

2018 Fall

Advanced Solidification

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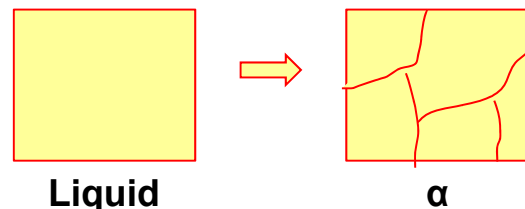
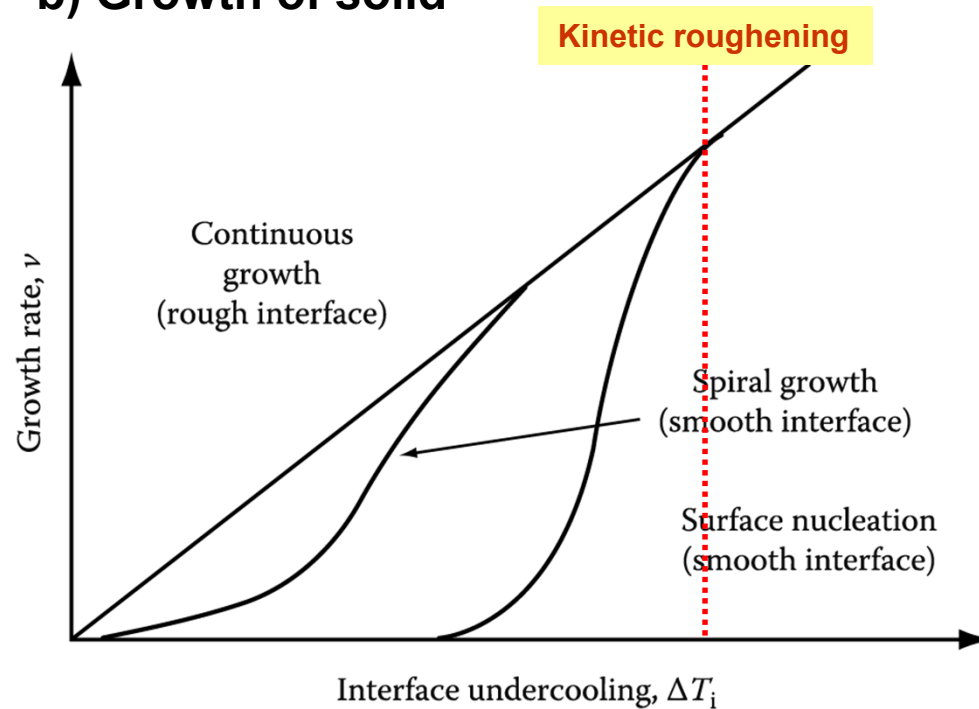
Office hours: by appointment

Solidification: Liquid \longrightarrow Solid

1) Pure Metals: Nucleation and Growth (thermally activated process)

a) homogeneous Nucleation or Heterogeneous Nucleation • Undercooling ΔT

b) Growth of solid



No compositional change during solidification

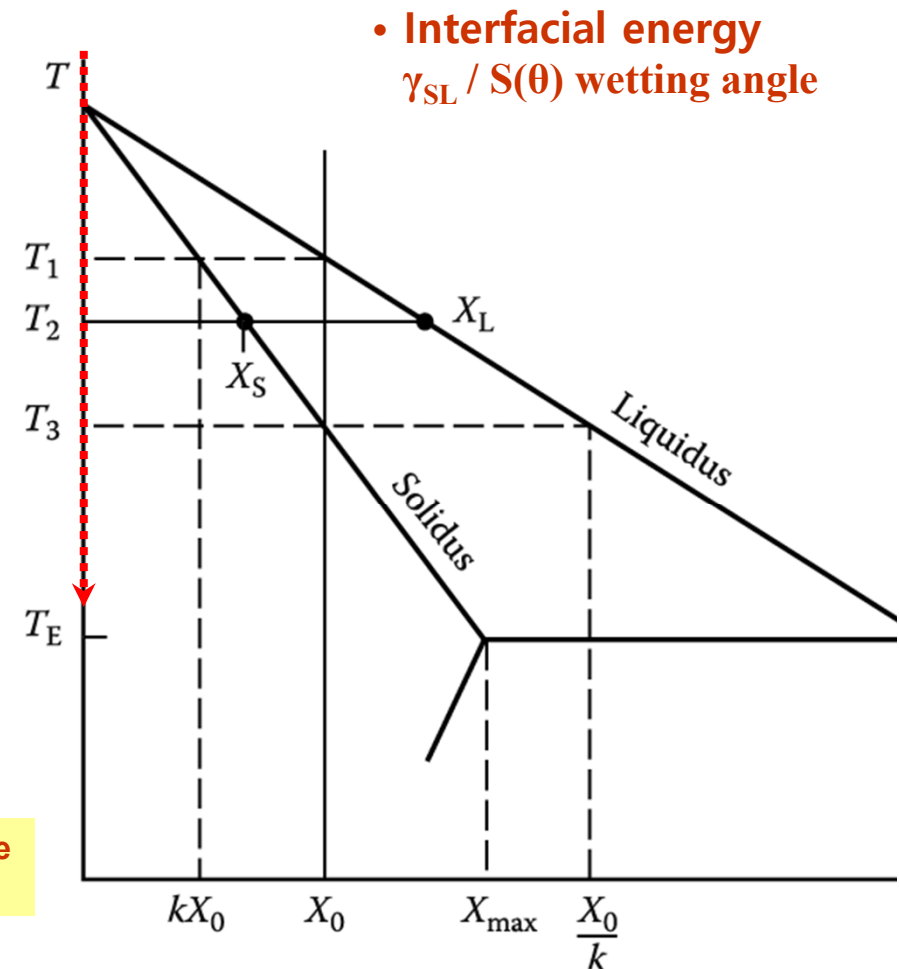


Fig. 4.19 A hypothetical phase diagram.

Chapter 5. Redistribution of solute during solidification

"Alloy solidification"

1. Solidification of single-phase alloys

- Three limiting cases

- 1) Equilibrium Solidification: perfect mixing in solid and liquid

- 2) No Diffusion on Solid, Diffusional Mixing in the Liquid

- 3) No Diffusion in Solid, Perfect Mixing in Liquid

- Planar S/L interface → unidirectional solidification

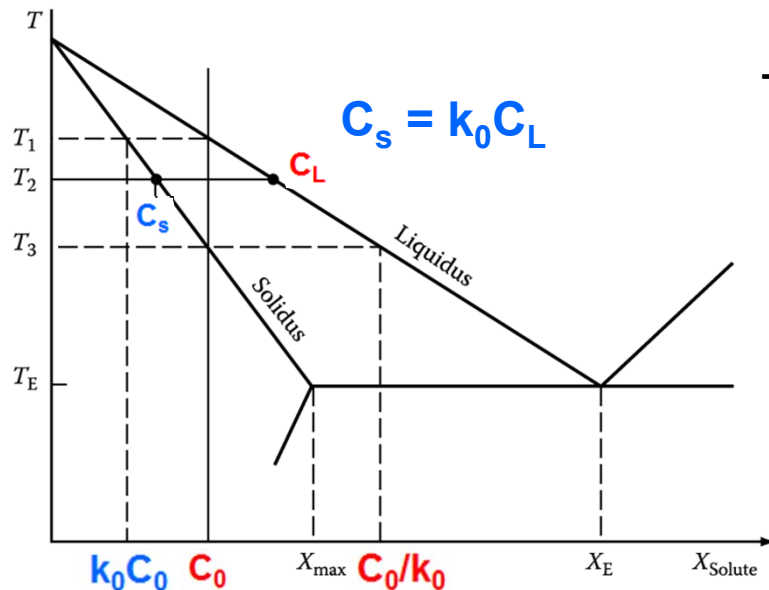


x → - Superheated liquid

- Cellular and Dendritic Solidification

- Constitutional Supercooling

1) Equilibrium Solidification : perfect mixing in solid and liquid

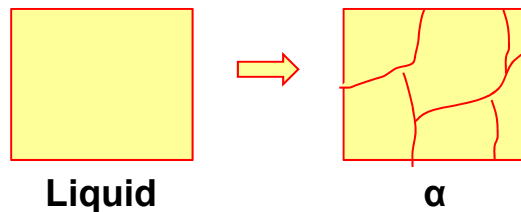


Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

$$k_0 C_0 \leq C_s \leq C_0$$

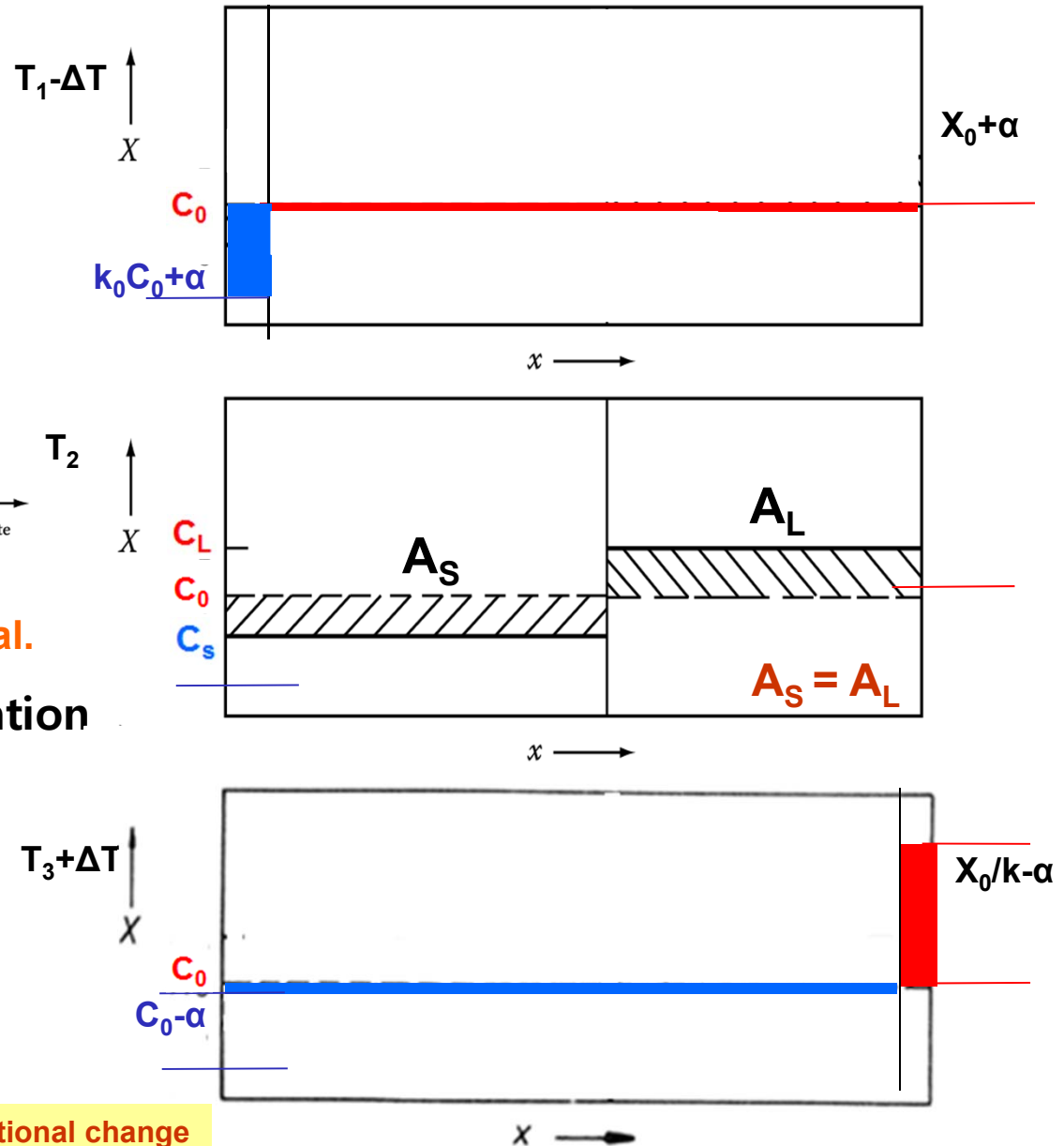
$$C_0 \leq C_L \leq C_0/k_0 < X_{\text{Eutectic}}$$



Liquid

α

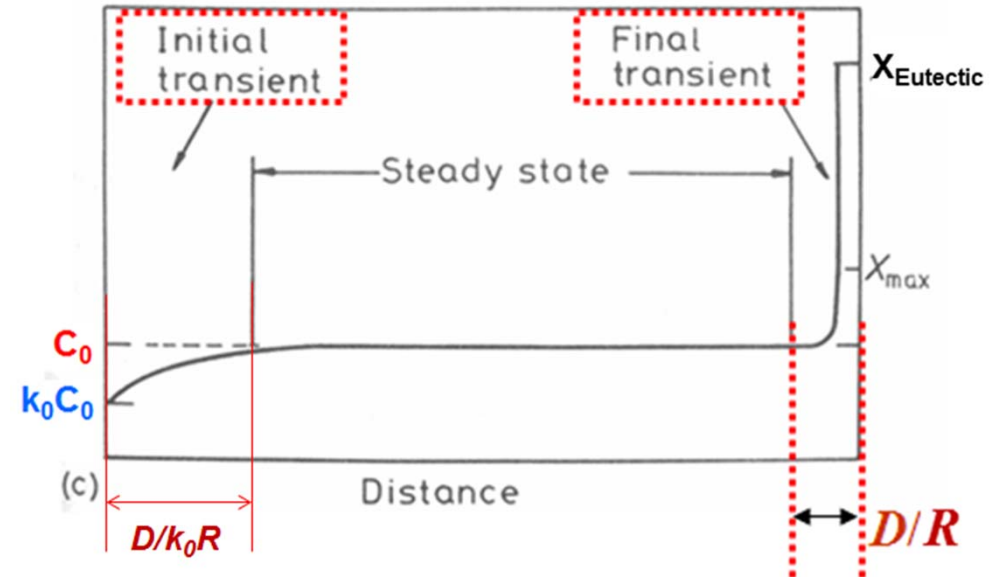
Compositional change during solidification



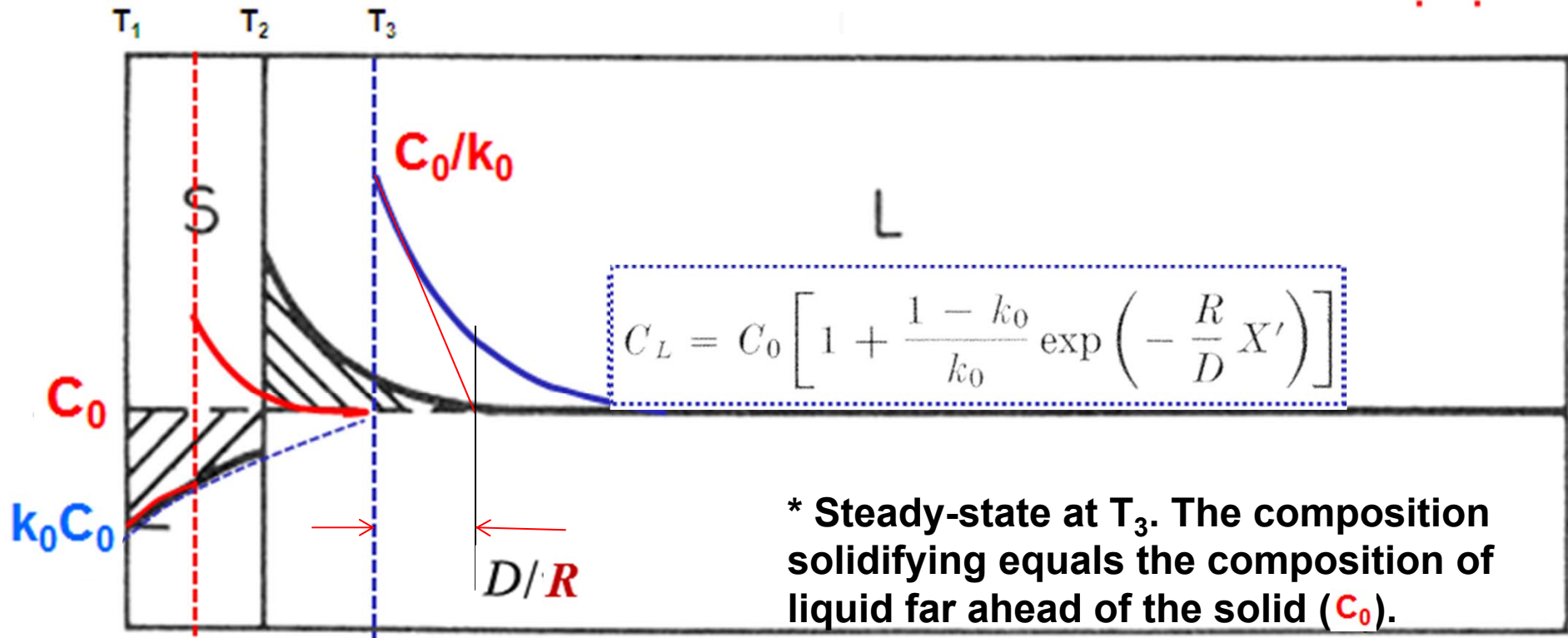
“Alloy solidification”

- Solidification of single-phase alloys

2) No Diffusion on Solid, Diffusional Mixing in the Liquid



Interface temperature

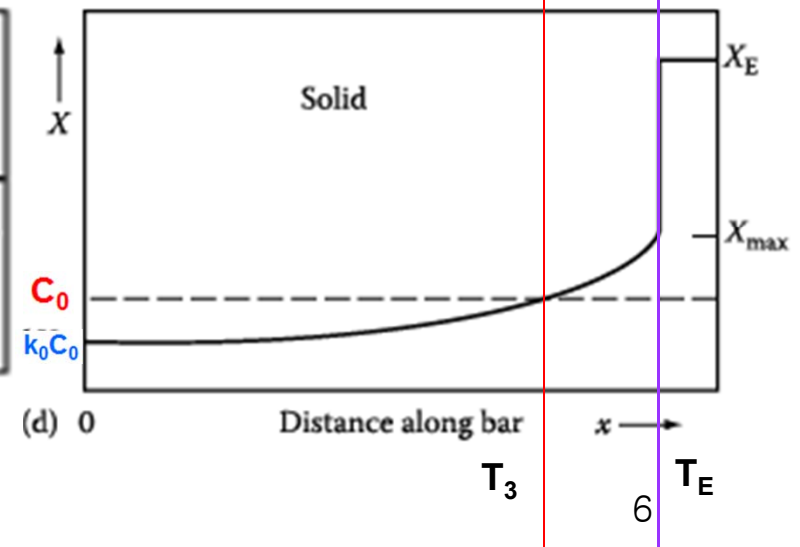
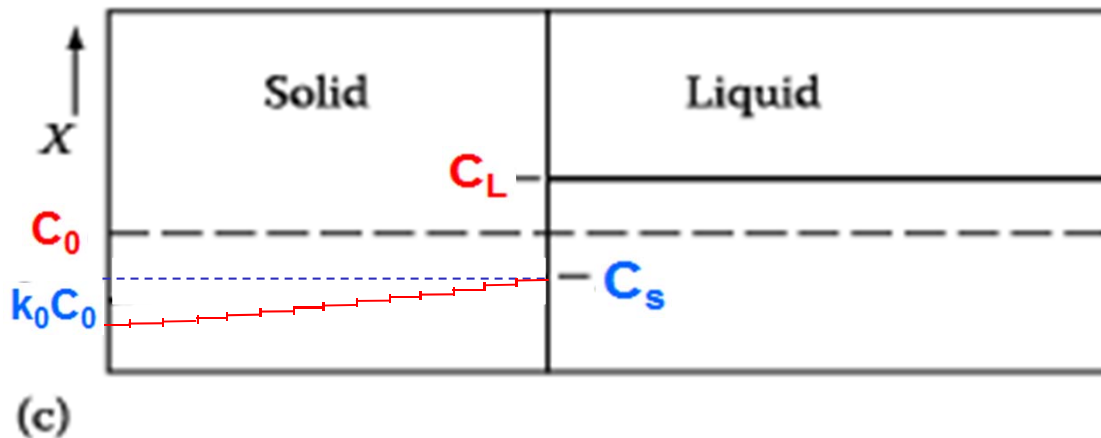
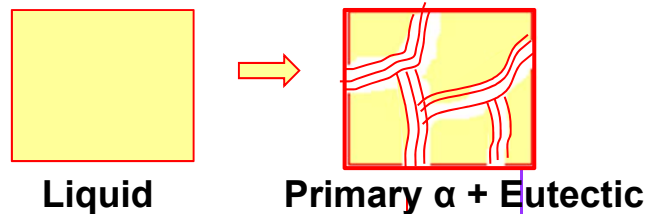
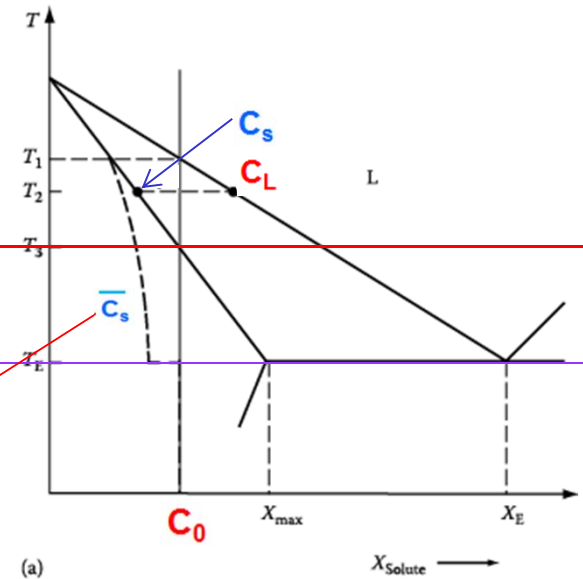
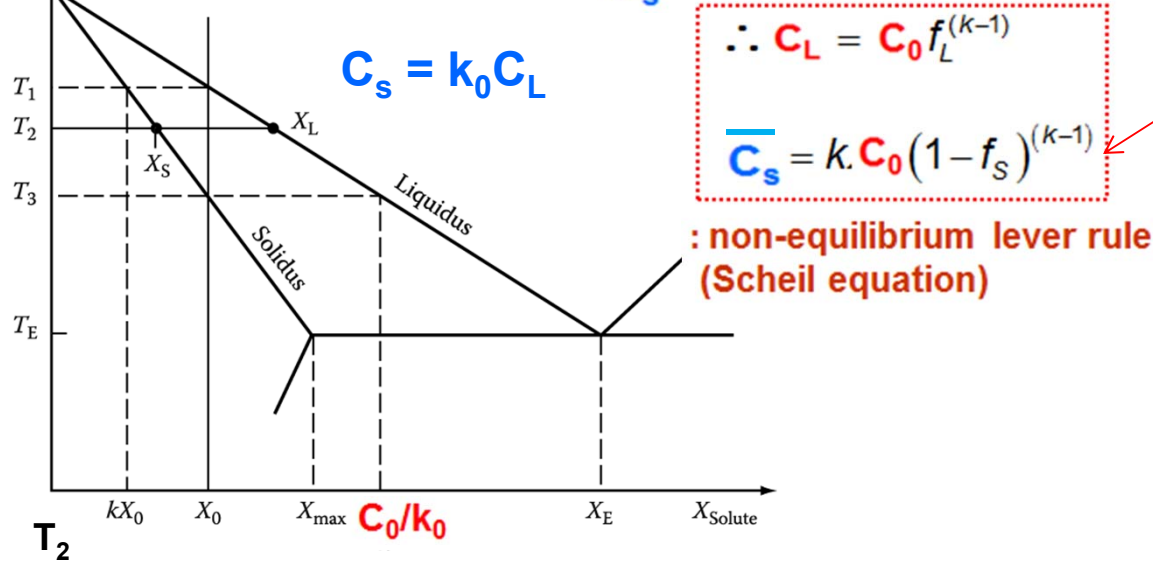


3) No Diffusion in Solid, Perfect Mixing in Liquid

: high cooling rate, efficient stirring

- Separate layers of solid retain their original compositions

- mean comp. of the solid (\bar{C}_s) < C_s



$\text{solid} \rightarrow \bar{X}_s < C_s$

$\text{liquid} > C_0/k_0 \rightarrow X_E$

Concentration profiles
in practice
: exhibit features
between two cases

➡ Zone Refining

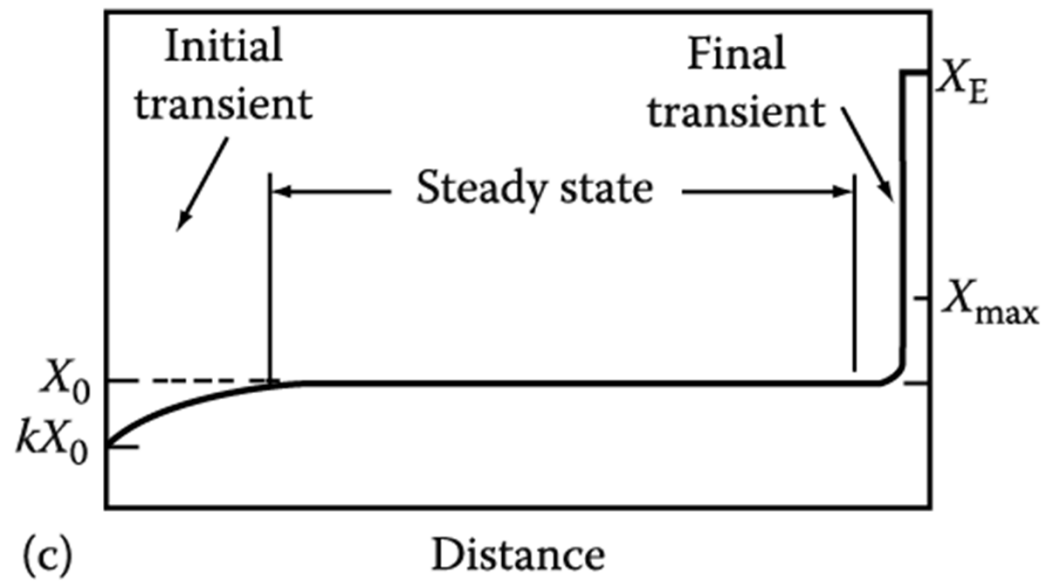
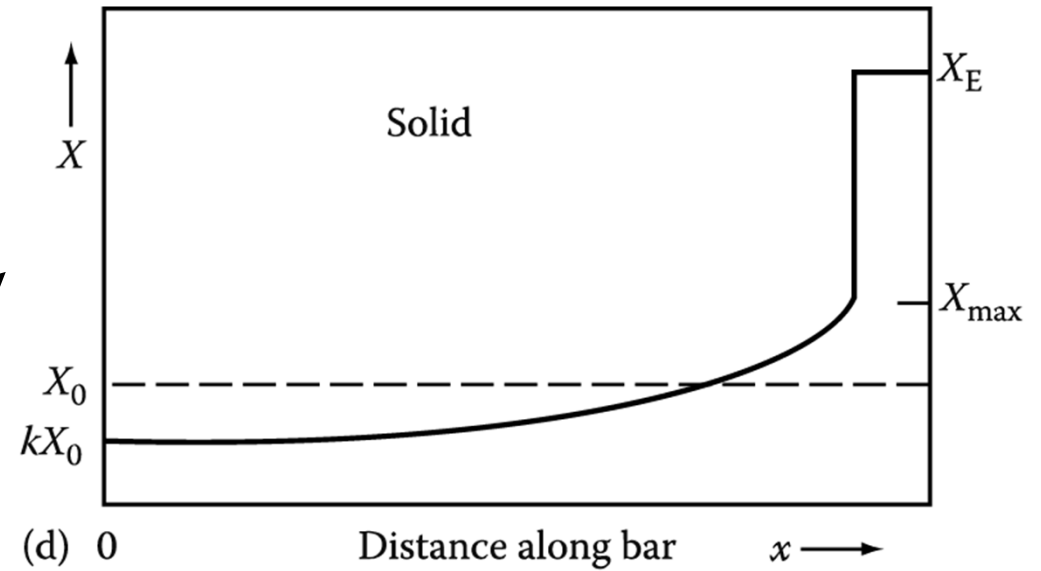
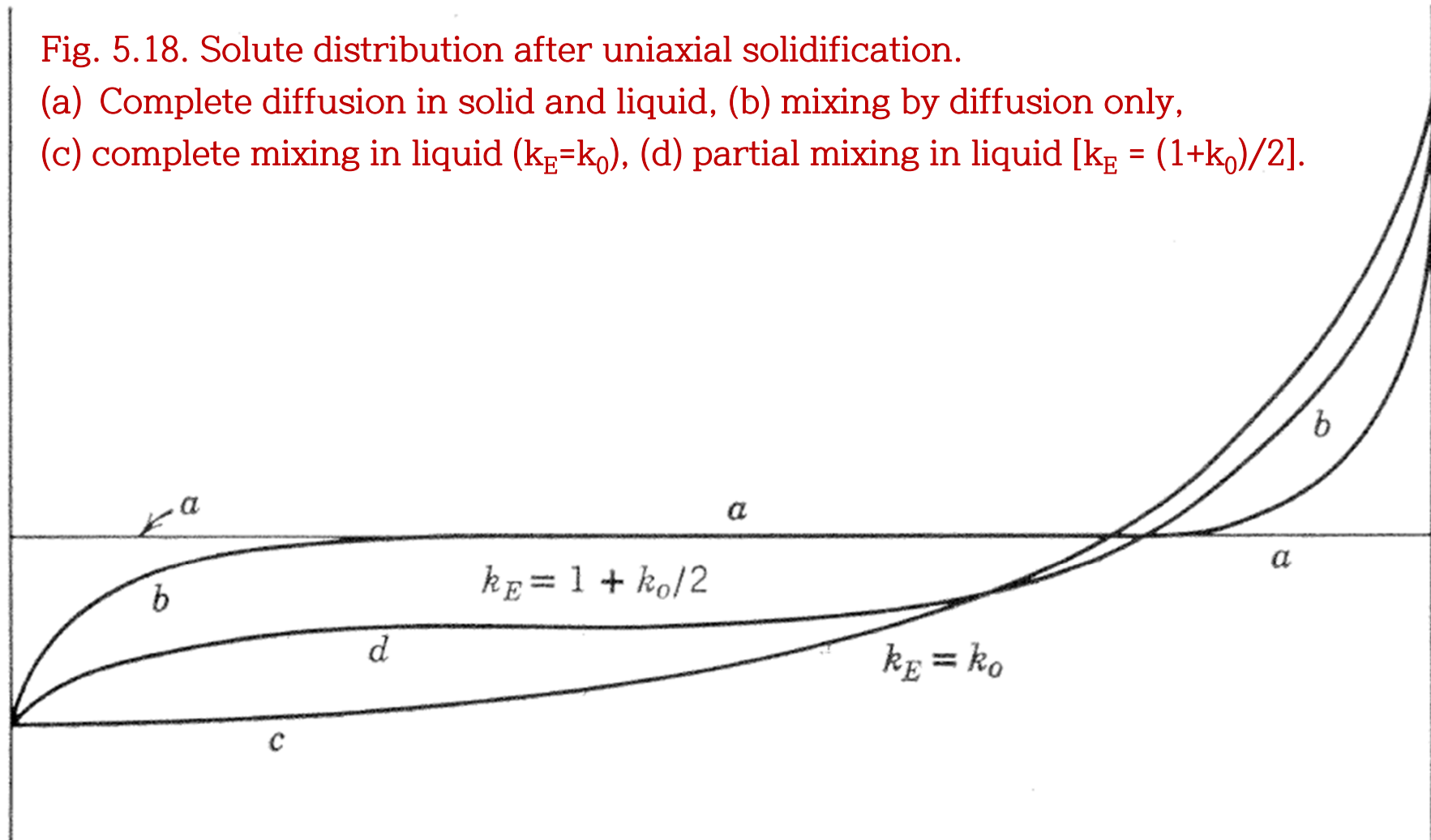


Fig. 5.18. Solute distribution after uniaxial solidification.

- (a) Complete diffusion in solid and liquid, (b) mixing by diffusion only,
(c) complete mixing in liquid ($k_E = k_0$), (d) partial mixing in liquid [$k_E = (1 + k_0)/2$].



* Comments: Solidus temperature of an alloy

T_L : Solidification start \rightarrow supercooling $\rightarrow T_L$ (recalescence) $\rightarrow T_S$: Solidification finish

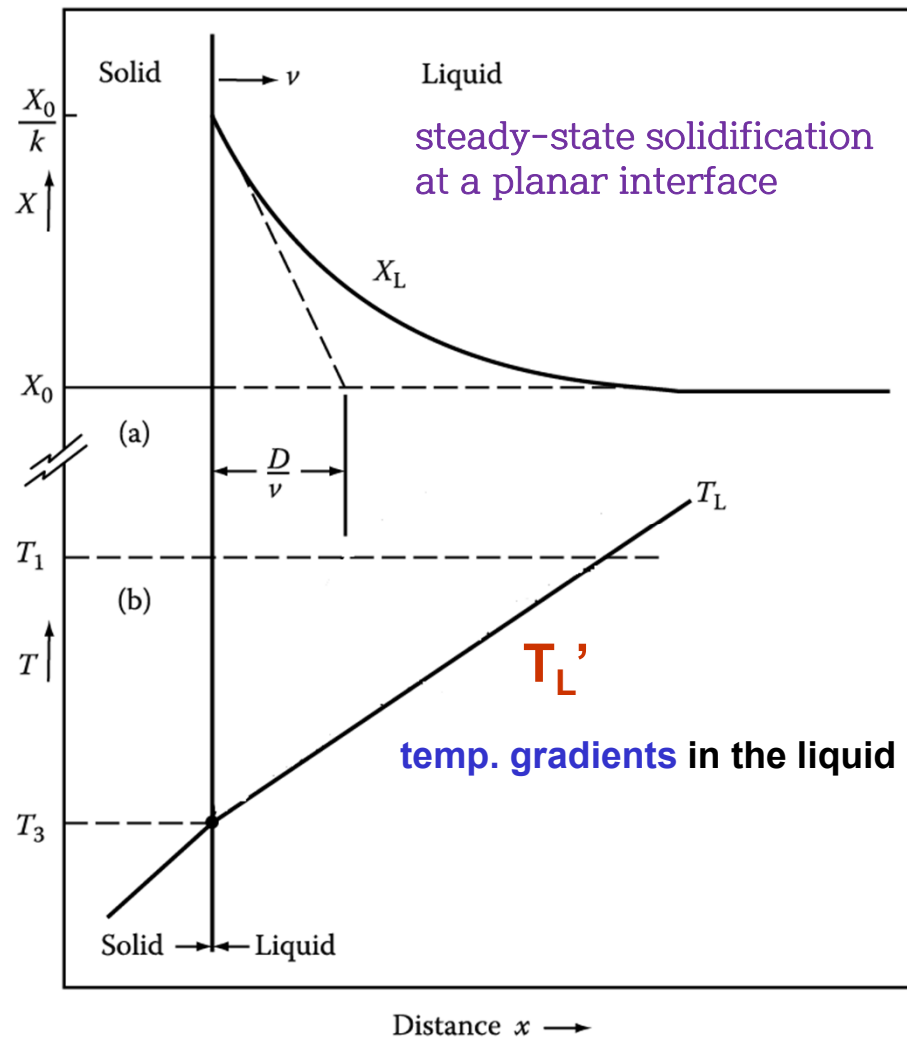
Phase diagram \rightarrow determined from cooling curve $\therefore T_L$ satisfactory, T_S large errors

When a single-phase solid is formed, the last liquid always solidifies at a temperature below the solidus for the original liquid (of composition C_0) some times by a large amount \rightarrow Please check "Zone refining".

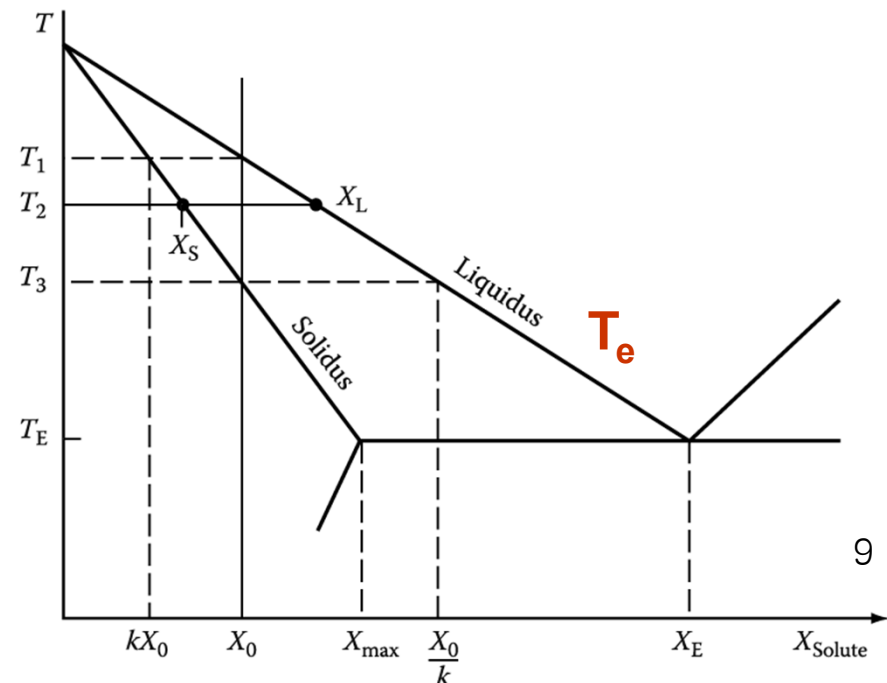
5.5 Constitutional supercooling

Fast Solute diffusion similar to the **conduction of latent heat** in pure metal, possible to break up the **planar front** into **dendrites**.

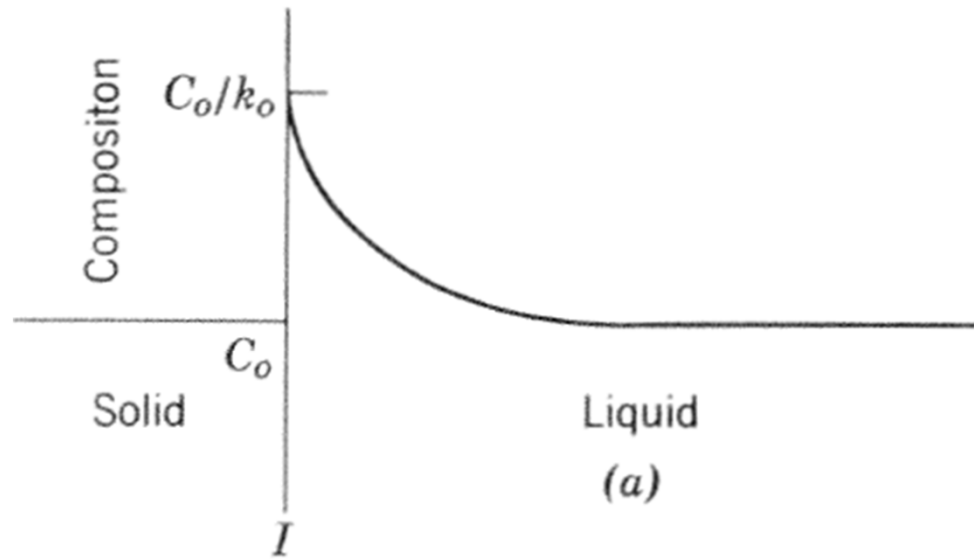
+ complicated by the **possibility of temp. gradients** in the liquid.



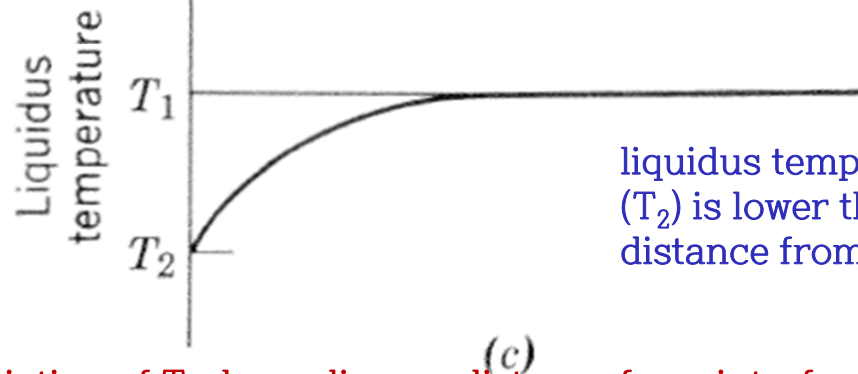
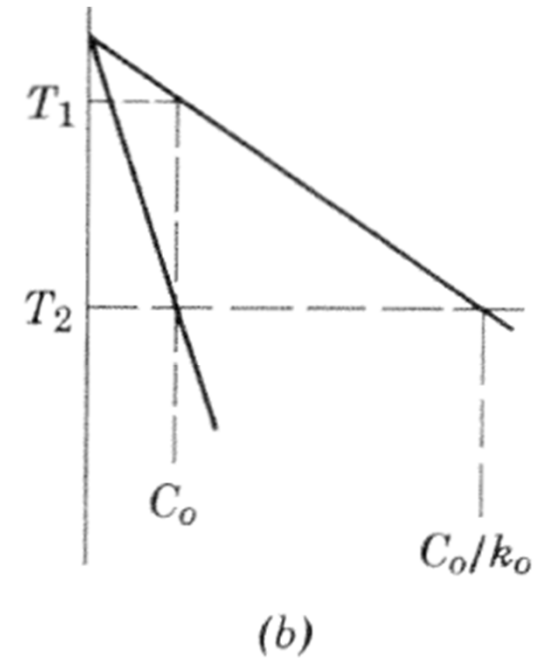
What would be “ T_e ” along the concentration profile ahead of the growth front during steady-state solidification?



Assumption: Steady state condition



Typical binary alloy with $k_o=0.2$



liquidus temp, of liquid in contact with the interface (T_2) is lower than that of the liquid at a greater distance from the interface (T_1).

Variation of T_e depending on distance from interface

Fig. 5.26. Variation of concentration and liquidus temperature ahead of an interface.
(a) Variation of concentration, (b) relationship between concentration and liquidus temperature, (c) variation of liquidus temperature.

→ Actual temp. of liquid at interface < Temp. of bulk liquid: superheated condition

: Undercooling may occur in front of the solidification interface due to the change of the equilibrium solidification temperature (T_e) by the solute released from the solid phase.

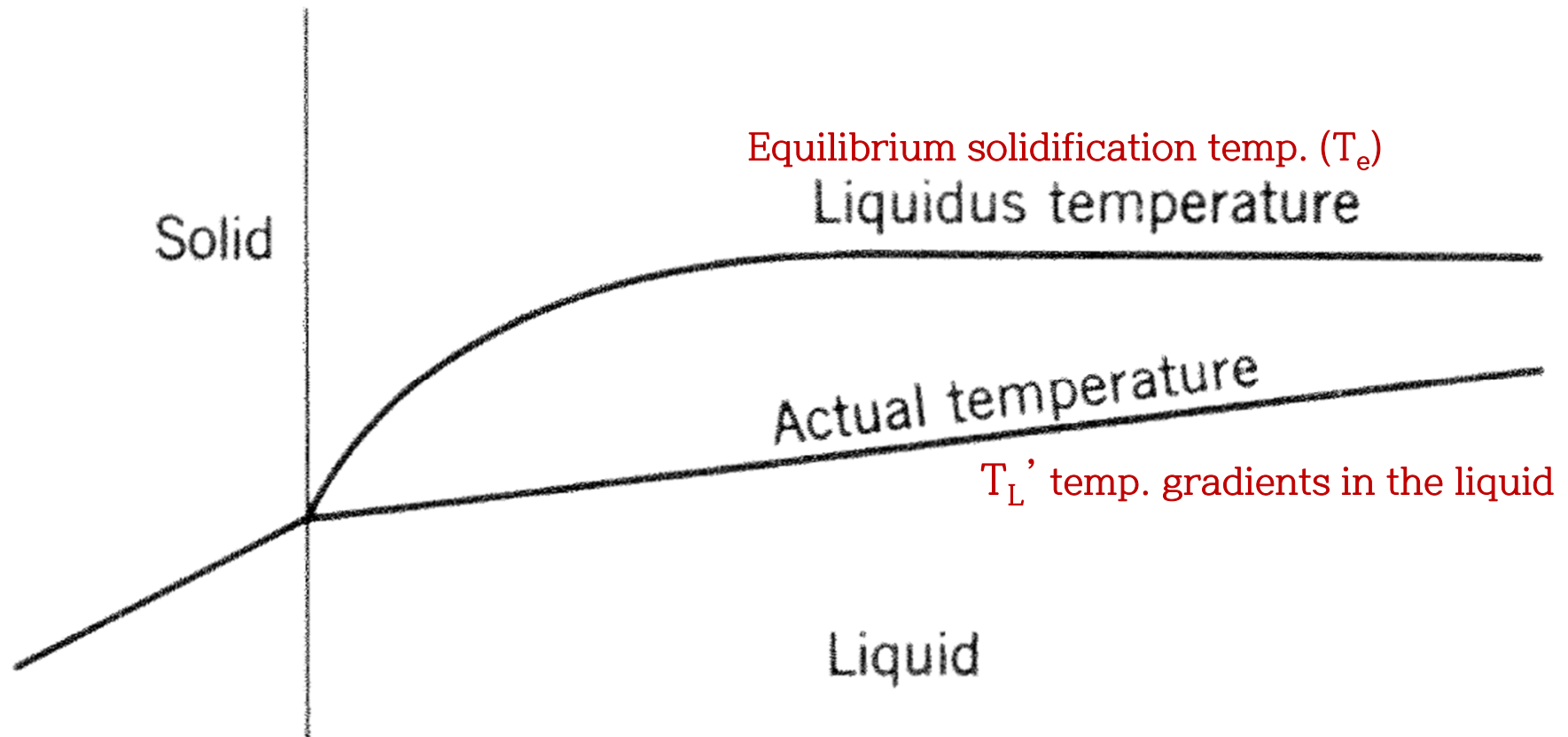
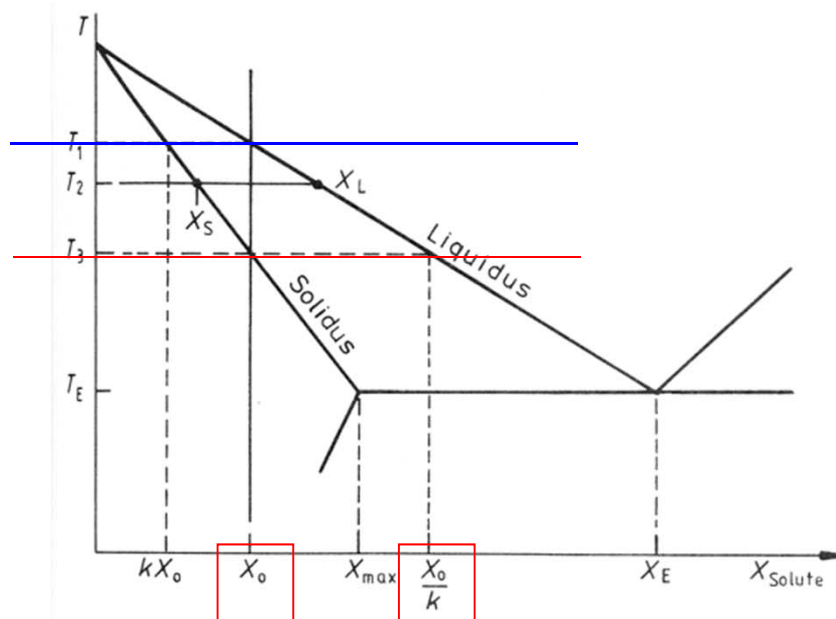


Fig. 5.27. Actual temperature of the liquid and its liquidus temperature

* Constitutional Supercooling

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

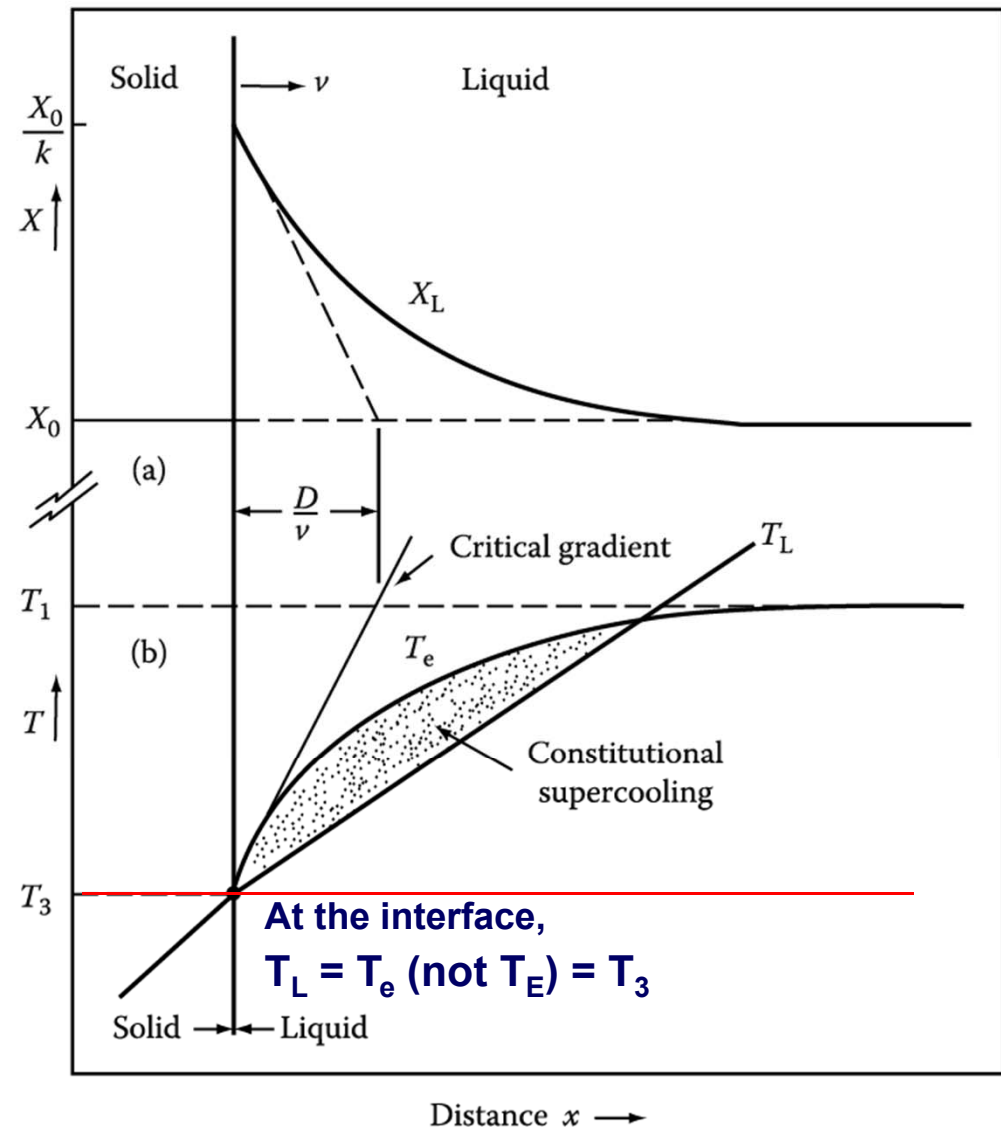


* Actual temperature gradient in Liquid

T_L'

* equilibrium solidification temp. change

T_e



$T_L' > (T_1 - T_3)/(D/v)$: the protrusion melts back \rightarrow **Planar interface: stable**

Cellular and Dendritic Solidification

At the interface, $T_L = T_e$ (not T_E) = $T_3 \rightarrow T_{L, \text{liquid}} = T_1 : T' = T_1 - T_3$

- **Criterion for the stable planar interface:**

$T_L' > (T_1 - T_3)/(D/v)$: the protrusion melts back_steeper than the critical gradient

$T_L' / v > (T_1 - T_3)/D$ ($T_1 - T_3$: Equilibrium freezing range of alloy)

→ Large solidification range of $T_1 - T_3$ or high v promotes protrusions.

⇒ need to well-controlled experimental conditions (temp. gradient & growth rate)

- **Constitutional supercooling:**

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

1) **Solute effect** : addition of a very small fraction of a percent solute with

very small k ($k = \frac{X_s}{X_L}$) $\rightarrow (T_1 - T_3) \uparrow$ promotes dendrites.

2) **Cooling rate effect** : Higher cooling rate allow less time for lateral diffusion of the rejected solute and therefore require smaller cell or dendrite arm spacings to avoid constitutional supercooling.

* **Instability due to constitutional supercooling**

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

- 1) **Solute effect** : addition of a very small fraction of a percent solute with very small k ($k = \frac{X_s}{X_L}$) $\rightarrow (T_1 - T_3) \uparrow$ promotes dendrites.

- (a) Freezing range of 90Cu-10Sn
 ~ very large (190 K) \rightarrow the liquid ahead of the advancing interface could be constitutional supercooling by 190 K.
- (b) This condition (= large undercooling) is never even approached because a very much smaller amount of supercooling is sufficient to set up an instability

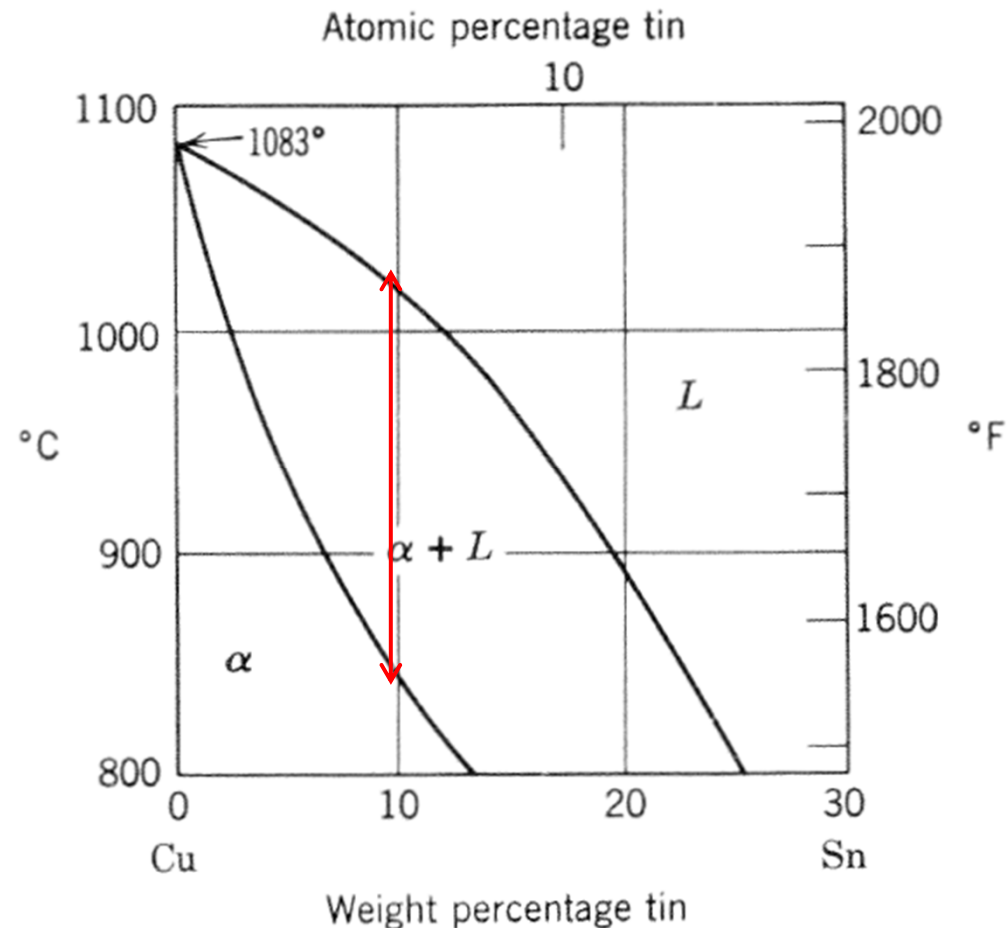


Fig. 5.28. Freezing range in copper-tin alloys

* **Constitutional supercooling** → **Interface instability** →
compositional fluctuation of solid → “Periodicity of solute”

1) Axial periodicity of solute (Landau proposal)

(a) Solute content of solid varies periodically in the direction of travel of the solid-liquid interface.

→ Uniform in any plane parallel to the interface

Assumption: (a) whole of the interface advances together/ (b) Accumulation of solute, as a result of the “initial transient”, increase progressively until some concentration is reached where either independent nucleation would occur in the most supercooled region, or the existing crystal would grow into that region.

(b) Landau cite evidence for periodic variation of concentration of antimony in Ge crystals grown by the Kyropoulos method, but no quantitative comparison btw this theory and experiment is available. →

No conclusive evidence btw Landau type of instability and periodic fluctuation in the thermal characteristics of the system

2) Transverse periodicity of solute (opposite with axial periodicity)

5.6 Cellular Substructure : Due to instability by constitutional supercooling at superheated liquid

The instability due to constitutional supercooling can be resolved by the development of a transverse periodicity in the solidification process. → The phenomenon can be readily observed on the top (free) surface of a crystal of tin grown from the melt.

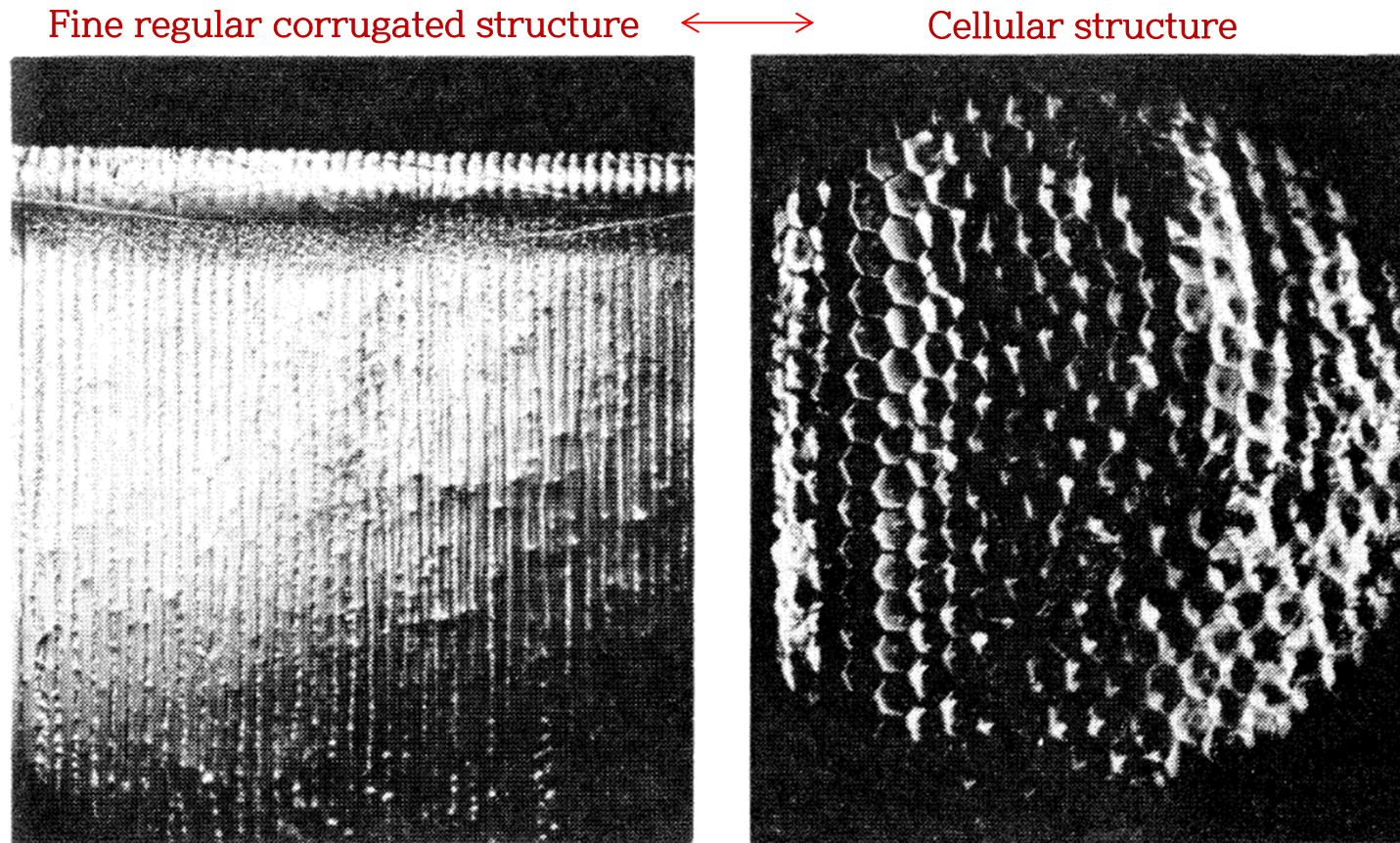


Fig. 5.29. Cellular structure (a) view of top (free) surface of tin crystal (x 75);
(b) view of decanted interfaces of tin crystal (x 75)

5.6 Cellular Substructure : Due to instability by constitutional supercooling at superheated liquid

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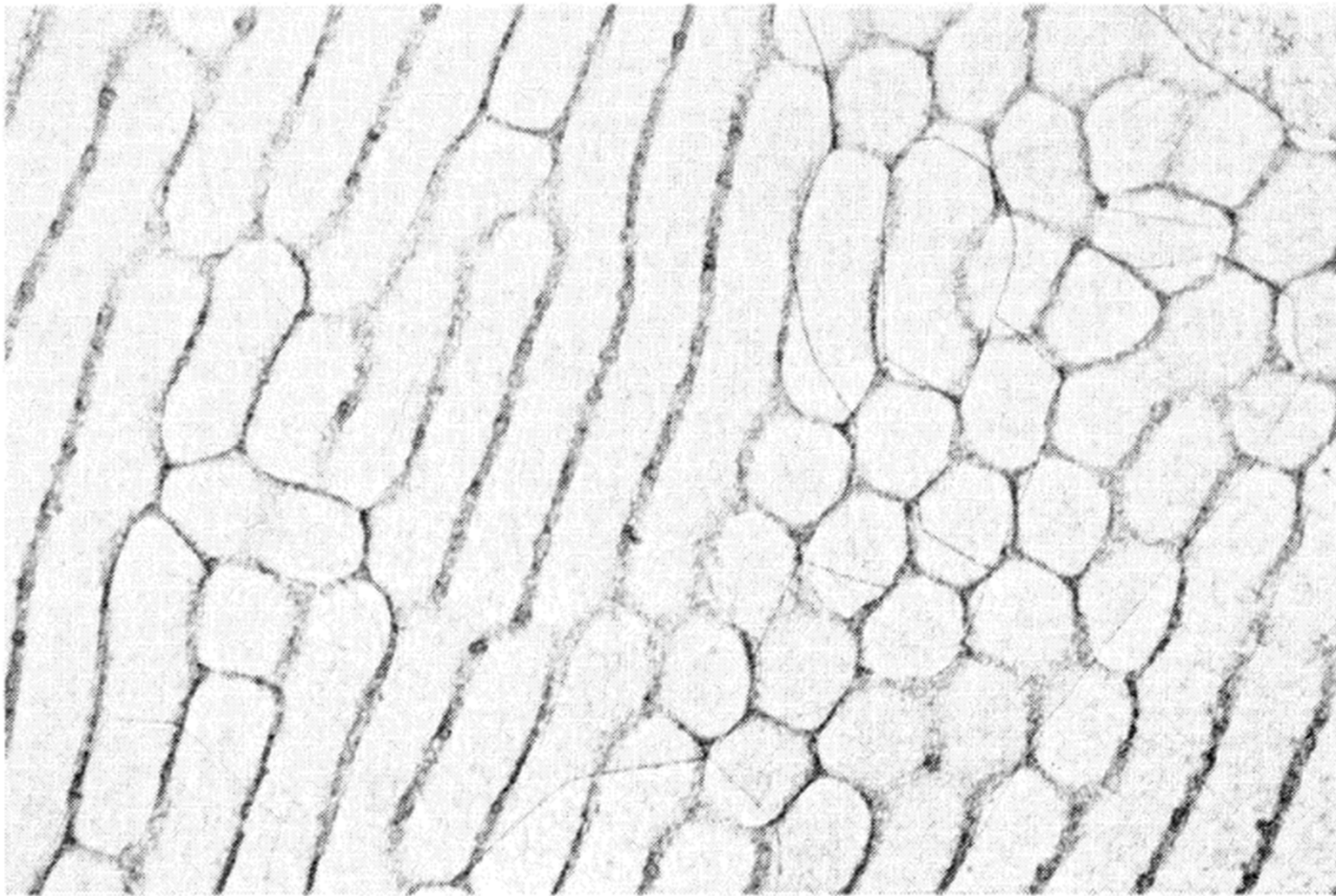


Fig. 5.29. (continue) Cellular structure (c) Less regular forms of cell

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))

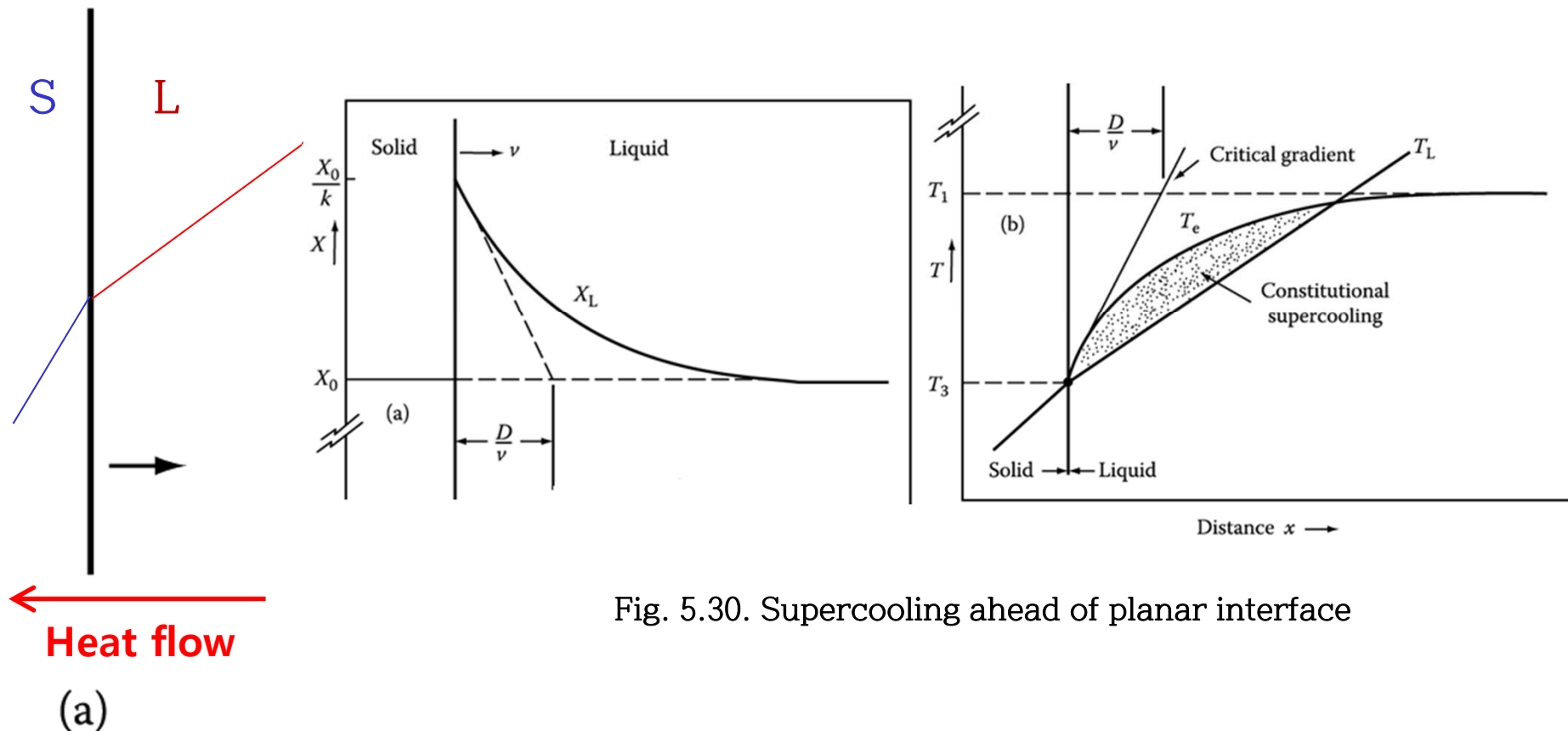


Fig. 5.30. Supercooling ahead of planar interface

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

5.6 Cellular Substructure : Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure: discussed by solute redistribution theory

Cell formation can be suppressed by a) reducing the solute content, $(T_1 - T_3) \downarrow$ / b) reducing the speed of growth, $v \downarrow$, or/ c) increasing the temperature gradient, T_L' to eliminate the region of supercooling (\overline{AV} in Fig. 5.30).

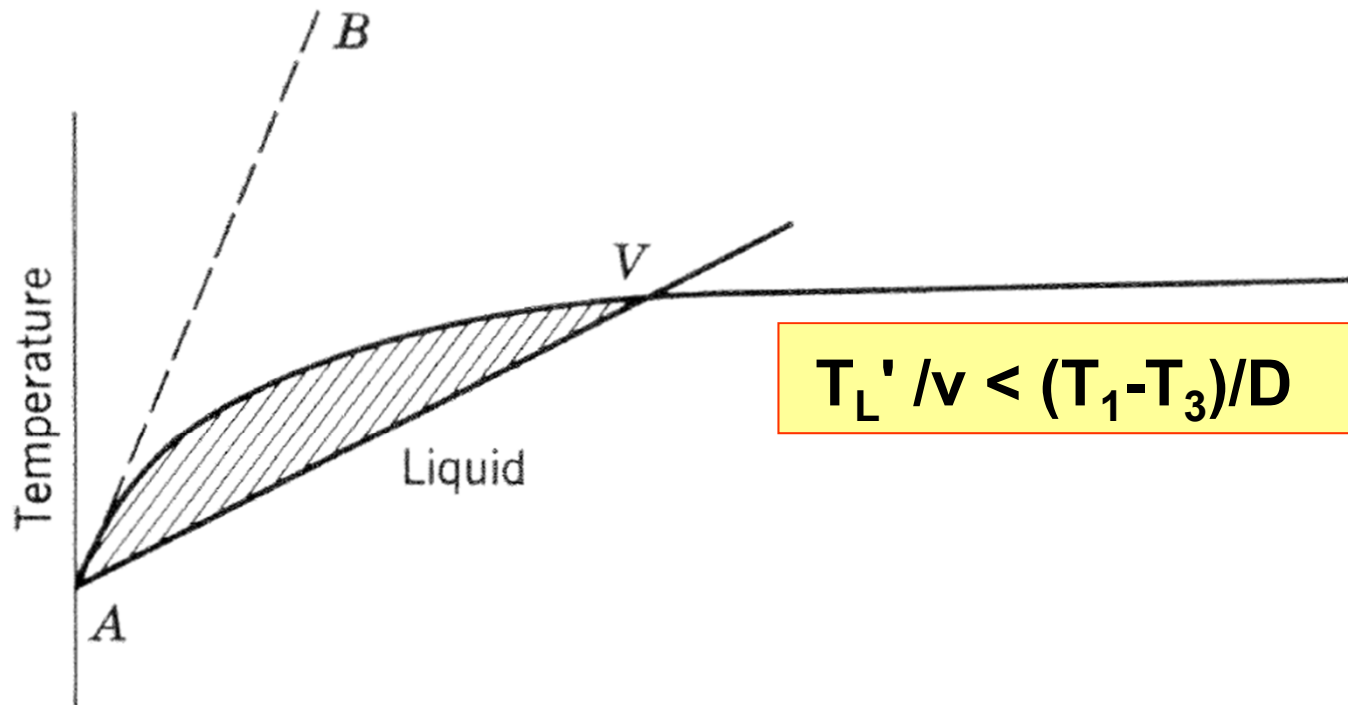


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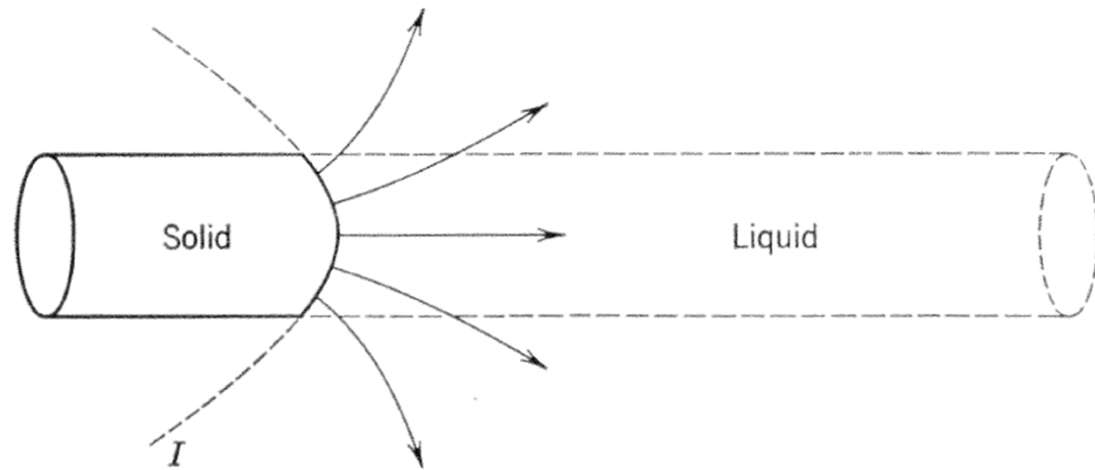
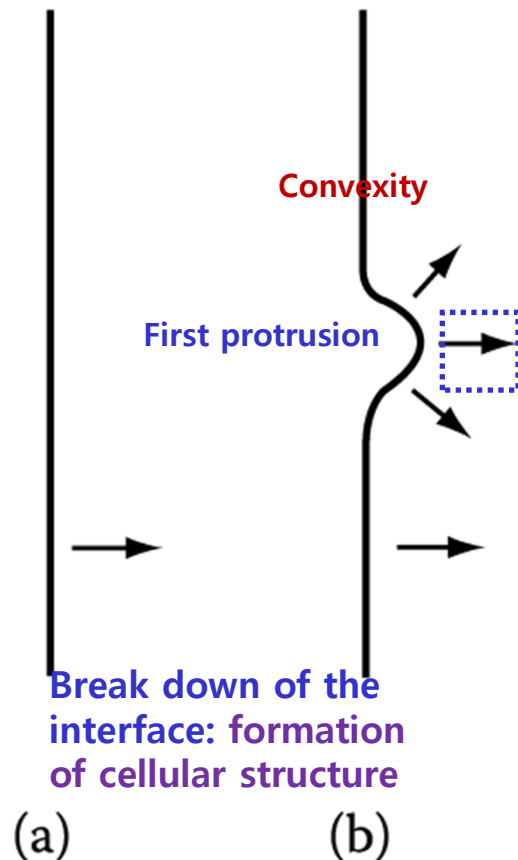


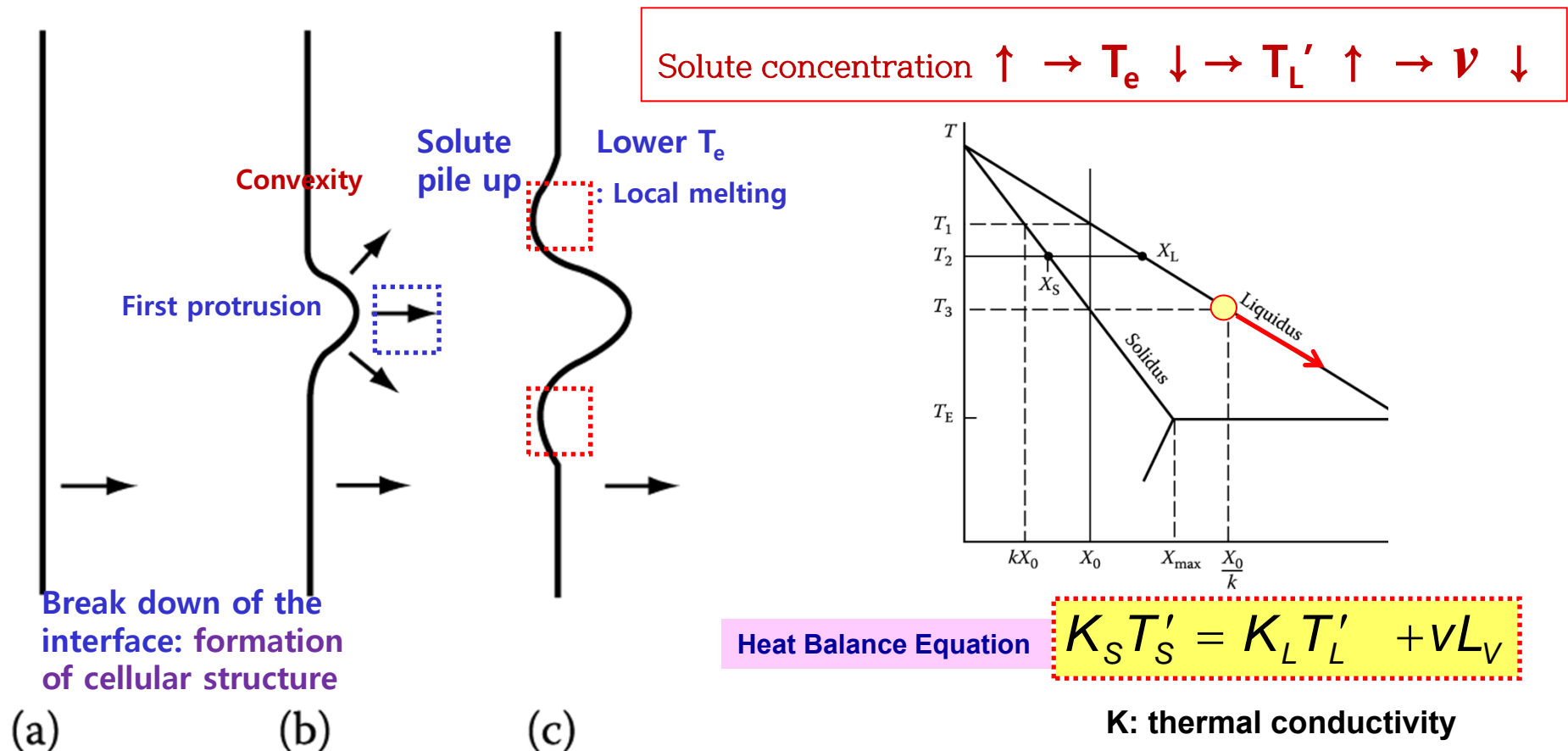
Fig. 5.14. Solute diffusion ahead of a convex interface

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

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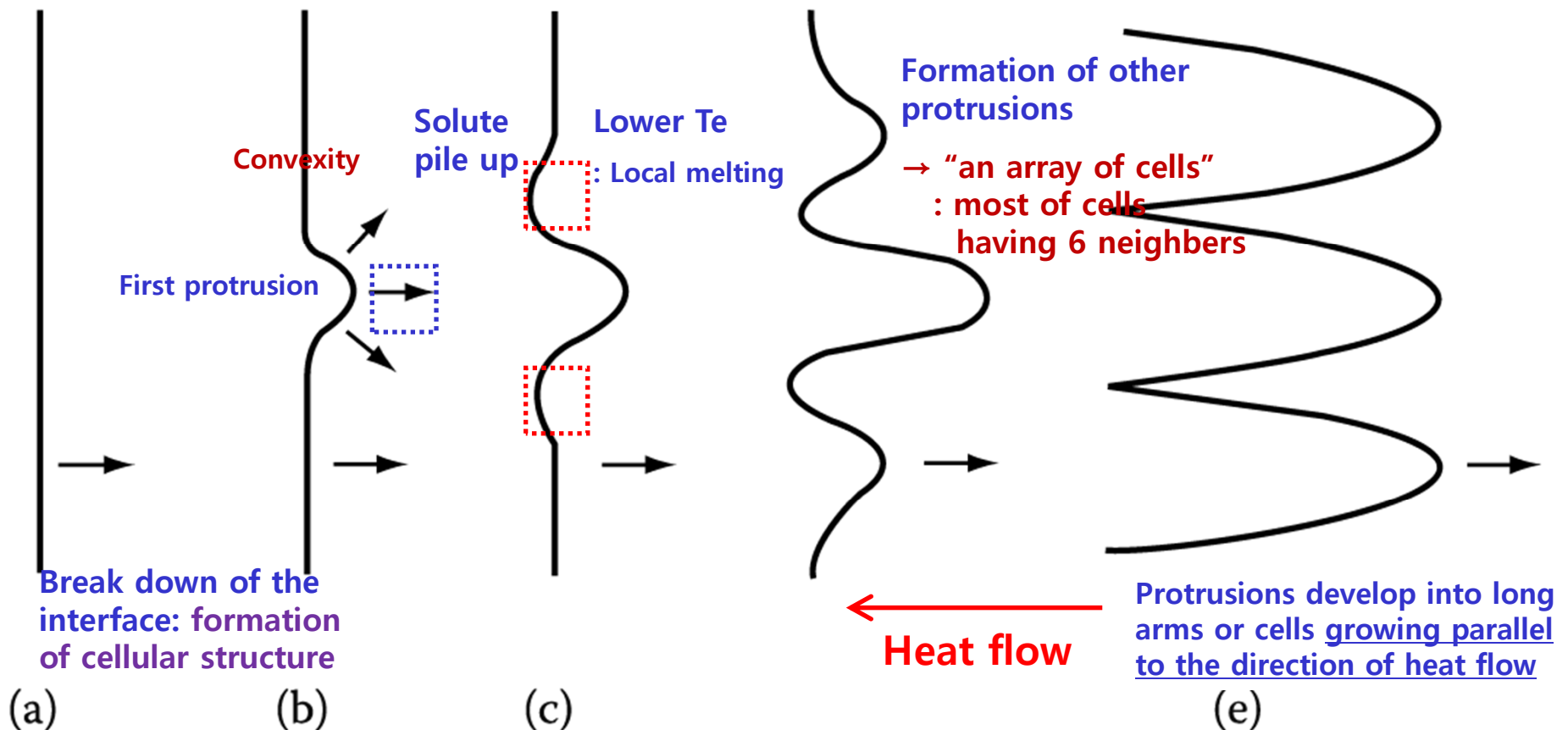


<The breakdown of an initially planar solidification front into cells>

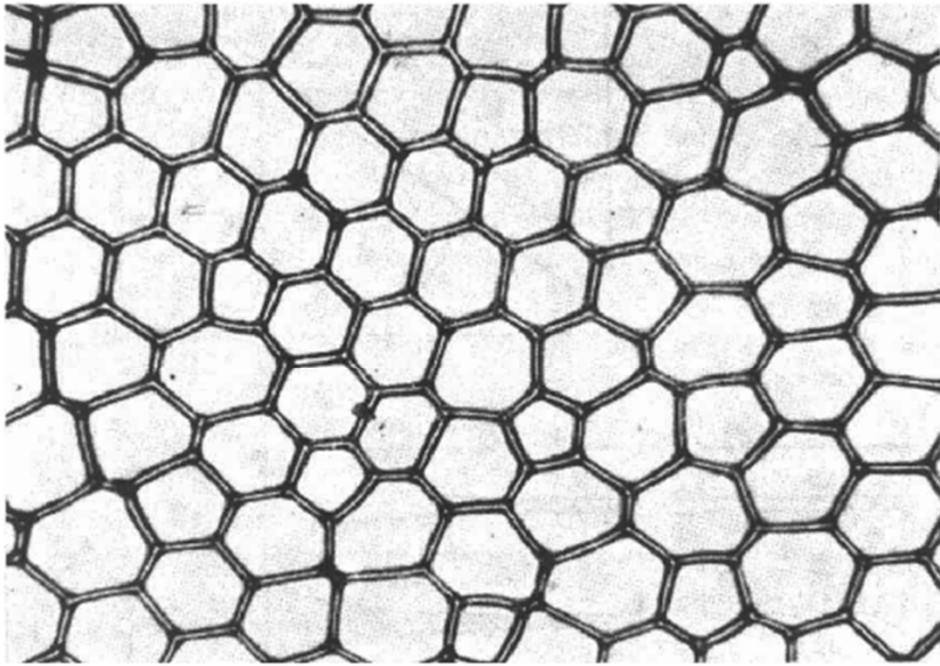
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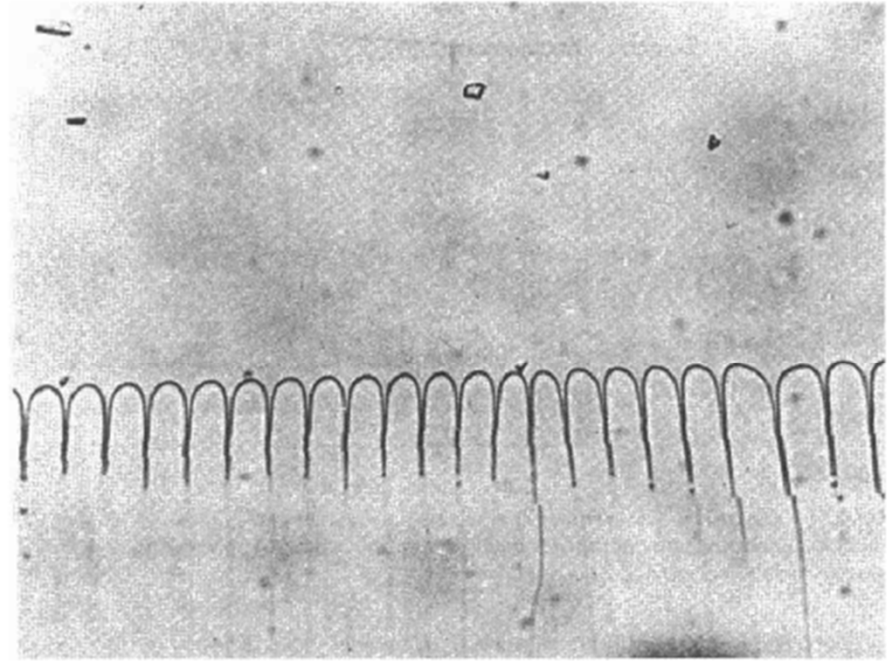
If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at interface, (a))



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



(a)



(b)

* Cellular microstructures

Note that each cell has virtually the same orientation as its neighbors and together they form a single grain.

(a) A decanted interface of a cellularly solidified Pb-Sn alloy (x 120)

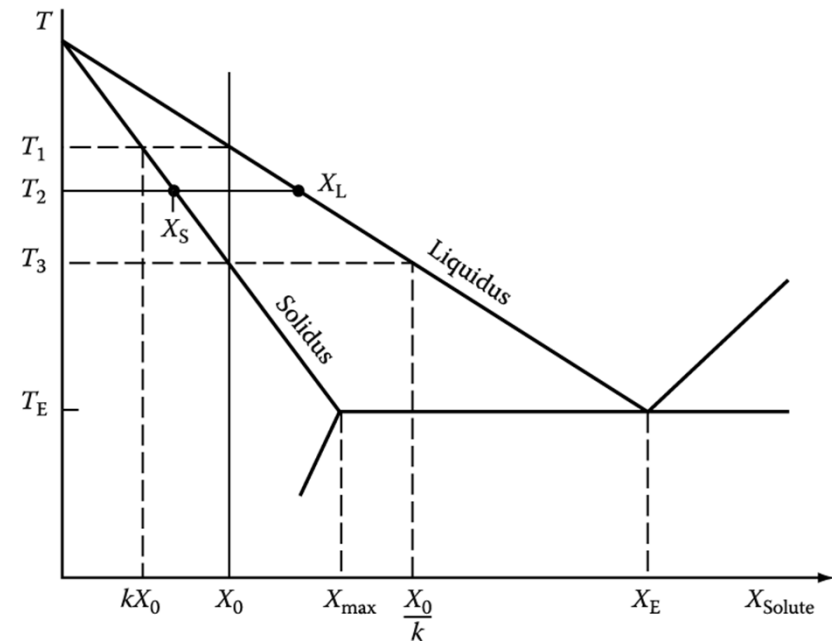
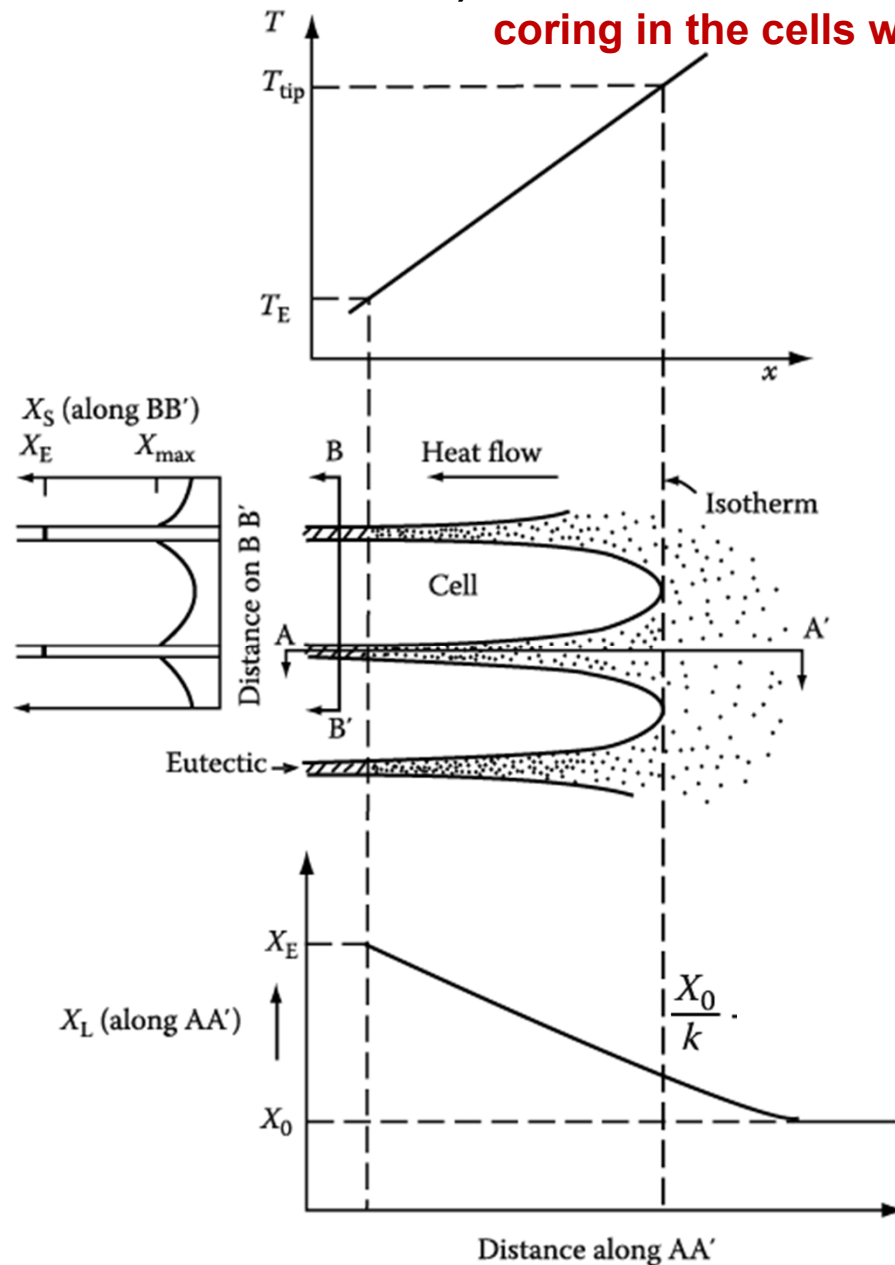
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(after K.A. Jackson and J.D. Hunt, Acta Metallurgica 13 (1965) 1212).

*** 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 pile up \rightarrow eutectic solidification \rightarrow formation of 2nd phases at the cell wall

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	$T \downarrow \rightarrow$ Increase of C.S. zone	formed by releasing the latent heat from the growing crystal toward the supercooled liquid
Dome type tip / (surrounding) hexagonal array	Pyramid shape of cell tip / Square array of branches / Growth direction change toward Dendrite growth direction	Dendrite growth direction / Branched rod-type dendrite

→ “Nucleation of new crystal in liquid”

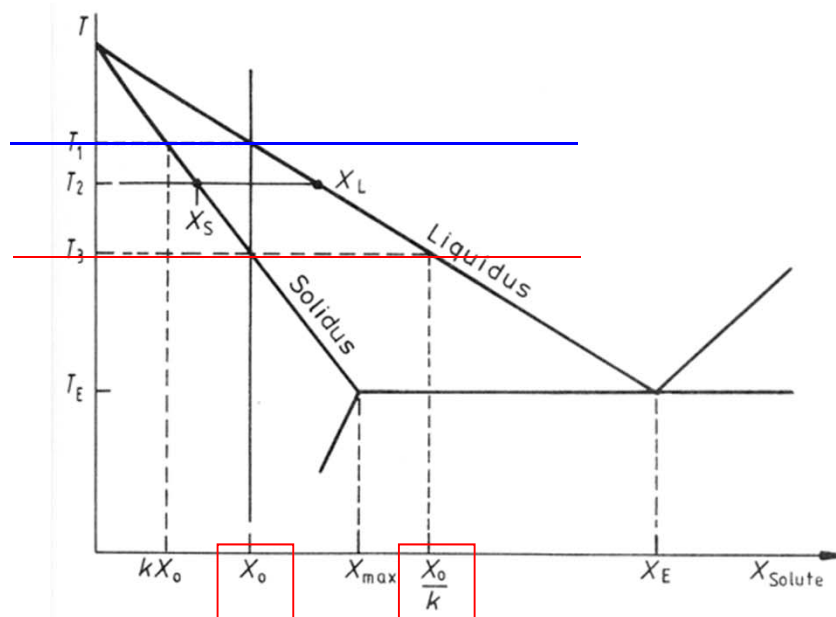
Temperature above the interface at which growth occurs

b) Segregation

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

* Constitutional Supercooling

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



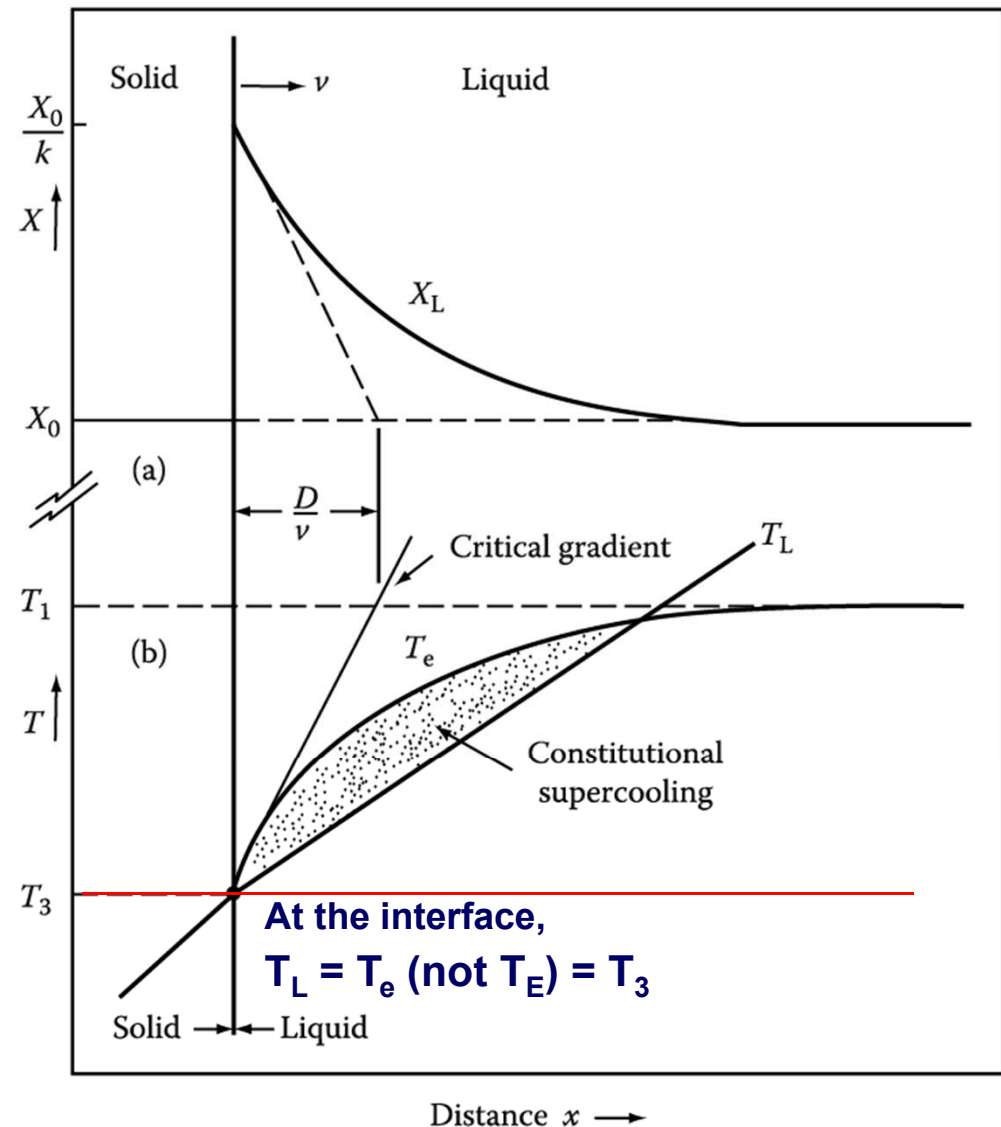
* Actual temperature gradient in Liquid

T_L'

* equilibrium solidification temp. change

T_e

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

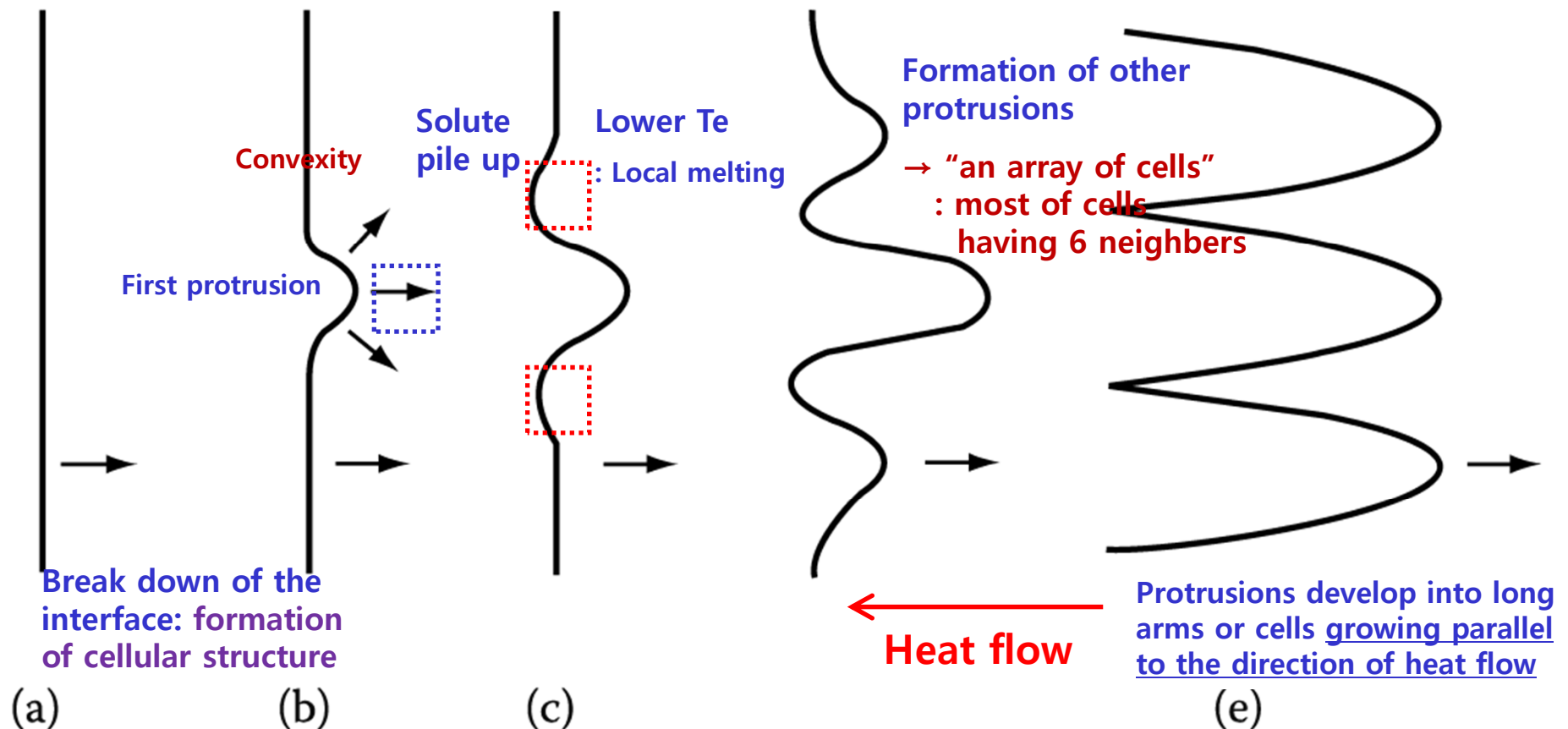


Constitutional supercooling

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

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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

$$T_E = T_0 - mC_L \quad (\text{Equip. temp. for the alloy})$$

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

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

R Growth rate

D diffusivity

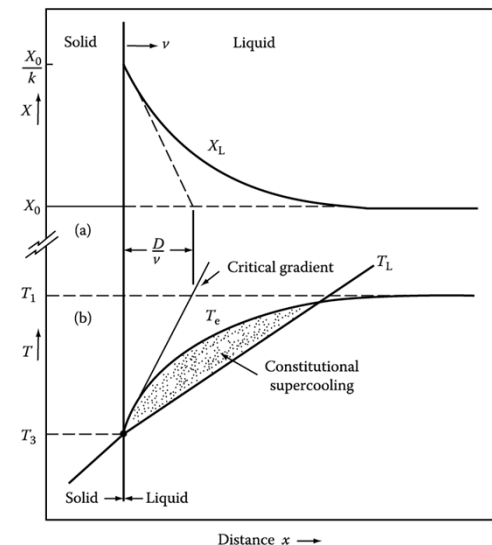
b) Actual temperature of alloy at distance X in front of interface

$$T = T_0 - m \frac{C_0}{k_0} + GX$$

Interface temperature

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

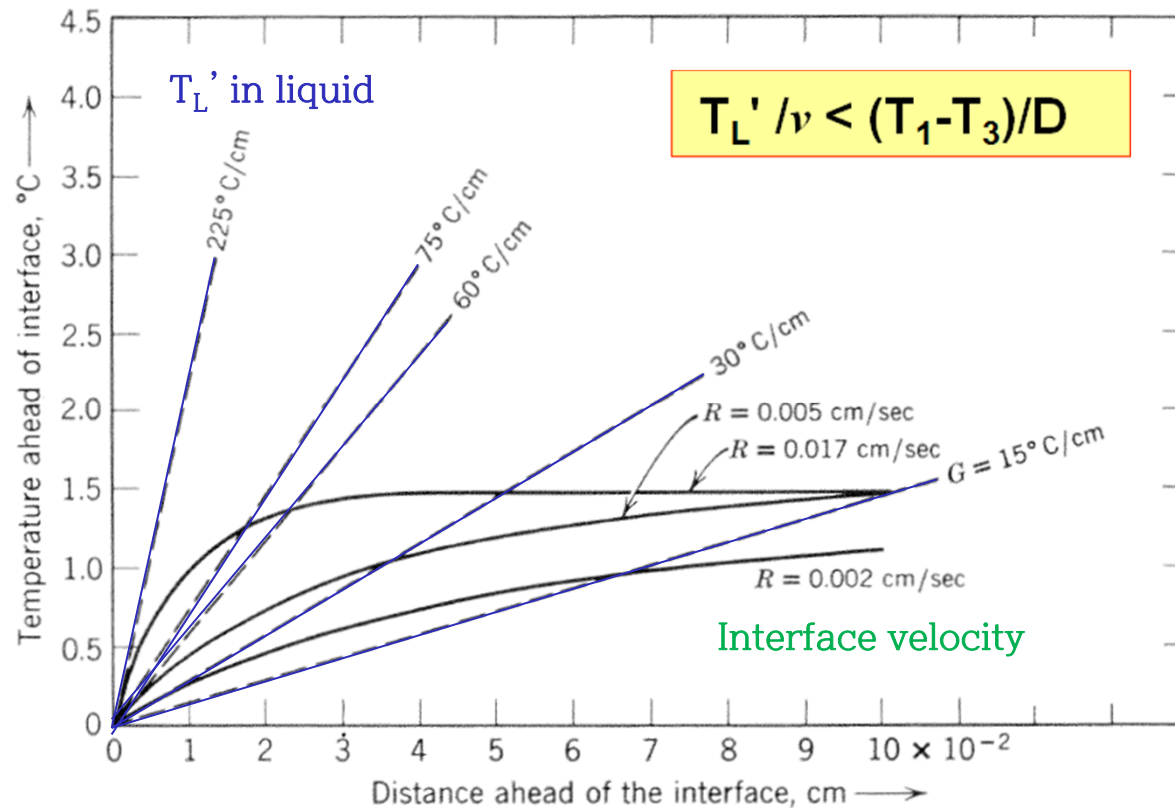
Temp gradient in the liquid in degrees per centimeter, T_L'



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



⇒ “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.

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

$G/R \propto$ solute concentration (C_0)

or $G/RC_0 = \text{constant}$

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

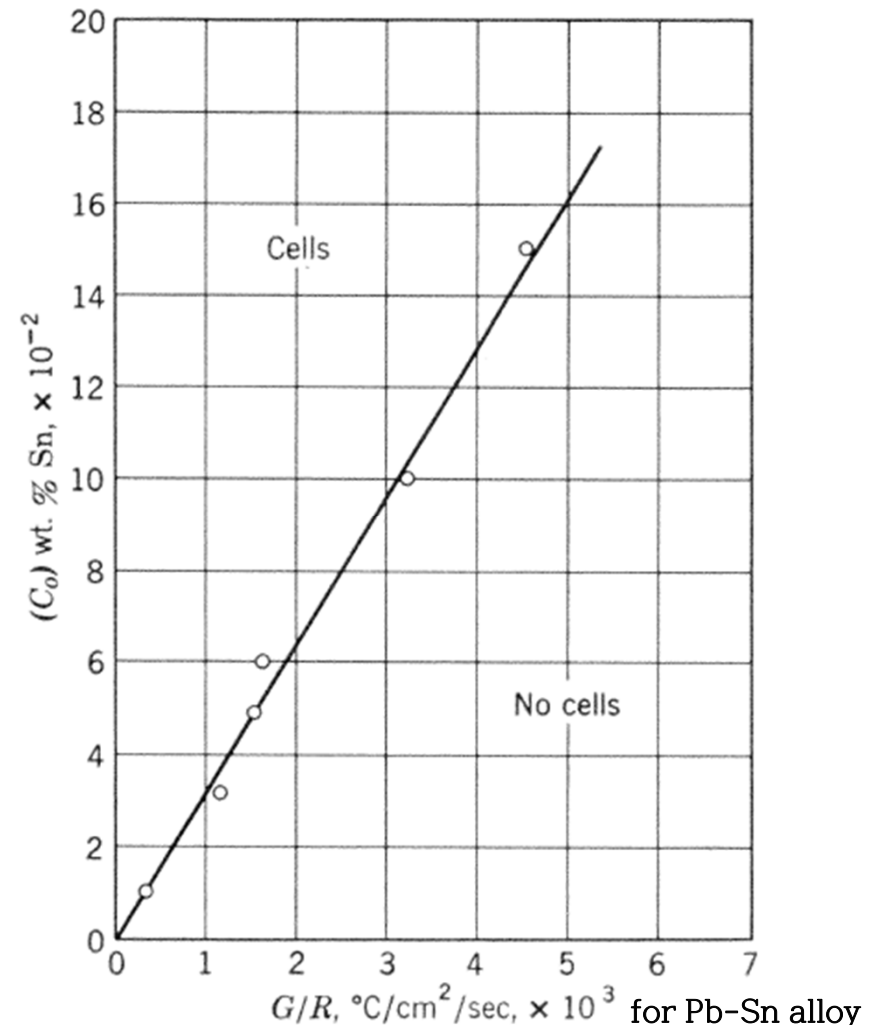


Fig. 5.33. Conditions for cellular solidification

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 (equil. Distribution coefficient)/ Using directly measured G and R values → C_0 composition calculation

$$C_0 = \frac{k_0}{1 - k_0} \cdot \frac{D}{m} \cdot \frac{G}{R} \quad \text{: for experimentally convenient values of } G \text{ and } R, \\ C_0 \text{ can be determined when it is btw } 6 \times 10^{-4} \sim 2 \times 10^{-1} \text{ wt.}\%$$

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

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

3) Geometry of cells

① Cell size

* Experimental data: **R (interface velocity: growth rate) $\downarrow \rightarrow$ cell size \uparrow**

but apparently independent of the temperature gradient

→ 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** ~ deviates toward the nearest “dendrite direction”, if this does not coincide with the normal to the interface.

→ **Degree of deviation from the growth direction** \propto **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

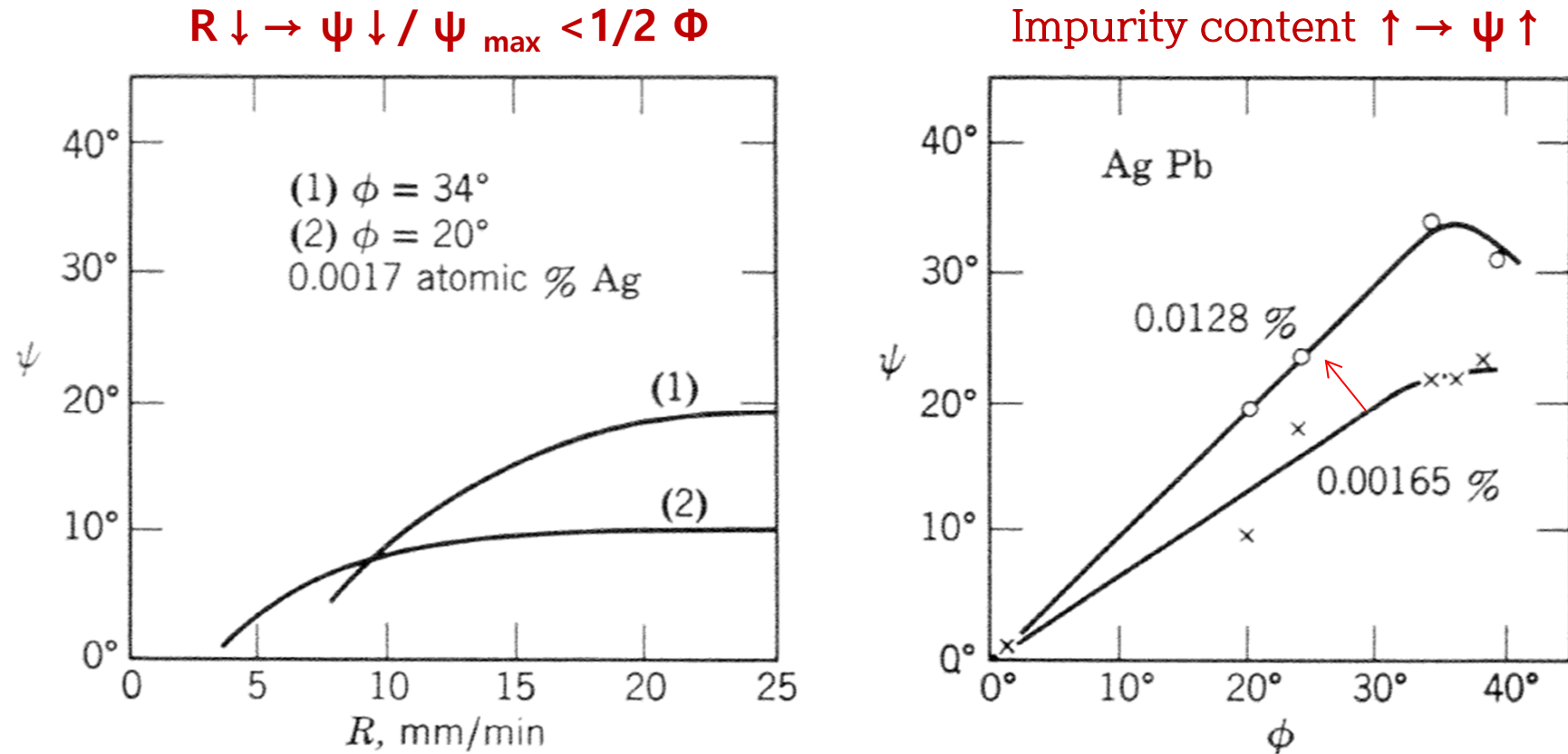


Fig. 5.34. deviation of cellular direction ψ as a function of R (Interface velocity) ,
dendrite orientation Φ , and solute content.

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.

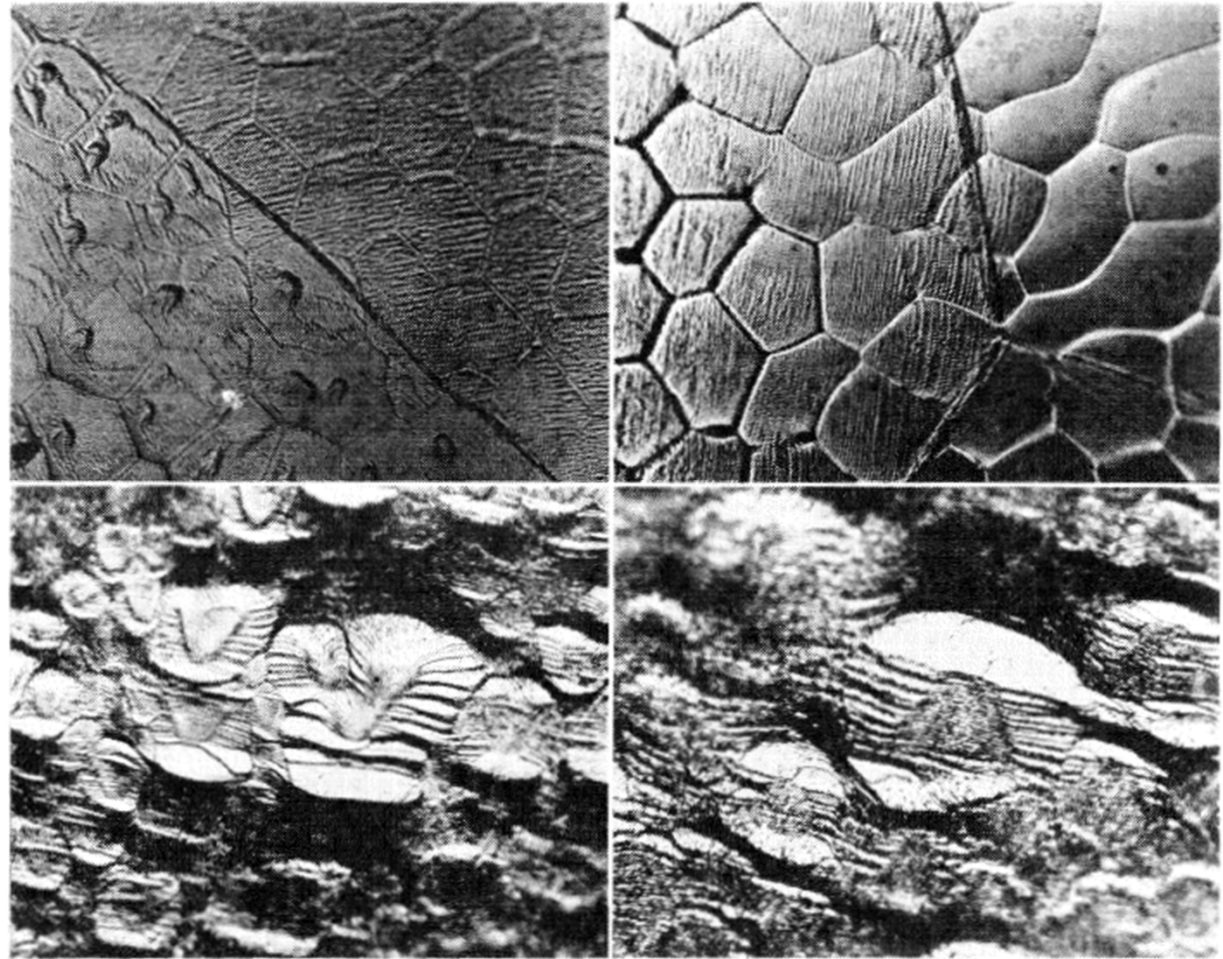


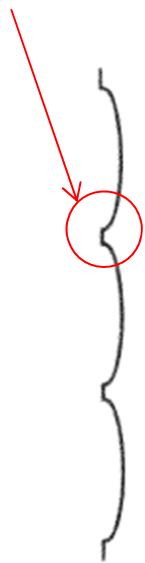
Fig. 5.35. appearance of decanted cellular interface.

3) Geometry of cells

③ Shape of cell surface

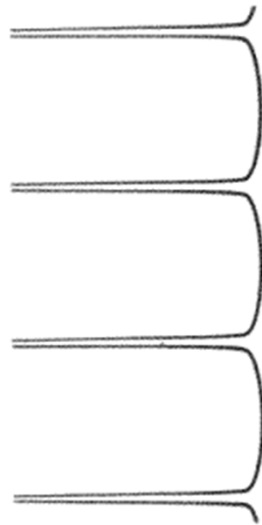
* Experimental observations are somewhat different from those predicted for the overall shape of the cell.

a) The cell wall is flat and somewhat thick.



(a)

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



(b)

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

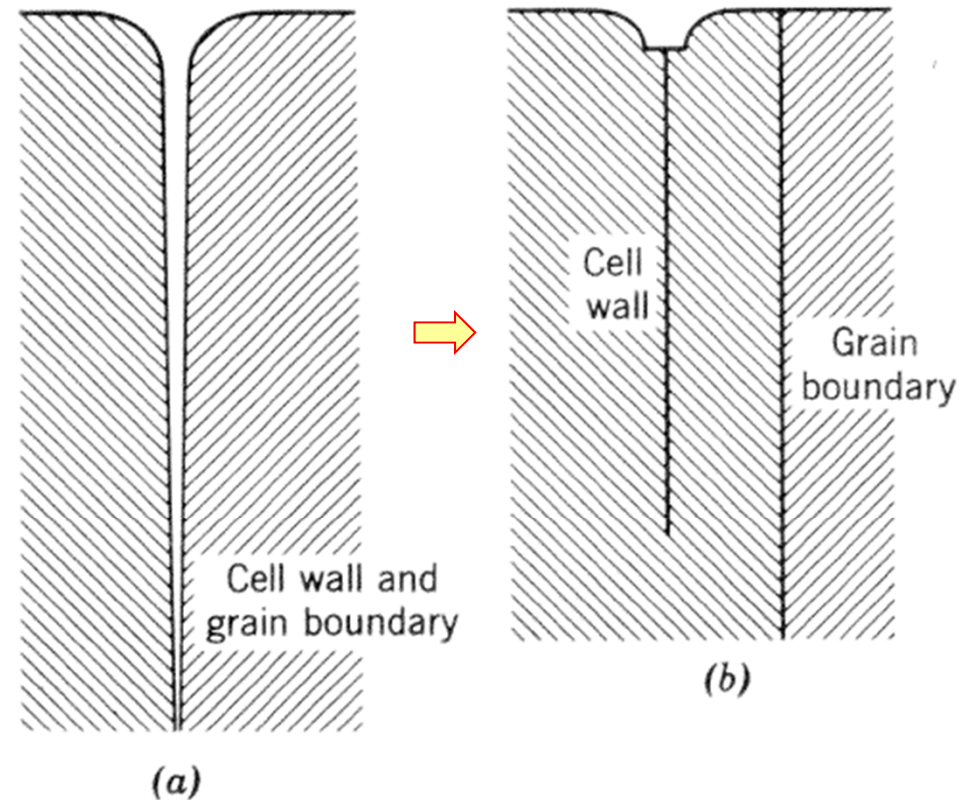


Fig. 5.37. Relative positions of grain boundary and cell wall. (a) During growth; (b) after decanting.

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 ($T \downarrow$), 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"**

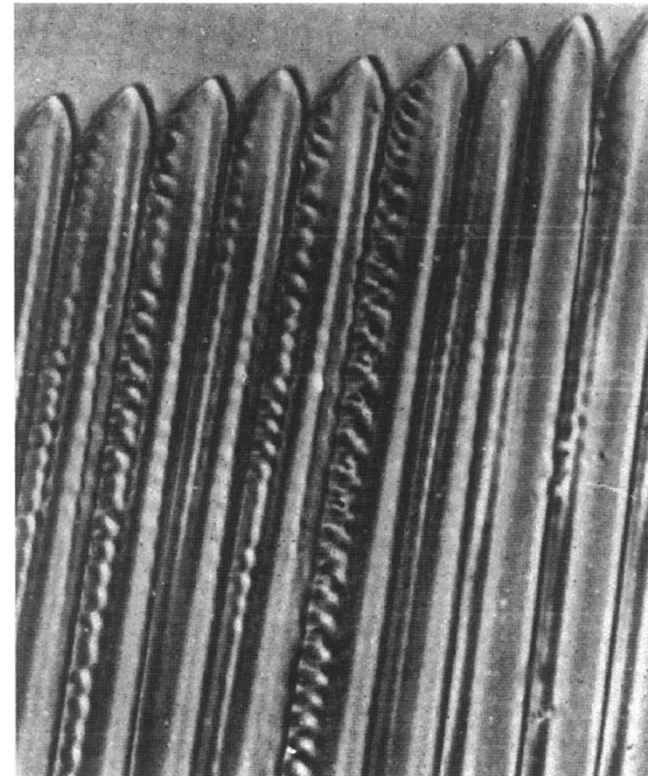


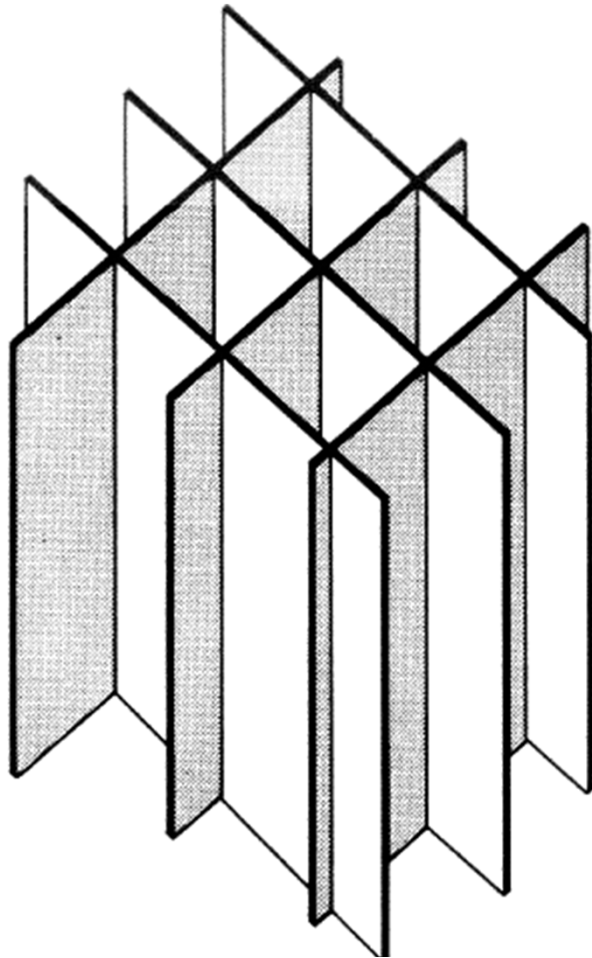
Fig. 4.27 Cellular dendrites in carbon tetrabromide.

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

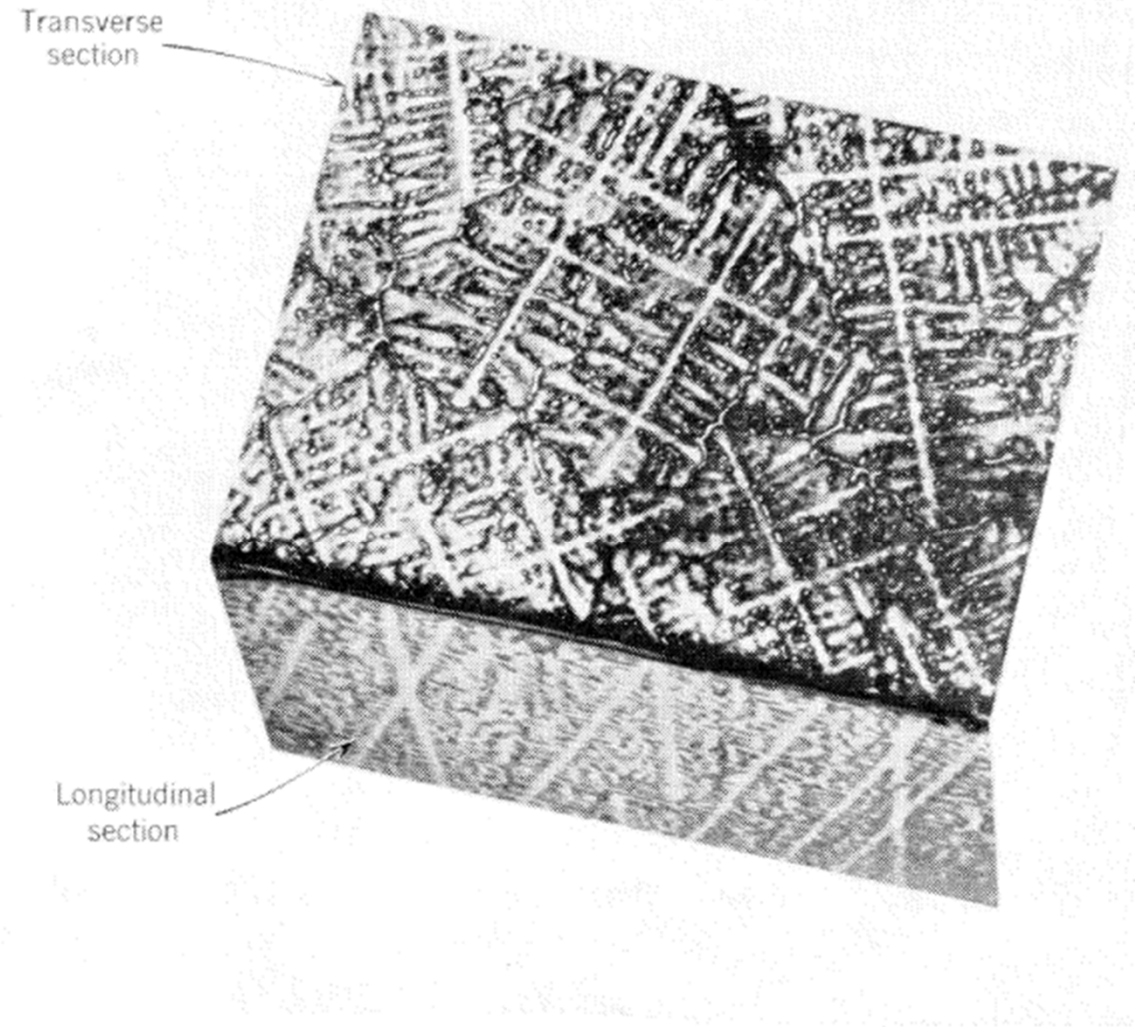
5.7 Cellular Dendrites

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

Each dendrite grows independent of its neighboring branches.



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



(b)

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.**

$$\mathbf{G/R < (T_1 - T_3)/D}$$

Constitutional supercooling

Cellular growth → Cellular dendritic solidification

$$G/R \quad G/R^{1/2} \sim C_0/k_0 \quad \therefore G/R^{1/2} \leq AC_0/k_0$$

(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) $\sim R^{-1/2} \therefore Z = a/R^{1/2}$

Thickness of supercooled layer, t

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

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

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

If $\exp(-R^{1/2}a/D)$ is less than 1,
 $Z=t$. ($\because G/R^{1/2} \sim C_0/k_0$)

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

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.→ \therefore 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.

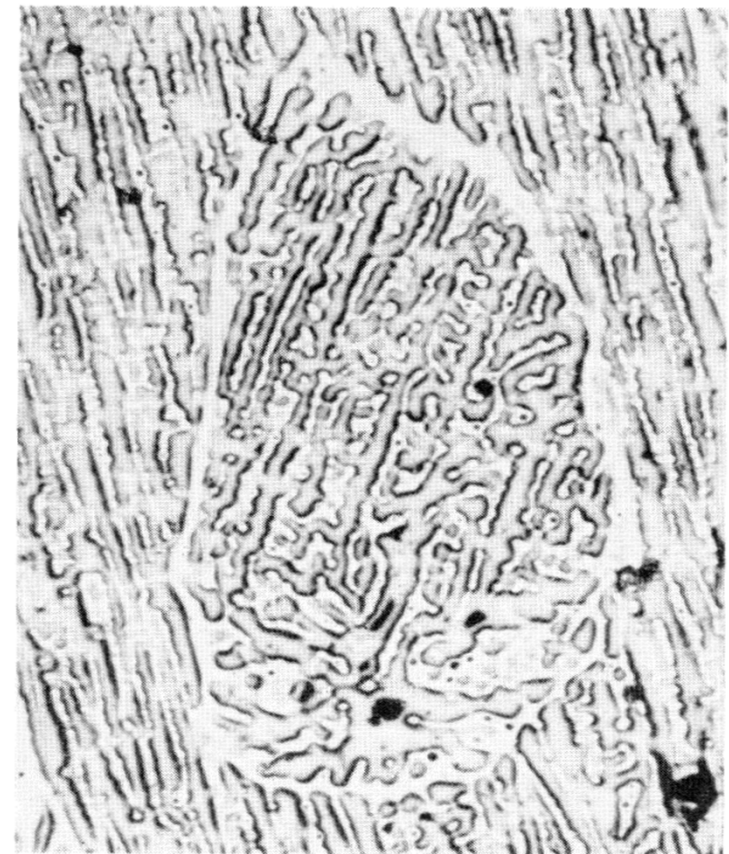


Fig. 5.39. Crystal showing free dendrites and Cellular dendritic substructure.

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 $T \downarrow \rightarrow$ 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 $T \downarrow \rightarrow$ 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 \rightarrow local $T_e \downarrow \rightarrow$ Effective supercooling \downarrow

: 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 supercooled alloy** has not yet been solved.

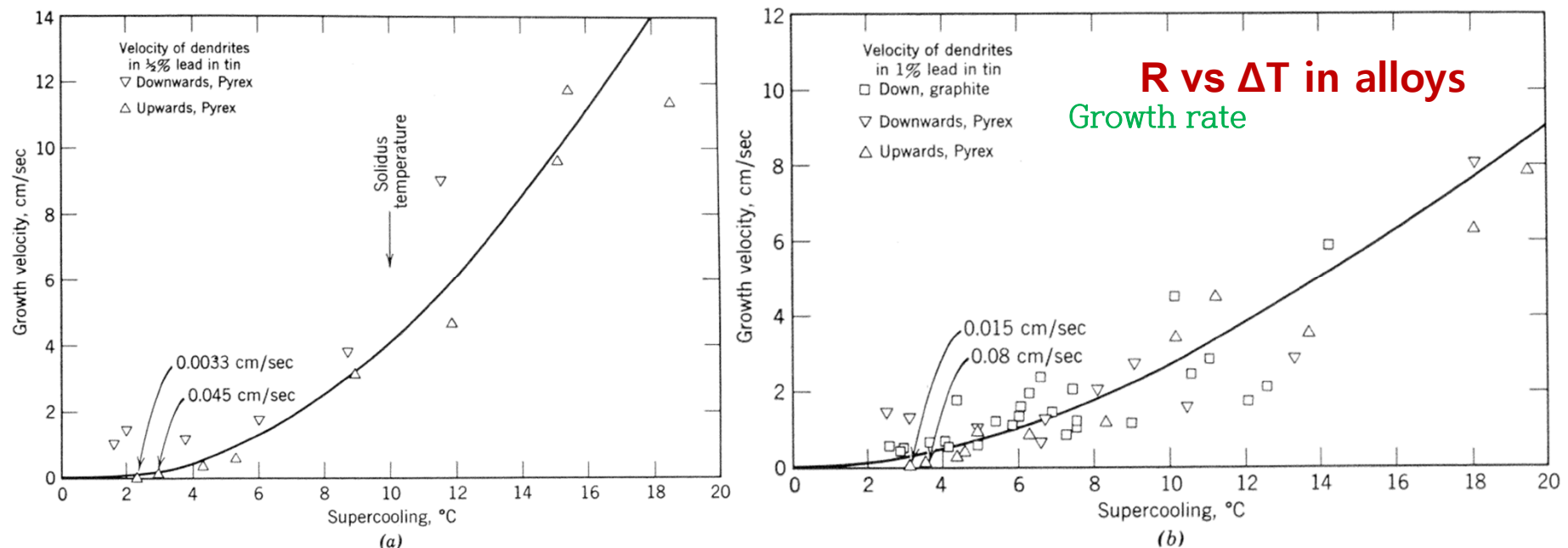


Fig. 5.40. Rate of growth of free dendrites of Pb-Sn in supercooled liquid (a) Tin with 1/2 percent lead, (b) tin with 1 percent lead.

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) $\uparrow \rightarrow S \downarrow$

(\because Solute's diffusion time is small)

② as the eutectic composition is approached $\rightarrow S \downarrow$

(\because 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.

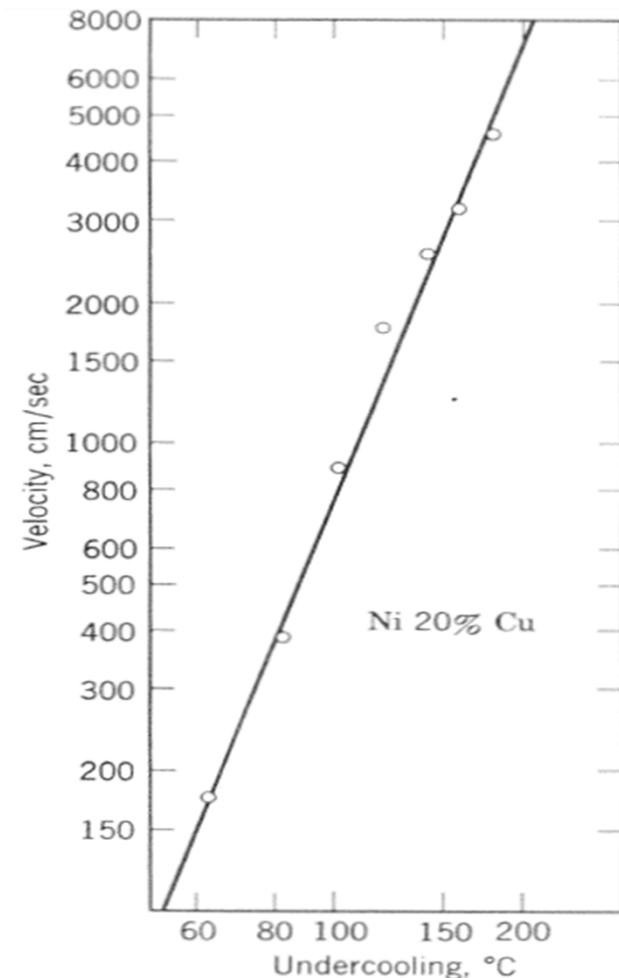


Fig. 5.40. Rate of growth of free dendrites in a supercooled melt of Ni-0.20% Cu

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 T_e ↓) & 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.

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).

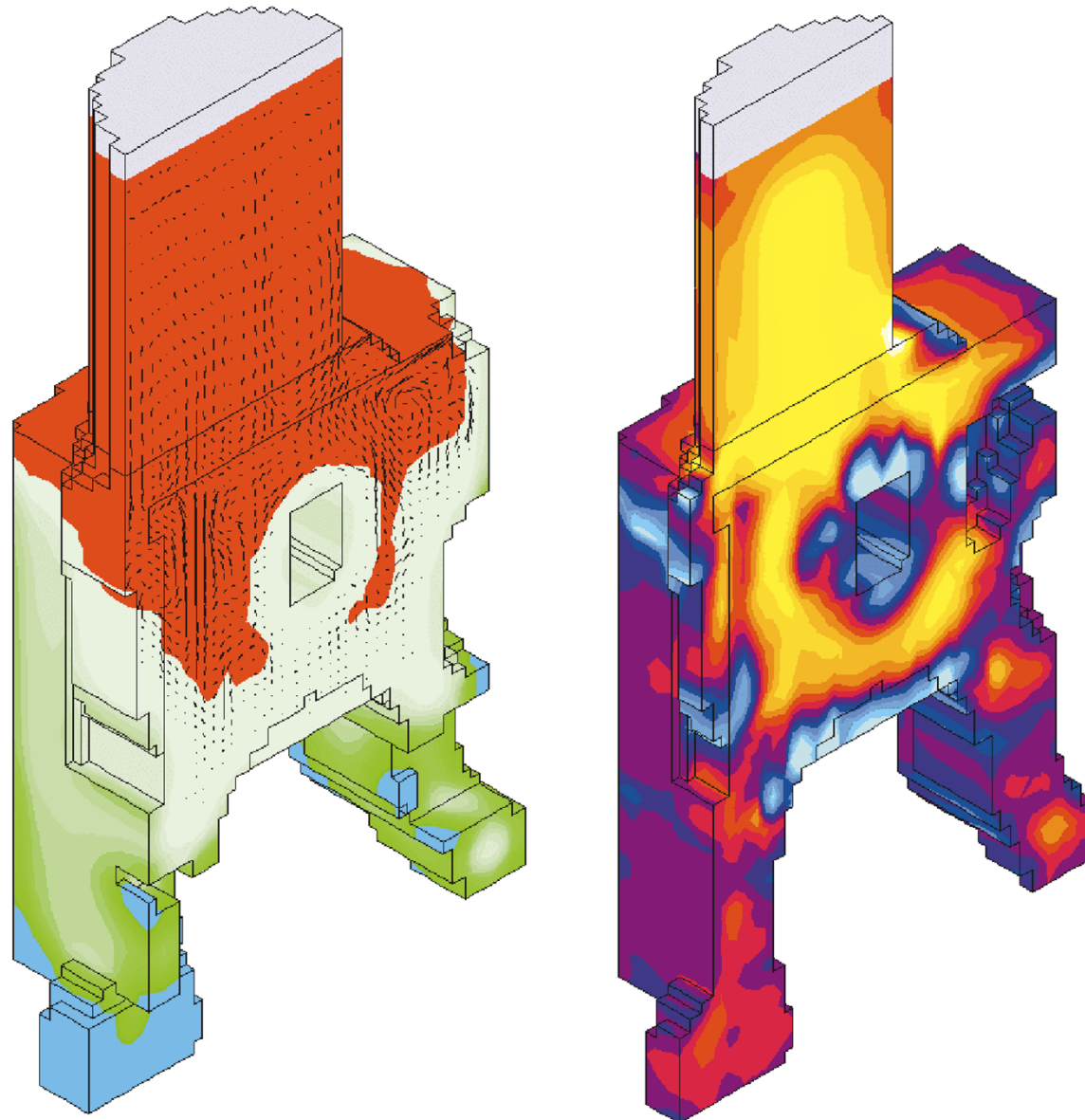


Fig.

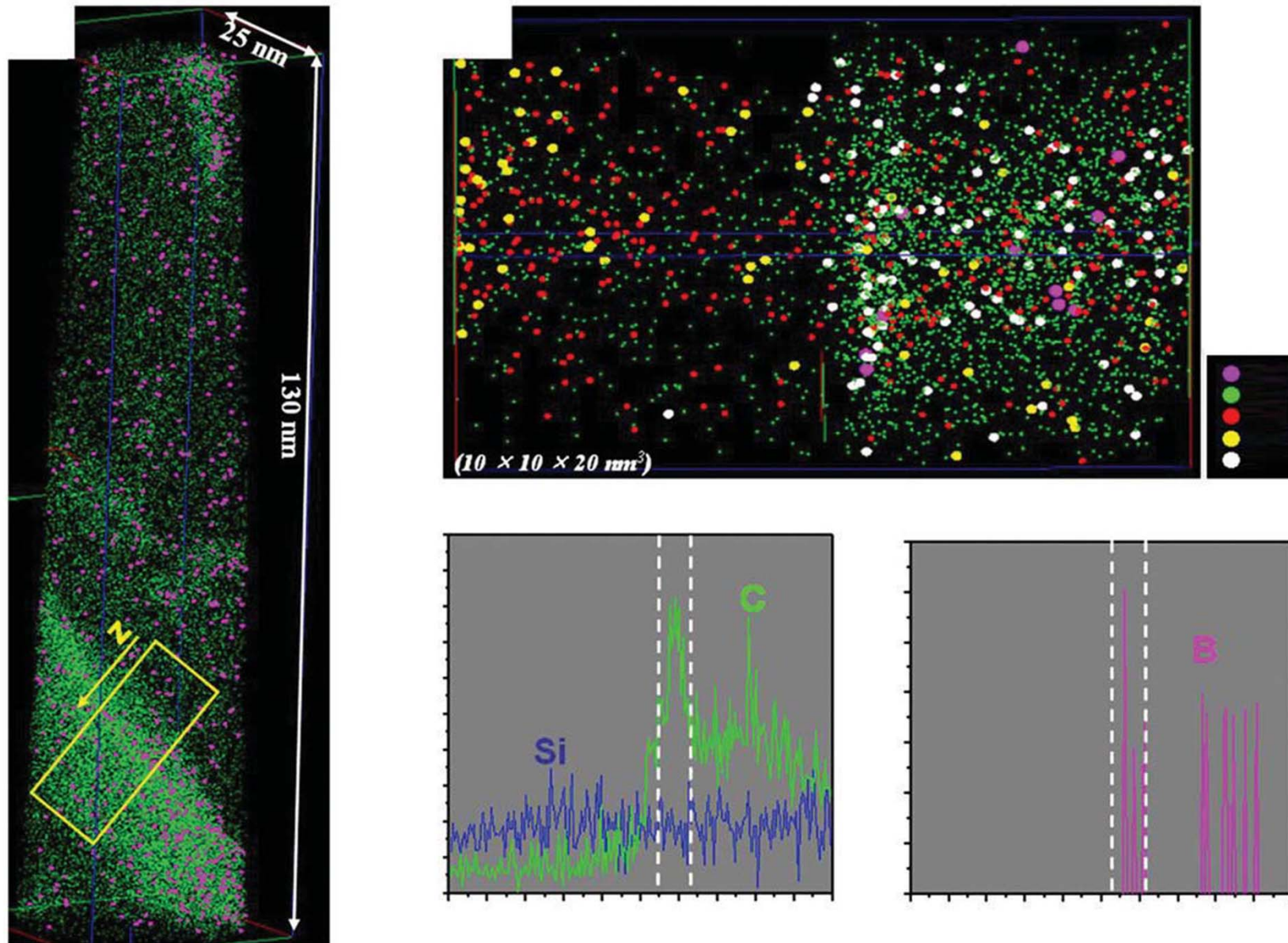
Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a single freckle (right) (courtesy of A. F. Giamei, United Technologies Research Center).



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

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

: undesirable ~ deleterious effects on mechanical properties

→ subsequent **homogenization heat treatment**, but diffusion in the solid is too slow

→ **good control of the solidification process**