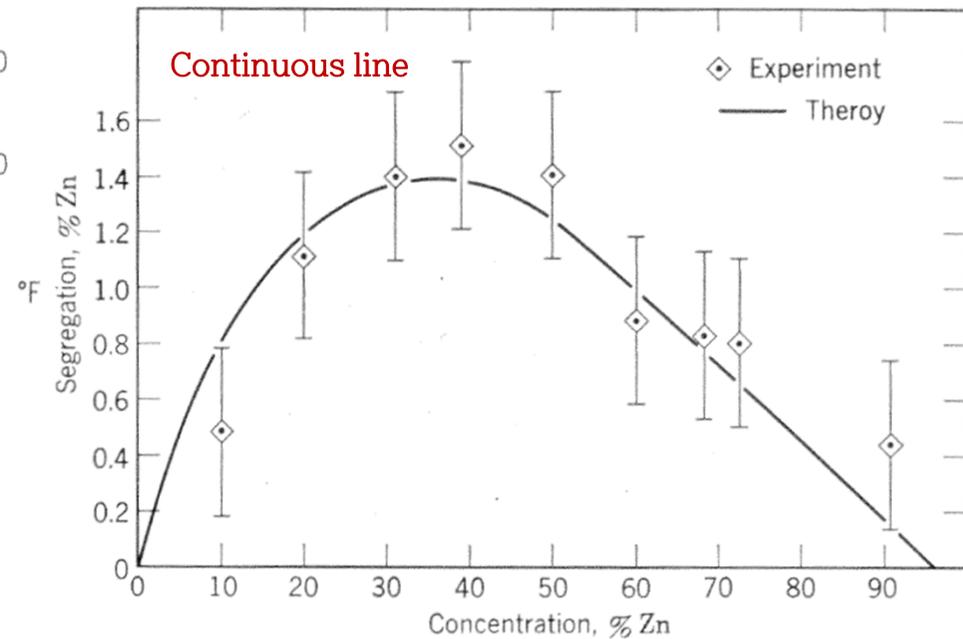
Fig. 5.54. Predicted and measured inverse segregation in Al-Zn

5) Inverse segregation

 * <u>A much more drastic form of inverse segregation</u> occurs when liquid is sucked out through the boundary QR (the first region to solidify) by a difference of the pressure arising from the separation of the metal from the mold.

→ The liquid which has exuded solidifies on surface of the metal btw it and the mold, in the form of <u>small "drops", known as "sweat",</u> which are <u>usually much harder</u> than the neighboring metal due to their high alloy content.
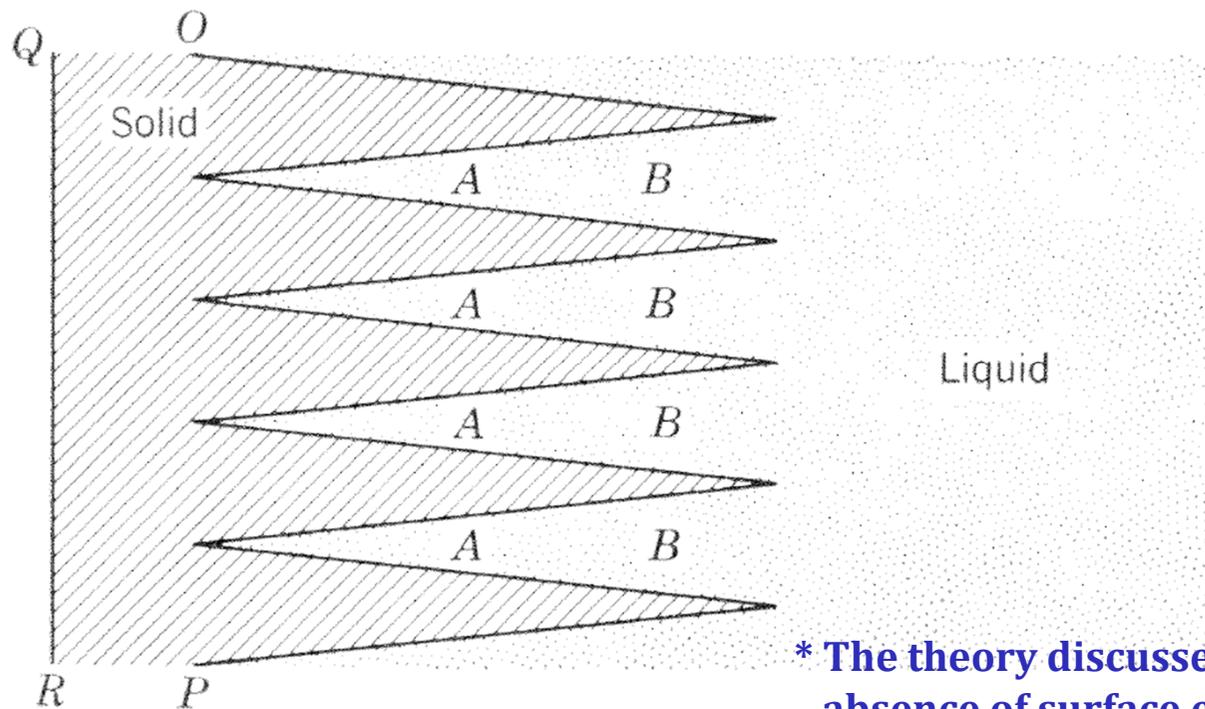
* The theory discussed above assumes the absence of surface exudation.

Fig. 5.50. mechanism of inverse segregation

6) Coring and intercrystalline segregation

 * The discussion of <u>normal segregation</u> was developed from a <u>macroscopics</u>
<u>point of view</u>. → **However, each crystal is likely to exhibit normal segregation on a microscopic scale; the earliest part of it to form has a lower concentration of solute (unless $k_0 > 1$) than the later parts;** **"Coring"****, locally highest solute content**

→ **found in <u>the terminal regions where two or more crystals</u> grow toward each other and finally form a** **grain boundary****.**

5. 10 Gravity segregation

* **When the mass of liquid is sufficiently large, convection causes motion of the solute away from the limit of the boundary layer.**

→ **If** **solute changes the density of the liquid****, it may set up a convection current that carries it toward the top or the bottom of the space in which the liquid can move.**

* **This is a type of** **transverse segregation** **that is much more significant in large, real system than in the idealized ones discussed in this chapter.**

* Segregation: undesiable ~ deleterious effects on mechanical properties

→ subsequent homogenization heat treatment, but diffusion in the solid far to slow

→ good control of the solidification process

"A" Segregates

Concentrates under hot-top segregation

"positive"

"V" Segregates

"Bands"

"negative"

Cone of negative segregation

Inverse segregation: As the columnar dendrites thicken solute-rich liquid (assuming k<1) must flow back between the dendrites to compensate for (a) shrinkage and this raises the solute content of the outer parts of the ingot relative to the center.

EX) Al-Cu and Cu-Sn alloys with a wide freezing range (relatively low k)

Negative segregation: The solid is usually denser than the liquid and sinks carrying with it less solute (initially solidified one)than the bulk composition (assuming k<1). This can, therefore, lead to a region of negative segregation near the bottom of the ingot. ((b) Gravity effects)

Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.) 26

Two of the most important application of solidification :

"Casting" and "Weld solidification"

Q: What kinds of ingot structure exist?

 Ingot Structure

- Chill zone

- Columnar zone

- Equiaxed zone

* Solidification of Ingots and Castings

a lump of metal, usually shaped like a brick.

an object or piece of machinery which has been made by pouring a liquid such as hot metal into a container

Later to be worked, e.g. by rolling, extrusion or forging>> blank (small)

Permitted to regain their shape afterwards, or reshaped by machining

Ingot Structure

- **outer Chill zone**
  : equiaxed crystals

- **Columnar zone**
  : elongated or column-like grains

- **central Equiaxed zone**
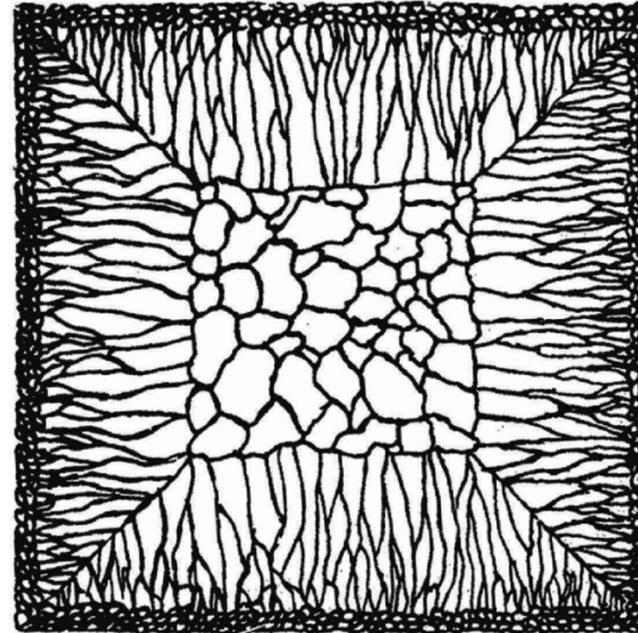
Chill zone

- **Solid nuclei form on the mould wall and begin to grow into the liquid.**

1) **If the pouring temp. is low**: liquid~ rapidly cooled below the liquidus temp. → **big-bang nucleation → entirely equiaxed ingot structure**, no columnar zone

2) **If the pouring temp. is high**: liquid~remain above the liquidus temp. for a long time → **majority of crystals~remelt under influence of the turbulent melt ("convection current") → form the chill zone**

Columnar zone

After pouring the temperature gradient at the mould walls decreases and the crystals in the chill zone grow dendritically in certain crystallographic directions, e.g. <100> in the case of cubic metals.

**→ grow fastest and outgrow less favorably oriented neighbors**

Crystals with very different direction btw thermal conduction and <100> direction stop growth

Nucleation sites

Mold wall

Heat flow

Mushy zone (or pasty zone) depends on temp. gradient and non-equil. Freezing range of the alloy

New primary arm grows from here

Mold wall

Nucleation sites

One columnar grain
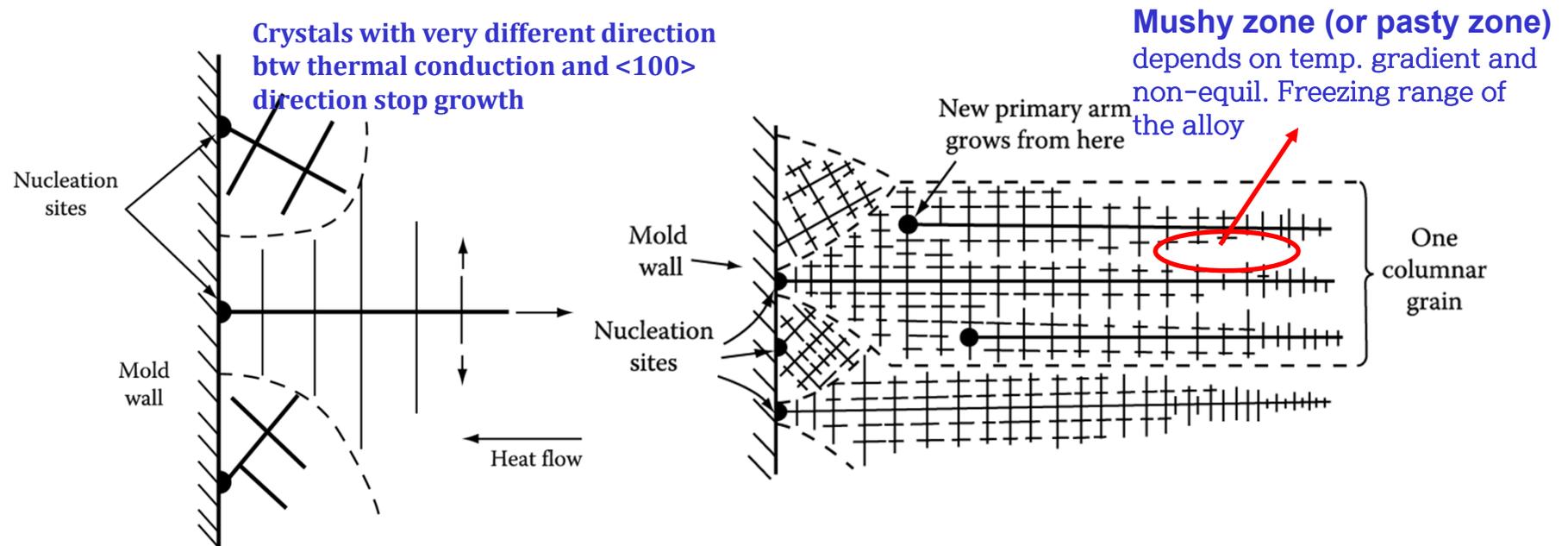
Fig. 4.41 Competitive growth soon after pouring. Dendrites with primary arms normal to the mould wall, i.e. parallel to the maximum temperature gradient, outgrow less favorably oriented neighbors.

Fig. 4.42 Favorably oriented dendrites develop into columnar grains. Each columnar grain originates from the same heterogeneous nucleation site, but can contain many primary dendrite arms.

1) In general, the secondary arms become coarser with distance behind the primary dendrite tips.

2) The primary and secondary dendrite arm spacing increase with increasing distance from the mold wall.
(∵ a corresponding decrease in the cooling rate with time after pouring)

⇒ **Mushy zone (or pasty zone)**
depends on temp. gradient and non-equil. freezing range of the alloy
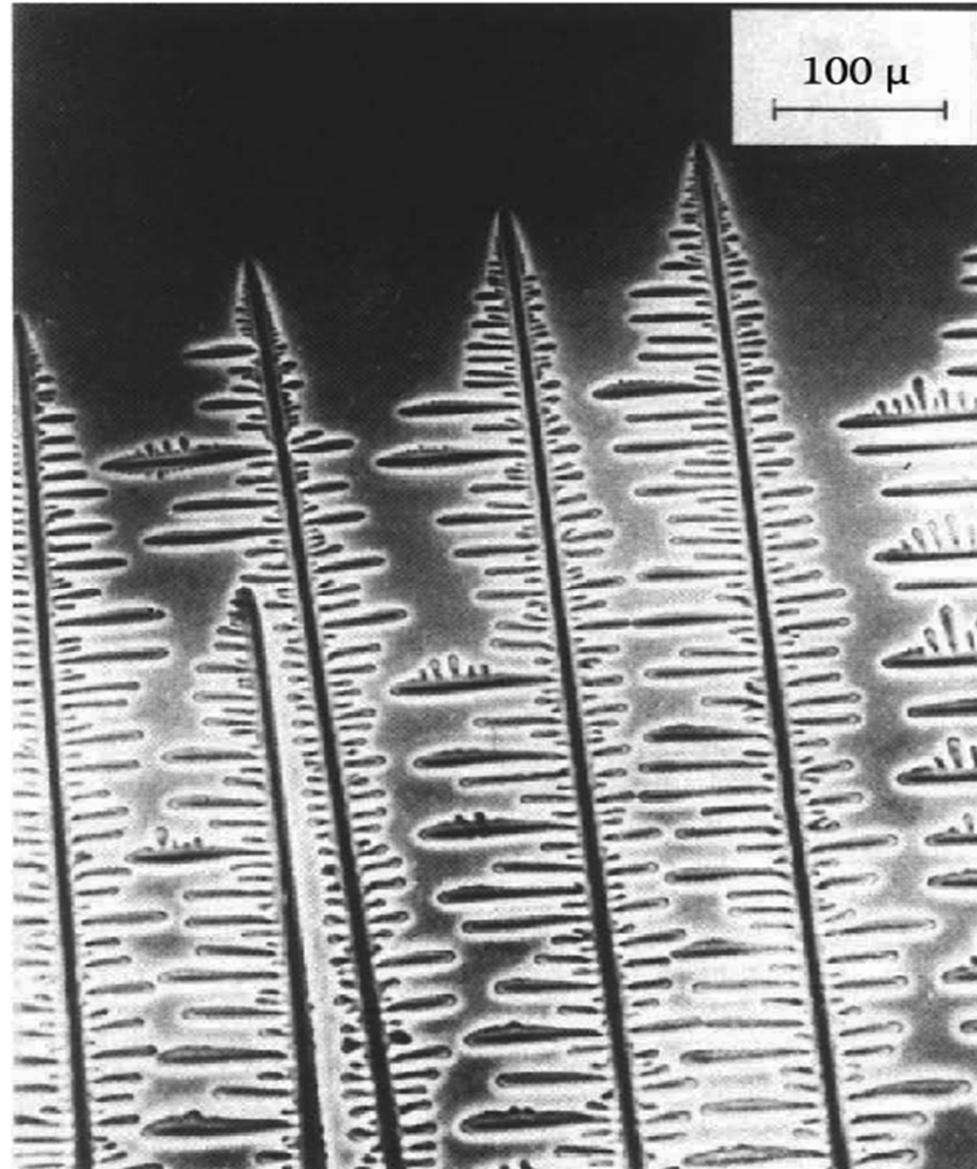
Fig. 4.28 Columnar dendrites in a transparent organic alloy.
(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

Equiaxed zone

The equiaxed zone consists of equiaxed grains randomly oriented in the centre of the ingot. An important origin of these grains is thought to be melted-off dendrite side-arms + convection current
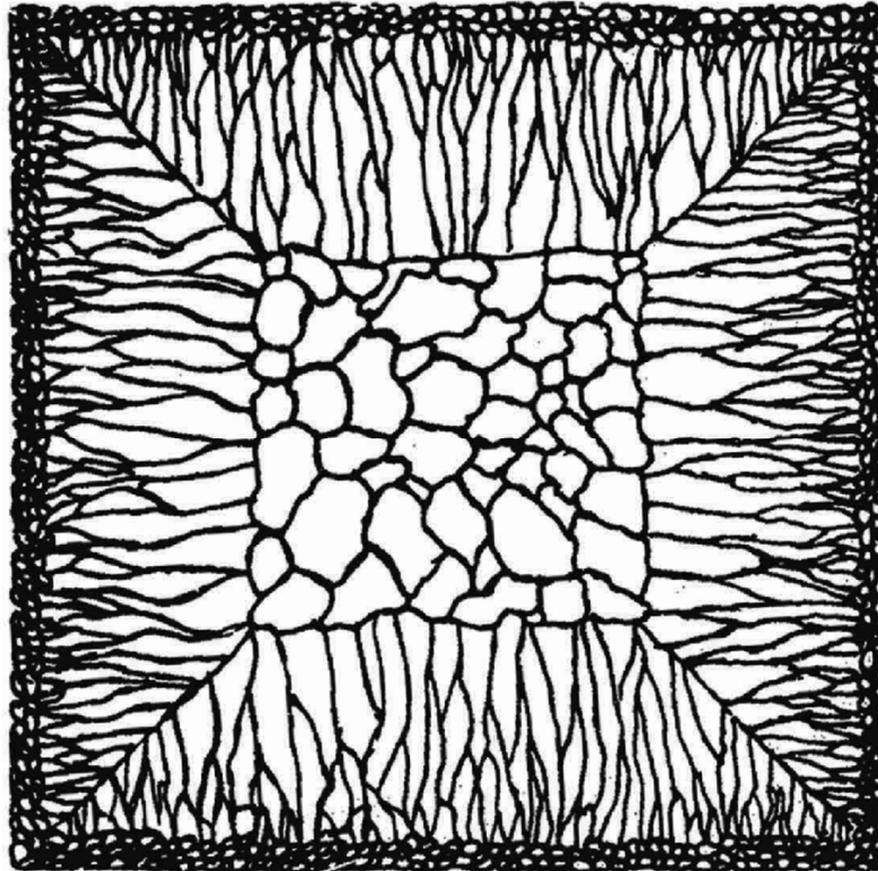
Fig. 4.40   Schematic cast grain structure.
(After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.) 31

Liquid

Liquid

Nuclei

Chill grains

Equiaxed grains

Columnar grains

Liquid

32

Solidification of Pure Metal   **: Thermal gradient dominant**

⇕

Solidification of single phase alloy: Solute redistribution dominant

  a) Constitutional Supercooling (C.S.)

Planar → Cellular growth → cellular dendritic growth → Free dendritic growth

Thin zone formation by
C.S. at the sol. Interface
Dome type tip / (surrounding)
hexagonal array

T↓ → Increase of C.S. zone
Pyramid shape of cell tip /
Square array of branches /
Growth direction change toward
Dendrite growth direction

formed by releasing the latent
heat from the growing crystal
toward the supercooled liquid
Dendrite growth direction/
Branched rod-type dendrite

→ "Nucleation of new crystal in liquid"**which is at a higher temp. than the interface at**
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    segregation, gravity segregation

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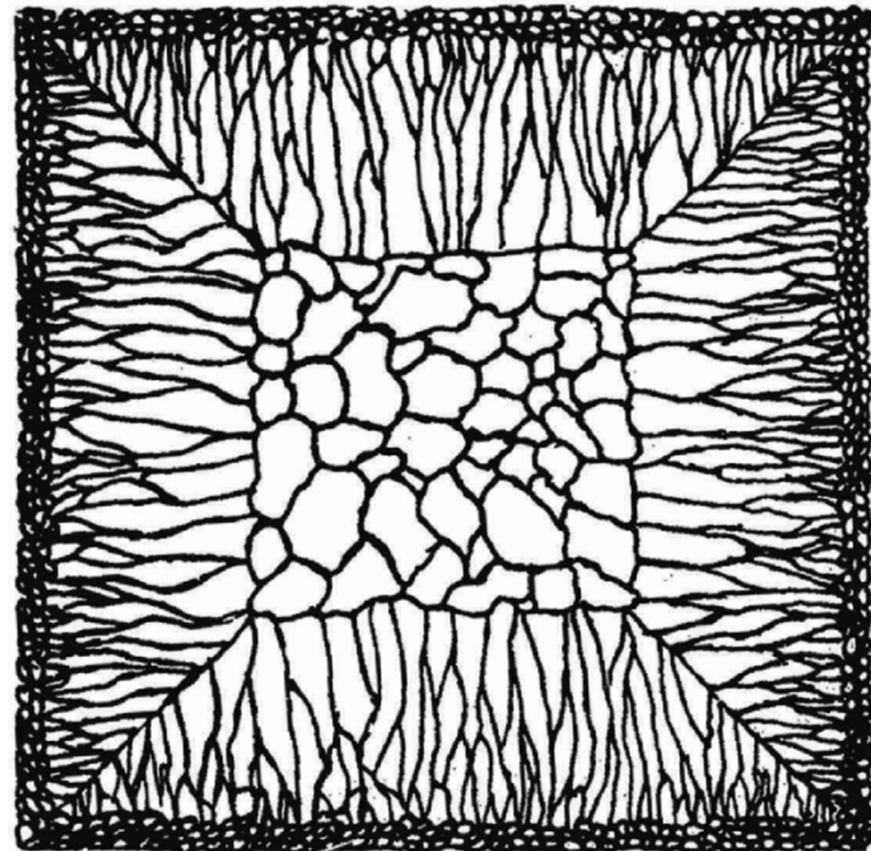
Chapter 6 Polyphase solidification

* <u>Chapter 5 : discussion of the redistribution of solute during solidification </u>was based on the implicit assumption that the whole of the solute could be accommodated in <u>solution to a single solid phase</u>.

However, many important cases_more than one solid phase is formed

Chapter 6 → Binary poly-phase solidification

6.1. Evolution of a Gas during solidification

(a) Gas-metal equilibria

- metallic system: ignore the pressure (except pressure appear to be relevant is for the consideration of nucleation under transient pressure resulting from cavitation, see Chapter 3)   → However, <u>when one of the phases is a gas (other than the vapor of the metal) the pressure has an important influence on the equilibrium relationships: Phase diagram with P, T, composition variables</u>

→ However, it is seldom necessary to consider the phase diagram as a whole, because the variation in melting point or in the liquidus and solidus temperatures, due to the presence of the gas is always small, unless a new phase, such as a metal-gas compound is formed.

→ ∴ The important characteristic of gas-metal system from the present point of view is the solubility of the gas in the metal (= the concentration of gas in solution in the solid or the liquid _ pressure or partial pressure)

Chapter 6 Polyphase solidification

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.
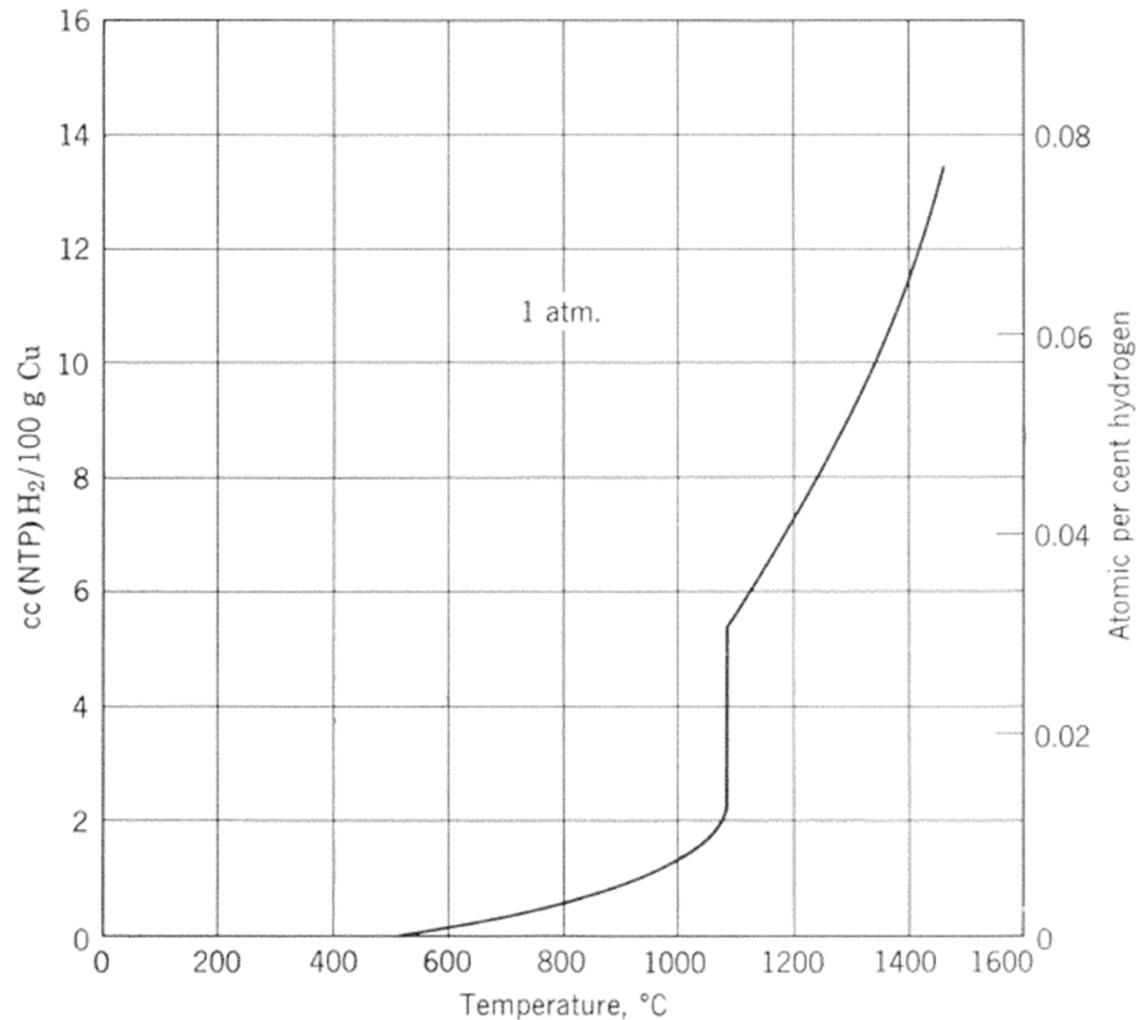
Fig. 6.1. Solubility of hydrogen in copper.

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.

A typical solubility diagram

* The solubility of gas is less in the solid than in the liquid; this is equivalent the statement that the value of k_0 is less than unity ($k_0 < 1$).

* A case which is very important technologically is the solubility of hydrogen in iron; that at atmospheric pressure 100 g of liquid iron dissolves 27 cm^2 of hydrogen, while the corresponding figure for the solid at the melting point is 13 cm^2 .

Y-axis: Solubility, atomic per cent (10^{-4})

X-axis: Temperature, °C

Solid   Liquid
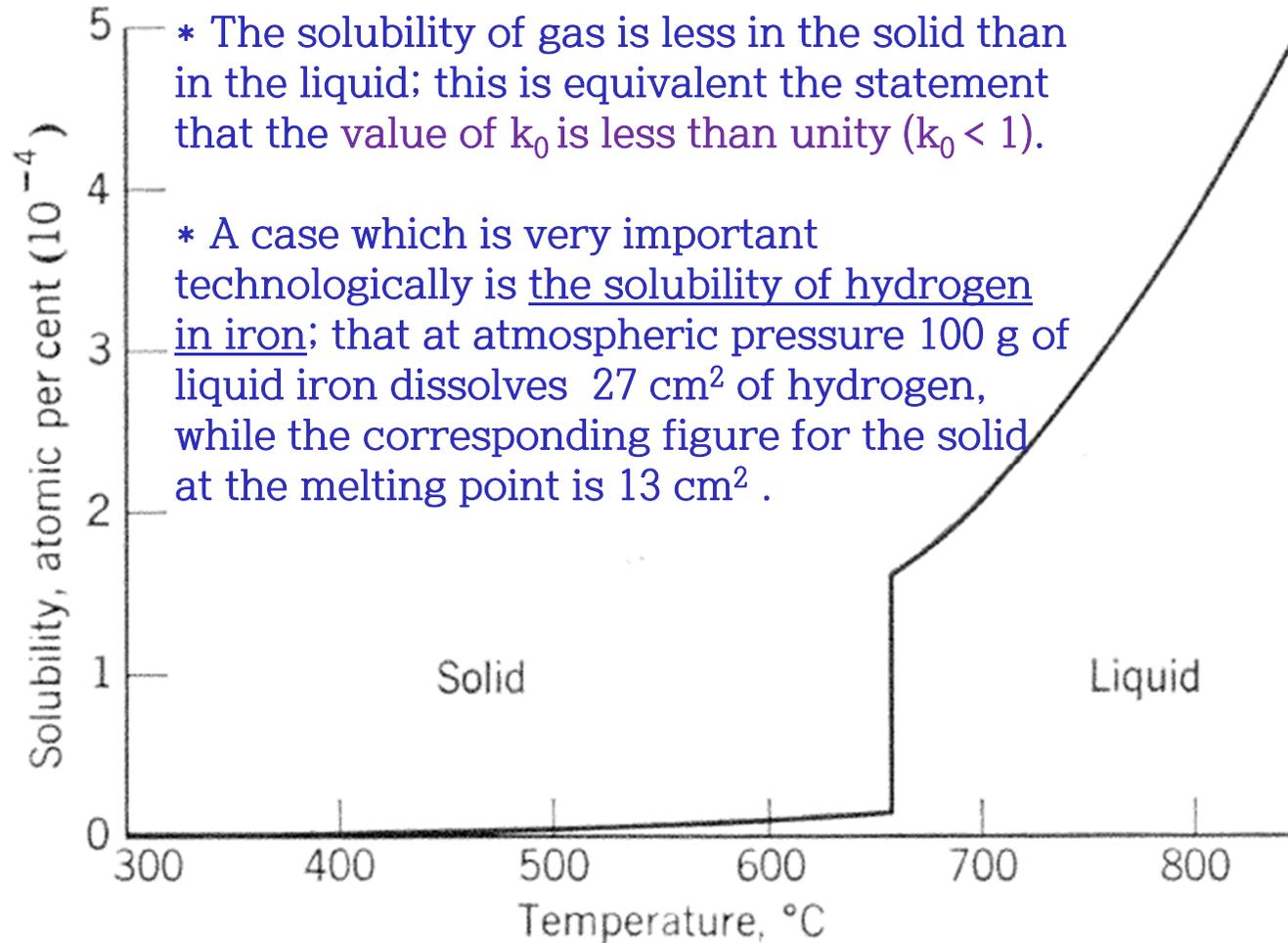
Fig. 6.2. Solubility of hydrogen in aluminum.

* A diagram relating solubility with temperature for a single pressure (for example, a pressure of one atmosphere) will convey the significant information.

A typical solubility diagram
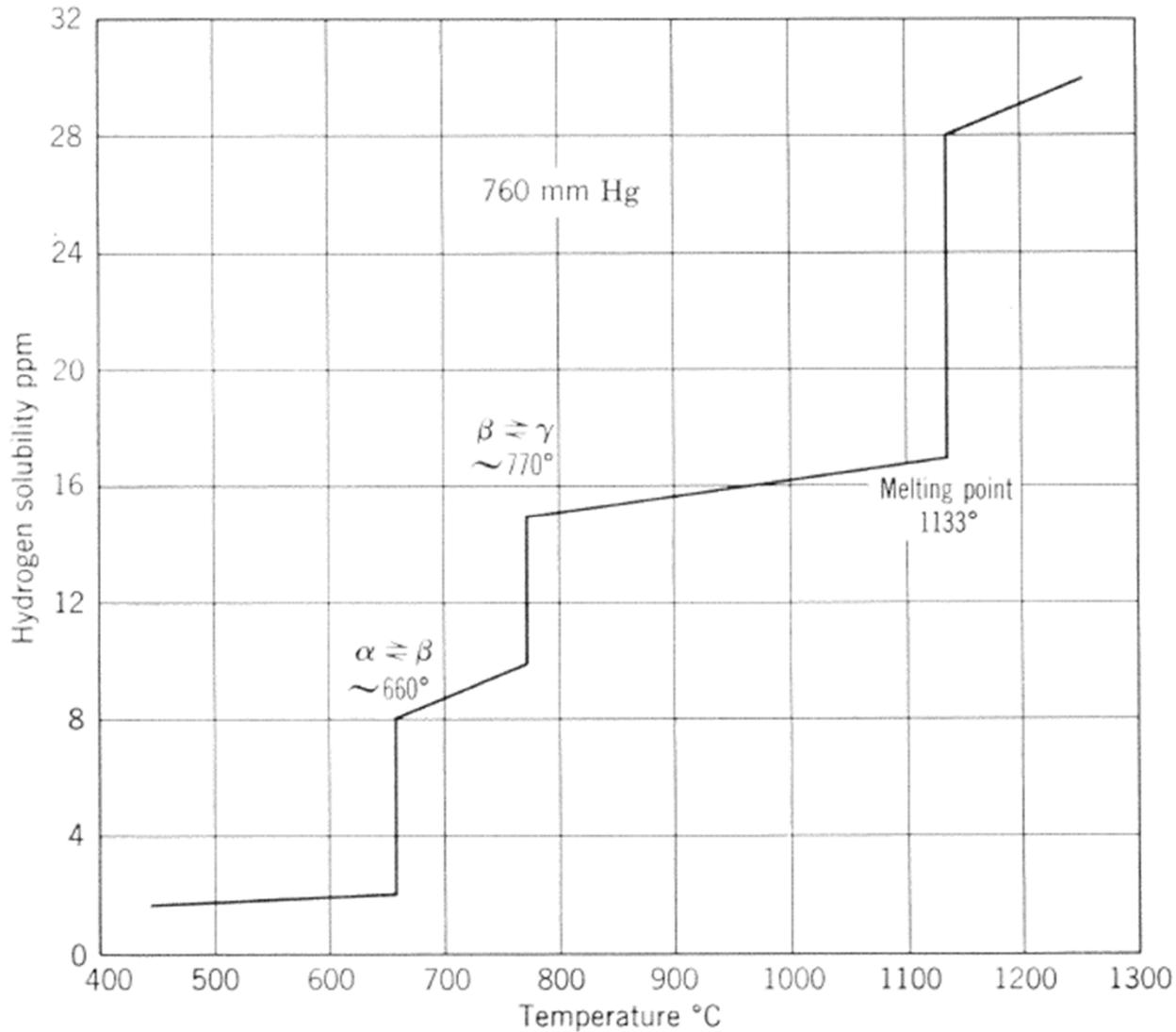
Fig. 6.3. Hydrogen–Uranium phase diagram.

(b) Bubble formation

- When a metal or alloy containing a gas (such as Oxygen, Nitrogen or hydrogen) in solution solidifies, <u>gas will be rejected at the interface, exactly in the same way as any other solute for which the $k_0 < 1$</u>.

→ If the gas in the liquid was already saturated (i.e. if it was at the limit of solubility for the prevailing pressure at T_m) then it becomes supersaturated as soon as an enriched layer begins to form at the interface. This means that there is more gas in solution than the equilibrium amount, as therefore there is a thermodynamic driving force tending to reduce the gas content.

→ The amount of gas in solution may decrease either by escape of the gas at a free surface, if one is accessible within the range in which the gas can diffuse in the liquid, or by the formation of a gas bubble in the liquid.

→ <u>Formation of gas bubble requires homogeneous or heterogeneous nucleation</u> :
   "The condition for nucleation of a gas bubble is similar to that for nucleation of a solid phase, except that the effect of the pressure of the gas on its free energy must be considered."

But , a solid-liquid interface should not be an effective nucleant for a bubble;

Equilibrium corresponds to Θ < 180 °,

$$\sigma_{SL} = \sigma_{SG} + \sigma_{LG} \cos \theta$$

$$\cos \theta = \frac{\sigma_{SL} - \sigma_{SG}}{\sigma_{LG}}$$

Fig. 6.4. Solid-liquid as nucleant for a gas bubble.

$\sigma_{SG} \gg \sigma_{SL}$ & $\sigma_{SG} > \sigma_{LG}$

∴ cosθ < -1

→ Surface E of the bubble is increased by contact with the solid-liquid interface.

However, gas bubbles are formed at solid-liquid interfaces.

This location is in part due to the fact that the gas concentration would be highest there during solidification; but it may also be due to the fact that any re-entrant in the interface, such as a cell wall, grain boundary, or inter-dendritic space, would have an even higher gas content because of lateral segregation, as shown in Fig. 6.5.

* gas bubbles are formed at solid-liquid interfaces.

In detail, in regions such as A, the terminal transient condition is entered as the 2 walls approach each other; the concentration of solute (in this case, gas rises far above the C_0/k that would occur at a flat interface, and which might not be sufficient to cause nucleation of gas bubbles.
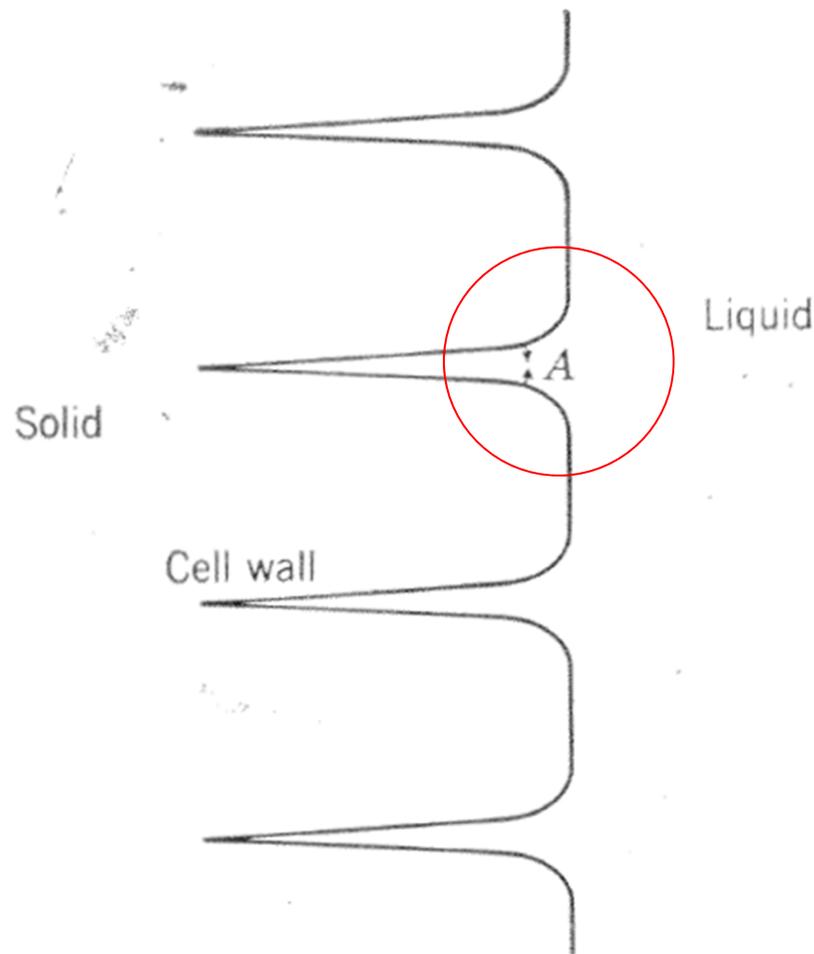
* Experimental observations leave no doubt that gas bubbles are in fact nucleated during solidification, when transport of gas away from the interface by diffusion is not sufficiently fast, in terms of the rate of rejection at the interface, to hold the gas content below the nucleation level.

Liquid

Solid

Cell wall

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Fig. 6.5. Conditions for the nucleation of gas bubbles in cell wall.

* Subsequent behavior of bubble;

depends upon whether they float away from the surface or remain attached.

a) If a bubble escapes from the region where it was nucleated, it may float to the surface of the melt , or it may be trapped by other crystals, in which case its subsequent behavior is similar to that of a bubble that remained at its point of origin.

b) If the bubble is trapped where it forms, it immediately becomes a "sink" into which gas from the neighboring supersaturated liquid can escape. This sets up a concentration gradient which causes gas to diffuse to the bubble from the surrounding liquid. The bubble there fore grows; but while it is doing so, the interface continues to advance.

→ The relative rates of growth of the bubble and of advance of the interface determine whether the bubble will increase in diameter, remain of constant diameter but increase in length, or be overgrown by the solid.

These three possibilities :

43
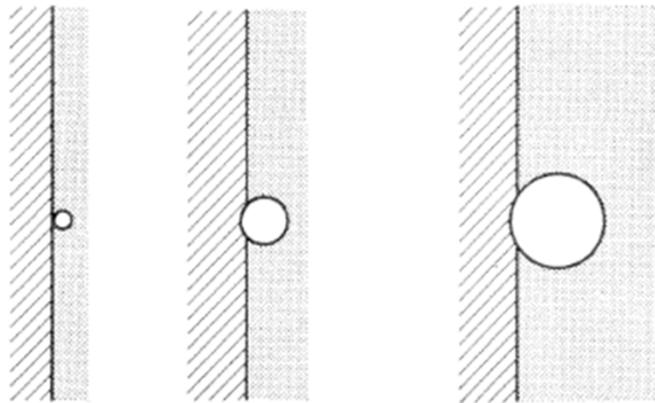
* **Growth rate of bubble > Advanced speed of interface**
→ **increase of bubble diameter**

The diameter of the bubble is maintained in the longitudinal direction

(a)
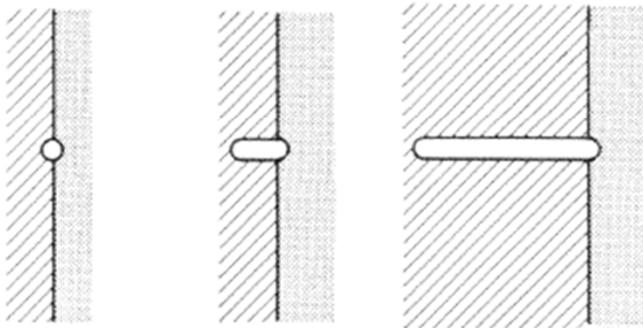
* **Growth rate of bubble ~ Advanced speed of interface**
→ **Bubble growth progresses in the longitudinal direction while maintaining bubble diameter**

(b)
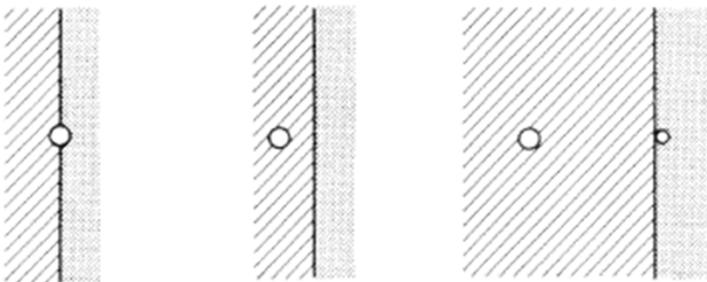
* **Growth rate of bubble < Advanced speed of interface**
→ **bubble are trapped in the solid.**

(c)

Fig. 6.6. Effect of speed of growth of a bubble on its shape and size.   44
(a) Slow growth, (b) intermediate speed, (c) fast growth.

* A bubble that starts by growing (Fig. 6.6a) may reach a size at which the conditions of Fig. 6.6b are satisfied, and a cylindrical bubble becomes stable. The stability of the cylindrical bubble at intermediate speeds, and it breakdown at high and at low speeds, has been demonstrated for water containing dissolved air.

* Cylindrical type of bubble (=wormhole) can easily be seen in ice cubes produced by freezing water containing dissolved air; an example is shown in Fig. 6.7.
→ The bubbles do not nucleate until the ice has grown inward for a few millimeters; this is presumably distance required for the critical supersaturation to be produced.

* Clear ice (=wormhole free ice) can be obtained by causing the water to flow continuously over the freezing interface. This prevents the concentration of dissolved air from reaching the critical level.
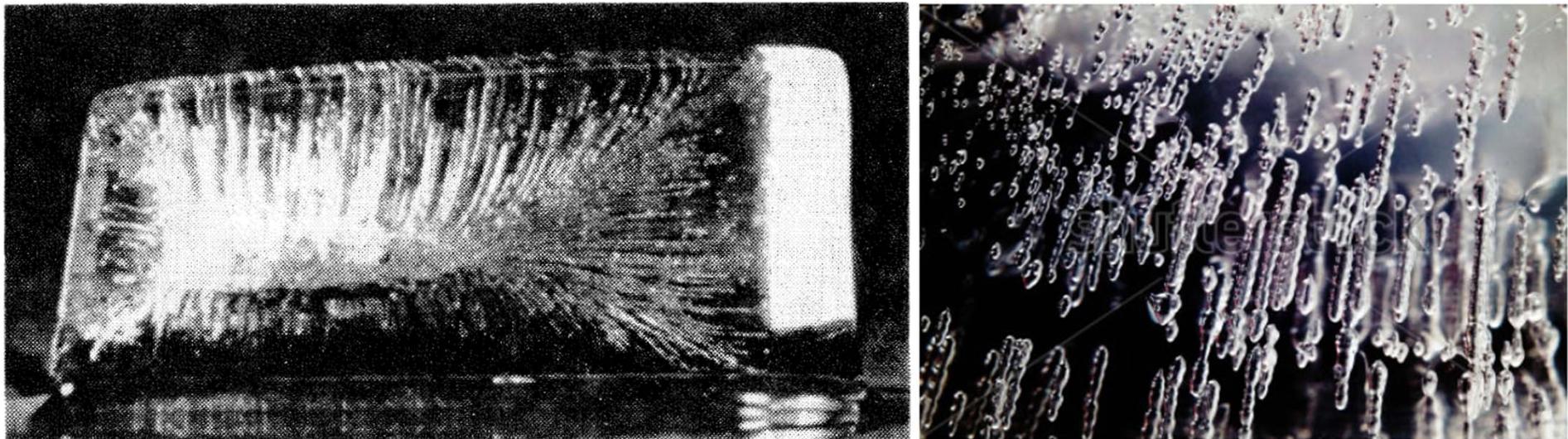
Fig. 6.7. Bubbles in ice cube

- **Growth of gas bubbles in a solidifyingmetal**

The process is essential the same as in water. → The pressure at a point in a solidifying liquid may be lower than would be expected from purely hydrostatic conditions. In the extreme case, a region of liquid may be completely surrounded by solid. Further solidification, accompanied by decrease in volume, would rapidly decrease the pressure, leading to the nucleation of bubbles.
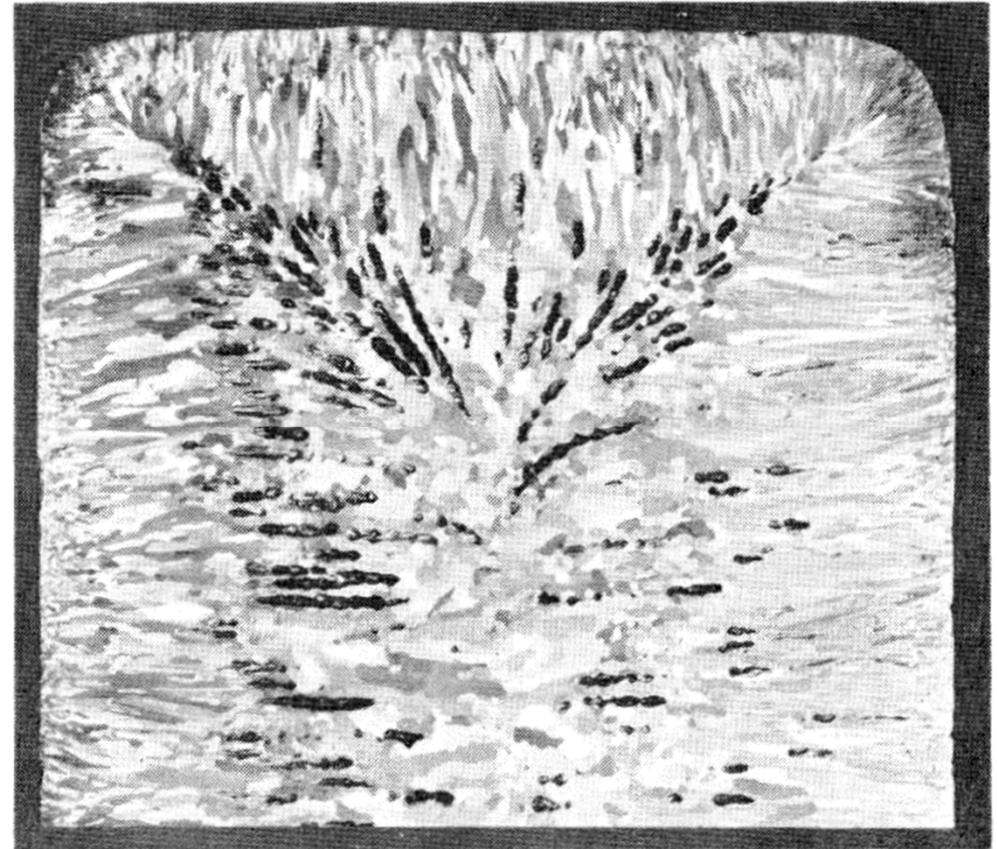
Fig. 6.8. Gas bubbles in a metal.

(c) Formation of compounds by dissolved gases

* A second possible effect of dissolved gasses on solidification is that compounds, such as oxides, may be formed when the gas concentration reaches a high level, especially during the terminal transient stage of solidification.

→ Oxide and other inclusions that are often found at grain boundaries in cast metals may have been formed in this way, rather than being present in the liquid prior to solidification.

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6.2 Eutectics: limited solubility, most fusible (가장 잘 녹는, Greek)

* Most of the discussion of eutectic solidification will be based on binary eutectic.
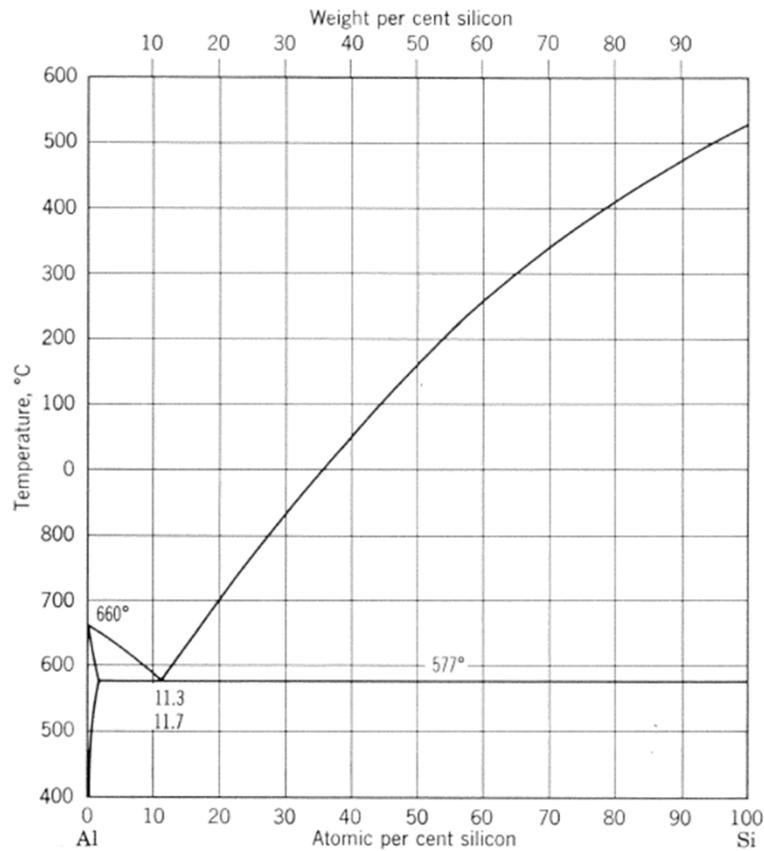
Fig. 6.9. Phase diagram for the Al-Si system
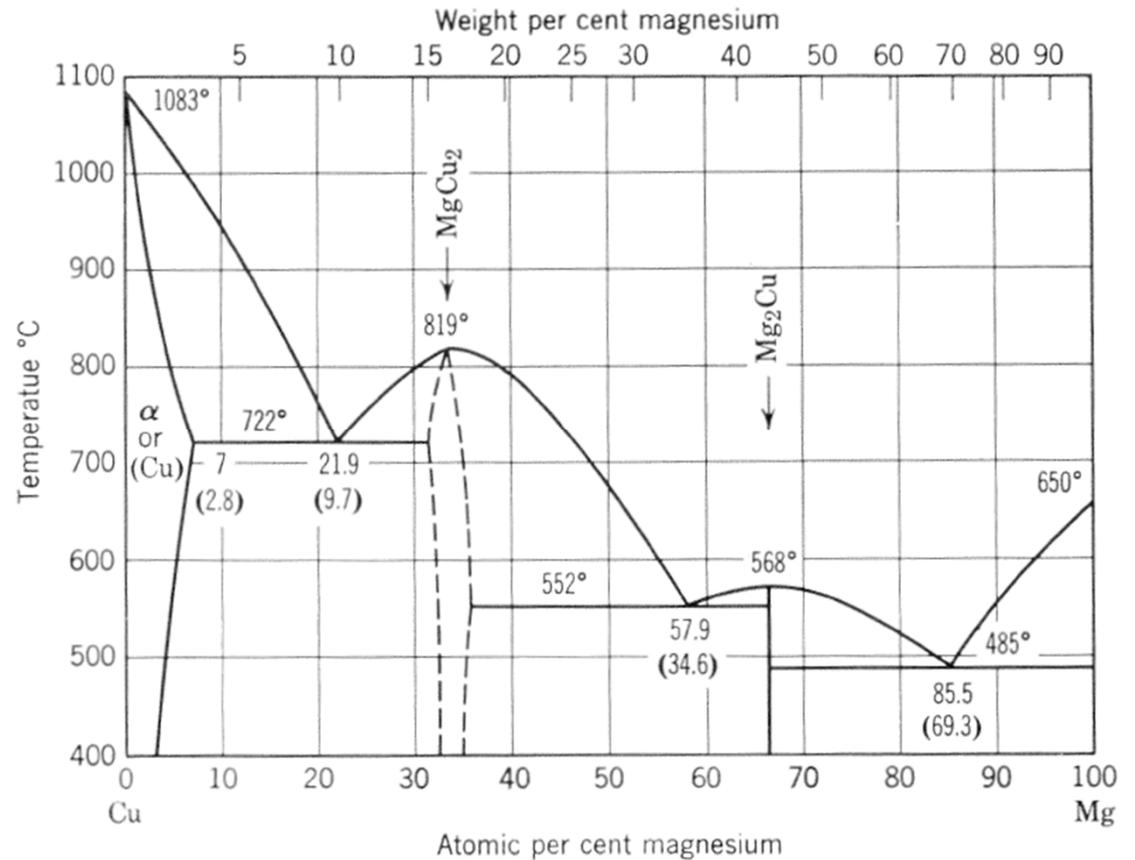
Fig. 6.10. Phase diagram for the Cu-Mg system
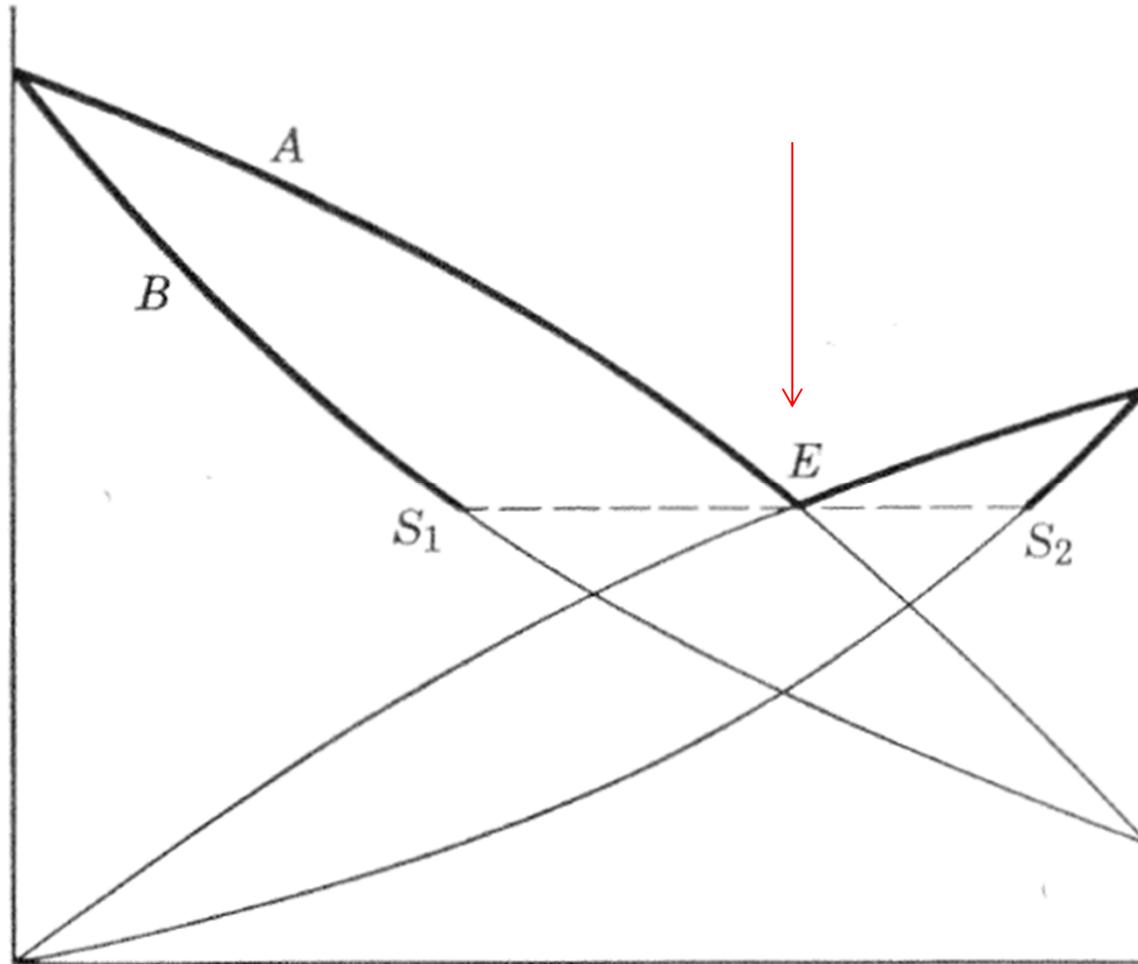
Fig. 6.11. Eutectic phase diagram

* Ternary eutectic system

: Minimum point of the liquidus surface
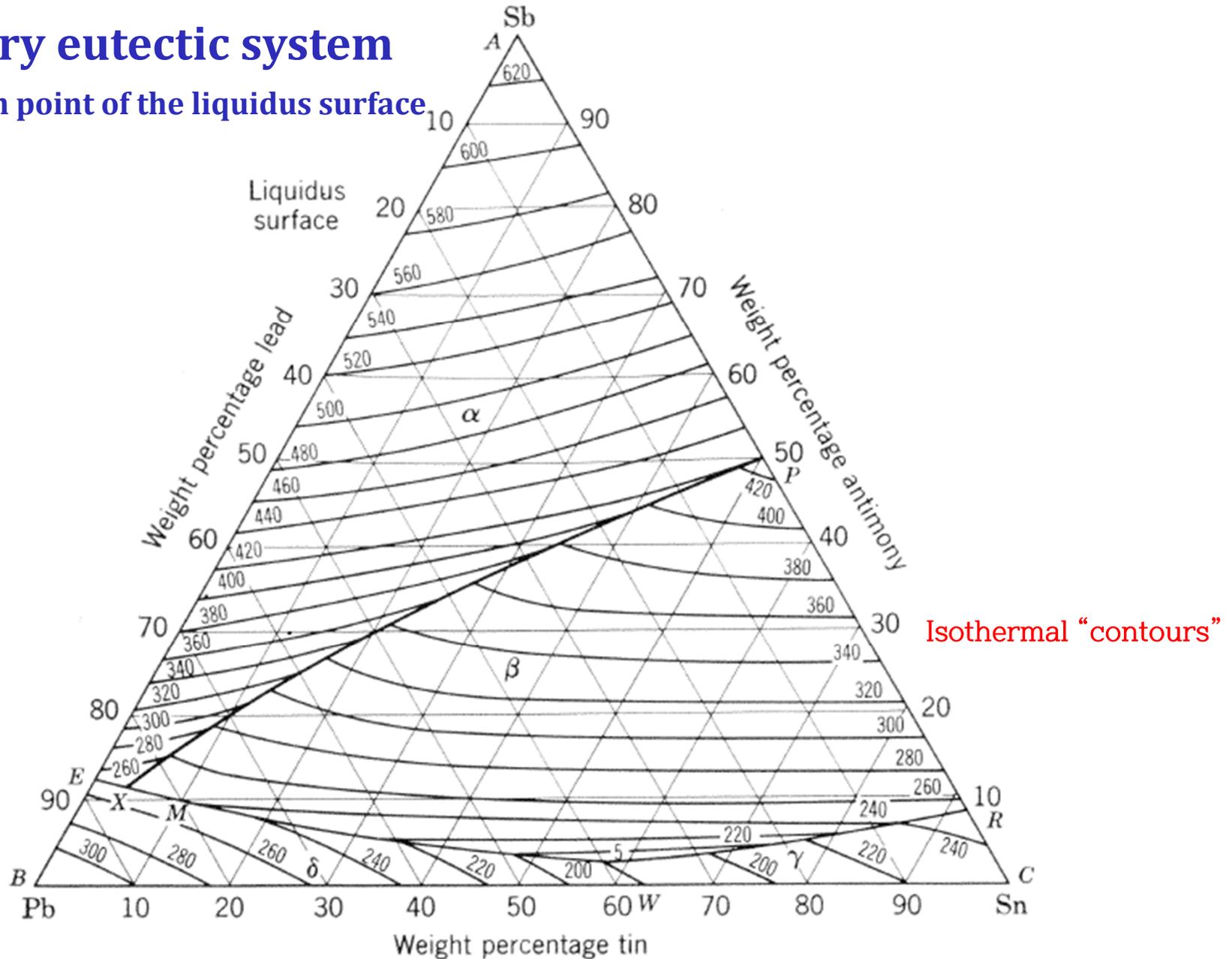
Fig. 6.12. The liquidus surface of the Pb–Sb–Sn system (X is the ternary eutectic point; liquidus temperature, 239 °C)

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* Ternary eutectic system

: Minimum point of the liquidus surface
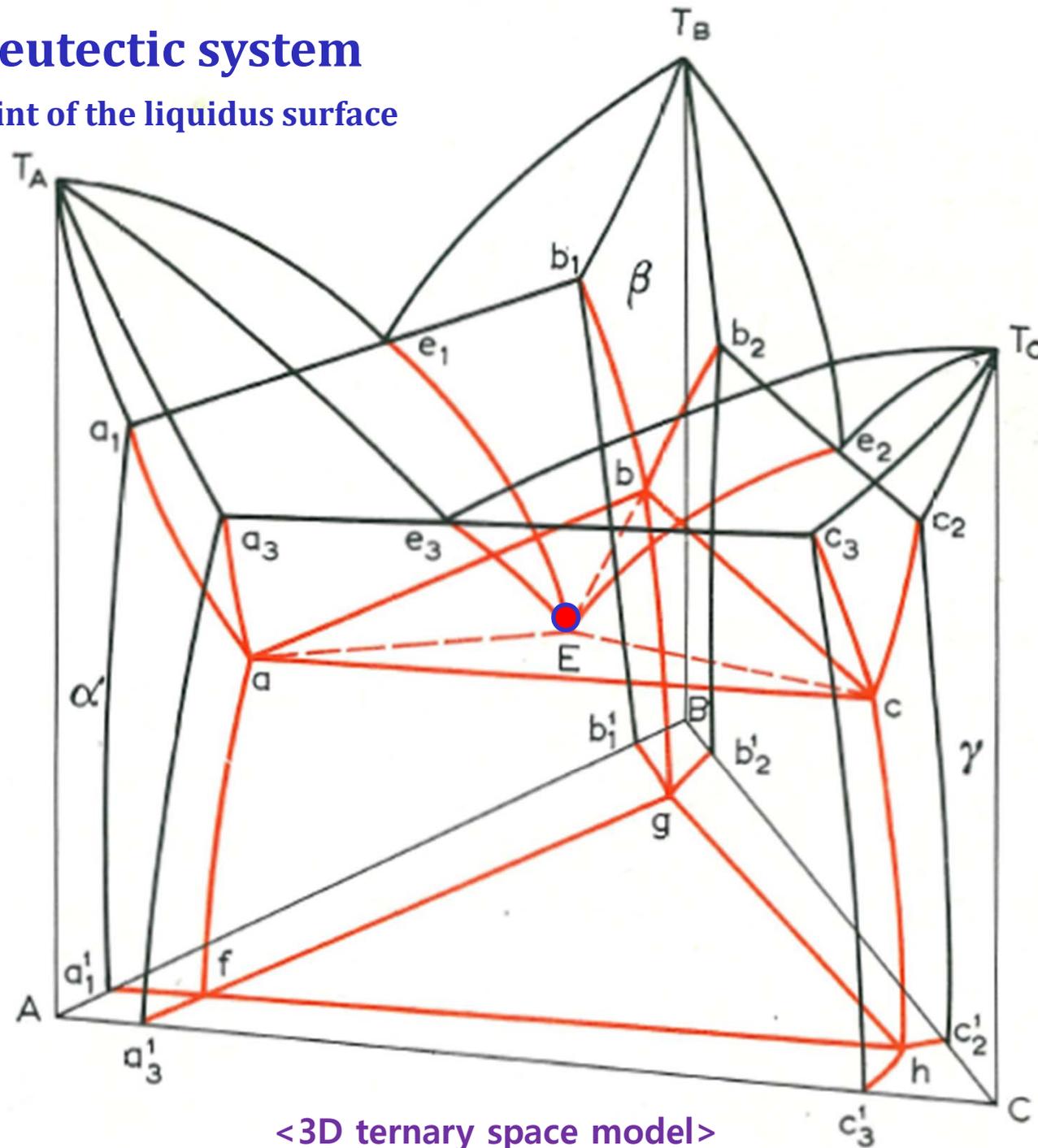

<3D ternary space model>

* Ternary eutectic system

**: Minimum point of the liquidus surface**

Location of vertical section
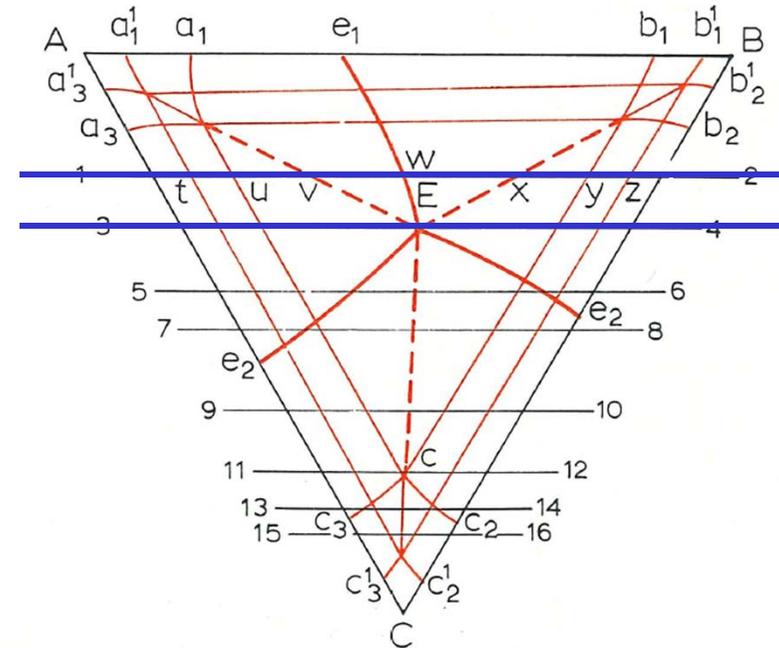
* Vertical section : Solidification Sequence

* The horizontal lines are not tie lines.
  (no compositional information)

* Information for equilibrium phases at
  different temperatures
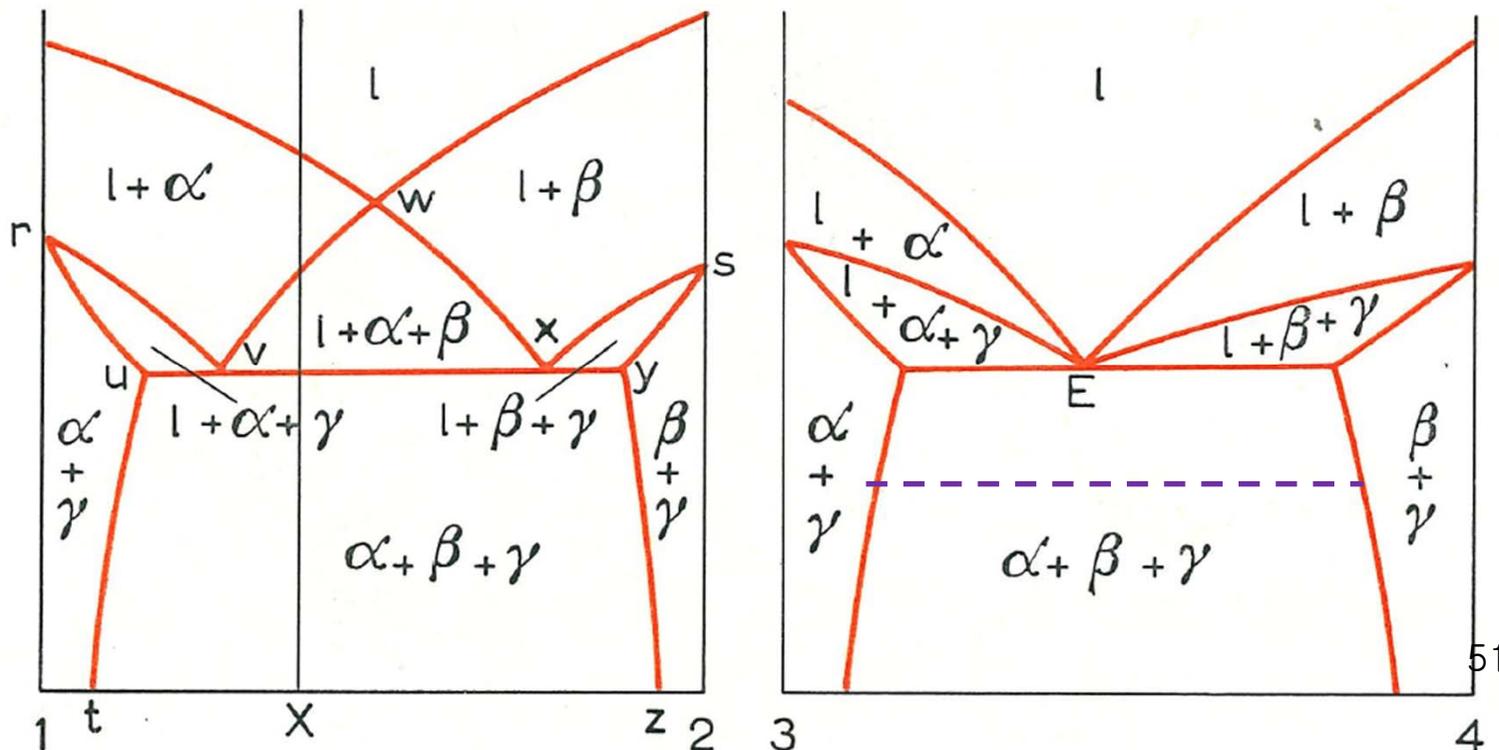
* Ternary eutectic system

: Minimum point of the liquidus surface
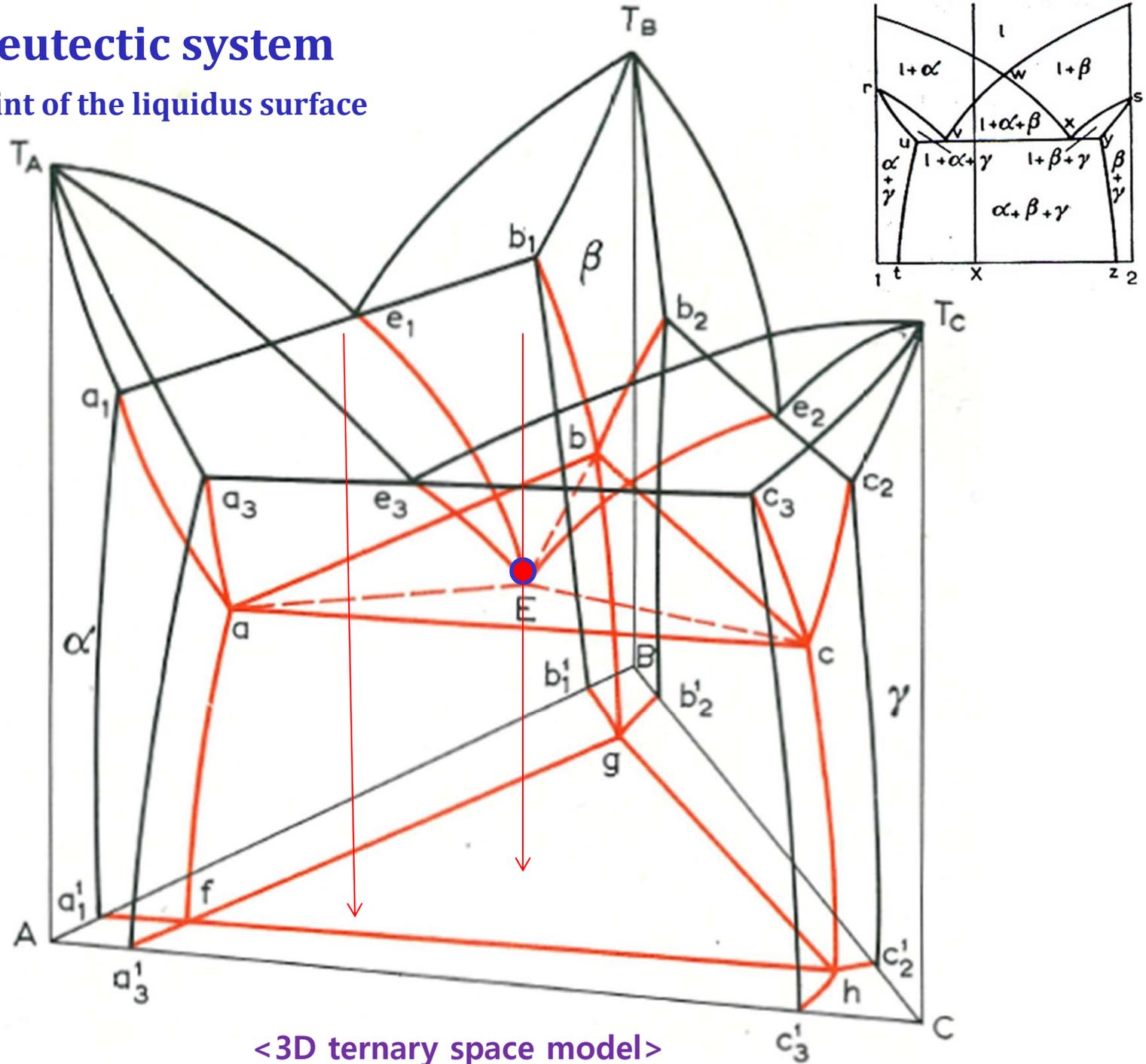
<3D ternary space model>

* THE EUTECTIC EQUILIBRIUM (l = α + β + γ)

- **Isothermal section ($T_A > T > T_B$)**
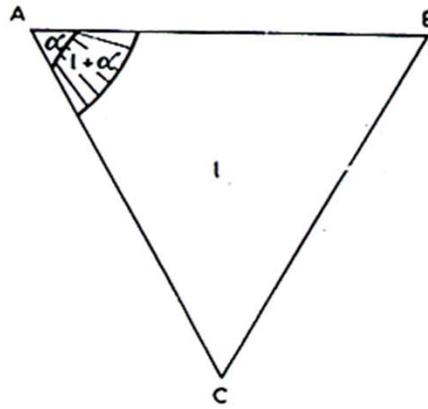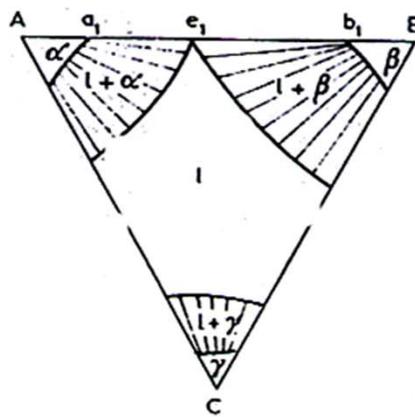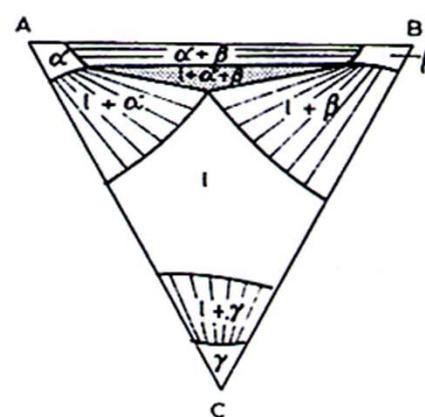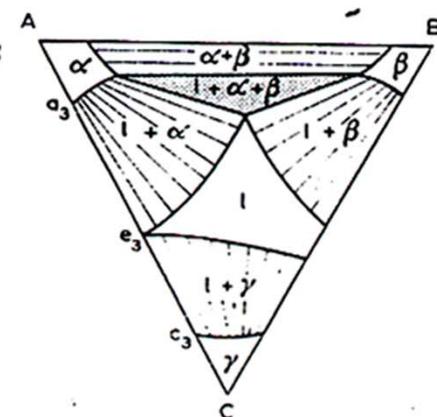
(a) $T_A > T > T_B$ (b) $T = e_1$ (c) $e_1 > T > e_3$ (d) $T = e_3$
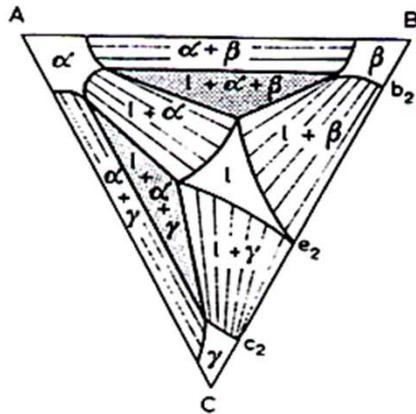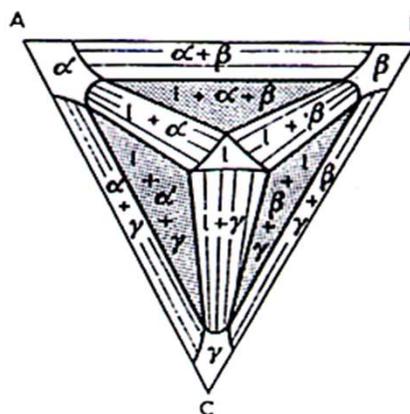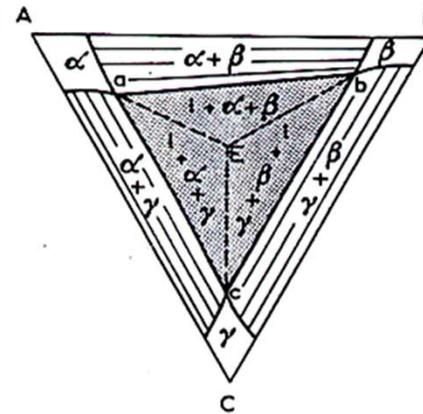
(e) $T = e_2$ (f) $e_2 > T > E$ (g) $T_A = E$ (h) $E = T$

* Quaternary eutectic l ⇄ α + β + γ + δ

Four tie tetrahedra

decreasing temperature

54
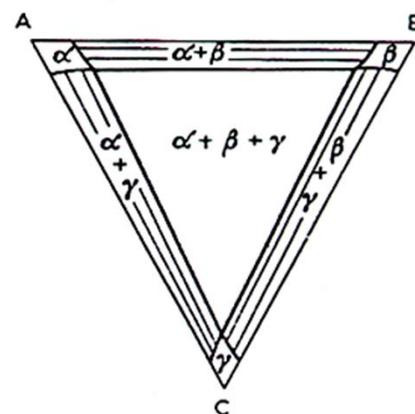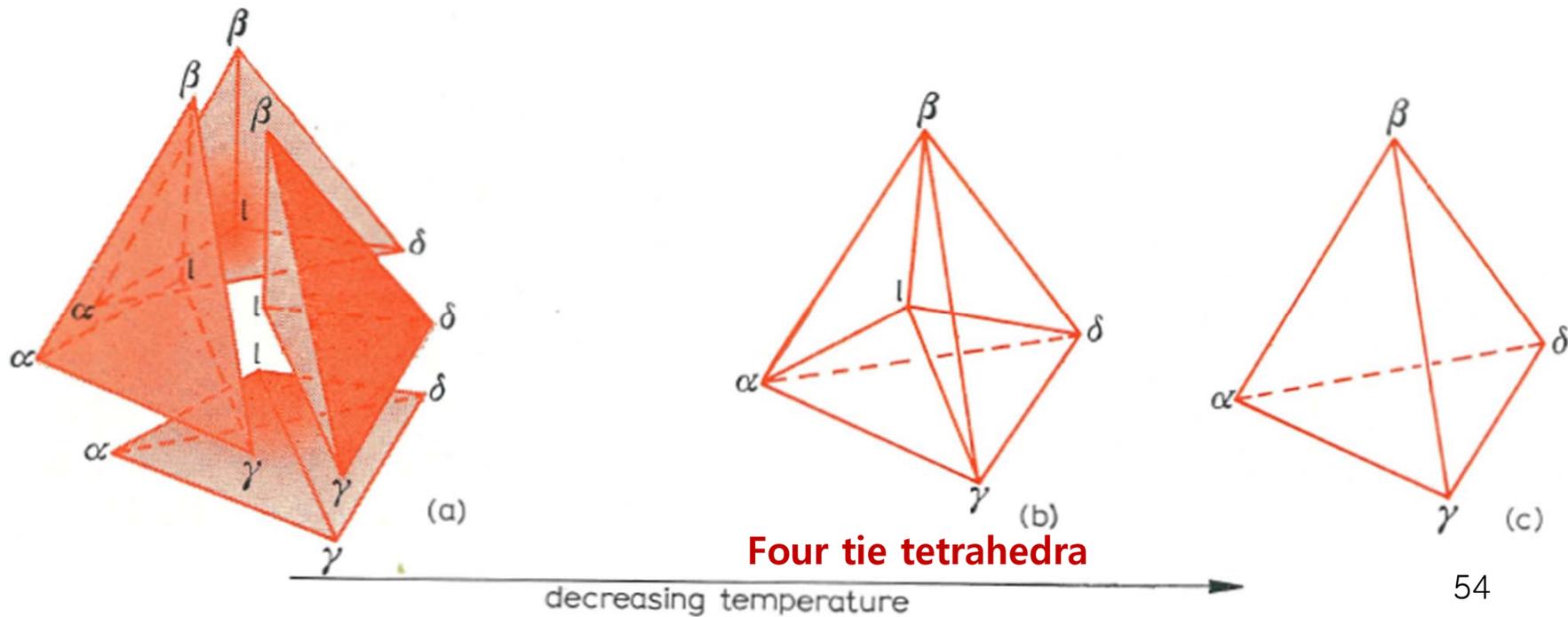
Fig. Sequence of tie-tetrahedron on cooling through the quaternary eutectic temperature

Polythermal projectin of a quaternary system involving five-phase equilibrium of the type l ⇄ α + β + γ + δ (schematic representation of the Bi-Cd-Pb-Sn quaternary eutectic system).
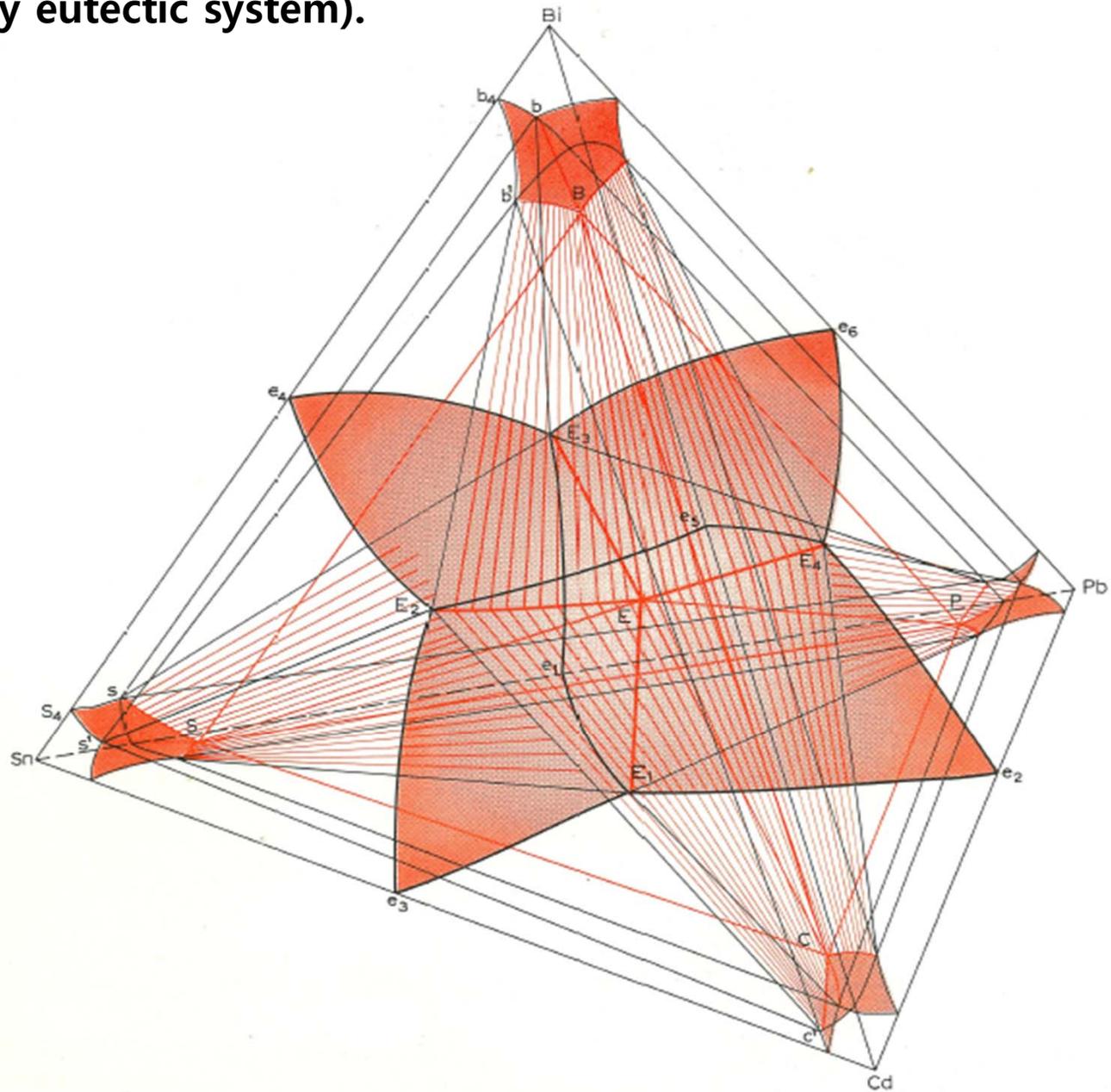
Q: Various different types of eutectic solidification (L→α + β) ?

1) Microstructure of Eutectics

* **Many eutectics are lamellar with a very regular structure if the metals used are sufficiently "pure" and that may of the other structures that are observed are degenerate forms of the lamellar structure cause by impurities.**
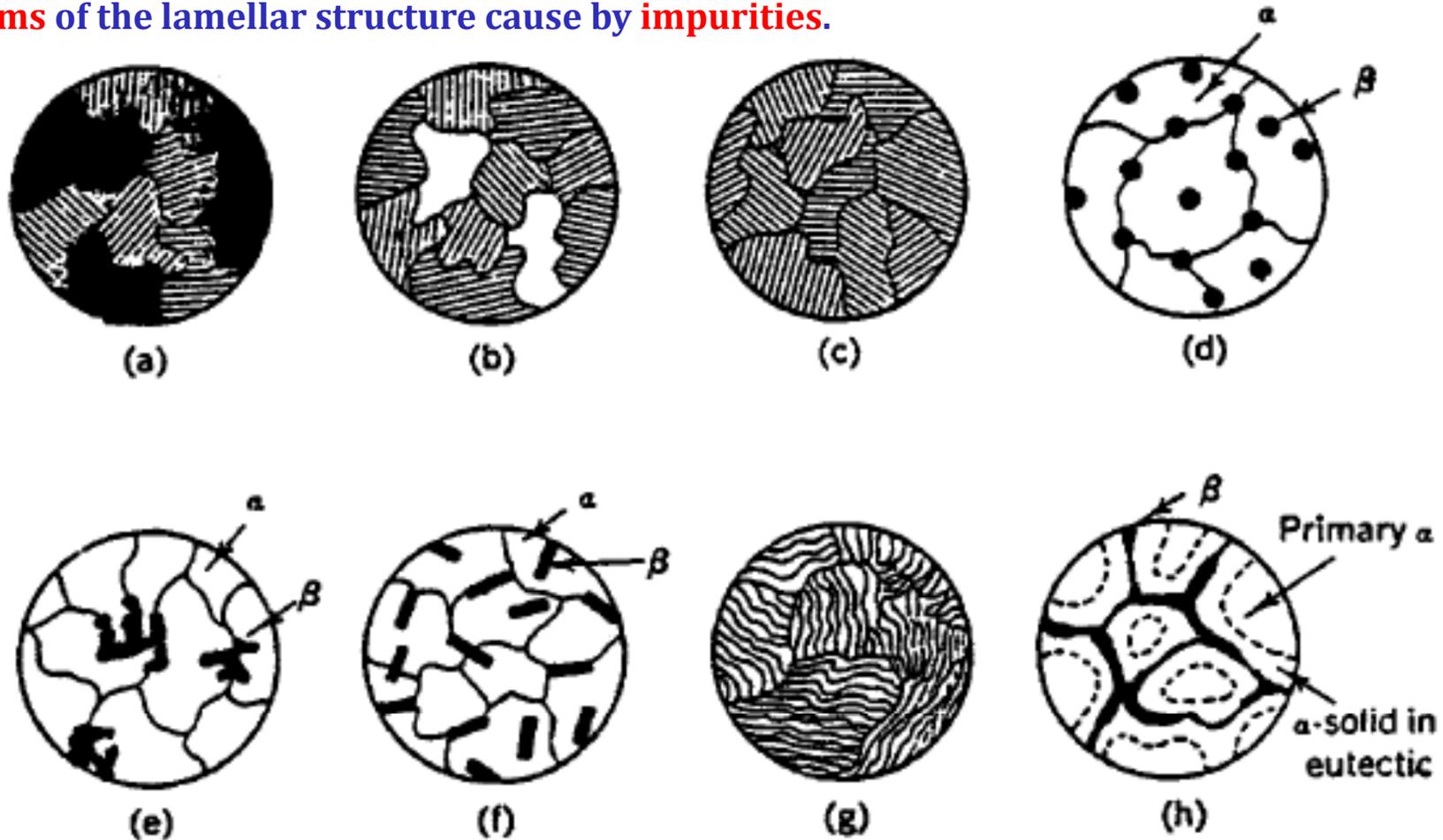
various

Fig. 14   Schematic representation possible in eutectic structures. (a), (b) and (c) are alloys shown in fig. 13; (d) nodular; (e) Chinese script; (f) acicular; (g) lamellar; and (h) divorced.

4.3.2 Eutectic Solidification

Various different types of eutectic solidification → Both phases grow simultaneously.

Normal eutectic

both phases have low entropies of fusion.

Fig. 4.30   Rod-like eutectic. Al_6Fe rods in Al matrix. Transverse section. Transmission electron micrograph (x 70000}.

Anomalous eutectic

One of the solid phases is capable of faceting, i.e., has a high entropy or melting.
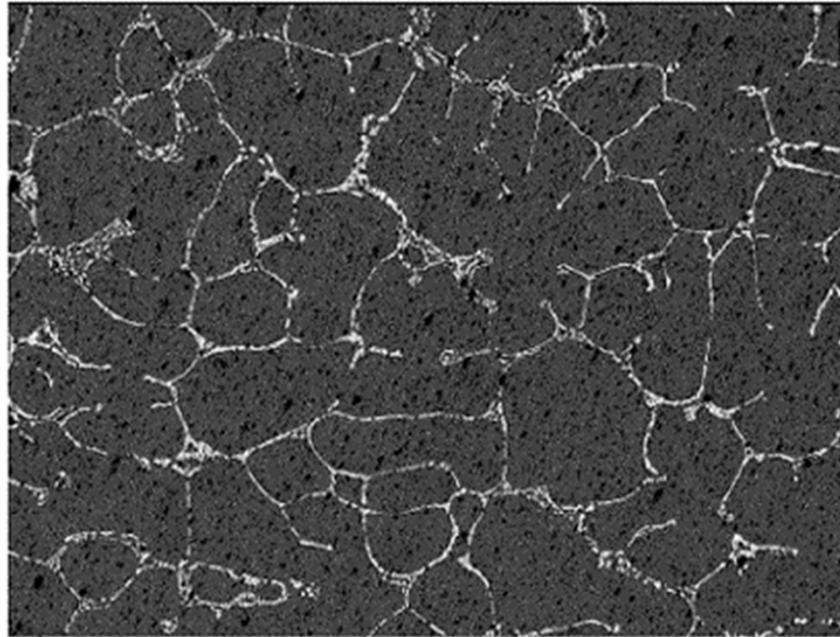
The microstructure of the Pb-61.9%Sn (eutectic) alloy presented a coupled growth of the (Pb)/βSn eutectic. There is a remarkable change in morphology increasing the degree of undercooling with transition from regular lamellar to anomalous eutectic.

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http://www.matter.org.uk/solidification/eutectic/anomalous_eutectics.htm
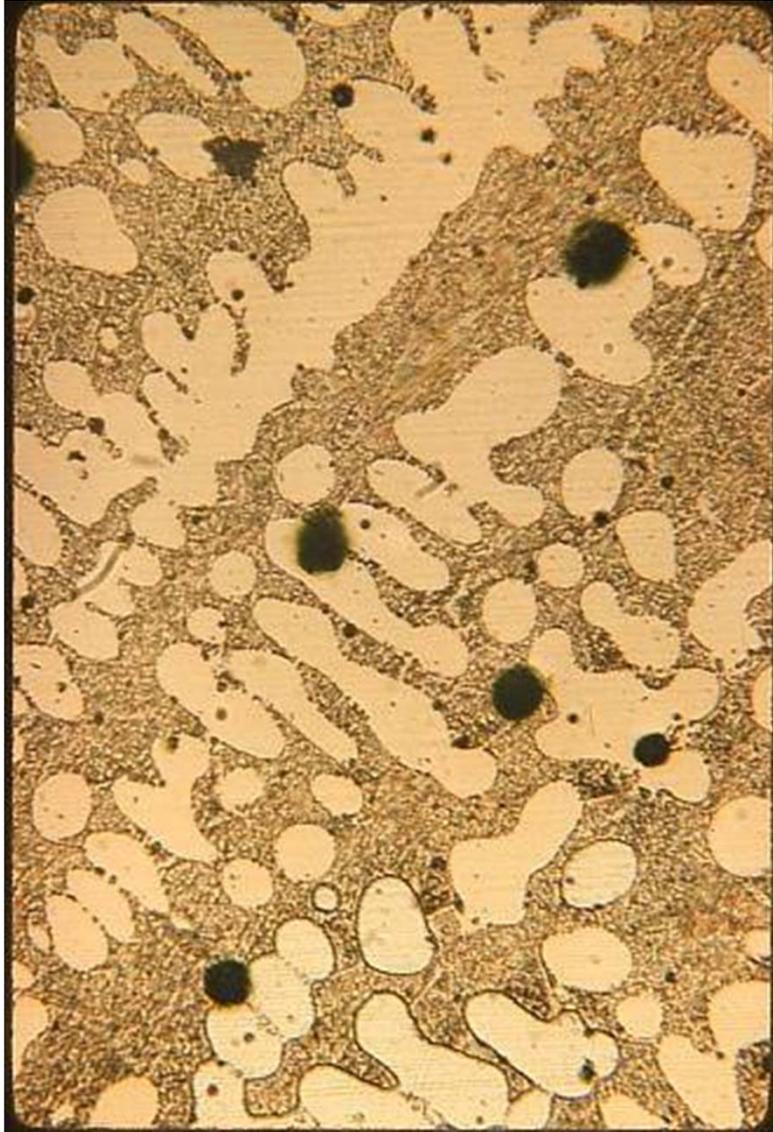
Eutectic

Divorced Eutectic
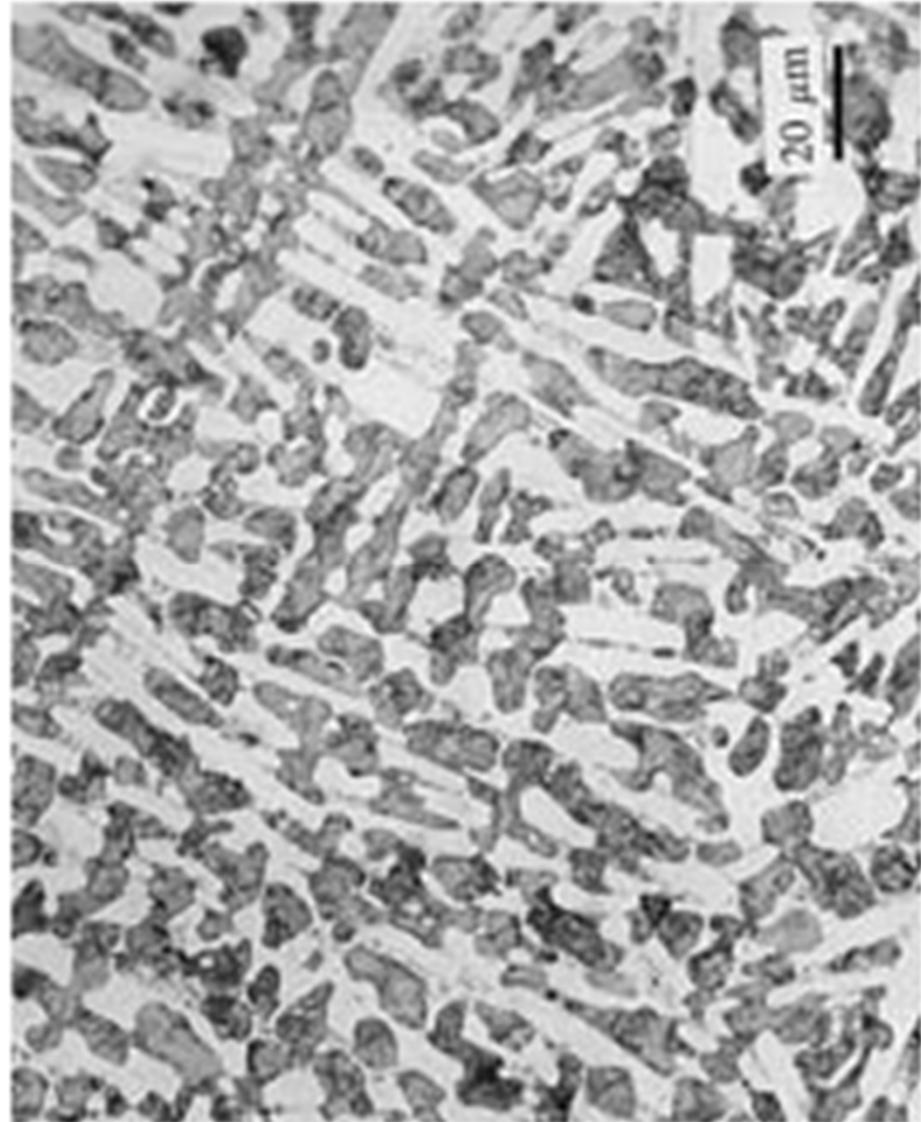
2) Pure binary eutectic

(zone-refined) high purity tin-lead

→ extremely regular lamellar structure
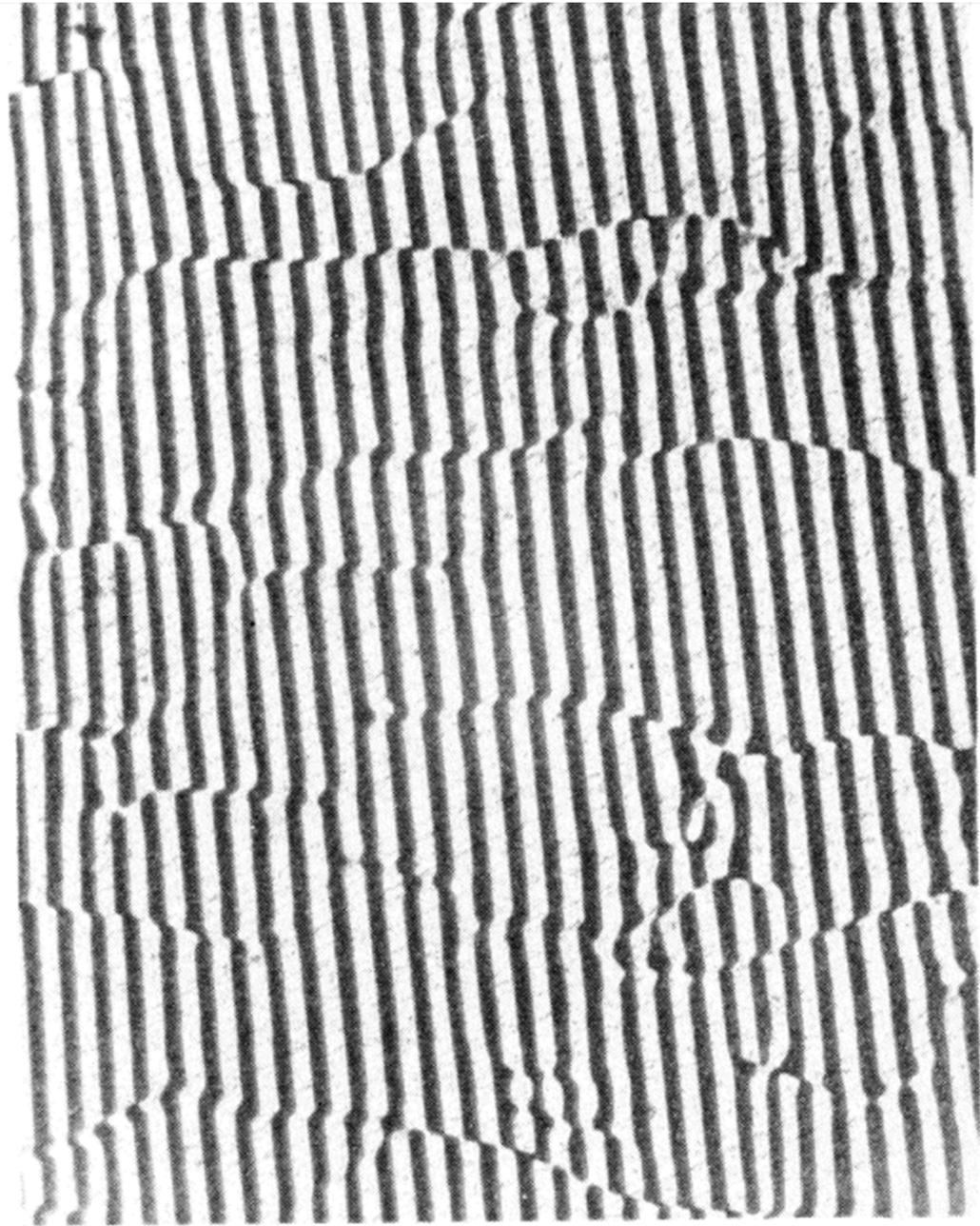
Fig. 6.13. Morphology of a pure eutectic (tin–lead).

Lamellae: straight and uniform thickness (ex, Al-Cu eutectic: several centimeters)

except where an "offset" or "termination" occurs

a) Constant orientation → simple crystallographic relationship

Sn-Zn (100) Sn $\parallel$ (0001) Zn; $[001]$ Sn $\parallel$ $[01\bar{1}0]$ Zn

Sn-Pb (101) Sn $\parallel$ (111) Pb; $[010]$ Sn $\parallel$ $[112]$ Pb

Ag Cu: all planes and directions parallel

b) Cu-CuAl$_2$ eutectic→ preferred relationship develops during the growth of a eutectic "single crystal"

: a relationship not only btw the orientation of the two phases, but also btw the interlamellar surface and the crystal orientations

(111) Al $\parallel$ (211) CuAl$_2$

$[101]$ Al $\parallel$ (120) CuAl$_2$

Lamellar interface parallel to (111) Al

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3) Solidification of lamellar eutectic

Two representative opinions:

1) Tammann : alternation of layers of the two phases

2) Vogel: two phase grew simultaneously → interlamellar interfaces were approximately normal to the mean solid–liquid interface
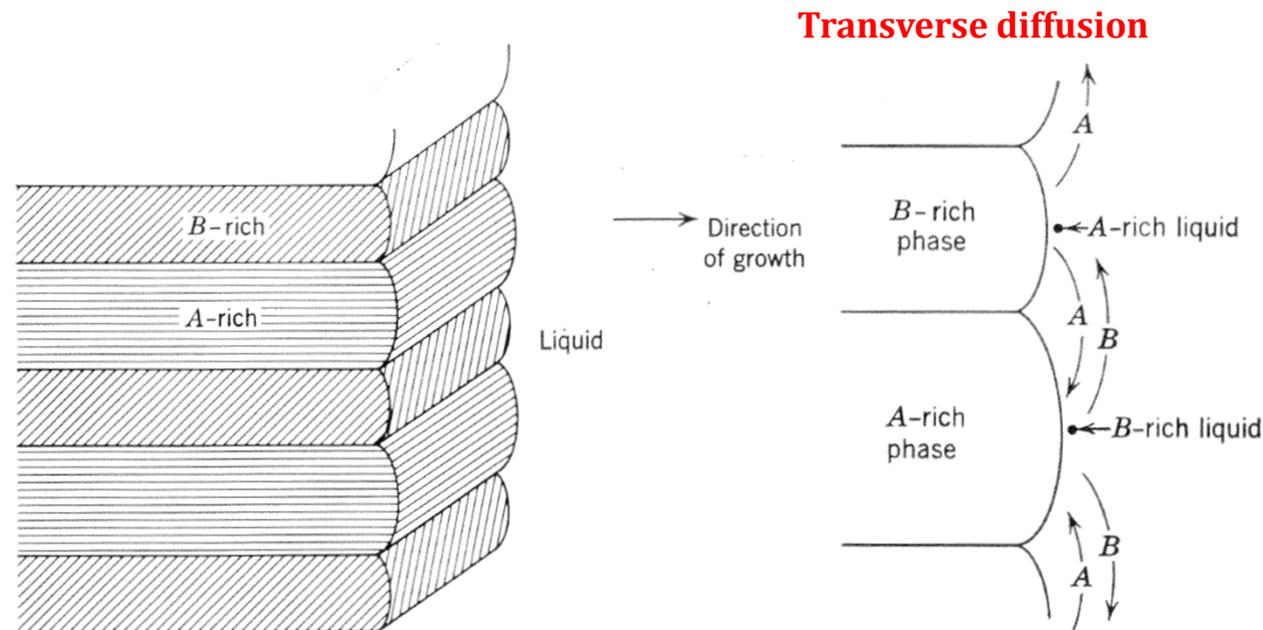
Fig. 6.14. Growth, mechanism, and diffusion paths for lamellar eutectic.

* Formation of Lamellae: a single nucleus of each phases → a nucleus of one phase forms first → second phase nucleates on the surface of the first

Reference: Pearlite Reaction in Fe-C Alloys: nucleation and growth

(a)
γ₁ | γ₂
Coherent interface | Incoherent interface
Fe₃C
(a) (i) (ii) (iii) (iv)
Branching

(b)
γ₁ γ₂
Semicoherent | Incoherent
Peralite will nucleate and grow on the incoherent side
(b) (i) (ii) (iii)

(c) A perlite colony at a later stage of growth

10 µm

Nucleation: depend on **GB structures and composition**
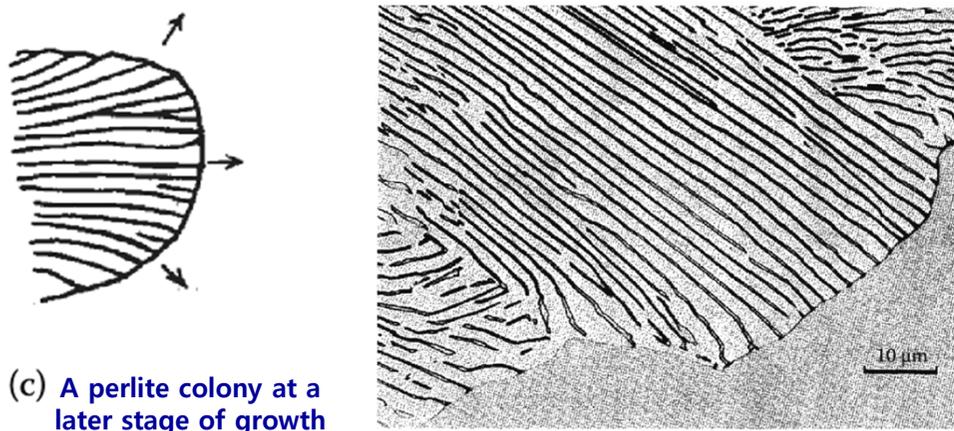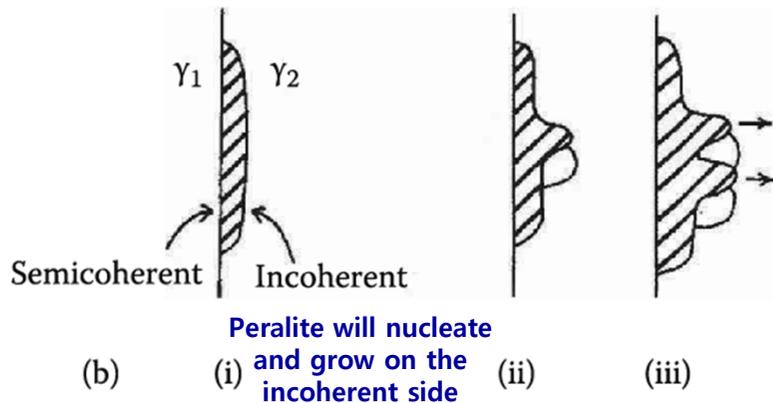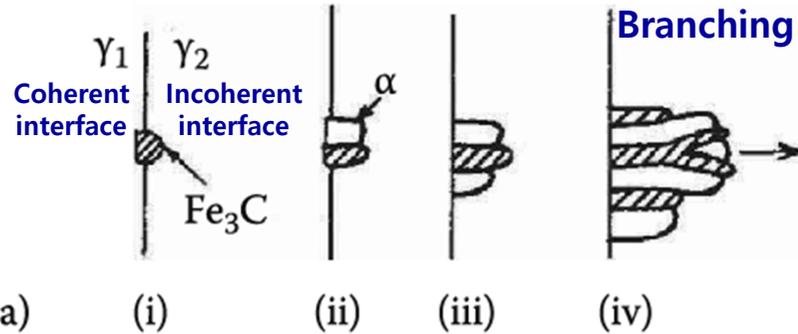
(a) On a "clean" GB.

(i) **Cementite nucleates on GB** with coherent interface and orientation relationship with γ₁ and incoherent interface with γ₂.

(ii) **α nucleates adjacent to cementite** also with a coherent interface and orientation relationship with γ₁. (This also produces an orientation relationship between the cementite and the ferrite).

(iii) The **nucleation process repeats side ways**, while incoherent interfaces grow into γ₂.

(iv) New plates can also form by a **branching** mechanism.

(b) When a proeutectoid phase (cementite or ferrite) already exists on that boundary, pearlite will **nucleate and grow on the incoherent side**. A different orientation relationship between the cementite and the ferrite results in this case.

(c) **Pearlite colony** at a latest stage of growth. Pearlite grows into the austenite grain with which it <u>does not have an orientation relationship</u>.

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4) Shape of the interface

Fig. 6.15. Possible interface shapes.

Normally convex   **Extreme case Concave**
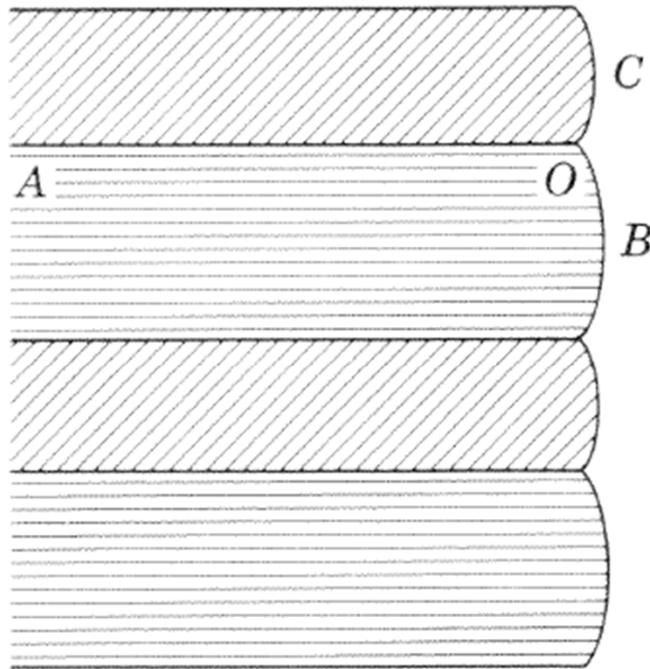
– Equilibrium of vector OA, OB, OC
  (O point → line in the real 3D case)

: the composition of the liquid in contact with
the interface is constant over each lamella
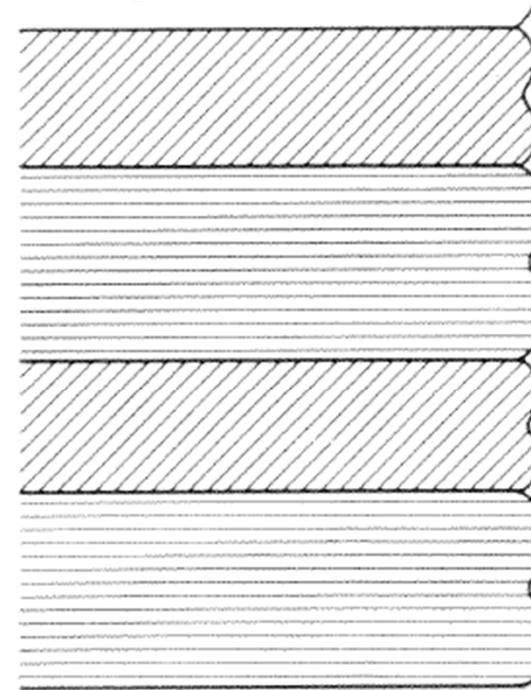
: Max. concentration of solute at Lamellae
center & Min. concentration of solute at
Lamellae edge

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Q: Thermodynamics and Kinetics of eutectic solidification (L→α + β) ?

2. Eutectic Solidification (Thermodynamics)
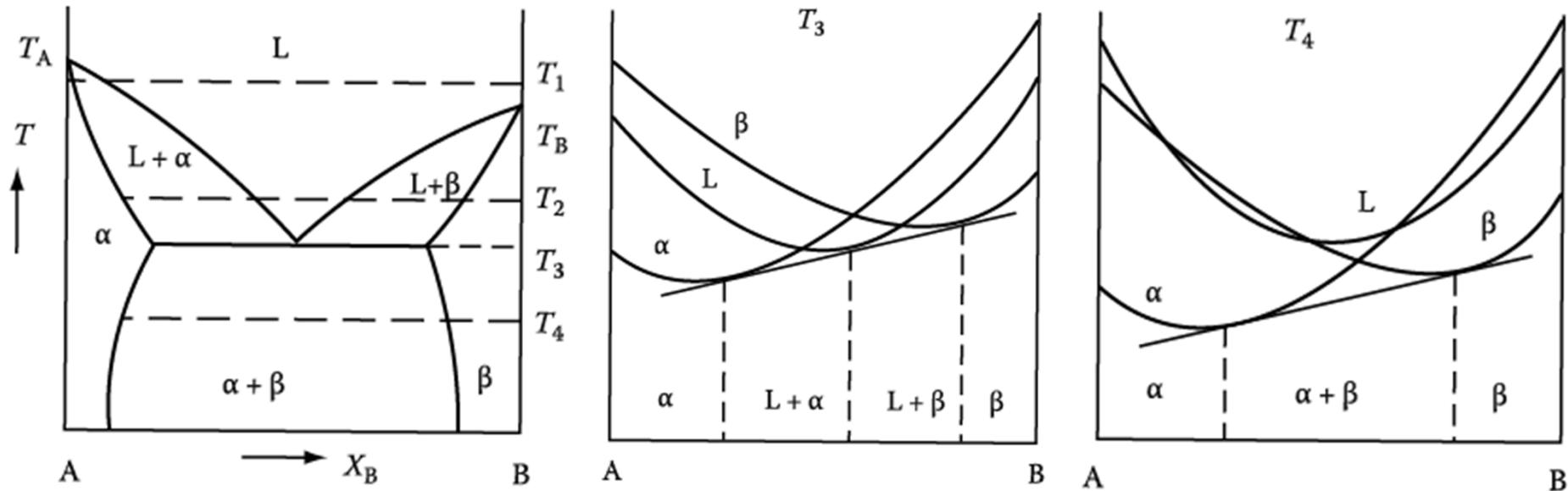
Plot the diagram of Gibbs free energy vs. composition at T_3 and T_4.

What is the driving force for the eutectic reaction (L $\rightarrow \alpha + \beta$) at T_4 at C_{eut}?

What is the driving force for nucleation of α and β? " ΔT "

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Eutectic Solidification (Kinetics)

: ΔT→ formation of interface + solute redistribution

If α is nucleated from liquid and starts to grow, what would be the composition at the <u>interface</u> of α/L determined?

→ **rough interface (diffusion interface) & local equilibrium**

How about at β/L?   Nature's choice? Lamellar structure

$$\rightarrow \quad G = G_{bulk} + G_{interface} = G_0 + \gamma\,A$$

$$\sum A_i \gamma_i + \Delta G_S = minimum$$

Interface energy $+$ Misfit strain energy

interlamellar spacing →
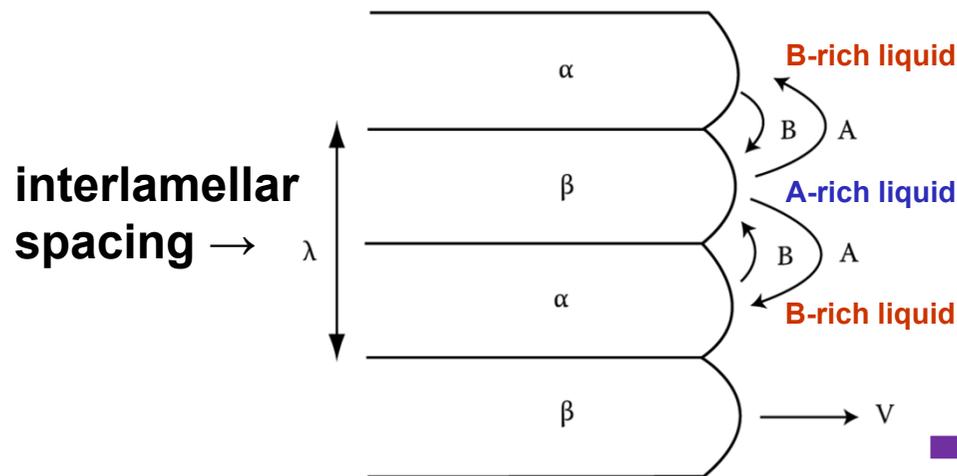
Eutectic solidification
: diffusion controlled process

1) $\lambda \downarrow \rightarrow$ eutectic growth rate ↑

but 2) $\lambda \downarrow \rightarrow \alpha/\beta$ interfacial E, $\gamma_{\alpha\beta}\uparrow$

→ lower limit of λ

➡ <u>fastest growth rate at a certain λ</u>

What would be a role of the <u>curvature</u> at the tip?

→ **Gibbs-Thomson Effect**

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Eutectic Solidification (Kinetics)

: ΔT→ a) formation of interface + b) solute redistribution

How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$
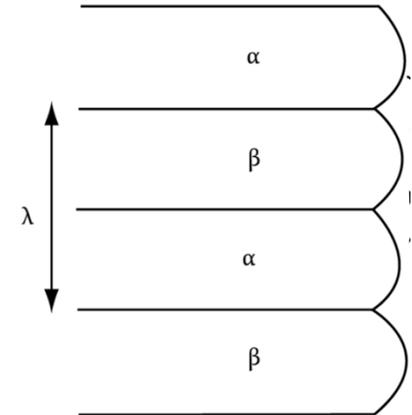
a) Formation of interface: **ΔG**

For an interlamellar spacing, λ, there is <u>a total of (2/ λ) m²</u> <u>of α/β interface per m³ of eutectic</u>.

$$\Delta G = \Delta \mu \cong \frac{L \Delta T}{T_m}$$

$$\rightarrow \Delta G = \Delta \mu = \frac{2\gamma}{\lambda} \times V_m \quad \text{Molar volume}$$

Driving force for nucleation = Total interfacial E of eutectic phase

For very large values of λ, interfacial E~ 0

$$\boldsymbol{\lambda \rightarrow \infty} , \quad \Delta G(\infty) = \Delta \mu = \frac{\Delta H \Delta T_0}{T_E} \quad \text{Total undercooling}$$

No interface (ideal case)

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda} \quad \text{Interfacial E term}$$

With interface (real case)

Solidification will take place if ΔG is negative (-).

@ $T_E - \Delta T_0$

G^L

$G^\alpha(\lambda^*)$ $G^\beta(\lambda^*)$

$\Delta G(\infty)$

$G^\alpha(\infty)$ $G^\beta(\infty)$

$\frac{2\gamma_{\alpha\beta}V_m}{\lambda^*}$

A X_E $X_B \longrightarrow$ B
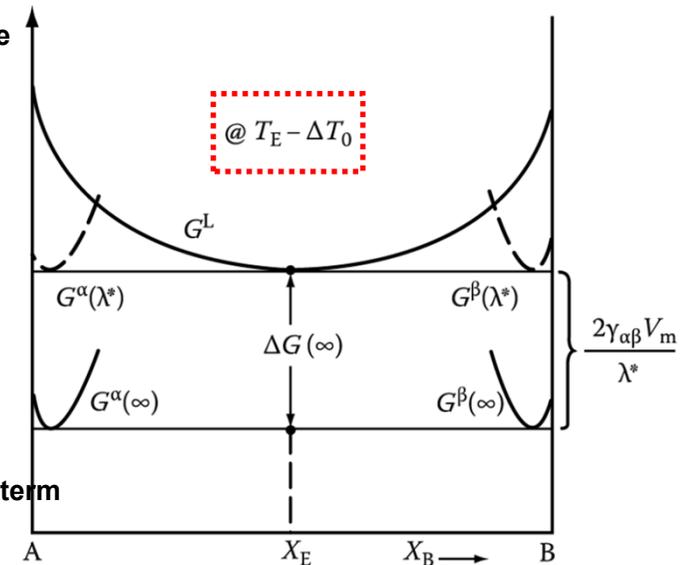
a) All **ΔT→ use for interface formation= min. λ**

What would be the minimum λ?   **Critical spacing,** $\lambda^* : \Delta G(\lambda^*) = 0$

최소 층상 간격

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda^*}$$

$$\lambda^* = +\frac{2T_E \gamma V_m}{\Delta H \Delta T_0}$$

$$\lambda^* = -\frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \rightarrow \text{identical to critical radius}$$

of dendrite tip in pure metal

Gibbs-Thomson effect

$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

L_V : *latent heat per unit volume*

$L = \Delta H = H^L - H^S$

* Growth Mechanism: Gibbs-Thomson effect in a ΔG-composition diagram?

1) At λ=λ* (<∞),

@ $T_E - \Delta T_0$

All 3 phases are in equilibrium.

G^L

$G^\alpha(\lambda^*)$ $G^\beta(\lambda^*)$

$\Delta G(\infty)$

$\frac{2\gamma_{\alpha\beta}V_m}{\lambda^*}$

$G^\alpha(\infty)$ $G^\beta(\infty)$

A X_E $X_B \longrightarrow$ B
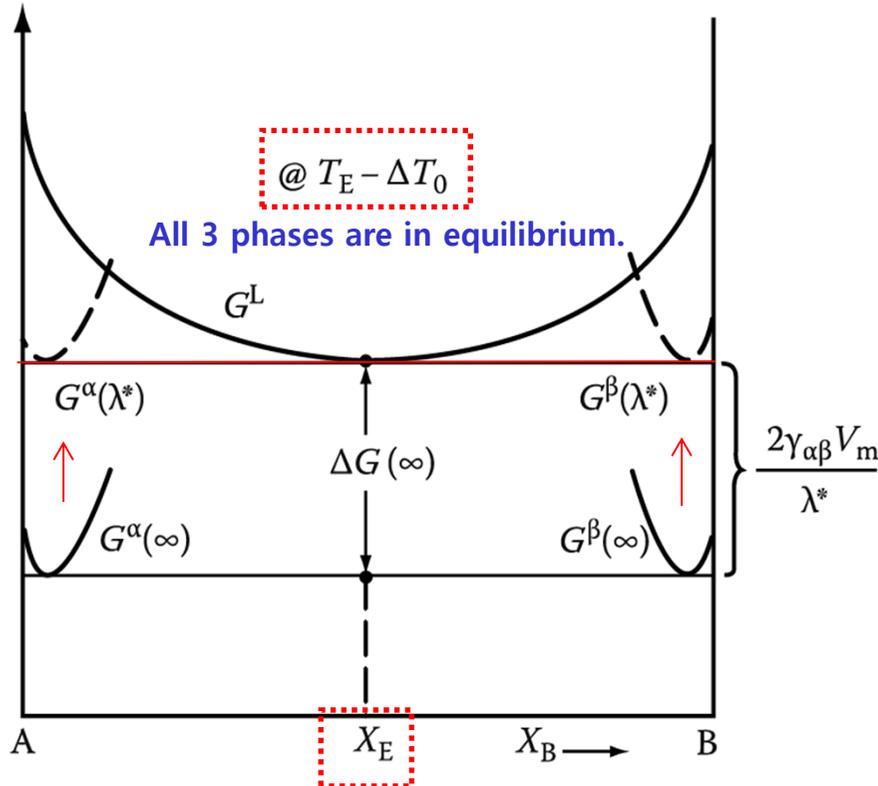
The cause of G increase is the curvature of the α/L and β/L interfaces arising from the need to balance the interfacial tensions at the α/ β/L triple point, therefore the increase will be different for the two phases, but for simple cases it can be shown to be

$\frac{2\gamma_{\alpha\beta}V_m}{\lambda}$ **for both.**

1) If λ=λ*, growth rate will be *infinitely slow* because the liquid in contact with both phases has the same composition, X_E in Figure 4.32.

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2) At λ= (∞>) λ (>λ*),   If ∞> λ > λ*, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. → $X_B^{L/\alpha} > X_B^{L/\beta}$

@ $T_E - \Delta T_0$

Concentration of B must be higher ahead of the α phase
B rejected from the α phase → the tips of the growing β

G^L

ΔX

$G^\alpha(\lambda)$ $G^\beta(\lambda)$

Formation of interface: ΔG

$G^\alpha(\infty)$ X_B $G^\beta(\infty)$ $\dfrac{2\gamma_{\alpha\beta}V_m}{\lambda}$

A $X_B^{L/\beta}$ $X_B^{L/\alpha}$ B

(a)
B concentration ahead of the β phase   **<**   B concentration ahead of the α phase

$V\uparrow$ l —   B   L

β   α

|← λ →|

(b)

Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case **λ* < λ < ∞**, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

* Eutectic growth rate, v

→ if α/L and β/L interfaces are highly mobile

→ proportional to flux of solute through liquid

→ **diffusion controlled process**

$$v \propto D\frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})$$

$\propto$ **1/effective diffusion distance.. 1/λ**

$$v = k_1 D\frac{\Delta X}{\lambda} \quad (1)$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

$$\Delta X = \Delta X_0(1 - \frac{\lambda^*}{\lambda}) \quad (2)$$

(next page)

$$\Delta X_0 \propto \Delta T_0 \quad (3)$$

(2)+(3) → (1) $$v = k_2 D\frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})$$

Maximum growth rate at a fixed ΔT₀→ $\boxed{\lambda = 2\lambda^*}$

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ΔX will it self depend on λ. ~ maximum value, ΔX₀

$$\lambda = \lambda^*, \Delta X = 0$$

$$\lambda = \infty, \Delta X = \Delta X_0$$

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

If undercooling is small,

$$\Delta X_0 \propto \Delta T_0$$

* **Total Undercooling**

$$\Delta T_0 = \Delta T_r + \Delta T_D$$

Undercooling required to overcome the interfacial curvature effects

ΔT_r Undercooling for curvature, r

ΔT_D Undercooling for Diffusion

Undercooling required to give a sufficient composition difference to drive the diffusion

L

$\lambda = \lambda^*$

λ

T_E

ΔT_0

ΔX

ΔX_0
$(\lambda = \infty)$

A X_B ⟶   B

Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX₀ (exaggerated for clarity)

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2) At $\lambda = (\infty >) \lambda (> \lambda^*)$, If $\infty > \lambda > \lambda^*$, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. $\rightarrow$ $X_B^{L/\alpha} > X_B^{L/\beta}$

* Eutectic growth rate, v

$\rightarrow$ if α/L and β/L interfaces are highly mobile

$\rightarrow$ **proportional to flux of solute through liquid**

$\rightarrow$ **diffusion controlled process**

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$\propto$ **1/effective diffusion distance.. 1/λ**

$$v = k_1 D \frac{\Delta X}{\lambda} \qquad (1)$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

(next page)

$$\Delta X = \Delta X_0 (1 - \frac{\lambda^*}{\lambda}) \qquad (2)$$

$$\Delta X_0 \propto \Delta T_0 \qquad (3)$$

(2)+(3) → (1) $\quad v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})$

Maximum growth rate at a fixed $\Delta T_0 \rightarrow$ $\boxed{\lambda = 2\lambda^*}$

In figure (a):

G

@ $T_E - \Delta T_0$

Concentration of B must be higher ahead of the α phase

B rejected from the α phase → the tips of the growing β

G^L

ΔX

$G^\alpha(\lambda)$ $\quad G^\beta(\lambda)$

Formation of interface: ΔG

$G^\alpha(\infty)$ $\quad X_B \quad G^\beta(\infty)$

$\dfrac{2\gamma_{\alpha\beta}V_m}{\lambda}$

A $\quad X_B^{L/\beta} \quad X_B^{L/\alpha} \quad$ B

(a)

B concentration ahead of the β phase $\;<\;$ B concentration ahead of the α phase

In figure (b):

V $\quad$ l $\quad$ B $\quad$ L

β $\quad$ α

λ

(b)

Fig. 4.33 (a) Molar free energy diagram at $(T_E - \Delta T_0)$ for the case $\lambda^* < \lambda < \infty$, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

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Closer look at the tip of a growing dendrite

different from a planar interface because heat can be conducted away from the tip in three dimensions.

Assume the solid is isothermal $\left(T_S' = 0\right)$

From $K_S T_S' = K_L T_L' + v L_v$

If $T_S' = 0,$ $v = \dfrac{-K_L T_L'}{L_v}$

A solution to the heat-flow equation for a hemispherical tip:

$T_L'(negative) \cong \dfrac{\Delta T_C}{r}$ $\Delta T_C = T_i - T_\infty$

$v = \dfrac{-K_L T_L'}{L_v} \cong \dfrac{K_L}{L_v} \cdot \dfrac{\Delta T_C}{r}$ $v \propto \dfrac{1}{r}$
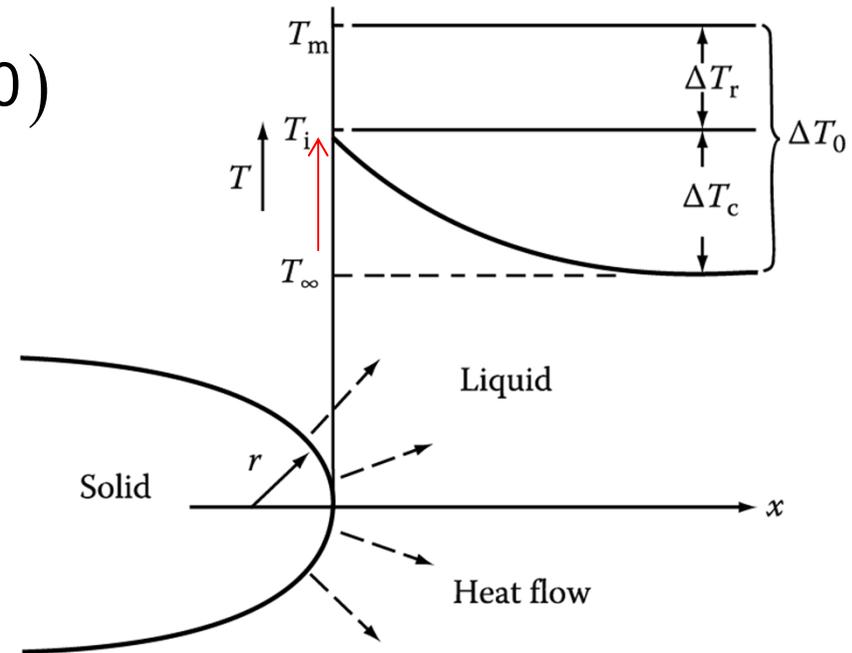
However, ΔT also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect: melting point depression

$\Delta G = \dfrac{L_v}{T_m} \Delta T_r = \dfrac{2\gamma}{r}$ $\Delta T_r = \dfrac{2\gamma T_m}{L_v r}$

Minimum possible radius (r)?

$$r_{min} : \Delta T_r \rightarrow \Delta T_0 = T_m - T_\infty \rightarrow r^*$$

The crit.nucl.radius

$$r^* = \frac{2\gamma T_m}{L_V \Delta T_o}$$

$$\Delta T_r = \frac{2\gamma T_m}{L_V r}$$

Express ΔT_r by r, r^* and ΔT_o.

$$\Delta T_r = \frac{r^*}{r} \Delta T_o$$
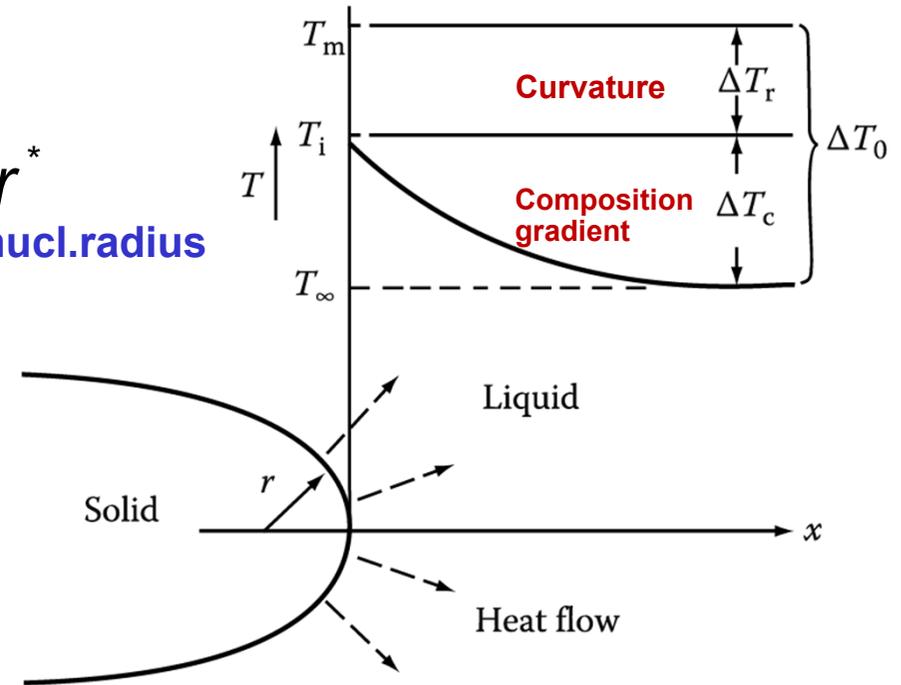
$$v \cong \frac{K_L}{L_V} \cdot \frac{\Delta T_c}{r} = \frac{K_L}{L_V} \cdot \frac{(\Delta T_0 - \Delta T_r)}{r} = \frac{K_L}{L_V} \cdot \frac{\Delta T_0}{r} \left(1 - \frac{r^*}{r}\right)$$

$v \rightarrow 0 \ as \ r \rightarrow r^* \ due \ to \ Gibbs\text{-}Thomson \ effect$

$as \ r \rightarrow \infty \ due \ to \ slower \ heat \ condution$

Maximum velocity?

$$\rightarrow \ r = 2r^*$$

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Undercooling ΔT_0

$$\Delta T_0 = \boxed{\Delta T_r} + \boxed{\Delta T_D}$$

Curvature   Composition gradient

$$\Rightarrow \quad \Delta G_{total} = \boxed{\Delta G_r} + \boxed{\Delta G_D}$$

$$\Rightarrow \quad v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})$$

$$\Delta G_r = \frac{2\gamma_{\alpha\gamma} V_m}{\lambda}$$

$\rightarrow$ *free energy dissipated in forming α/β interfaces*

$\Delta G_D \rightarrow$ *free energy dissipated in diffusion*

By varying the interface undercooling (ΔT_0) it is possible to vary the growth rate (v) and spacing (λ) independently.

Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX₀ (exaggerated for clarity)

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Undercooling ΔT_0

$$\Delta T_0 = \boxed{\Delta T_r} + \boxed{\Delta T_D}$$

Curvature   **Composition gradient**

$$\Delta G_{total} = \boxed{\Delta G_r} + \boxed{\Delta G_D}$$

$$v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})$$

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By varying the interface undercooling (ΔT_0) it is possible to vary the growth rate (V) and spacing (λ) independently.

Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. <u>However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.</u>

* **For example,**

     Maximum growth rate at a fixed $\Delta T_0 \rightarrow$ $\boxed{\lambda_0 = 2\lambda^*}$

(4) $v = k_2 D \dfrac{\Delta T_0}{\lambda}(1 - \dfrac{\lambda^*}{\lambda})$ $\Longrightarrow$ $\boxed{v_0 = k_2 D \Delta T_0 / 4\lambda^*}$ **(5)**

From Eq. 4.39

$$\lambda^* = + \frac{2 T_E \gamma V_m}{\Delta H \Delta T_0}$$ $\Longrightarrow$ $\boxed{\Delta T_0 \propto 1/\lambda^*}$ **(6)**

So that the following relationships are predicted:

(5) + (6)

$$v_0 \lambda_0^2 = k_3 \text{ (constant)}$$

$$\frac{v_0}{(\Delta T_0)^2} = k_4$$

Ex) Lamellar eutectic in the Pb-Sn system

$k_3 \sim$ **33 μm³/s and** $k_4 \sim$ **1 μm/s·K²**

$\Longrightarrow$ **v = 1 μm/s, λ_0 = 5 μm and ΔT_0 = 1 K**

* Total Undercooling

$$\Delta T_0 = \Delta T_r + \Delta T_D$$

Strictly speaking,

ΔT_i term should be added   but, **negligible** for high mobility interfaces

Driving force for atom migration across the interfaces

Undercooling required to overcome the interfacial curvature effects

Undercooling required to give a sufficient composition difference to drive the diffusion

$\Delta T_D \rightarrow$ **Vary continuously from the middle of the α to the middle of the β lamellae**

$\Delta T_0 = const$ ← **Interface is essentially isothermal.**

$\Delta T_D \rightarrow \Delta T_r$ **The interface curvature will change across the interface.**

Should be compensated

* A planar eutectic front is not always stable.

Binary eutectic alloys contains **impurities** or **other alloying elements**

➡ **"Form a cellular morphology"**

analogous to single phase solidification restrict in a sufficiently high temp. gradient.

➡ **The solidification direction changes as the cell walls are approached and the lamellar or rod structure fans out and may even change to an irregular structure.**

➡ **Impurity elements (here, mainly copper) concentrate at the cell walls.**

10 μ

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A planar eutectic front is not always stable.

Binary eutectic alloys contains impurities or other alloying elements ➡ **"Form a cellular morphology"** analogous to single phase solidification restrict in a sufficiently high temp. gradient.

➡ **The solidification direction changes as the cell walls are approached and the lamellar or rod structure fans out and may even change to an irregular structure.**

➡ **Impurity elements (here, mainly copper) concentrate at the cell walls.**

**Fig. 4.35 Transverse section through the cellular structure of an Al-Al$_6$Fe rod eutectic (x3500).**
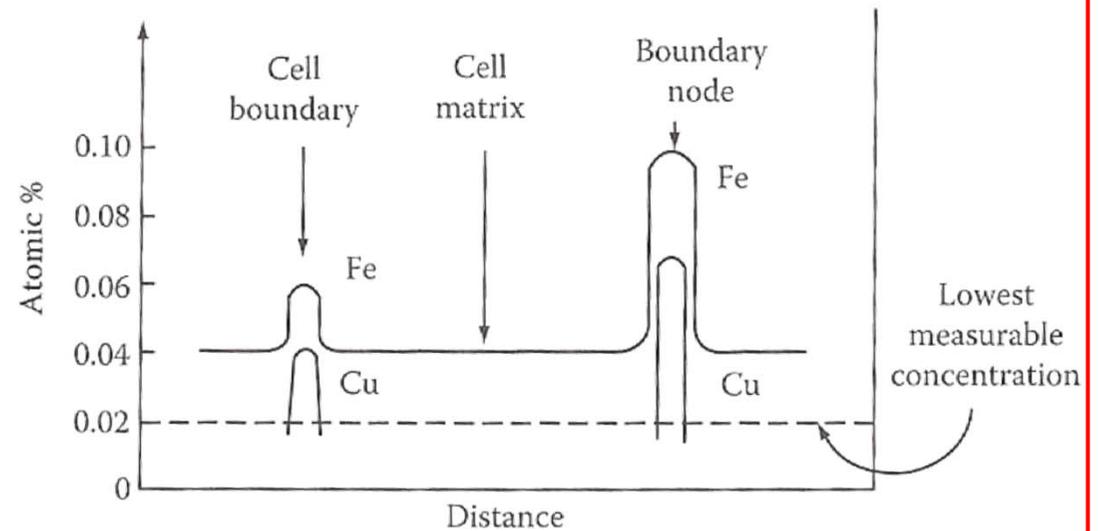
Fig. 4.36 Composition profiles across the cells in Fig. 4.35b.