2018 Fall

Advanced Solidification

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7. Macroscopic Heat Flow and Fluid Flow

7.2. Fluid Flow

* The ability of a molten metal to flow =

(1) poured from a container in which it was melted into a mold in which it is to solidify.

: effect of the macroscopic geometry of the casting (Chapter 7)

(2) Relative motion of different parts of the liquid can occur while it is solidifying.

: its implications in relation to the structure of the solidified metal (Chapter 8)

1) Viscosity of liquid metal

liquid metal : “Flow rate depends on the force” = “shear rate is proportional to the shear stress”

→ To compare “rates of flow”,

Reynolds’ number = $\gamma v l / \mu$

γ = density , v = velocity,
μ = viscosity, l = linear dimension

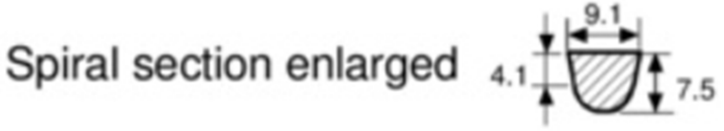
* If the value of Reynolds’ number is <u>high</u> (>1400) for a tube leading out of a containing vessel, <u>the flow becomes turbulent</u> and Q (the quantity flowing per unit time) drops below the value that would be calculated from the formula. → Derive the “Kinematic viscosity, μ/γ” from the above equation : <u>Used for calculation of flow rate when pressure difference is caused by flowing liquid</u> → For solidification it is considered more important.

* **Fluidity:** **The ability of being fluid or free-flowing_distinguished from viscosity**

Measurement of Fluidity

: Maximum length melt can reach

(a) Fluidity Spiral



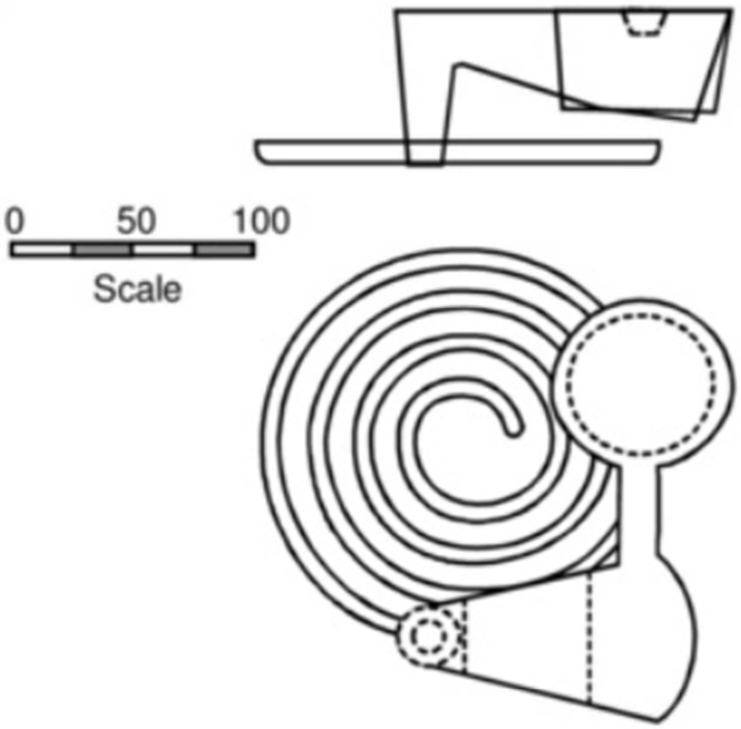
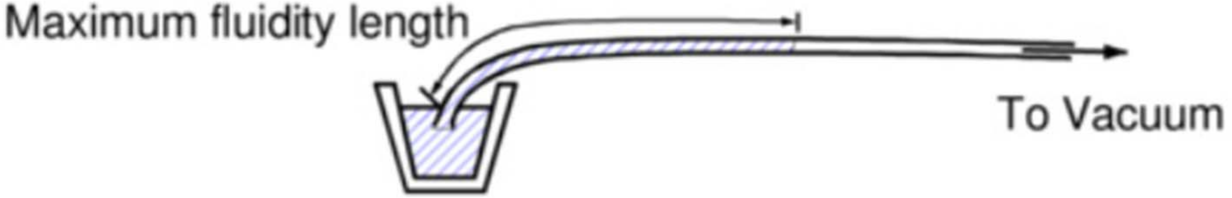


Fig. 7.1. Mold for fluidity test.

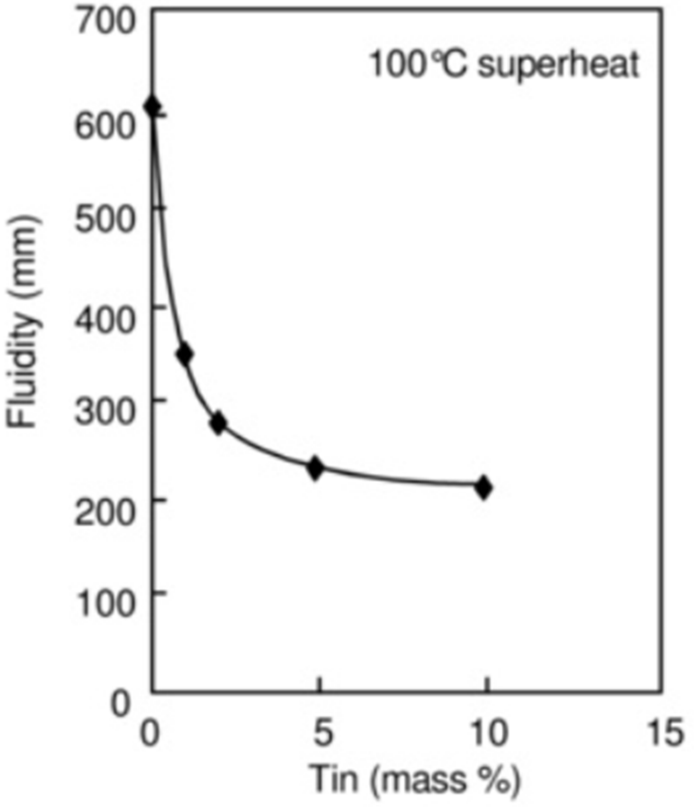
(b) Laboratory Test

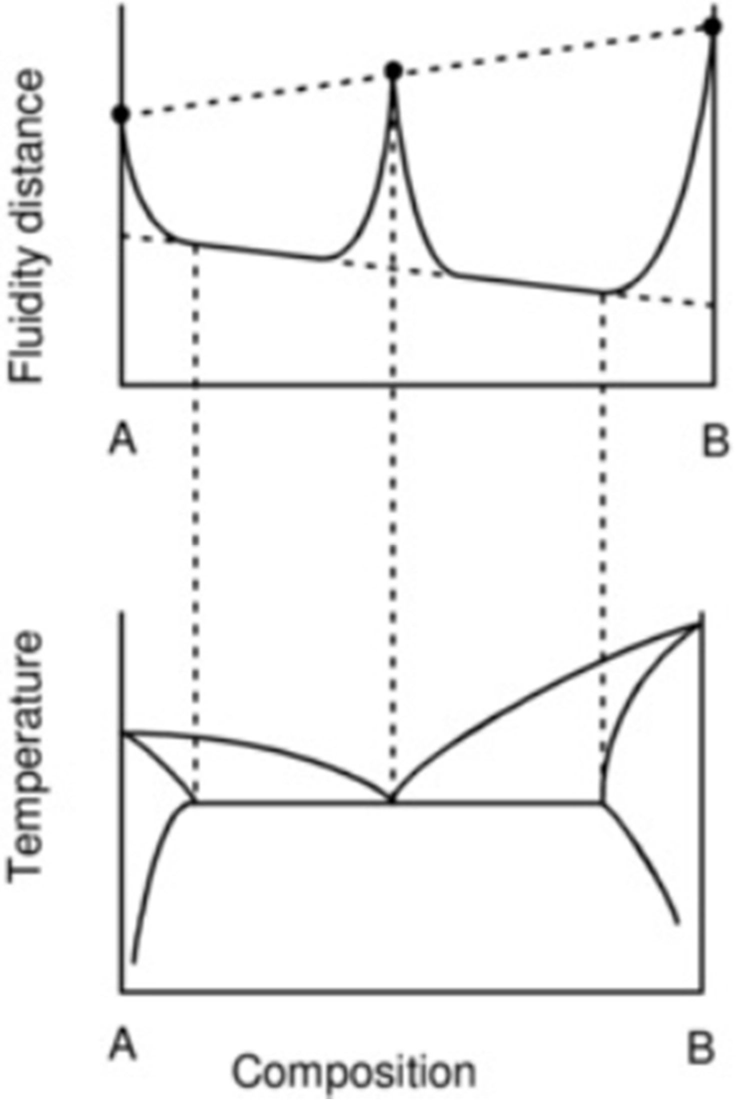


① Effect of composition

Mapping the Fluidity of Binary Alloys

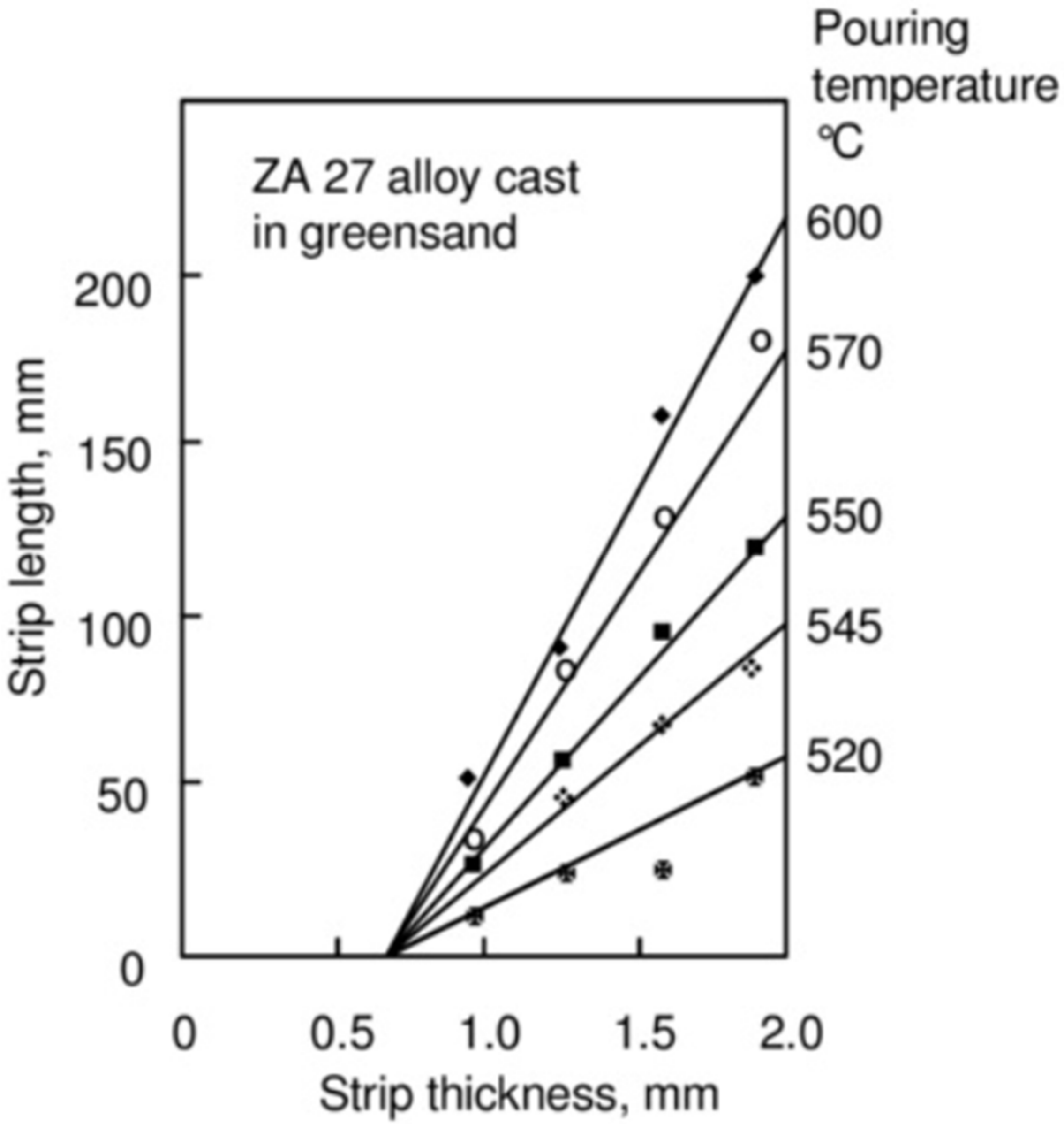
Fluidity of Al-Sn alloys



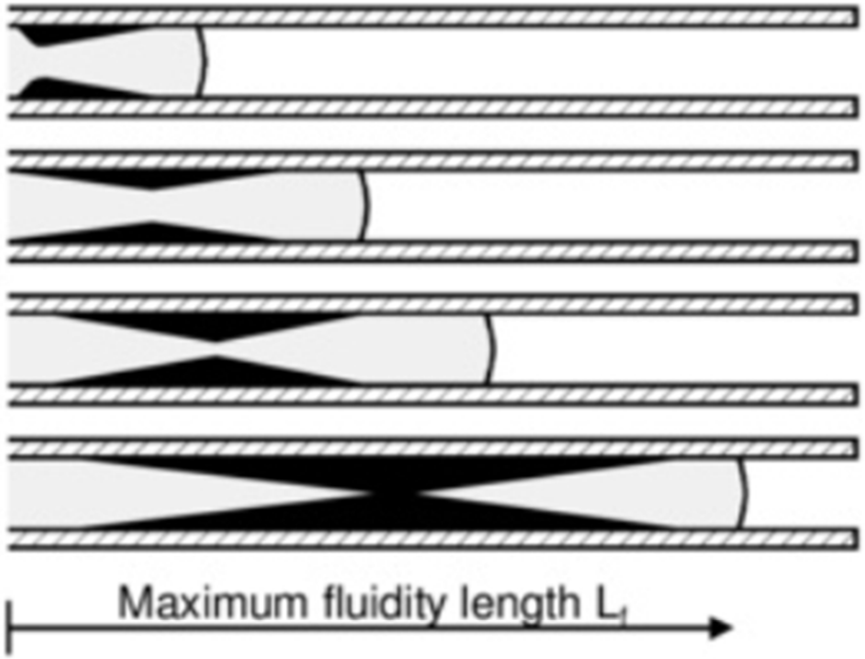


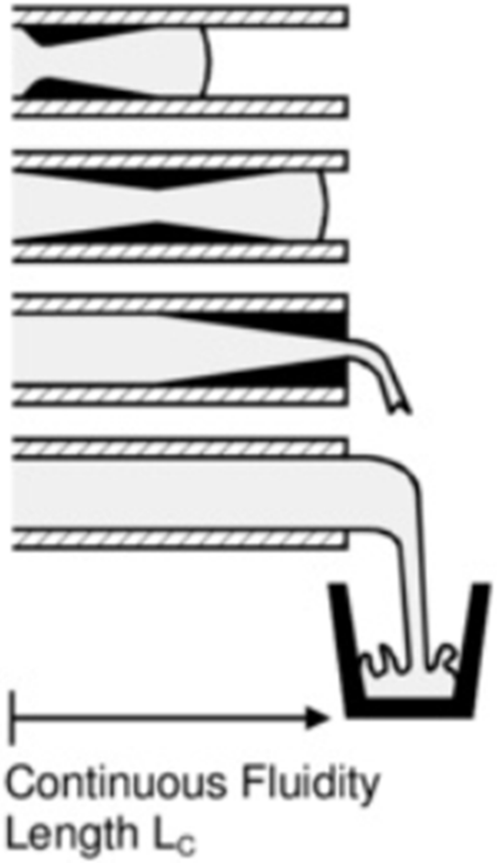
② Effect of temperature

The Fluidity of ZA 27 Zinc-Aluminum Alloy

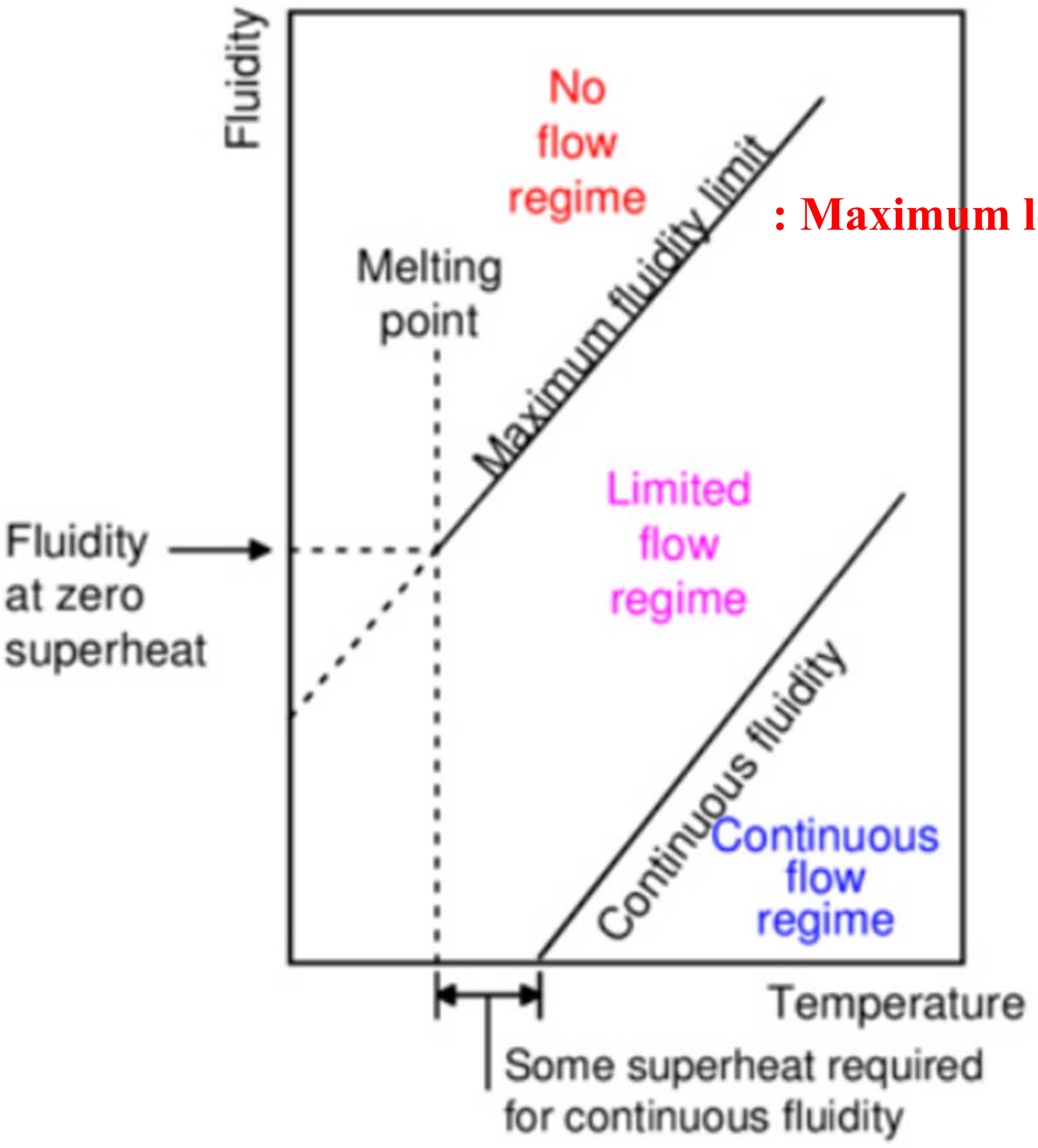


Continuous Fluidity

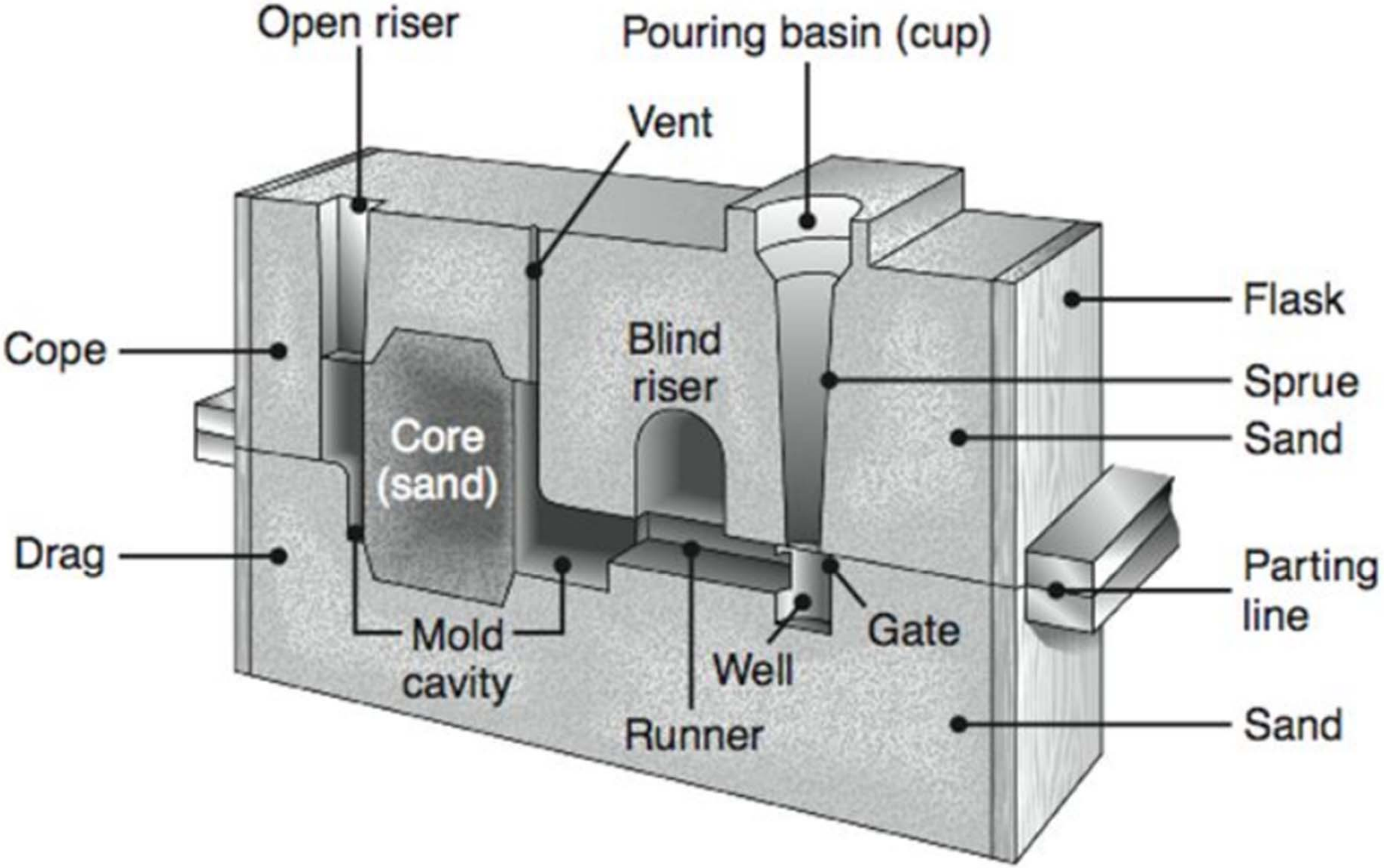




Regimes of continuous, partial and impossible flow



: Maximum length melt can reach



Fluid Flow : Molten metal → Pouring basin → Sprue → Runner → Cavity → Riser

7.3. Heat Flow

Heat Balance Equation

$$K_S T_S' = K_L T_L' + vL_V$$

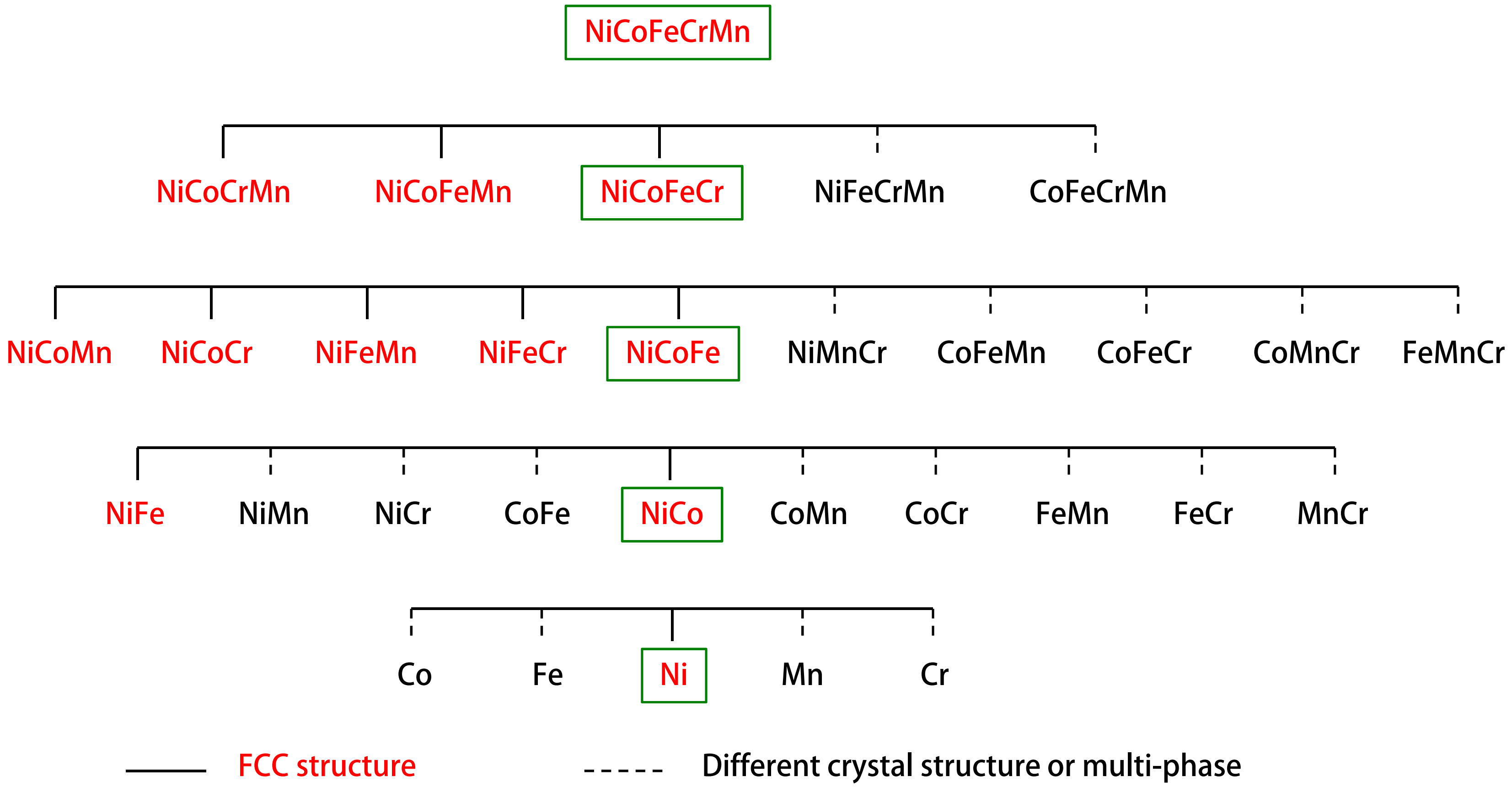
* **Solidification rate of solid/liquid interface ∝ $\Delta T = T_e - T$ (actual temp): To maintain ΔT, latent heat generated during solidification needs to be removed.**

→ the amount of solidification at a given time ∝ the amount of heat removed during that time, Q

* Heat transfer in the casting process

1) **Thermal conductivity:** **Generally in pure metals and low alloys, TC decreases/ in high alloys TC increases when T increases/ TC of metal >> TC of ceramic.**
2) **Convection heat transfer:** **Convection occurs <u>due to density difference by temperature difference in flowing of molten metal</u>.**
3) **Radiative heat transfer:** **in high-temperature molten metal or mold surface contacting the atmosphere, radiation heat transfer in which heat energy moves in the form of electromagnetic waves should be considered.**
4) **Phase transformation and latent heat:** **Release or absorption of latent heat occurs when there is a phase transformation/ in this case, exothermic or endothermic term should be added by heat energy conservation law.**

manipulation of σ_y/κ ratio in FCC solid solutions



NiCoFeCrMn

NiCoCrMn NiCoFeMn NiCoFeCr NiFeCrMn CoFeCrMn

NiCoMn NiCoCr NiFeMn NiFeCr NiCoFe NiMnCr CoFeMn CoFeCr CoMnCr FeMnCr

NiFe NiMn NiCr CoFe NiCo CoMn CoCr FeMn FeCr MnCr

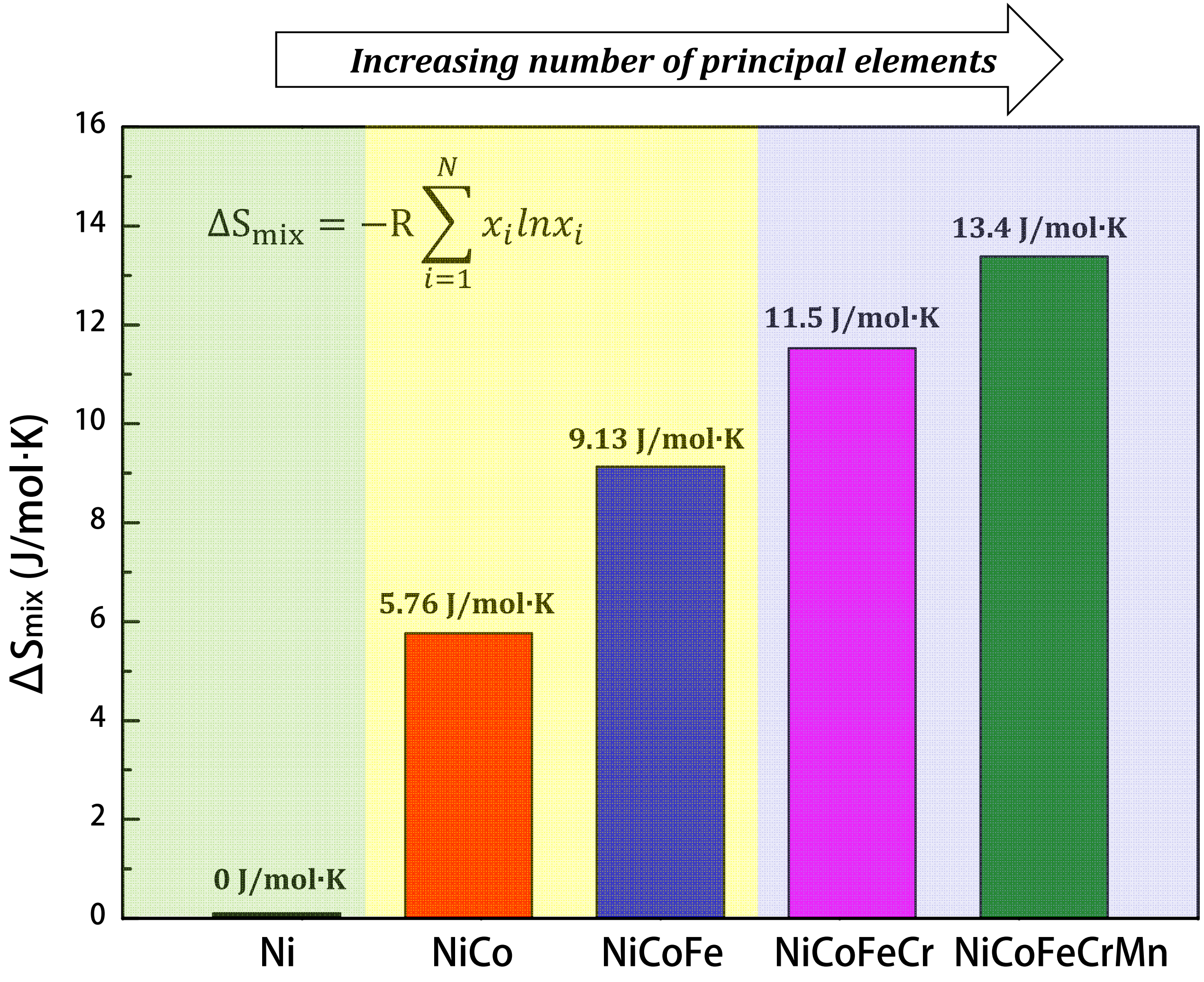
Co Fe Ni Mn Cr

—— FCC structure

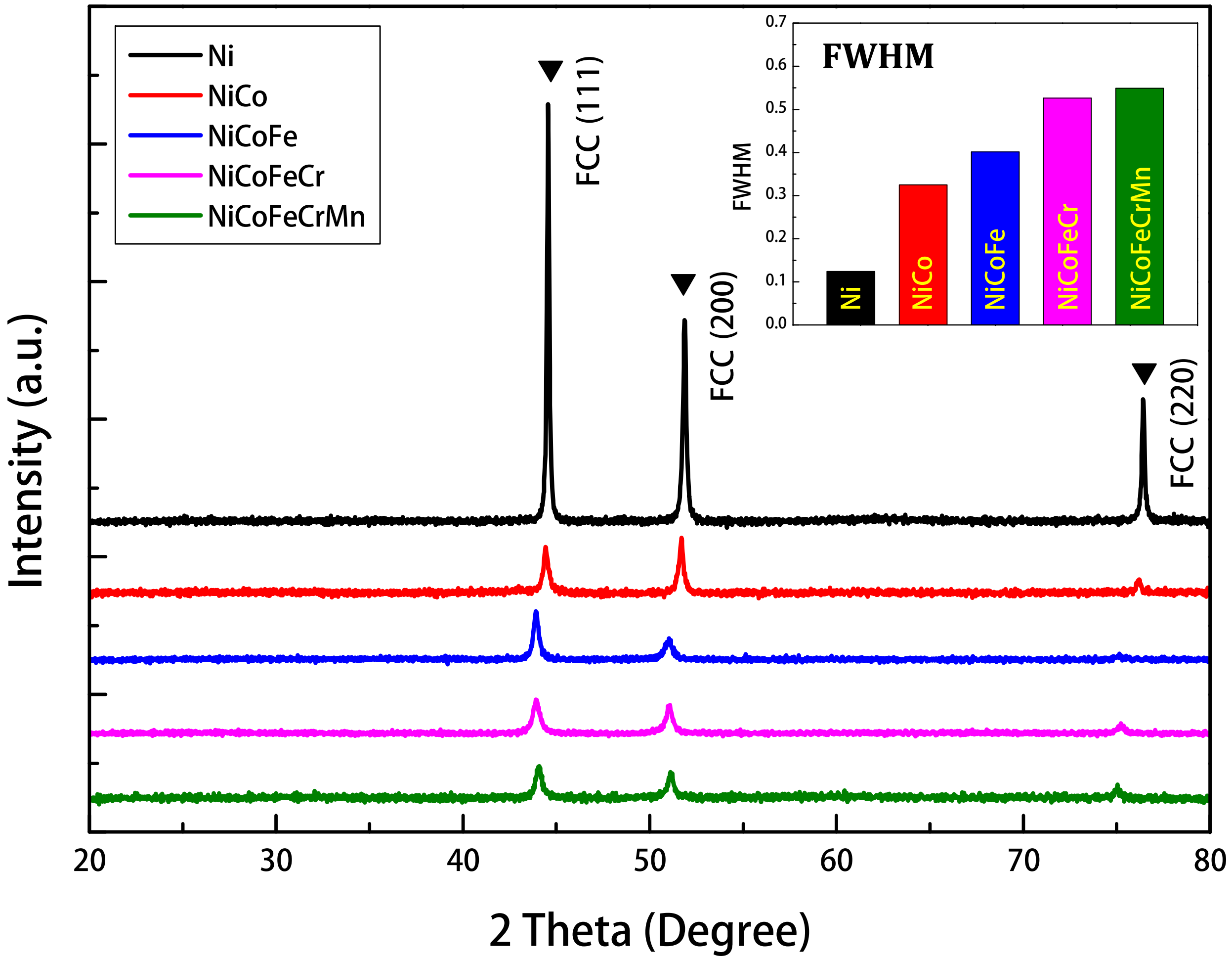
- - - - - Different crystal structure or multi-phase

→ Guideline for design of multi-principal elements alloys in cryogenic applications

Relationship btw # of principle elements (NPEs) & ΔS_{mix}



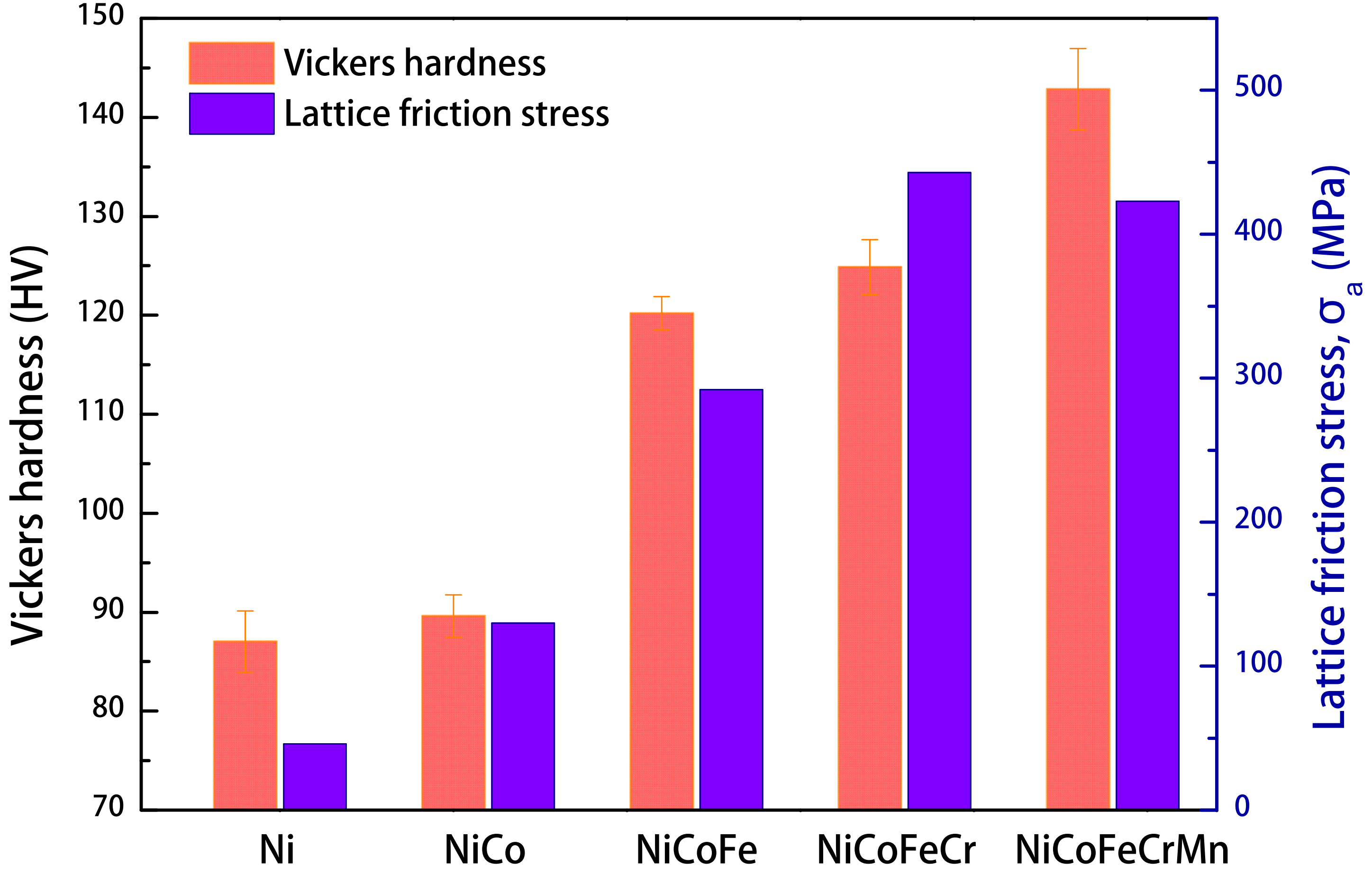
XRD results of the FCC solid solutions



Number of principal elements ↑ → Peak intensity ↓ & Full width at half maximum ↑

→ Increase in lattice distortion with increasing NPEs

Mechanical properties of the FCC solid solutions

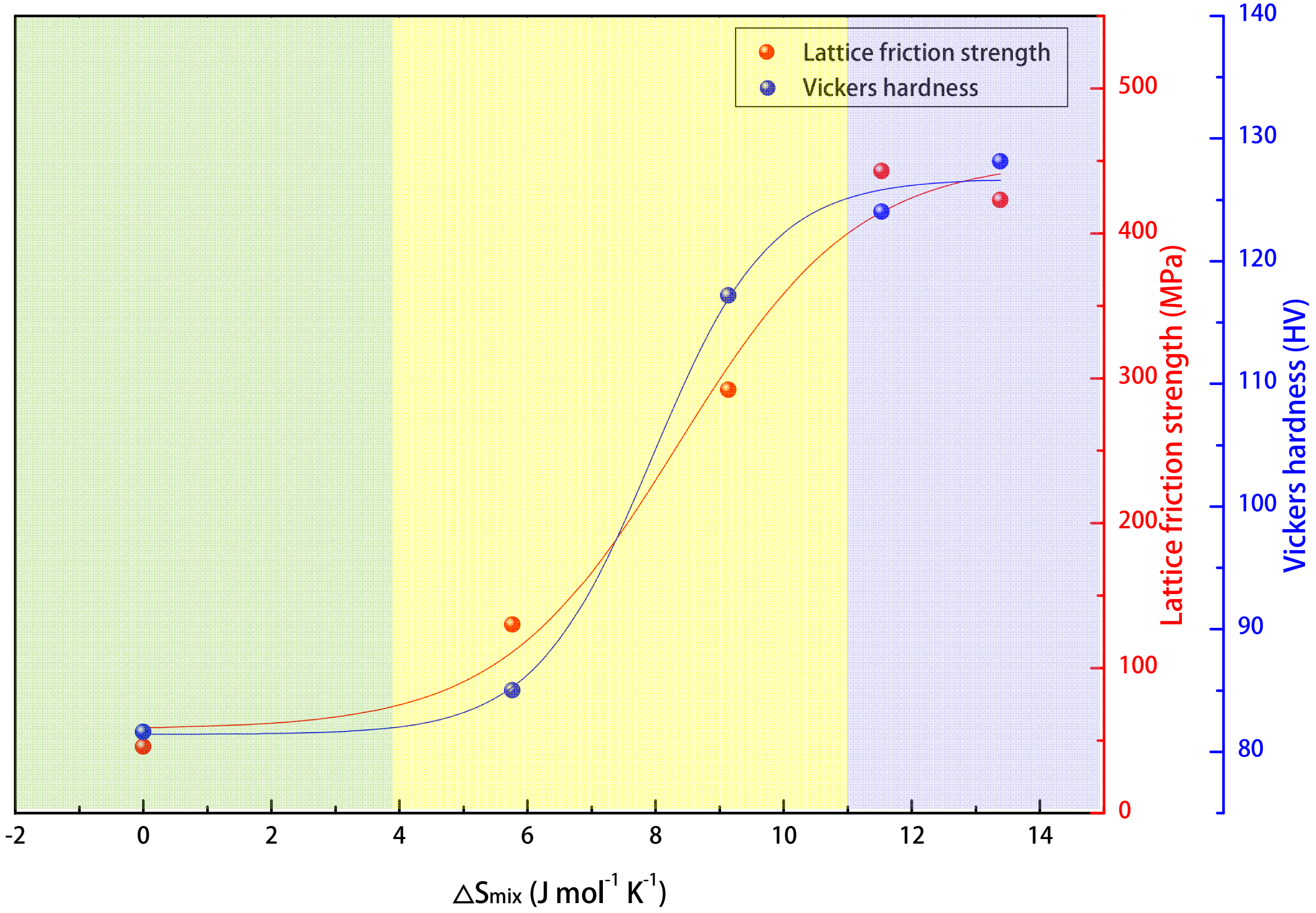


NPEs ↑ → Lattice distortion ↑ → Vickers hardness & Lattice friction stress ↑

: grain size and temperature-independent intrinsic lattice resistance to dislocation motions

Z.Wu et al. (2014)

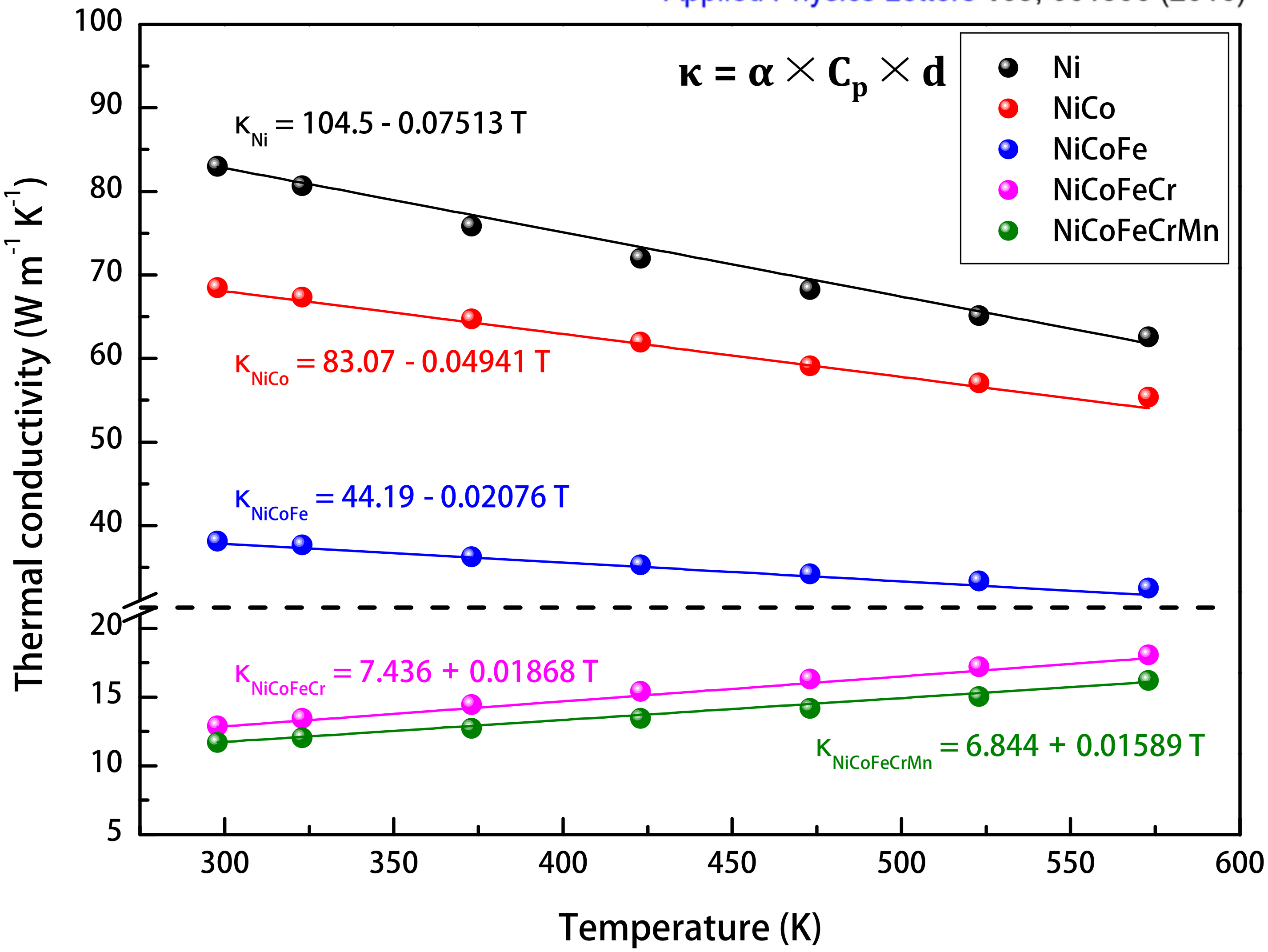
Mechanical properties of the FCC solid solutions



ΔS_{mix} (NPEs) ↑ → Lattice distortion & Compositional complexity ↑
→ Solid-solution hardening ↑ (HV & σ_a ↑)

Thermal conductivity (κ) of the FCC solid solutions

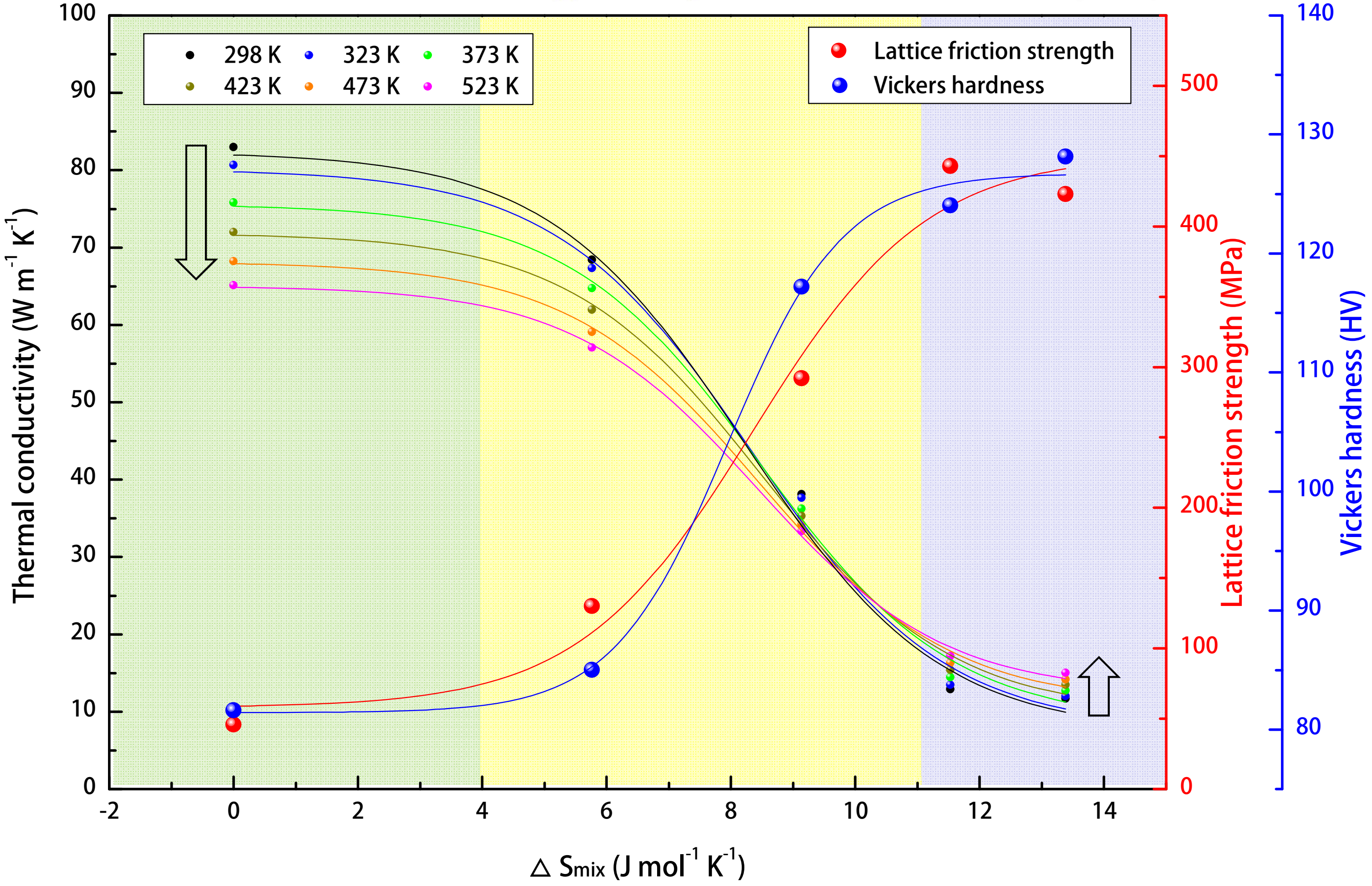
Applied Physics Letters **109**, 061906 (2016)



Ni, NiCo and NiCoFe: Negative trend / NiCoFeCr and NiCoFeCrMn: Positive trend

Reversed trends in κ and σ_y with increasing ΔS_{mix}

Applied Physics Letters **109**, 061906 (2016)



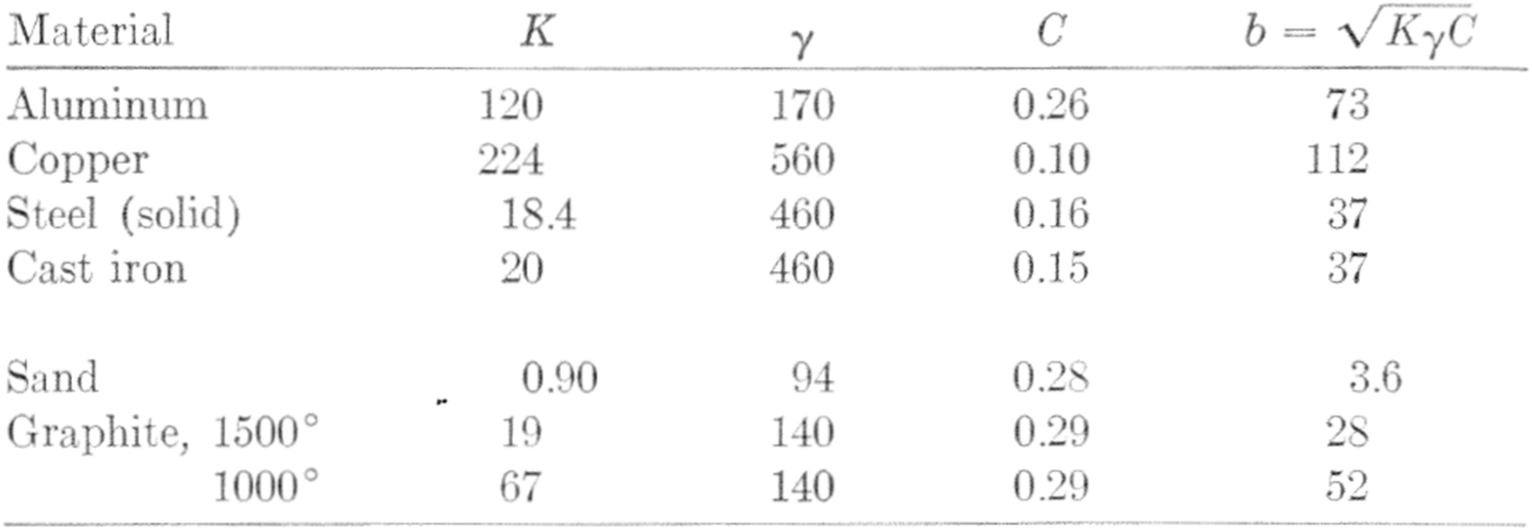
ΔS_{mix} (NPEs)↑→ Lattice distortion & Compositional complexity↑
→ Solid-solution hardening↑ (HV & σ_a↑) & Electron scattering↑ (ρ↑, κ↓)

* Possible to classify of various solidification processes according to thermal property of mold (Related to heat release associated with solidification rate)

* Heat diffusivity **b =** $\sqrt{K\gamma C}$

K= thermal conductivity/ γ = density/ C= specific heat

Table 7.2 (Values in feet, pounds, °F units)



Material	K	γ	C	$b = \sqrt{K\gamma C}$
Aluminum	120	170	0.26	73
Copper	224	560	0.10	112
Steel (solid)	18.4	460	0.16	37
Cast iron	20	460	0.15	37
Sand	0.90	94	0.28	3.6
Graphite, 1500°	19	140	0.29	28
1000°	67	140	0.29	52

A. For <u>metal molds</u> with thermal conductivity similar to solidifying metal

* n = (b of mold metal)/ (b of solidifying metal)

: Solidification of steel in cast iron mold n = 1.12 ~ close to 1.

* If the metal mold thickness is not larger than the section thickness to be cast,

Initial solidification: control by heat flow into mold

final solidification: Conduction through mold / Heat loss outside the mold

*** 3 different types of metal mold**

(1) Typical ingot mold: Heat release by radiation from outer surface and convection

(2) Metal mold cooled on surface relatively far from casting

→ - Most continuous casting is made by water cooling.
- Water cooling in the absence of mold has a similar effect.
- Arc melting also uses this type of mold.

(3) Huge metal mold compared to the solidification part

: Heat loss outside mold is not large until final solidification

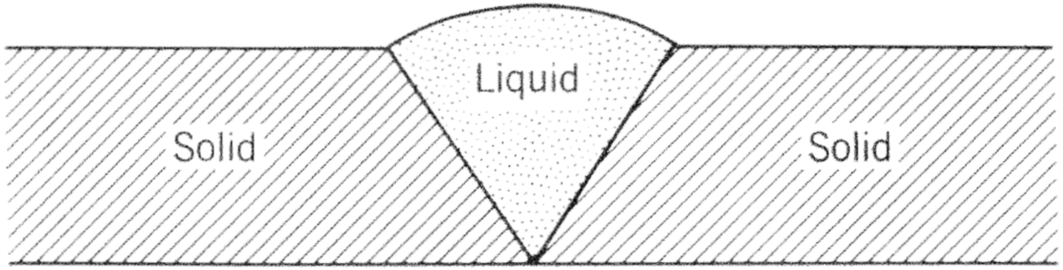


Fig. 7.2. cross section of butt weld (schematic).

B. Sand mold: Thermal conductivity is much smaller than solidifying metal

Ex) n = 0.13 → the dependence of the mold thickness is greatly reduced

(∵ heat loss from the mold surface is independent of thickness variation)

C. If the heat release is controlled by controlled heat supply control and heat sink to the liquid metal, as in the case of zone refining or single crystal growth: the process rate depends on the L-S temperature gradient and the interfacial velocity, v.

1. Solidification Rate

* The solidification rate *f*(t) is to obtain the increase in time of the solid layer in contact with the mold. Although in case of ①pure metal or eutectic without solidus-liquidus interval, it is possible to calculate the heat flow by solidifying while maintaining the planar interface, heat flow calculations and interpretation of results at the ②dendritic interface are complicated due to influence by various interface conditions → Solidification rate can be calculated by measuring the Temp.-time relationship in various parts of the solidifying metal.

Assumption: mold and metal: semi-infinite / initial liquid temperature T_m / liquid: pure metal & solid-liquid interface temperature~ constant / metal: constant temperature with mold interface

① **For heat conduction in one direction in the mold (i.e., perpendicular to the planar mold wall), Temp, θ of an element of volume at t**

Thermal conductivity

$$\frac{\partial \theta}{\partial t} = \frac{K}{\gamma C}\frac{\partial^2 \theta}{\partial x^2}$$

density Heat capacity

② **ΔT at a specific location in time t :**

initial temp. at the surface, θ_0 → instantly raised to θ_i at t=0 → change to θ_m at $t=t_1$

$$\theta_m = \theta_0 + (\theta_i - \theta_0)\,\mathrm{erfc}\left(\frac{X}{2\sqrt{\alpha t_1}}\right)$$

where, $\alpha = \dfrac{K}{\gamma C}$

③ **Heat removed by casting at any time t_1 :**

$$\frac{\partial Q}{\partial t} = -K\left[\frac{\partial \theta}{\partial x}\right]_{x=0} = \frac{K(\theta_i - \theta_0)}{\sqrt{\pi \alpha t}} = 0.564\frac{K(\theta_i - \theta_0)}{\sqrt{\alpha t}} = 0.564b\frac{(\theta_i - \theta_0)}{\sqrt{t}}$$

By differentiation of the efrc equation

④ **Total heat conducted into the mold Q up to time t : (where, b =** $\sqrt{K\gamma C}$

$$Q = b(\theta_i - \theta_0)\int_0^t \frac{0.564}{\sqrt{t}} = 1.128b(\theta_i - \theta_0)\sqrt{t}$$

⑤ Thickness of the solidified layer, D:

$$\boxed{D = q\sqrt{t}}$$

where, q = solidification constant

$$1.128\ [b(\theta_i - \theta_0)/L\gamma'];$$

L: latent heat/ density of solidified metal: γ'

⑥ Reflection of Superheat condition: more complicated problem

Total heat to be extracted from solidifying metal = $W[L + S(\theta_c - \theta_f)]$

where W = weight of casting
θ_c = initial temperature of the liquid
θ_f = final solidification temperature

→ This amount of heat must be conducted into the mold during the time t taken for solidification.

<u>If the area of the surface of contact of mold and metal is A</u>, then

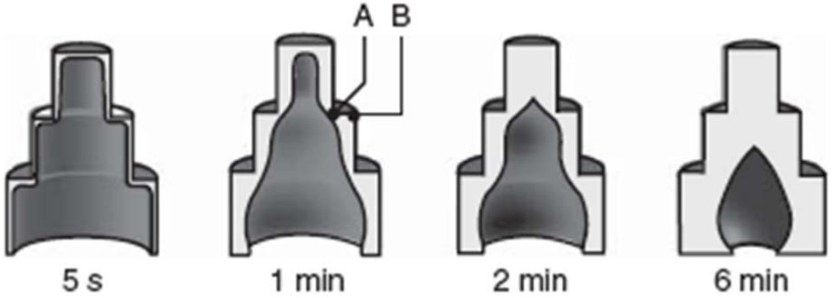
$$\sqrt{t} = \frac{W[L + S(\theta_c - \theta_f)]}{1.128A\sqrt{K\gamma C}\,(\theta_i - \theta_0)}$$

from which

$$\boxed{t = \left(\frac{V}{A}\right)^2 \times \text{constant}}$$

(Chvorinov's rule)

Solidification Time



- Total solidification time T_{TS} = time required for casting to solidify after pouring
- T_{TS} depends on size and shape of casting by relationship known as *Chvorinov's Rule*

$$T_{TS} = C_m \left(\frac{V}{A} \right)^n$$

where T_{TS} = total solidification time; V = volume of the casting; A = surface area of casting; n = exponent with typical value = 2; and C_m is *mold constant.*

$$T_{TS} = C_m \left(\frac{V}{A} \right)^n$$

$$\sqrt{t} = \frac{W[L + S(\theta_c - \theta_f)]}{1.128A\sqrt{K\gamma C}\,(\theta_i - \theta_0)}$$

Mold Constant in Chvorinov's Rule

- Mold constant C_m depends on:
  - Mold material
  - Thermal properties of casting metal
  - Pouring temperature relative to melting point

- Value of C_m for a given casting operation can be based on experimental data from previous operations carried out using same mold material, metal, and pouring temperature, even though the shape of the part may be quite different.

Solidification times for various shapes

Three metal pieces being cast have the same volume but different shapes: On is a sphere, one a cube, and the other a cylinder with its height equal to its diameter.
Which piece will solidify the fastest, and which one the slowest? Assume that n = 2

Solution The volume of the piece is taken as unity. Thus from Eq.

$$\text{Solidification time} \propto \frac{1}{(\text{Surface area})^2}$$

The respective surface areas are as follows:

Sphere:

$$V = \left(\frac{4}{3}\right)\pi r^3,\ r = \left(\frac{3}{4\pi}\right)^{1/3}$$

$$A = 4\pi r^2 = 4\pi\left(\frac{3}{4\pi}\right)^{2/3} = 4.84$$

Cube:

$$V = a^3,\ a = 1,\ \text{and}\ A = 6a^2 = 6$$

Cylinder:

$$V = \pi r^2 h = 2\pi r^3,\ r = \left(\frac{1}{2\pi}\right)^{1/3}$$

$$A = 2\pi r^2 + 2\pi r h = 6\pi r^2 = 6\pi\left(\frac{1}{2\pi}\right)^{2/3} = 5.4$$

The respective solidification times are therefore

$$t_{\text{sphere}} = 0.043C,\ t_{\text{cube}} = 0.028C,\ t_{\text{cylinder}} = 0.033C$$

Hence, the cube-shaped piece will solidify the fastest, and the spherical piece will solidify the slowest.

What Chvorinov's Rule Tells Us

- Casting with a higher volume-to-surface area ratio cools and solidifies more slowly than one with a lower ratio
  - To feed molten metal to the main cavity, T_{TS} for riser must be greater than T_{TS} for main casting

- Since mold constants of riser and casting will be equal, design the riser to have a larger volume-to-area ratio so that the main casting solidifies first
  - This minimizes the effects of shrinkage & waste metal.

*** In the case of sand mold,**

the superheat of the liquid phase is uniformly reflected throughout and delays the start of solidification until the liquid reaches the liquidus temp.

*** Thickness of the solidified layer D in sand mold casting**

$$D = q\sqrt{t} - c$$

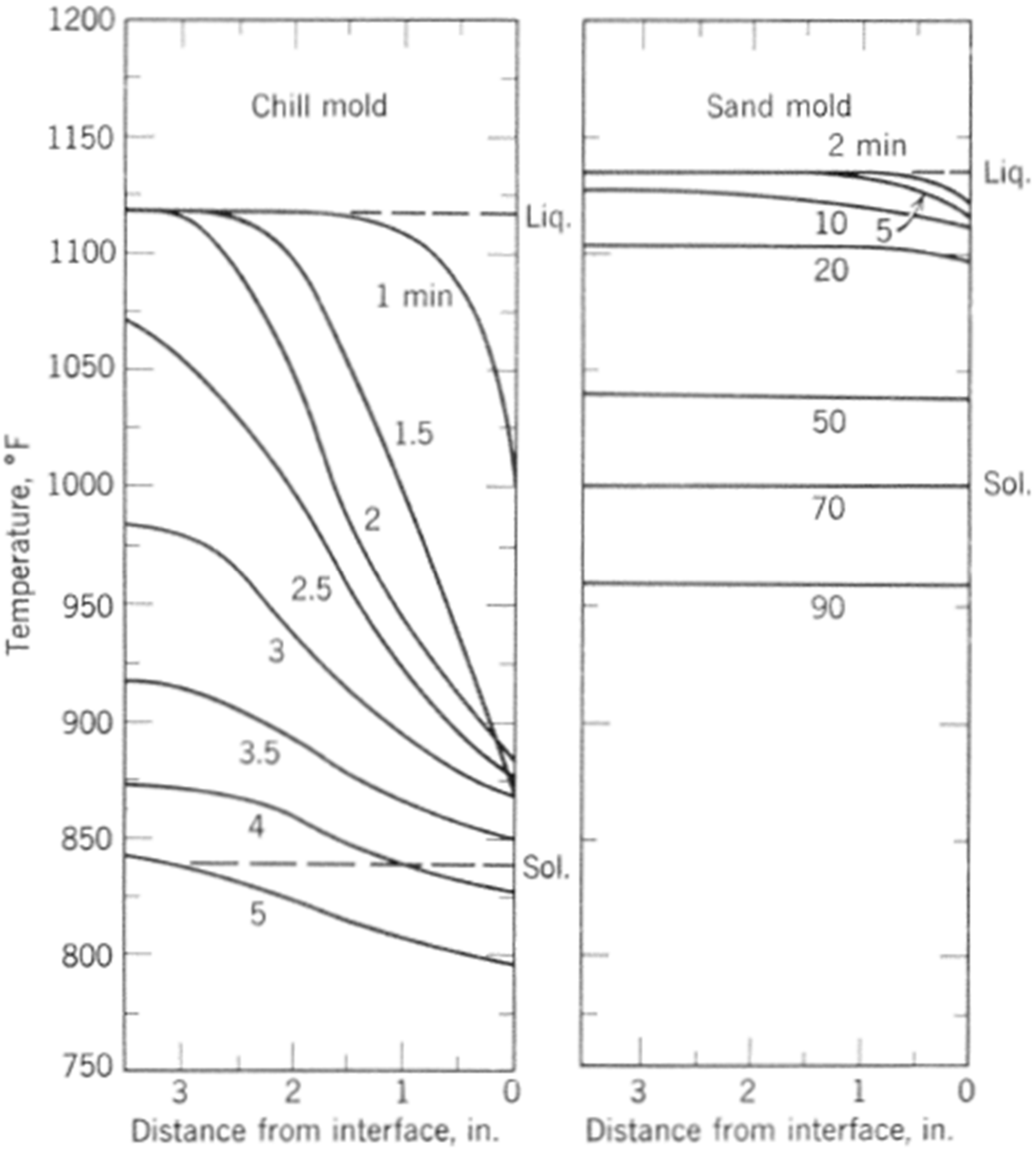


Fig. 7.3. Variation of temperature during solidification of Al 5% Mg alloy in a 7-inch square mold. (a) Metal mold, (b) sand mold.

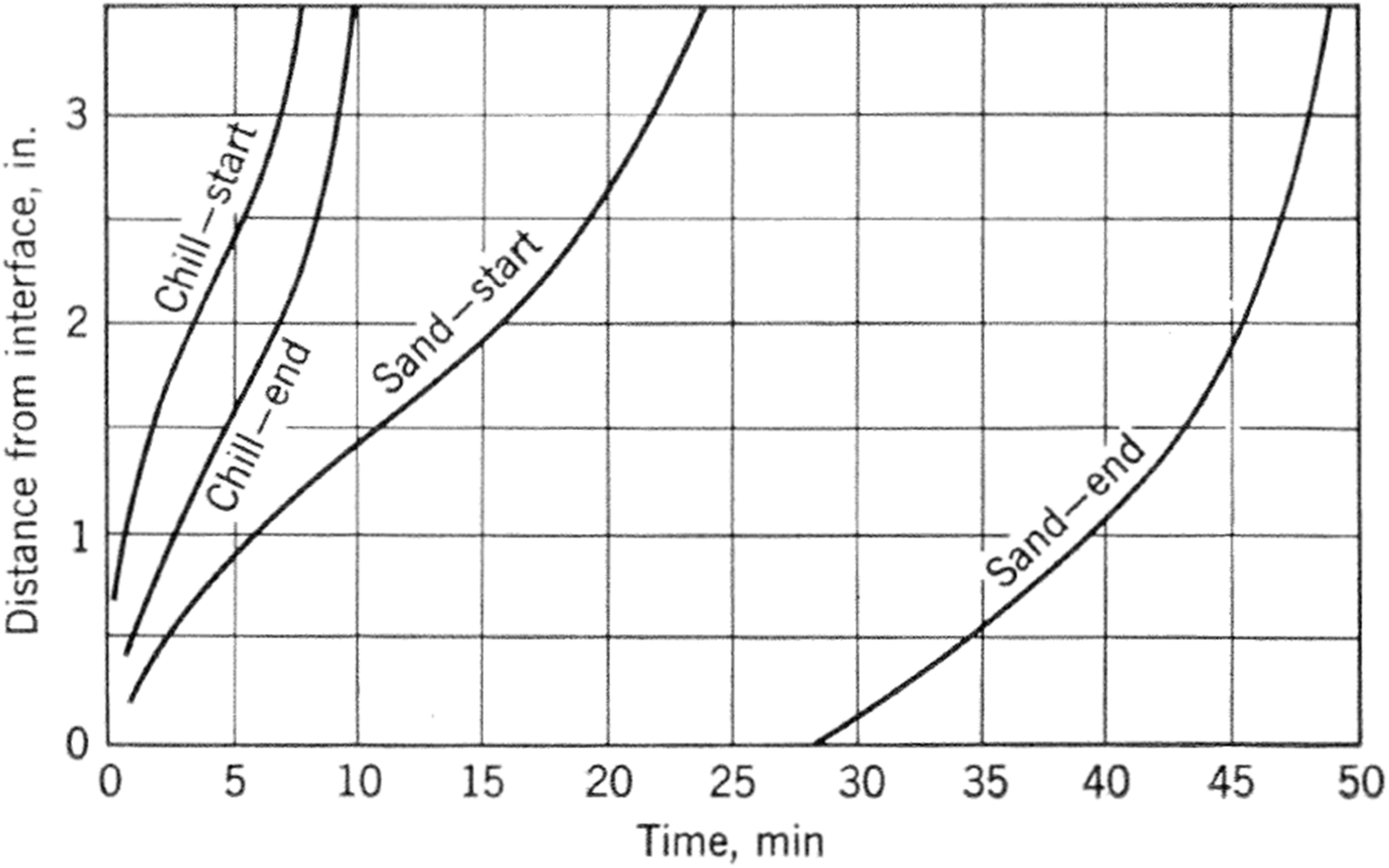
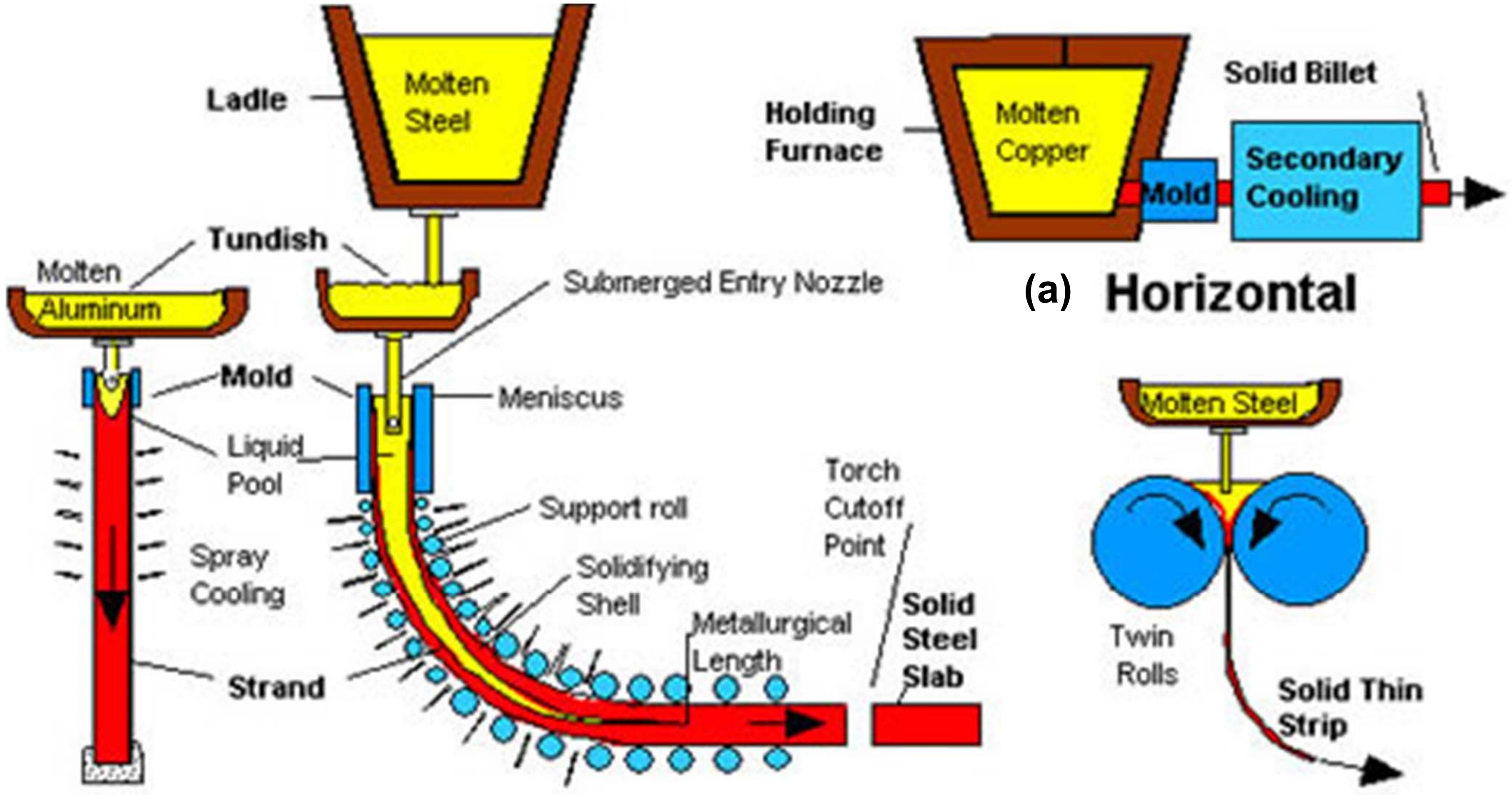


Fig. 7.4. Movement of liquidus and solidus tempeeratures during solidification of a 0.6% carbon steel.

2. continuous casting: a number of dynamic industrial process

The molten metal is poured continuously into a water-cooled mold from which the solidified metal is continuously withdrawn in plate or rod form. (solid-liquid interface)



(a) Horizontal

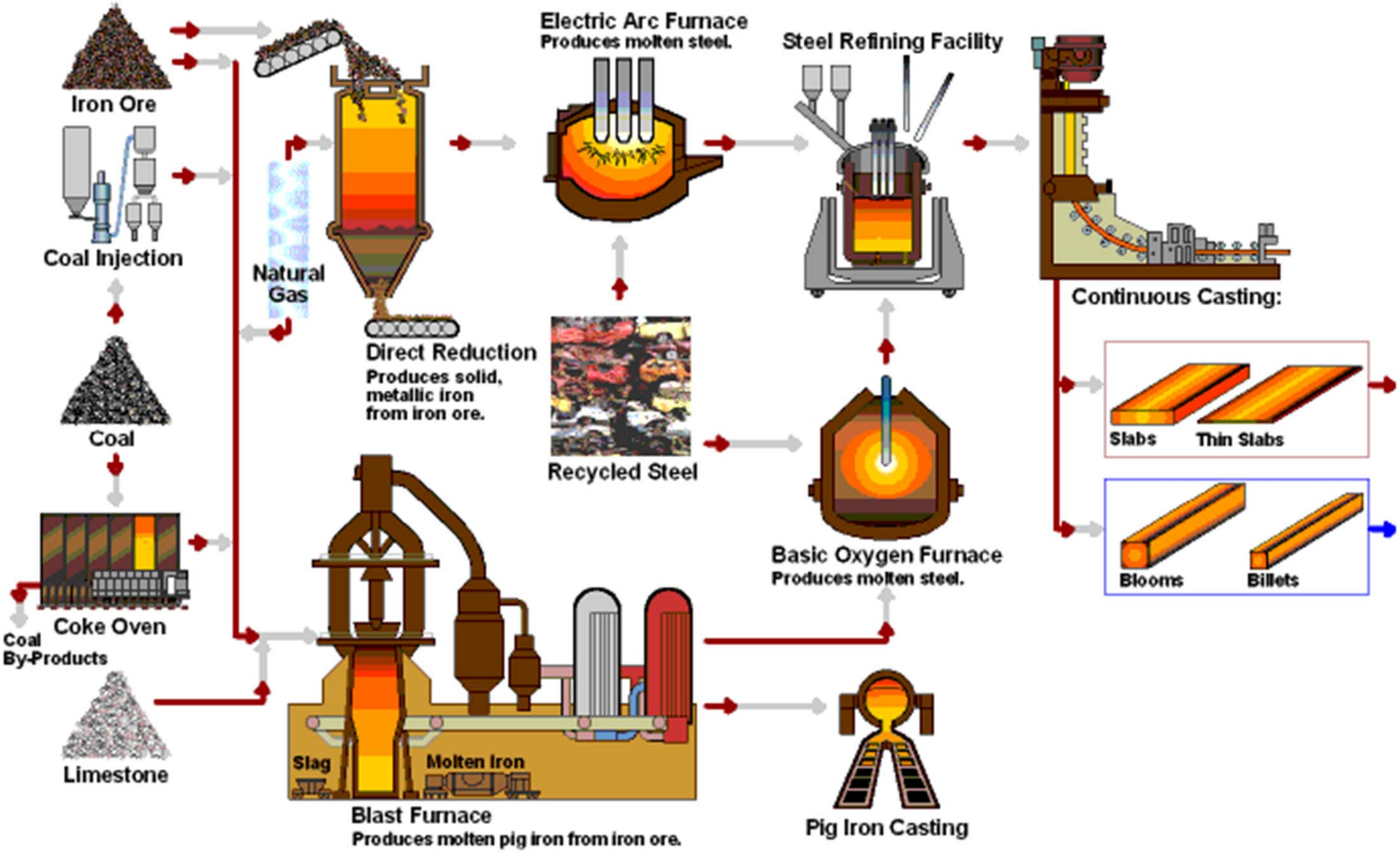
(b) Vertical

(c) Curved

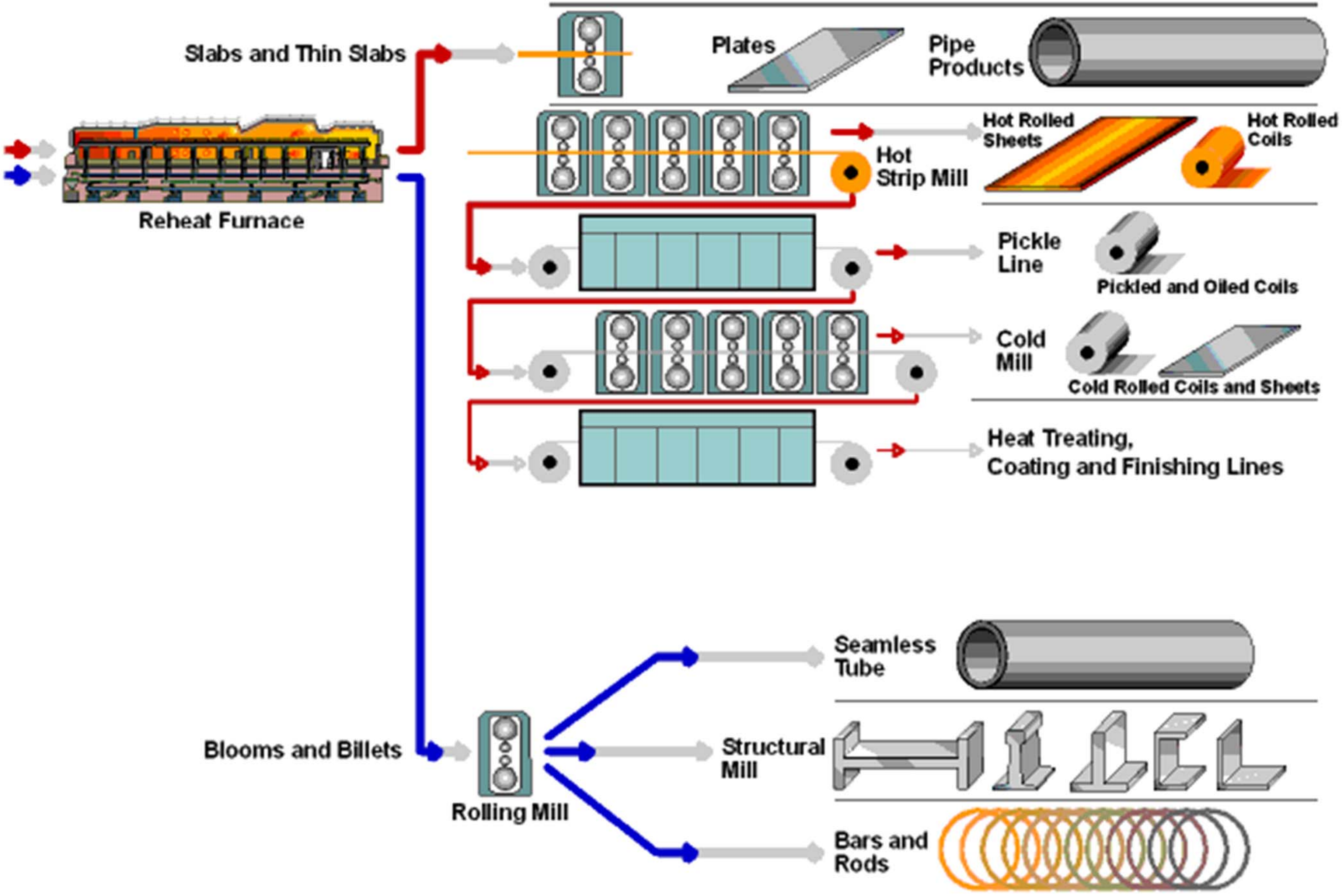
(d) Strip Casting

continuous casting

continuous casting



4.4.3 continuous casting

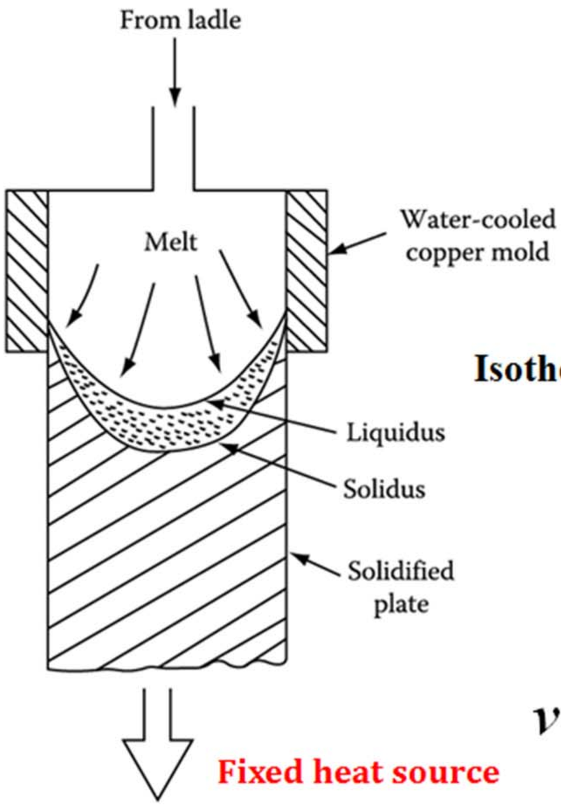


continuous casting: a number of dynamic industrial process

: large mass (economic advantage)/ high speed (property good)

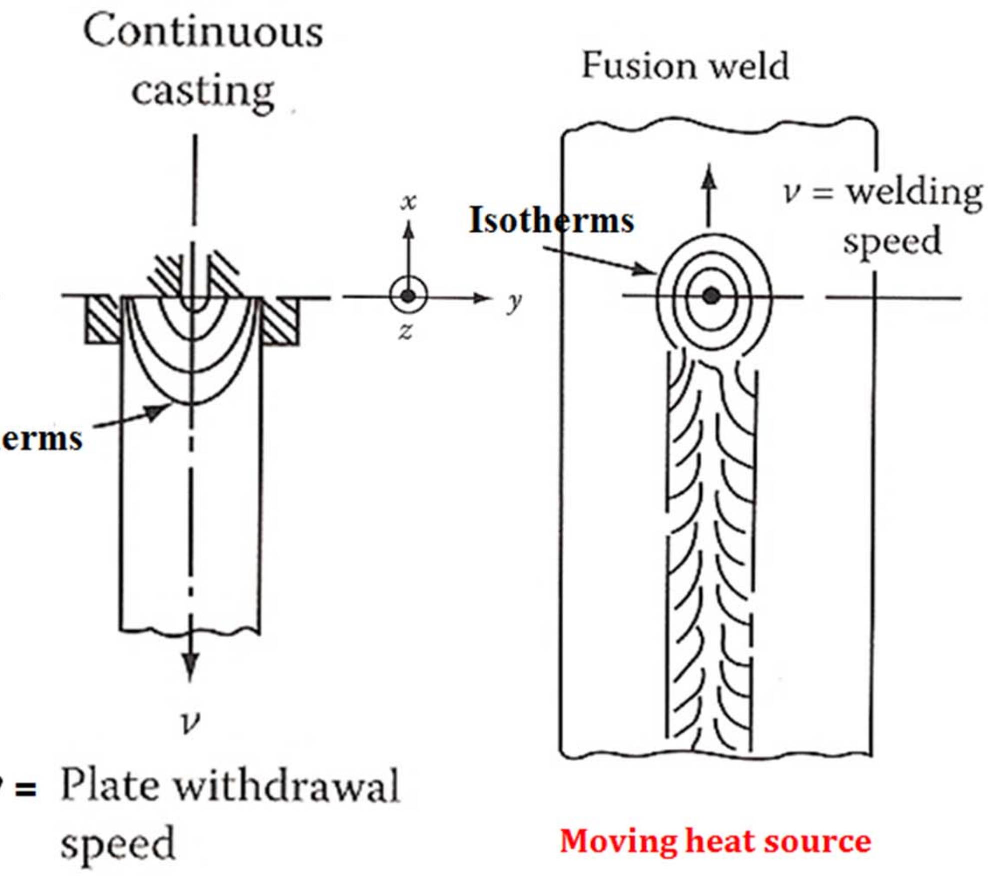
→ Process speed: related to latent heat removal & metal flow during solidification.

① Dynamic process: importance of isotherm distribution



Fixed heat source

Fig. 4.44 Schematic illustration of a continuous casting process



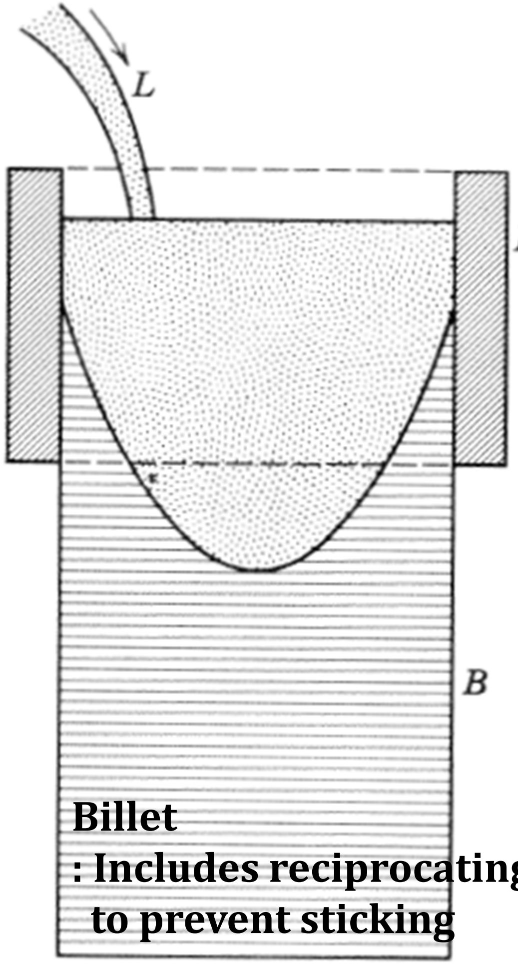
v = Plate withdrawal speed

Moving heat source

Fig. 4.45 Illustrating the essential equivalence of isotherms about the heat sources in fusion welding and continuous casting

continuous casting: a number of dynamic industrial process

② the temperature gradient is maintained in a steady state→ **related to constant shape of the interface and the solidification rate (<u>here, the solidification rate is changed by not to time but to position from the surface</u>)**



Mold
: Square or circular section

a) cooling by water spray or water jet/

b) Extra cooling for the metal extracting from the mold

Billet
: Includes reciprocating motion to prevent sticking

Fig. 7.5. Continuous casting (schematic).

* solidification rate varies depending on the position as shown in the following figure

(∵ Since solidification occurs in a direction perpendicular to the solidification interface)

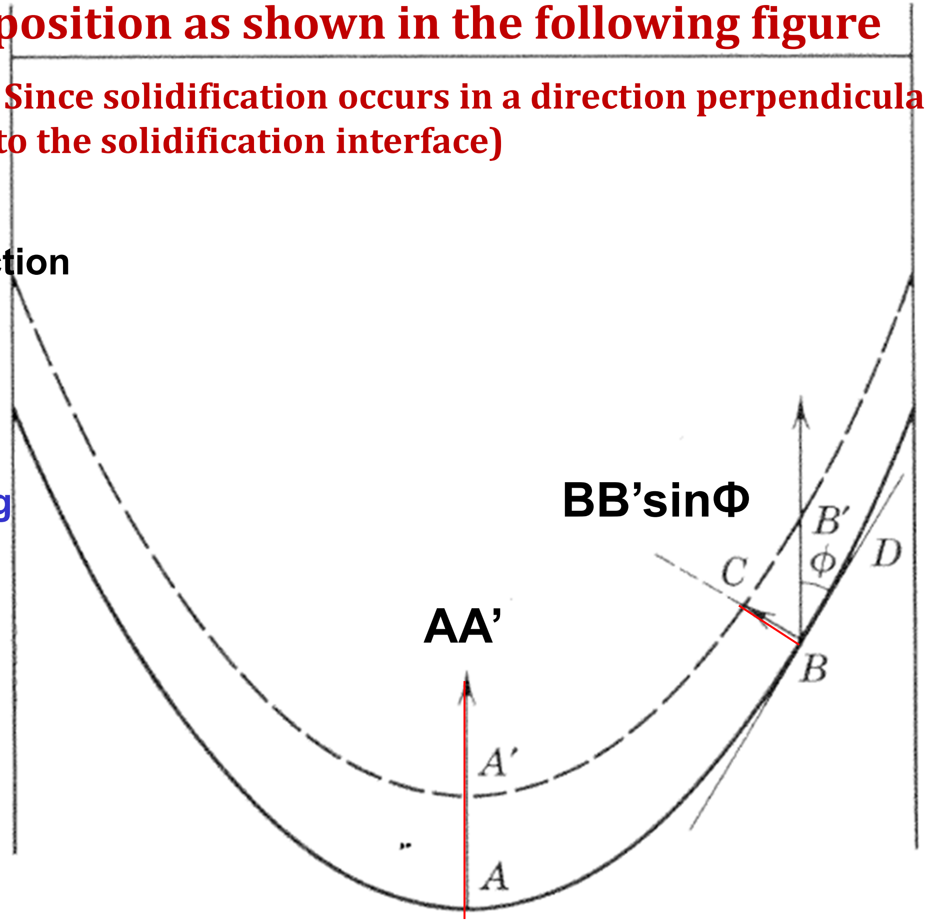


Fig. 7.6. Interface shape and rate of solidification in continuous casting.

* To obtain the interface shape of Fig. 7.6,

in the case of max. emission of latent heat at A/ min. emission of latent heat at D

→ For this, efficient cooling of the billet beyond the mold is necessary.

* To obtain solid-liquid interface shape of Fig. 7.7,

At the billet center, the solidification rate becomes minimum.

→ In this case. a large tendency of segregation and porosity by shrinkage in the center line where solidification ends

→ additional cooling of the lower part of the mold is required

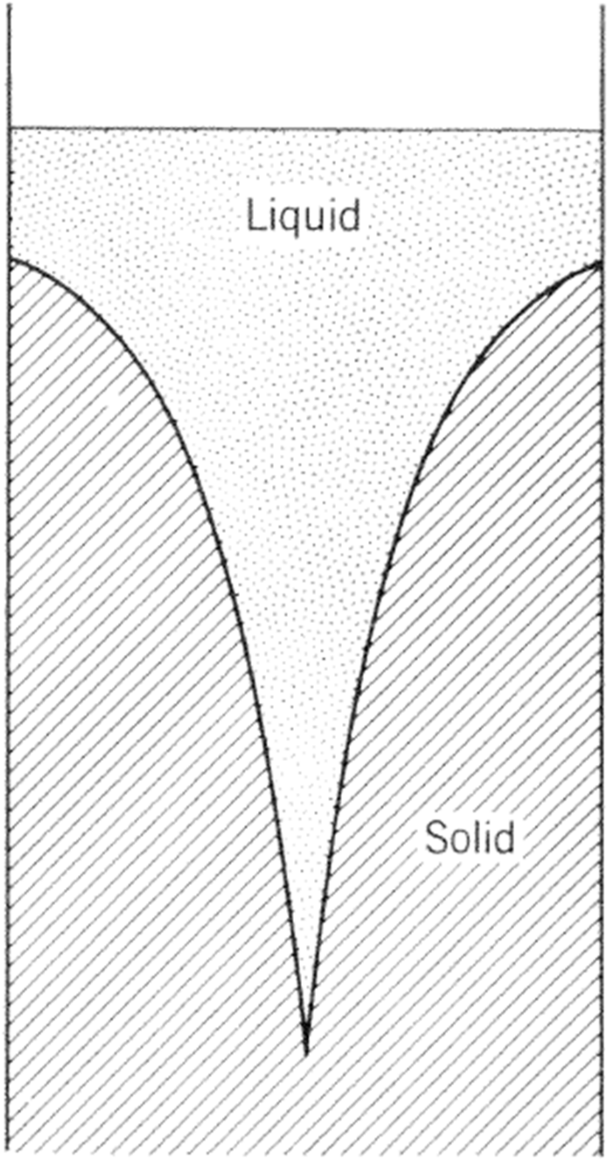


Fig. 7.7. Alternative interface shape in continuous casting

* Quantitative aspects of continuous casting

① depth of liquid core h_c:

$$\boxed{h_c = \frac{I\gamma R^2 v_c}{4K(\theta_f - \theta_s)}}$$

where I = latent heat plus heat extracted, for unit mass, during fall of temperature from θ_f to $(\theta_f + \theta_s)/2$
γ = density
R = radius of billet (assumed cylindrical)
v_c = rate of withdrawal of the billet
K = thermal conductivity of the solid metal
θ_f = melting point
θ_s = surface temperature (assumed uniform)

(1) Depth of core for billets of equal diameter ∝ casting rate (v_c)

(2) Depth of Liquid core ∝ (billet dia.)^2

(3) For billets of a given diameter and a given alloy composition,
v_l = impossible to exceed in practice

limiting rate of solidification v_l

$$v_l = \frac{4K(\theta_f - \theta_s)}{I\gamma R}$$

→ The existence of this limit follows from the consideration that as casting velocity ↑ → length of liquid core ↑ → changing angle Φ → a much greater normal freezing rate is required to give the required longitudinal rates.

→ In practice, a very long liquid core produces segregation and porosity difficulties of the kind mentioned in connection with interfaces of reverse curvature

* Figure 7.8 shows the validity of the calculation of the liquid core depth.

casting rate ↑ → depth of liquid core (hc) ↑

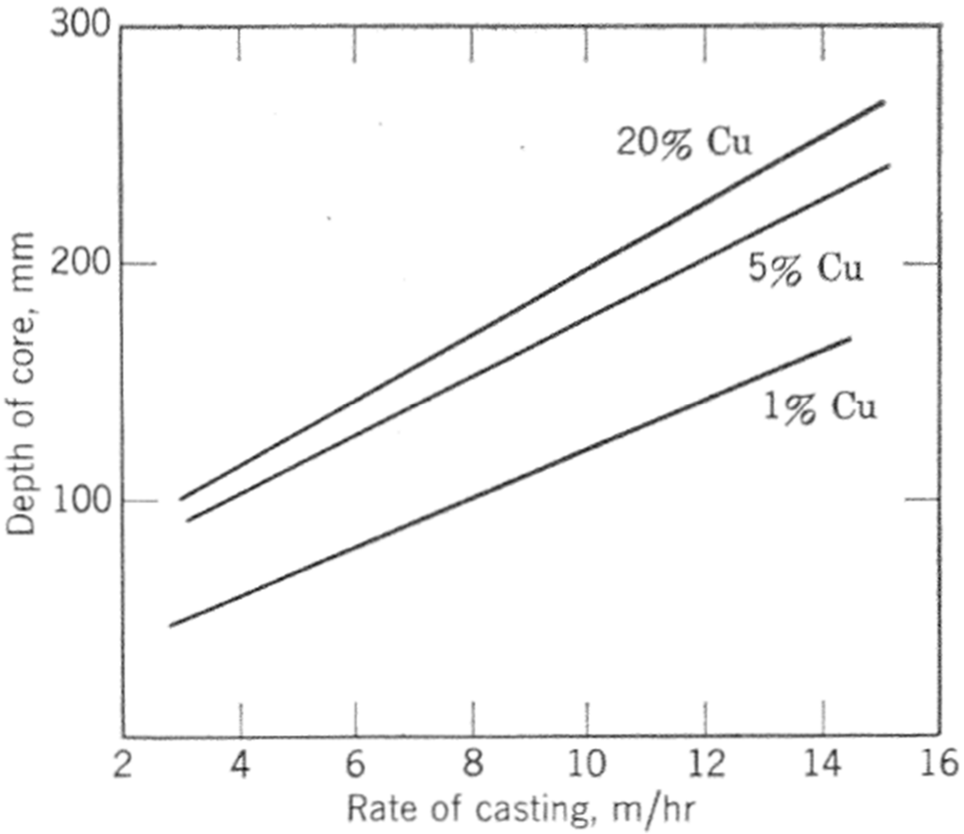


Fig. 7.8. Relationship between depth of liquid core and rate of casting.

TC Find temp. Surface temp.

$$f(h) = \frac{K(\theta_f - \theta_s)}{L + \frac{1}{2}\gamma_c(\theta_f - \theta_s)}$$

Latent heat density

is inversely proportional to the pool depth (*hc*) for a given combination of casting speed and billet size

$$h_c = \frac{I\gamma R^2 v_c}{4K(\theta_f - \theta_s)}$$

*** Table 7.3 shows *f* (*h*) of various alloys.**

Metal	K	L	K/γ_c	$f(h)$
Aluminum	0.53	93	0.82	0.72
Copper	0.92	50	0.98	1.02
Brass	0.28	37	0.33	0.36
Mild steel	0.11	78	0.09	0.10

→ ***f*(*h*) steel < *f*(*h*) Al → pool depth (*hc*) of steel >> pool depth (*hc*) of Al**

① **A very long liquid pool increases the danger of the liquid breaking out through the solid skin** (Strong solid skin is required to withstand the hydrostatic pressure induced by the liquid head at the liquid interface/ more important when <Speed ↑>) **limiting speed or cross section for continuous casting of steel is much less than for other metals due to low *f*(*h*)**

② **Billet size ↑ → liquid pool depth ↑**

→ The billet can not be cut until the liquid area is completely solidified

→ a very long device is needed for high speed casting

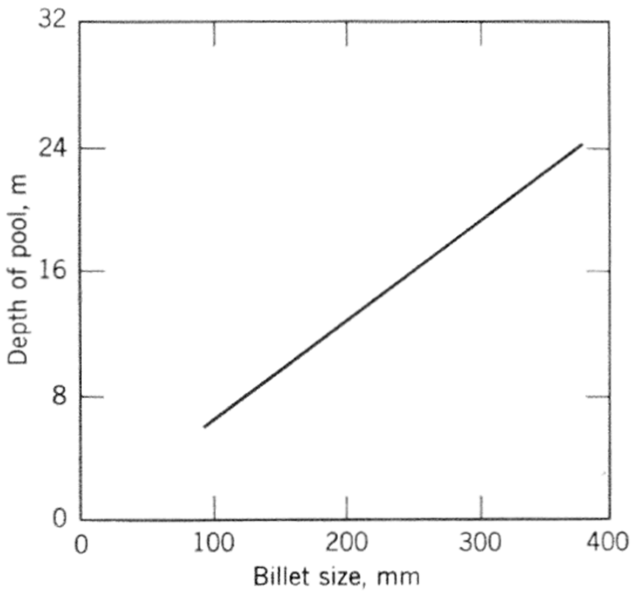
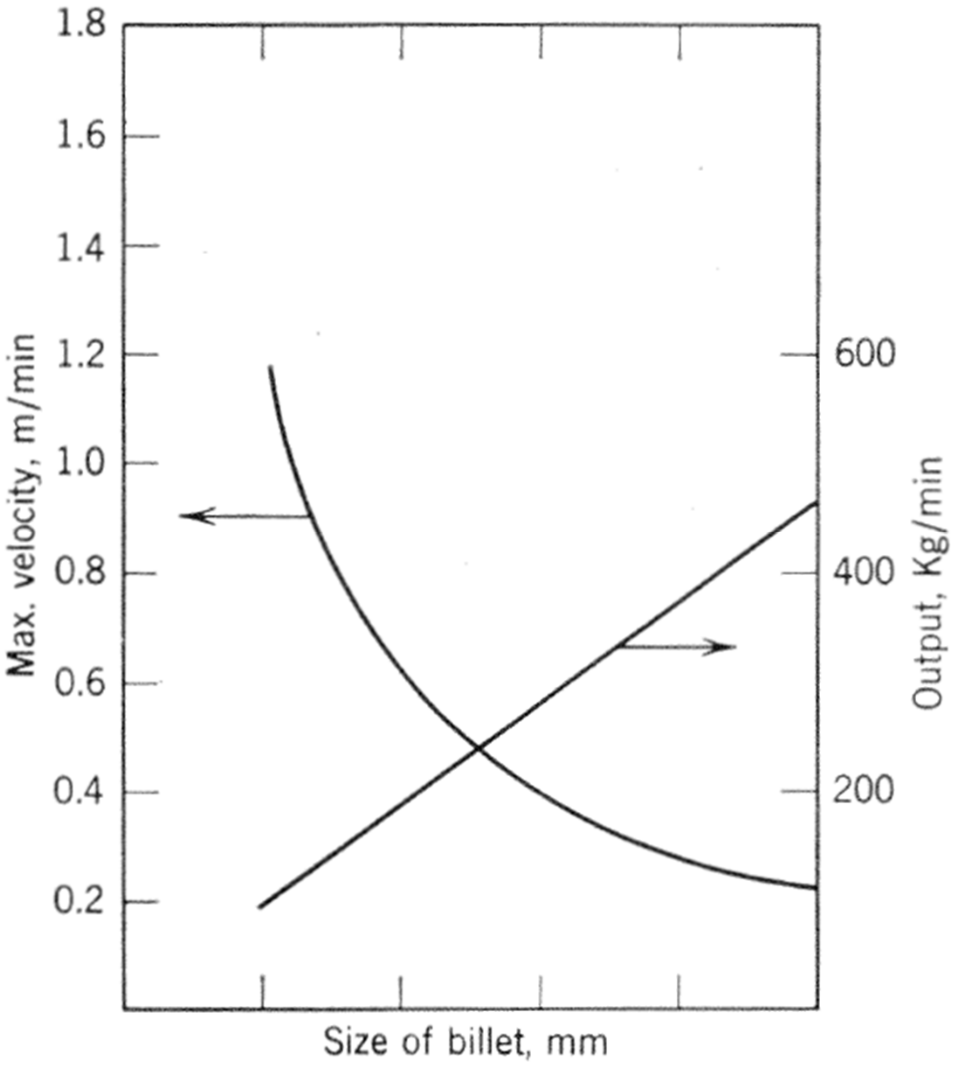


Fig. 7.9. Pool depth for continuously cast steel billets as a function of billet size.

③ **By theoretical considerations a) Increasing the cross section size of the billet is obtained by slower solidification / b) Increasing output is obtained by increasing cross section size.**

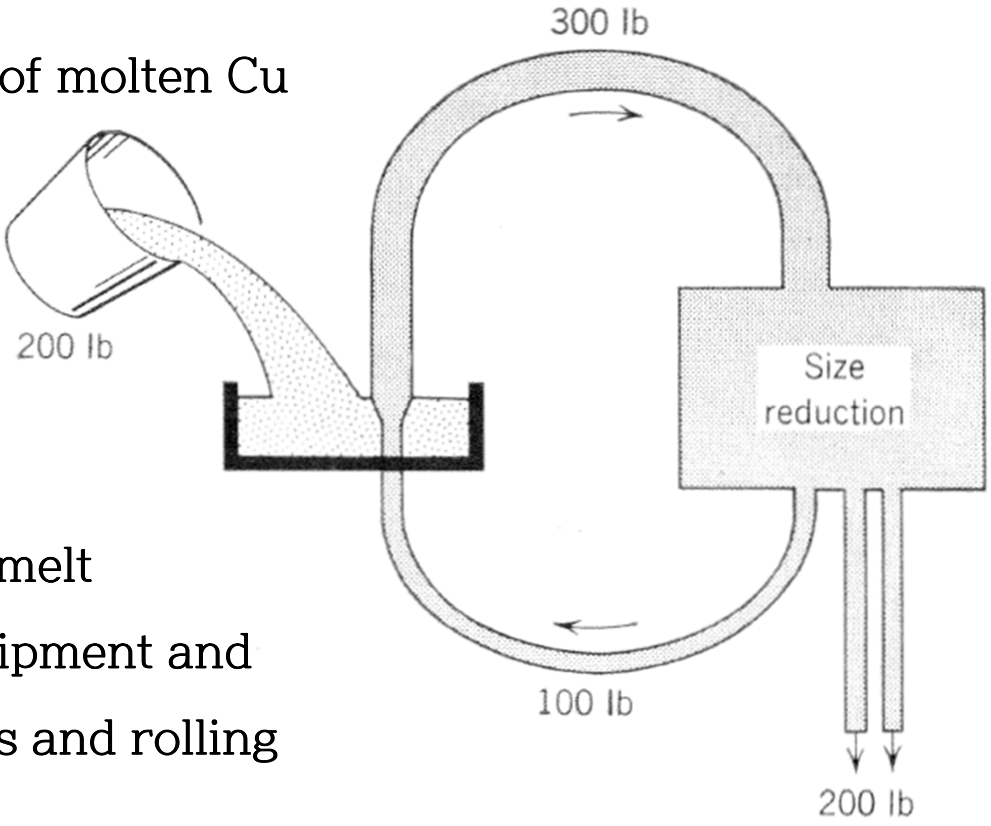


7.10. Maximum casting speed and output per unit time as a function of bullet size.

3. Dip forming: 2nd type of continuous casting

: the amount and shape of solidified metal is controlled by a heat sink rather than by a mold/ <u>developed for fabrication of Cu rod</u>: Cu rod (cold when it enters) → heated up by the bath & some of which solidifies on the rod → increase of thickness

100 lb rod → pass through a bath of molten Cu =300 lb rod → 1/3 of it is used for further dip forming (100 lb rod)/ 2/3 200lb rod_ready for further processing



7.11. Principle of dip forming.

① Direct production of rod from melt

② high speed, eliminating the equipment and time required for pouring ingots and rolling them into rod

Dip Casting

- Dip a part or mold into liquid resin
- Resin can be it’s own part (gloves) or it can be a portion of a larger part

* Calculation of thermal factor for Dip forming

① thickness of added metal ~ *f* (time in bath melt, speed of bar, temperature, thermal property, geometry of the system)

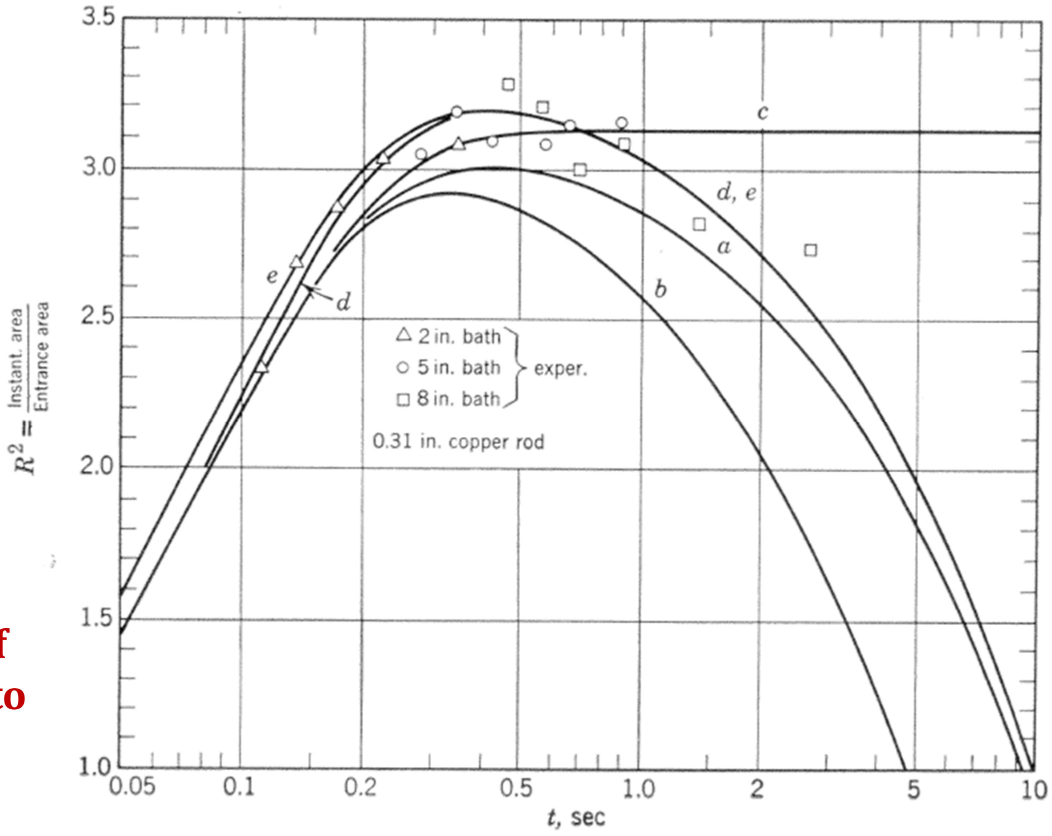
② amount of added metal ~ if depth of the bath is sufficient, increase to max. and then decreases

Fig. 7.12 shows some experimental points (for speeds ranging from 15 ft/min to 90ft/min & bath temp. of about and theoretical curves using different values of the effective temp. of the bath and the rod.

→ Calculation and experimental
: good similarity

But calculations are made on the assumption of a smooth interface. This condition would be satisfied in the case of pure Cu, but when the process is applied to an alloy, a dendritic or cellular-dendritic interface is to be expected.

∴ Max. amount solidified would be somewhat greater for an alloy



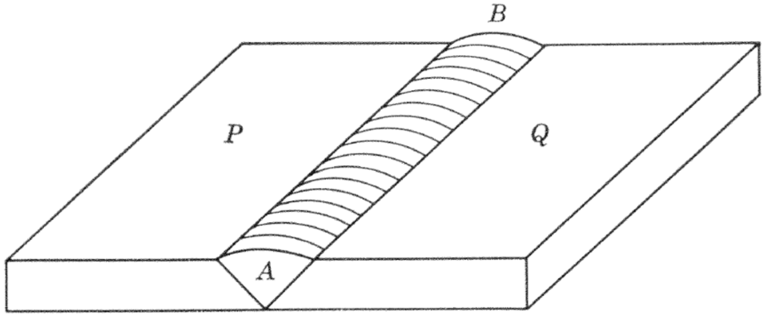
7.12. Comparison of experimental and theoretical results of dip forming of copper.

7.4. Thermal stresses in a solidifying Body

: Effect of macroscopic heat flow during solidification → Temperature gradient in the solidified metal
→ different contraction of the solid metal
→ thermal stresses within the solid metal ↑

① Extreme case : welded joint

: Unless the plates are pre-heated, the "bead" contracts far more, after it is solid, than do this plates, and high stresses is in a welded joint btw two metal plates.
→ Plastic deformation may relieve the stresses, but cracking often occurs instead.



7.13. Origin of stresses in a weld.

② stress arise as a result of contraction of solidified metal

: if alloy solidifies over a long temp. range, the contraction of the first part to solidify may tear the metal apart where there is still some liquid, resulting in extreme weakness, although the casting may appear to be sound.

→ "hot tearing"

Shrinkage of the mold btw A and B

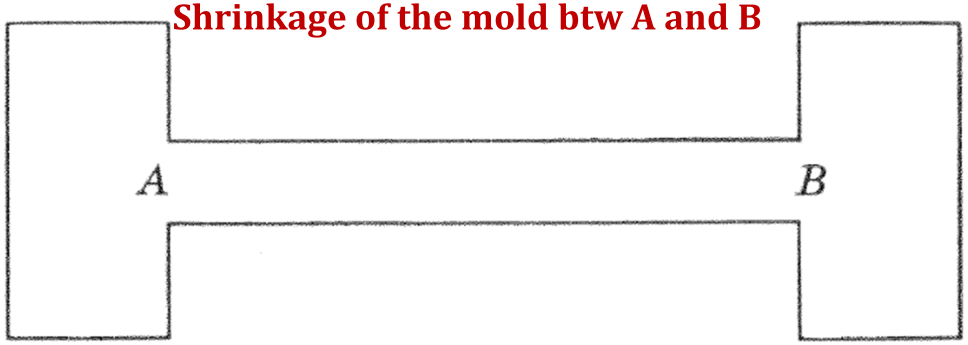


Fig. 7.14. Origin of contraction stresses in a casting.

8. The Structure of Cast Metal

8.1. General Consideration

*** "Structure" of cast metal**

① metallographic sense
: Size, Shape, Orientation and perfection of the crystals

② Distribution in the metal of the various chemical elements
: macro- and micro-segregation

③ Internal and external topography of metal
: Porosity, soundness, surface shape, and finish

→ **Main variables: "chemical composition" & "solidification rate"**

Gasses/ impurity/ elements

Different parts of metal freeze at different rates/ liquid metal may not be stationary during solidification

*** Three main categories for solidification**

"Casting" ↔ "Ingots and Billets" ↔ "Cast metal with a more complicated structure"

Welds, brazed and soldered joints and hot dipped and sprayed coating

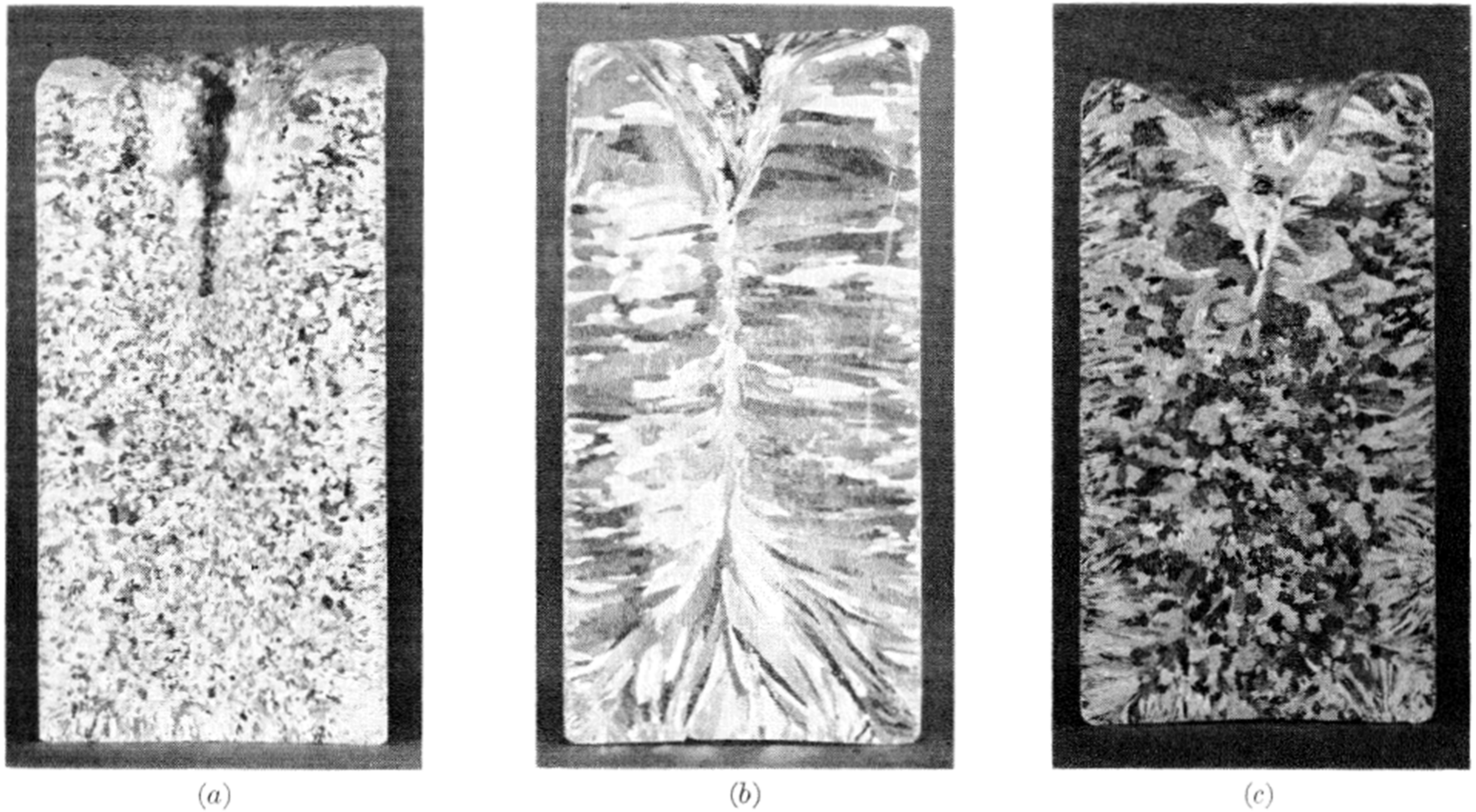
1) casting: the structure that is produced by the solidification process is preserved, which may followed by further heating like homogenization

2) Ingots & billets: the structure formed during solidification is changed by subsequent deformation and annealing; this produces an entirely new grain structure but it does not completely cure either porosity or segregation

8.2. The macrostructure of cast metals

a. Description of cast structure

→ Main factors: **heat release rate, amount of metal, composition, amount of nucleus**



Metal & cooled rapidly of small mass → large # of equiaxed crystals → “casting structure”

Metal & cooled slowly of large mass→ Columnar growth perpendicular to mold wall

Partially columnar structure → “Ingot structure”

Fig. 8.1. “As cast” structures. (a) Completely equiaxed, (b) Completely columnar, (c) partially columnar.

* **When columnar and equiaxed crystals begin to dendritically grow, they develop into cellular dendrite (Fig. 8.2):** **Control of degree of formation btw two microstructures**

→ Main process variables: "metal"_ composition, nucleation characteristics, temperature when it is poured, its motion as it enters the mold, "mold"_ thermal property of mold, temperature, and geometry

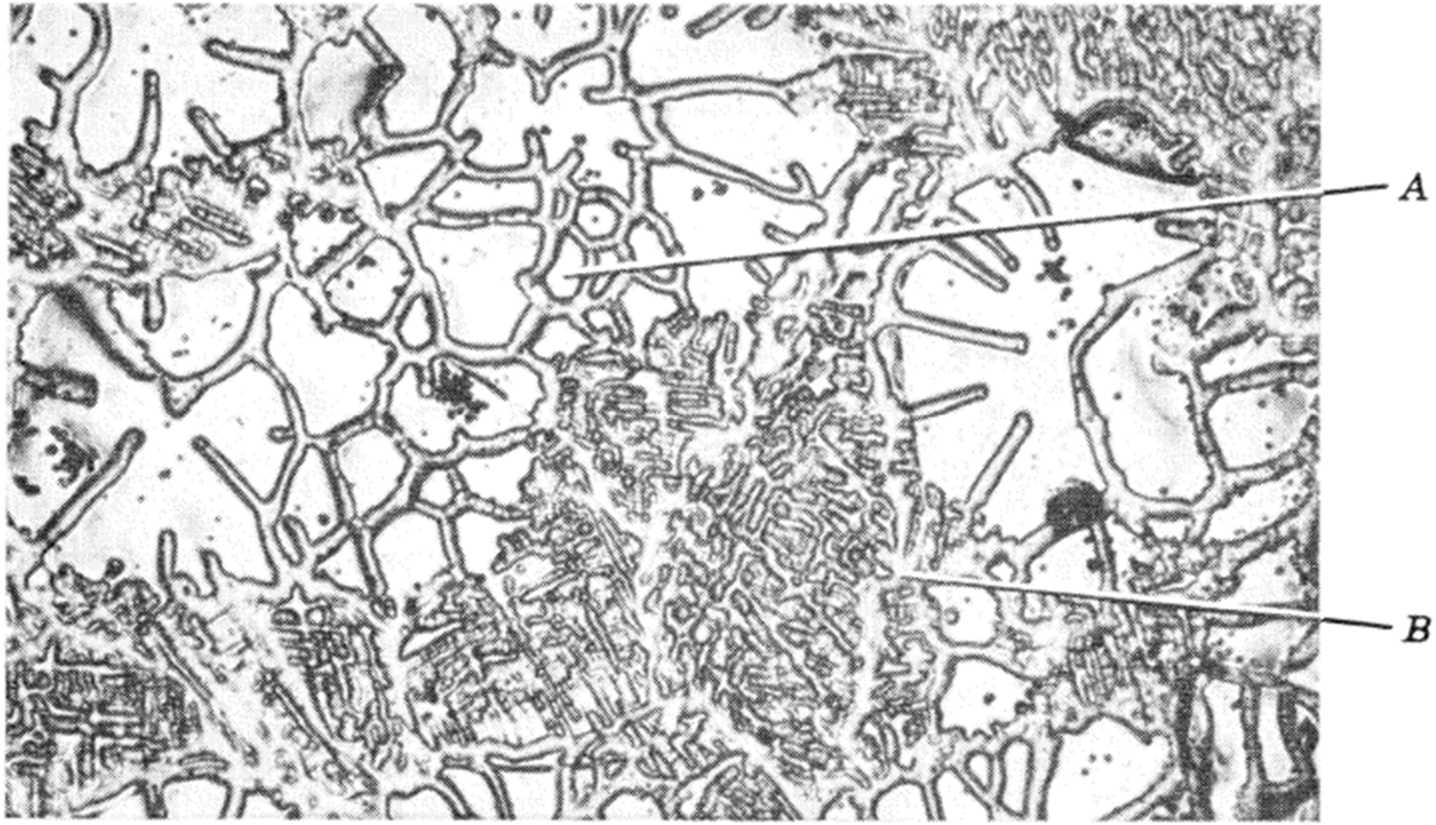
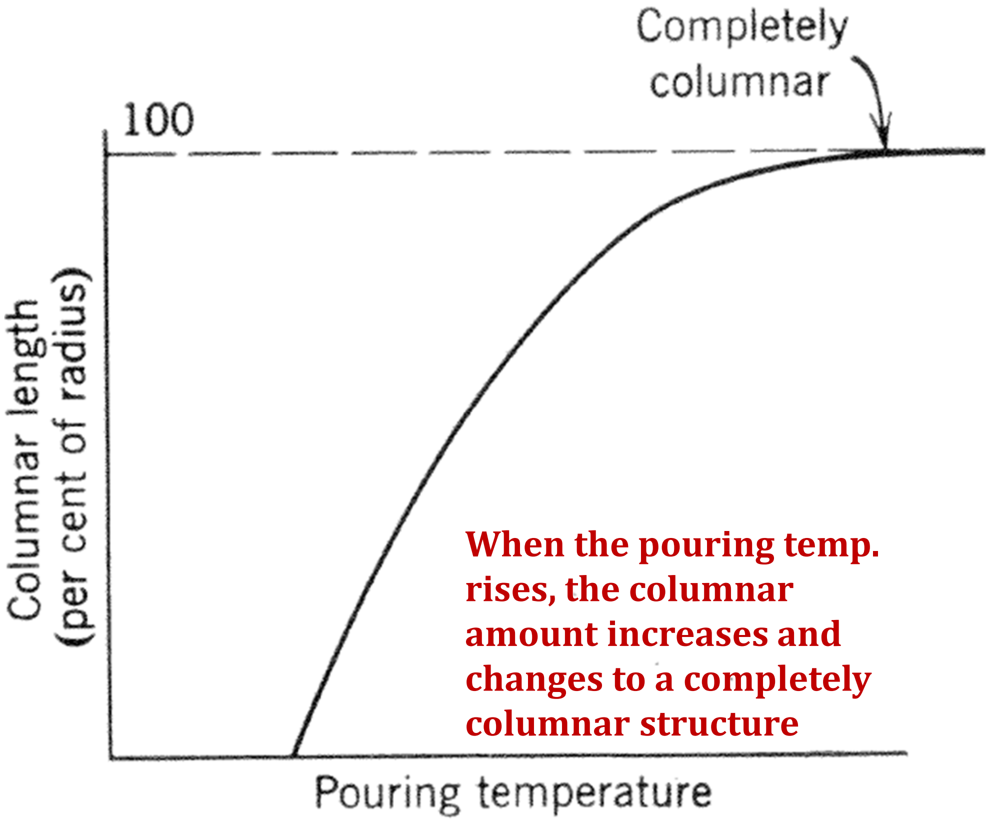


Fig. 8.2. Equiaxed grain in an ingot of Al-2% Cm, showing pre-dendritic region (A) and cellular dendritic region (B).

b. Experimental observation: Effect of process variables for controlling structure

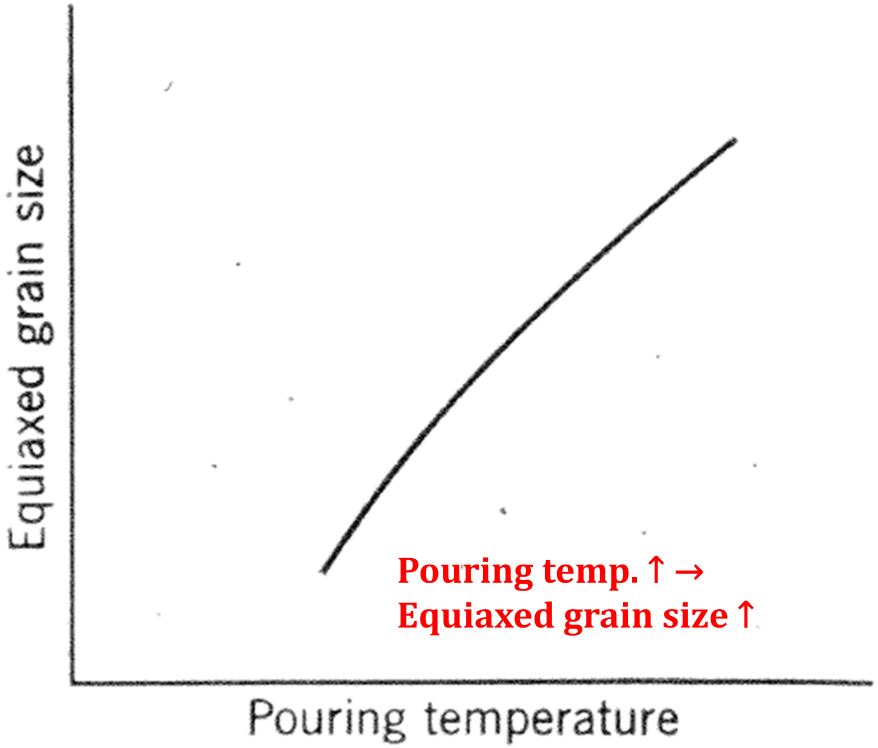
→ Au-Cu alloy + graphite mold (3 inch height/ 2 inch diameter)

Columnar length and Equiaxed grain size measurements at different pouring temperatures



When the pouring temp. rises, the columnar amount increases and changes to a completely columnar structure

Fig. 8.3. Variation of length of columnar zone with pouring temperature.



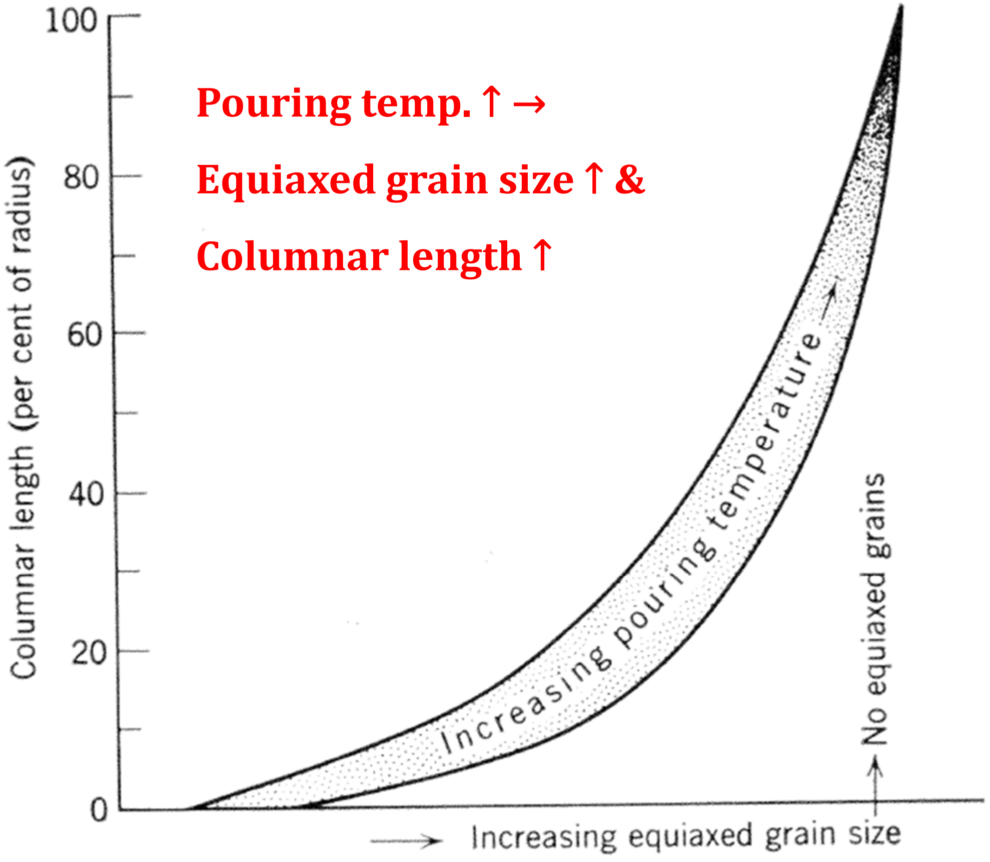
Pouring temp. ↑ → Equiaxed grain size ↑

Fig. 8.4. Variation of equiaxed grain size with pouring temperature.

b. Experimental observation: Effect of process variables for controlling structure

→ Au-Cu alloy + graphite mold (3 inch height/ 2 inch diameter)

Columnar length and Equiaxed grain size measurements at different pouring temperatures

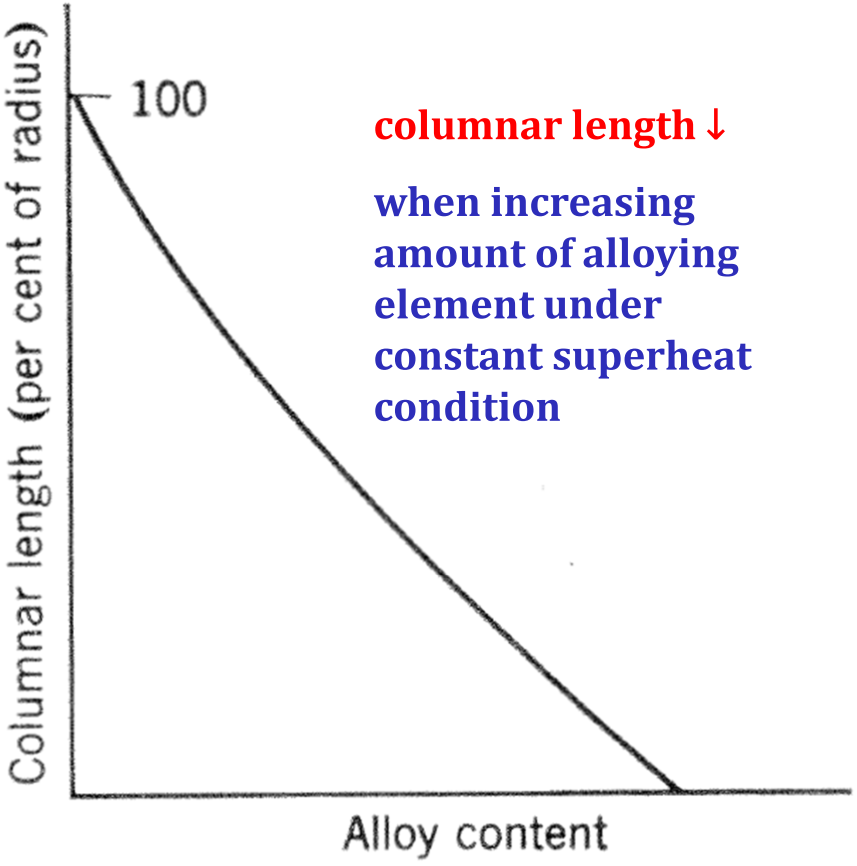


Pouring temp. ↑ →

Equiaxed grain size ↑ &

Columnar length ↑

Fig. 8.5. Variation of equiaxed grain size with columnar length.



columnar length ↓

when increasing amount of alloying element under constant superheat condition

Fig. 8.6. Variation of columnar length with alloy content; constant superheat.

c. Solidification in a mold

(1) Chill zone

- When the molten metal is poured into the mold, nucleation increases due to ΔT of the mold wall and melt

→ small ΔT → slow growth of nuclei → easy extra nucleation

large ΔT → fast growth of nuclei → difficult extra nucleation

* Crystal # in chill zone ∝ the availability of nucleants, the rate of heat release, the volume of chilled liquid, the temperature of the metal surface when metal reaches T_l, and the thermal properties of the mold and metal.

Ex ① During pouring at high T, the metal is heated while the metal is chilled on the surface, reducing the rate of heat release until the nucleation temp is reached

high pouring temp → # of nuclei ↓/ low pouring temp → # of nuclei ↑

Ex ② Metal with high thermal diffusivity & metal with low thermal diffusivity :

heat release ↑ → More nucleation density in larger liquid volumes

Ex ③ Composition: Excess solute rejection from Alloy → Decrease dendrite growth rate in given supercooling → Alloying element ↑ → Increase nucleation

c. Solidification in a mold

(1) Chill zone

* **Just after nucleation: Not all nuclei are in good contact with the mold wall**

→ Convection current of liquid metal

1) **Low pouring temp.: Many nuclei falling off due to the mold temp. increase continue to grow due to the reduction of the melt temp. = big-bang wall nucleation → Equiaxed structure**
2) **High pouring temp.: Most of the separated nuclei are re-melted and form a chilled zone on the mold wall**

* **Initial solidification: Pre-dendritically grow in chilled zone → Residual liquid rapidly drops to Sol.-Liq. temp. of the crystal growing in the superheated state.**

1) **If this temperature is above the nucleation temperature of the melt → No extra nucleation→ ingot type structure**
2) **If this temperature is below the nucleation temperature of the melt → extra nucleation in whole melt → casting type structure**

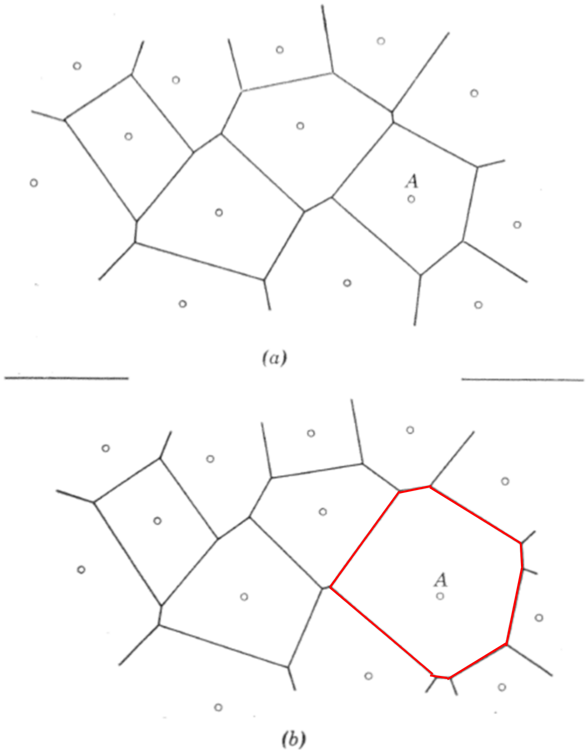
(2) Columnar zone: Produced as a result of heat flow towards mold

→ Fast growth rate with preferred orientation & obstructing growth by forming branches

* The interface between the columnar crystal and liquid forms smooth, cellular, cellular-dendritic structures (most alloys) depending on alloy composition and solidification rate

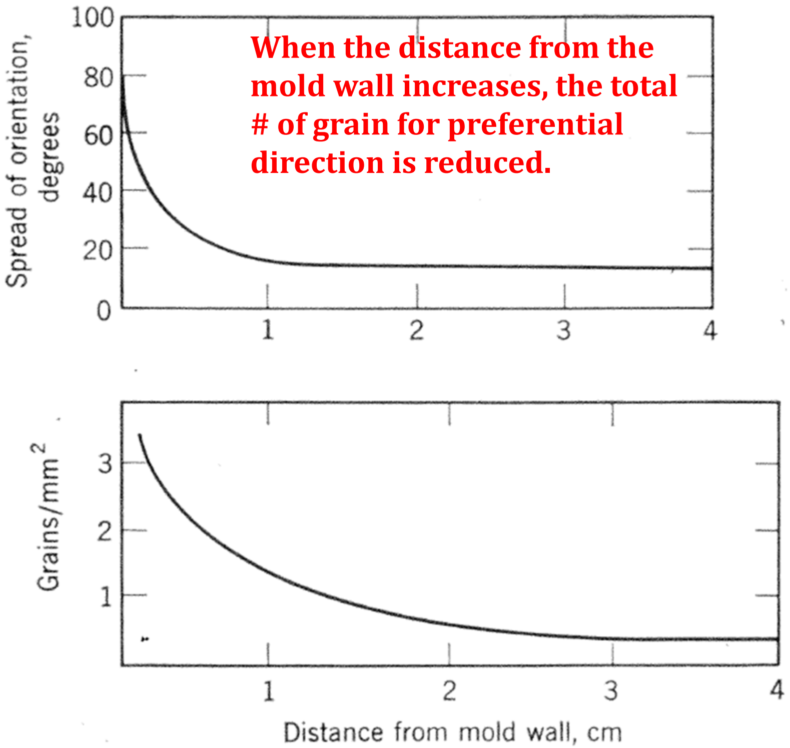
* Favorable orientation: Perpendicular to mold wall

FCC, BCC → <100> direction/ HCP → $\langle 10\bar{1}0 \rangle$ direction



Grain A: fast longitudinal growth rate, & fast transverse growth rate

Fig. 8.7. Shapes of crystals growing from randomly selected points. (a) Equal rates, (b) crystal A growing twice as fast as the others.



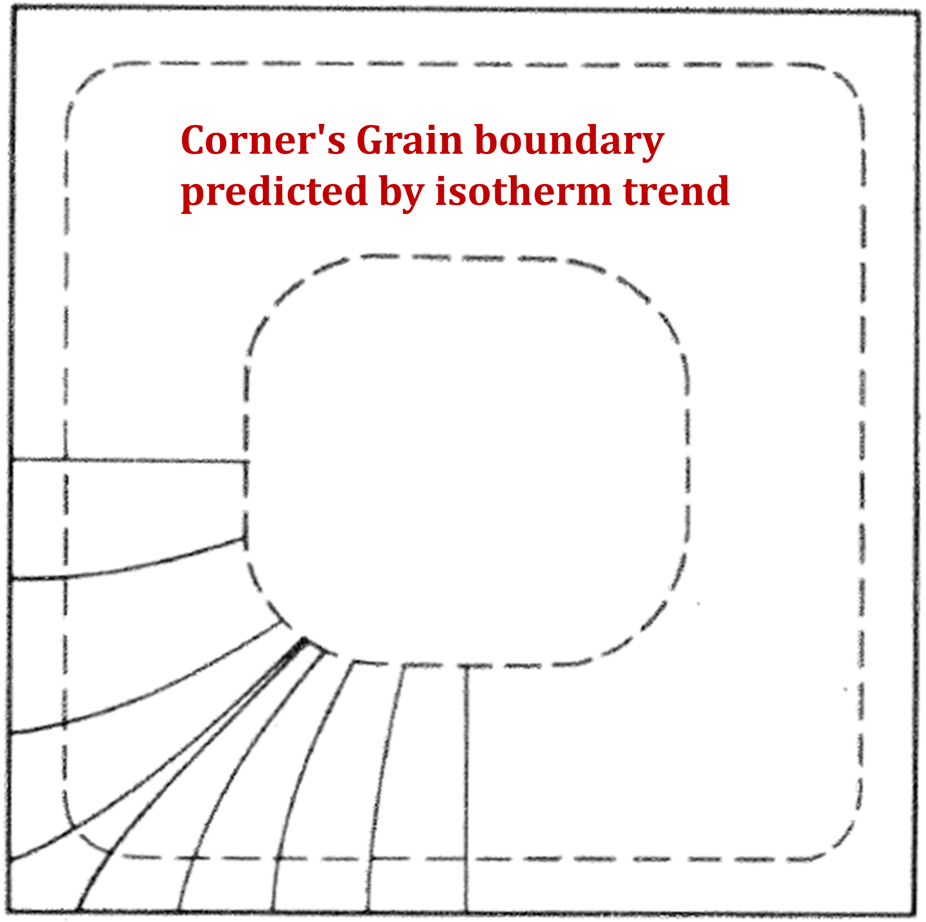
When the distance from the mold wall increases, the total # of grain for preferential direction is reduced.

Fig. 8.8. Variation of grain size and preferred orientation with distance from mold wall.

(2) Columnar zone: Produced as a result of heat flow towards mold

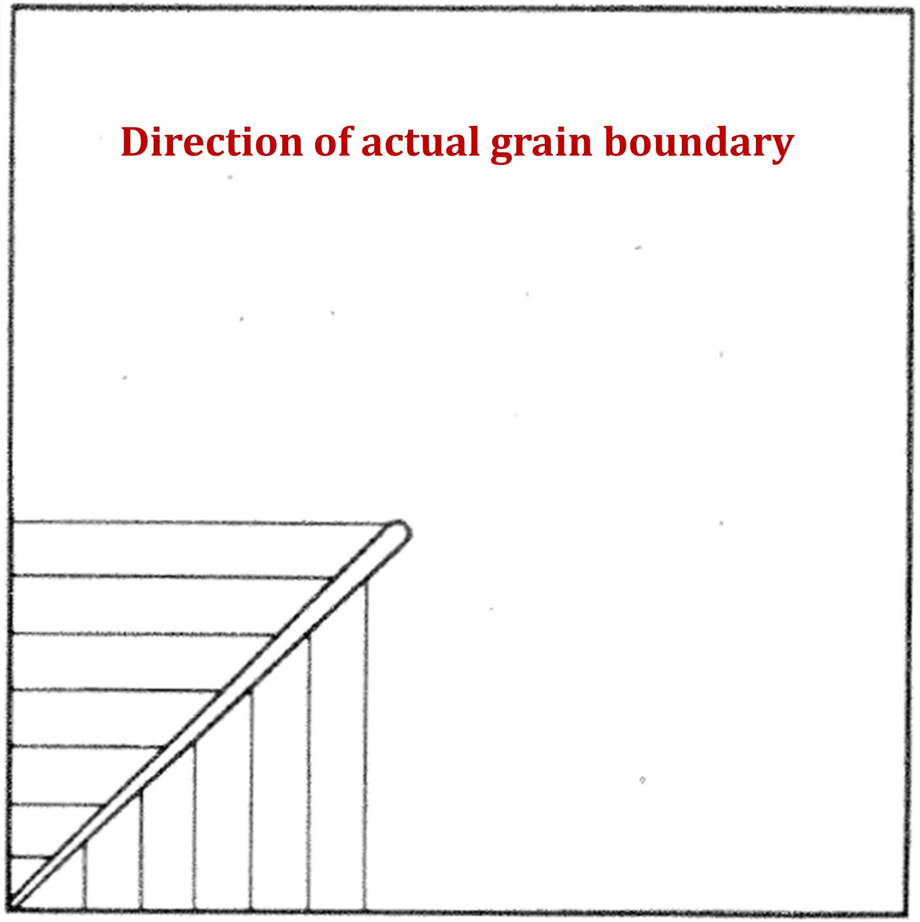
→ Fast growth rate with preferred orientation & obstructing growth by forming branches

*** Boundaries near the mold corner**



Corner's Grain boundary predicted by isotherm trend

Fig. 8.9. Grain boundaries orthogonal to isotherms (schematic).

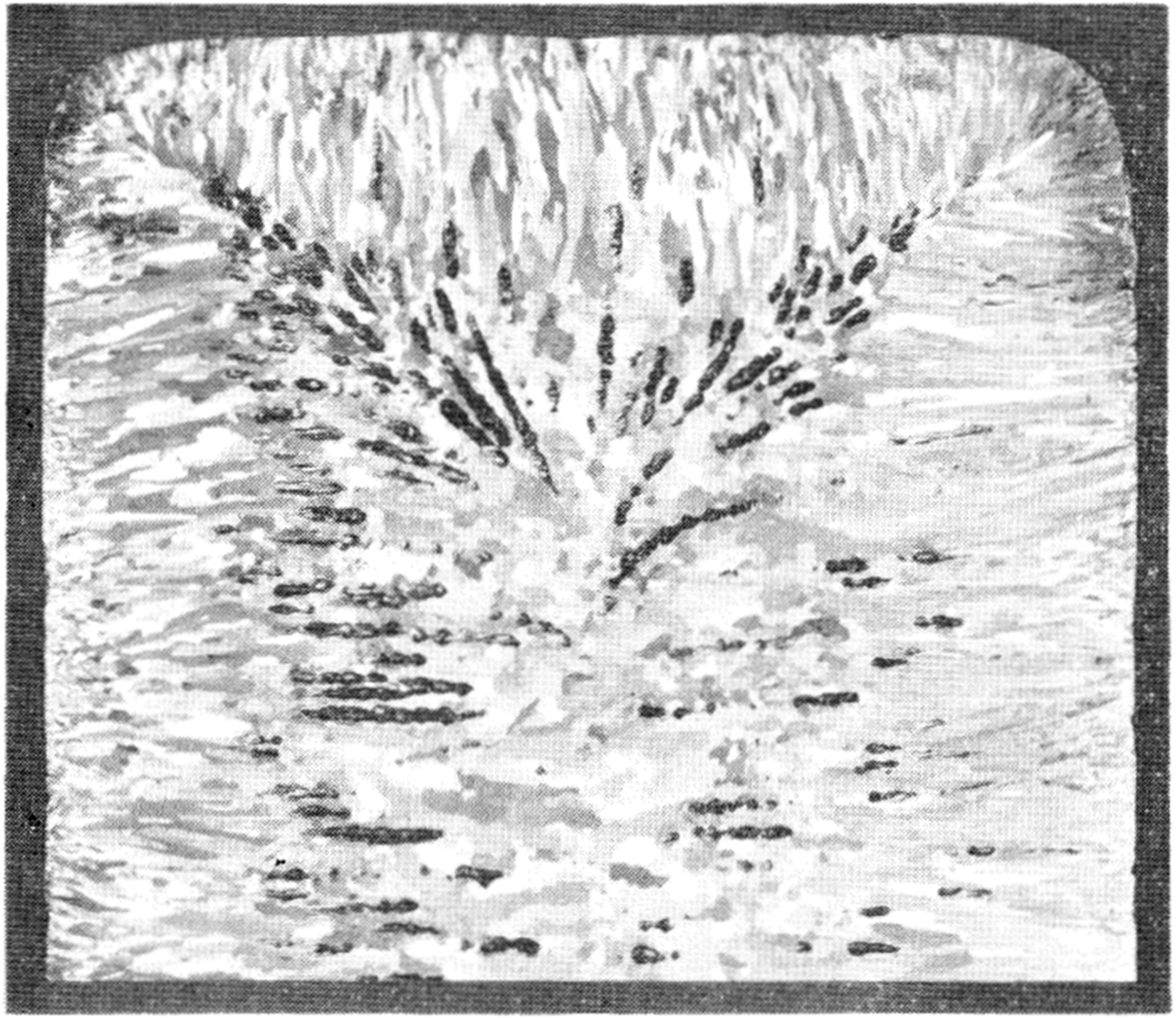


Direction of actual grain boundary

Fig. 8.10. Grain boundaries maintaining original directions (schematic).

* Actual Photograph of structure shown in Figure (8.10)

: This structure is due to the large crystallographic orientation dependence of cellular-dendritic type growth.



* It is considered that the nuclei of the columnar zone were all formed on the mold wall. But it is recently investigated that equiaxed crystals of pre-dendritic structure within the columnar zone as shown in Fig. 8. 12.

→ **Growth of crystal fallen from cold mold wall.**

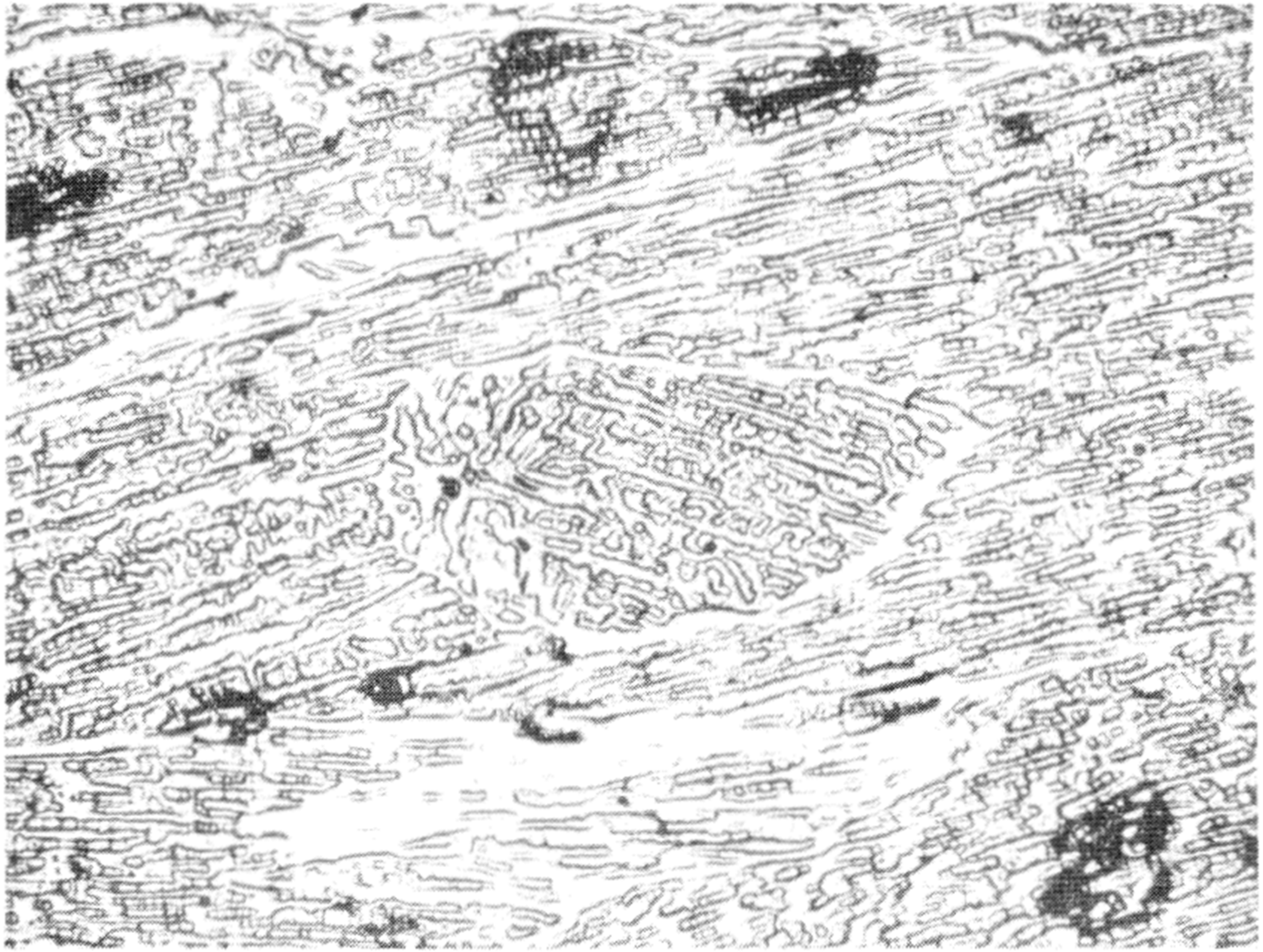
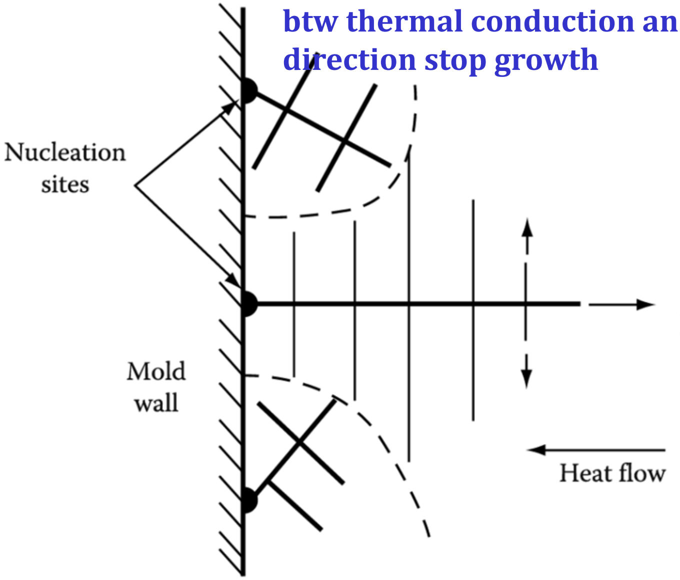


Fig. 8.12. Equiaxed crystals in columnar zone.

(2) Columnar zone

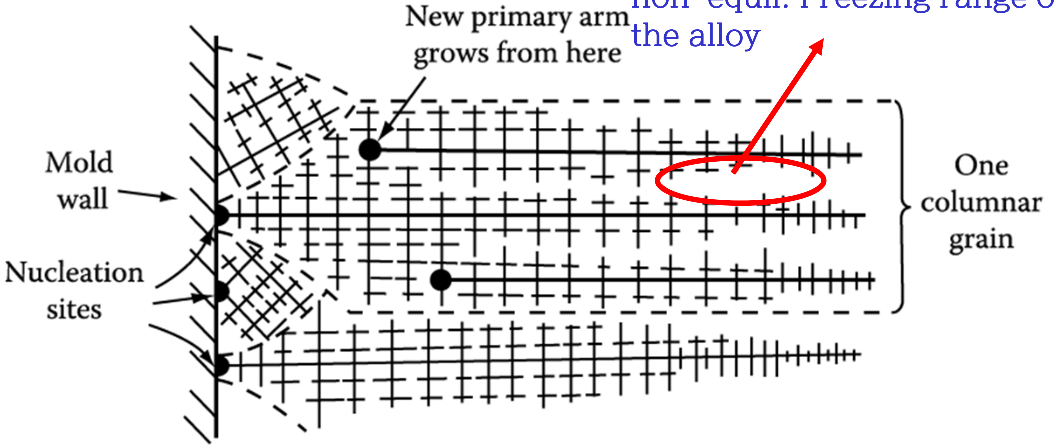
After pouring the temperature gradient at the mould walls decreases and the crystals in the chill zone grow dendritically in certain crystallographic directions, e.g. <100> in the case of cubic metals.

→ 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

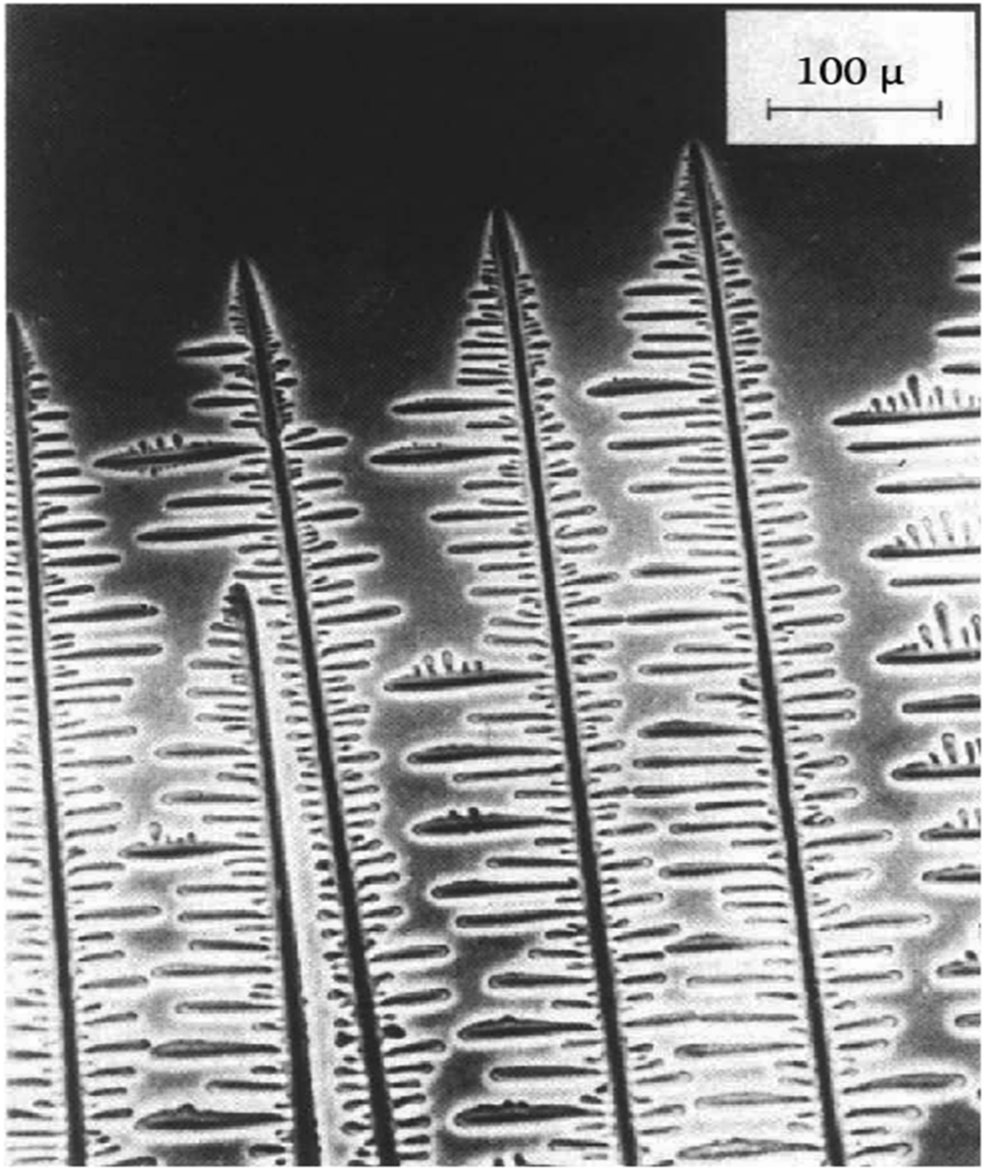


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

(3) 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

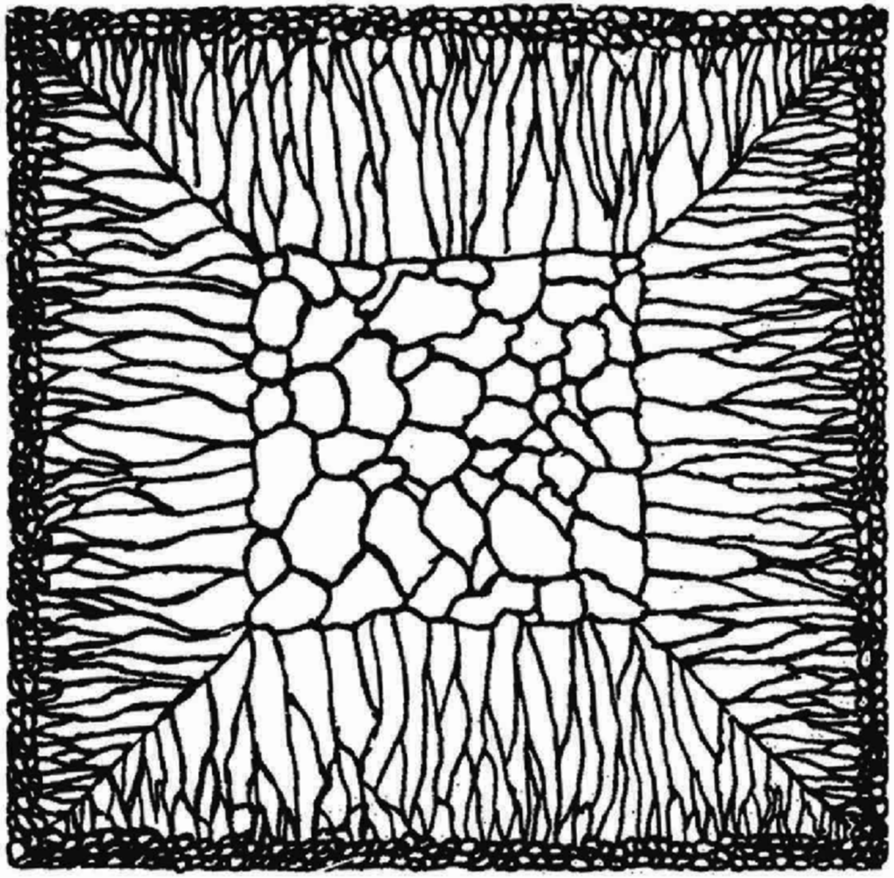
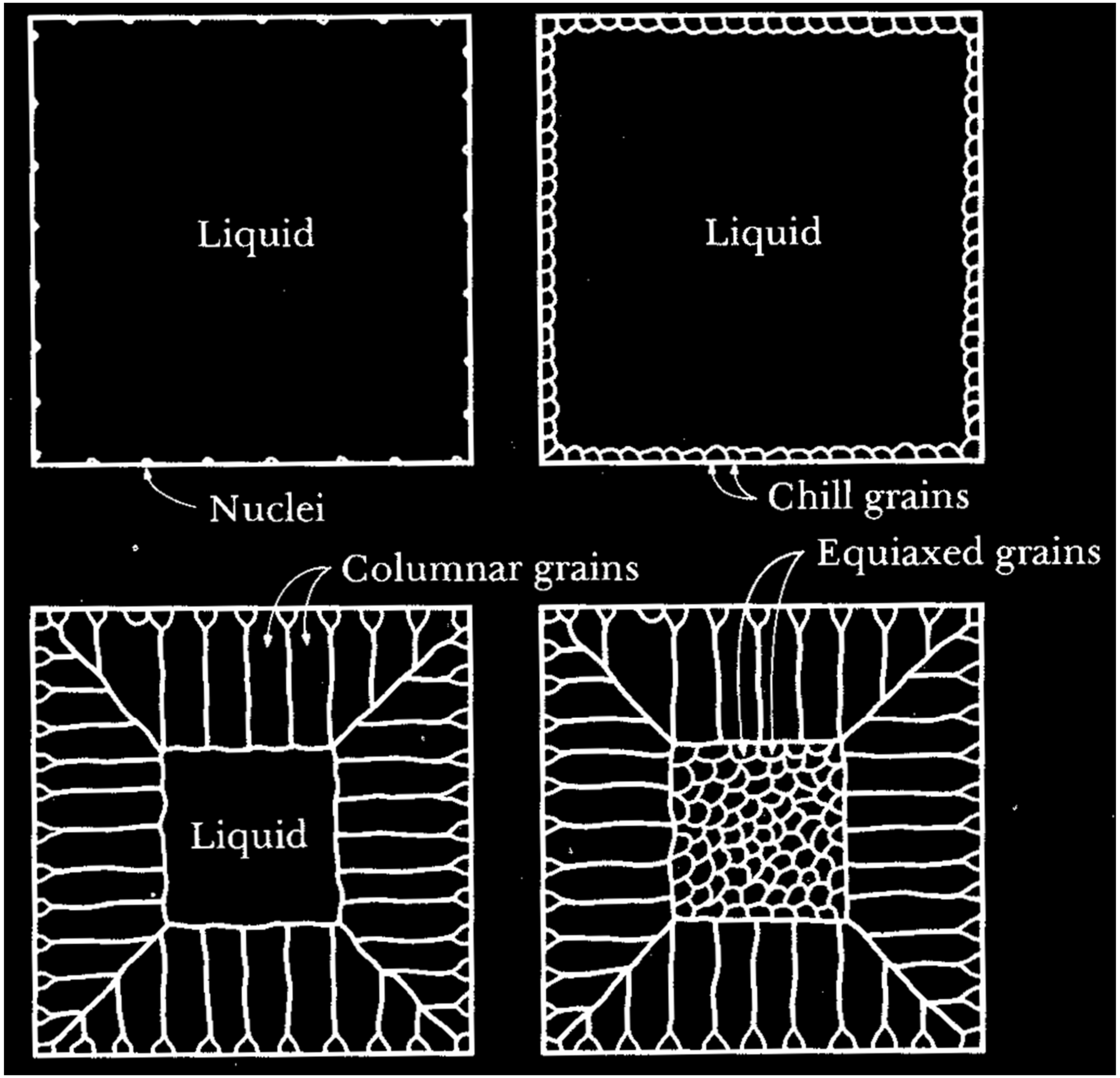


Fig. 4.40 Schematic cast grain structure.
(After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.)


Liquid
Liquid
Nuclei
Chill grains
Columnar grains
Equiaxed grains
Liquid

(4) Effect of gravity and of rotation

① Mixed structure by gravity due to “settling” of crystals

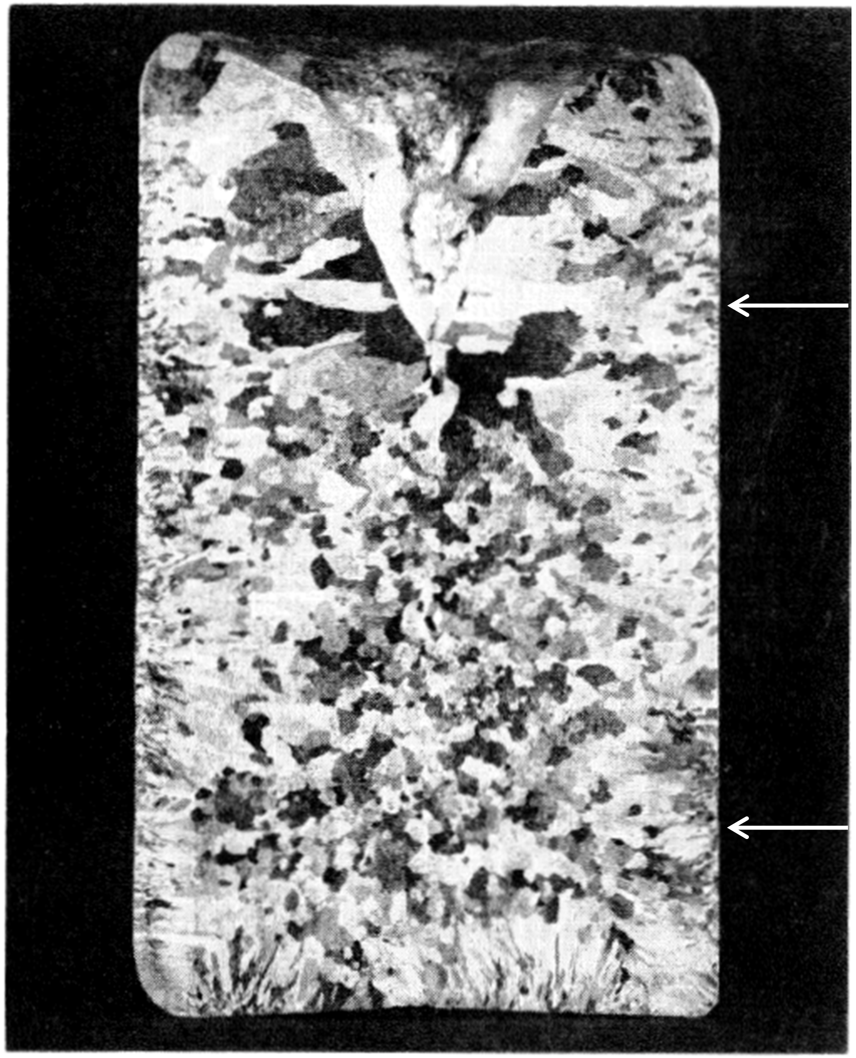


Fig. 8.16. “Mixed” structure due to “settling” of crystals.

Columnar

Equiaxed

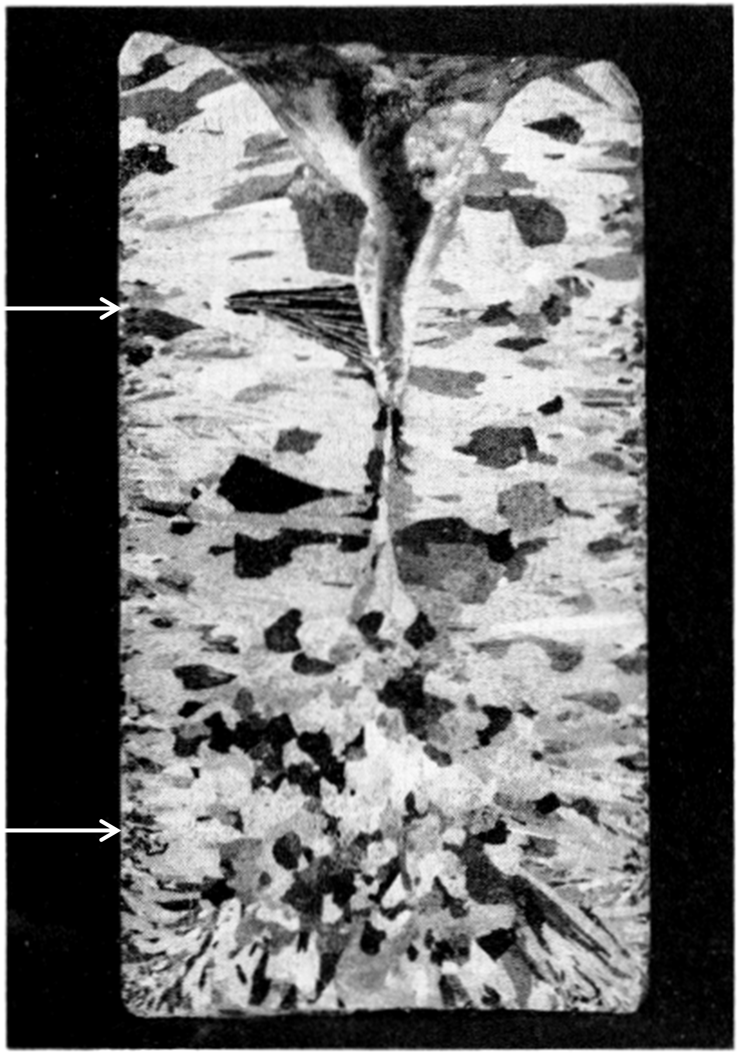


Fig. 8.17. Variation of equiaxed grain size with position in the ingot.

(4) Effect of gravity and of rotation

② Melt rotation during electromagnetic stirring

a) Grain refinement and shorten columnar zone

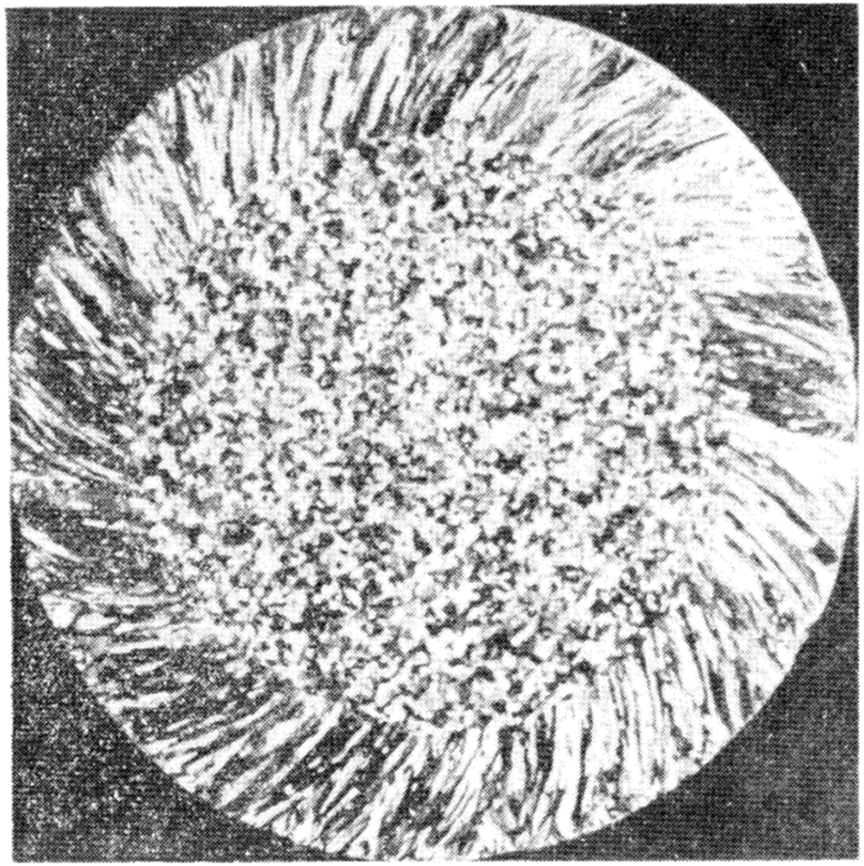


Fig. 8.18. Effect of rotation of the liquid on grain size and columnar length.

b) Tilted to the top of the interface

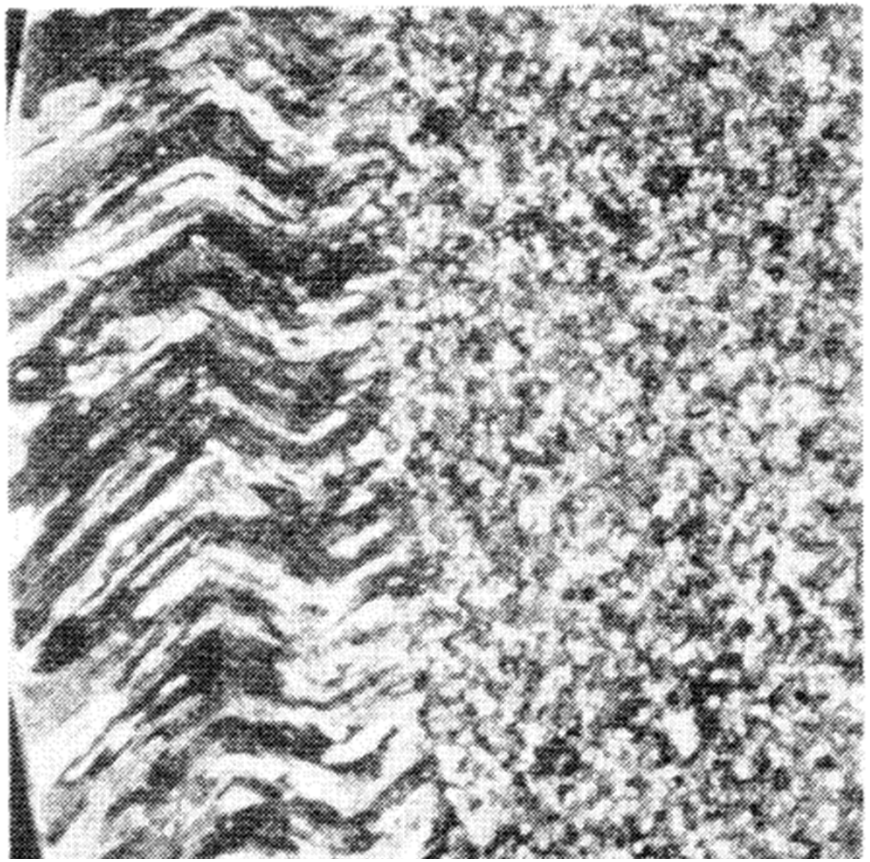


Fig. 8.19. Effect of rotation on the columnar structure. (effect of rotation reversing)

(5) Thermal measurement: superheat ~ very soon disappear

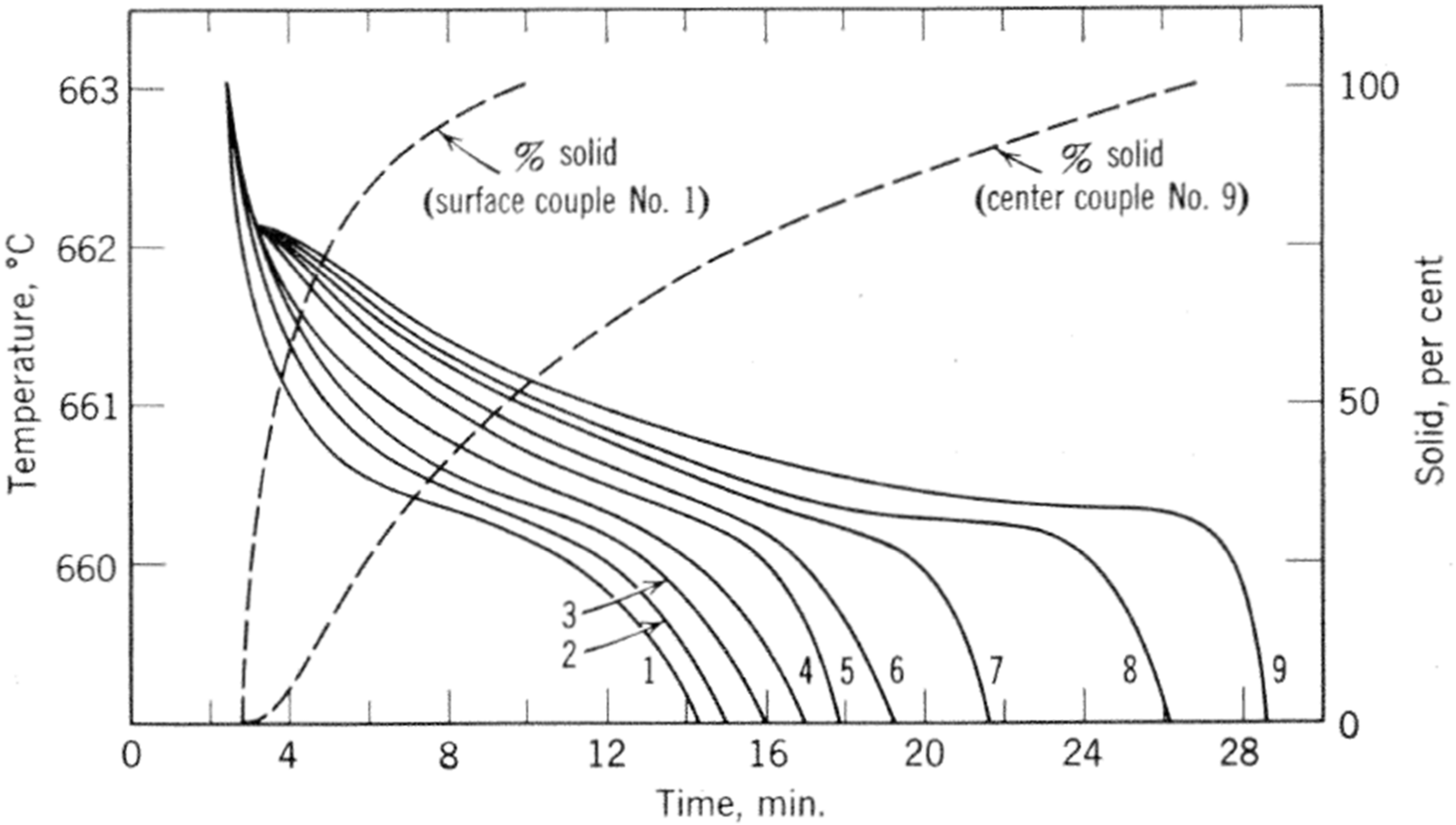


Fig. 8.23. Cooling curves for an ingot of super purity aluminum with 0.11% titanium.

(6) Grain refiners

: empirical findings

Ex.

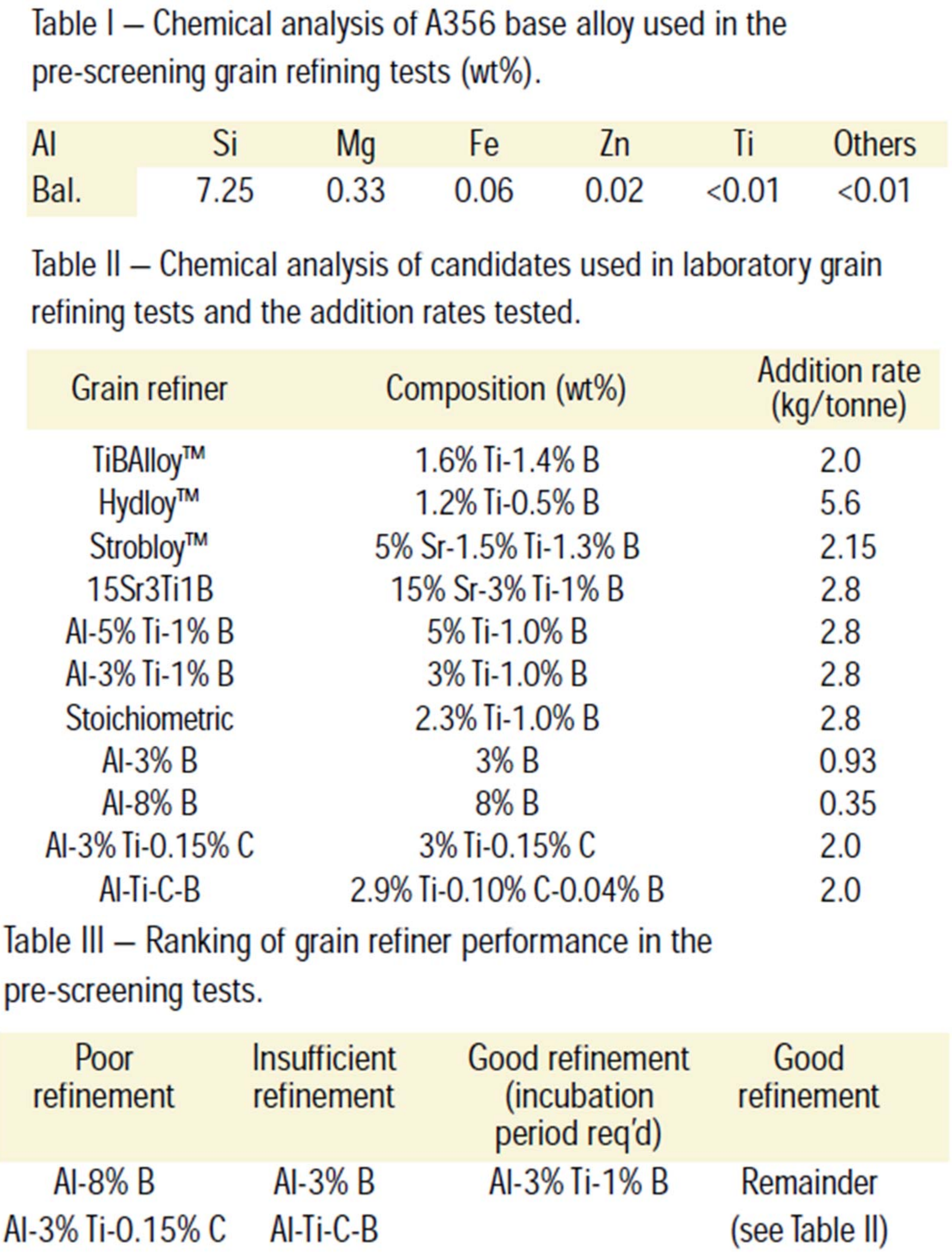


Table I – Chemical analysis of A356 base alloy used in the pre-screening grain refining tests (wt%).

Al	Si	Mg	Fe	Zn	Ti	Others
Bal.	7.25	0.33	0.06	0.02	<0.01	<0.01

Table II – Chemical analysis of candidates used in laboratory grain refining tests and the addition rates tested.

Grain refiner	Composition (wt%)	Addition rate (kg/tonne)
TiBAlloy™	1.6% Ti-1.4% B	2.0
Hydloy™	1.2% Ti-0.5% B	5.6
Strobloy™	5% Sr-1.5% Ti-1.3% B	2.15
15Sr3Ti1B	15% Sr-3% Ti-1% B	2.8
Al-5% Ti-1% B	5% Ti-1.0% B	2.8
Al-3% Ti-1% B	3% Ti-1.0% B	2.8
Stoichiometric	2.3% Ti-1.0% B	2.8
Al-3% B	3% B	0.93
Al-8% B	8% B	0.35
Al-3% Ti-0.15% C	3% Ti-0.15% C	2.0
Al-Ti-C-B	2.9% Ti-0.10% C-0.04% B	2.0

Table III – Ranking of grain refiner performance in the pre-screening tests.

Poor refinement	Insufficient refinement	Good refinement (incubation period req'd)	Good refinement
Al-8% B	Al-3% B	Al-3% Ti-1% B	Remainder
Al-3% Ti-0.15% C	Al-Ti-C-B		(see Table II)

(7) Structure of continuous casting

* To reduce segregation, grain size and porosity in casting or ingot
→ Solidification rate ↑→ But, in case of casting, possible to obtain by mold wall conductivity ↑ or casting size ↓ → ∴ "continuous casting"

* Key process parameters: Advance rate of isotherm + temp. gradient of liquid
→ Determination of supercooling (temp. reduction measurement at given point)

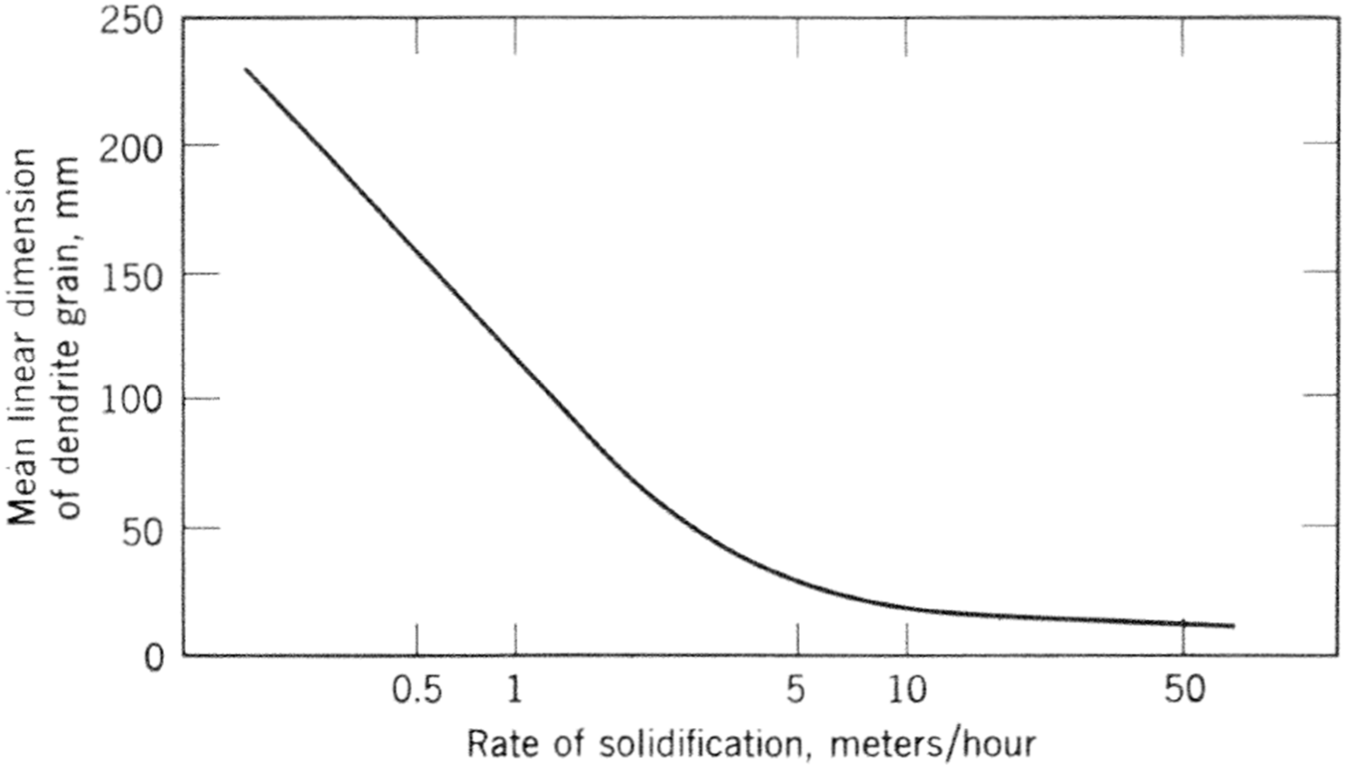


Fig. 8.24. Relation between rate of solidification and "dendritic grain size" for duralumin.

(8) Effect of vibration on structure

*** Vibration: Effective when exposed during solidification rather than grain refinement / superheating**

→ ① More nucleation ② Small crystal dispersion similar with turbulence formation.

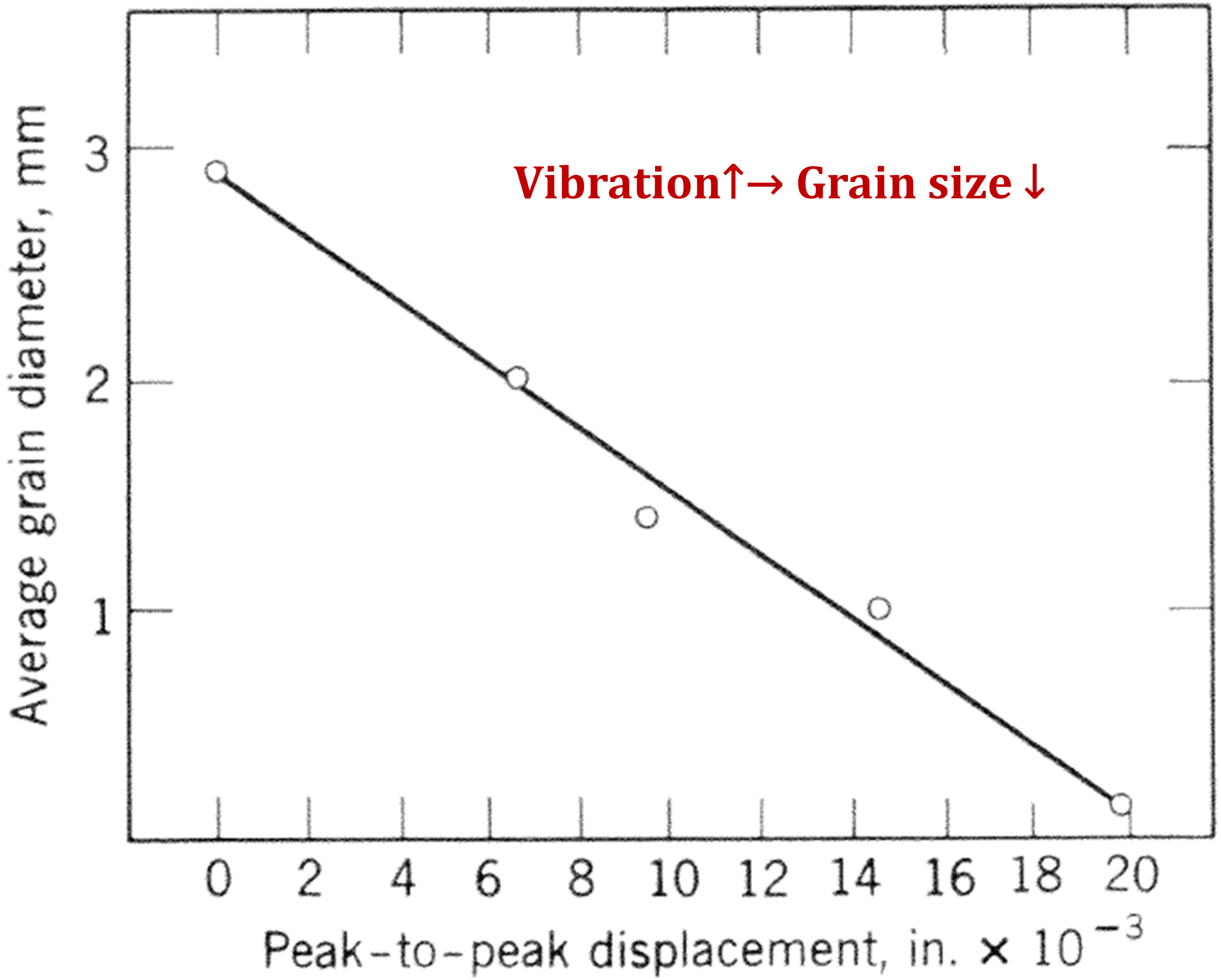


Fig. 8.25. Effect of amplitude of vibration on grain size.

(8) Effect of vibration on structure

*** Vibration: Effective when exposed during solidification rather than grain refinement / superheating**

→ ① More nucleation ② Small crystal dispersion similar with turbulence formation.

a) Effect of Vibration amplitude

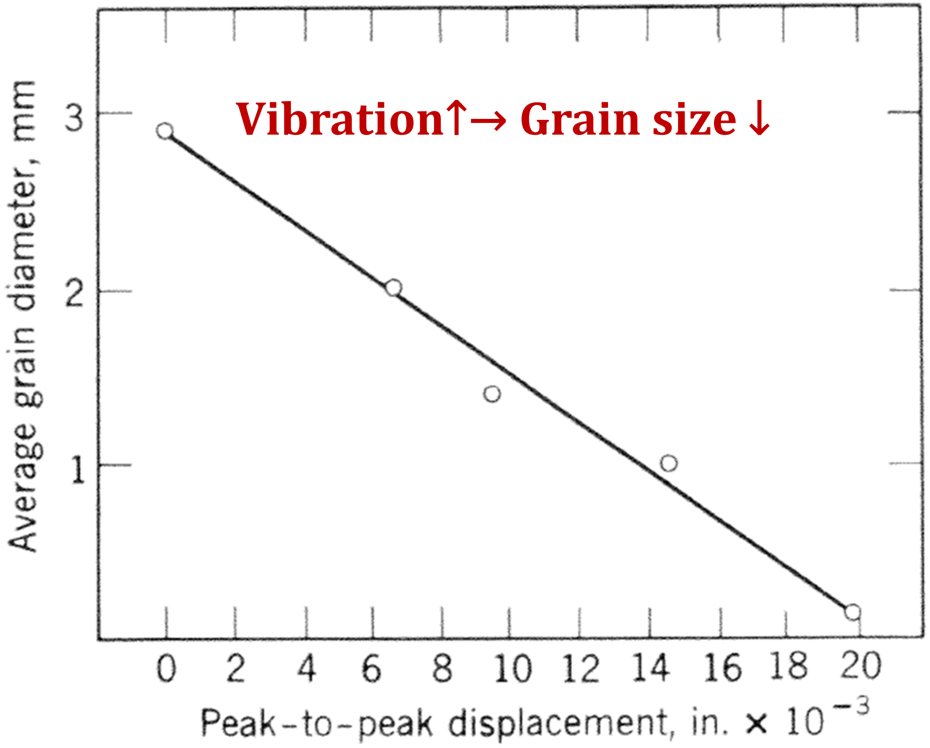

Vibration↑→ Grain size↓

Fig. 8.25. Effect of amplitude of vibration on grain size.

b) Effect of pouring temp. in vibrated, unvibrated condition

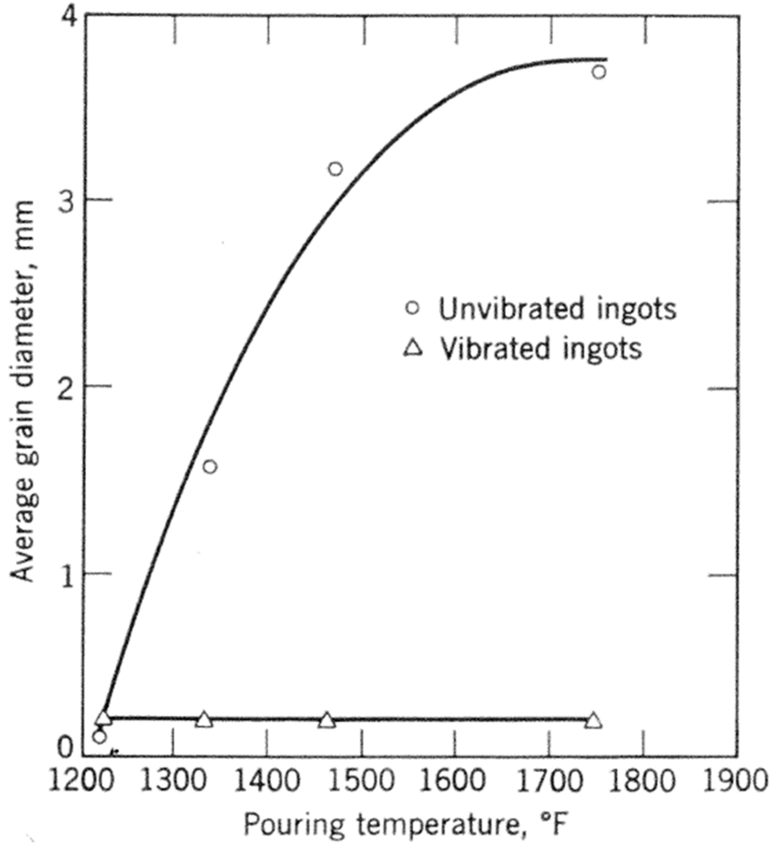


Fig. 8.26. Effect of pouring temperature on grain size.

8.3 Segregation

Solution rejection for solidification of alloy or impure metal → Redistribution by diffusion and mass flow → Effect of interface growth and propagation speed

Ex) Zone refining: possible to control of solute distribution
Other solidification: Interfacial shape complexity, difficult prediction of mass flow prediction → difficulty in quantitative prediction

*** Factors affecting solute transport in liquids**

① liquid motion

② Convection caused by density difference due to temperature difference

③ Convection due to density differences due to liquid composition changes as a result of solute rejection

④ Motion due to gravity of crystal growing in liquid

⑤ liquid motion due to solidification shrinkage

a) Micro segregation (short-range): inter-dendritic region (predictable)

b) Macro segregation (long-range): diffusion of en-riched liquid and mass movement
→ normal segregation (difficult to predict), inverse segregation (predictable) and gravity segregation (difficult to predict_need to understanding of fluid motion)

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

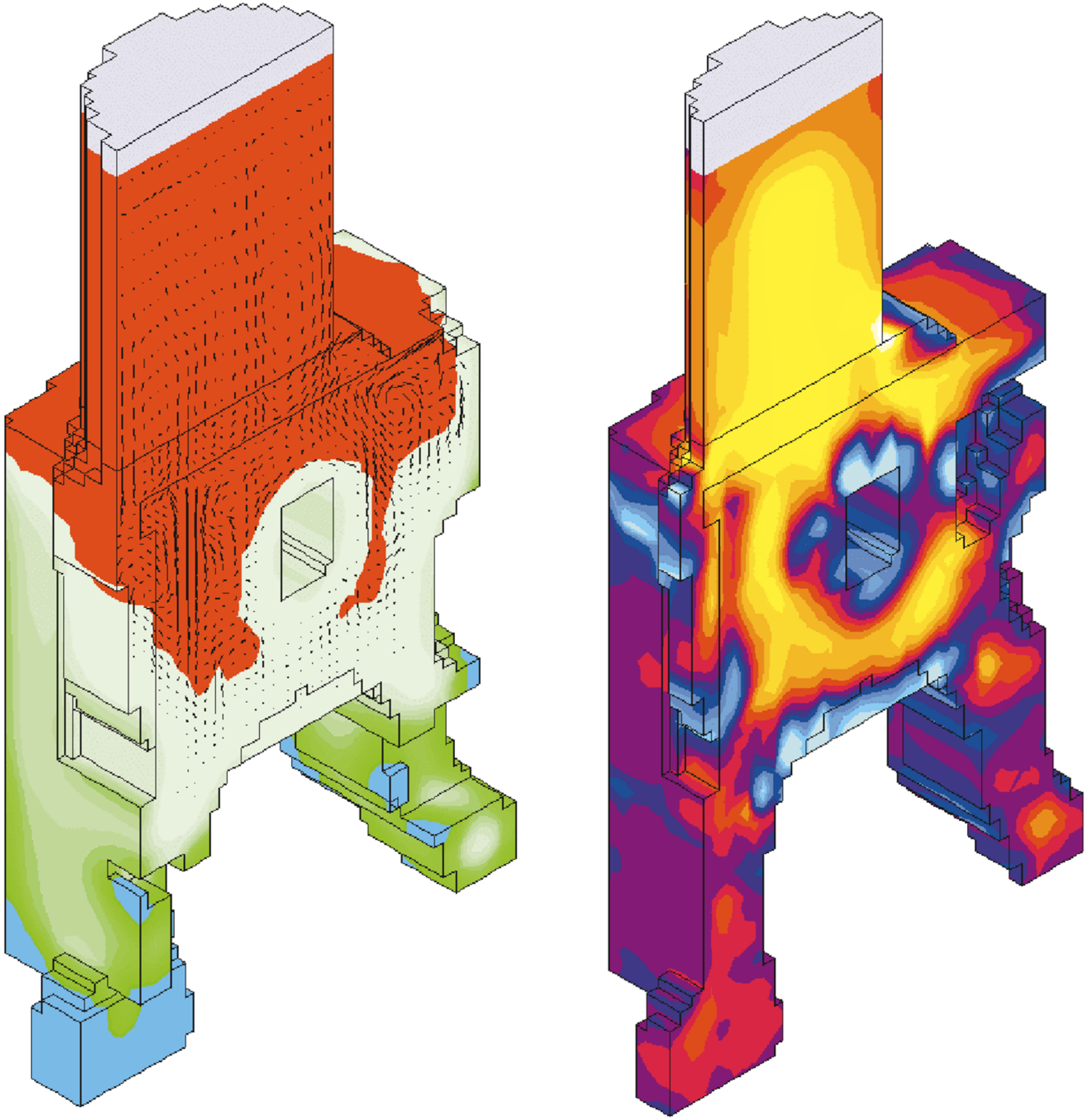


Fig.

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).

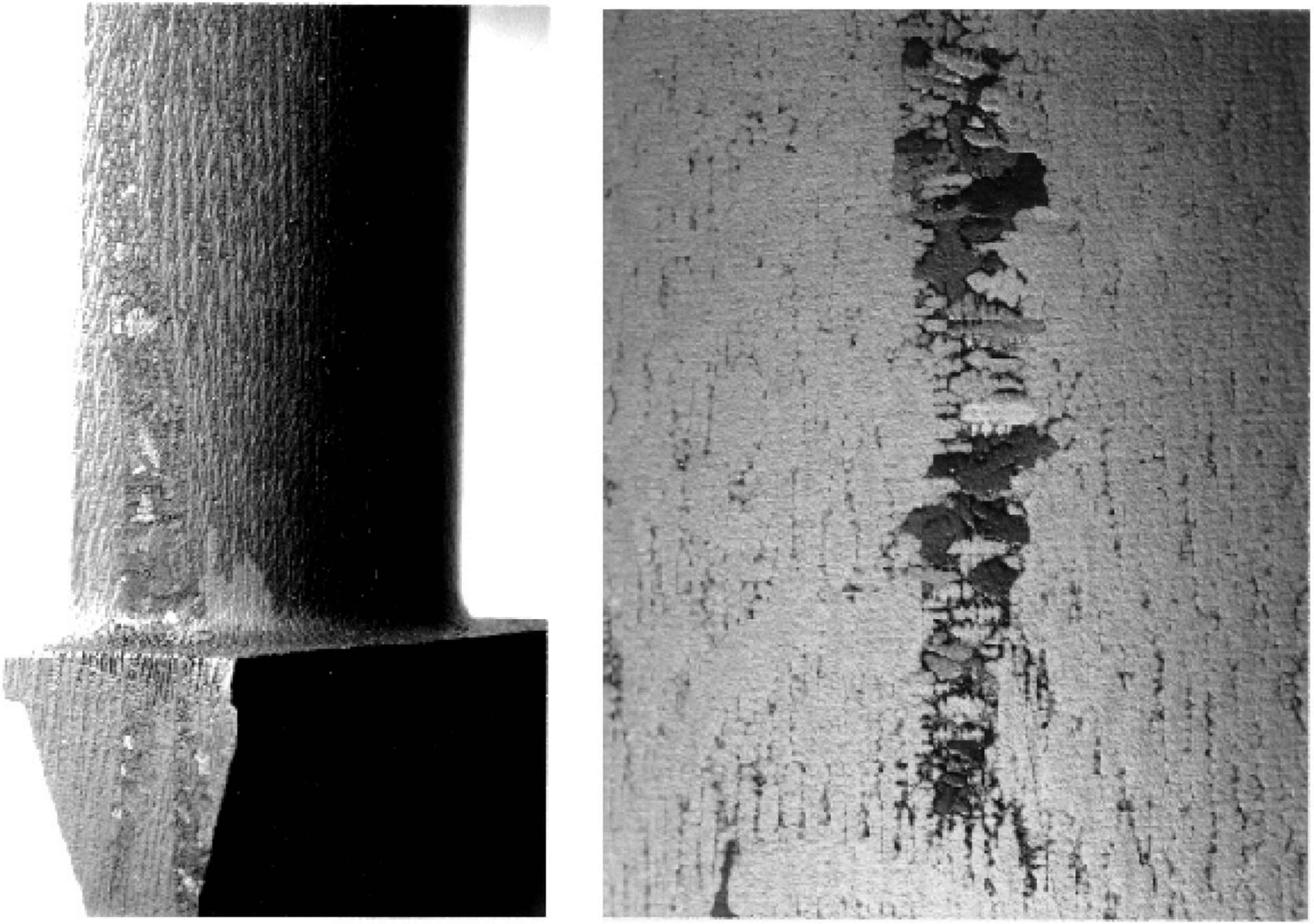
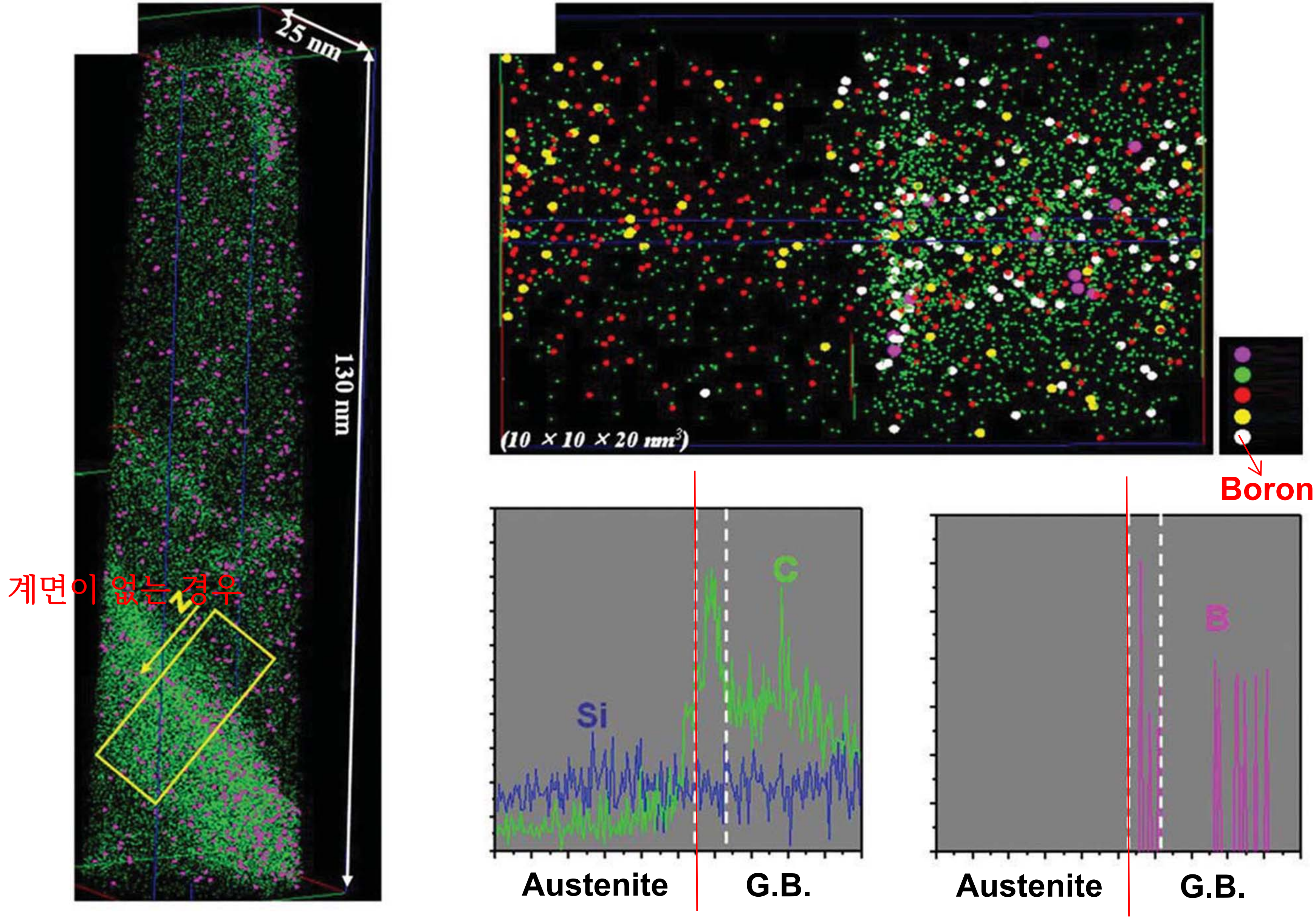


Fig.

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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8.4. The significant of small-scale experiments

-Prediction of full scale structure and characteristics by small scale experiment
But there are various variables to consider.

8.5. change of volume on Freezing

T_m: liquid → solid ΔV positive (general) → exsistance → where? location

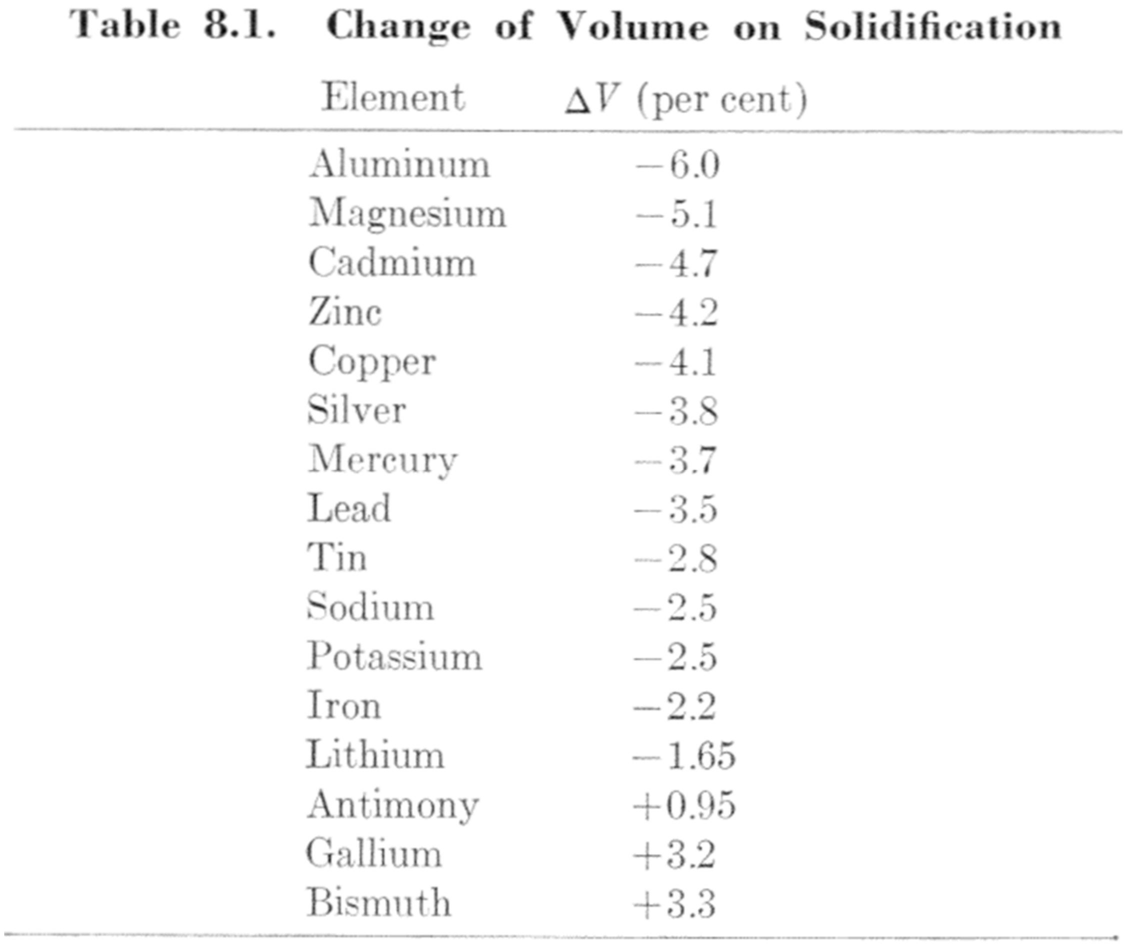


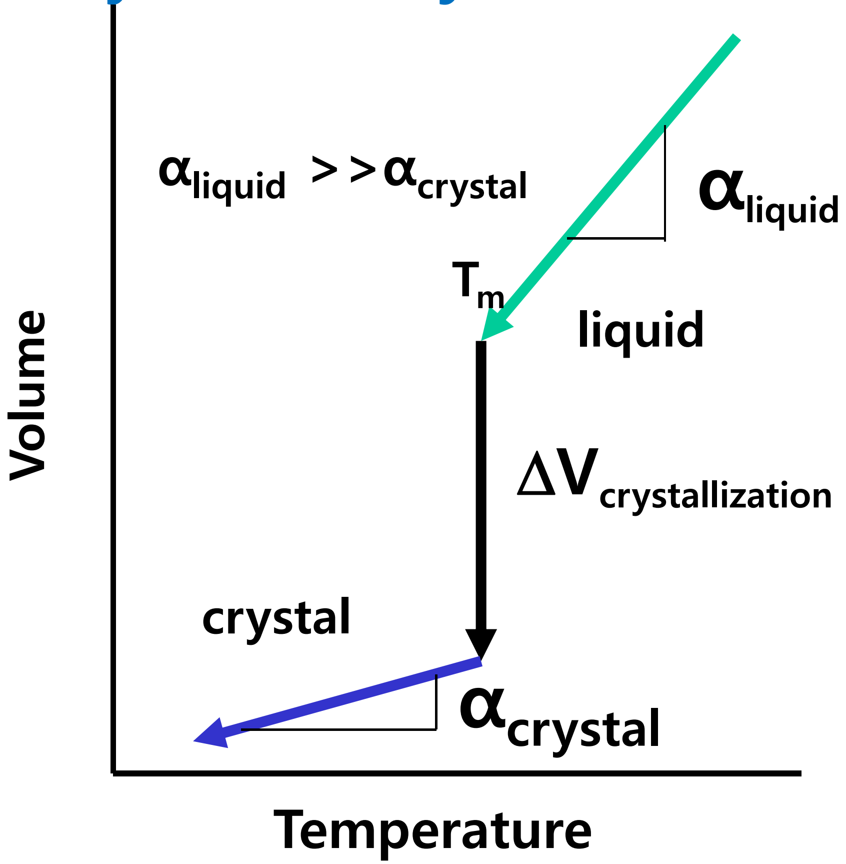
Table 8.1. Change of Volume on Solidification

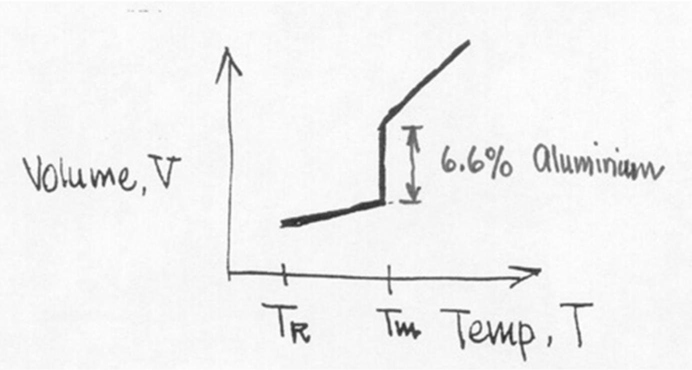
Element	ΔV (per cent)
Aluminum	−6.0
Magnesium	−5.1
Cadmium	−4.7
Zinc	−4.2
Copper	−4.1
Silver	−3.8
Mercury	−3.7
Lead	−3.5
Tin	−2.8
Sodium	−2.5
Potassium	−2.5
Iron	−2.2
Lithium	−1.65
Antimony	+0.95
Gallium	+3.2
Bismuth	+3.3

* Shrinkage

Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α





Shrinkage effect

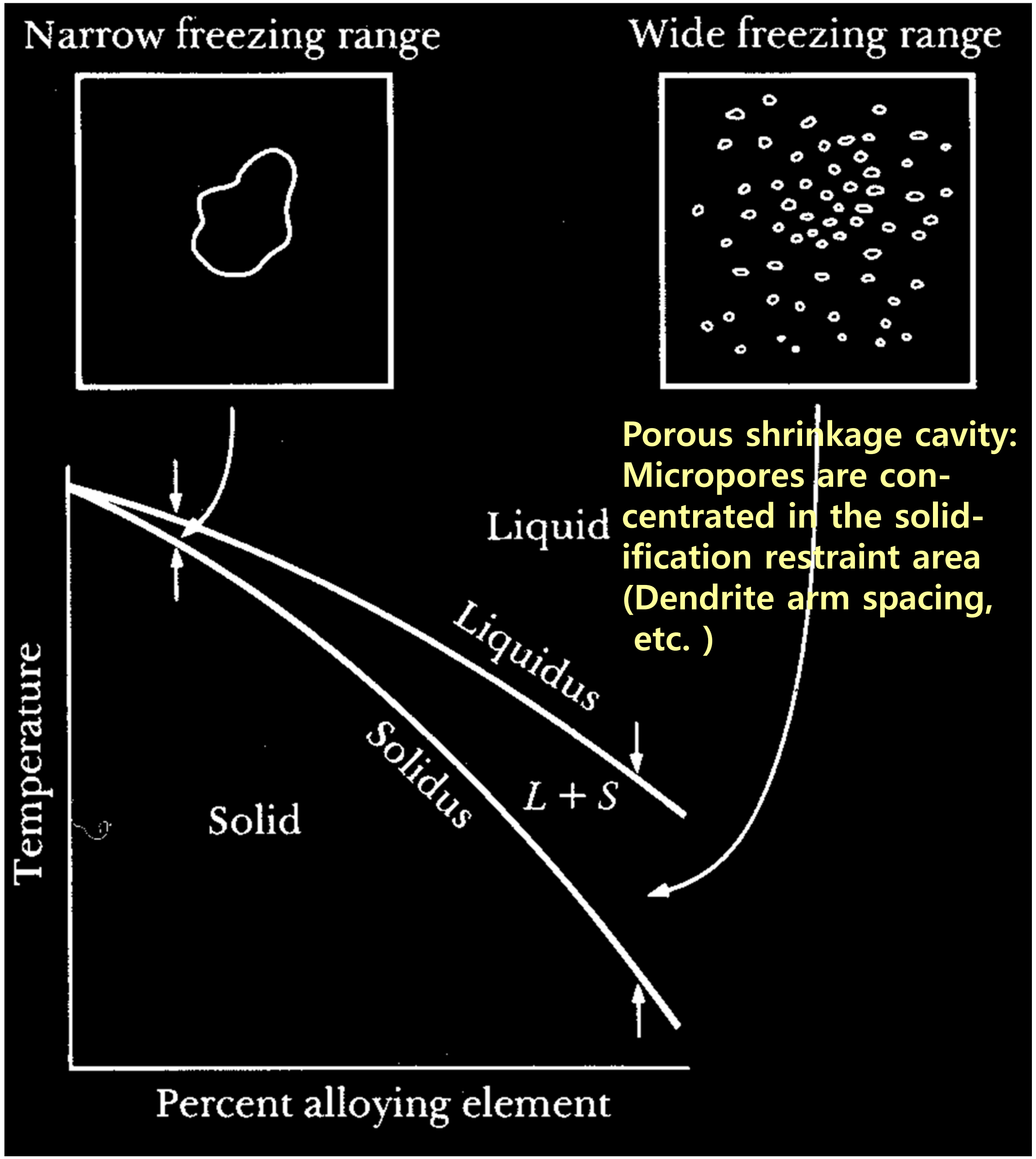
* Formation of Voids during solidification

Center shrinkage cavity: occurs at the casting center caused by ΔV (solidification shrinkage at the time of solidification of castings with little change in composition)

Dispersed micropores:
A very wide range of scattered micropores

Except for external shrinkage (around the mold) and primary shrinkage hole (surface), these shrinkage voids are mainly bubble defects

In the bubbles, there are CO, nitrogen, oxygen, and hydrogen in the iron alloy, hydrogen, oxygen in the copper alloy, and hydrogen in the aluminum alloy.



Porous shrinkage cavity: Micropores are concentrated in the solidification restraint area (Dendrite arm spacing, etc.)

Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

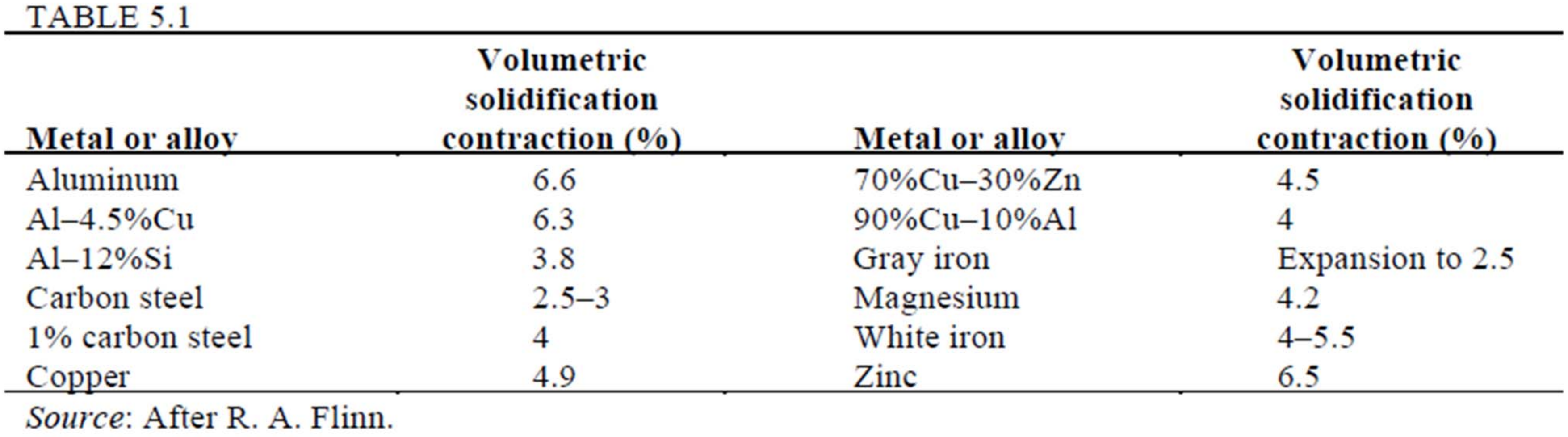


TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

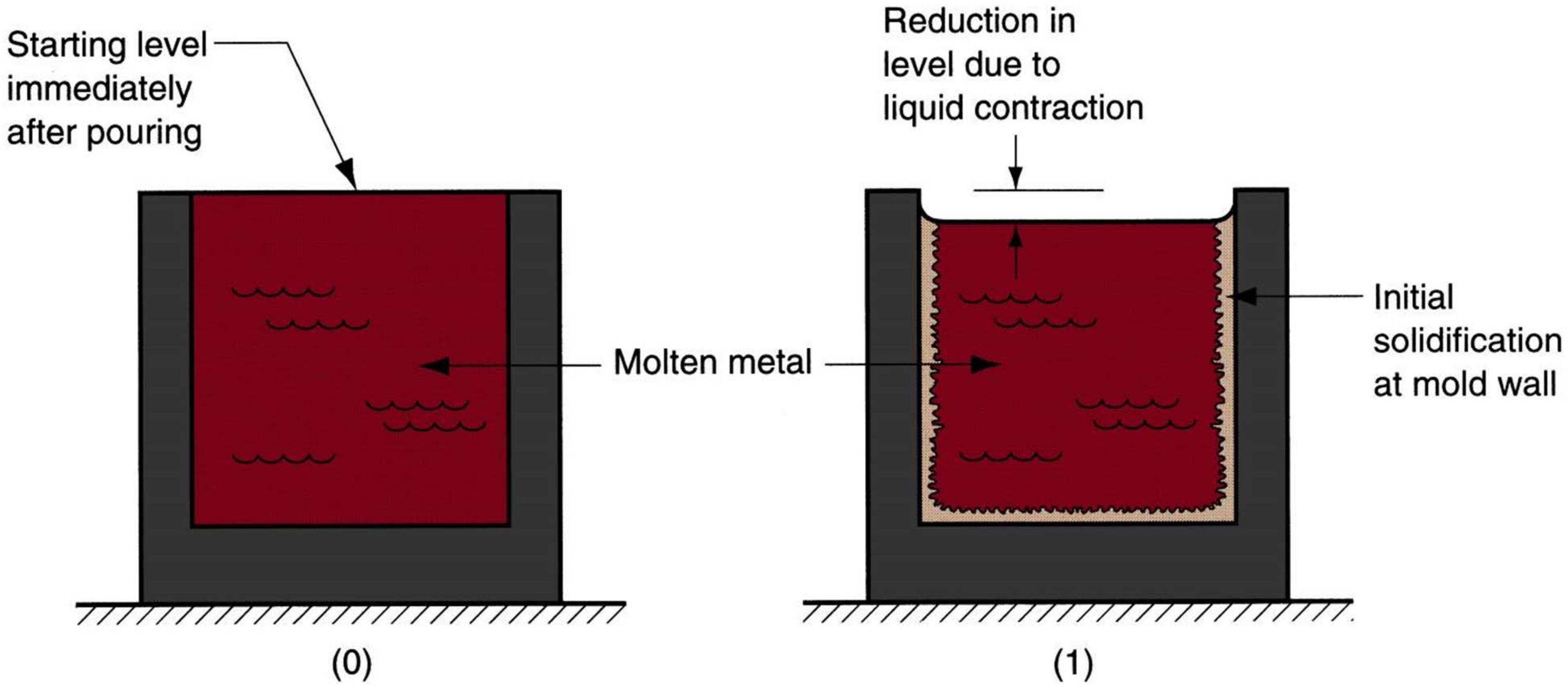
*** Volumetric solidification expansion: H_2O (10%), Si (20%), Ge**

ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

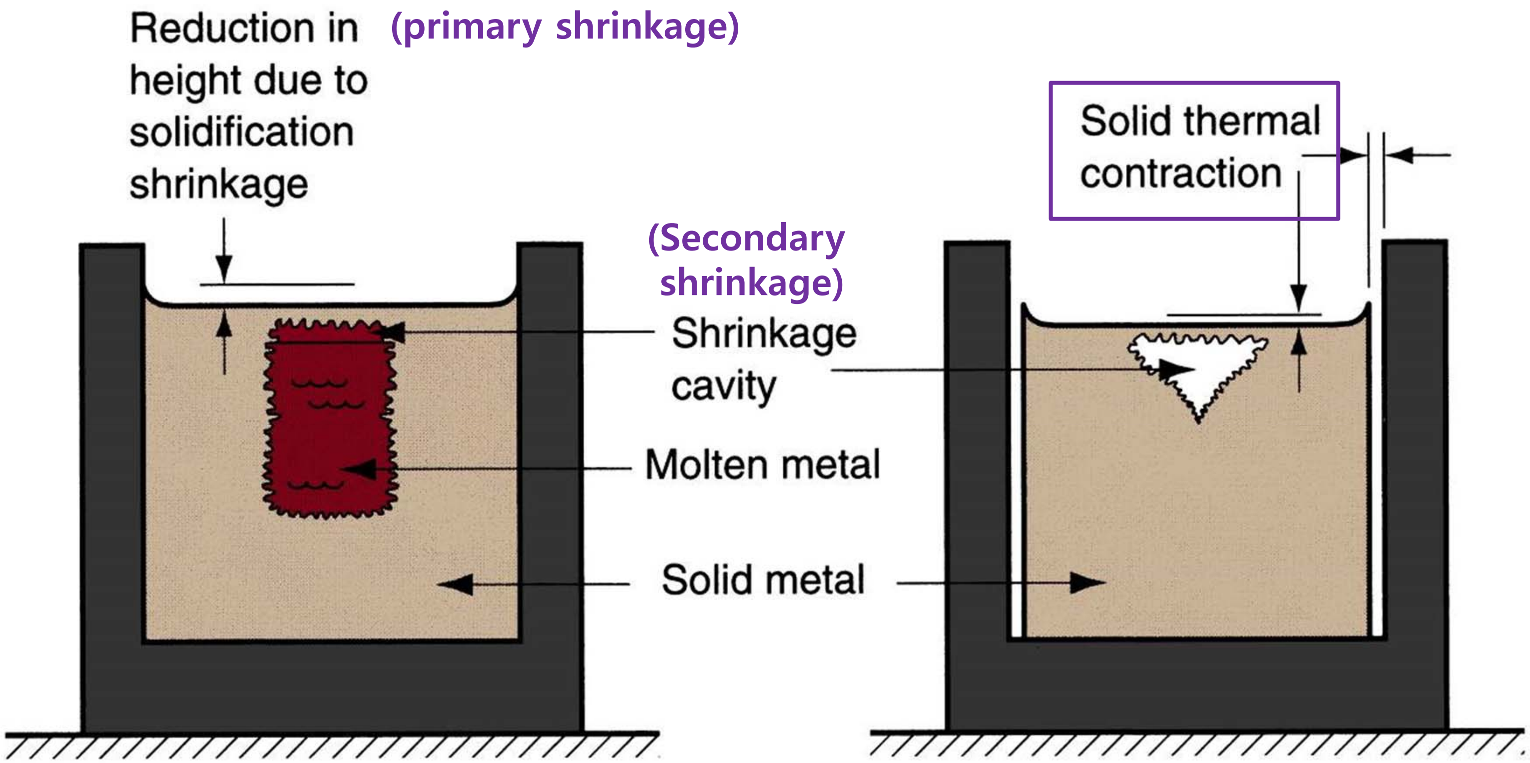
→ precipitation of graphite during solidification reduces shrinkage.

Shrinkage in Solidification and Cooling



* Shrinkage of a cylindrical casting during solidification and cooling: (0) starting level of molten metal immediately after pouring; (1) reduction in level caused by liquid contraction during cooling (dimensional reductions are exaggerated for clarity).

Shrinkage in Solidification and Cooling



(2) (3)

* (2) reduction in height and formation of shrinkage cavity caused by solidification shrinkage; (3) further reduction in height and diameter due to thermal contraction during cooling of solid metal (dimensional reductions are exaggerated for clarity).

Fig. 8.27 Five types of Shrinkage

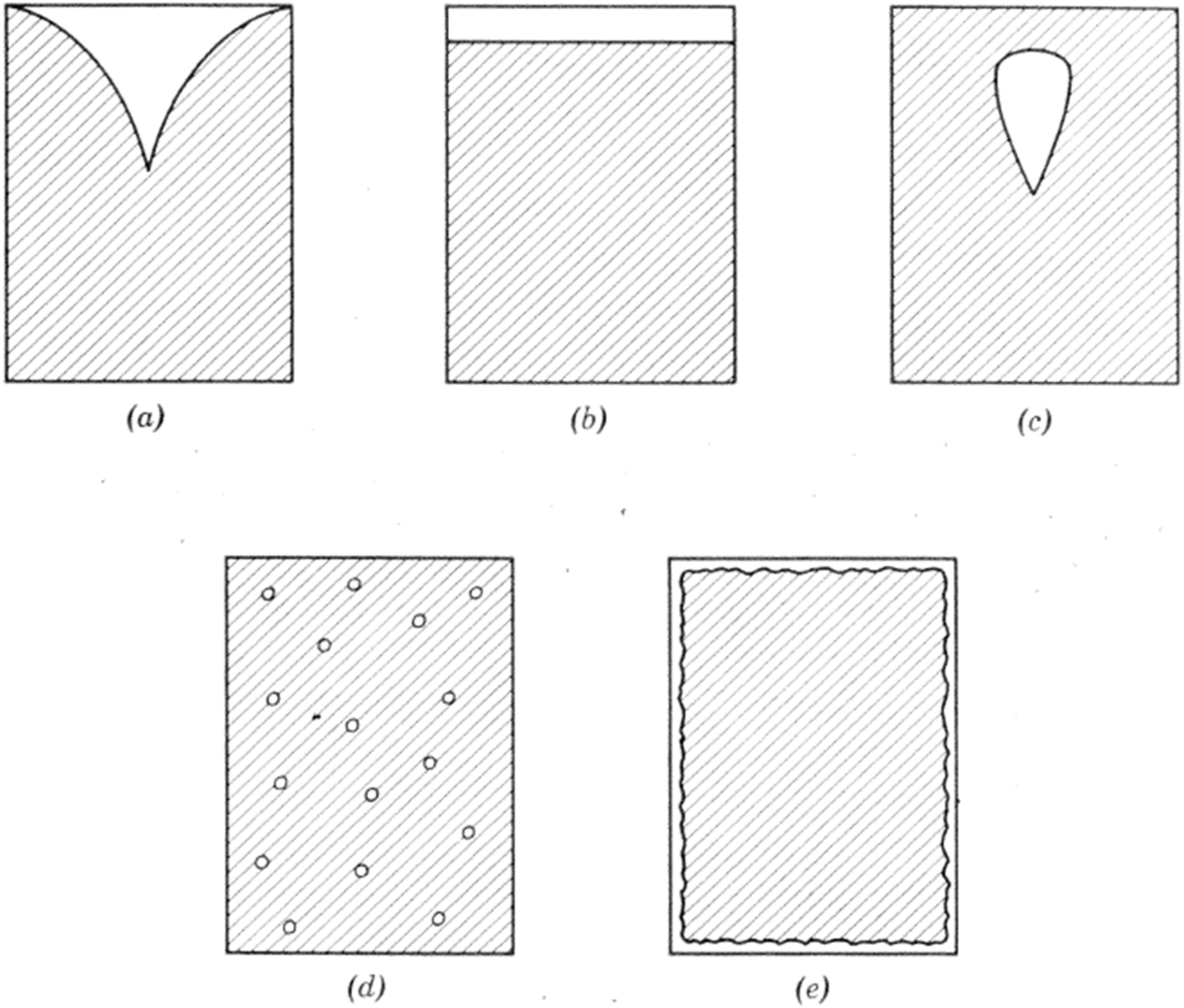
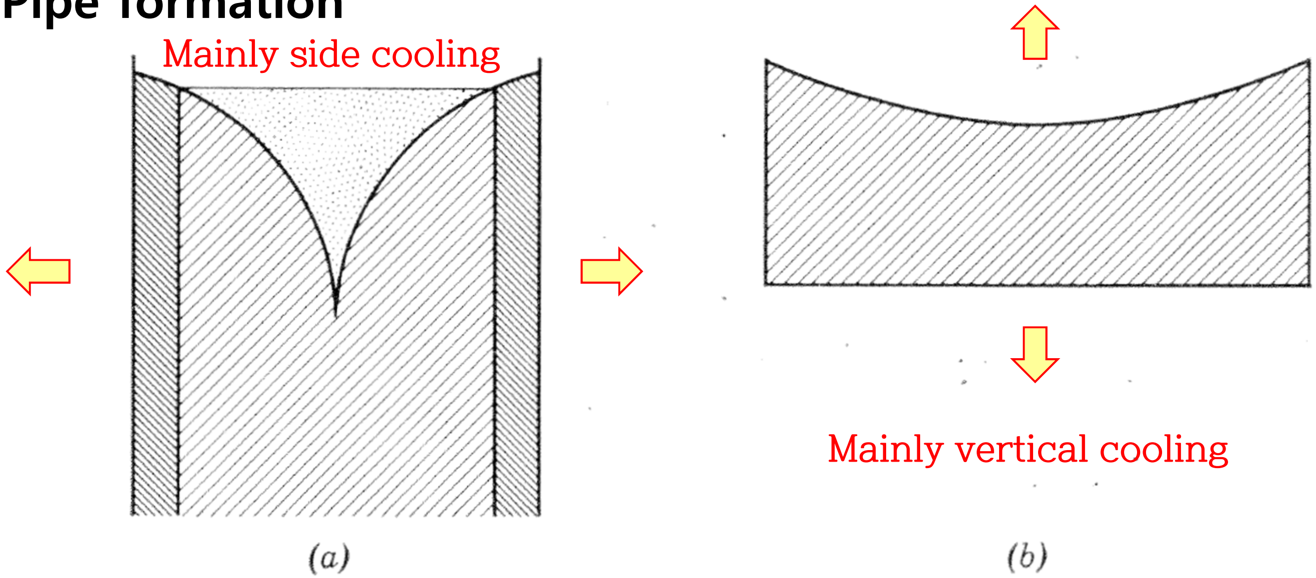


Fig. 8.27. Shrinkage effects. (a) Pipe, (b) unidirectional shrinkage, (c) cavity, (d) distributed porosity, (e) surface porosity.

① Pipe formation

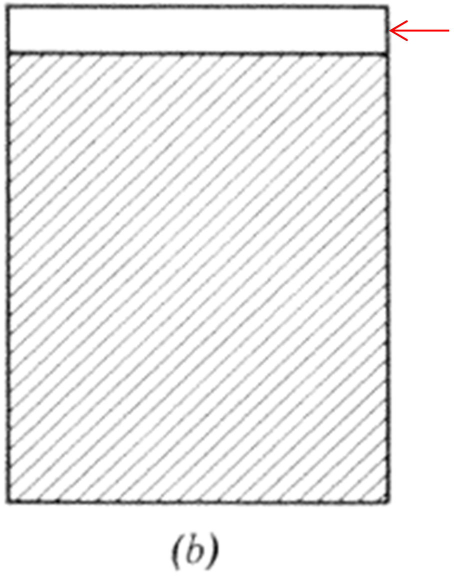


Mainly side cooling

Mainly vertical cooling

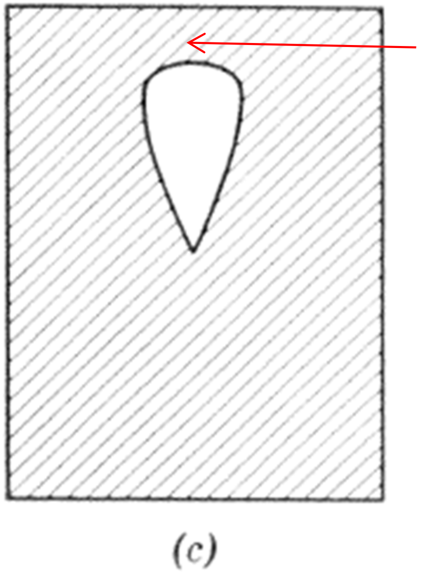
Fig. 8.28. Geometry of pipe. (a) Mainly lateral cooling, (b) mainly vertical cooling.

② Unidirectional Shrinkage



Total **ΔV**

③ Cavity formation: in many practical cases



Many Crust (껍질부분) disappear from atmospheric pressure

These ①, ②, and ③ are macro shrinkage: difficult to prevent due to inherent characteristics of solidification = Heat flow_ direction and speed control

* **These ①, ②, and ③ are macro-shrinkage: difficult to prevent due to inherent characteristics of solidification. However, the presence of a pipe or cavity causes degradation of the material properties → The shrinkage position depends on the relative heat release of the mold in different regions.**

* **Three ways of heat flow direction and speed control**

  a) Chill application: allows high conductivity for low conductivity mold
  b) Padding: interferes with heat extraction by using low thermal conductivity material or by local preheating
  c) Exothermic compounds: retarding the cooling of adjacent metals by supplying heat through mold material or casting

→ These methods are ancillary and the most important factor controlling cooling is the cross section related to the casting geometry, the ratio between the thermal capacity and the heat release area.

→ The most desirable shape to induce the heat flow of the part containing the rejected solute is to ensure that it is not isolated from the last part by any liquid provided by the raisers.

④ Porosity

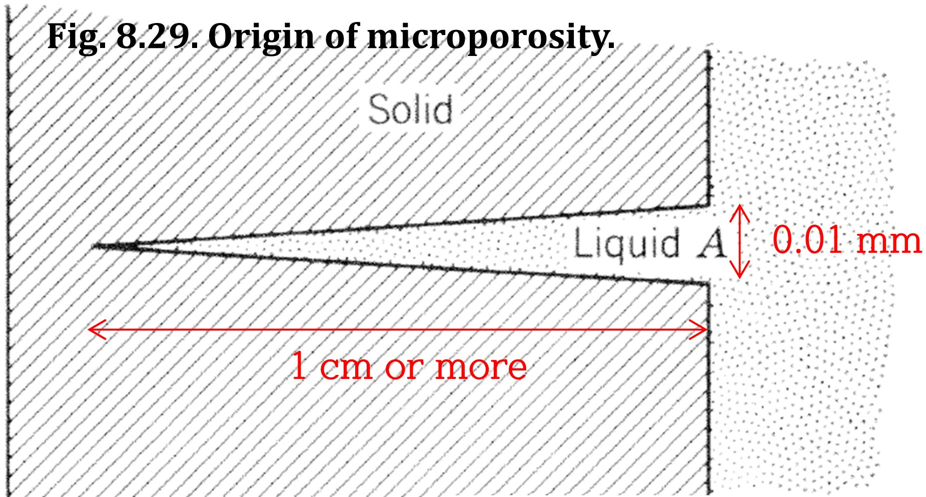


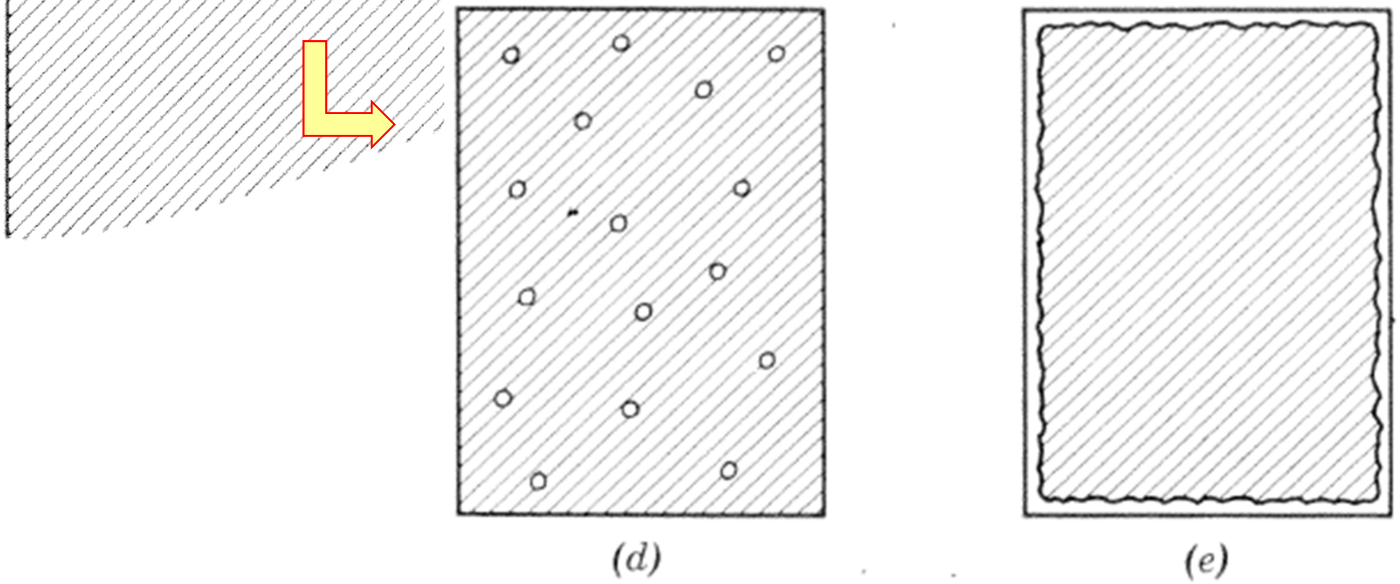
Fig. 8.29. Origin of microporosity.

: Dendrite or Cellular-dendrite solidification = Liquid A with high viscosity is difficult to suck into the groove sufficiently

→ Pore occurrence in groove of wall

→ micropores

⑤ surface porosity



8.6. Blow holes (page 191)

= cylindrical cavities

→ exist a <u>hydrogen upper limit</u> for sound ingot production

Carbon steel	6.5 cm^3/100 gm
Low alloy steel	7 cm^3/100 gm
Chromium (ferritic) stainless	10 cm^3/100 gm
Austenitic stainless	12 cm^3/100 gm

8.7. Surface Topography Resulting from Solidification

- Prediction of successful solidification → From surface observation

: In most cases, the as-cast surface departs from the topography of the mold by amounts that would be measured in millimeters.

① Surface tension effects: Difficult to fill completely due to liquid pressure at sharp edge or corner of mold.

② Cold shut
③ Trapped gas
④ Surface dendrite

⑤ Extrudation (→ inverse segregation) and surface porosity
⑥ Topography of the free surface → decided by surface tension & shrinkage
⑦ metal coating by hot dipping

8.7. Surface Topography Resulting from Solidification

* Prediction of successful solidification → From surface observation

: In most cases, the as-cast surface departs from the topography of the mold by amounts that would be measured in millimeters.

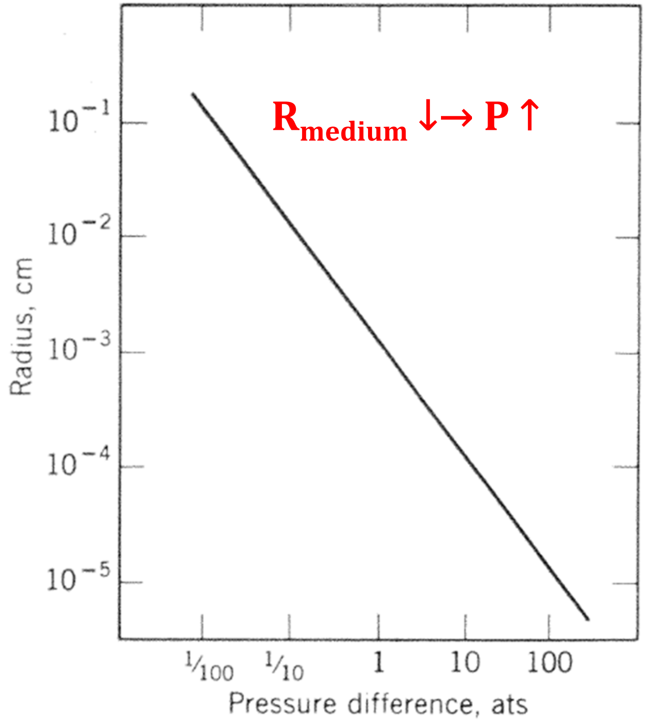
① **Surface tension effects:** The surface tension of the liquid results in the pressure difference btw liquid (R1) and adjacent medium (R2)

$$\boxed{P = \sigma(1/R_1 + 1/R_2)}$$

→ As a result, it is difficult to completely fill the sharp edge or corner of the mold due to the liquid pressure.

Ex) In the case of metal ~ generally surface tension ~ 500 dynes/cm

→ A radius of 1/100 mm (10^{-3} cm) adds additional pressure to the liquid up to 1 atm.



R_{medium} ↓→ P ↑

Fig. 8.30. Limiting radius of curvature of surface of a liquid as a function of pressure difference.

② **Cold shut:** Some liquids solidify in a discontinuous state that is not in contact with previously solidified liquid.

a) Occurs in the presence of an oxide film on a solid substrate or liquid surface.

b) Occurs due to metal splashing when molten metal is poured.

→ Drops or splashes are precooled in contact with mold above liquid level.

③ **Trapped gas**: Interference of contact between solid skin and mold
→ trapped gas at cleavage of mole wall/ Water vapor from mold or mold-dressing/ Separation of solid skin and mold by gas bubble from mold-metal reaction_ Rapid decrease in thermal conductivity

④ **Surface dendrite**: dendritic growth at surface layer

→ Small crystal formed during rapid chilling

→ rapid growth in parallel to the surface

→ Failed to fill Interdendritic space completely

* Formation of surface dendrite

a) Large supercooling ⟷ b) Remelting & slow cooling

→ formation of large crystal

→ Formation of fewer crystals but formation of dendrite by effect of supercooling

Fig. 8.31. Surface dendrites. (a) Supercooled, x100; (b) slowly cooled, x1.

⑤ Extrudation and surface porosity

a) Extudation (스며나옴) : Melt-back effect in the formation of the Dendrite skeleton can be occurred by extrusion toward the mold prior to complete solidification of the inter-dendritic liquid

: These drops come from the interdendritic region → much richer in solute → lead to inverse segregation

b) Surface porosity : In the formation of Dendrite skeleton, the surface skin is rapidly solidified and then the solidification contraction occurs when the inner interdendritic area is solidified.

⑥ Topography of the free surface→Determined by surface tension and shrinkage

* Surface change mechanism after solidification

a) chemical reaction → formation of oxide, etc.

b) thermal etching → surface terrace formation or groove formation in G.B.

c) vacancy pit formation: Reduction of equil. vacancy concentration when temperature decreases → If there is sufficient time, the excess vacancy diffuses to the surface to form pit. → Generally, the pit is small and has a pyramidal shape.

⑦ metal coating by hot dipping

: Coating by dipping on metal bath with low melting temperature

a) Tin-plated steel sheet (주석도금 강판)

Formation of "River structure": Separation of roller and tin surfaces by surface cavitation causing instability during rolling

b) Hot dipped Zinc_galvanized steel sheet (아연도금강판)

Formation of <u>Spangle</u>: Large undercooling occurs during cooling

→ relatively few crystal nuclei are formed

→ <u>each crystal can be visually confirmed by surface etching effect</u>

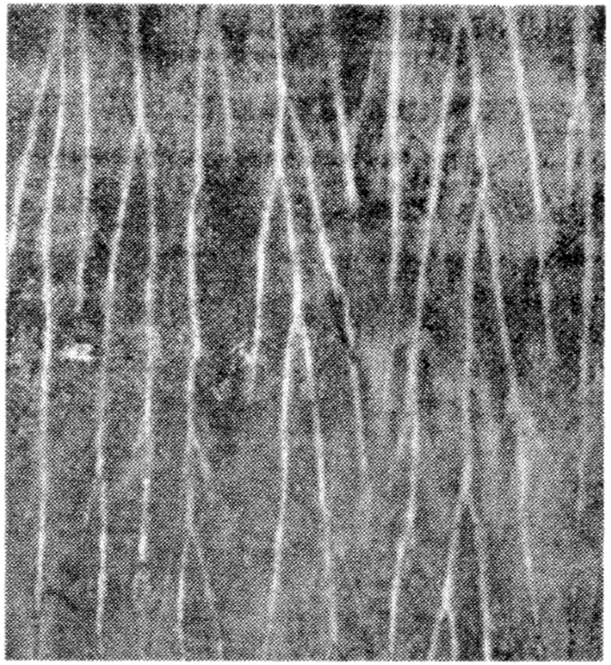
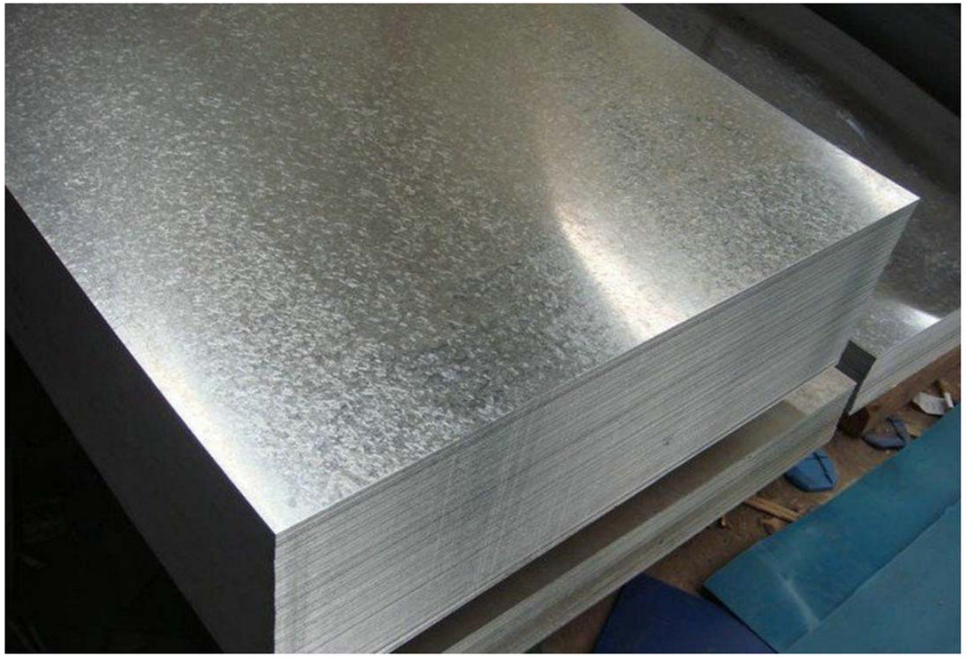


Fig. 8.32. River structure on tinplate.



< Spangle phenomenon >

Principles of Solidification

week 1 Brief introduction : the relevant thermodynamic laws, properties, and relationships
week 2 Solidification as an Atomic Process I
week 3 Solidification as an Atomic Process II
week 4 Nucleation I
week 5 Nucleation II
week 6 Microscopic Heat Flow Consideration I
week 7 Microscopic Heat Flow Consideration II
week 8 Reduction of Solute during solidification I
week 9 Reduction of Solute during solidification II
week 10 Polyphase Solidification I
week 11 Polyphase Solidification II
week 12 Macroscopic Heat Flow and Fluid Flow I
week 13 Macroscopic Heat Flow and Fluid Flow II
week 14 The Structure of Cast Metals I
week 15 The Structure of Cast Metals II