2020 Spring

Advanced Solidification

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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

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

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

Free dendritic growth:
- **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"

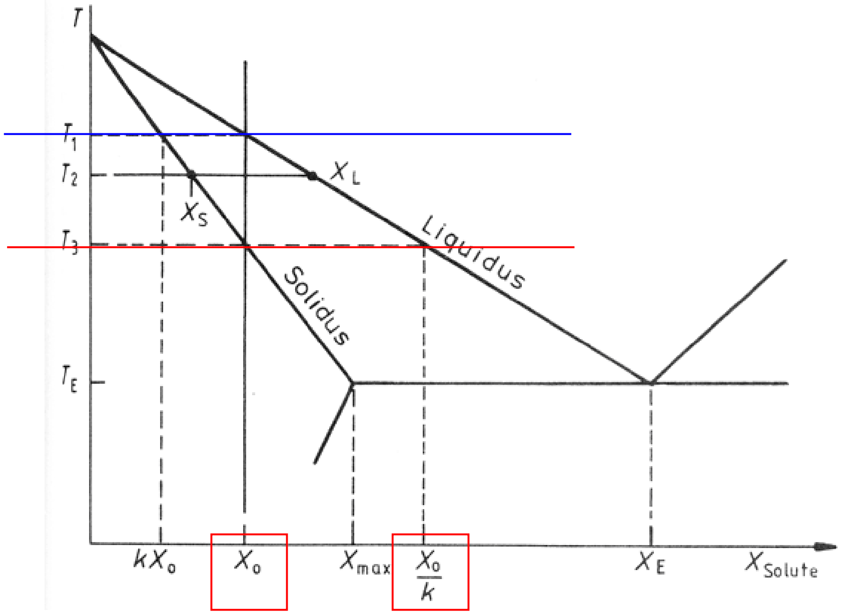
Temperature above the interface at which growth occurs

b) Segregation

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

* Constitutional Supercooling

No Diffusion on Solid, Diffusional Mixing in the Liquid ➡ **Steady State**



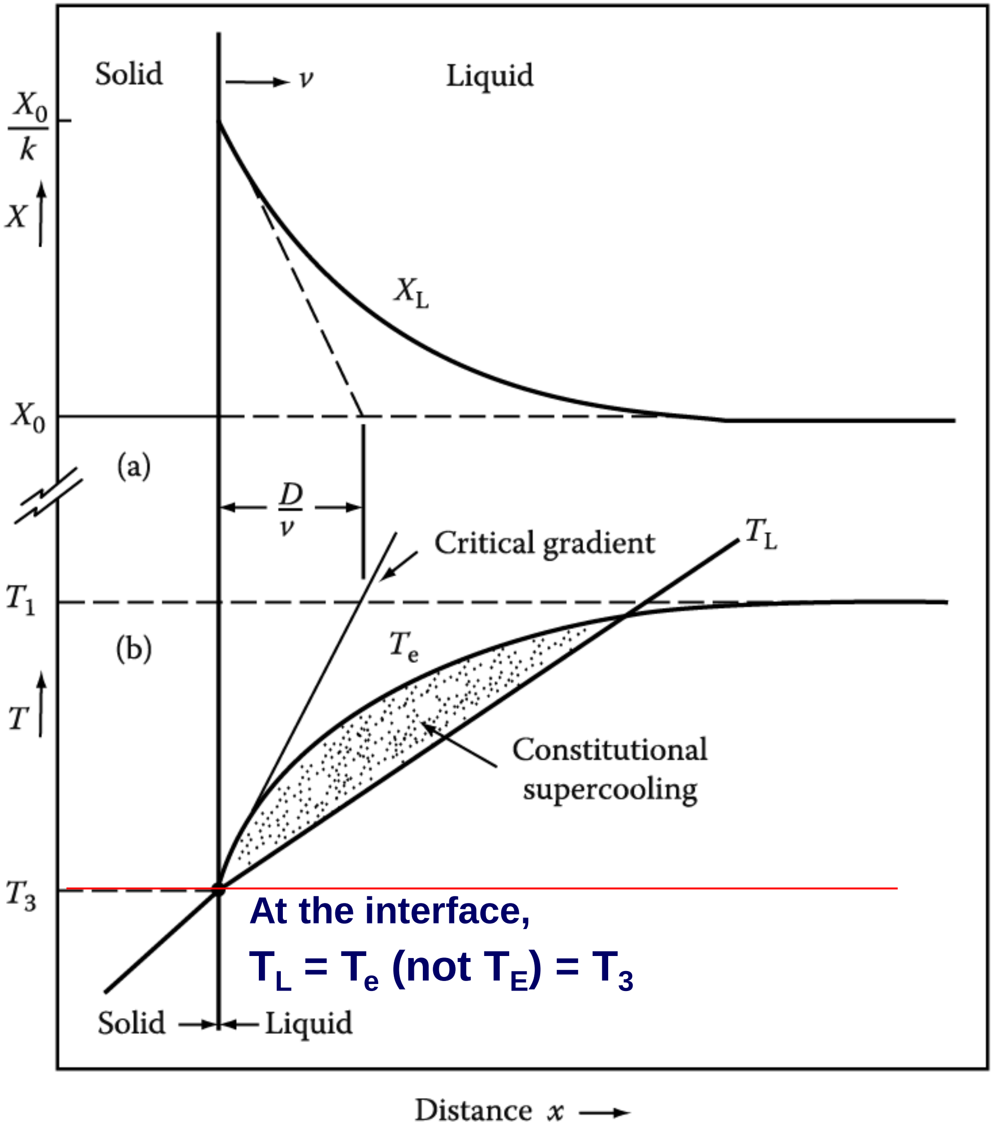
*** Actual temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

T_e

$T_L'/v < (T_1-T_3)/D$



At the interface,

$T_L = T_e$ (not T_E) $= T_3$

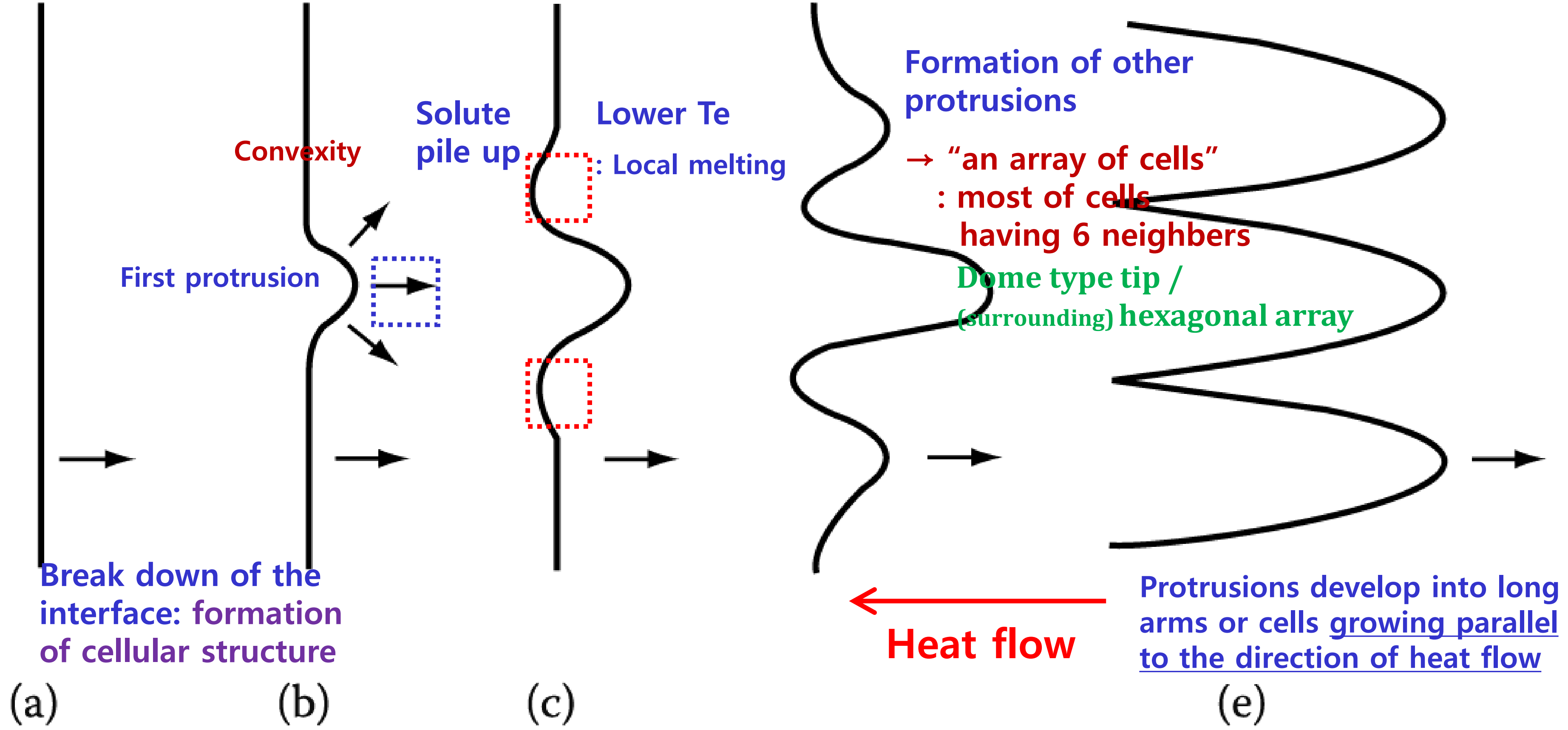
Constitutional supercooling

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at interface, (a))



Convexity

First protrusion

Solute pile up

Lower Te : Local melting

Formation of other protrusions

→ "an array of cells" : most of cells having 6 neighbors

Dome type tip / (surrounding) hexagonal array

Break down of the interface: formation of cellular structure

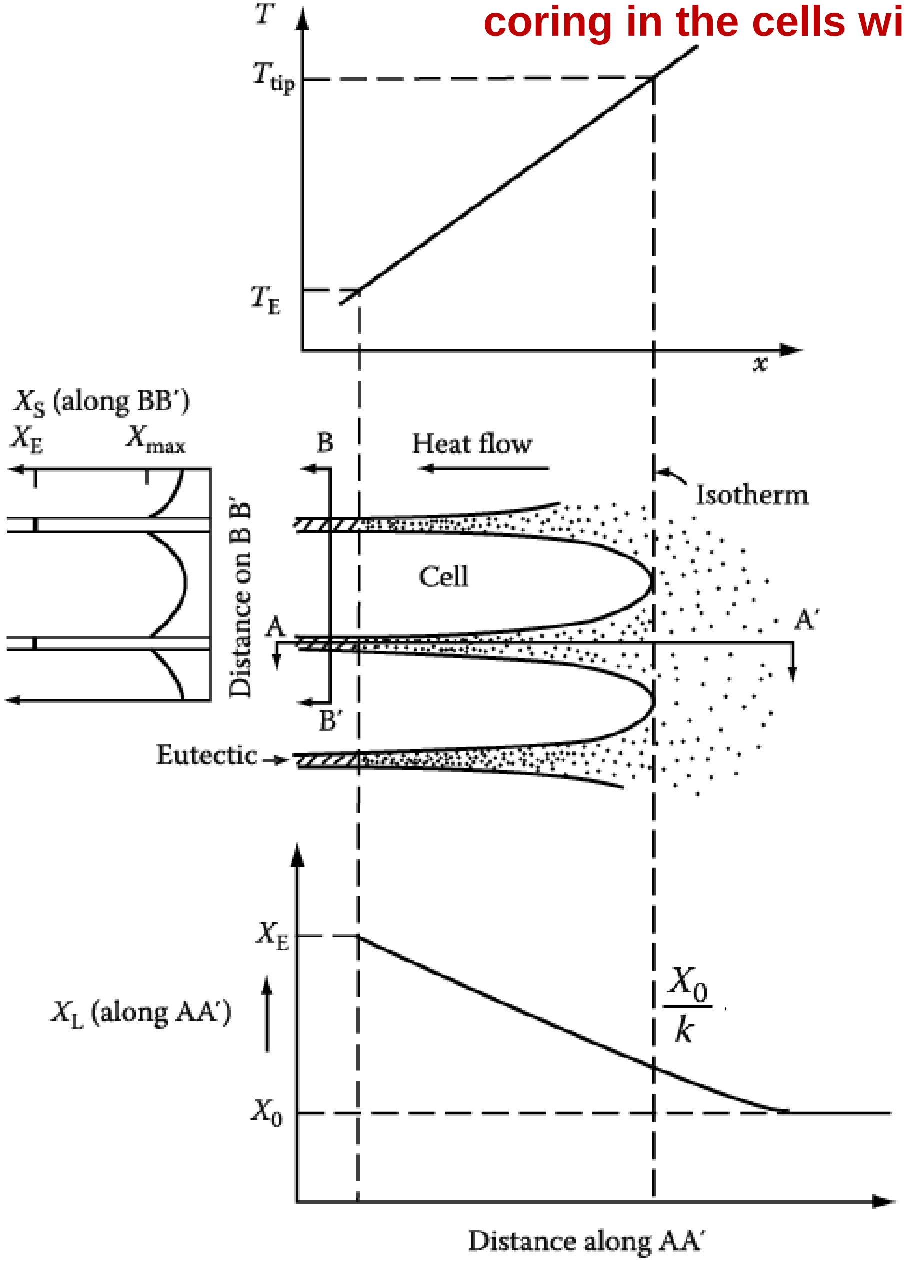
Heat flow

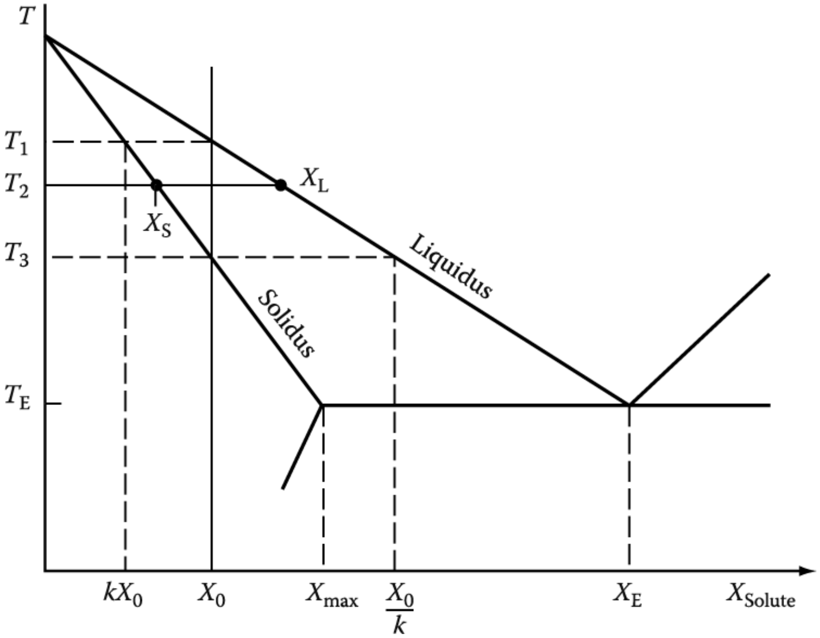
Protrusions develop into long arms or cells <u>growing parallel to the direction of heat flow</u>

<The breakdown of an initially planar solidification front into cells>

* 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 $X_0 << X_{max}$

Solute file up → eutectic solidification → formation of 2nd phases at the cell wall

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

2) Quantitative studies of cell formation

* Critical temp gradient where no constitutional supercooling occurs

Assumption: Steady state distribution of solute

⇨ If m = slope of liquidus line, dT_E/dC_L & T_0: Equip. temp. for the pure metal

$$\boxed{T_E = T_0 - mC_L}$$

(Equip. temp. for the alloy)

a) Equilibrium temperature of alloy at distance X in front of interface

R Growth rate

$$T_E = T_0 - mC_0\left[1 + \frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X\right)\right]$$

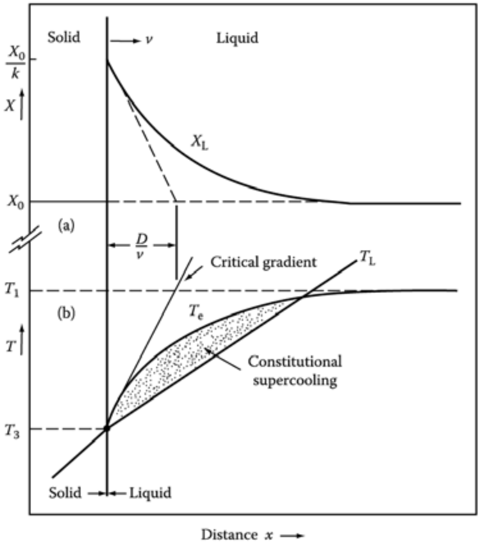
D diffusivity

b) Actual temperature of alloy at distance X in front of interface

$$T = \boxed{T_0 - m\frac{C_0}{k_0}} + \boxed{G}X$$

Interface temperature
(Ignoring the supercooling required
to provide the kinetic driving force)

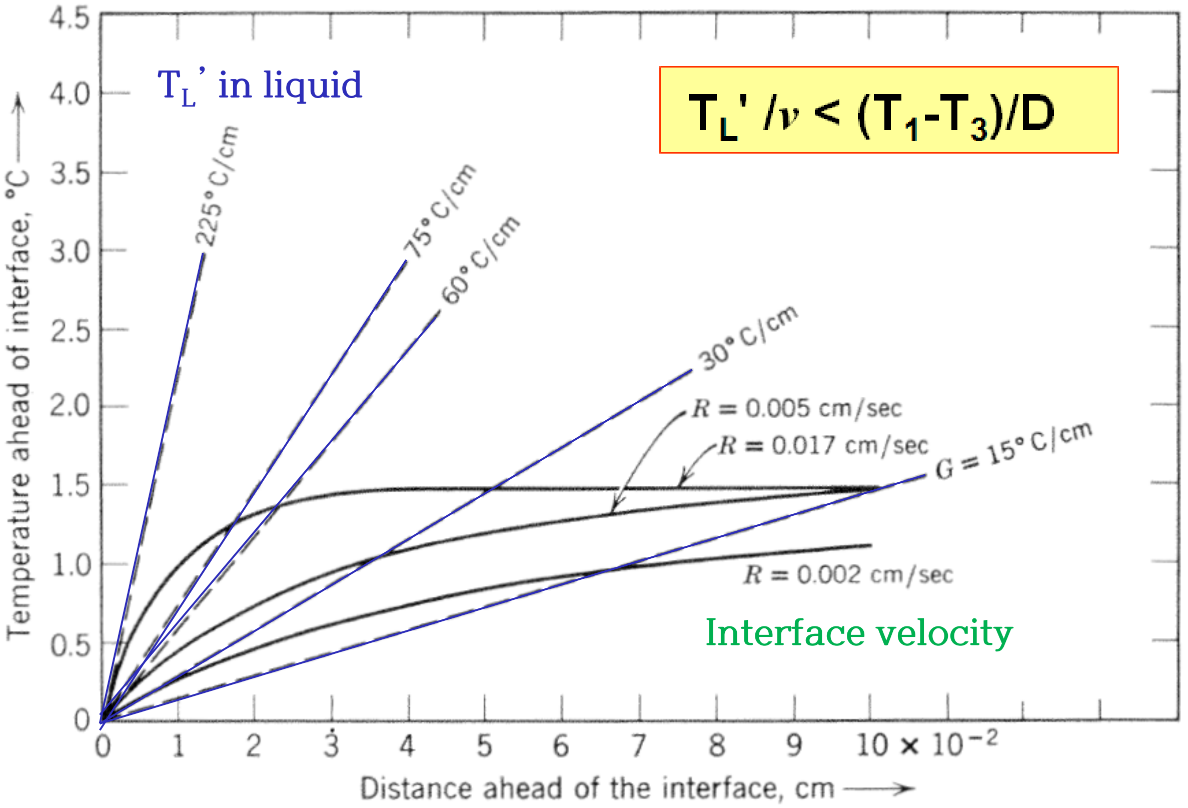
Temp gradient in the liquid
in degrees per centimeter, T_L'



2) Quantitative studies of cell formation

Fig. 5.32. distribution of temperature and liquid temperature ahead of an advancing planar interface, for selected values of R and G. (From Ref. 3, p. 434.)

Interface velocity T_L' in liquid



$T_L' / v < (T_1 - T_3)/D$

"Length of the supercooled zone" is given by the value of X (distance) at $T=T_E$.

$$1 - \exp\left(\frac{R}{D}X\right) = \frac{G}{mC_0(1-k_0)/k_0}X$$

2) Quantitative studies of cell formation

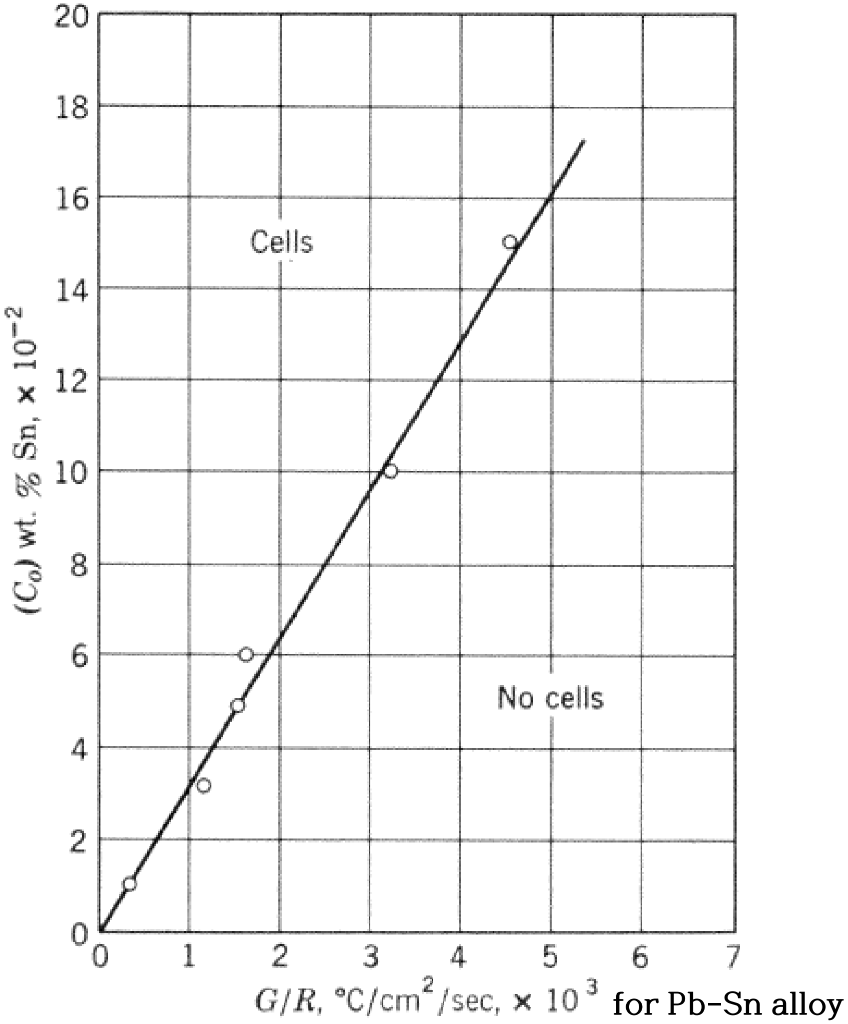
⇨ **The critical ratio of temperature gradient (G) to growth rate (R) is that at which the length of the supercooled zone is zero, or the slopes at the origin of the "liquidus temperature" lines are equal.**

$$\boxed{\frac{G}{R} = \frac{mC_0}{D} \cdot \frac{1 - k_0}{k_0}}$$

G/R ∝ solute concentration (C_0)

or G/RC_0 = constant

⇨ **These experiments confirm the cell formation is a result of the instability produce by constitutional supercooling.**



for Pb–Sn alloy

Fig. 5.33. Conditions for cellular solidification

2) Quantitative studies of cell formation

* Since C.S. cannot exist until an enriched (or depleted) boundary layer has been formed, it follows that cells should not form immediately when solidification begins, even if uniform values of G and R are immediately established.

⇨ There "must" be an "incubation distance" for the formation of cells.

$$Z = \frac{D}{k_0 R} \ln\left[1 - \frac{GD}{C_0 R m (1 - k_0)/k_0}\right]$$

: typical experimental case ~ order of one millimeter

* Rutter : Suggesting a method to find the purity of a metal as a critical condition of cell formation ① Assumption: single solute with $k_{0\ (\text{equil. Distribution coefficient})}$/ Using directly measured G and R values → C_0 composition calculation

$$C_0 = \frac{k_0}{1 - k_0} \cdot \frac{D}{m} \cdot \frac{G}{R}$$

: for experimentally convenient values of G and R, C_0 can be determined when it is btw $6\text{x}10^{-4}$ ~ $2\text{x}10^{-1}$ wt.%.

② If there is more than one solute→still possible to obtain information about purity; but the information is restricted to an assessment of the combined effect of solutes.

Assumption : solution ~ so dilute = no interaction between solutes

$$\frac{G}{R} = \Sigma\{C_0{}^1 \cdot [(1 - k_0{}^1)/k_0{}^1] \cdot (m^1/D)\}$$

3) Geometry of cells

① Cell size

* Experimental data: R (interface velocity: growth rate) ↓→ cell size↑

but apparently <u>independent of the temperature gradient</u>

→ Approximate calculations are possible, but not in good agreement with the experimental results.

② Growth direction: more complicated

* Lineage structure (page 60) → directly related to the direction of growth of the cellular structure

a) These studies, mainly on tin and on lead,

→ Direction of Cell growth ~ <u>deviates toward the nearest "dendrite direction"</u>, if this does not coincide with the normal to the interface.

→ Degree of deviation from the growth direction ∝ speed/ impurity content/ the inclination of the dendrite direction to the growth direction

→ Deviation ~ minimum at low speed/ less than half of the deviation of the dendrite direction/ increases with increase of impurity content

3) Geometry of cells

② Growth direction: more complicated

$R \downarrow \rightarrow \psi \downarrow / \psi_{max} < 1/2\ \Phi$

Impurity content $\uparrow \rightarrow \psi \uparrow$

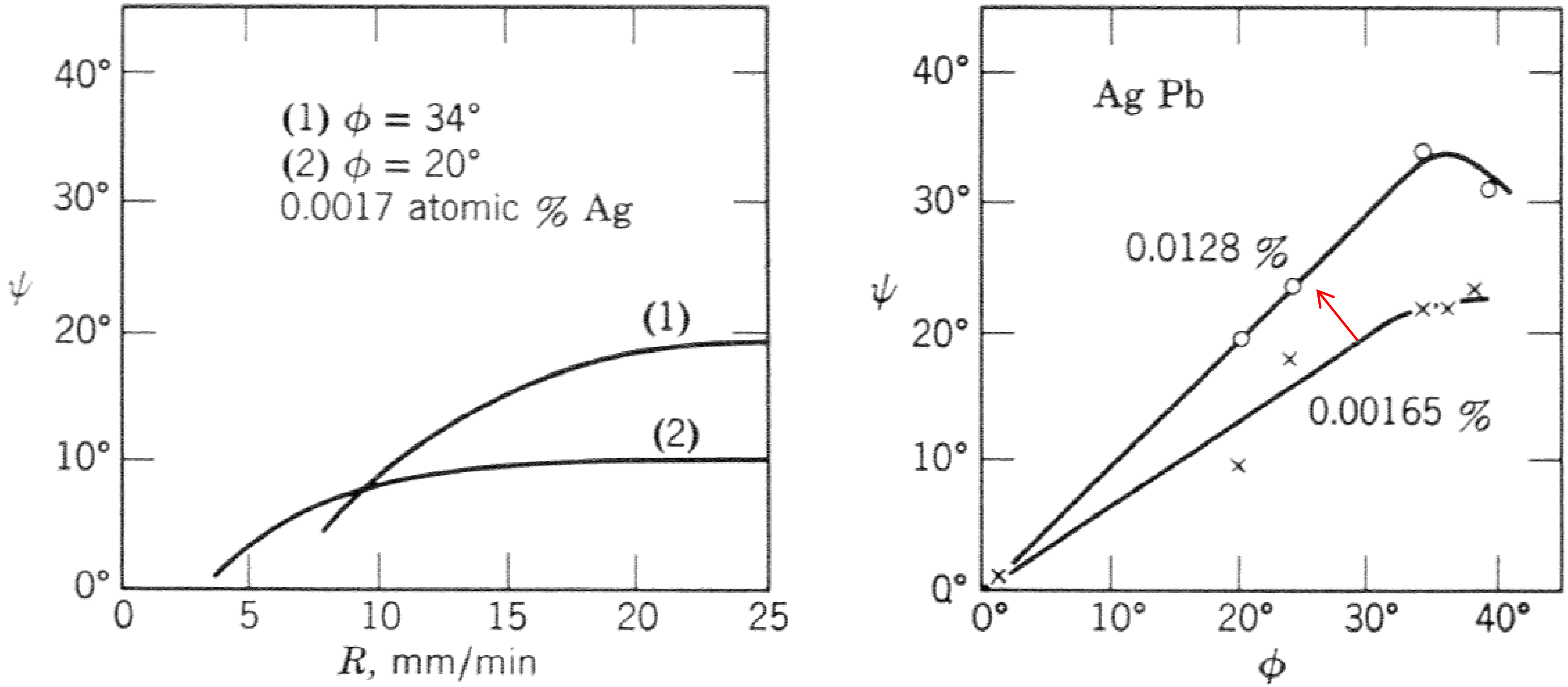


Fig. 5.34. deviation of cellular direction ψ as a function of R (Interface velocity) , dendrite orientation Φ, and solute content.

3) Geometry of cells ③ Shape of cell surface

* Experimental evidence for cell shape is somewhat different from theoretical predictions.

a) Surface with a stepped or terraced structure

b) Surface with terrace structure ~ within 10° of {100} plane or 20° of a {111} plane

c) This observation can be interpreted as evidence that the cell tip grows into a terrace structure while the interface grows → a reference to infer the cell growth direction.

d) Chadwick, however, showed that the terrace structure observed by other mechanisms could be formed after solidification.

a) In conclusion, there is no evidence that the terrace forms on the cell surface during growth.

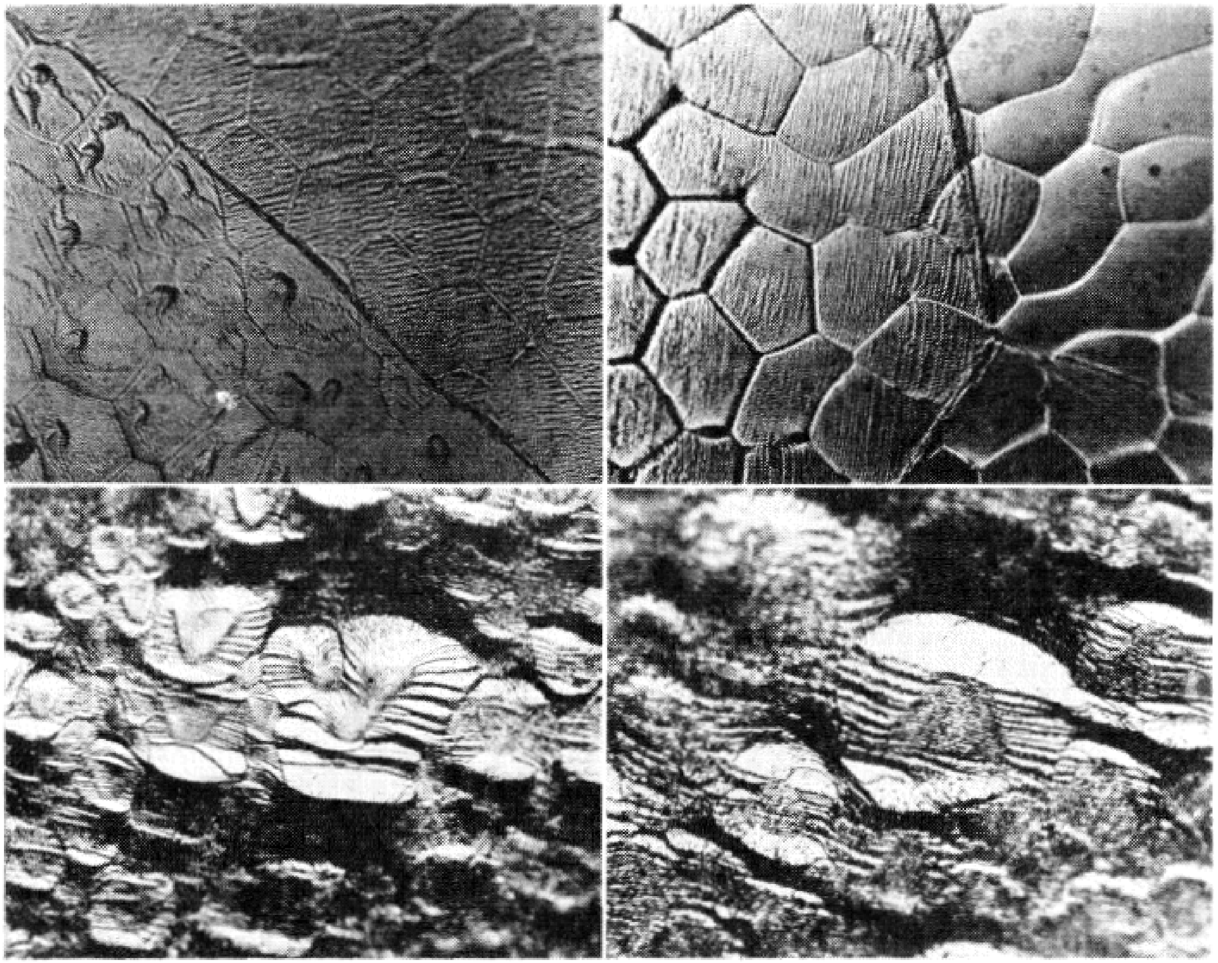


Fig. 5.35. appearance of decanted cellular interface.

3) Geometry of cells

③ Shape of cell surface

*** Experimental observations are somewhat different from those predicted for the overall shape of the cell.**

a) The cell wall is flat and somewhat thick.

b) The walls extending relatively far back into the crystal. → Pores often occur in cell wall.

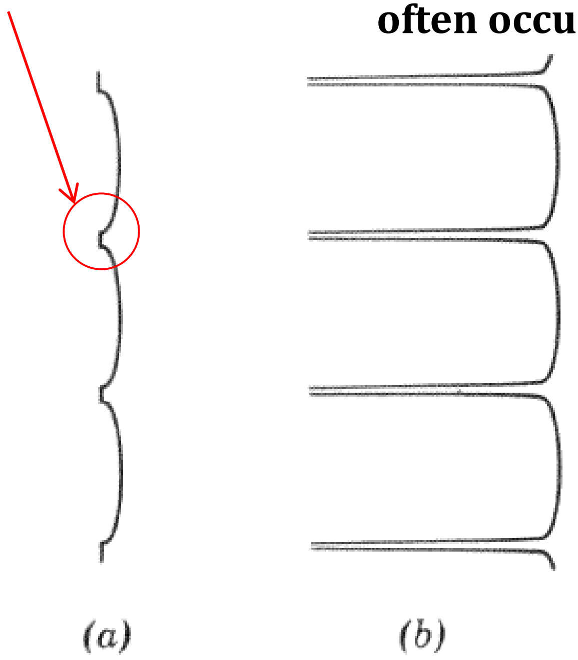


Fig. 5.36. Cross sectional shape of cells. (*a*) As observed after decanting; (*b*) presumed shape during growth.

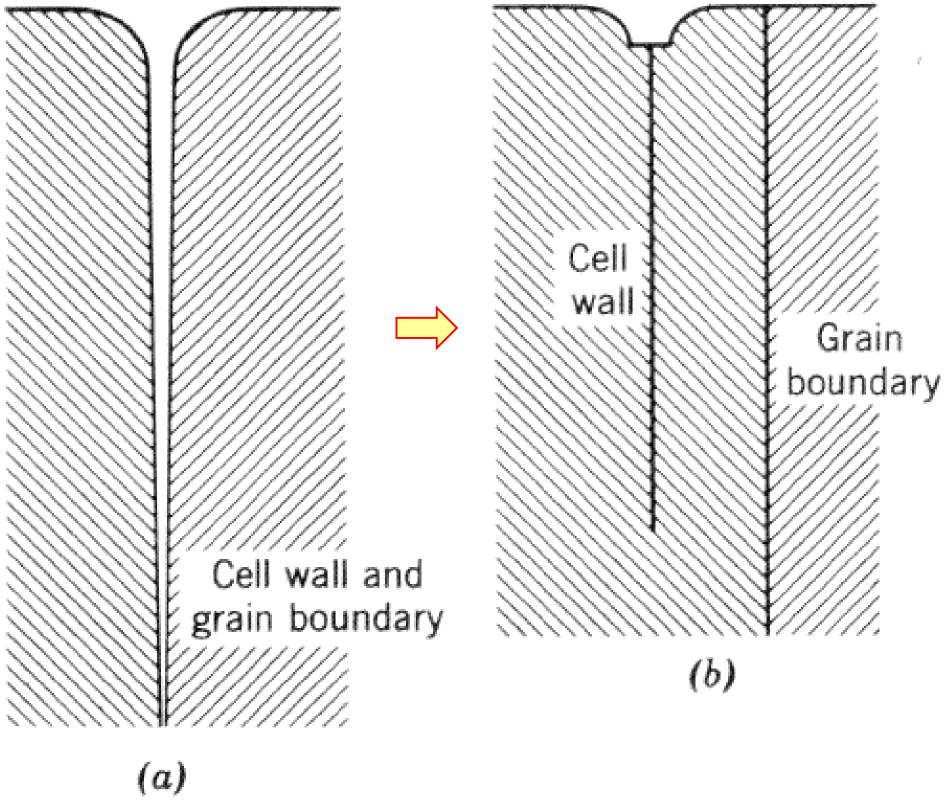


Fig. 5.37. Relative positions of grain boundary and cell wall. (*a*) During growth; (*b*) after decanting.

5.7 Cellular Dendrites

* **During cell structure formation, the liquid is still in a positive temp. gradient (= superheated condition) and the constitutional supercooling region is very limited.**
→ However, if the liquid temp. decreases (T ↓), the supercooled zone will increase.

→ Cell structure → some of characteristics of dendrite=cellular dendrites

* **In this condition, the cell tip has a square pyramidal shape instead of a flat curved "dome". The cells form a square array instead of a conventional hexagonal array and grow in the direction of growth of a specific dendrite.**

* **Develop arms, i.e. dendrites form & change in the direction of the primary arms away from the direction of heat flow into the crystallographically preferred directions**
i.e. (100) for cubic metals.

→ "Cellular dendrite"

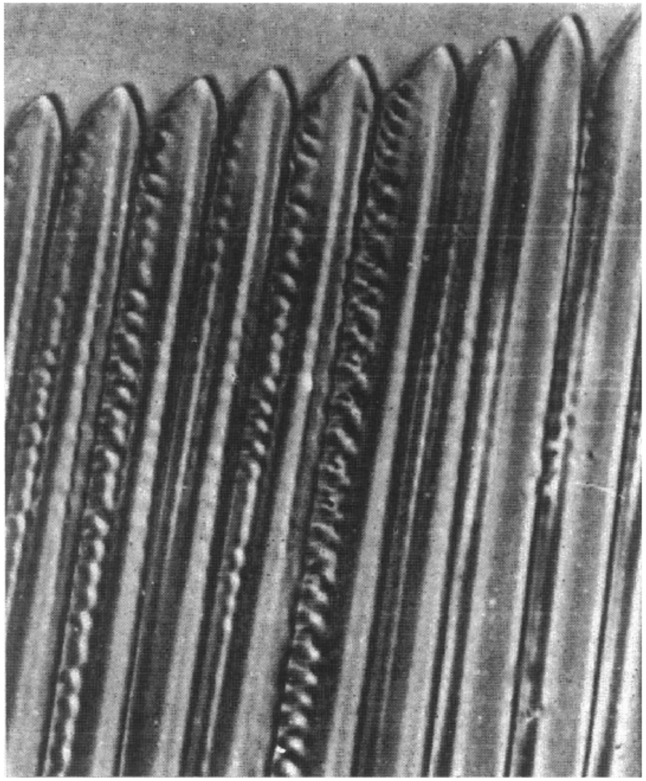
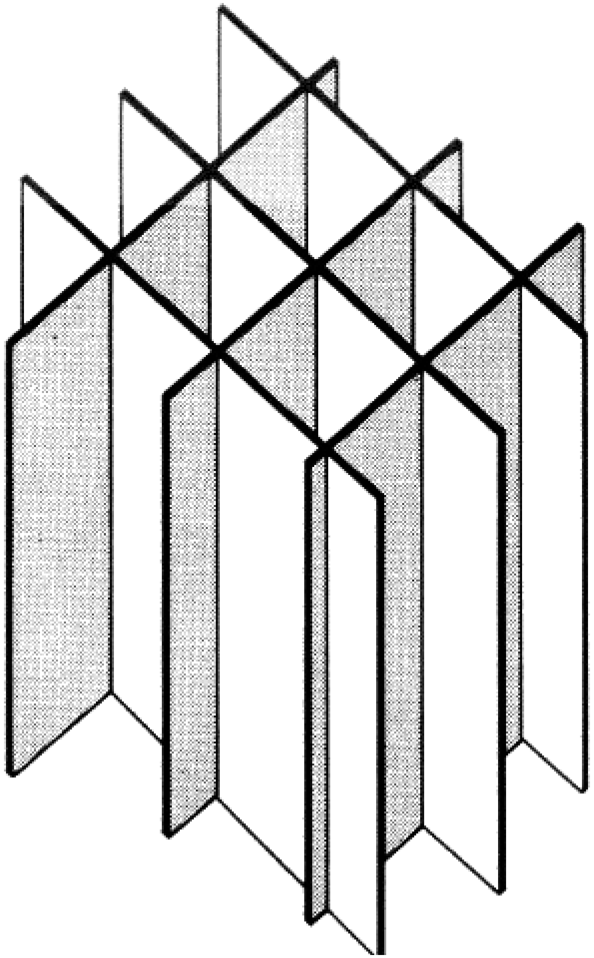


Fig. 4.27 Cellular dendrites in carbon tetrabromide.

(After L.R. Morris and W.C. Winegard, Journal of Crystal Growth 6 (1969) 61.)

5.7 Cellular Dendrites

: This structure is distinguished from "cellular structure" and "free dendritic growth".



Branches were formed in {100} planes perpendicular to main growth direction.

Each dendrite grows independent of its neighboring branches.

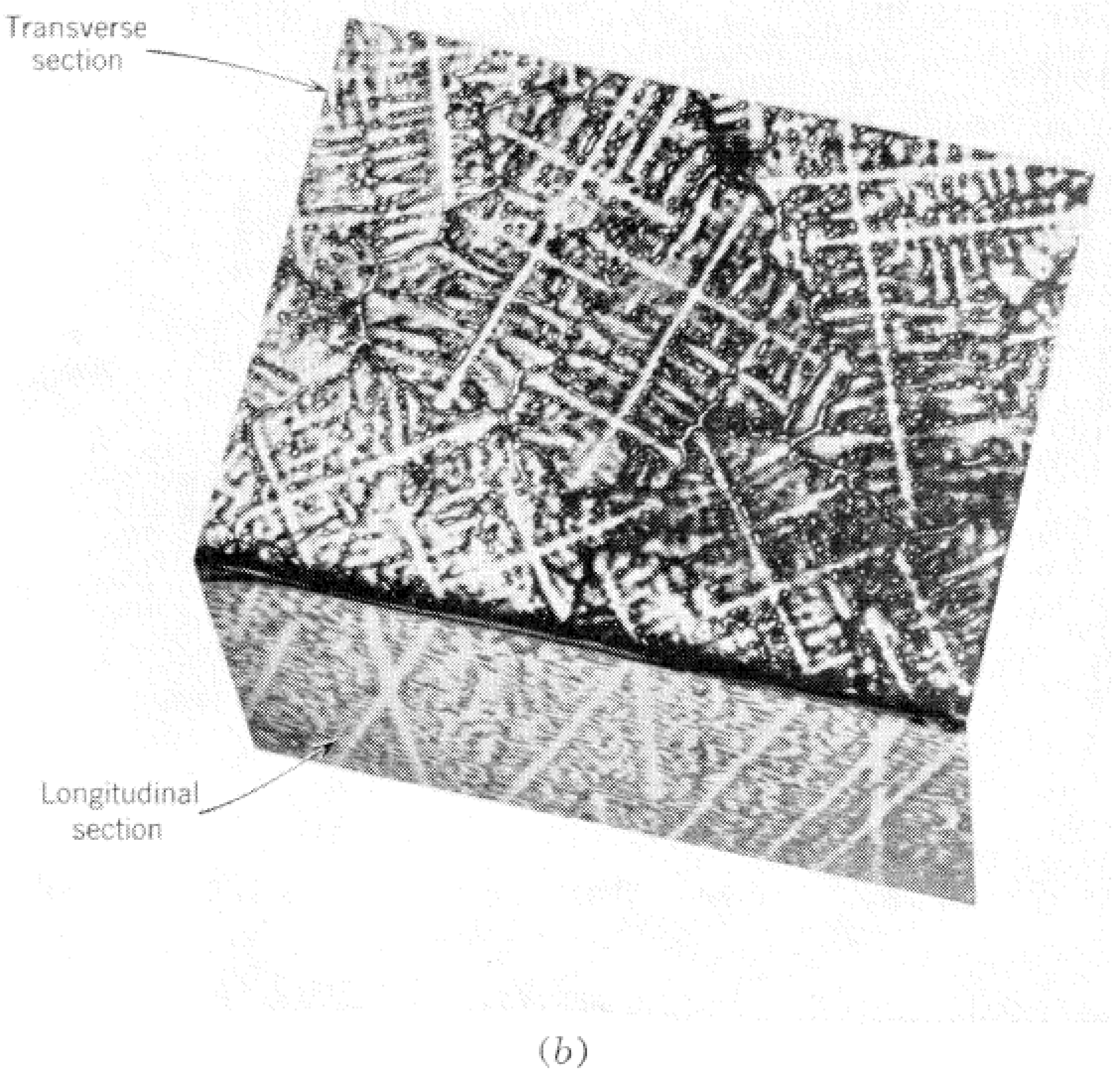


Fig. 5.38. Cellular-dendritic structure.

5.7 Cellular Dendrites

* Cellular dendritic growth occurs when the liquid temperature gradient is positive but small. Thus, the latent heat is still released into the solid while the rejected solute diffuses into the liquid.

1) When the temperature gradient is sufficiently small, the crystallographic factors can control the shape and growth direction, as in the case of dendrites in a pure metal.

2) The alignment of the dendrites to form a square array in this kind of dendritic growth may arise from the fact that if the braches join to form webs, they provide a better conducting path for heat flow from the liquid to the crystal than would exist if the branches were separate. → For example, a web in (010) plane between two (100) dendrites is a stable growth form.

3) Most studies on the conditions for dendritic solidification in alloys are related to the "Cellular dendrite" mentioned here.

5.7 Cellular Dendrites

*** How to determine if Growth will form Cellular or Cellular dendrite structures**

(Morris, Tiller, Rutter= “experimental identification”)

→ **liquid comp. (C_0/k_0), Temp. gradient (G), Growth rate (R) factors are important.**

$\boxed{G/R < (T_1-T_3)/D}$ Constitutional supercooling

Cellular growth → Cellular dendritic solidification

G/R $\underline{G/R^{1/2}} \sim C_0/k_0$ $\therefore G/R^{1/2} \leqq AC_0/k_0$

(Interface solute concentration) A: Changes depending on system/ The first sign that changes to cellular dendritic solidification

Cellular growth → Cellular dendritic type growth: “$G/R^{1/2} \sim C_0/k_0$”

Cell size, Z (Determined by diffusion distance) ~ $R^{-1/2}$ ∴ $Z= a/R^{1/2}$

Thickness of supercooled layer, t

$$1 - \exp\left(-\frac{R}{D}t\right) = \frac{G}{mC_0(1-k_0)k_0}\mathbf{t}$$

substituting $a/R^{1/2}$ for t

$$1 - \exp\left(-\frac{Ra}{DR^{1/2}}\right) = \frac{aG}{R^{1/2}} \cdot \frac{1}{mC_0(1-k_0)/k_0}$$

$$1 - \exp\left(-\frac{R^{1/2}a}{D}\right) = \frac{aG}{R^{1/2}} \cdot \frac{1}{mC_0(1-k_0)/k_0}$$

If exp ($-R^{1/2}a/D$) is less than 1,

Z=t. ($\because G/R^{1/2} \sim C_0/k_0$)

5.7 Cellular Dendrites

1) Cellular-dendritic growth differs from cellular growth:

Because the depth of supercooled zone is greater, the cells become more pointed, with the result that the factors that determine the direction of growth of dendrites are able to exercise control ; that is growth is relatively slow in four {111} directions, accounting for both

"pyramidal morphology and growth direction."

2) The growth rate of the dendrite tip of Cellular-dendrite structure is controlled by the rate of heat extraction through the solid and by the rate of advance of the appropriate isotherm into the liquid.→ ∴ The shape of freezing front, is controlled by the shape of the isothermal surface, which depends on the geometry and thermal characteristics of the system.

→ When supercooling increases at the interface, the transition from the cellular dendrite structure to the free dendrite structure occurs naturally.

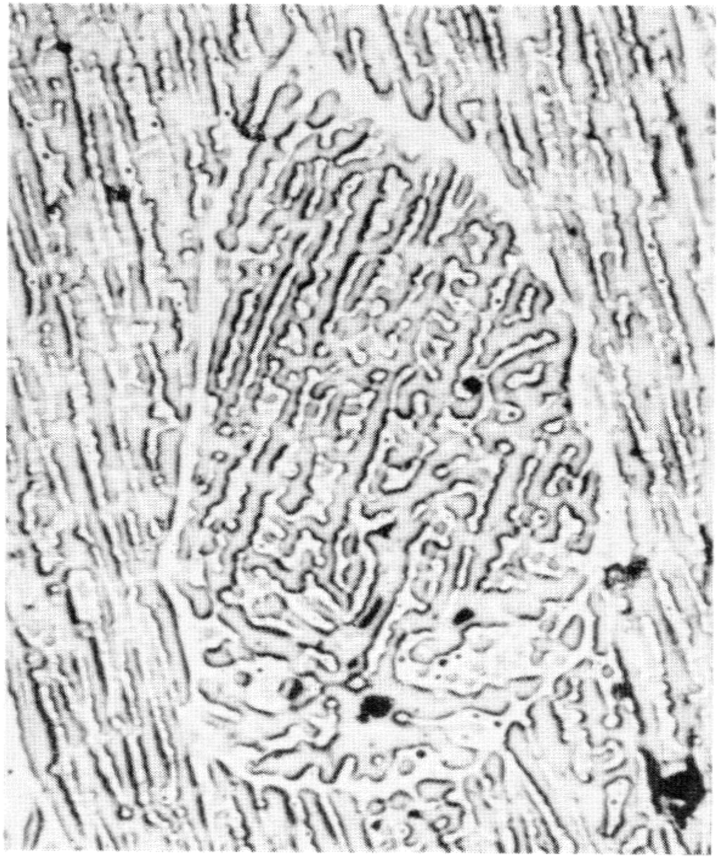


Fig. 5.39. Crystal showing free dendrites and Cellular dendritic substructure.

5.8. Free Dendritic Growth in Alloys

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

Thin zone formation by C.S. at the sol. Interface

T↓ → Increase of C.S. zone

formed by releasing the latent heat from the growing crystal toward the supercooled melt

1) In free dendritic growth, the rate of advance of the growing points is determined only by the "temperature" and "composition“, and the shape of a crystal growing in this way is similarly determined by the local conditions of growth and not by any externally imposed temperature gradient.

→ this type of growth is conducive to the formation of “branched rod” type dendrites, with a morphology similar to that of pure metals, while an imposed temp. gradient tends to produce the plate type of structure described as cellular dendritic.

→ The reason for this difference may be that, while the branches of the free type of dendrite do not grow after they have “used up” the local supercooling, those of the cellular type do so, because of the continuous extraction of heat; the consequent thickening of the branches may lead to their coalescence as plates.

2) Free dendritic growth in alloys takes place in a manner very similar to that already described for pure metals. However, the rejection of solute presents an additional complication, which results in slower growth than would be found for the pure metal.

5.8. Free Dendritic Growth in Alloys

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

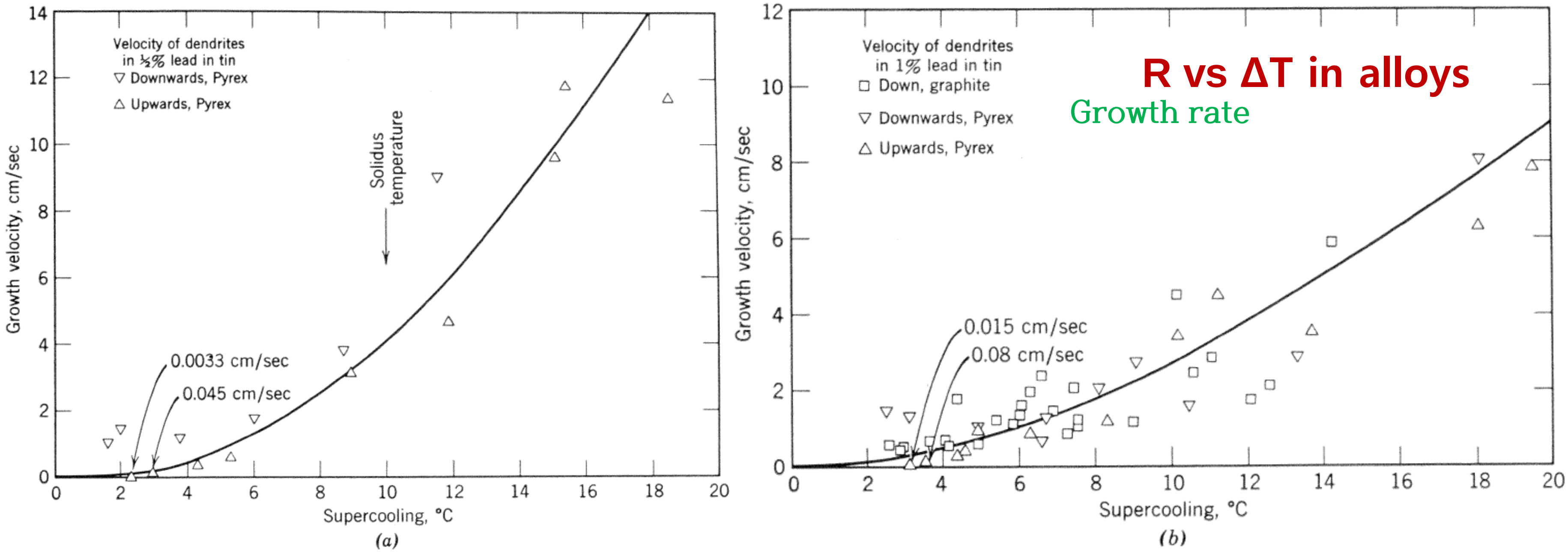
Thin zone formation by C.S. at the sol. Interface

T↓ → Increase of C.S. zone

formed by releasing the latent heat from the growing crystal toward the supercooled melt

3) **Liquid in contact with interface at the tip of growing dendrite has a greater solute content than that of ambient liquid → local T_e ↓→ Effective supercooling ↓**

: **However, the solute diffusion equation that would give the equilibrium temperature itself depends on the rate of growth and the radius of the tip; the problem of predicting the growth rate in a superdooled alloy has not yet ben solved.**



R vs ΔT in alloys

Growth rate

Fig. 5.40. Rate of growth of free dendrites of Pb-Sn in supercooled liquid (a) Tin with ½ percent lead, (b) tin with 1 percent lead.

4) Spacing of dendrite arms

: The dendritic arm spacing in the alloy is well matched with the cooling rate (expressed in deg/sec) rather than the rate of motion of the isotherms (expressed in cm/sec)

Spacing

$$S = A\exp(B\ln R + CM)$$

R: cooling rate
M: Molar fraction of Cu
A, B, C ~ constant

① R (cooling rate) ↑→ S ↓

(∵ Solute's diffusion time is small)

② as the eutectic composition is approached → S ↓

(∵ With increasing rejected solute amount the composition moves further away from pure metal)

⇨ **In conclusion, S is controlled by diffusion and not by heat transfer, and that the S is determined by the characteristic thickness of the diffusion zone around a growing dendrite.**

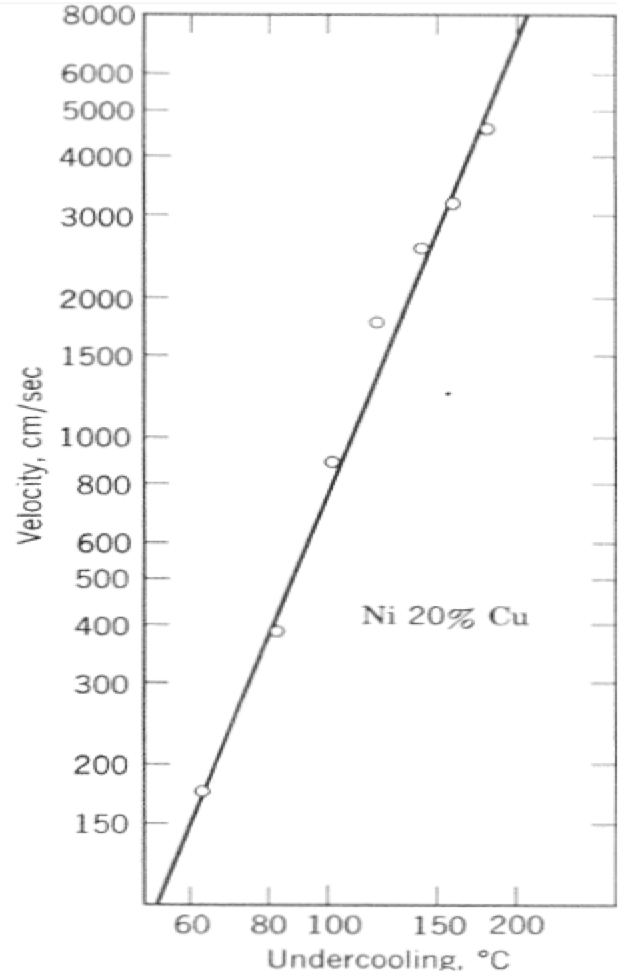


Fig. 5.40. Rate of growth of free dendrites in a supercooled melt of Ni-0.20% Cu

5.9. Nucleation of Crystals ahead of the Existing Interface

Constitutional supercooling

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

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

* **Constitutional supercooling zone is sufficient- Possibility of nucleation ↑ by presence of nucleant particles due to enriched boundary layer**

If the growth rate of the interface ↓ (= local Te ↓) & temperature gradient ↑,

Nucleation probability ↑ → formation possibility of "stray" crystal ↑

For example, the Al-Mg alloy is solidified at a R (rate) / G (temp. gradient).

→ Nucleation of new crystals occurs ahead of an advancing interface when the value of $G/R^{1/2}$ is less than a value that is roughly proportional to Mg content of the alloy.

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, inversegregation, 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

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

composition changes over distances 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 on the scale of the secondary dendrite arm spacing.

Fig. Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).

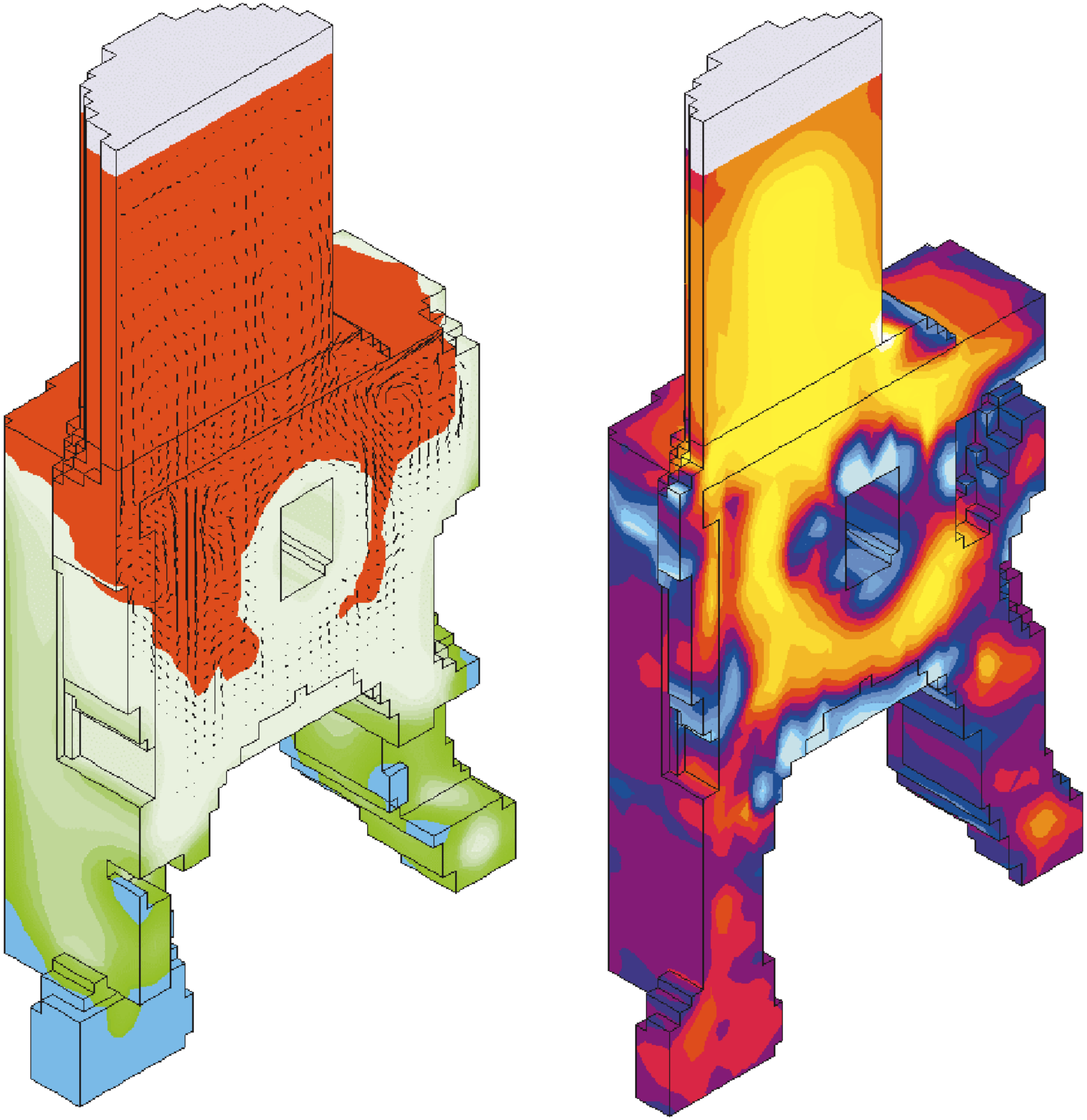


Fig.

Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a single freckle (right) (courtesy of A. F. Giamei, United Technologies Research Center).

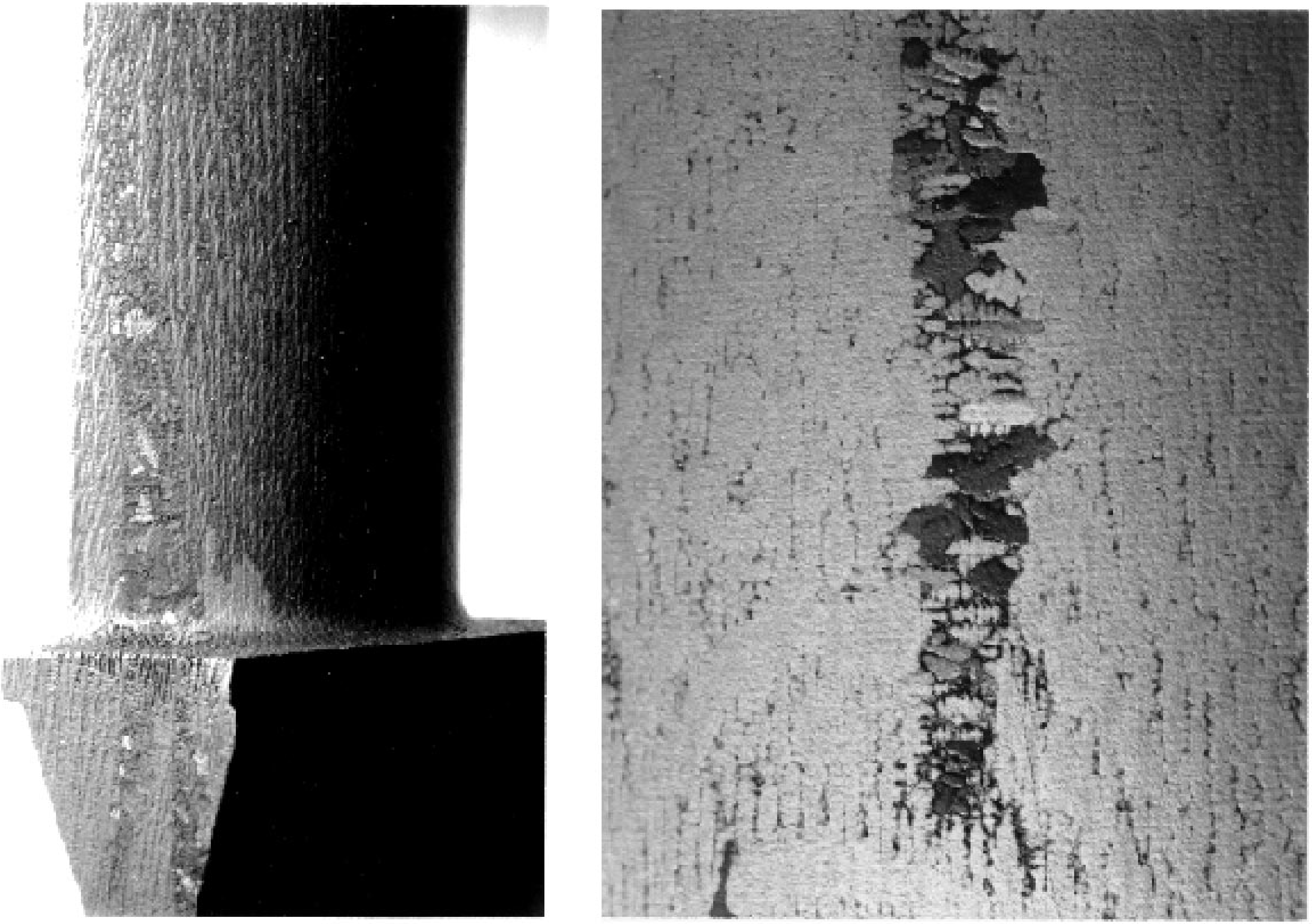
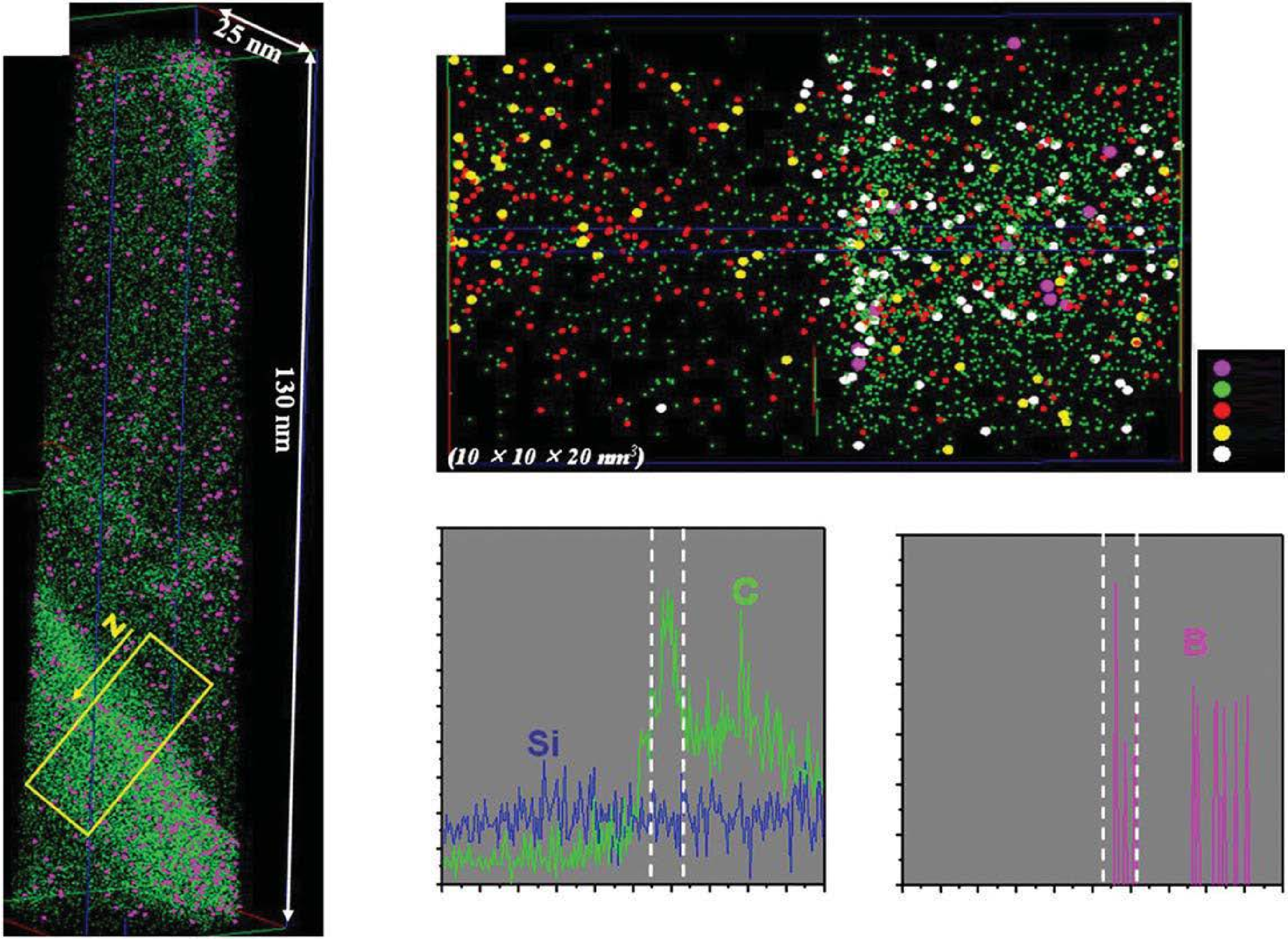


Fig.
Sulfur print showing centerline segregation in a continuously cast steel slab (courtesy of IPSCO Inc.).



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

Korean J. Microscopy Vol. 41, No. 2, 2011

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

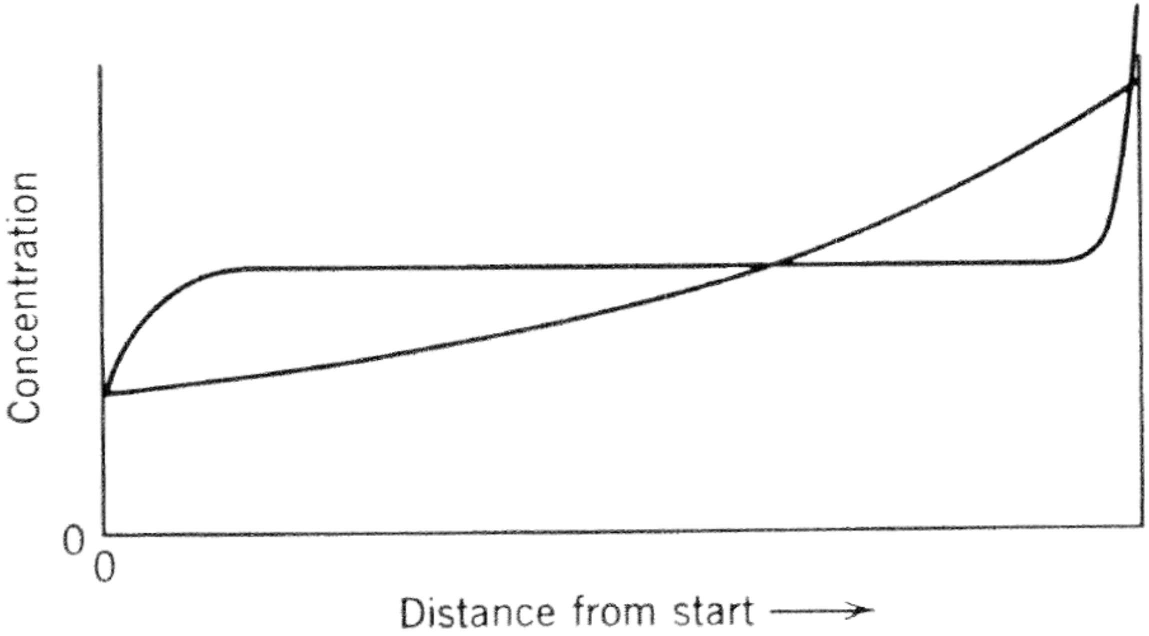


Fig. 5.42. Extreme cases of normal segregation

1) Normal segregation

: 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

- **Variation of Segregation pattern**

Solidification rate

Below 2 cm/hr ⟷	Above 20 cm/hr
Mixing dominant	Diffusion control

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

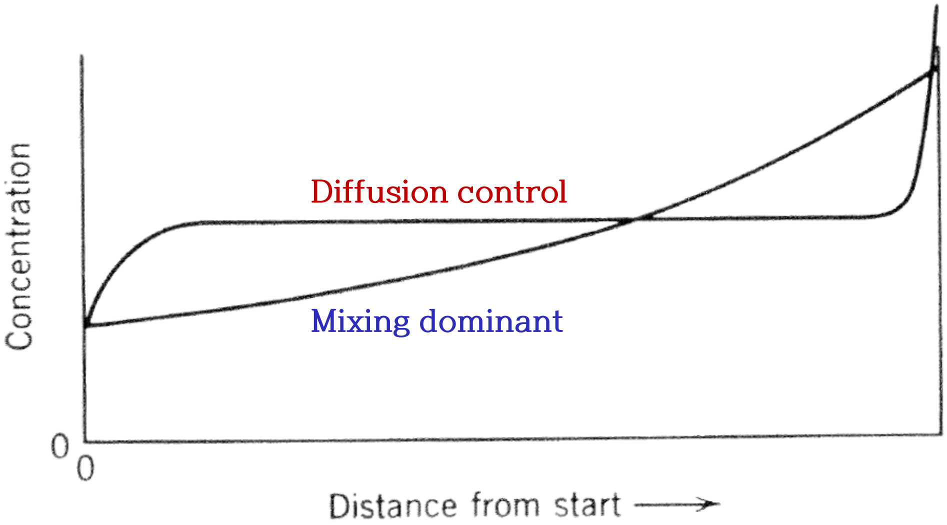
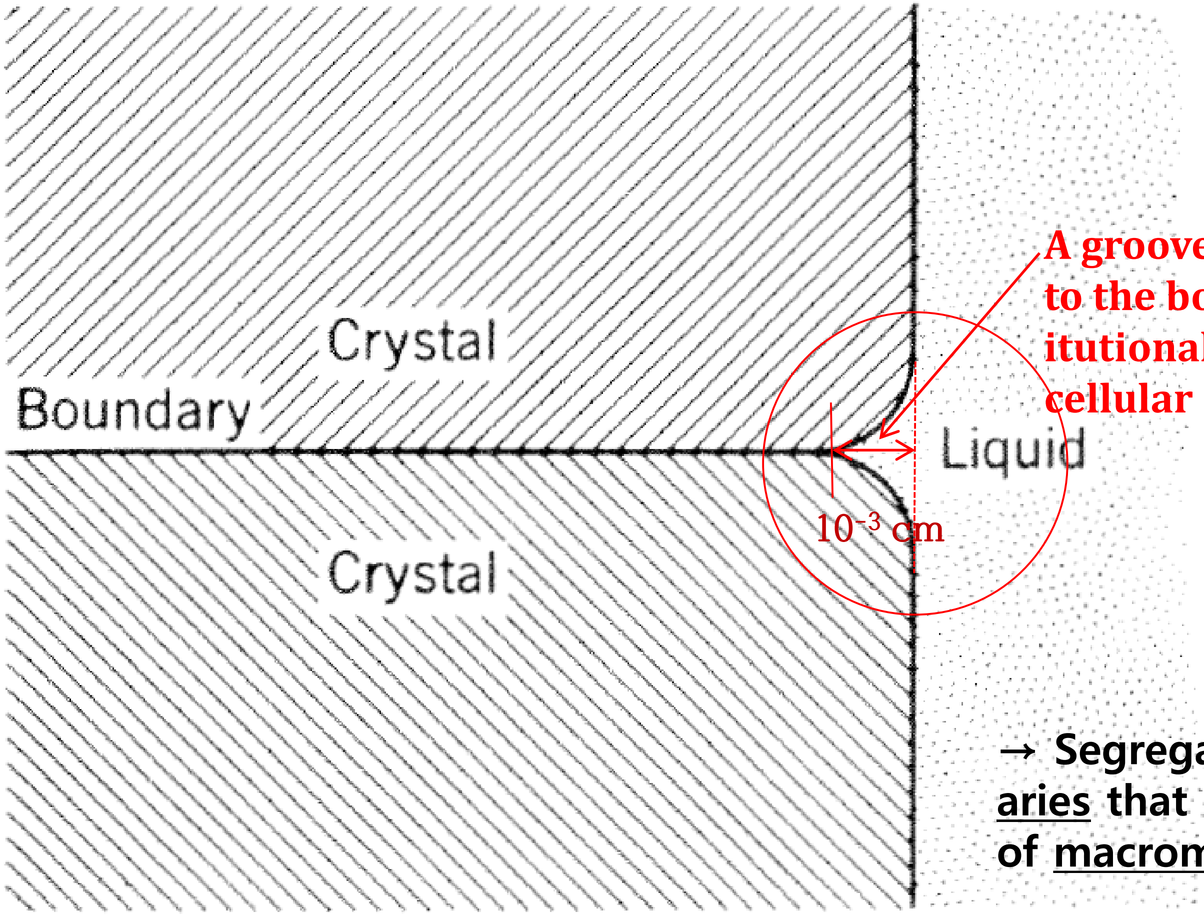


Fig. 5.42. Extreme cases of normal segregation

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**

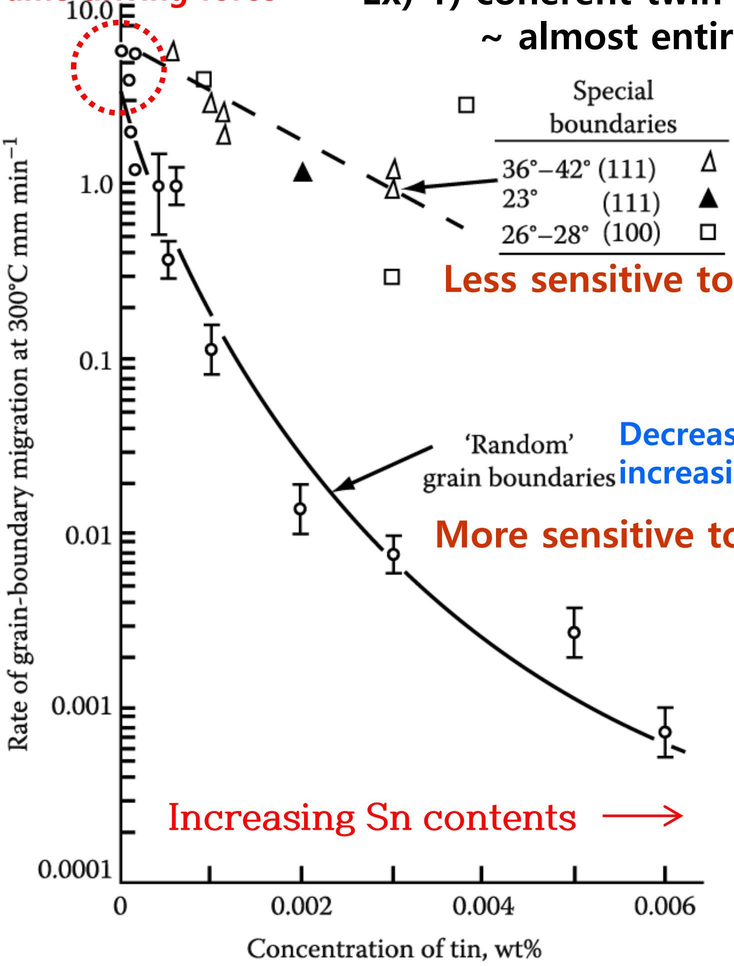
2) The other special boundaries are usually more mobile than random high-angle boundary. Why?

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**

Ex) 1) coherent twin boundary ~ almost entirely immobile

Same driving force



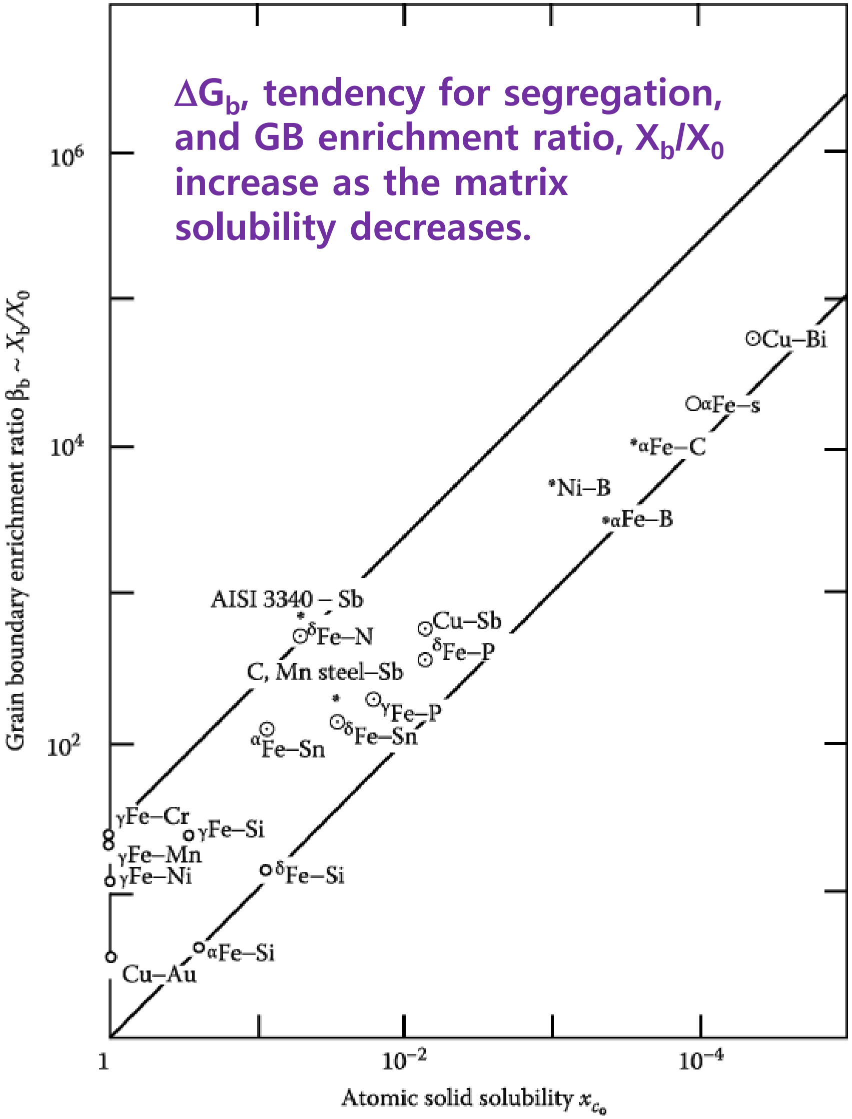
Less sensitive to impurities

Decreases rapidly with increasing alloy content

More sensitive to impurities

Increasing Sn contents →

Migration rate of special and random boundaries at 300 °C in zone-refined lead alloyed with tin under equal driving forces



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

<Increasing GB enrichment with decreasing solid solubility in a range of system>

* 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 segregation, 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.

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.

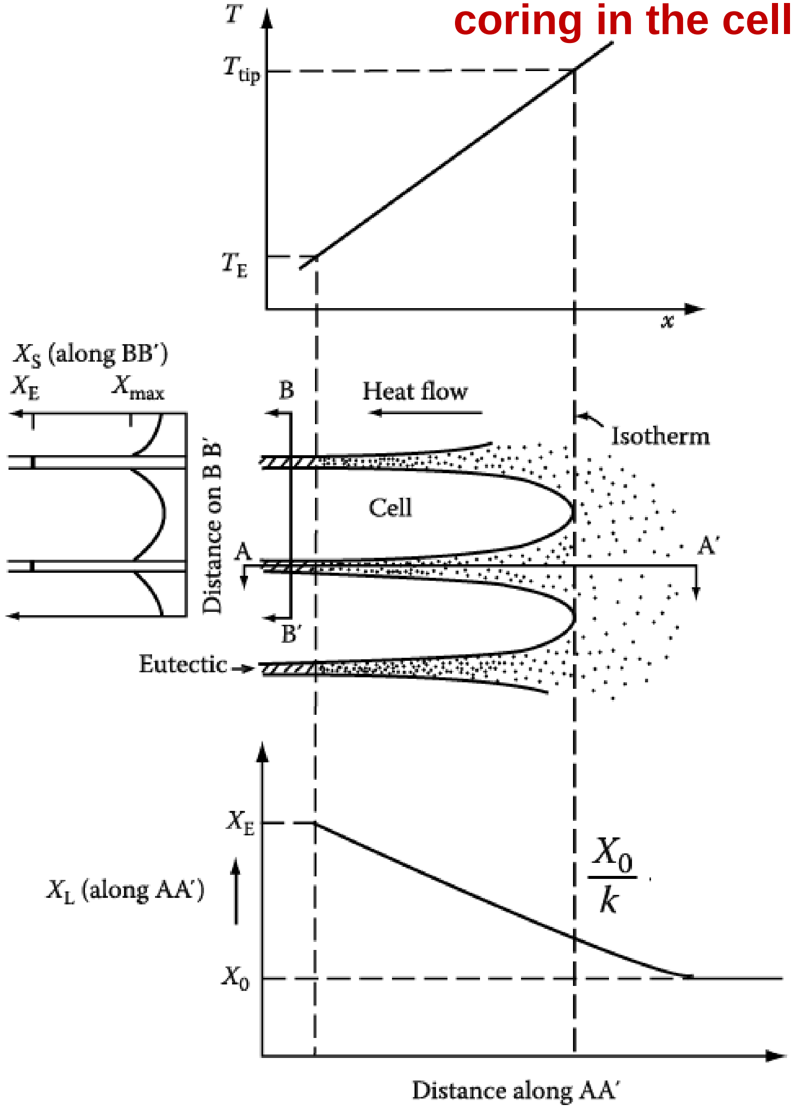
→ The high mobility of special boundaries can possibly be attributed to a low solute drag on account of the relatively more close-packed structure of the special boundaries.

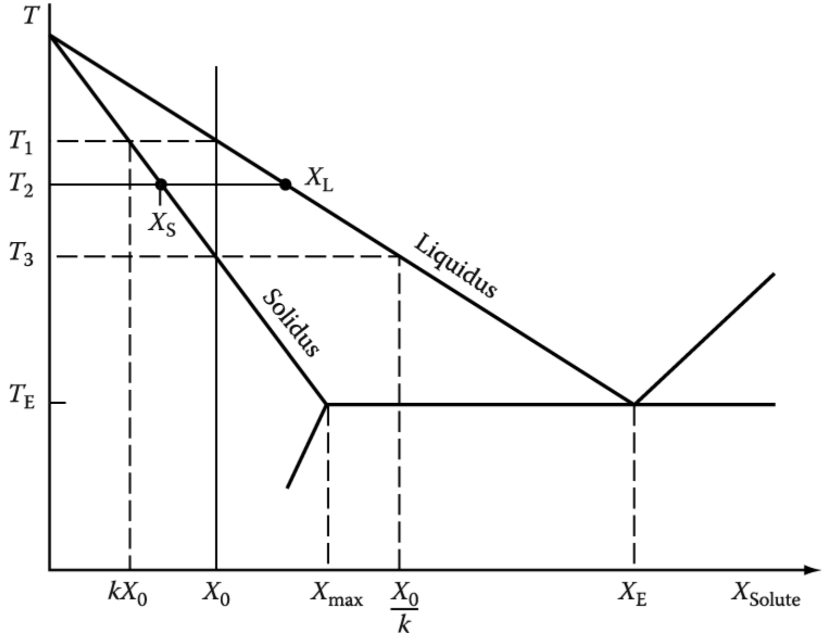
3) Cellular segregation

: 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 $X_0 << X_{max}$**
Solute file up → eutectic solidification
→ formation of 2nd phases at the cell wall

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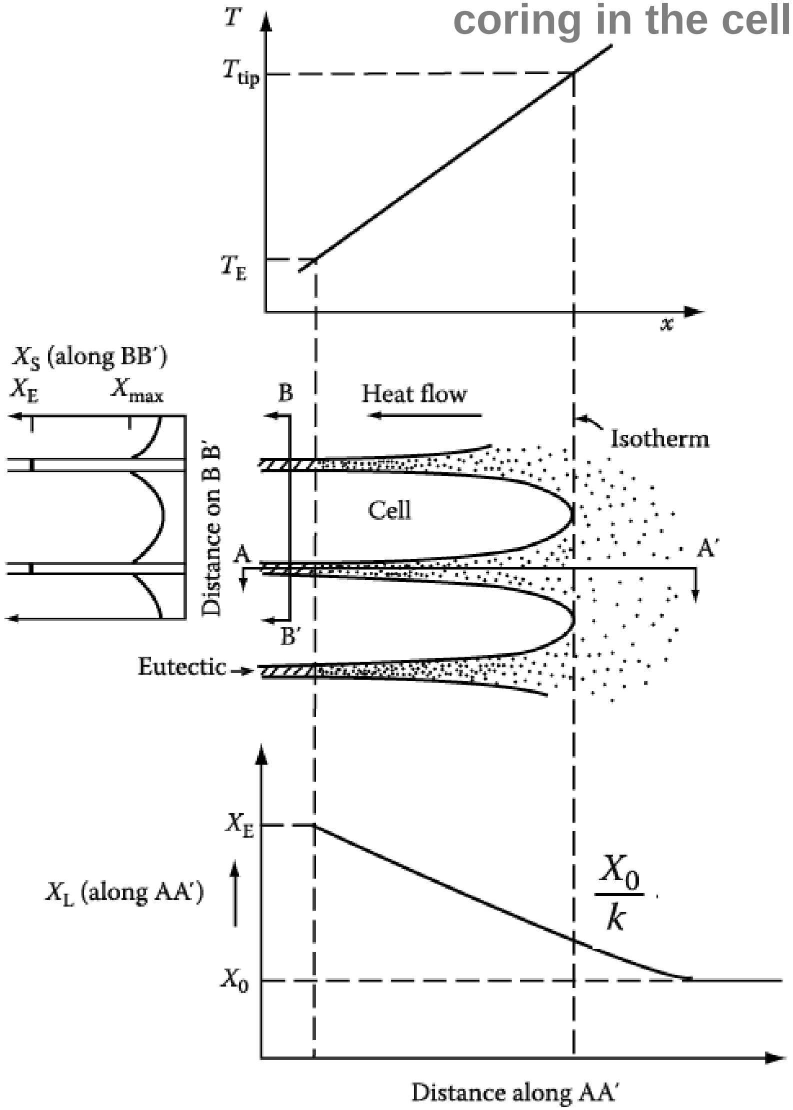

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- **Segregation deceases as a result of diffusion**

  ① during cooling down after solidification

  ② any subsequent annealing process

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