2017 Fall

"Calculation and Applications Phase Equilibria"

Principles *of* Solidification

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Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

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

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).

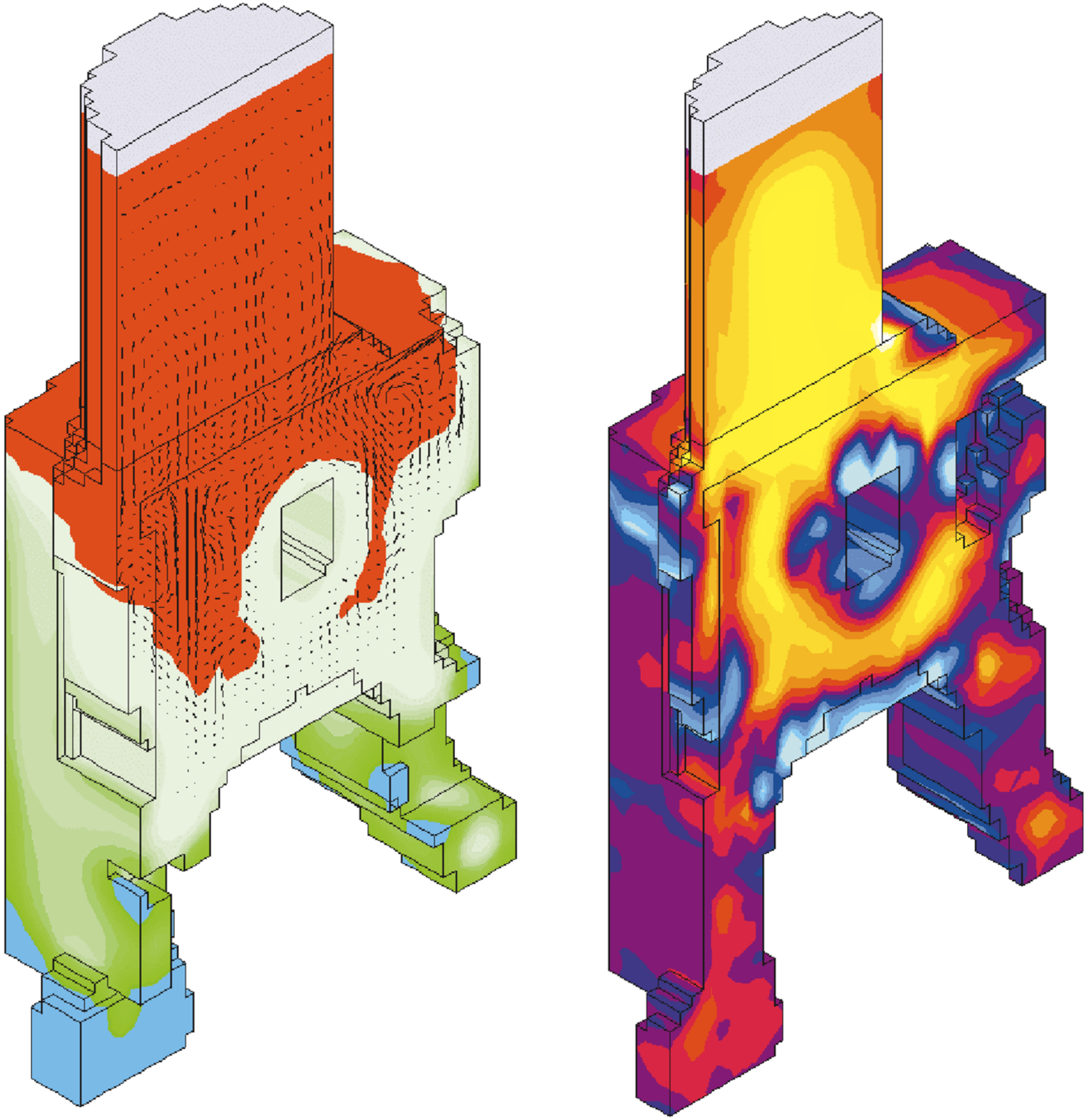


Fig.

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).

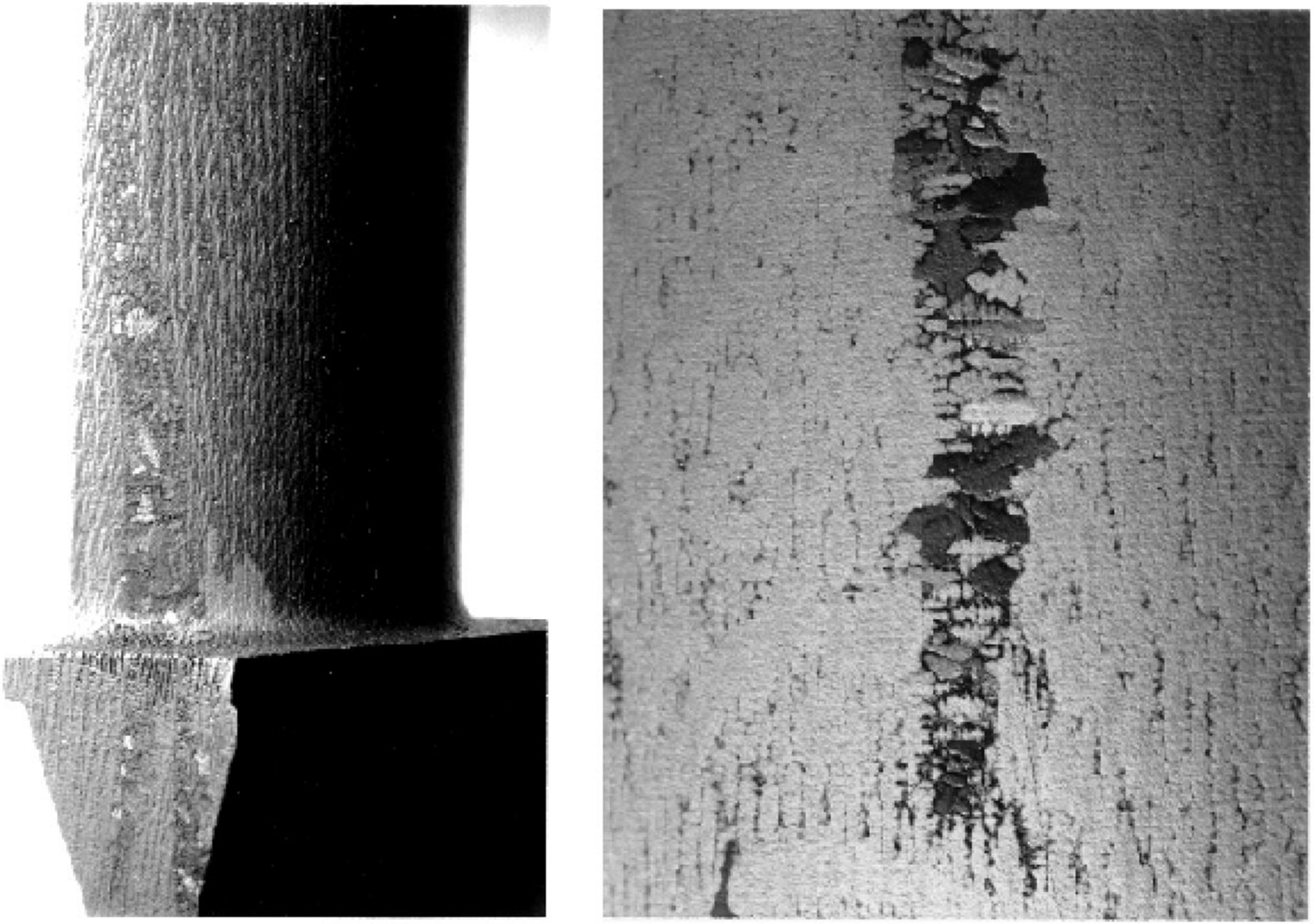
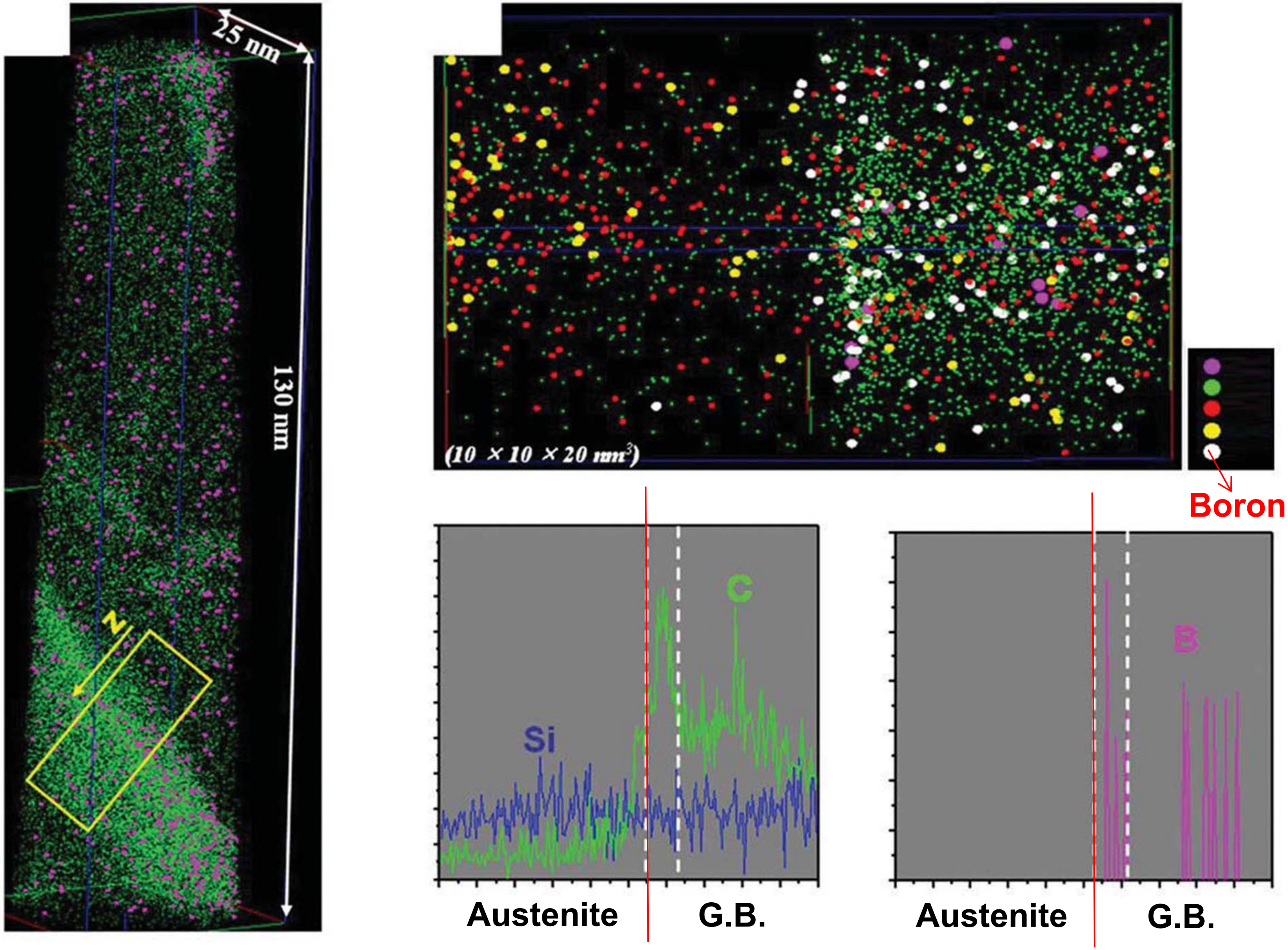


Fig.

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**

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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

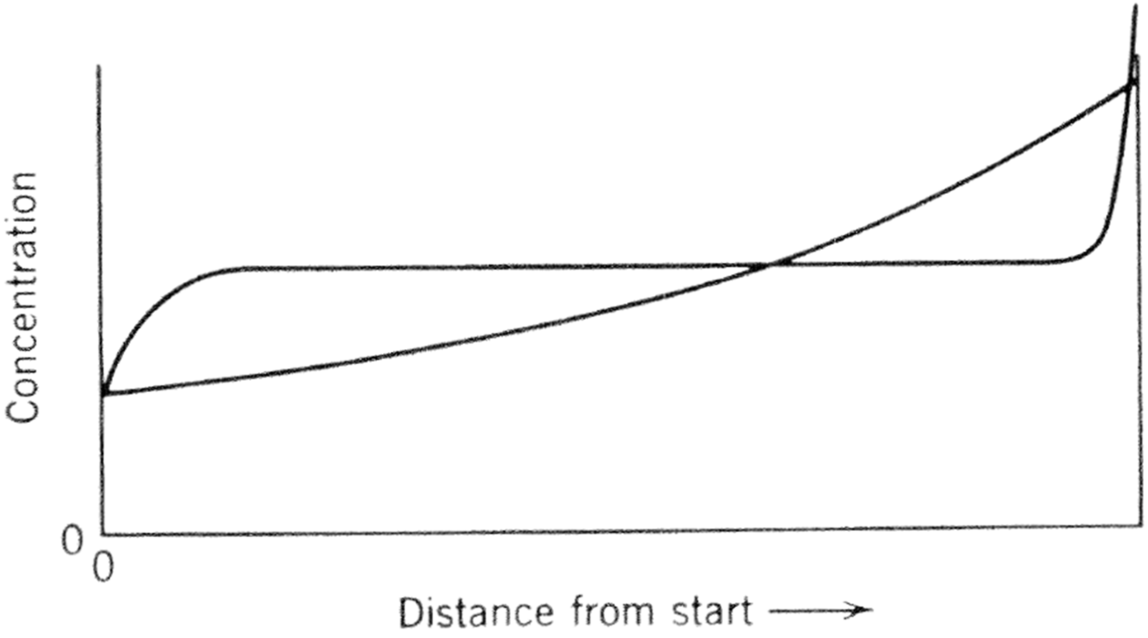

Fig. 5.42. Extreme cases of normal segregation

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

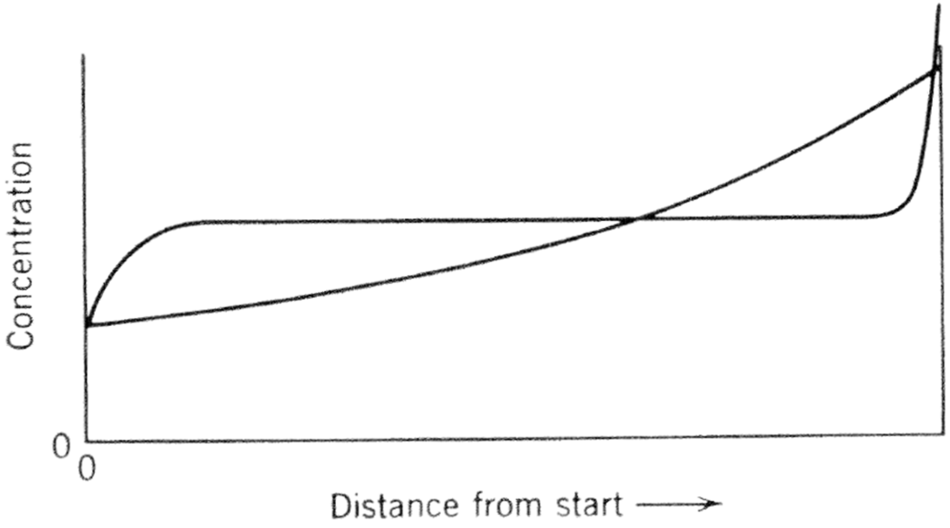
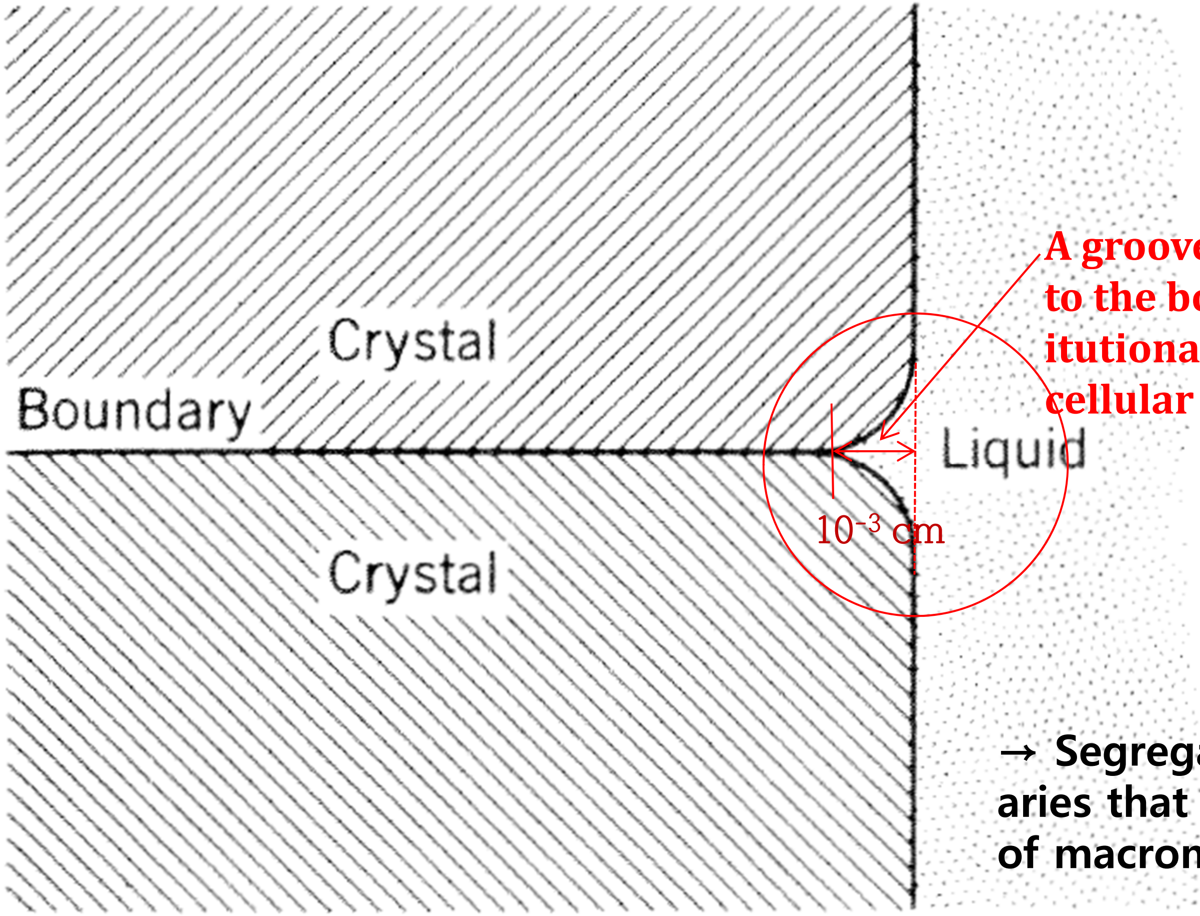


Fig. 5.42. Extreme cases of normal segregation

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

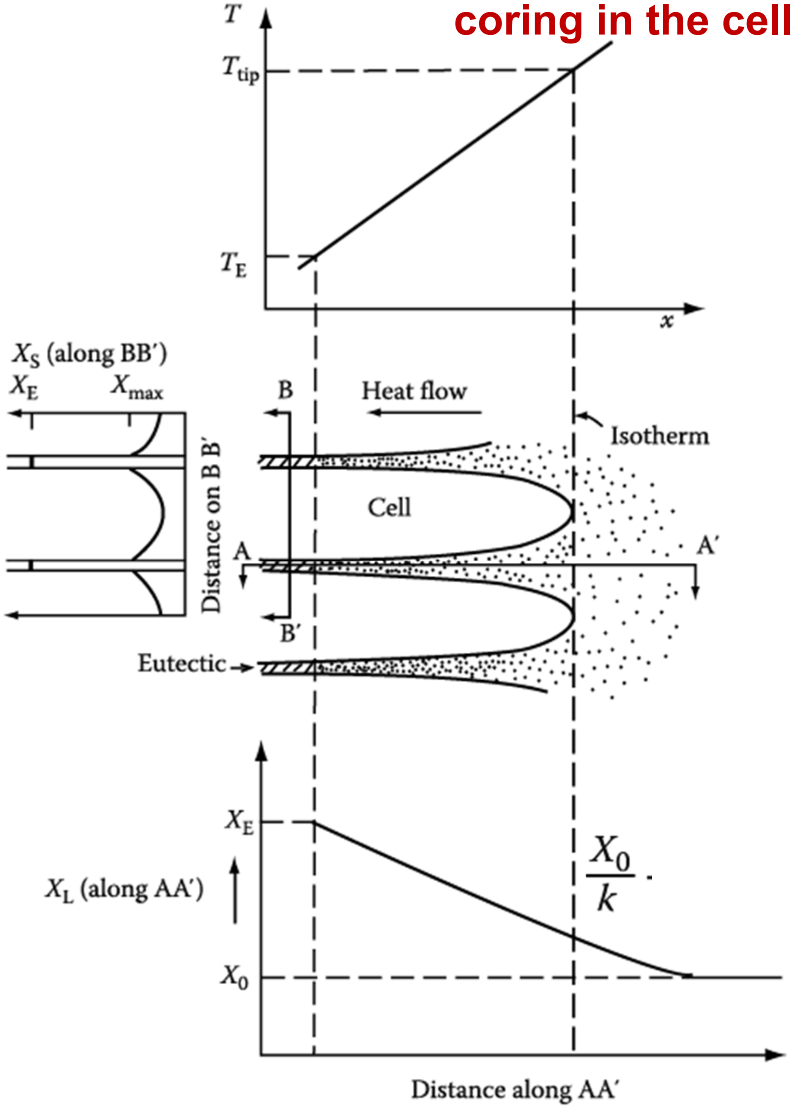
Fig. 5.43. Conditions for grain boundary segregation

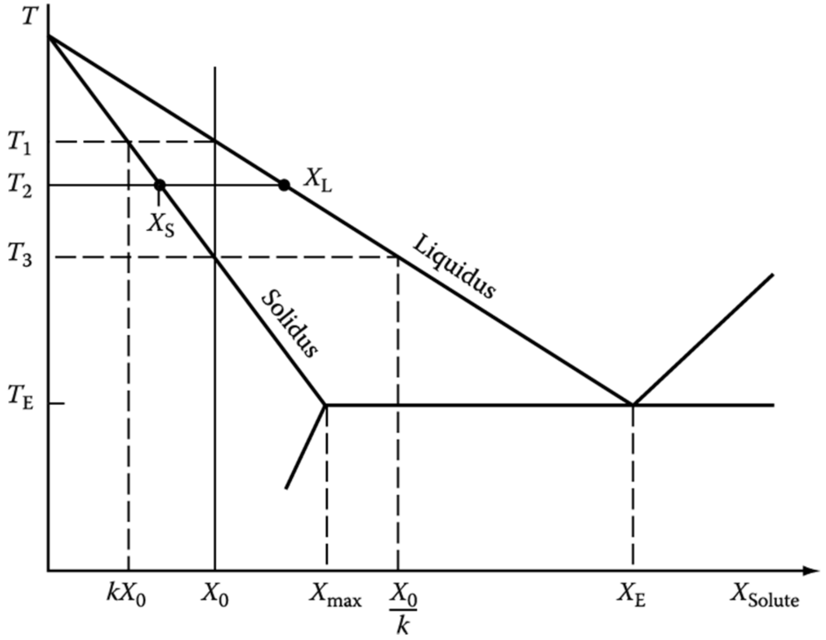
3) Cellular segregation

: 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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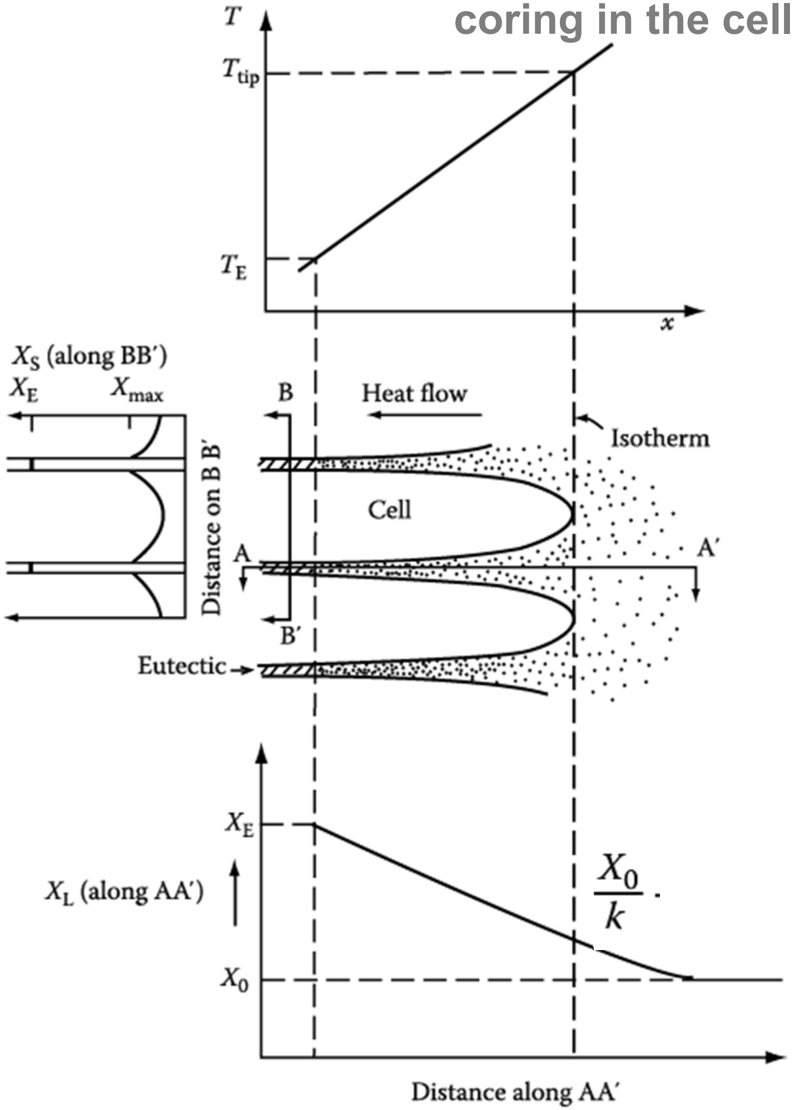


2) Tips of the cells grow into the hottest liquid and therefore contain the least solute.

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

- **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.

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.

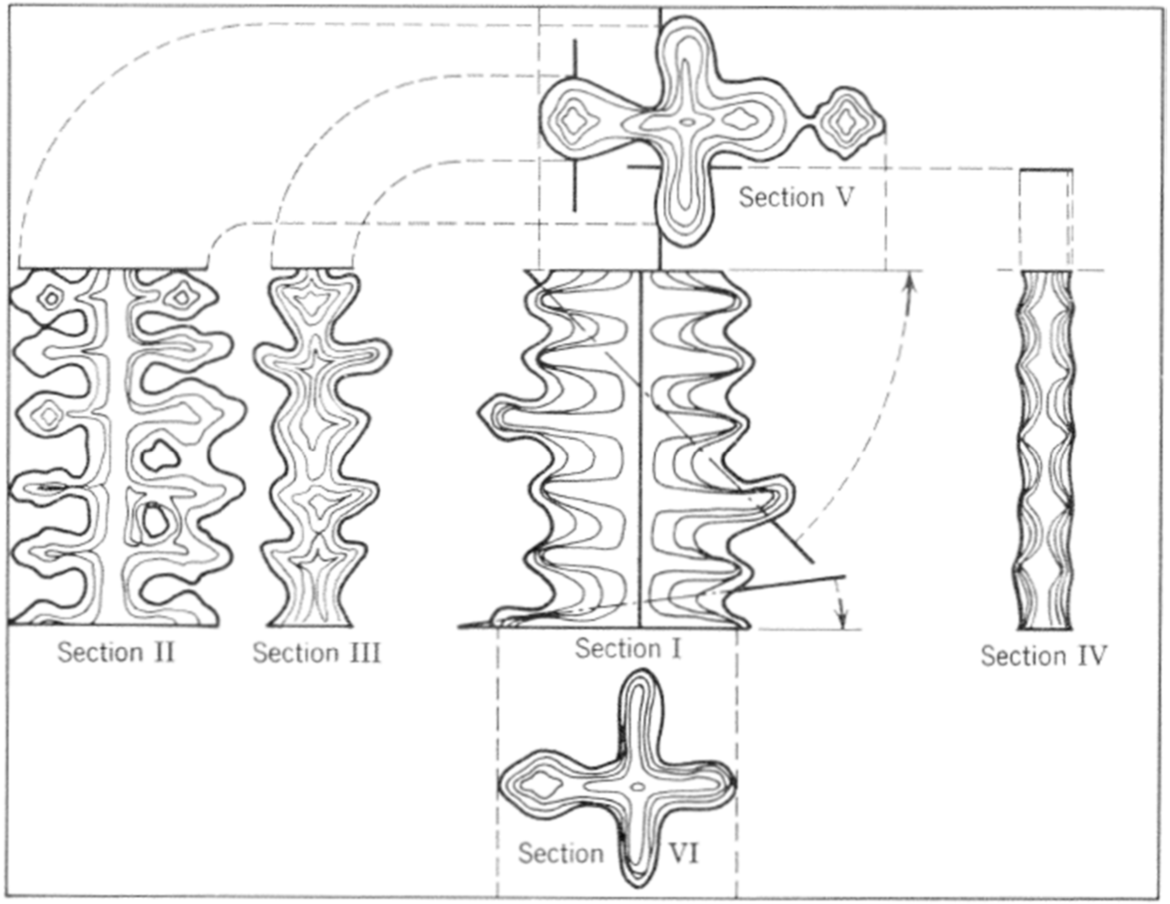


Fig. 5.46. Quantitative results on distribution of solute in columnar dendritic crystal

4) Dendritic segregation

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

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

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

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.

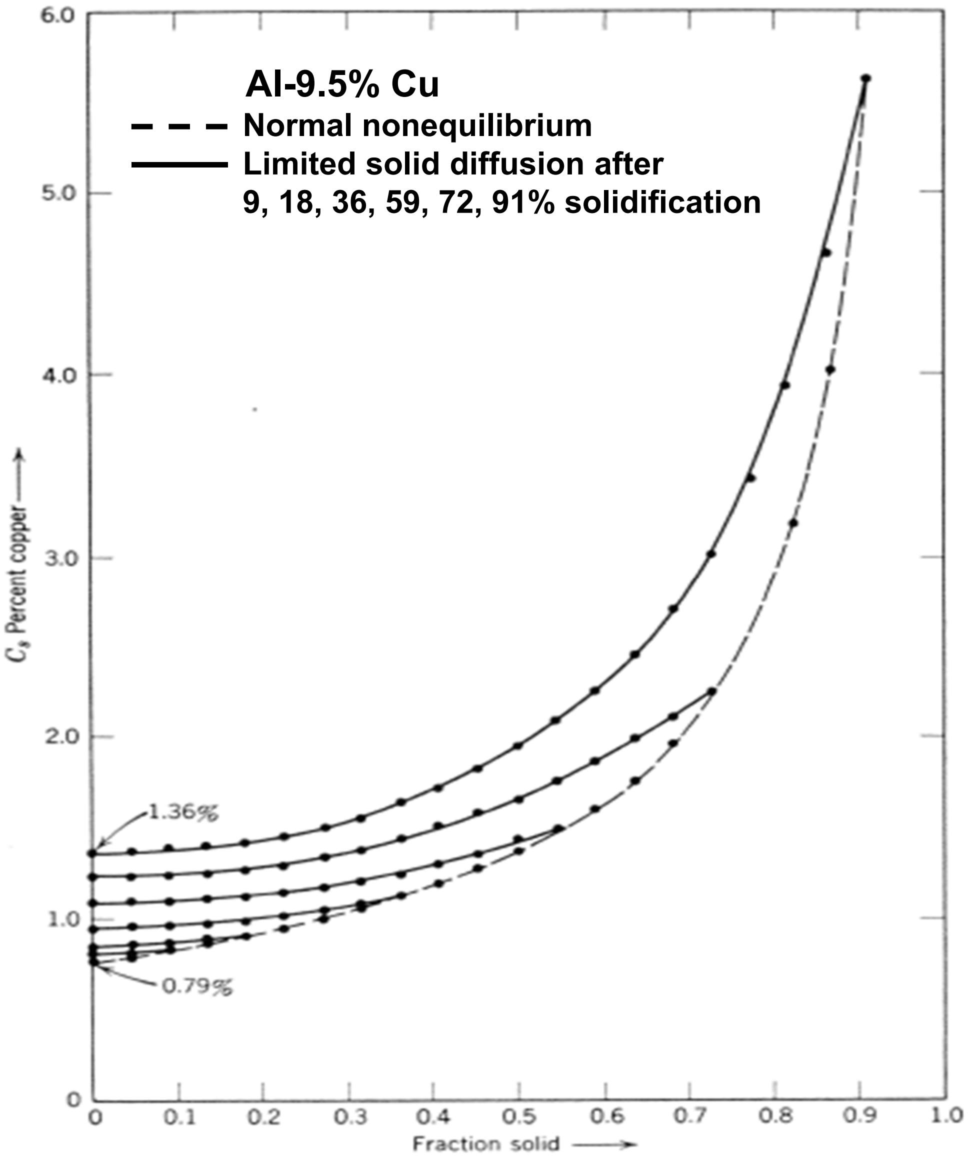
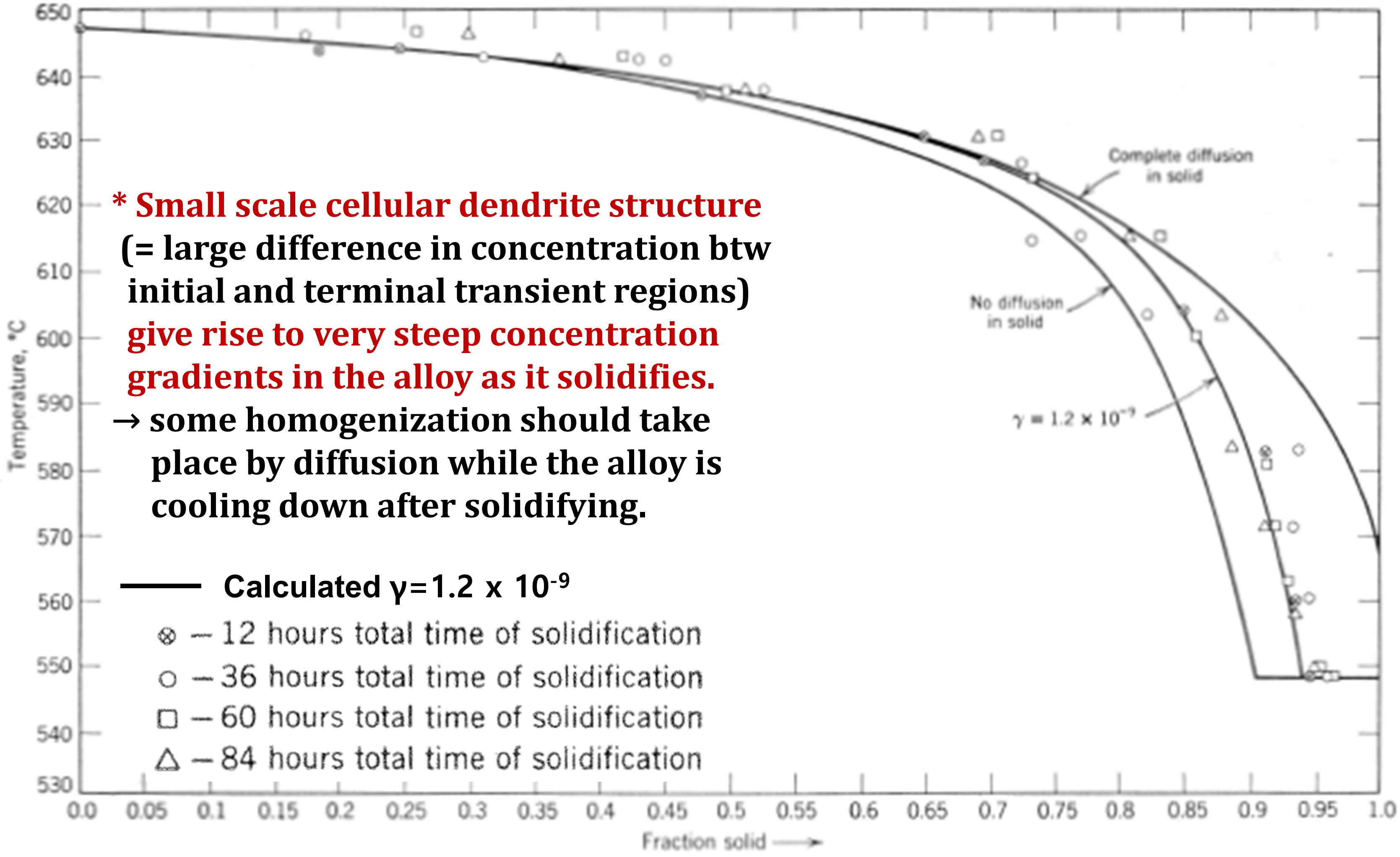


Fig. 5.47. Calculated distribution of solute between walls of cellular dendritic structure

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.

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.**

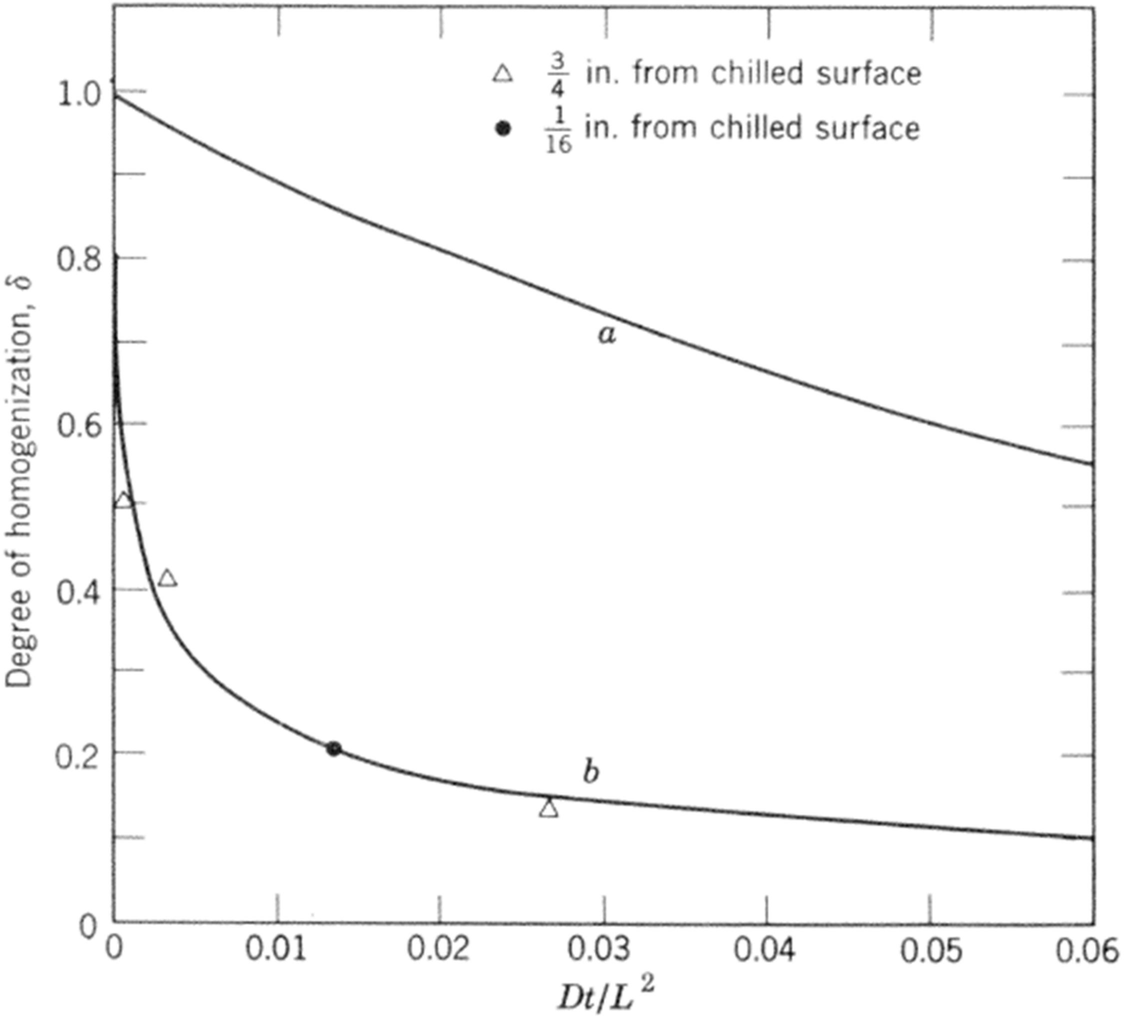


Fig. 5.49. Experimental and calculated results for homogenization during cooling.

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.**

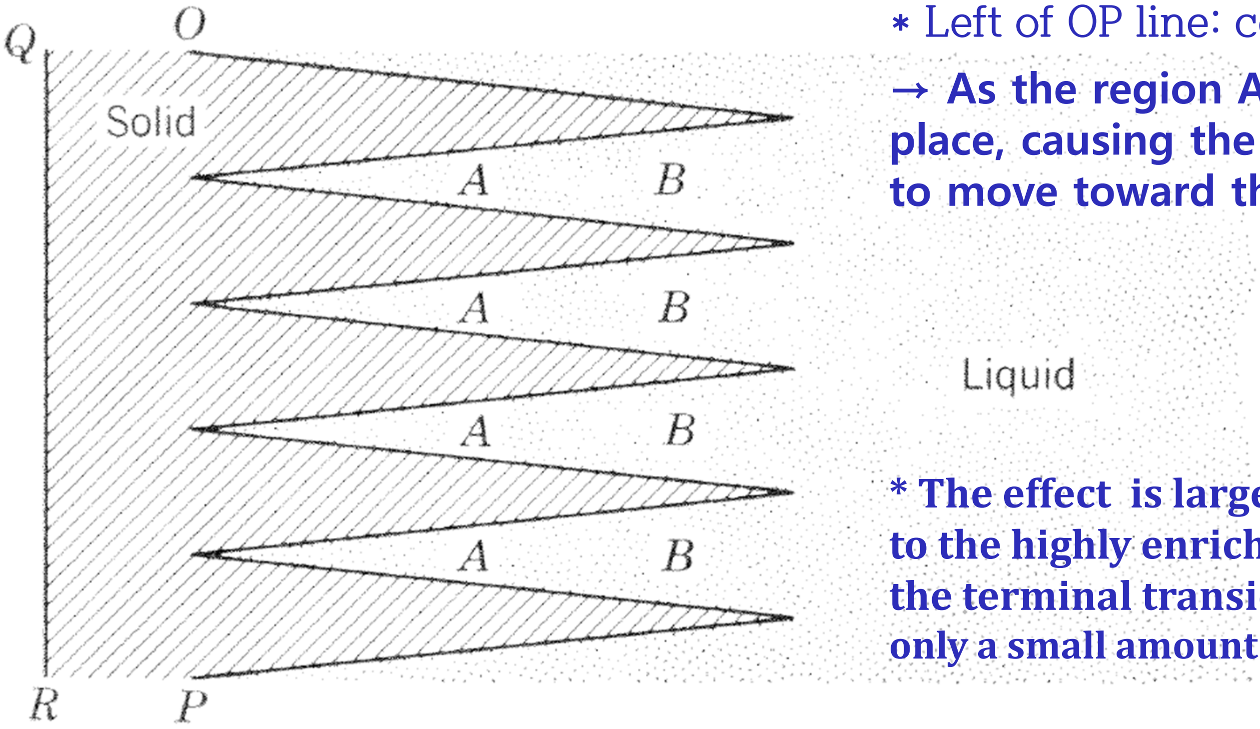


Fig. 5.50. mechanism of inverse segregation

* 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.**

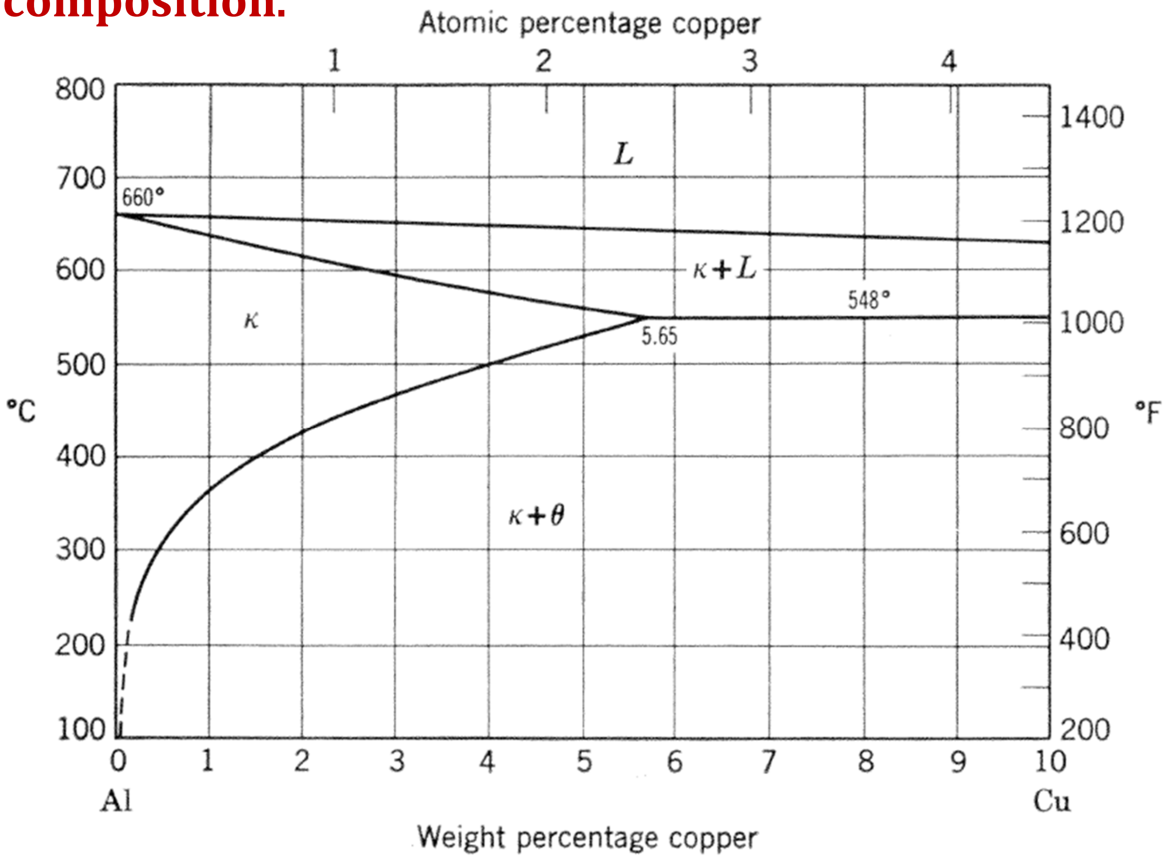


Fig. 5.51. Part of the phase diagram for the Cu-Al system.

* **Good agreement btw theory and experiment in inverse segregation of Al-Cu alloy.**

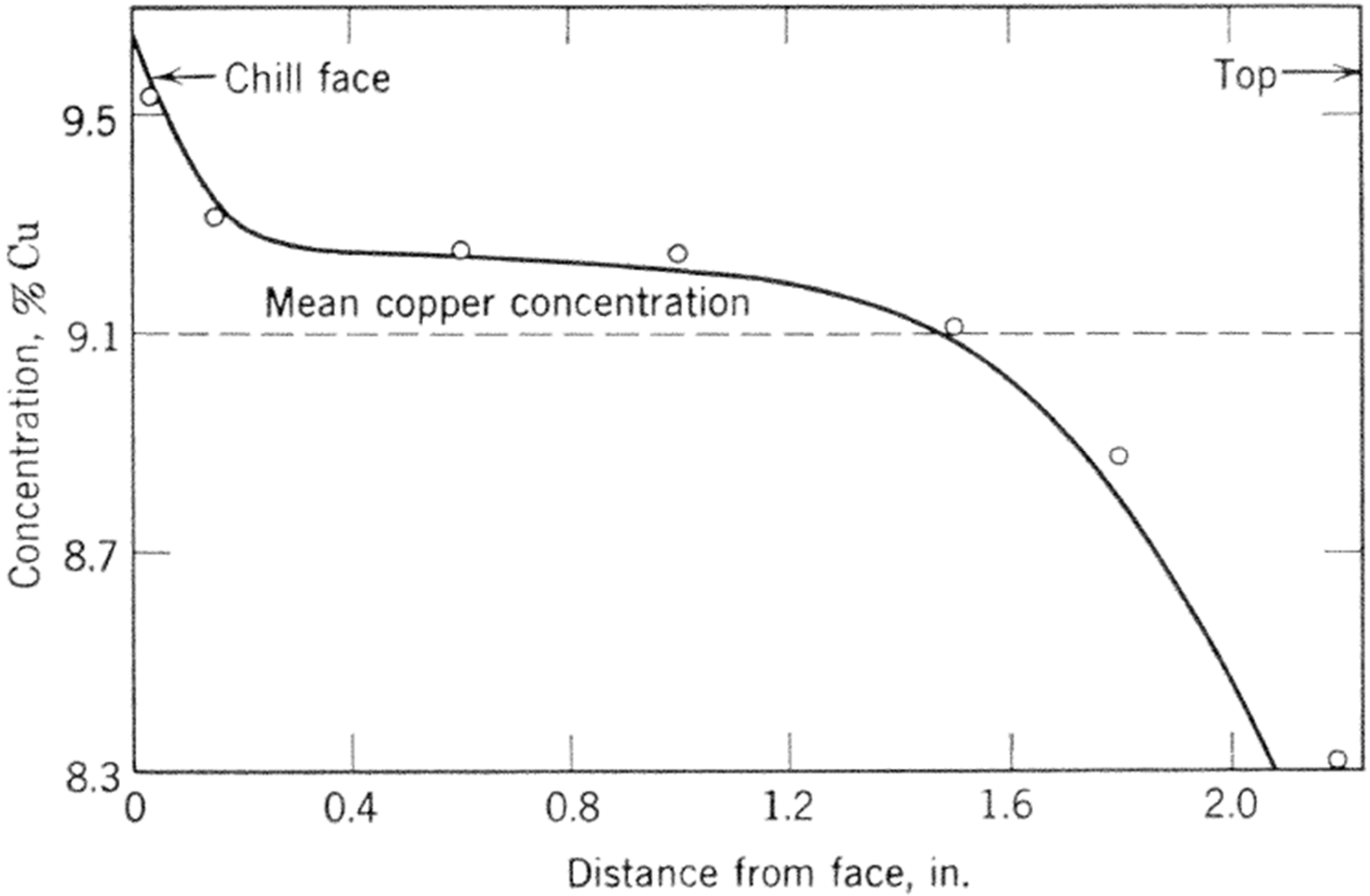


Fig. 5.52. Comparison between experimental and calculated inverse segregation in Al-Cu.

∗ 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.

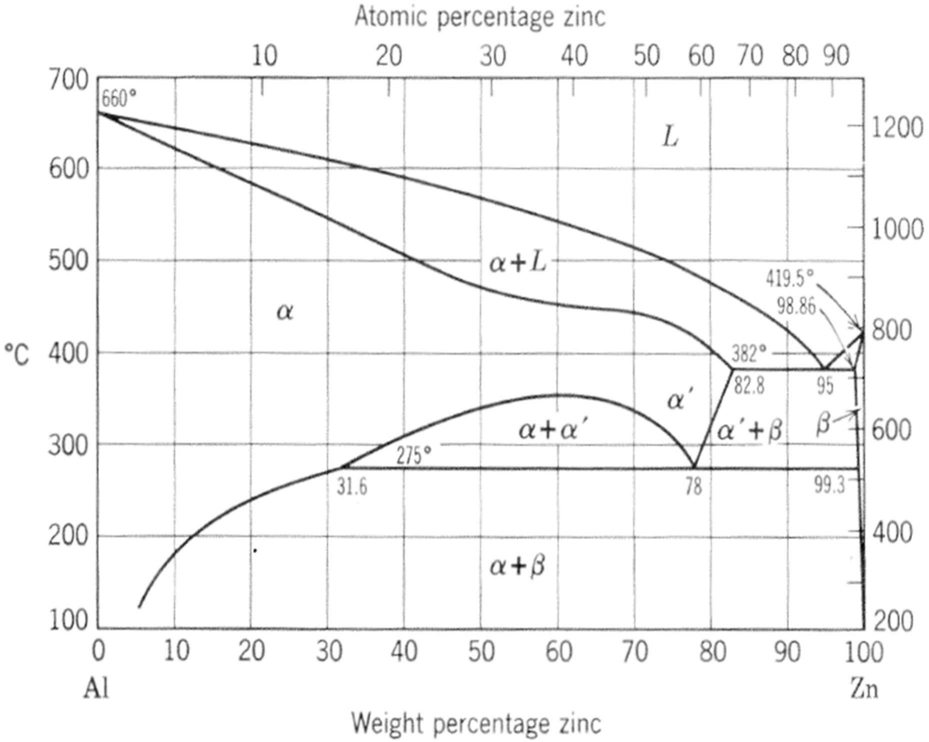


Fig. 5.53. Part of phase diagram for the Al-Zn system

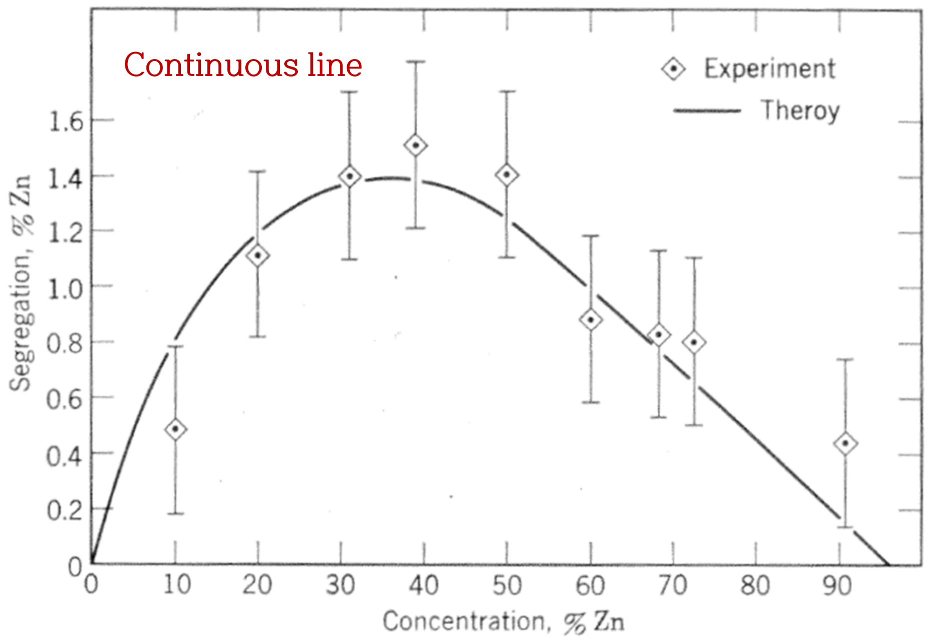
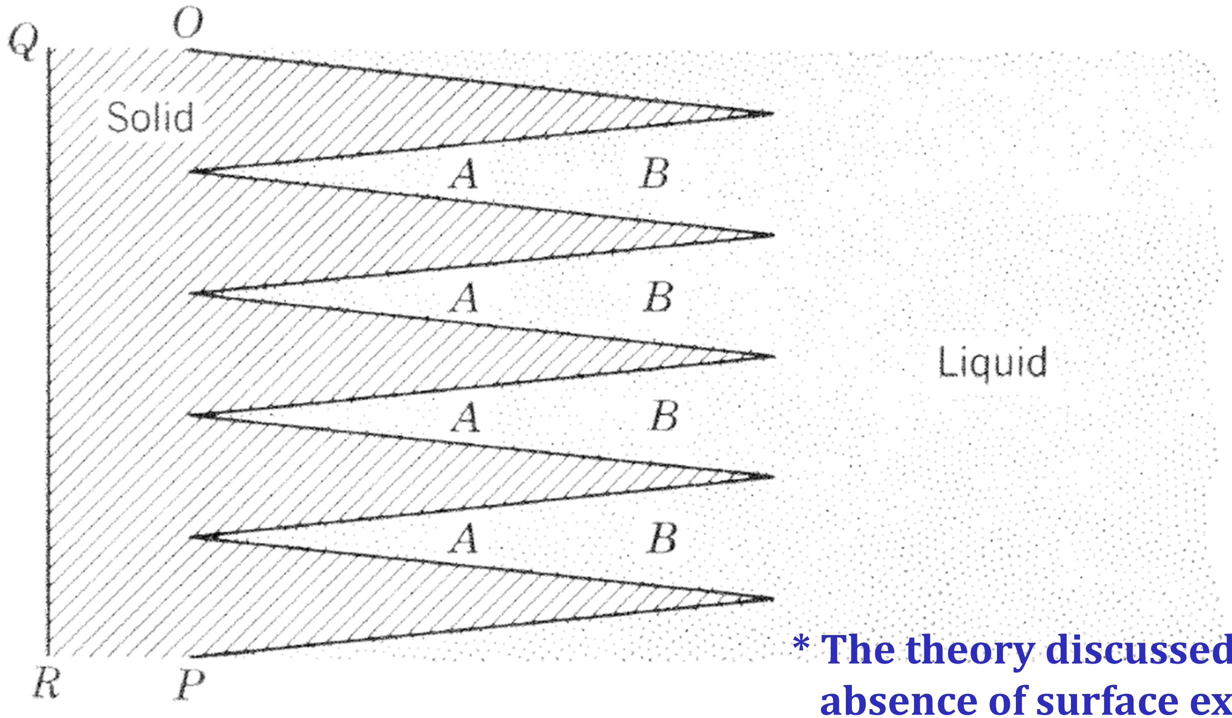

Continuous line

Fig. 5.54. Predicted and measured inverse segregation in Al-Zn

5) Inverse segregation

* A much more drastic form of inverse segregation 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 mod, in the form of small "drops", known as "sweat", which are usually much harder than the neighboring metal due to their high alloy conent.



* 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 normal segregation was developed from a macroscopics point of view. → **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 the terminal regions where two or more crystals 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

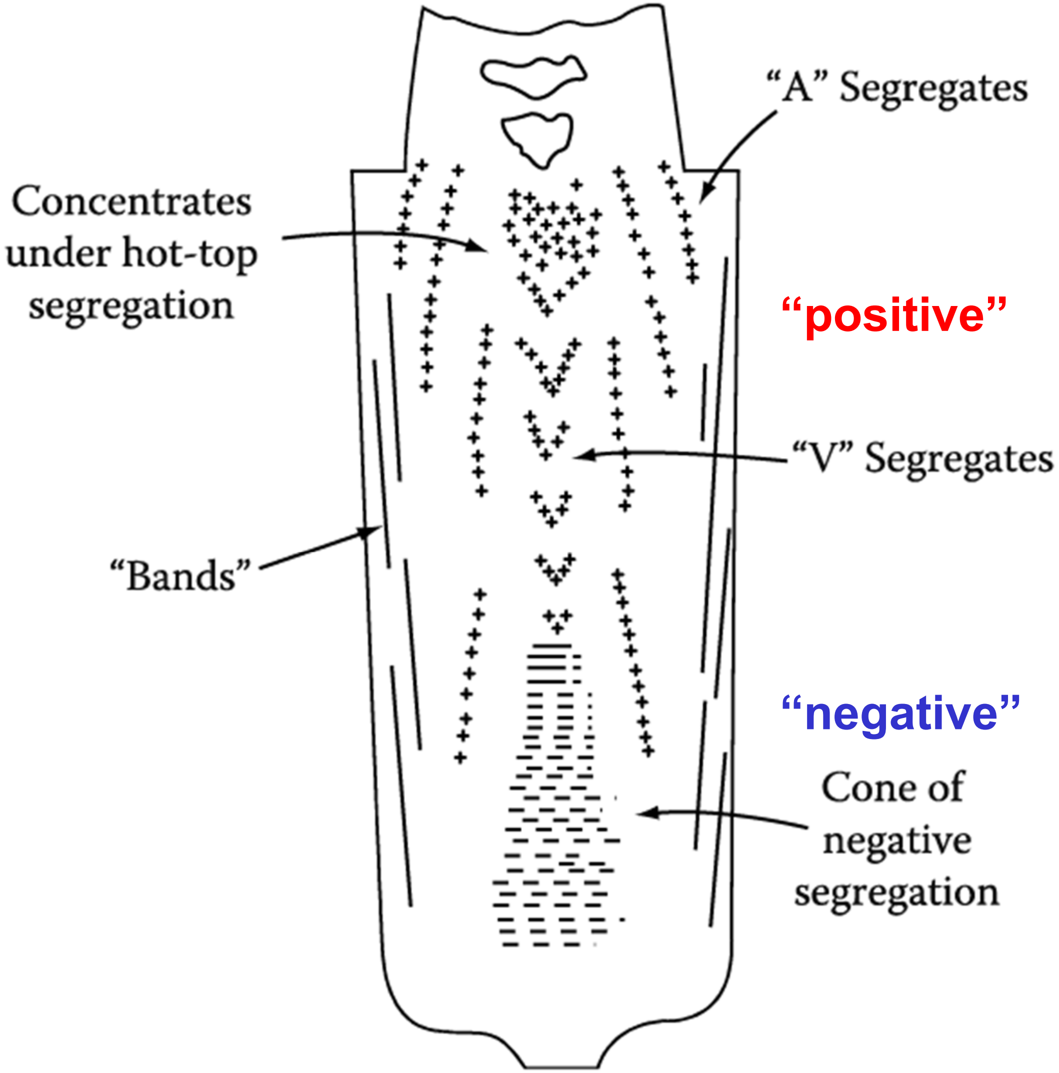


Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.)

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)

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

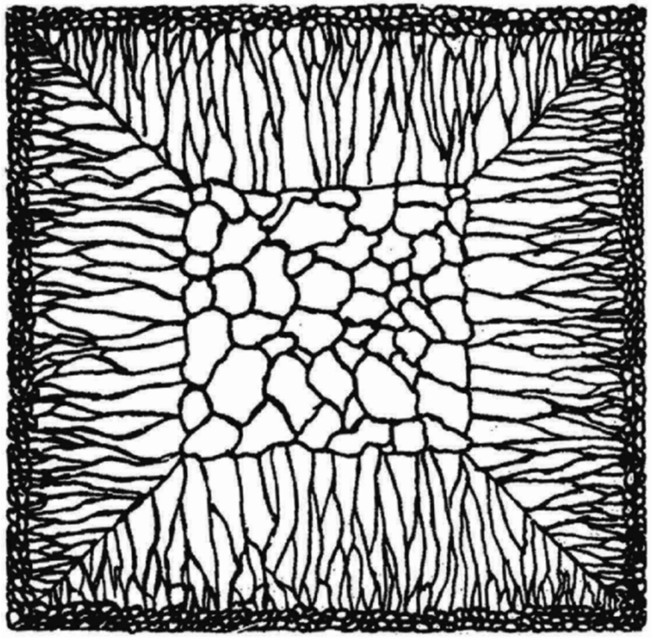
a lump of metal, usually shaped like a brick.

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

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

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.

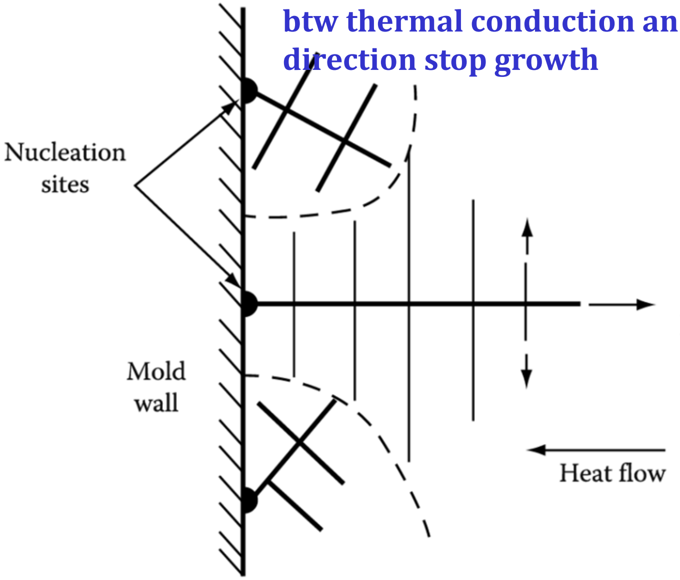
1) **If the pouring temp. is low**: liquid~ rapidly cooled below the liquidus temp. → **big-bang nucleation** → **entirely equiaxed ingot structure**, no columnar zone

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

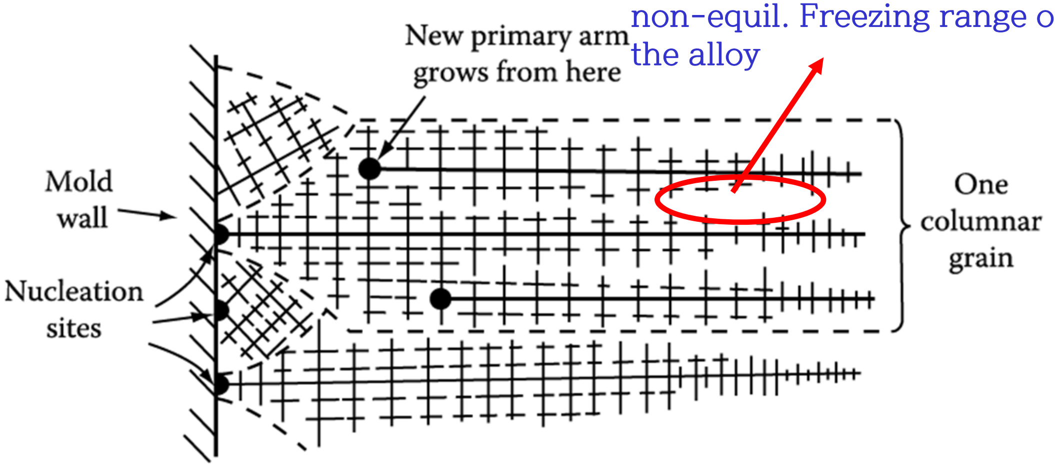
After pouring the temperature gradient at the mould walls decreases and the crystals in the chill zone grow dendritically in certain crystallographic directions, e.g. <100> in the case of cubic metals.

→ grow fastest and outgrow less favorably oriented neighbors



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

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.



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

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

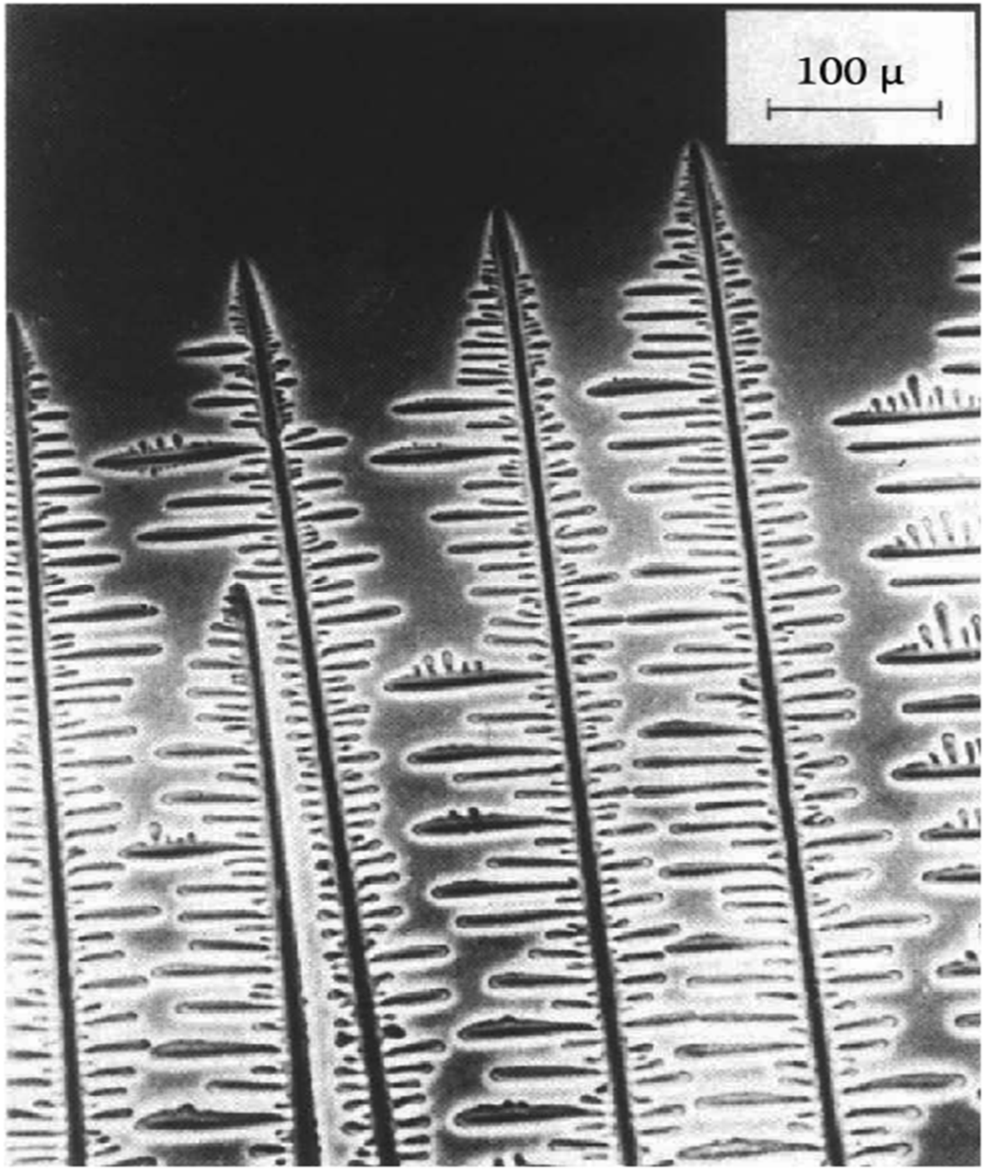


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(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

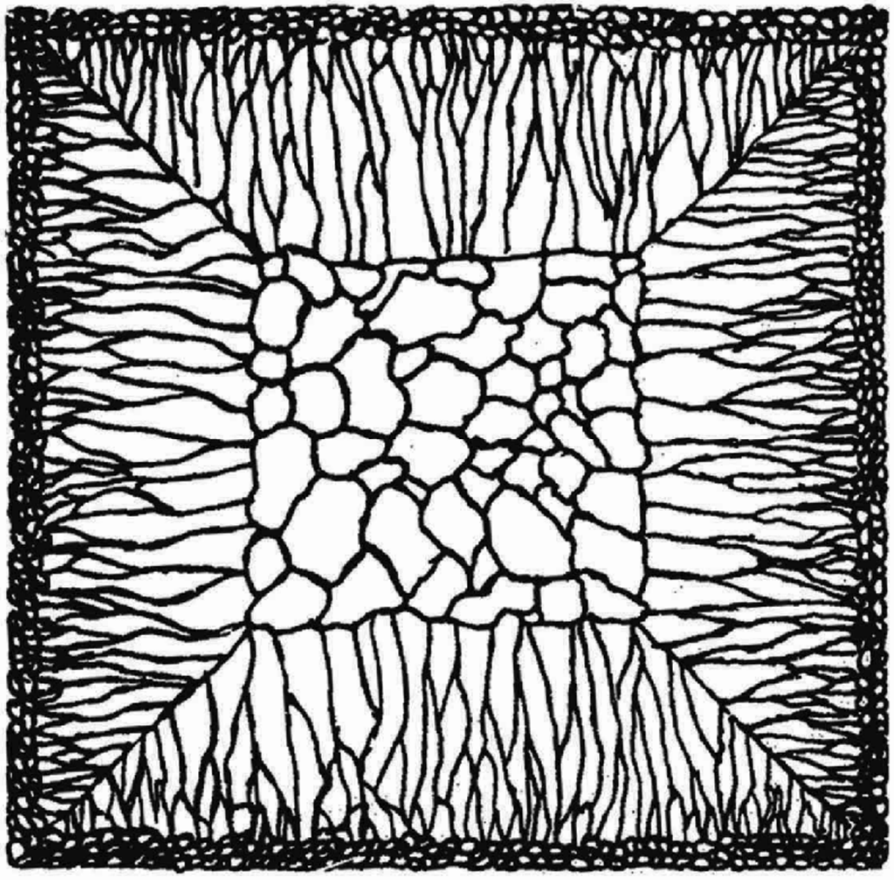
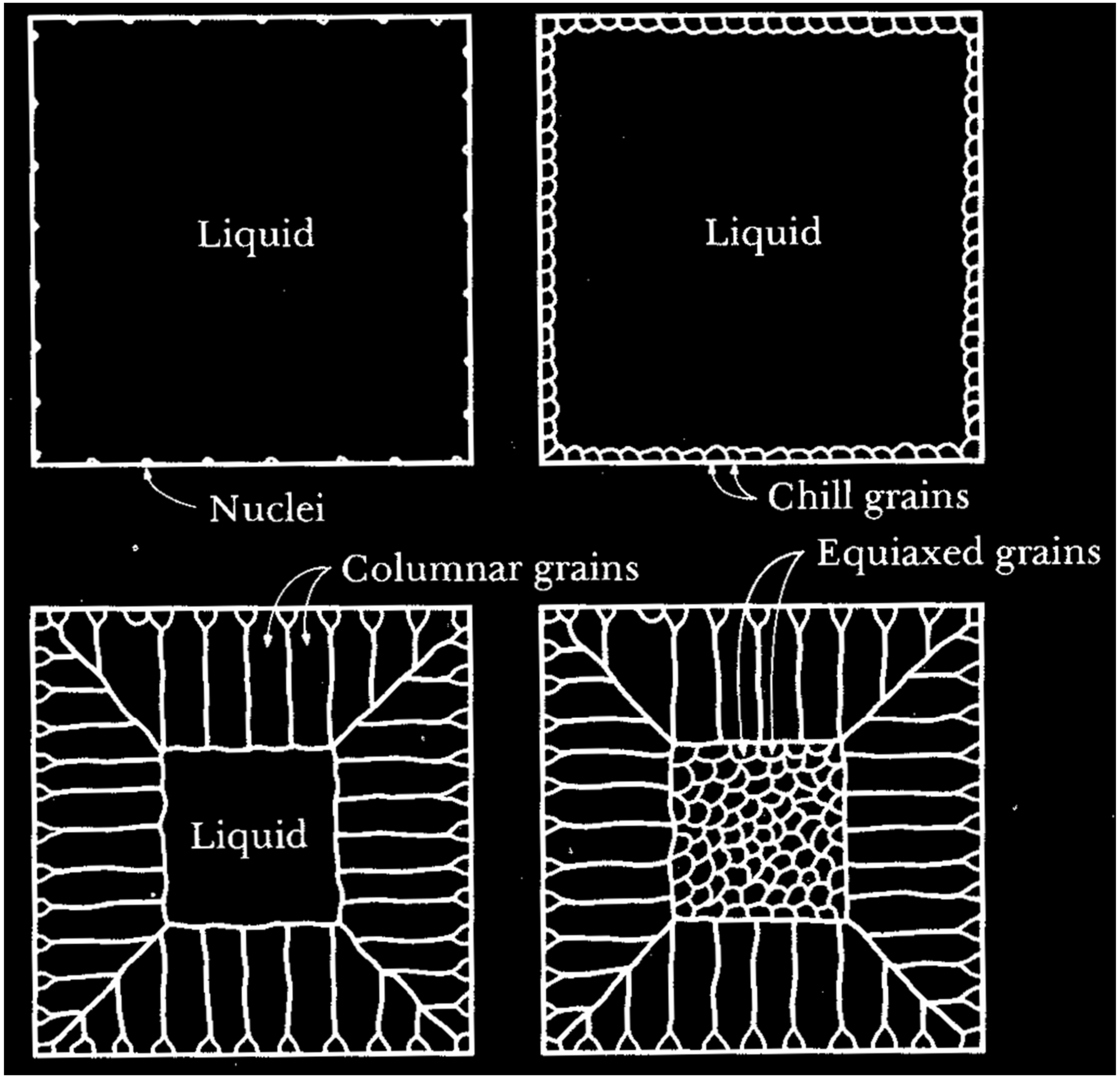


Fig. 4.40 Schematic cast grain structure.

(After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.)


Liquid
Liquid
Nuclei
Chill grains
Columnar grains
Equiaxed grains
Liquid