2009 fall

# Advanced Physical Metallurgy

# “Phase Equilibria in Materials”

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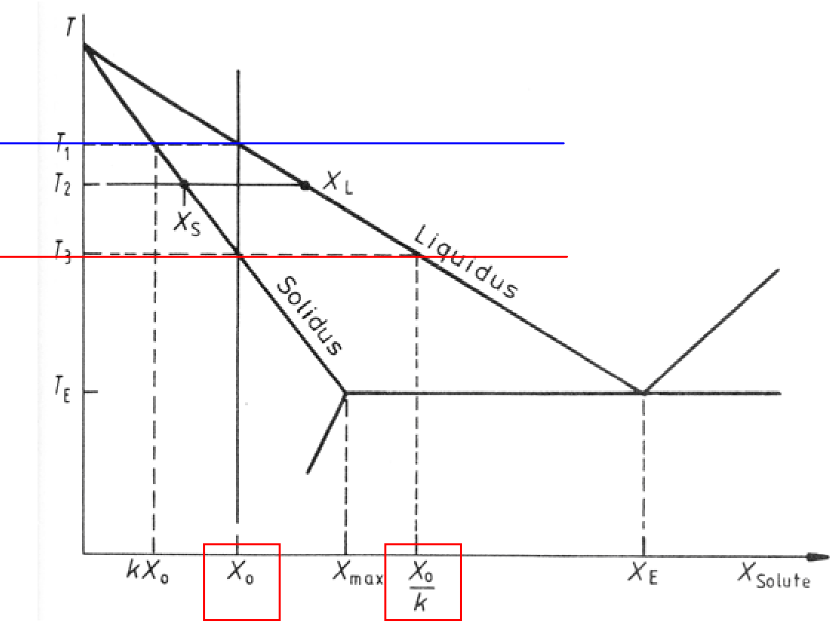
# Contents for previous class

# “Alloy solidification”

## Constitutional Supercooling

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



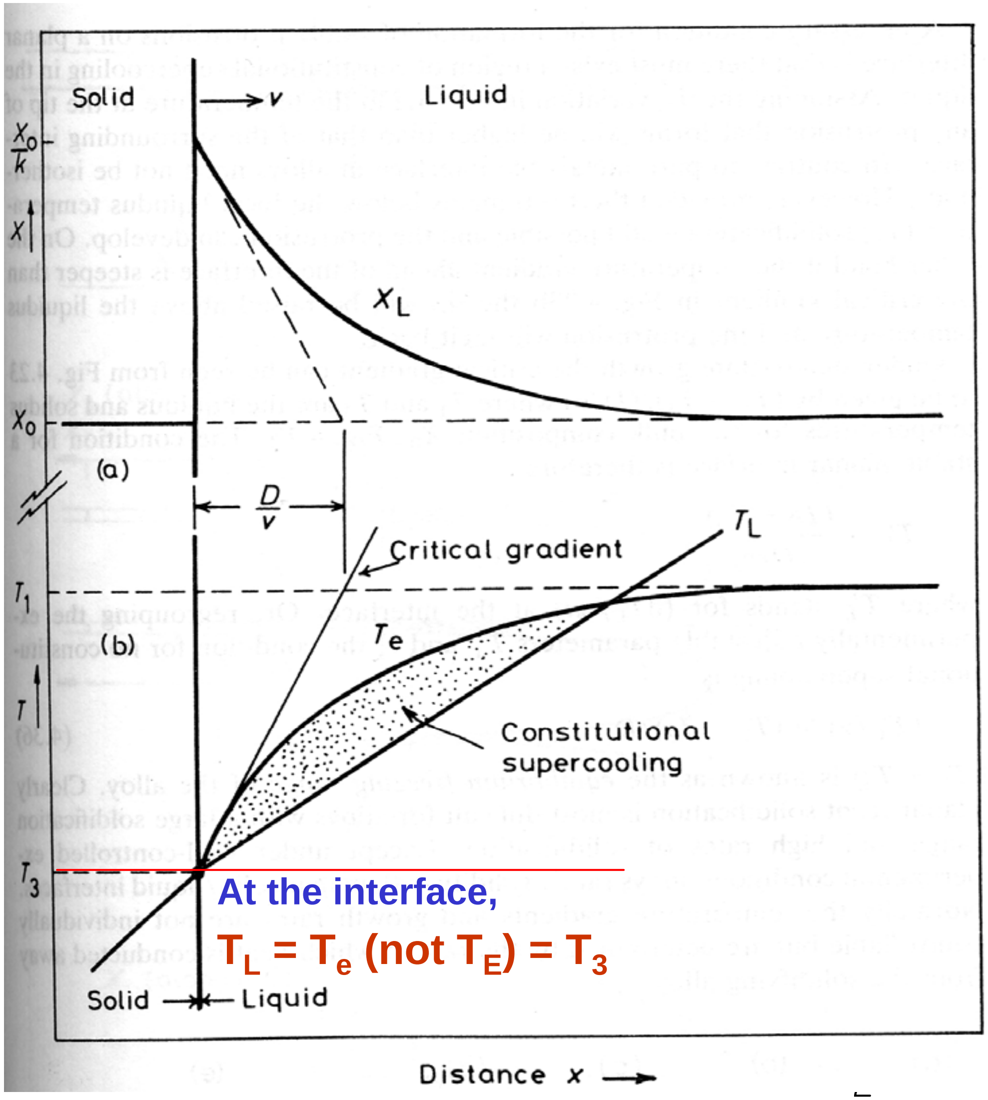
*** Temperature gradient in Liquid**

**$T_L'$**

*** equilibrium solidification temp. change**

**$T_e$**

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



**At the interface,**

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

# Contents for today's class

## 4.3 Alloy solidification

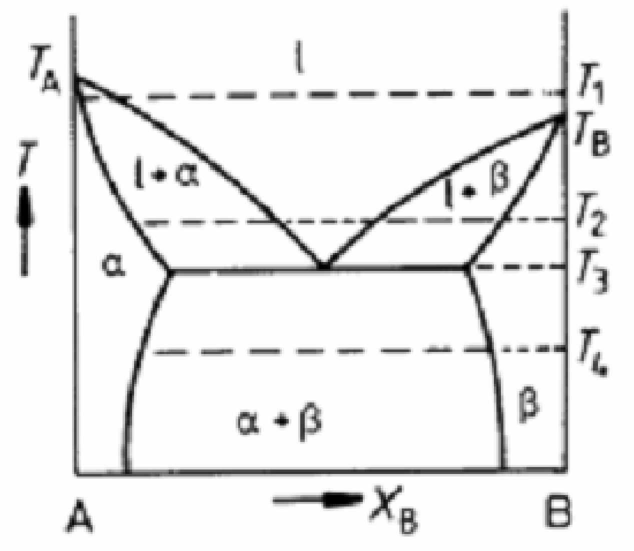
- Solidification of single-phase alloys
- Eutectic solidification
- Off-eutectic alloys
- Peritectic solidification

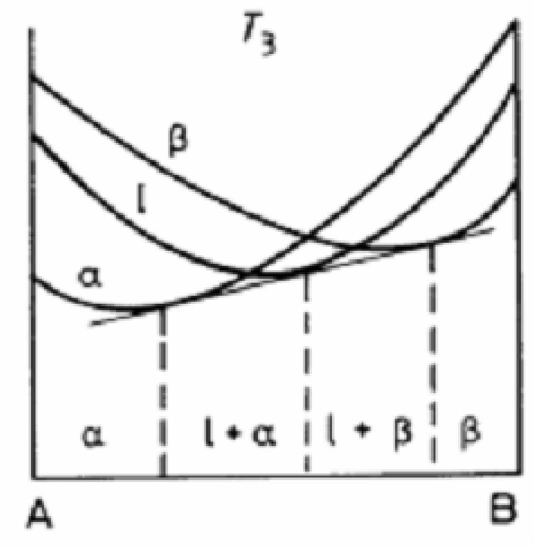
## 4.4 Solidification of ingots and castings

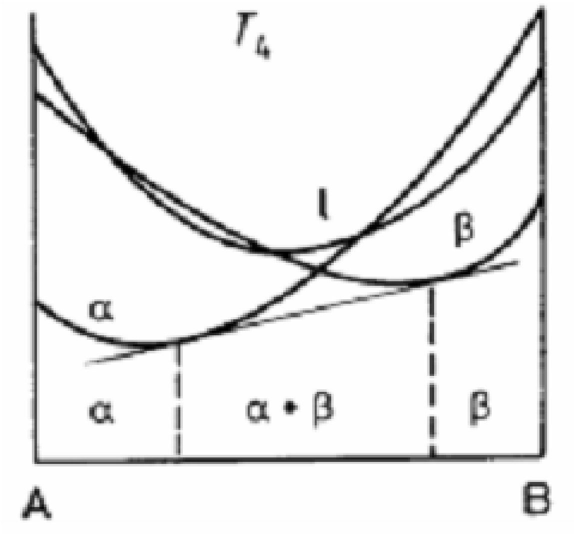
- Ingot structure
- Segregation in ingot and castings
- Continuous casting

## 4.6 Solidification during quenching from the melt

# 4.3.2 Eutectic Solidification (Thermodynamics)







Plot the diagram of Gibbs free energy vs. composition at $T_3$ and $T_4$.

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

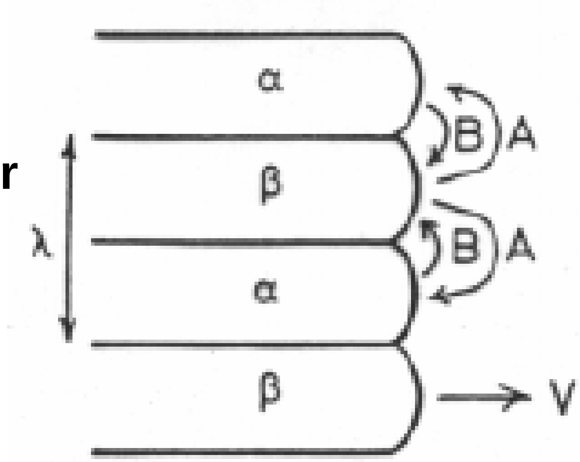
What is the driving force for nucleation of $\alpha$ and $\beta$?

# Eutectic Solidification (Kinetics)

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

→ rough interface (diffusion interface) & local equilibrium

How about at β/L? Nature's choice?



**interlamellar spacing →**

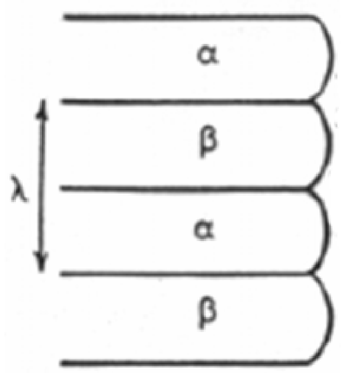
**1) λ ↓ → 성장속도 ↑**

**2) λ ↓ → $\gamma_{\alpha\beta}$ ↑ 로 계의 계면 E ↑**
**최소 λ 존재**

What would be a role of the curvature at the tip?

→ Gibbs-Thomson Effect

# Eutectic Solidification



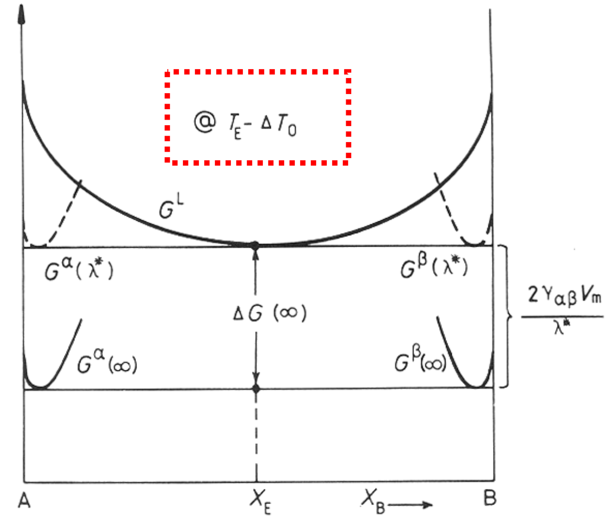
How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$

For an interlamellar spacing, λ, there is a total of (2/ λ) m$^2$ of α/β interface per m$^3$ of eutectic.

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

Driving force for nucleation

$$\rightarrow \Delta G = \Delta\mu = \frac{2\gamma}{\lambda} \times V_m$$



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

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda}$$

What would be the minimum λ?

**Critical spacing,** $\lambda^* : \Delta G(\lambda^*) = 0$

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

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

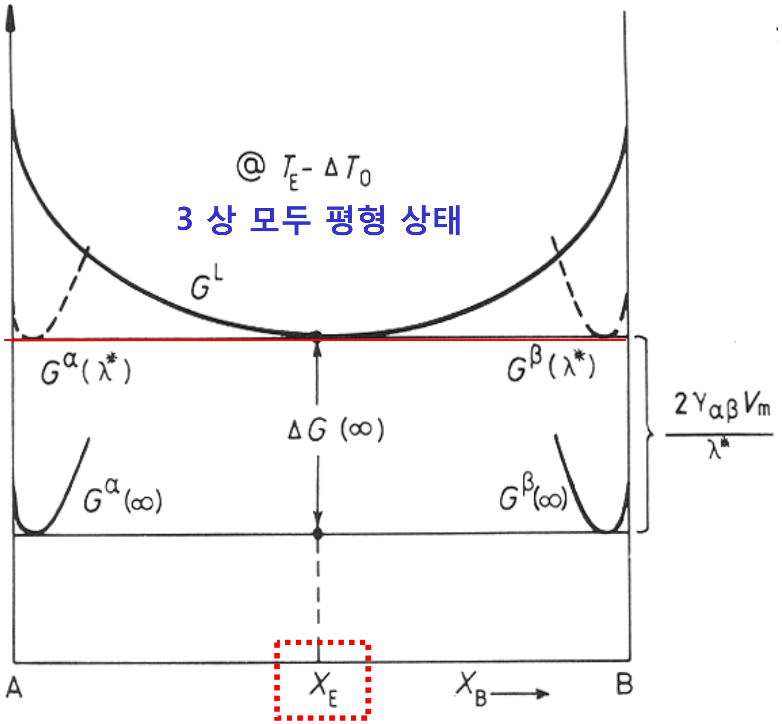
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL}T_m}{L_V}\right)\frac{1}{\Delta T}$$

$L_V$ : *latent heat per unit volume*

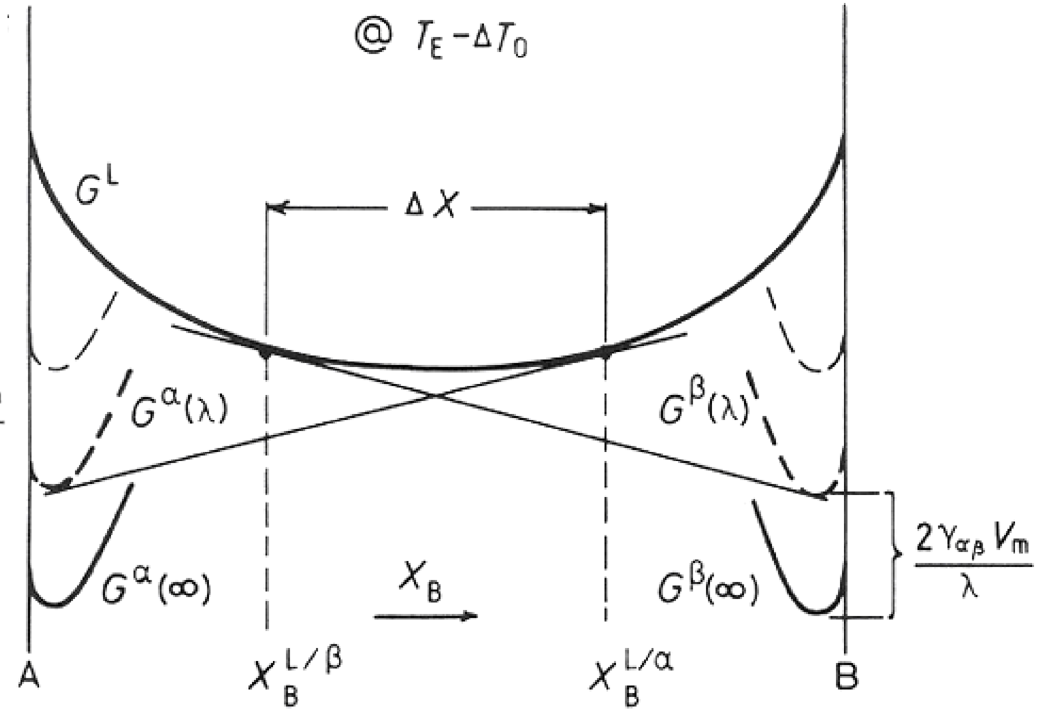
**$L$ = ΔH = $H^L$ - $H^S$**

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

# Gibbs-Thomson effect in a ΔG-composition diagram?



**3 상 모두 평형 상태**



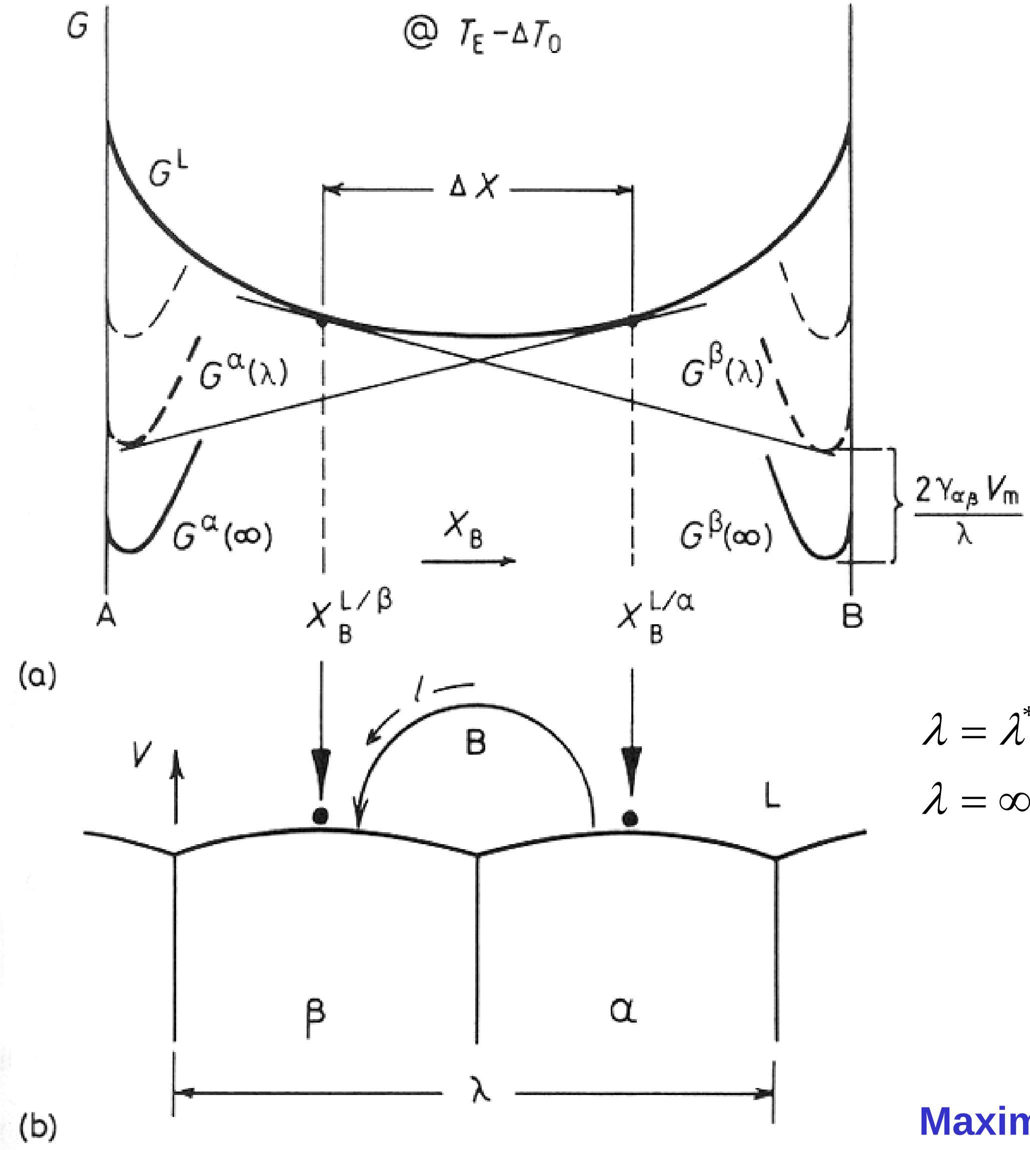
**G 증가의 원인은 α/β/L의 3중점에서 계면장력이 균형을 유지하기 위하여 α/L 계면과 β/L 계면이 곡률을 갖기 때문**

**β 상과 국부적 평형 이루는 액상의 B 조성** **<** **α 상과 국부적 평형 이루는 액상의 B 조성**

# 공정의 성장속도 $v$

→ α/L와 β/L 계면의 이동도가 커서
   액상을 통한 용질이동과 비례

→ 성장 확산 제어



$$\boxed{v \propto D\frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta}) \\ \propto \ \textbf{1/유효확산거리 ... 1/}\lambda}$$

$$\boxed{v = k_1 D\frac{\Delta X}{\lambda}}$$

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

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

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

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

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

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

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

계면 과냉 변화시킴에 따라 성장속도와 간격 서로 독립적으로 변화시킬 수 있음.

# Closer look at the tip of a growing dendrite

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

**Assume the solid is isothermal** $\left(T'_S = 0\right)$

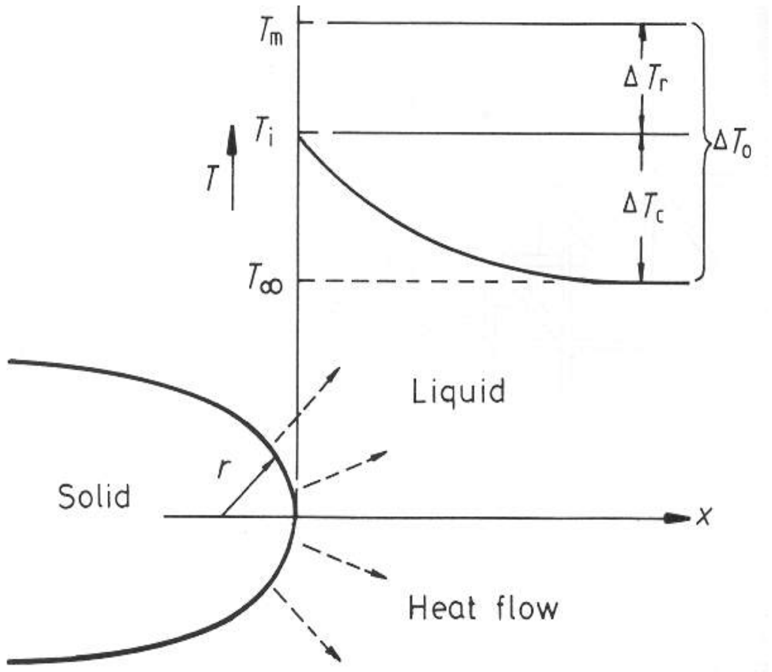
**From** $K_S T'_S = K_L T'_L + v L_V$

$$If\ \ T'_S = 0,\ \ v = \frac{-K_L T'_L}{L_V}$$

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

$$T'_L(negative) \cong \frac{\Delta T_C}{r} \qquad \Delta T_C = T_i - T_\infty$$

$$v = \frac{-K_L T'_L}{L_V} \cong \frac{K_L}{L_V} \cdot \frac{\Delta T_C}{r} \qquad v \propto \frac{1}{r}$$



**However, ΔT also depends on r.**

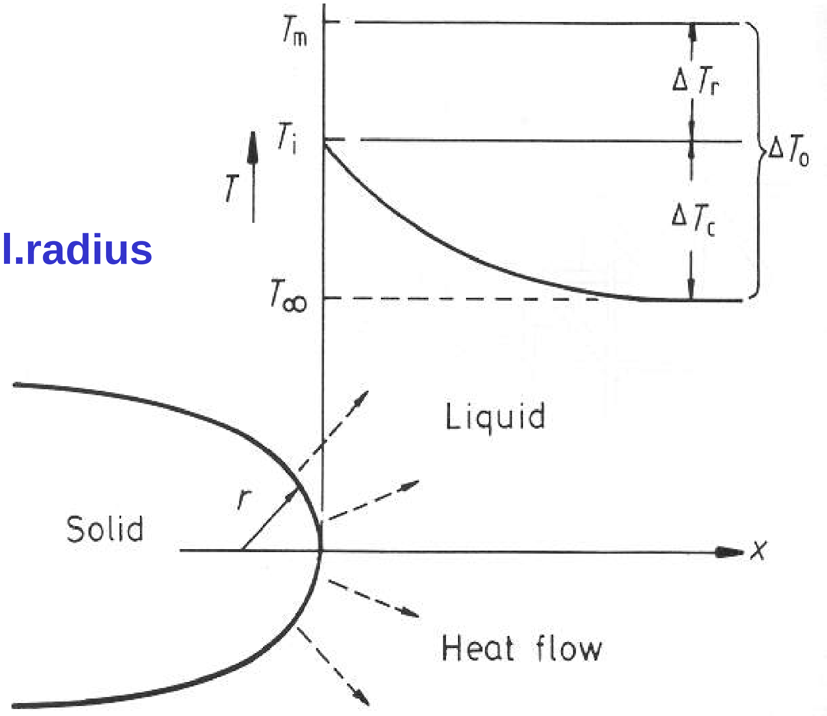
**How?**

Thermodynamics at the tip?

**Gibbs-Thomson effect:**
**melting point depression**

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

# Minimum possible radius ( r)?



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

The crit.nucl.radius

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

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

*Express $\Delta T_r$ by $r, r^*$ and $\Delta T_o$.*

$$\Delta T_r = \frac{r^*}{r}\Delta T_o$$

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

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

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

*Maximum velocity?*

$$\boxed{\rightarrow\ r = 2r^*}$$

# Corresponding location at phase diagram?

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

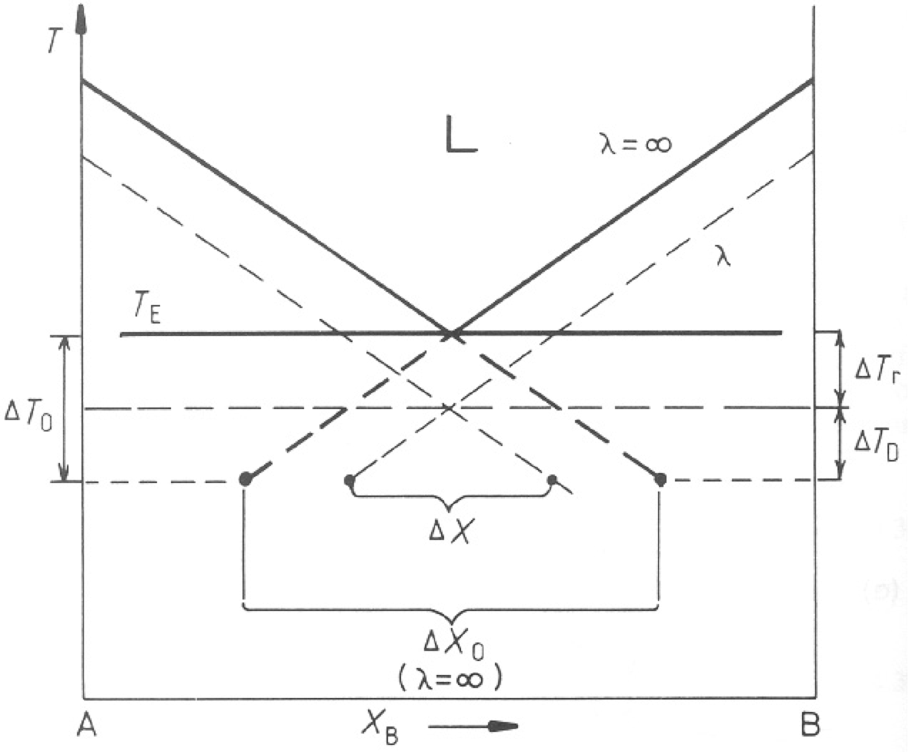
**curvature composition gradient**

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

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

$\rightarrow$ *free energy dissipated in forming $\alpha / \beta$ interfaces*

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



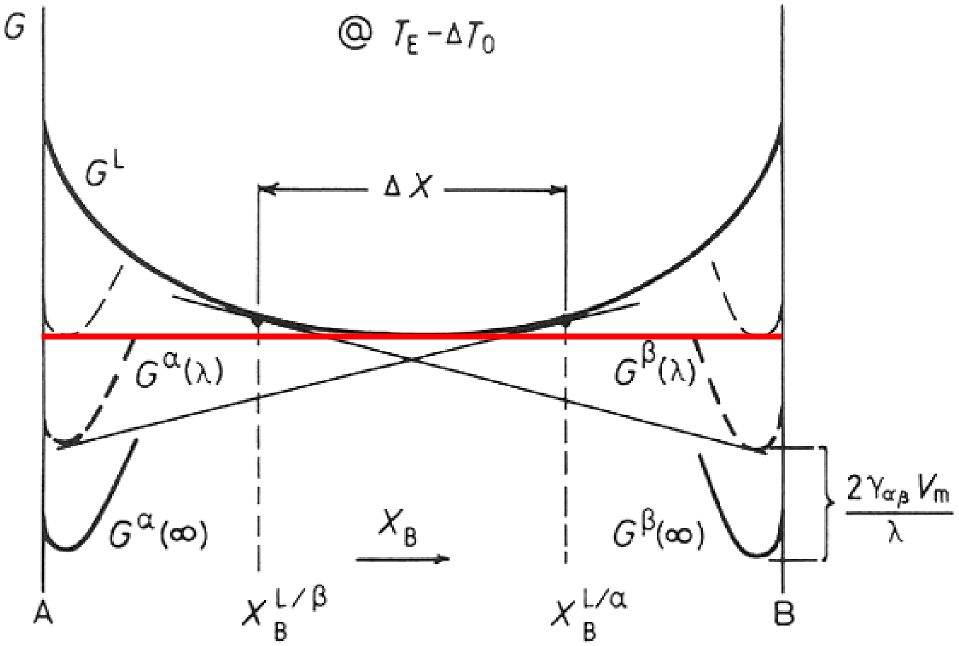


**Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and $\Delta X_0$ (exaggerated for clarity)**

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

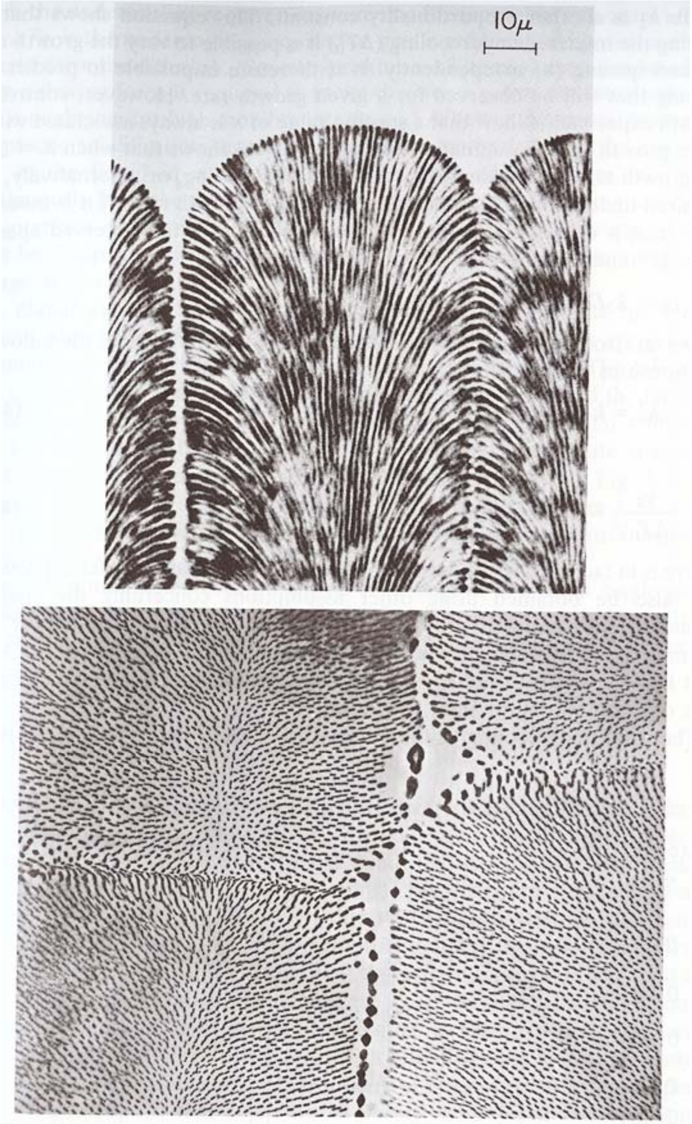
Maximum growth rate at a fixed $\Delta T_0 \rightarrow \boxed{\lambda = 2\lambda^*}$

$$v_0 = k_2 D \Delta T_0 / 4\lambda^*$$

$$\lambda^* = +\frac{2T_E \gamma V_m}{\Delta H \Delta T_0}$$ 로 부터, $\Delta T_0 \propto 1/\lambda^*$

$\lambda = \lambda_0$ 인 경우,

$$\boxed{v_0 \lambda_0^2 = k_3 \qquad \frac{v_0}{(\Delta T_0)^2} = k_4}$$



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

| | |
|---|---|
| 계면 곡률효과 극복 과냉도 | 확산 위한 충분한 조성차주기 위한 과냉 |

$\Delta T_D \rightarrow$ α층의 중간부터 β층의 중간까지 연속적으로 변화

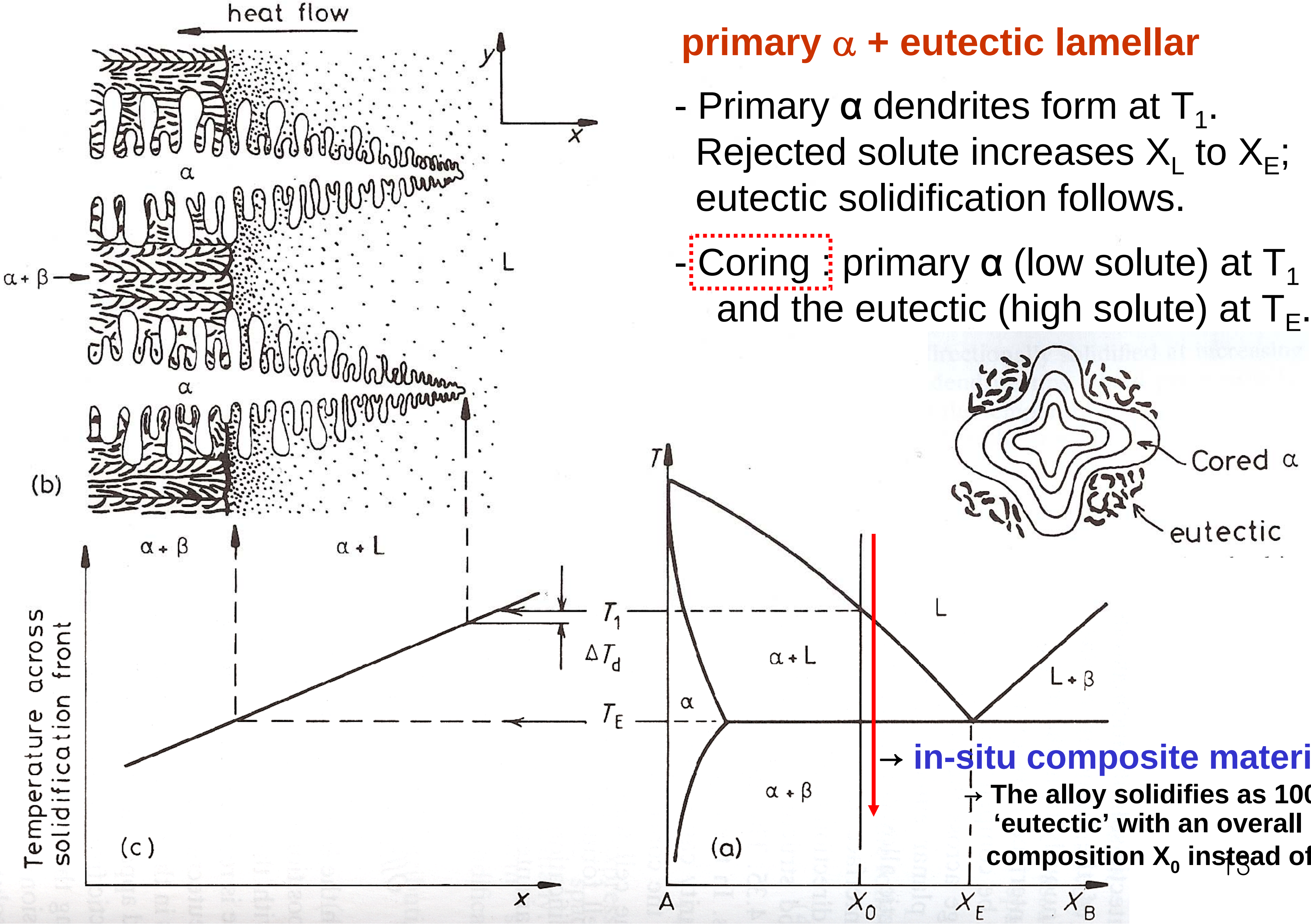
$\Delta T_0 = const$ 계면은 항상 등온

$\Delta T_r$ 로 극복해야 함 → 계면의 곡률을 따라 변화

# 4.3.3 Off-eutectic Solidification

**primary α + eutectic lamellar**

- Primary **α** dendrites form at $T_1$. Rejected solute increases $X_L$ to $X_E$; eutectic solidification follows.
- Coring : primary **α** (low solute) at $T_1$ and the eutectic (high solute) at $T_E$.



→ **in-situ composite materials**

→ **The alloy solidifies as 100% 'eutectic' with an overall composition $X_0$ instead of $X_E$.**

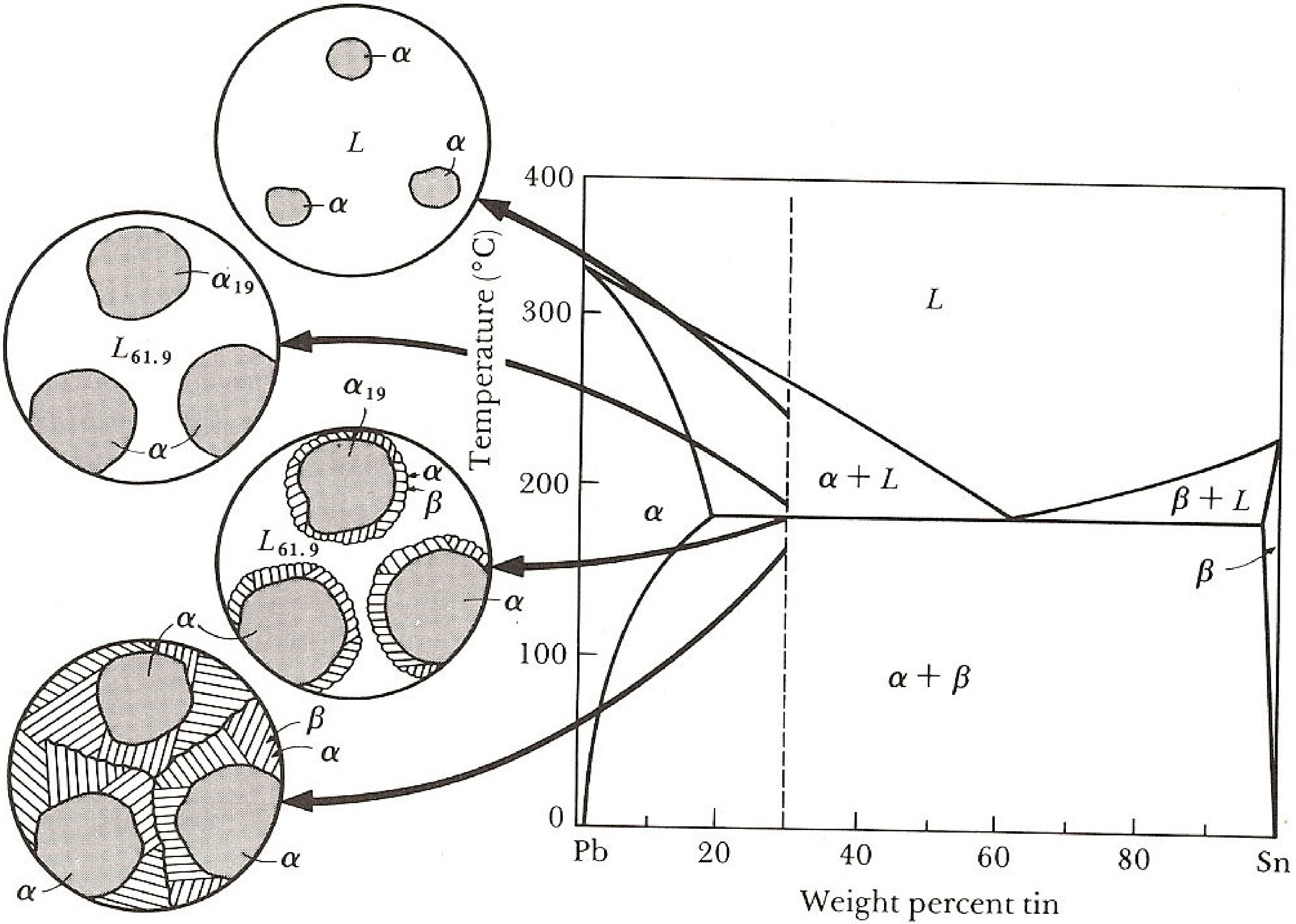
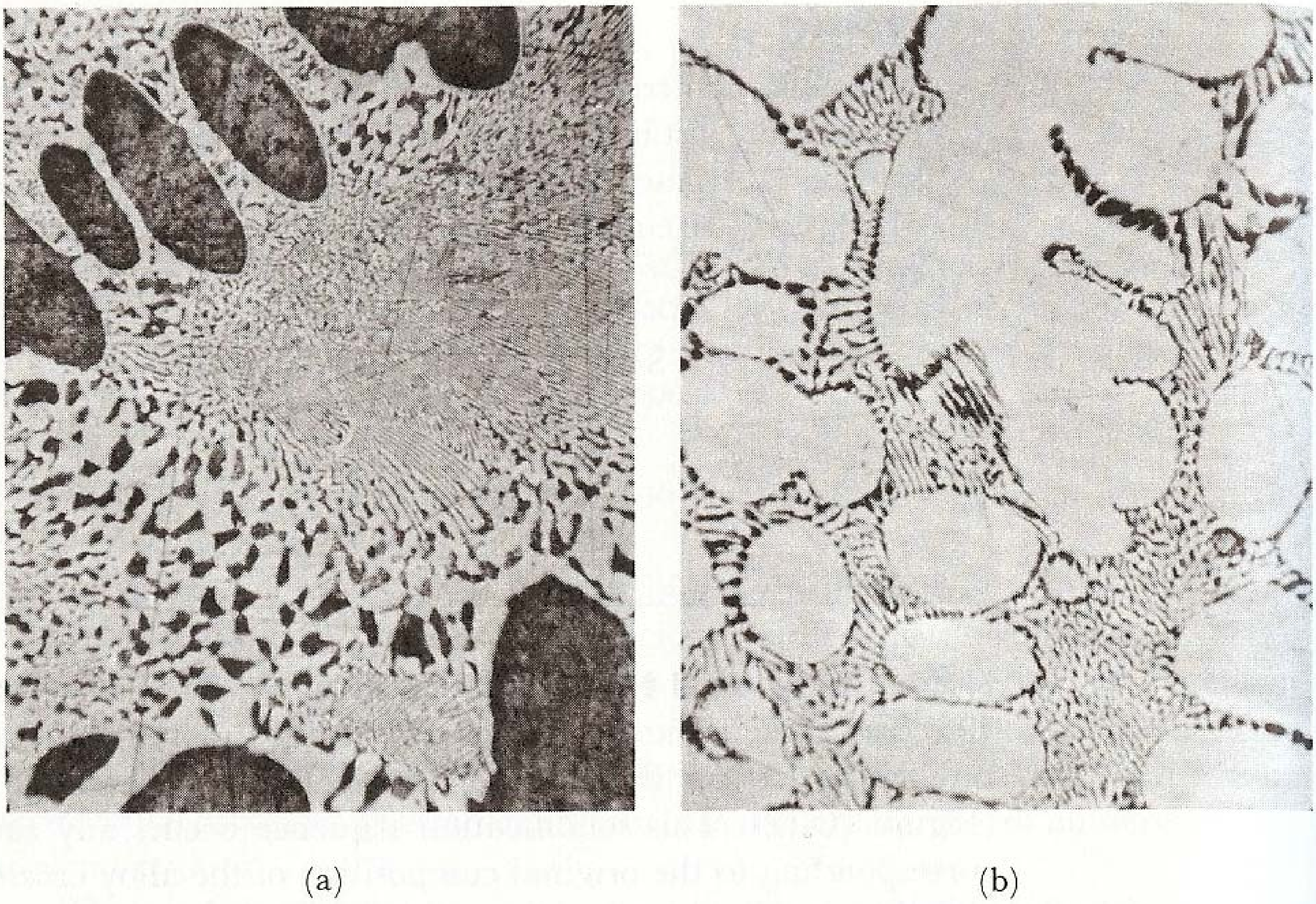


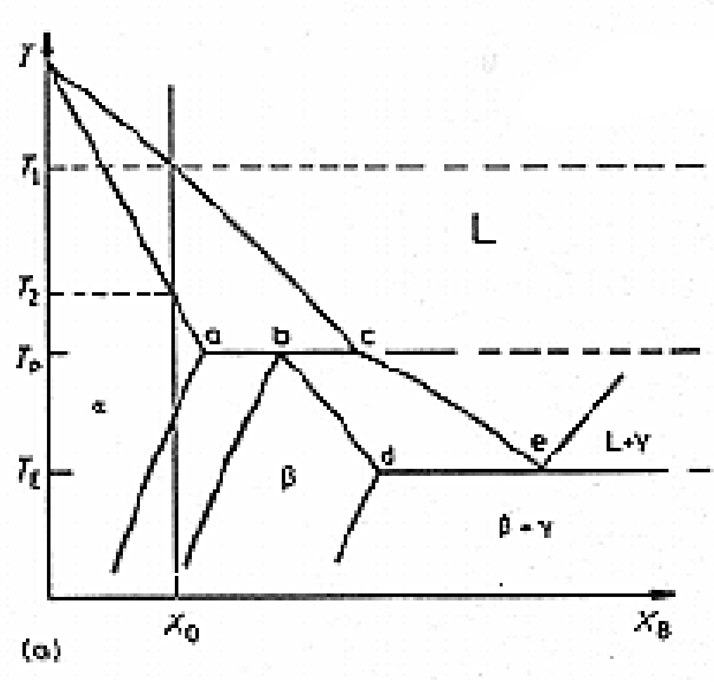
**FIGURE 10-12** The solidification and microstructure of a hypoeutectic alloy (Pb-30% Sn).

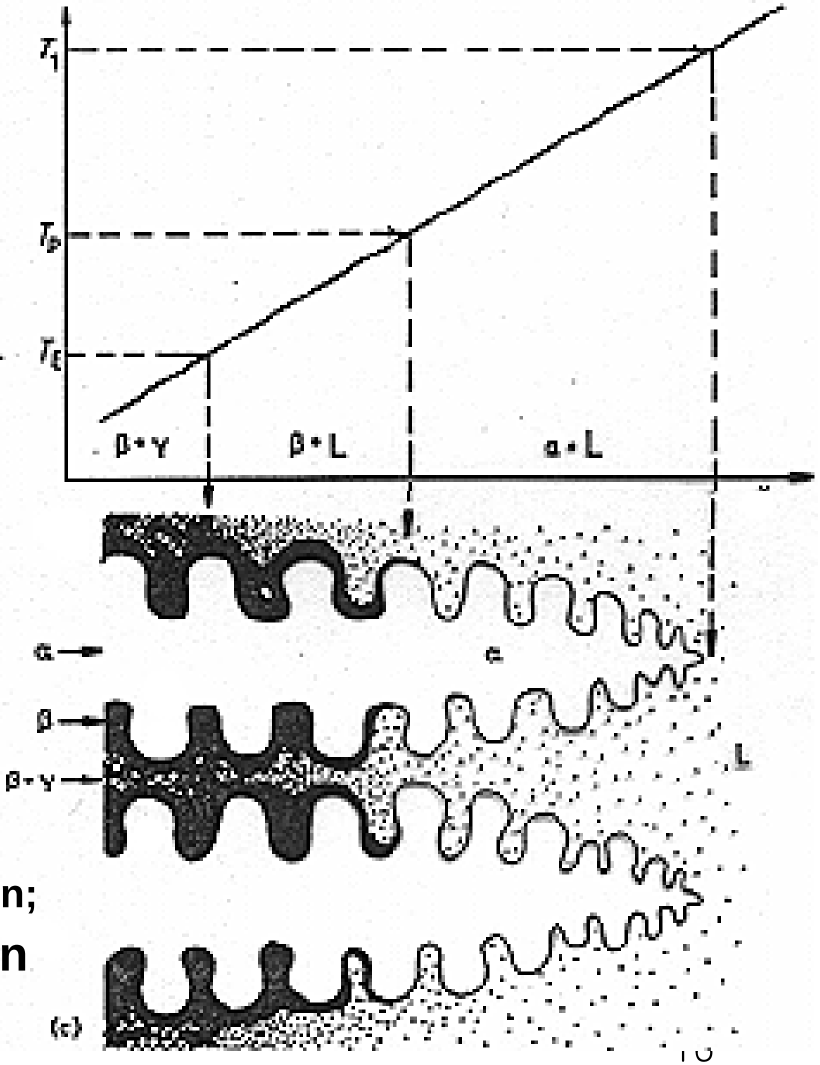


(a) (b)

**FIGURE 10-13** (a) A hypoeutectic lead-tin alloy. (b) A hypereutectic lead-tin alloy. The dark constituent is the lead-rich solid α, the light constituent is the tin-rich solid β, and the fine plate structure is the eutectic ( × 400).

# 4.3.4 Peritectic Solidification



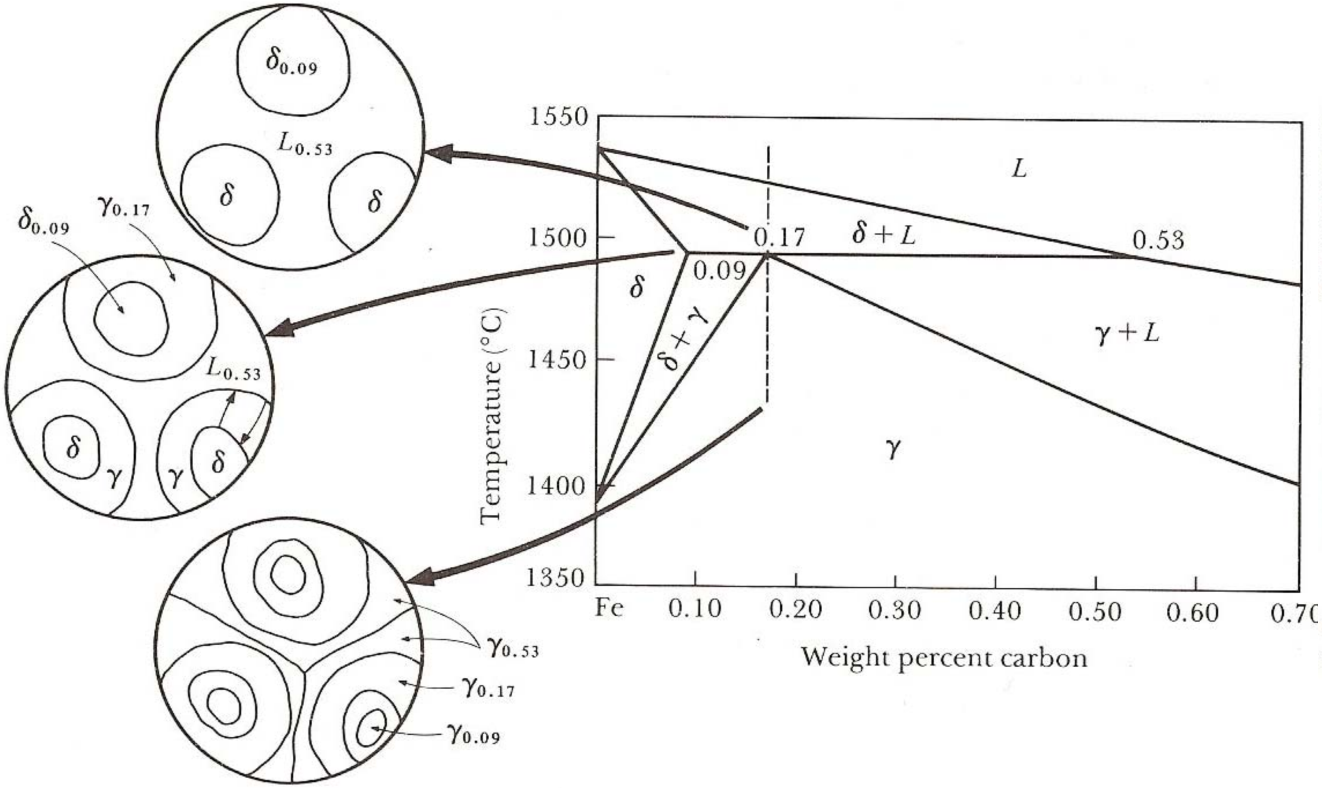


- **L + α → β , difficult to complete.**

- **α dendrites first form at $T_1$;**
  **Liquid reaches the composition 'c';**
  **β forms as the result of the peritectic reaction;**
  **α coring is isolated from further reaction**
  **finally β + γ eutectic forms.**

# Solidification and microstructure

## that develop as a result of the peritectic reaction



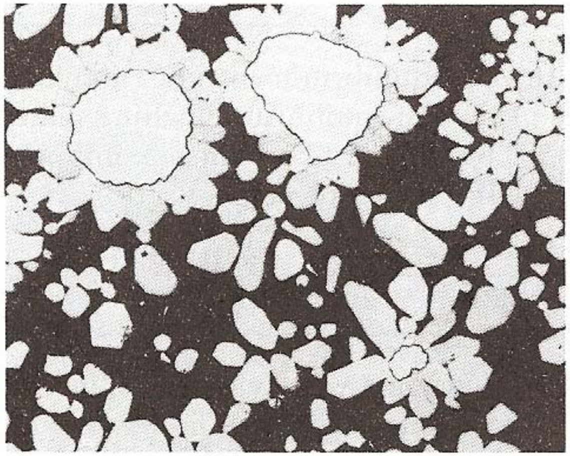


**FIGURE 10-24** The peritectic reaction in a Cd-10% Cu alloy begins when rounded

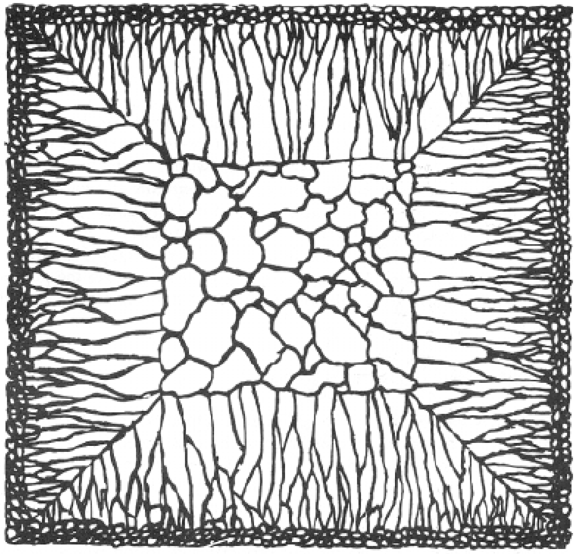
# 4.4 Solidification of Ingots and Castings

주조 후 압연, 압출 또는 단조 등에 의해 가공할 것 >> blank (작은 것)

주조된 제품이 최종 모양을 유지하거나 혹은 기계가공에 의해 최종 모양으로 된 것

## Ingot Structure

- Chill zone
- Columnar zone
- Equiaxed zone



## Chill zone

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

- As the mould wall warms up it is possible for many of these solidified crystals to break away from the wall under the influence of the turbulent melt.

# 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.

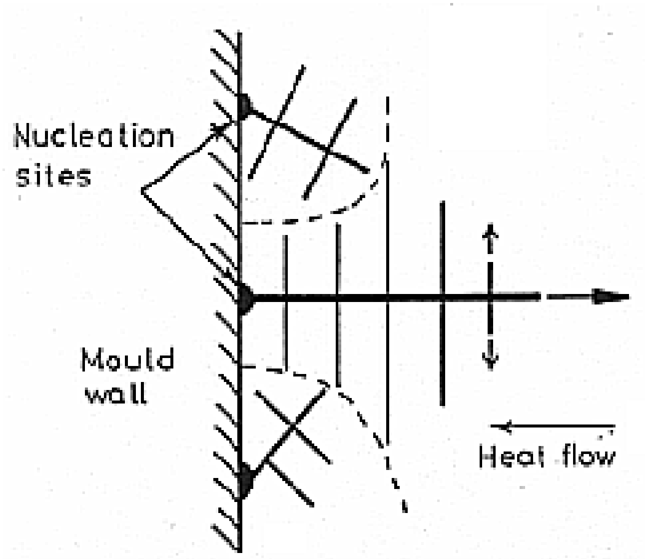


**Fig. 4.41** Competitive growth soon after pouring. Dendrites with primary arms normal to the mould wall, i.e. parallel to the maximum temperature gradient, outgrow less favorably oriented neighbors.

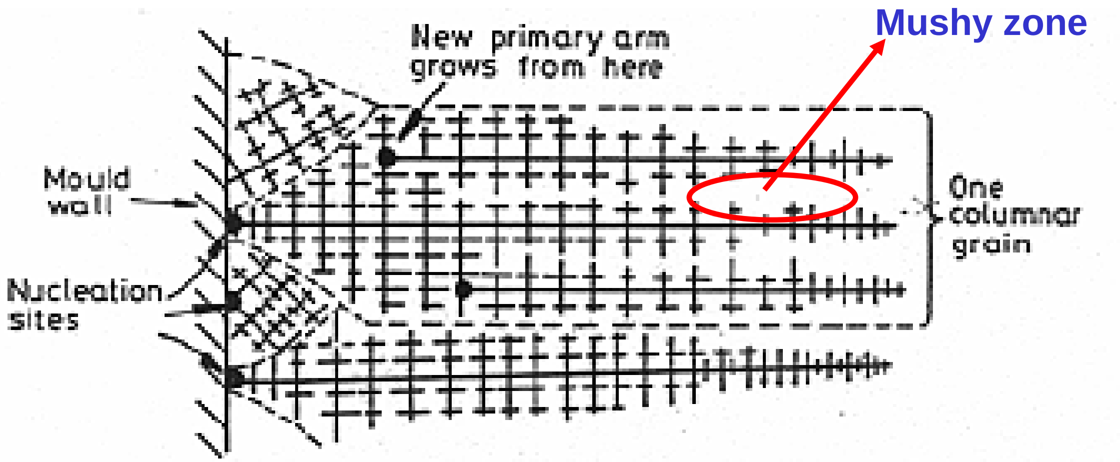


**Fig. 4.42** Favorably oriented dendrites develop into columnar grains. Each columnar grain originates from the same heterogeneous nucleation site, but can contain many primary dendrite arms.

1차 가지 성장 방향 변화

열전도 방향 → 결정학적 우선 방향

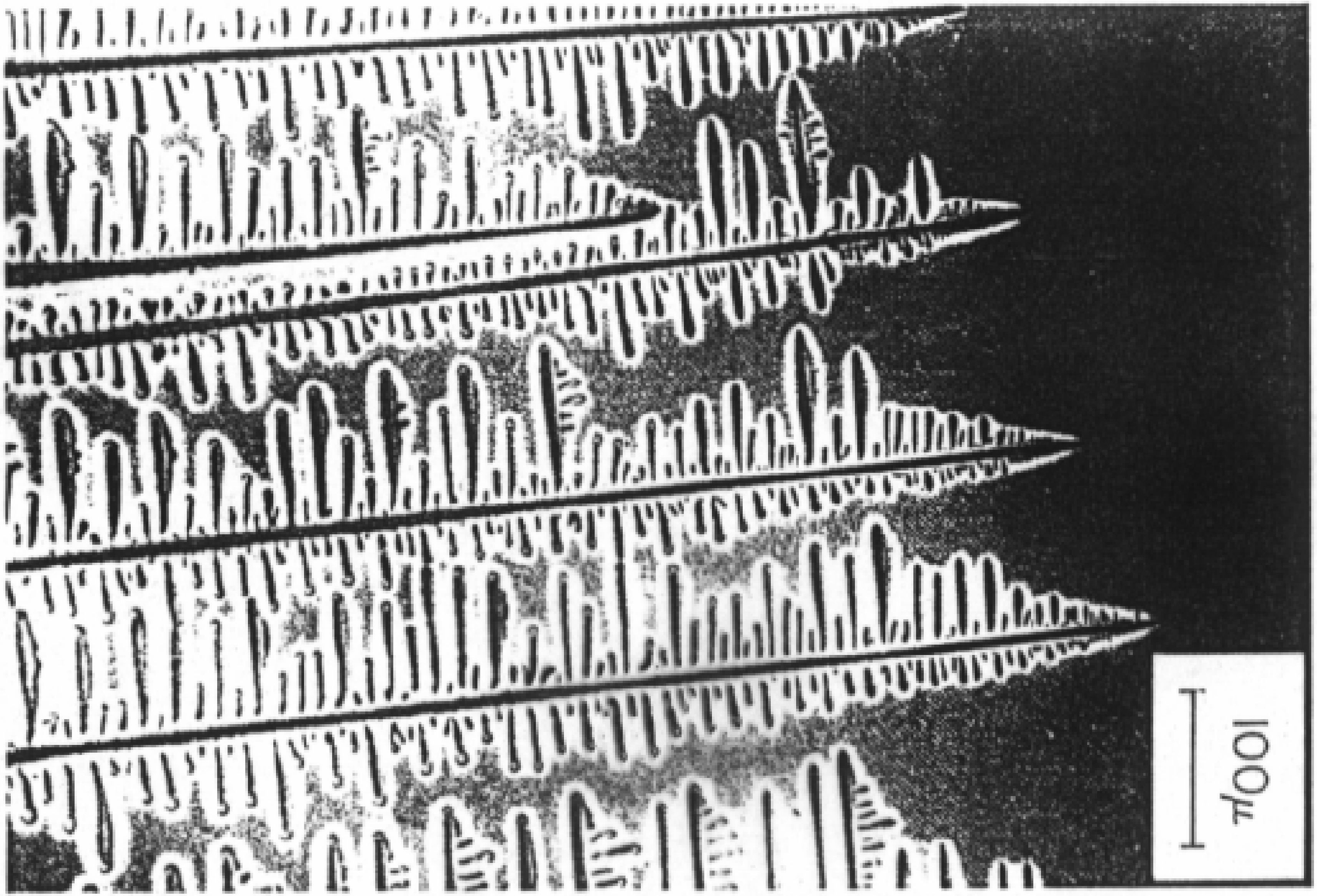


**Fig. 4.28 Columnar dendrites in a transparent organic alloy.**

**(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

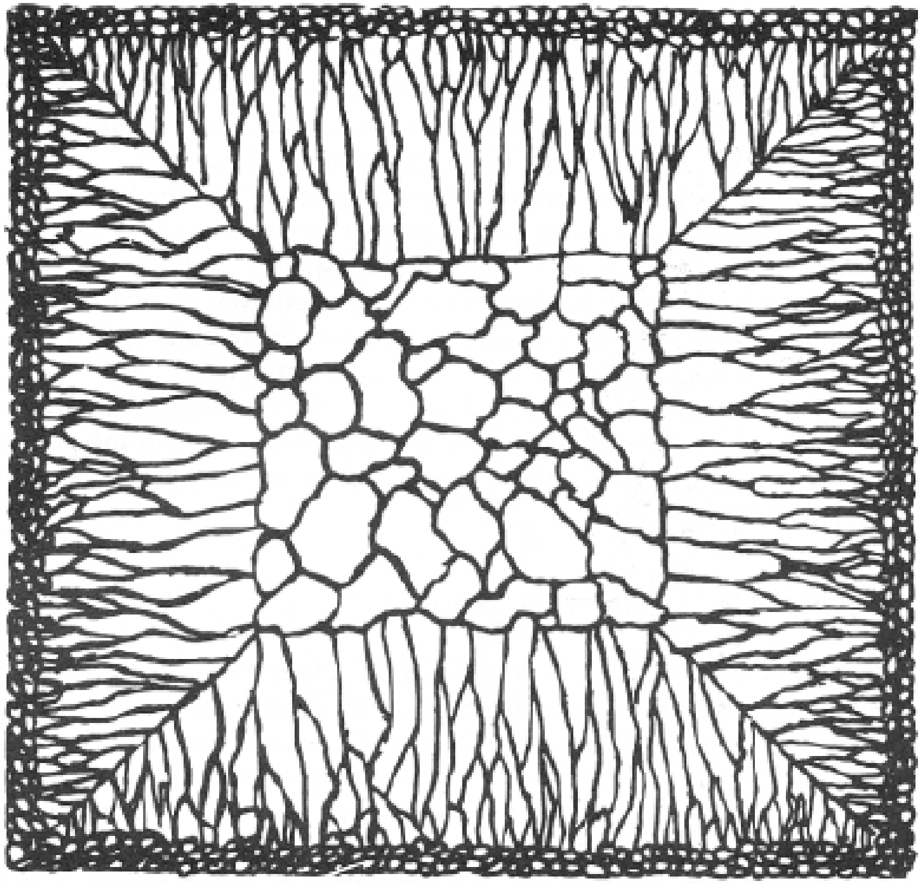
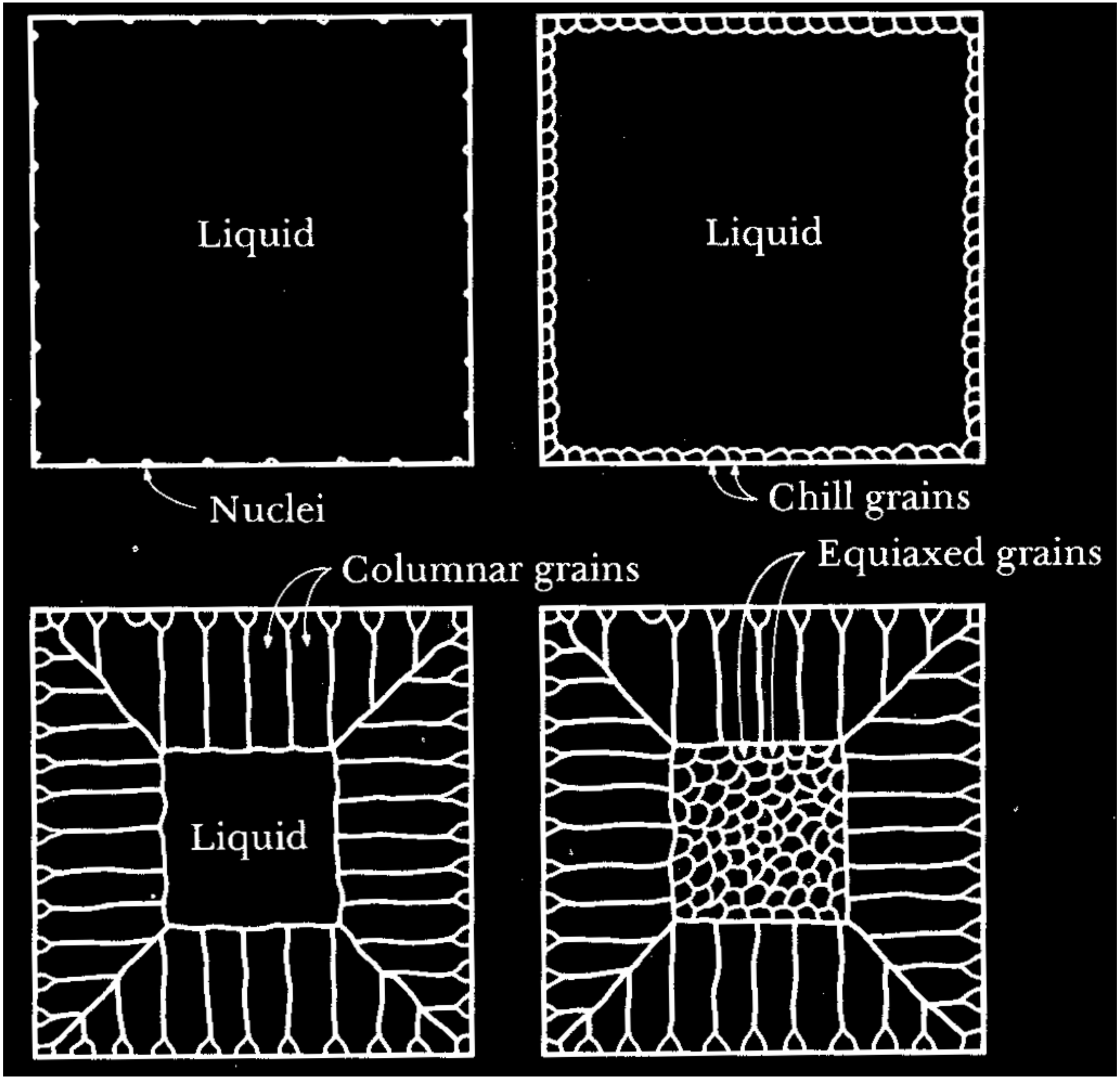
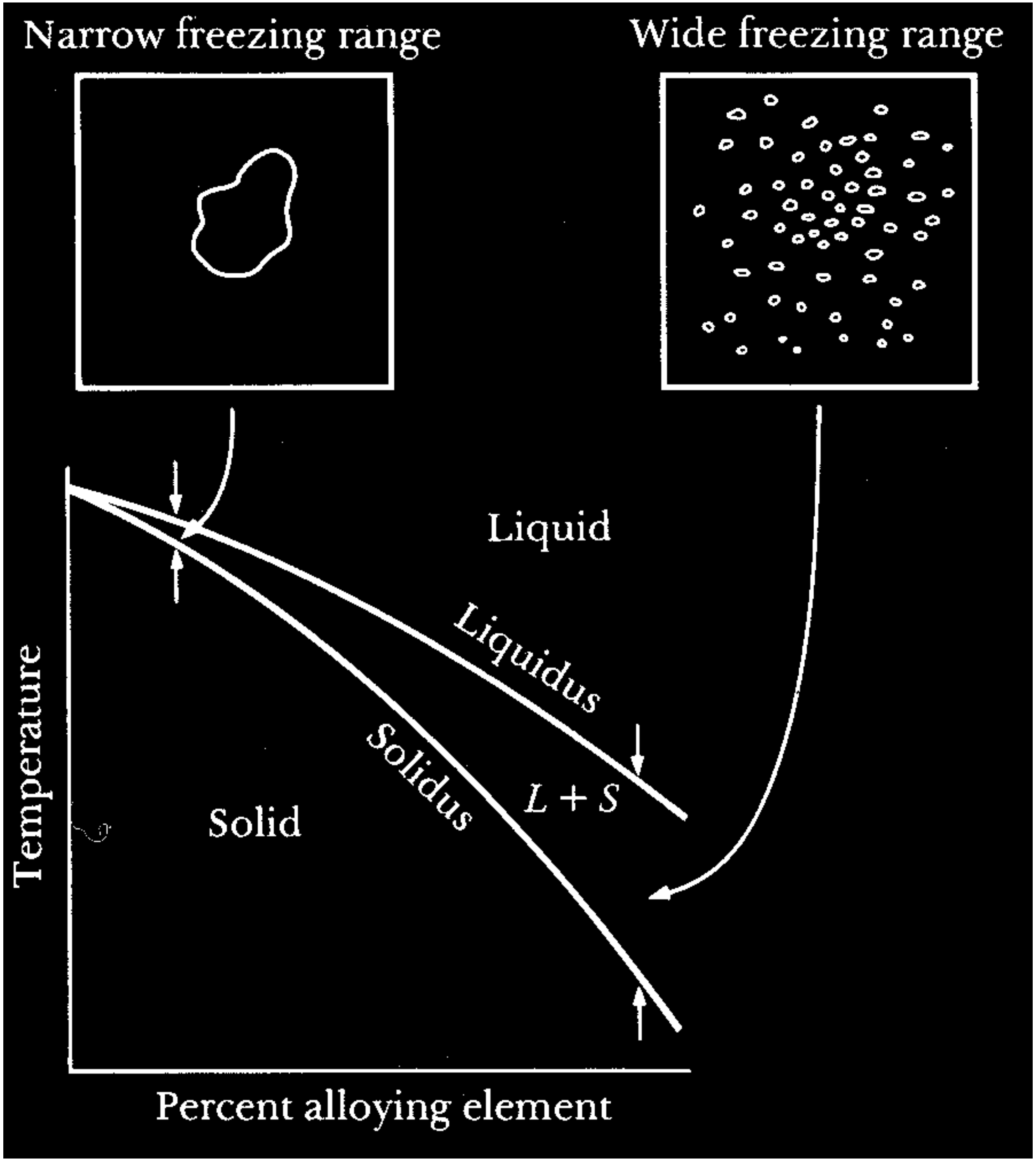


**Fig. 4.40 Schematic cast grain structure.**

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


Liquid
Nuclei
Liquid
Chill grains
Columnar grains
Equiaxed grains
Liquid

# Shrinkage effect



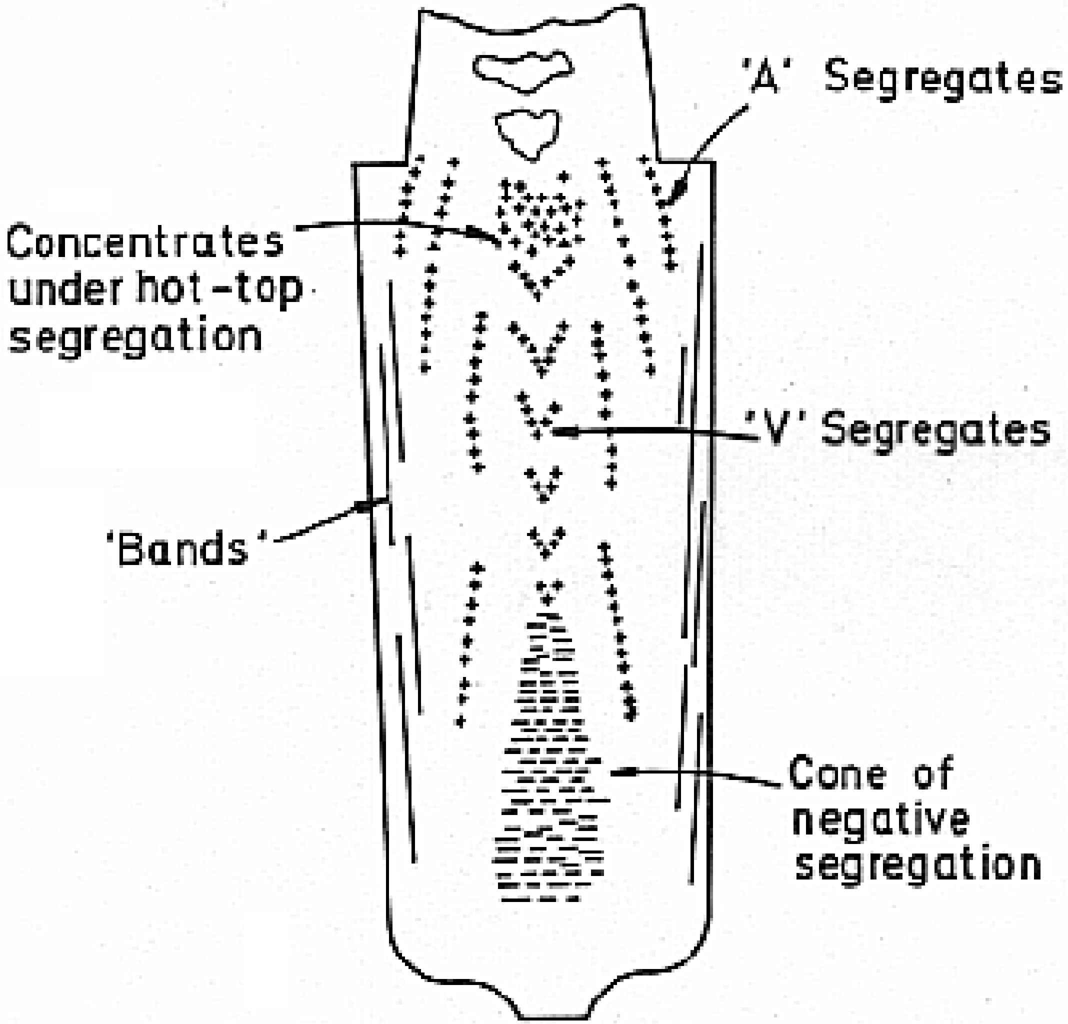
# 4.4.2 Segregation in Ingots and Castings

- Macrosegregation :
  Composition changes over distances comparable to the size of the specimen.

- Microsegregation :
  Occur on the scale of the secondary dendrite arm spacing.

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

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



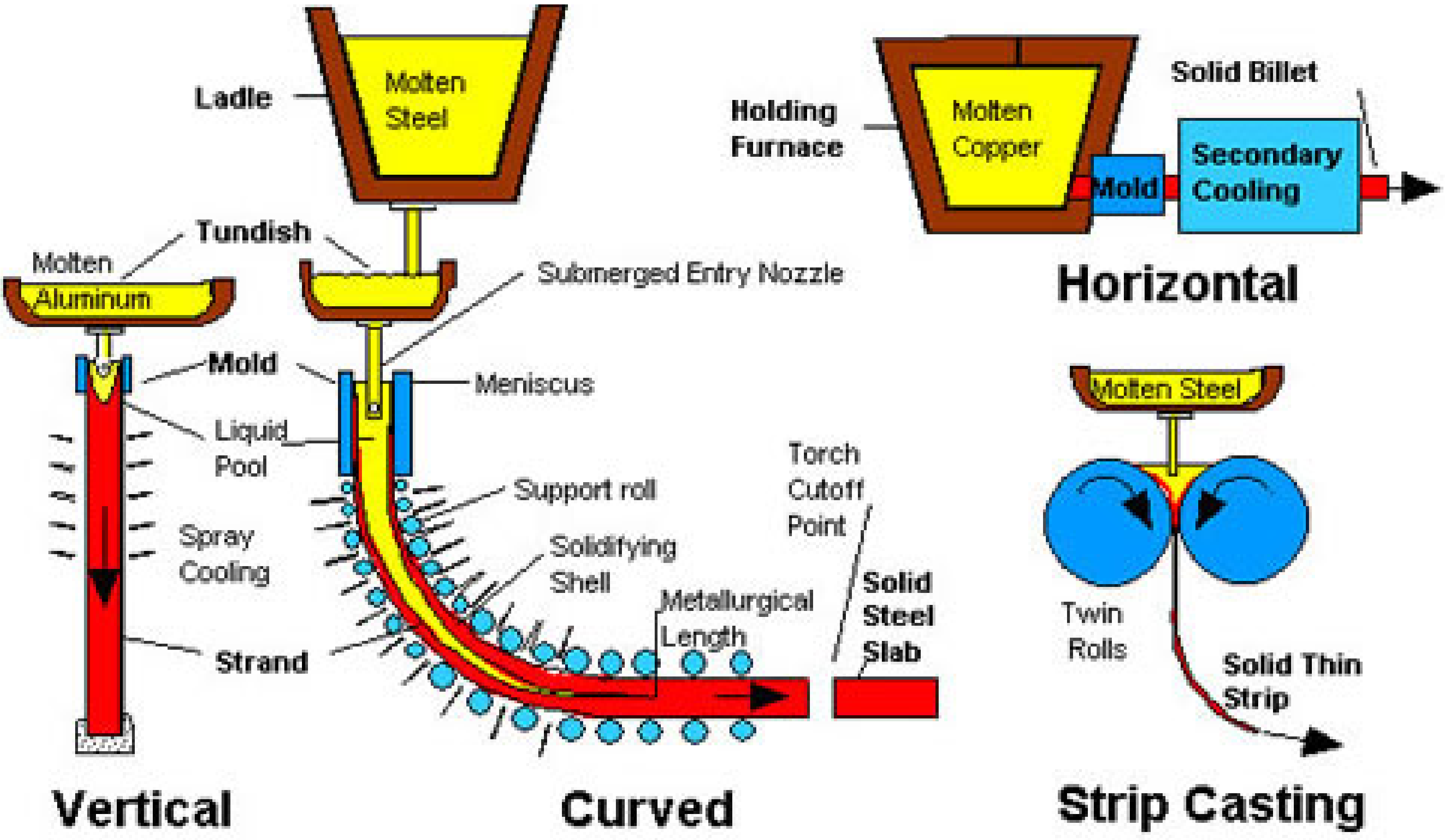
역편석: 주상정 수지상이 두꺼워지면 용질이 농축된 액상 (k<1인 경우)이 수축을 보충하기 위해 수지상 사이로 다시 흘려들어온다.

EX) Al-Cu나 Cu-Sn 등 응고범위가 넓은 합금의 응고시

음의 편석: 등축결정 형성시 중력효과에 의함. 일반적으로 고상은 액상보다 밀도 높고, k<1 이라면 고상의 조성은 본래의 조성보다 낮은 조성을 가짐.

**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.)

# 4.4.3 continuous casting



# 4.4.3 continuous casting

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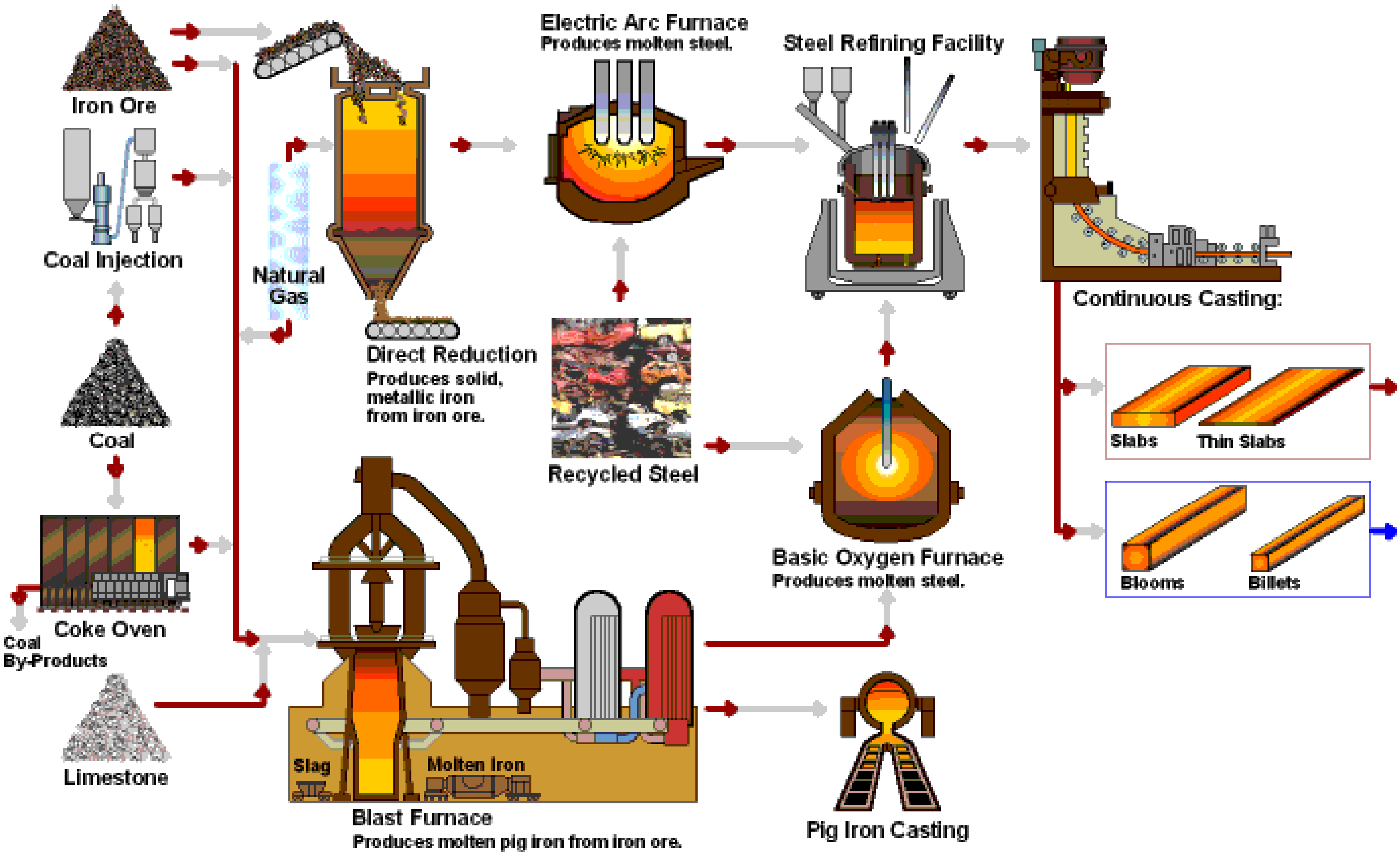
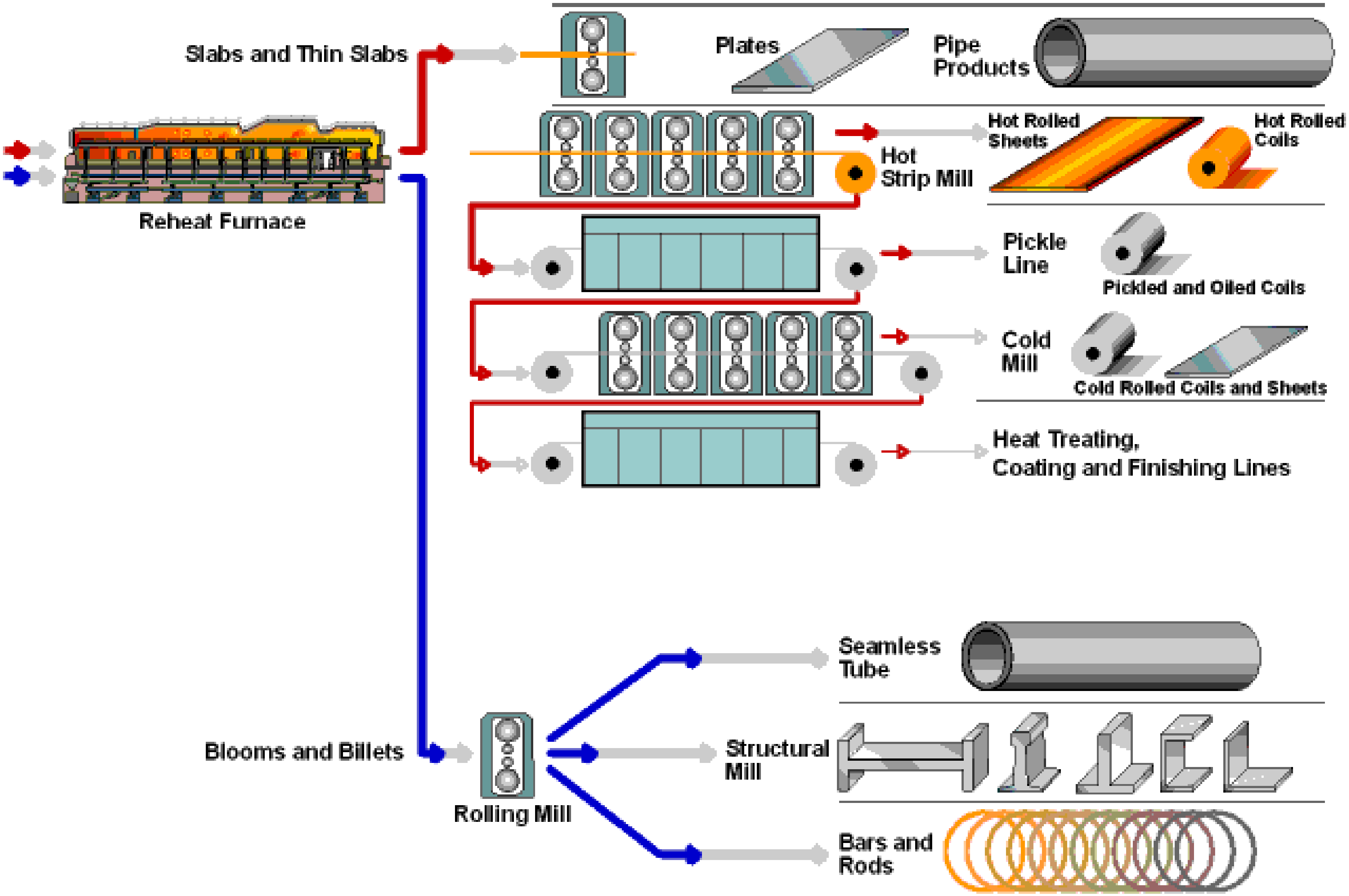
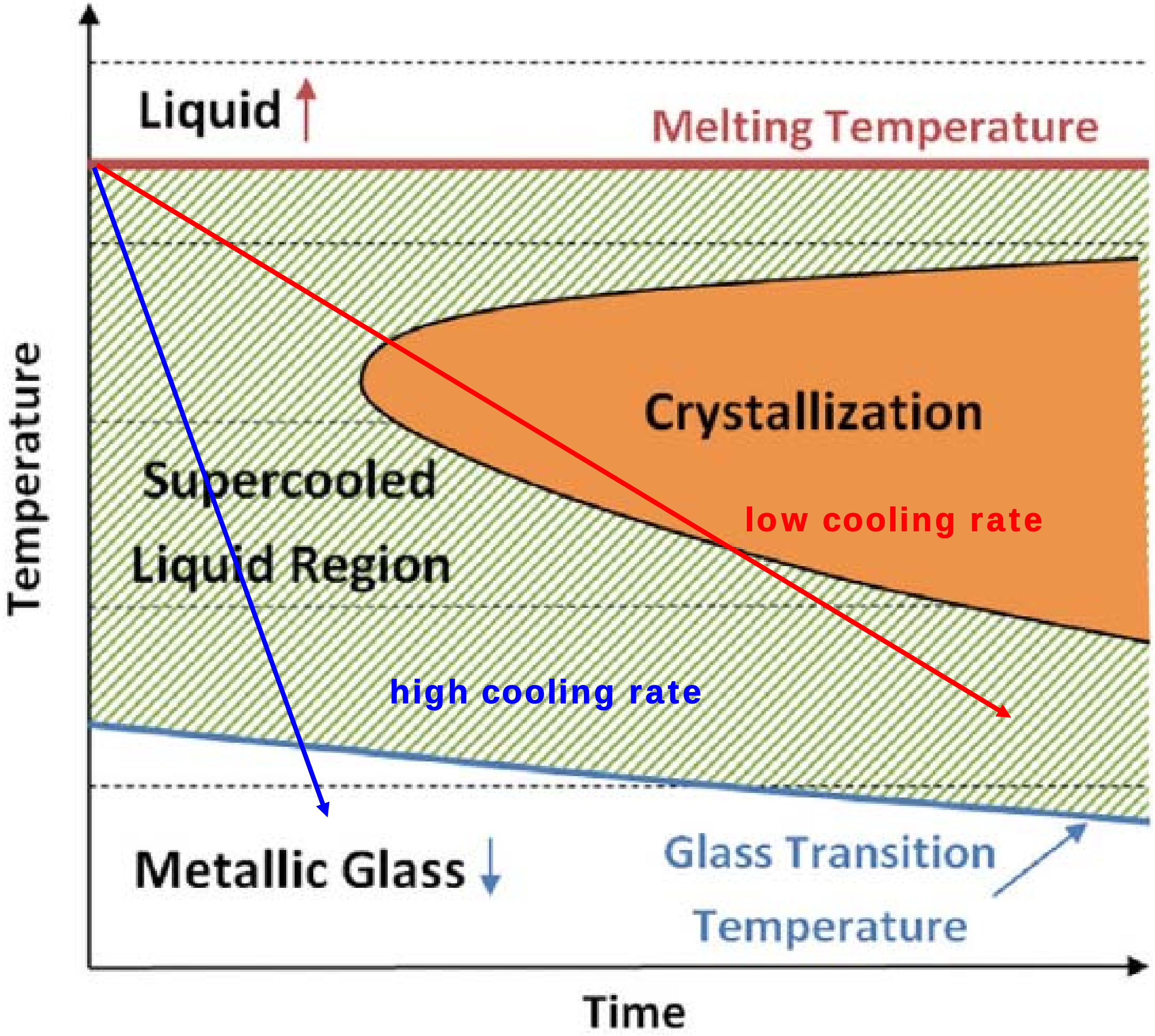


# 4.4.3 continuous casting

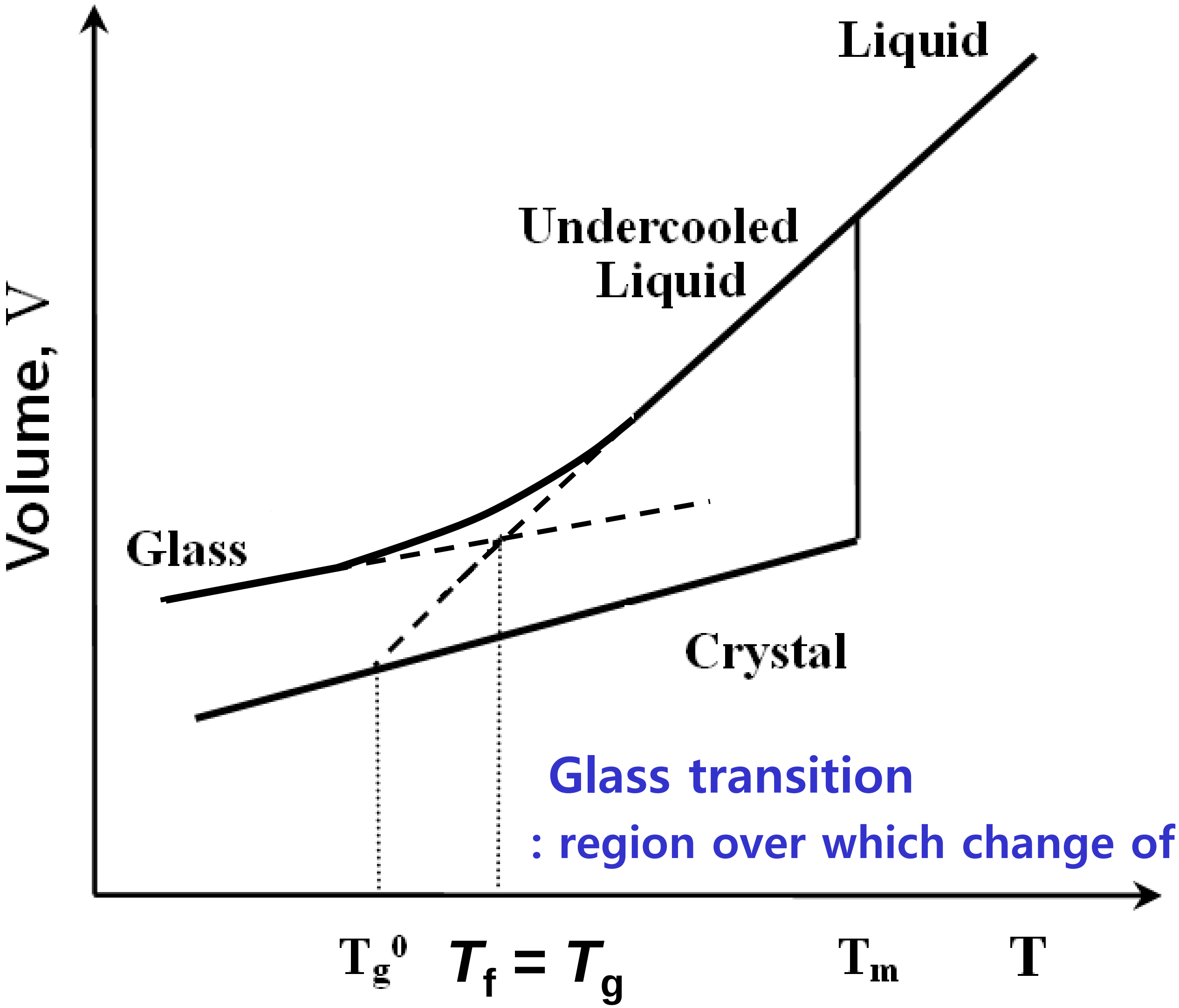


# 4.6 Solidification during quenching from the melt

## Time Temperature Transformation diagram



# ***$T_g$ = fictive temperature, $T_f$***

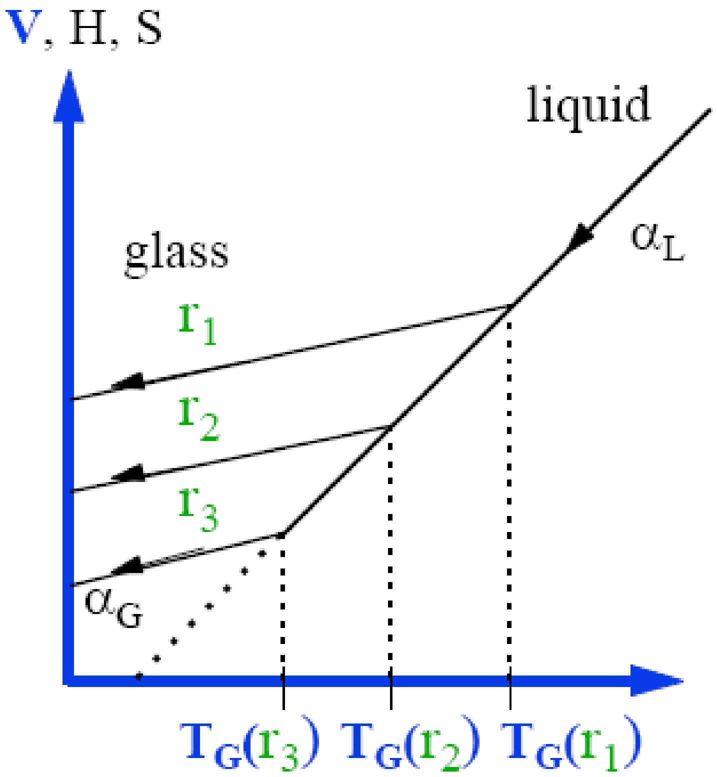


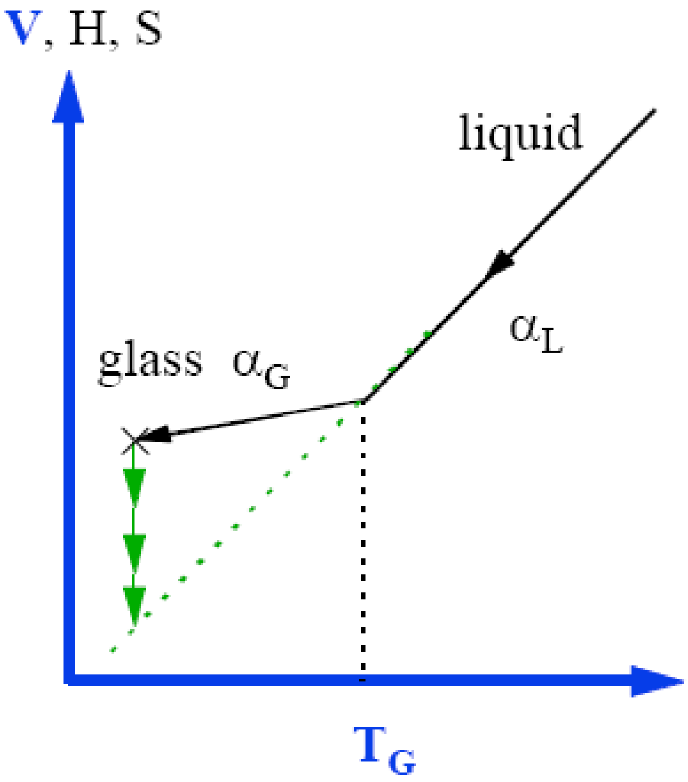
**Glass transition**

**: region over which change of slope occurs**

# * $T_g$ depends on thermal history.

## Kinetic Nature of the Glass Transition

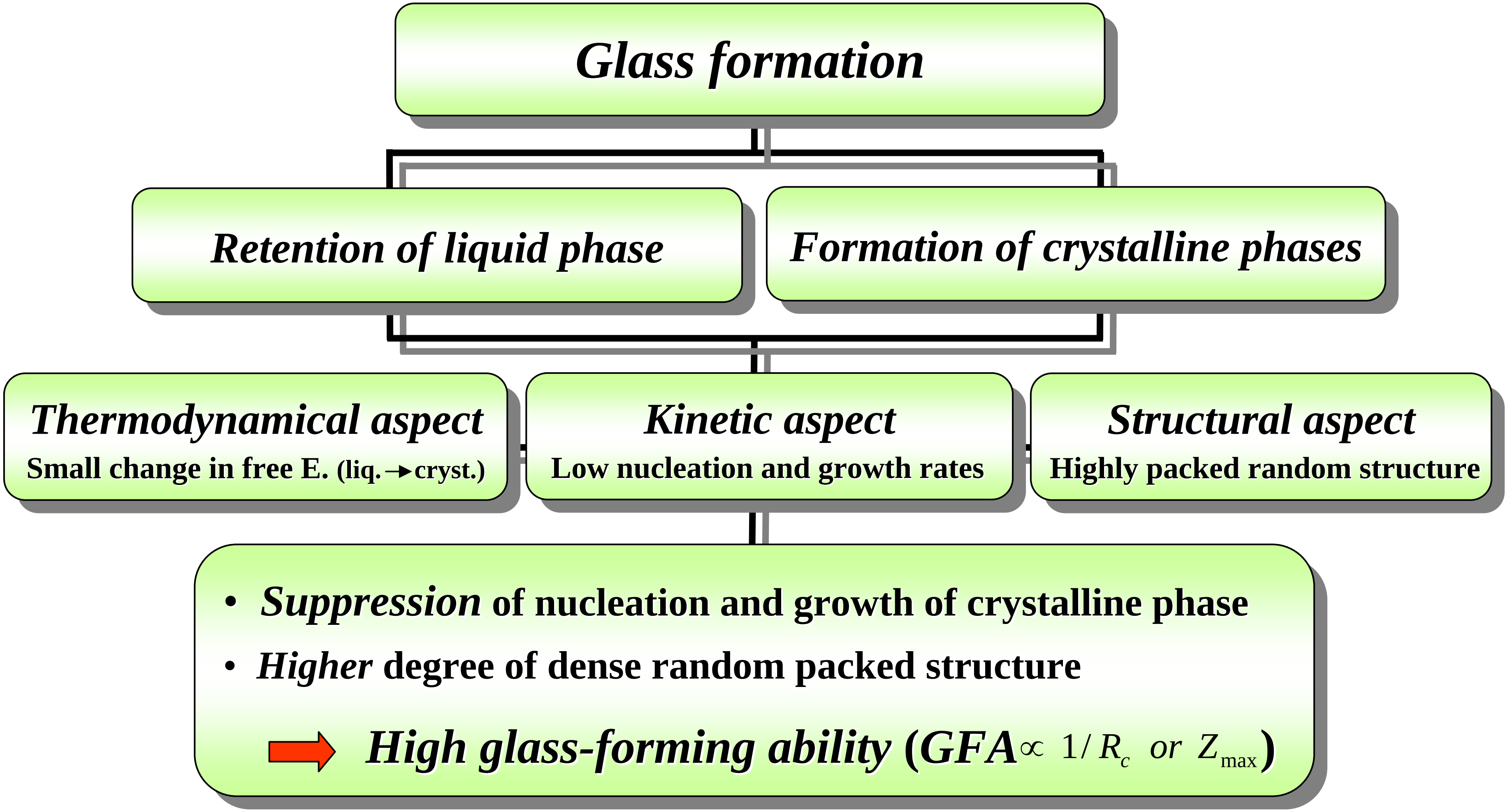




Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$

Specific Volume (density) of the glass depends on the time at a given $T < T_g$

# Glass formation



***Glass formation***

***Retention of liquid phase***

***Formation of crystalline phases***

***Thermodynamical aspect***

**Small change in free E. (liq.→cryst.)**

***Kinetic aspect***

**Low nucleation and growth rates**

***Structural aspect***

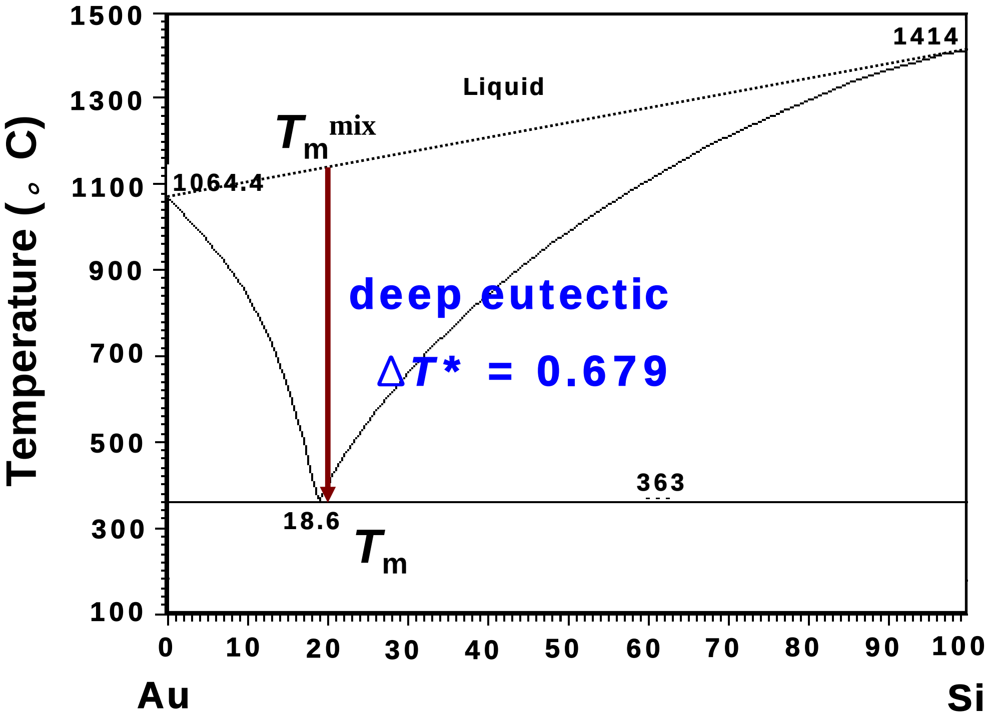
**Highly packed random structure**

- ***Suppression*** **of nucleation and growth of crystalline phase**
- ***Higher*** **degree of dense random packed structure**

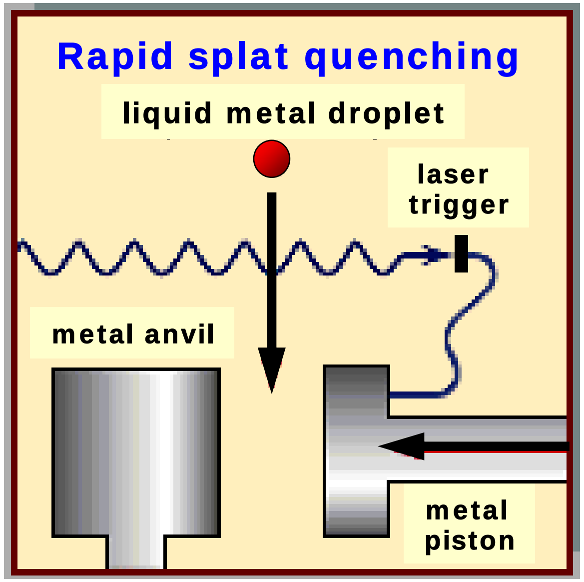
➡ ***High glass-forming ability*** **(*GFA*** $\propto 1/R_c \;\; or \;\; Z_{\max}$**)**

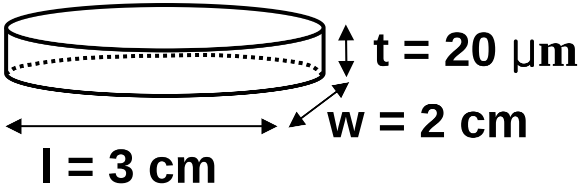
# Glass formation: stabilizing the liquid phase

- **First metallic glass ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.**



*W. Klement, R.H. Willens, P. Duwez, Nature 1960; **187**: 869.*



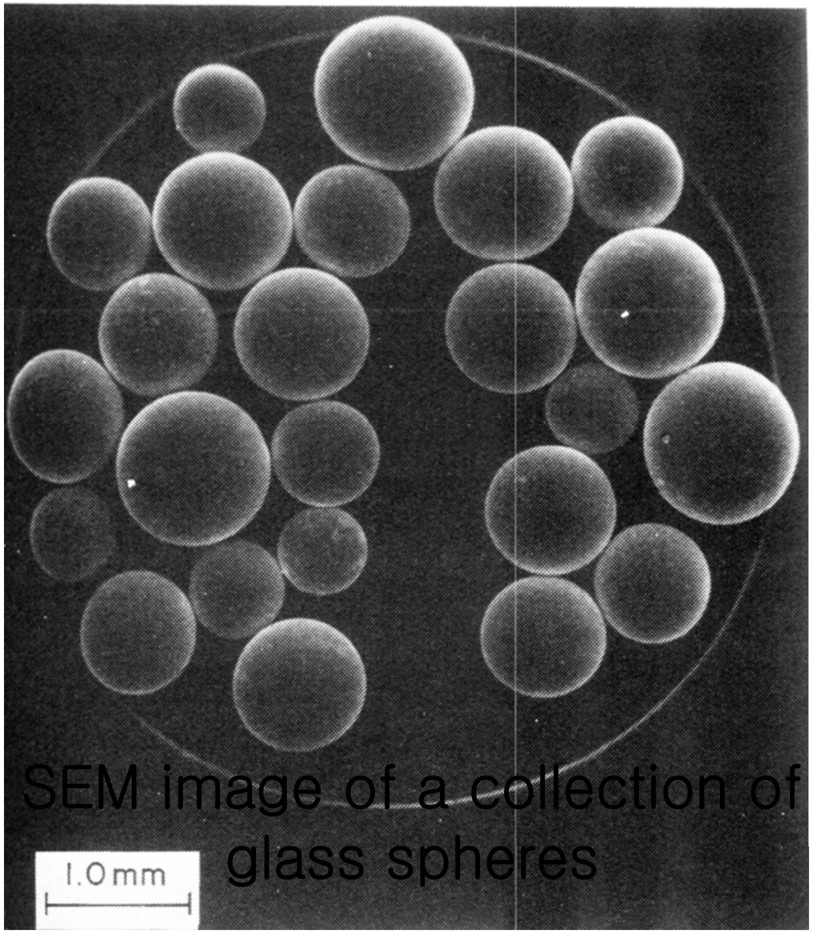


# Bulk formation of metallic glass

- **First bulk metallic glass**

**$Pd_{77.5}Cu_6Si_{16.5}$ ($T_{rg}$=0.64)**

**By droplet quenching (CR~800 K/s)**



SEM image of a collection of glass spheres

*H.S. Chen and D. Turnbull, Acta Metall. 1969; 17: 1021.*

**Alloy Selection: consideration of $T_{rg}$**

**$Pd_{40}Ni_{40}P_{20}$ ($T_{rg}$=0.67)**

**Suppression of heterogeneous nucleation**

- **Largest ingot**

**- minimum dimension 1 cm and mass of 4 g**
**- Critical cooling rate: ~ 1K/sec.**

*Drehman, Greer, and Turnbull, 1982.*

# Bulk glass formation in the Pd-Ni-P system

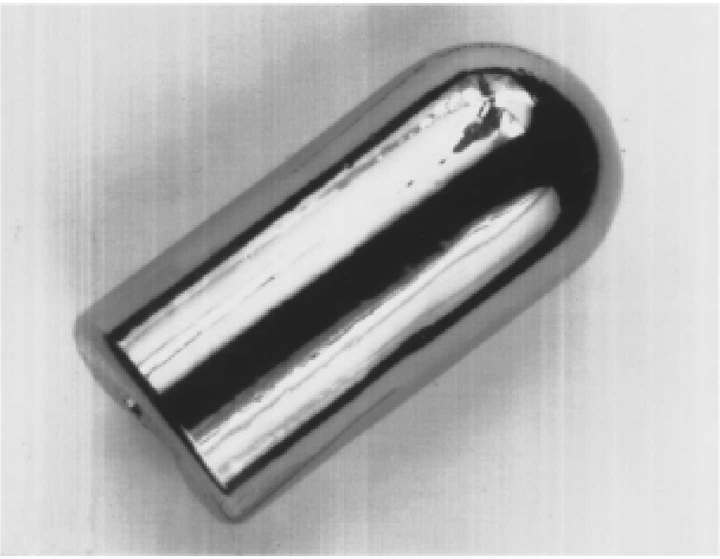
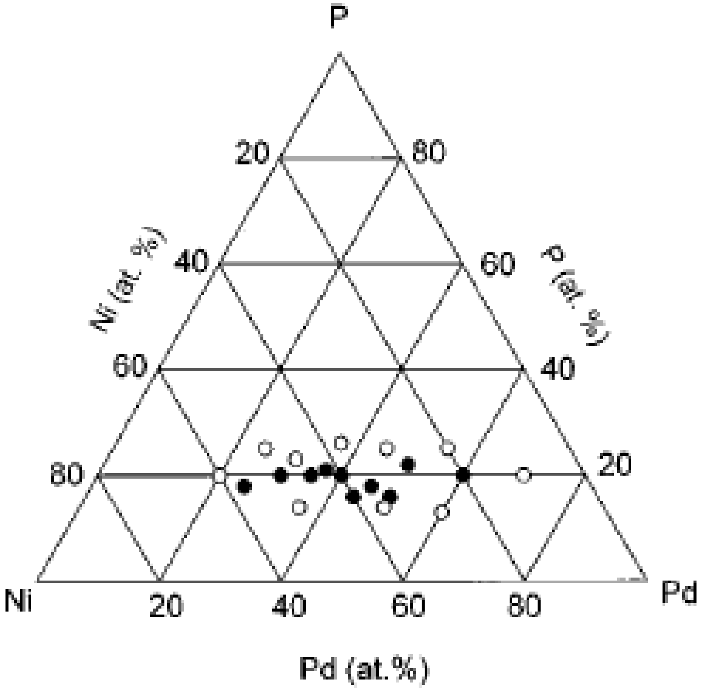


FIG. 1. 300-g ingot of bulk amorphous $Pd_{40}Ni_{40}P_{20}$ rod with 25 mm in diamter prepared by fluxing in $B_2O_3$ and water quenching.



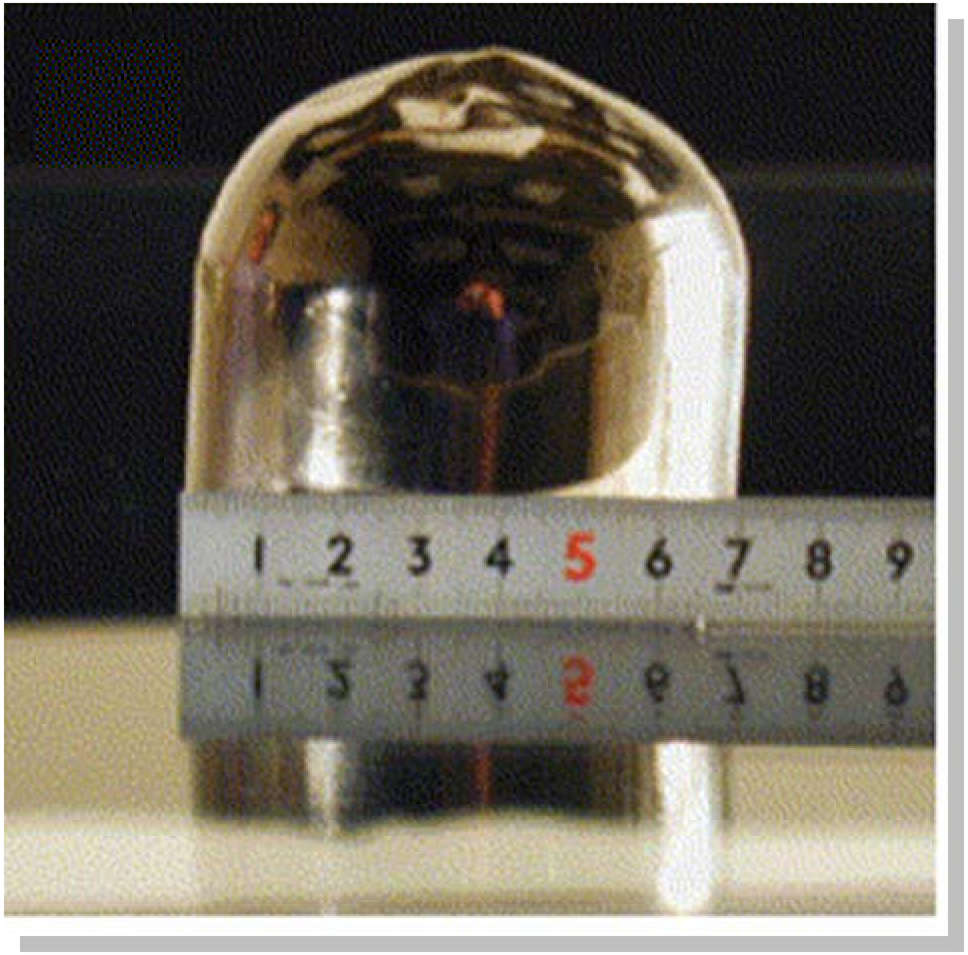
- **Experimental Difference**

**1. Arc melting for the ingot : process temperature > 3000 K**

**2. Water quenching : Improvement of cooling rate**

**Y.He, R.B. Schwarz, J.I. Archuleta, Appl. Phys. Lett. 1996; 69: 1861.*

# Bulk glass formation in the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ system



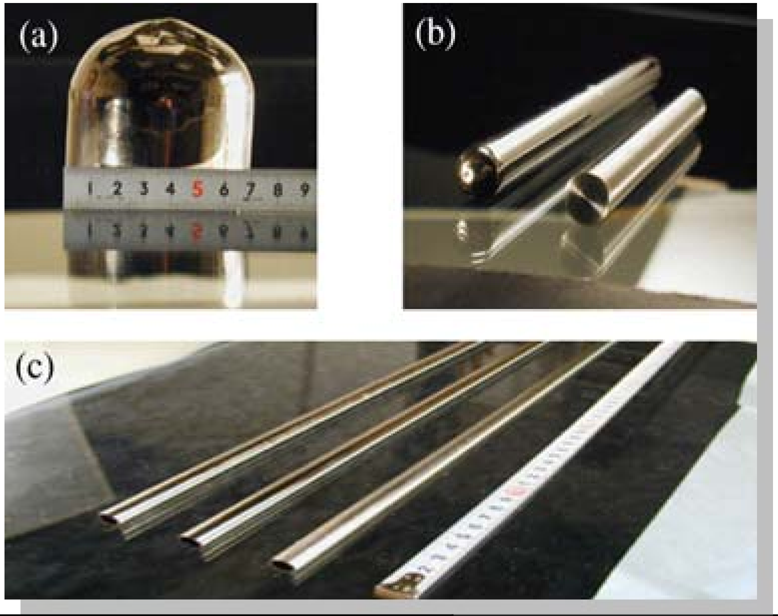
- **Largest ingot**

**maximum diameter for glass formation : 72 mm**

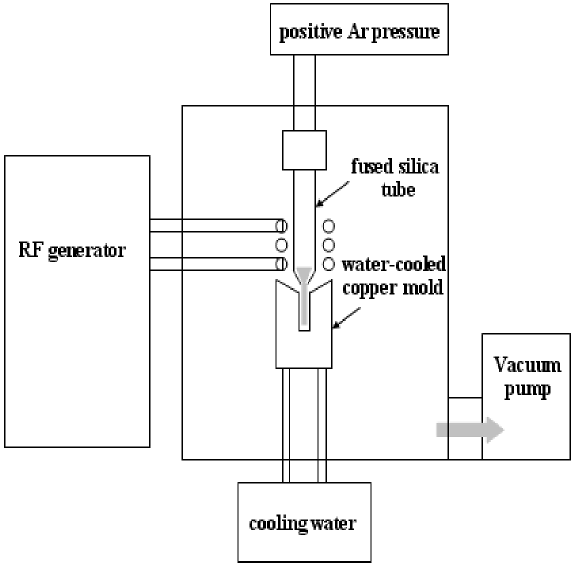
**Critical cooling rate: ~ 0.1K/sec.**

# How to make bulk metallic glasses

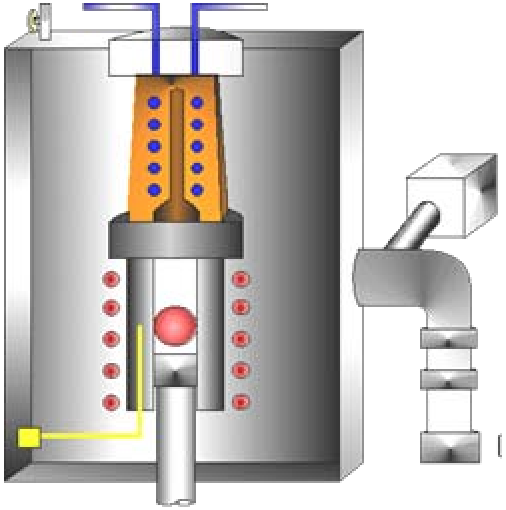
## < Casting >



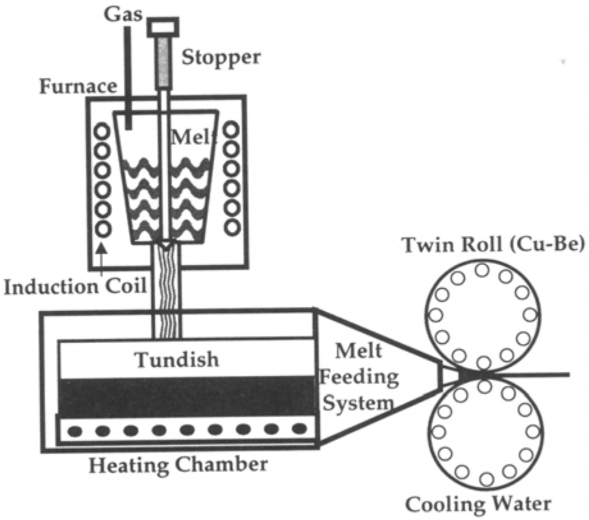
### 1) Injection casting



### 2) Squeeze casting



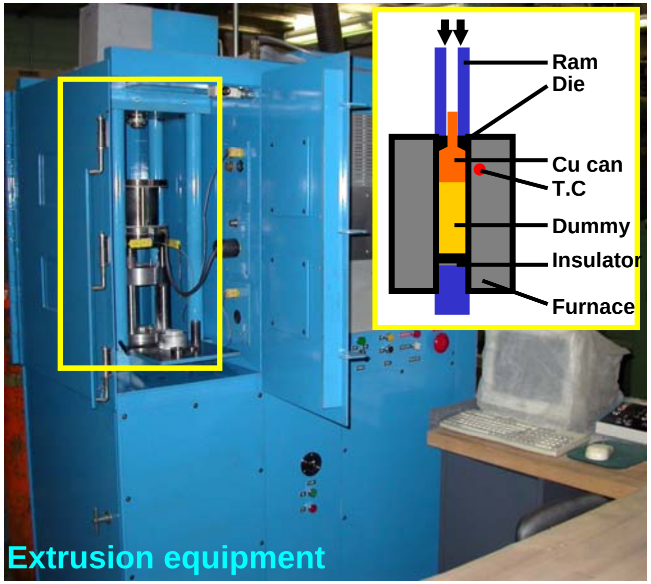
### 3) Strip casting



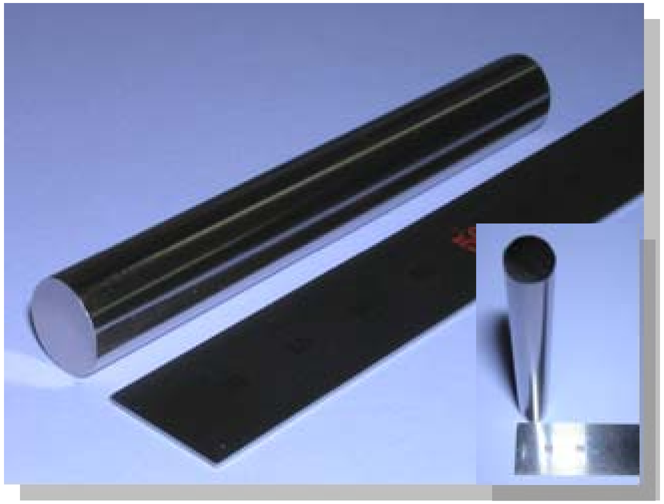
# How to make bulk metallic glasses

## < Powder Metallurgy>

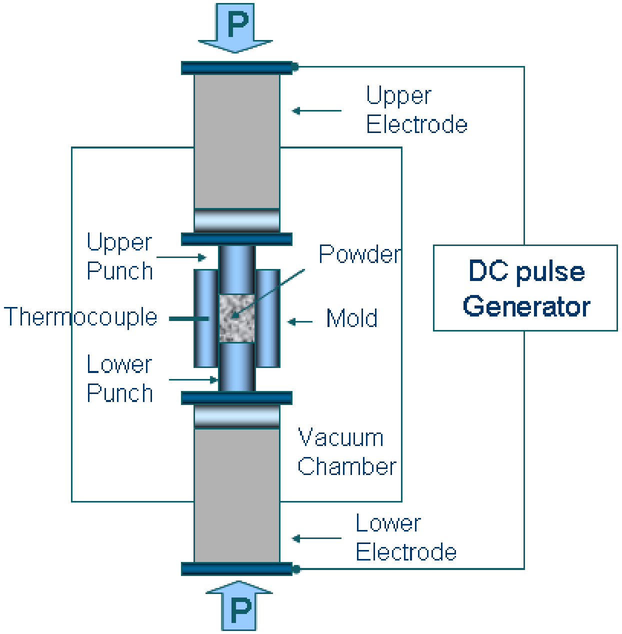
### 1) Extrusion

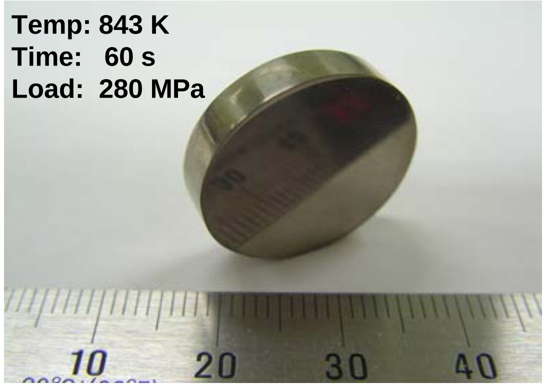


Extrusion equipment



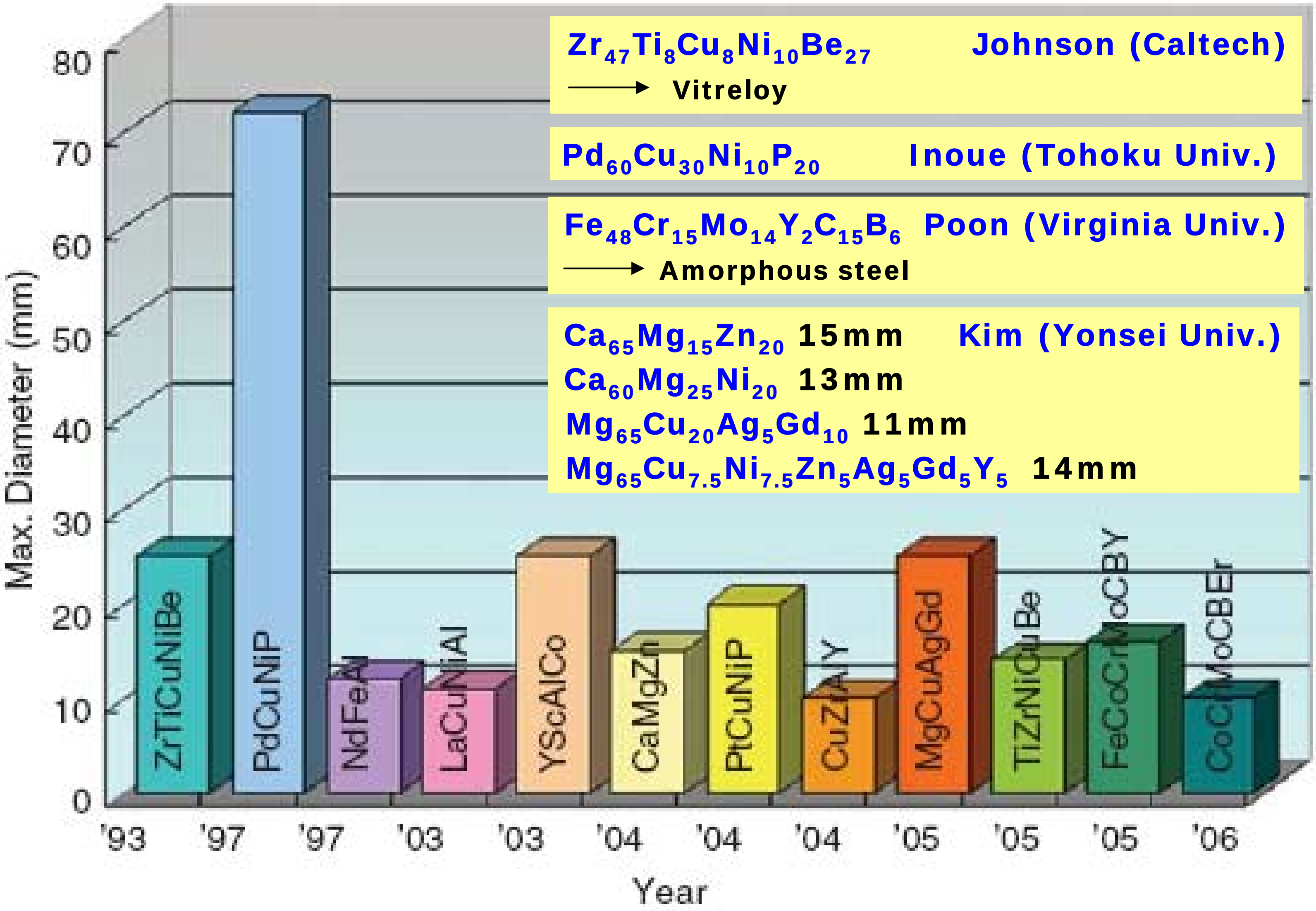
### 2) Spark Plasma Sintering





Temp: 843 K
Time: 60 s
Load: 280 MPa

# Recent BMGs with critical size ≥ 10 mm



**$Zr_{47}Ti_8Cu_8Ni_{10}Be_{27}$ Johnson (Caltech)**
**→ Vitreloy**

**$Pd_{60}Cu_{30}Ni_{10}P_{20}$ Inoue (Tohoku Univ.)**

**$Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ Poon (Virginia Univ.)**
**→ Amorphous steel**

**$Ca_{65}Mg_{15}Zn_{20}$ 15mm Kim (Yonsei Univ.)**
**$Ca_{60}Mg_{25}Ni_{20}$ 13mm**
**$Mg_{65}Cu_{20}Ag_5Gd_{10}$ 11mm**
**$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Gd_5Y_5$ 14mm**

*A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.*