

2017 Fall

“Phase Transformation *in* Materials”

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Solidification of Pure Metal

: Thermal gradient dominant



Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional supercooling

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

응고계면에 조성적 과냉의
thin zone 형성에 의함
Dome 형태 선단 / 주변에
hexagonal array

$T \downarrow \rightarrow$ 조성적 과냉영역 증가
Cell 선단의 피라미드형상/ 가지
들의 square array/ Dendrite
성장방향쪽으로 성장방향 변화

성장하는 crystal로 부터 발생한 잠
열을 과냉각 액상쪽으로 방출함에
의해 형성
Dendrite 성장 방향/ Branched
rod-type dendrite

→ “Nucleation of new crystal in liquid”

성장이 일어나는 interface 보다 높은 온도

b) Segregation

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

Eutectic Solidification (Kinetics)

: $\Delta T \rightarrow$ a) formation of interface + b) solute redistribution

How many α/β interfaces per unit length?

$$\rightarrow 1/\lambda \times 2$$

a) Formation of interface: ΔG

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

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

$$\rightarrow \Delta G = \Delta \mu = \frac{2\gamma}{\lambda} \times V_m^{\text{Molar volume}}$$

Driving force for nucleation = Total interfacial E of eutectic phase

For very large values of λ , interfacial E ~ 0

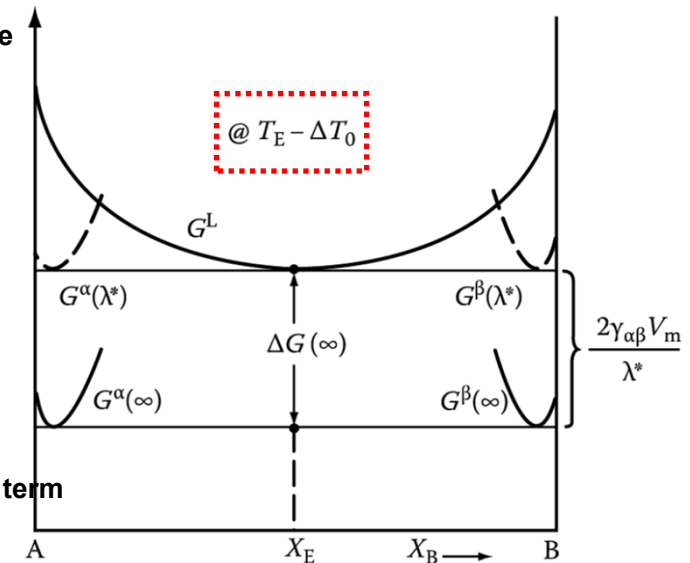
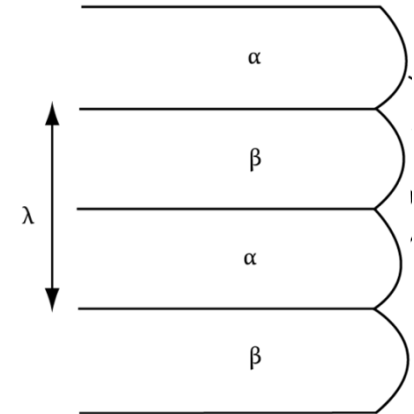
$$\lambda \rightarrow \infty, \quad \Delta G(\infty) = \Delta \mu = \frac{\Delta H \Delta T_0}{T_E} \quad \text{Total undercooling}$$

No interface (ideal case)

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda} \quad \text{Interfacial E term}$$

With interface (real case)

Solidification will take place if ΔG is negative (-).



a) All $\Delta T \rightarrow$ use for interface formation = min. λ

What would be the minimum λ ?

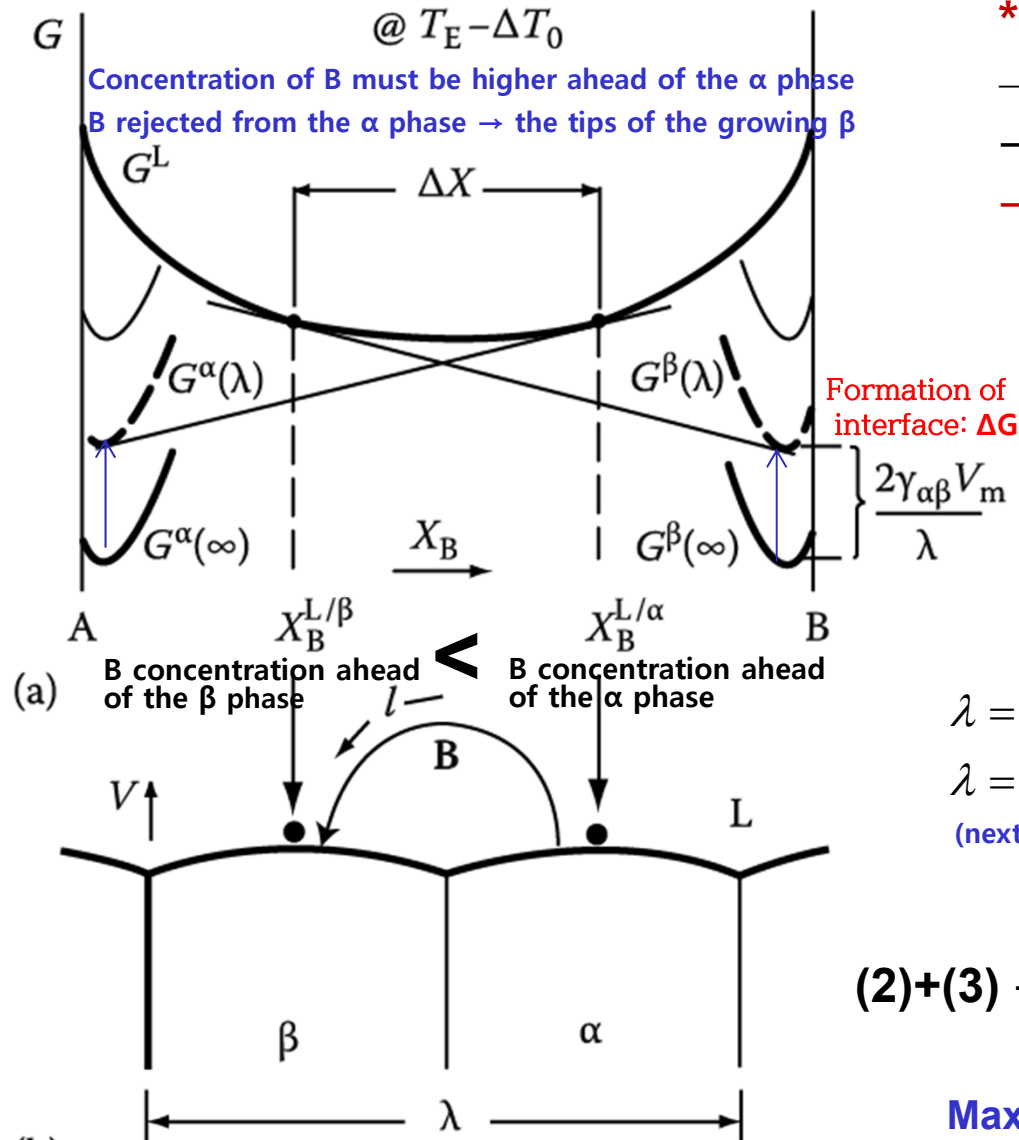
Critical spacing, $\lambda^* : \Delta G(\lambda^*) = 0$

최소 층상 간격

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

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

2) At $\lambda = (\infty >) \lambda (> \lambda^*)$, If $\infty > \lambda > \lambda^*$, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. $\rightarrow X_B^{L/\alpha} > X_B^{L/\beta}$



* Eutectic growth rate, v

\rightarrow if α/L and β/L interfaces are highly mobile

\rightarrow proportional to flux of solute through liquid

\rightarrow diffusion controlled process

$$v \propto D \frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})$$

$$\propto 1/\text{effective diffusion distance.. } 1/\lambda$$

$$v = k_1 D \frac{\Delta X}{\lambda} \quad (1)$$

$$\Delta X = \Delta X_0 \left(1 - \frac{\lambda^*}{\lambda}\right) \quad (2)$$

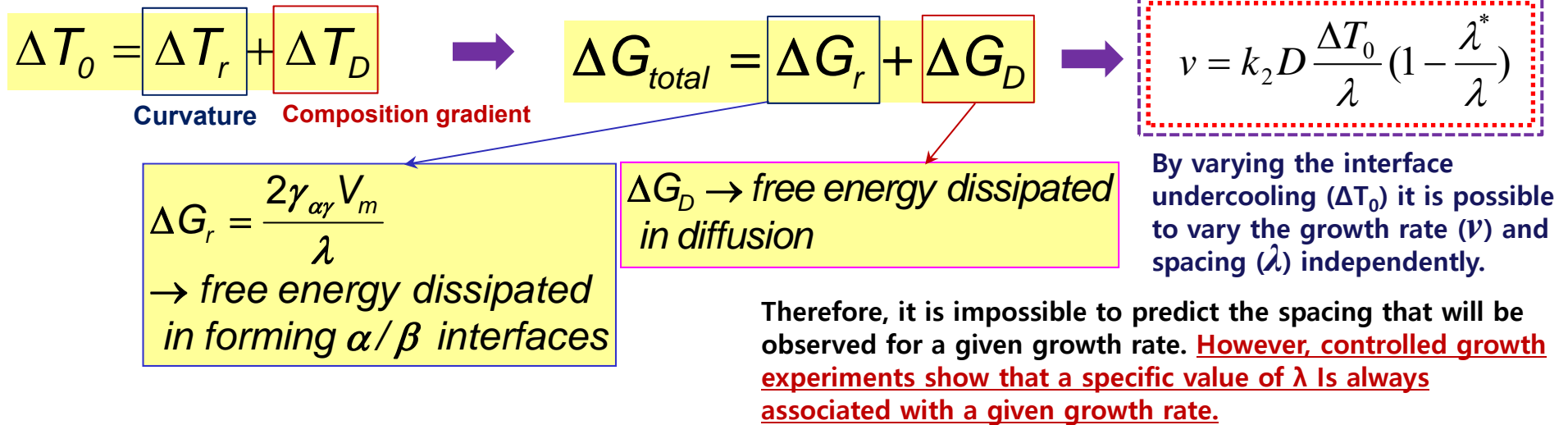
$$\Delta X_0 \propto \Delta T_0 \quad (3)$$

$$(2)+(3) \rightarrow (1) \quad v = k_2 D \frac{\Delta T_0}{\lambda} \left(1 - \frac{\lambda^*}{\lambda}\right)$$

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

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 (ΔX). (b) Model used to calculate the growth rate.

Undercooling ΔT_0



* For example,

Maximum growth rate at a fixed $\Delta T_0 \rightarrow \lambda_0 = 2\lambda^*$

$$(4) \quad v = k_2 D \frac{\Delta T_0}{\lambda} \left(1 - \frac{\lambda^*}{\lambda}\right) \quad \rightarrow \quad v_0 = k_2 D \Delta T_0 / 4\lambda^* \quad (5)$$

From Eq. 4.39

$$\lambda^* = + \frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \quad \rightarrow \quad \Delta T_0 \propto 1 / \lambda^* \quad (6)$$

So that the following relationships are predicted:

(5) + (6) →

$$v_0 \lambda_0^2 = k_3 \text{ (constant)}$$

$$\frac{v_0}{(\Delta T_0)^2} = k_4$$

Ex) Lamellar eutectic in the Pb-Sn system

$$k_3 \sim 33 \mu\text{m}^3/\text{s} \text{ and } k_4 \sim 1 \mu\text{m}/\text{s}\cdot\text{K}^2$$

$$\rightarrow v = 1 \mu\text{m}/\text{s}, \lambda_0 = 5 \mu\text{m} \text{ and } \Delta T_0 = 1 \text{ K}$$

* Total Undercooling

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

Undercooling required to overcome the interfacial curvature effects

Undercooling required to give a sufficient composition difference to drive the diffusion

Strictly speaking,

ΔT_i term should be added **but, negligible for high mobility interfaces**

Driving force for atom migration across the interfaces

$\Delta T_D \rightarrow$ Vary continuously from the middle of the α to the middle of the β lamellae

$\Delta T_0 = \text{const}$ \leftarrow Interface is essentially isothermal.

$\Delta T_D \rightarrow \Delta T_r$ **The interface curvature will change across the interface.**
Should be compensated

* A planar eutectic front is not always stable.

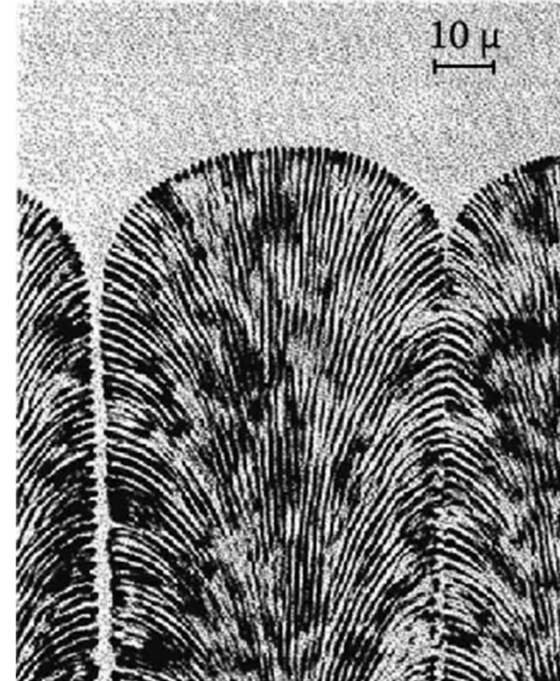
Binary eutectic alloys
contains **impurities** or
other alloying elements

"Form a cellular morphology"

\rightarrow analogous to single phase solidification
restrict in a sufficiently high temp. gradient.

\rightarrow The solidification direction changes as the cell walls are approached and the lamellar or rod structure fans out and may even change to an irregular structure.

\rightarrow **Impurity elements (here, mainly copper) concentrate at the cell walls.**



Q: Off-eutectic Solidification?

4.3.3 Off-eutectic Solidification _Pb-Sn system

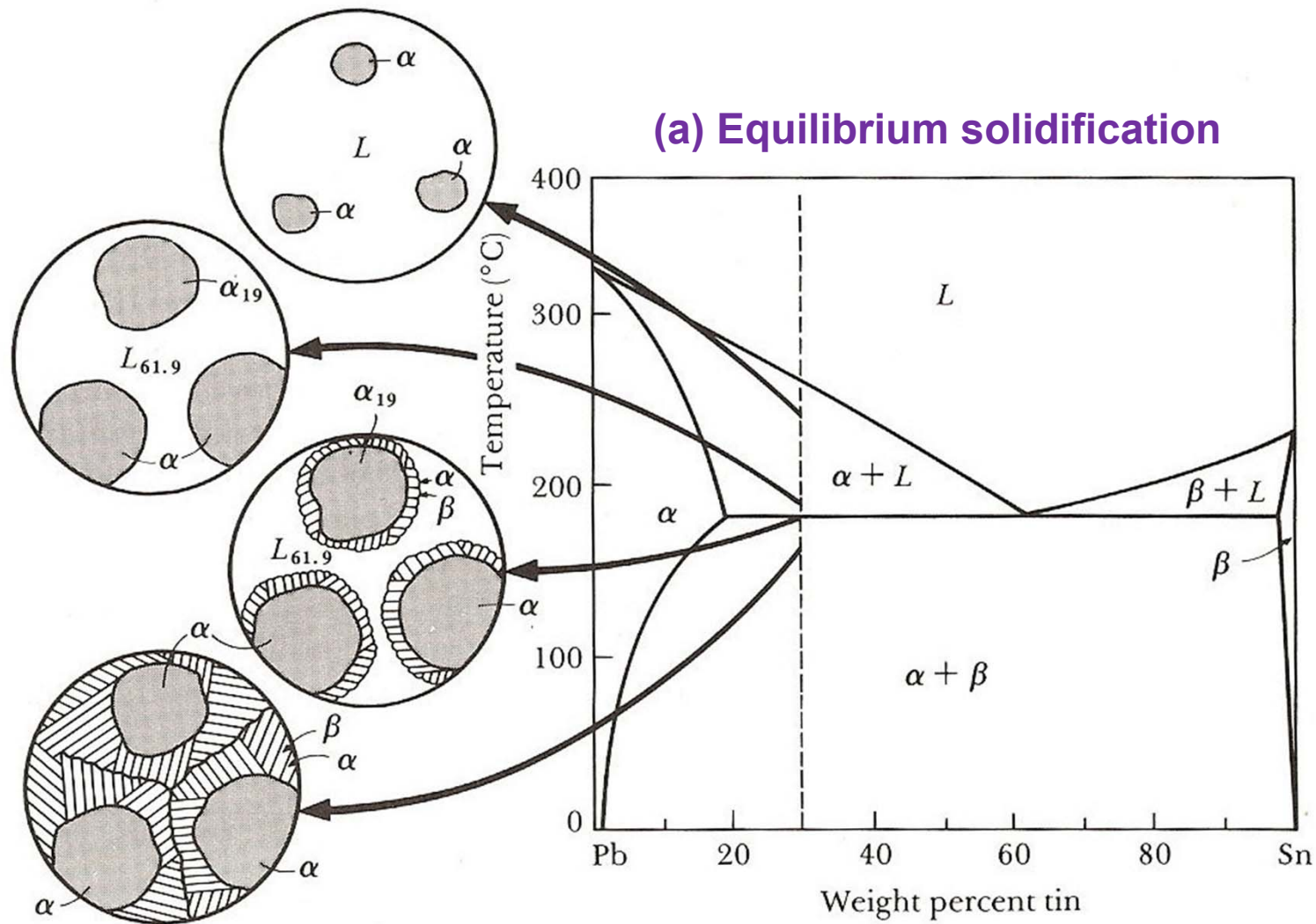
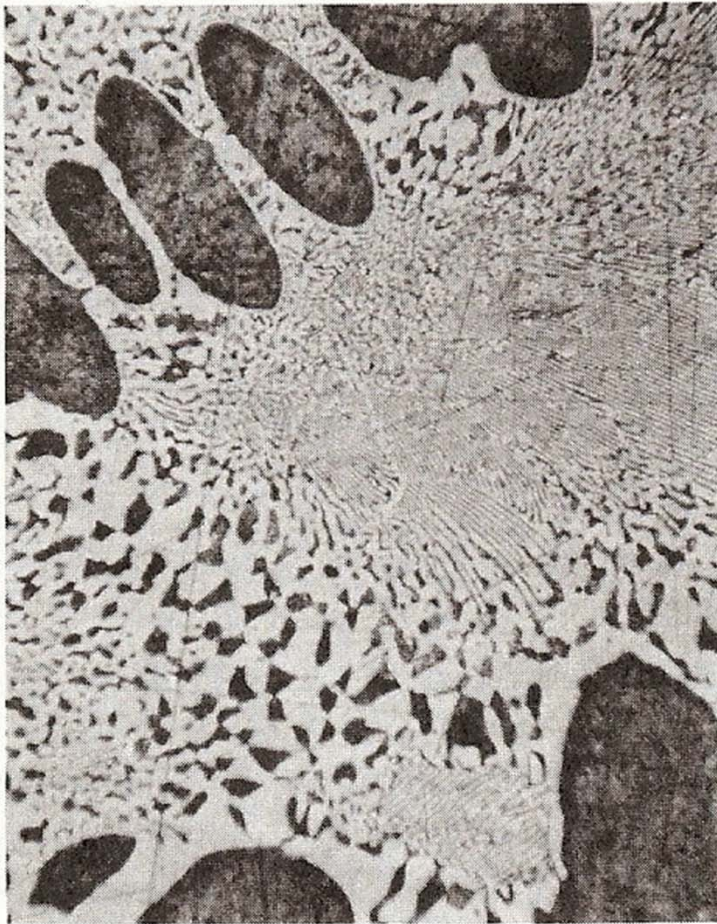
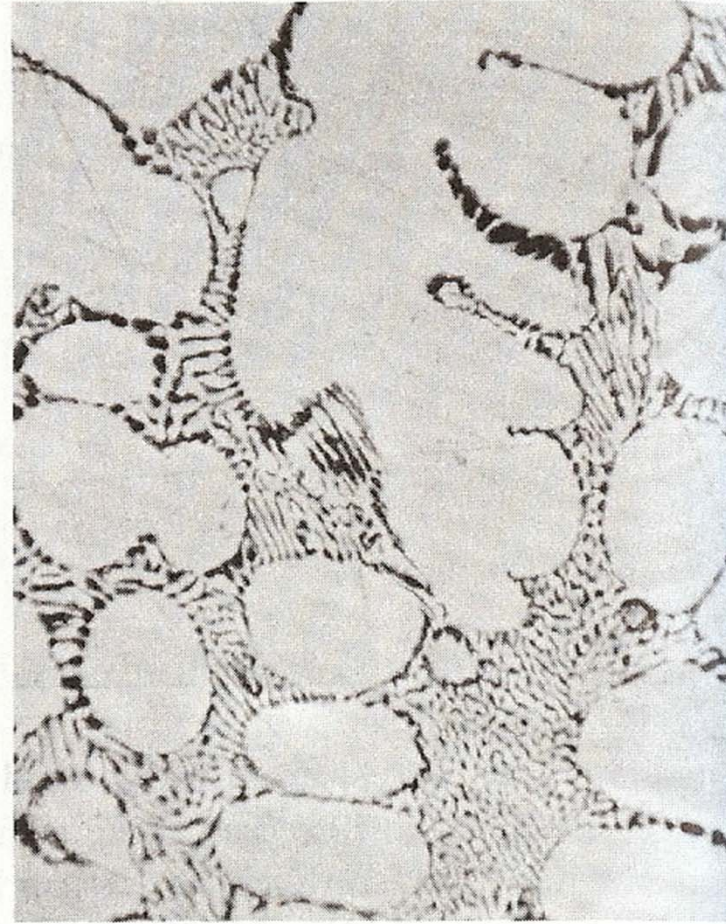


FIGURE 10-12 The solidification and microstructure of a hypo-eutectic alloy (Pb-30% Sn).

4.3.3 Off-eutectic Solidification _Pb-Sn system



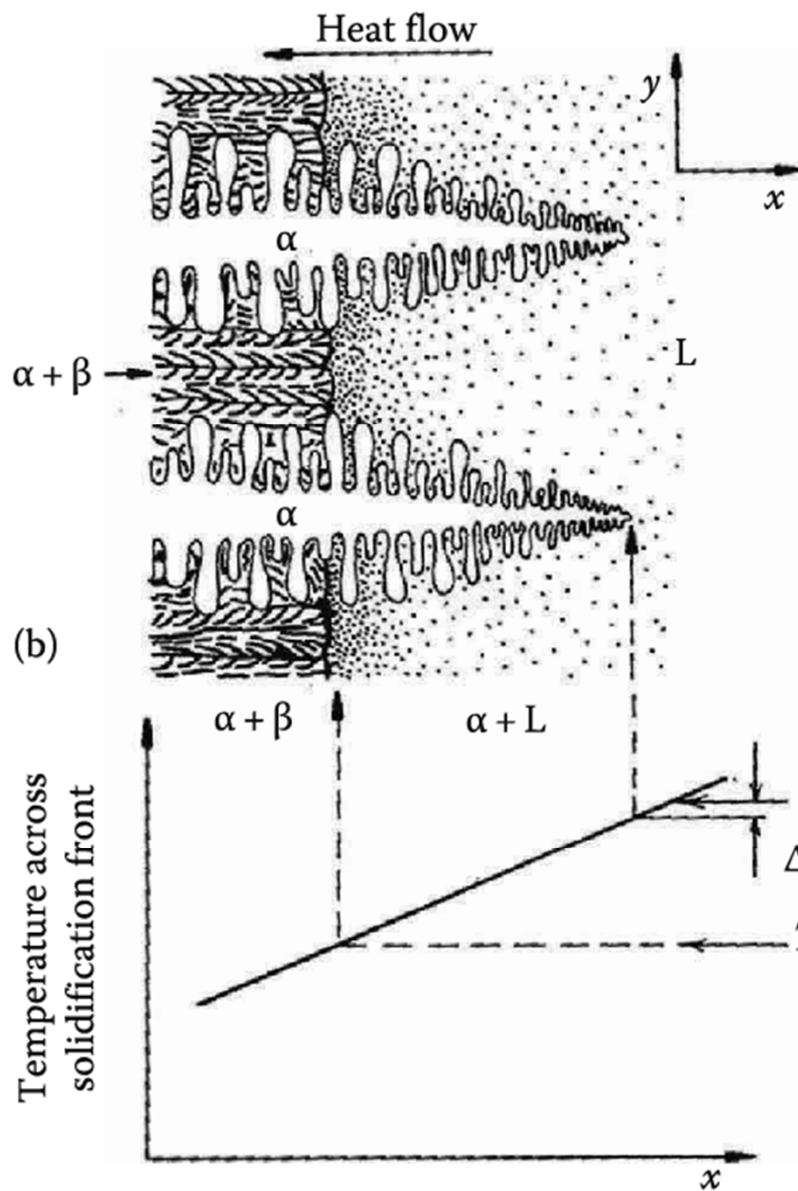
(a)



(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 ($\times 400$).

4.3.3 Off-eutectic Solidification



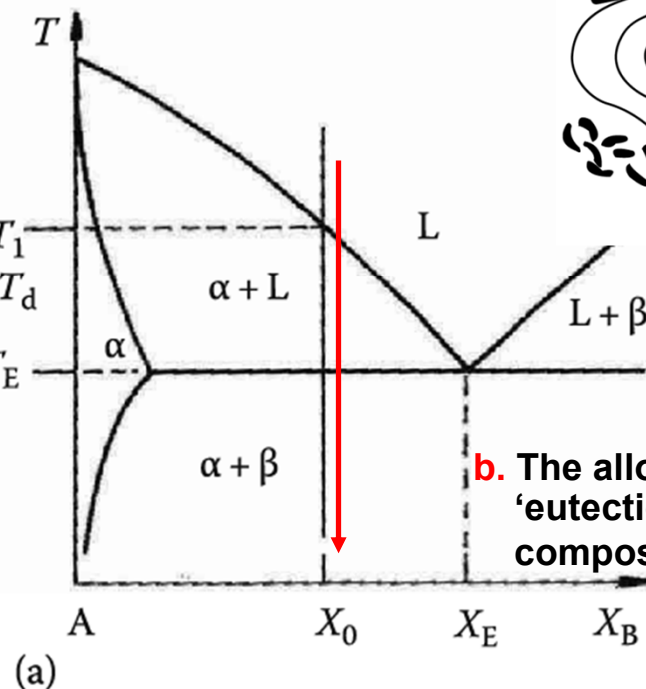
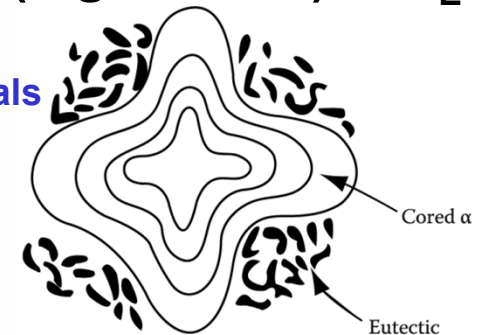
(b) Non-equilibrium solidification

a. 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



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

Q: Peritectic Solidification ($L + \alpha \rightarrow \beta$)?

Solidification and microstructure that develop as a result of the **peritectic reaction**

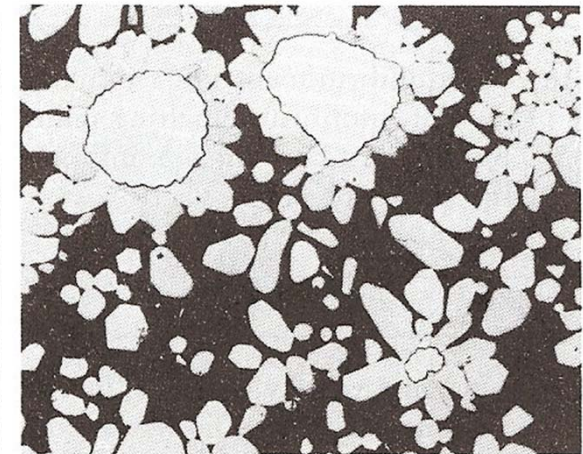
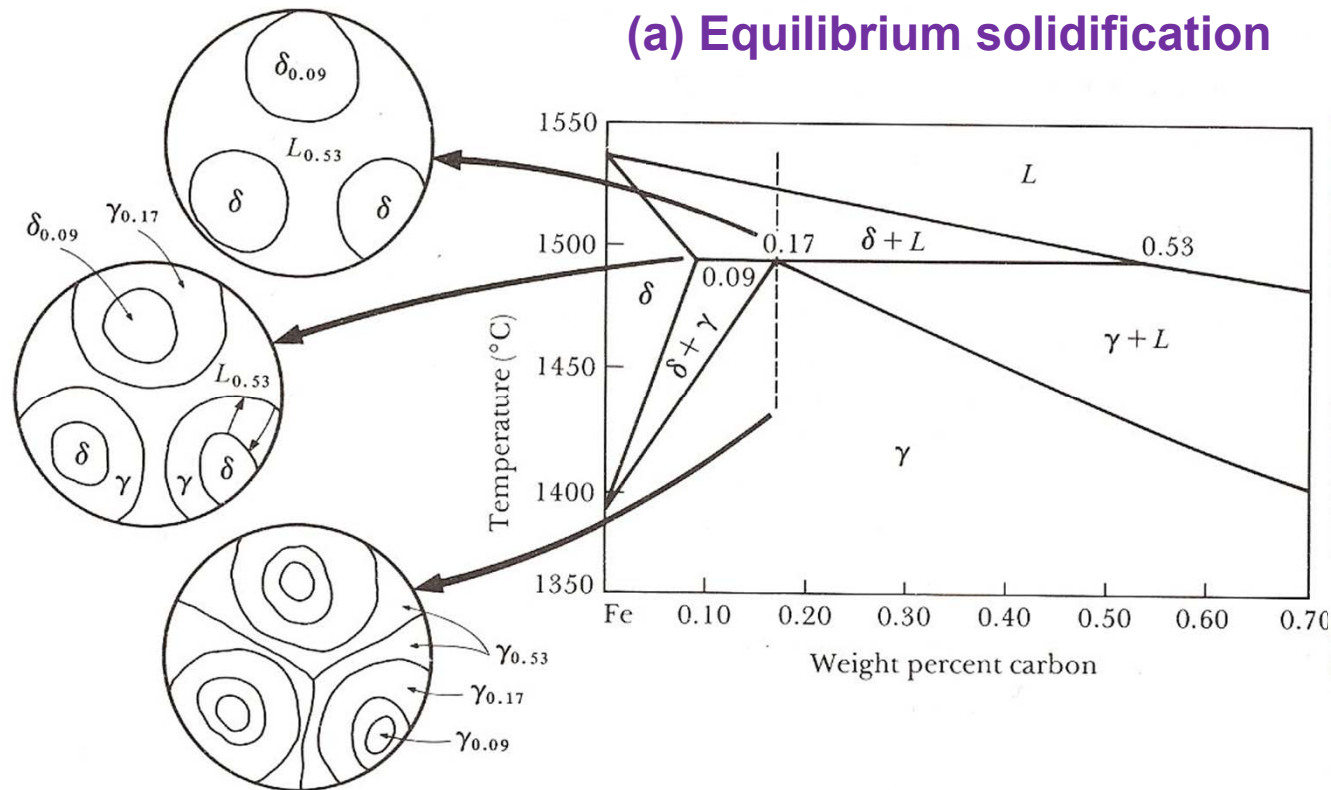
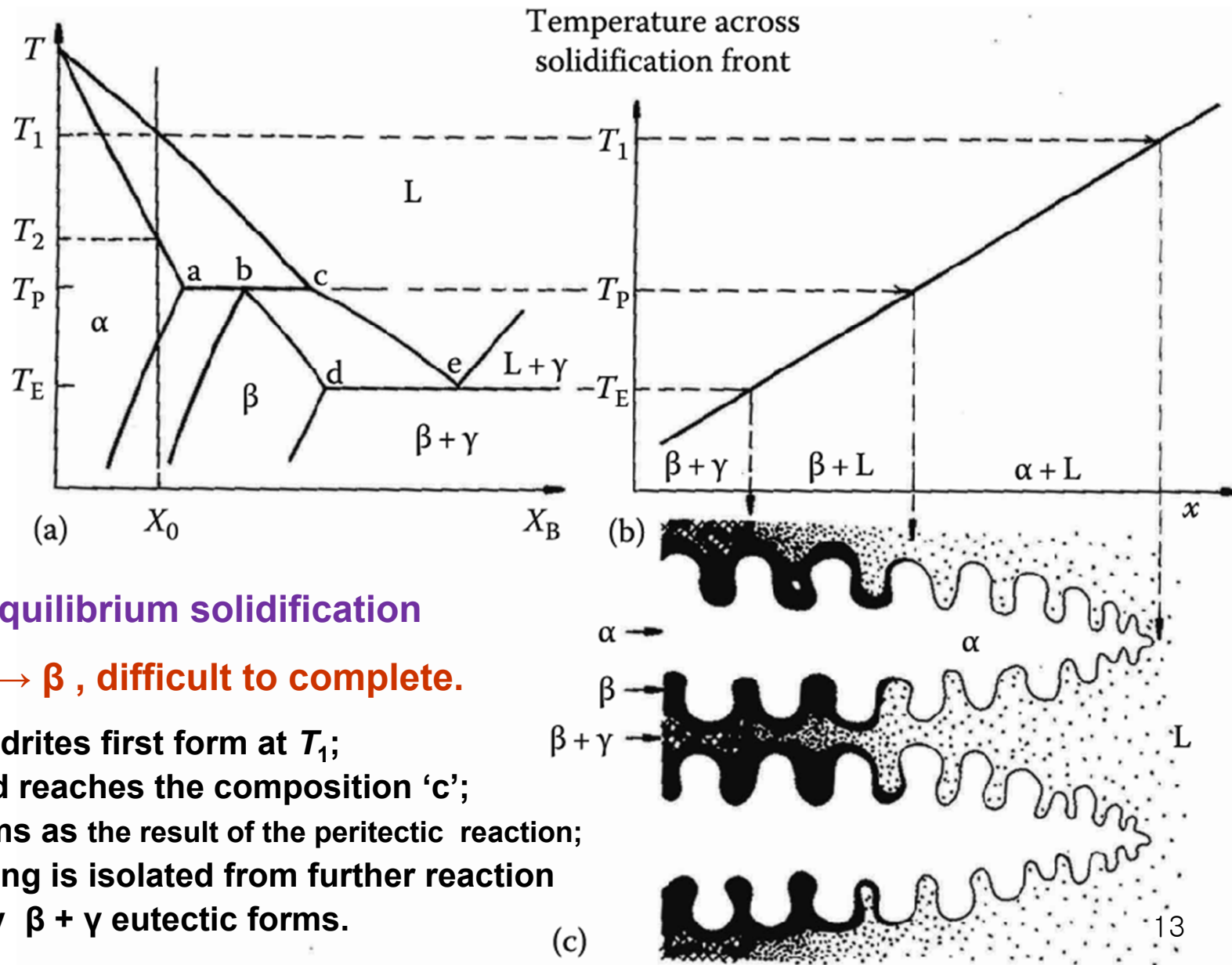


FIGURE 10-24 The peritectic reaction in a Cd-10% Cu alloy begins when rounded

4.3.4 Peritectic Solidification



**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**

4.4 Solidification of **Ingots** and **Castings**

a lump of metal, usually shaped like a brick.

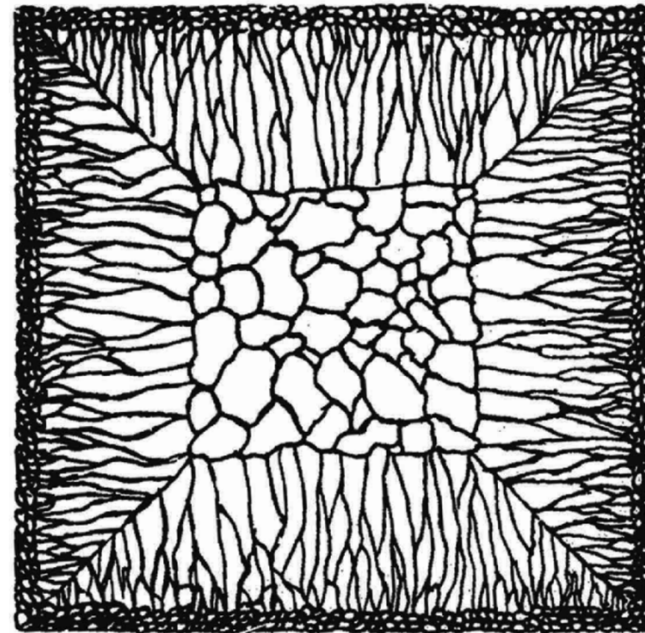
Later to be worked, e.g. by rolling, extrusion or forging >> blank (small)

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**

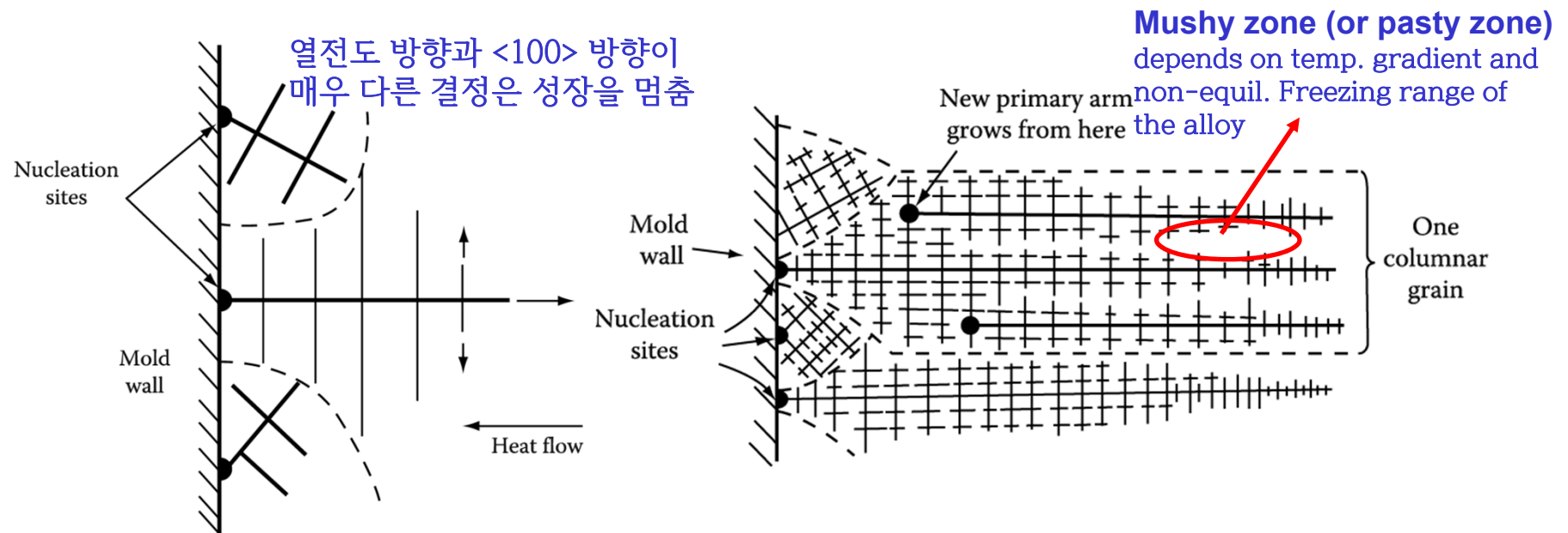


Fig. 4.41 Competitive growth soon after pouring. Dendrites with primary arms normal to the mould wall, i.e. parallel to the maximum temperature gradient, outgrow less favorably oriented neighbors.

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.

- 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.
(\because 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

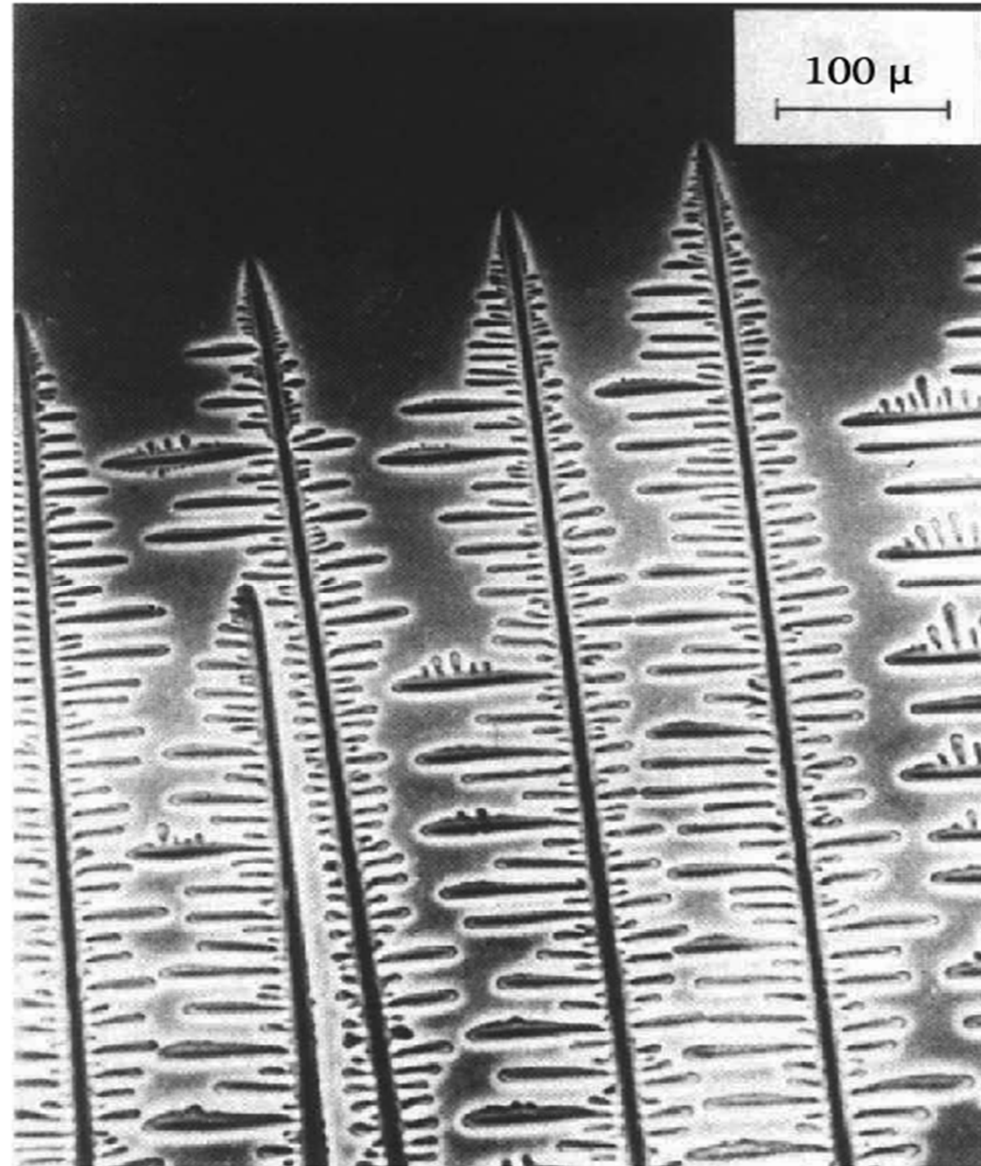


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(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**

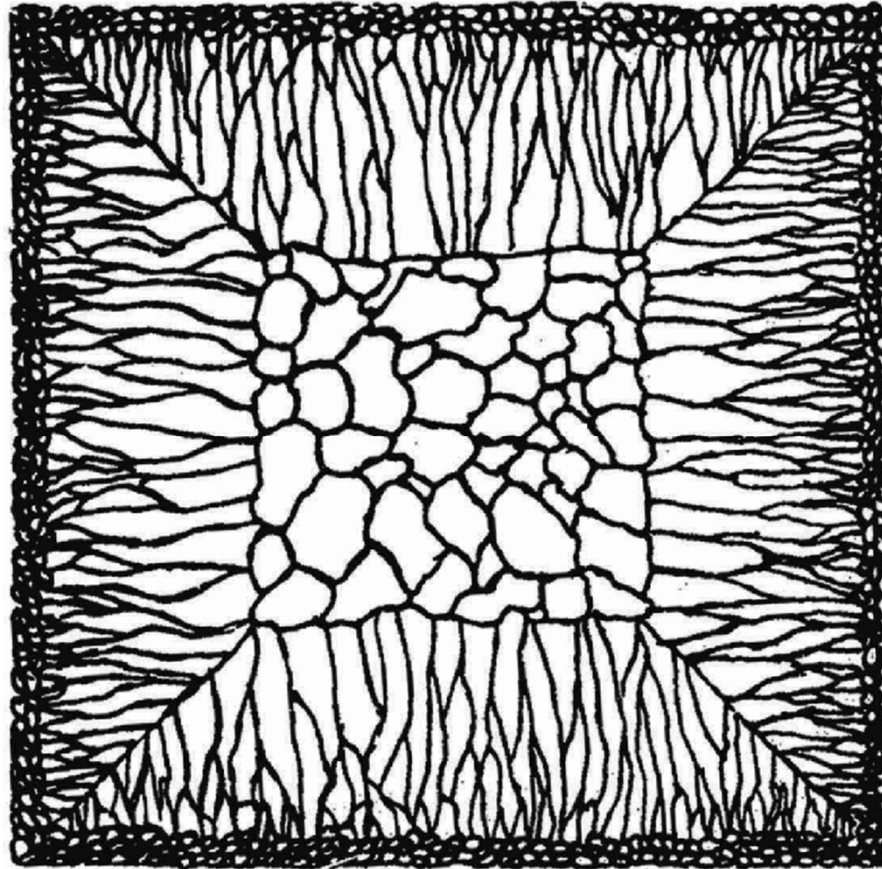
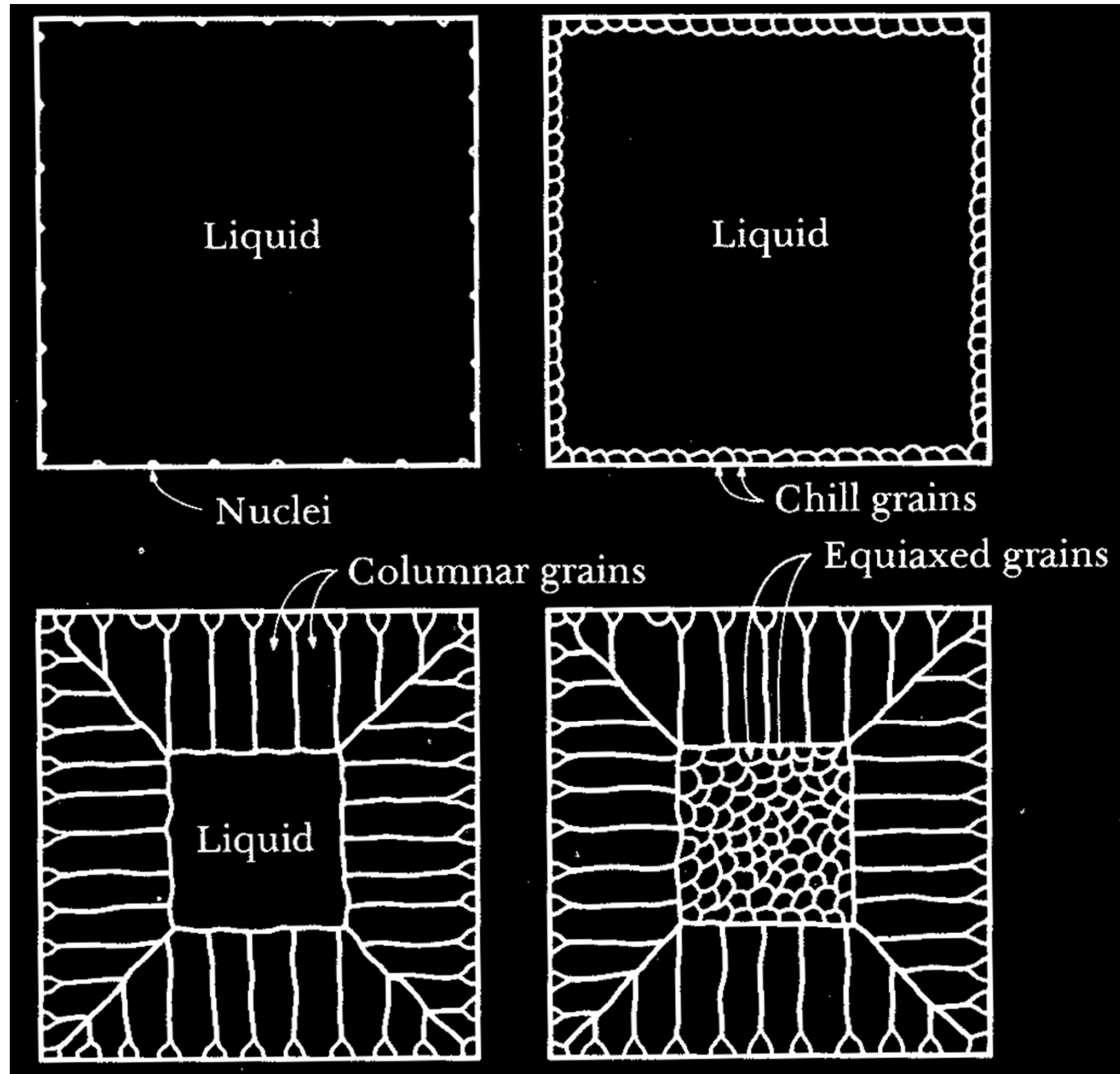


Fig. 4.40 Schematic cast grain structure.

(After M.C. Flemings, Solidification Processing, McGraw-Hill, New York, 1974.) 18



Q: What kind of segregations exist?

4.4.2 Segregation and Shrinkage in Ingots and Castings

(a) Segregation

- **Macrosegregation** : Large area composition changes over distances comparable to the size of the specimen.
- **Microsegregation** : In the secondary dendrite arm occur on the scale of the secondary dendrite arm spacing.

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.

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

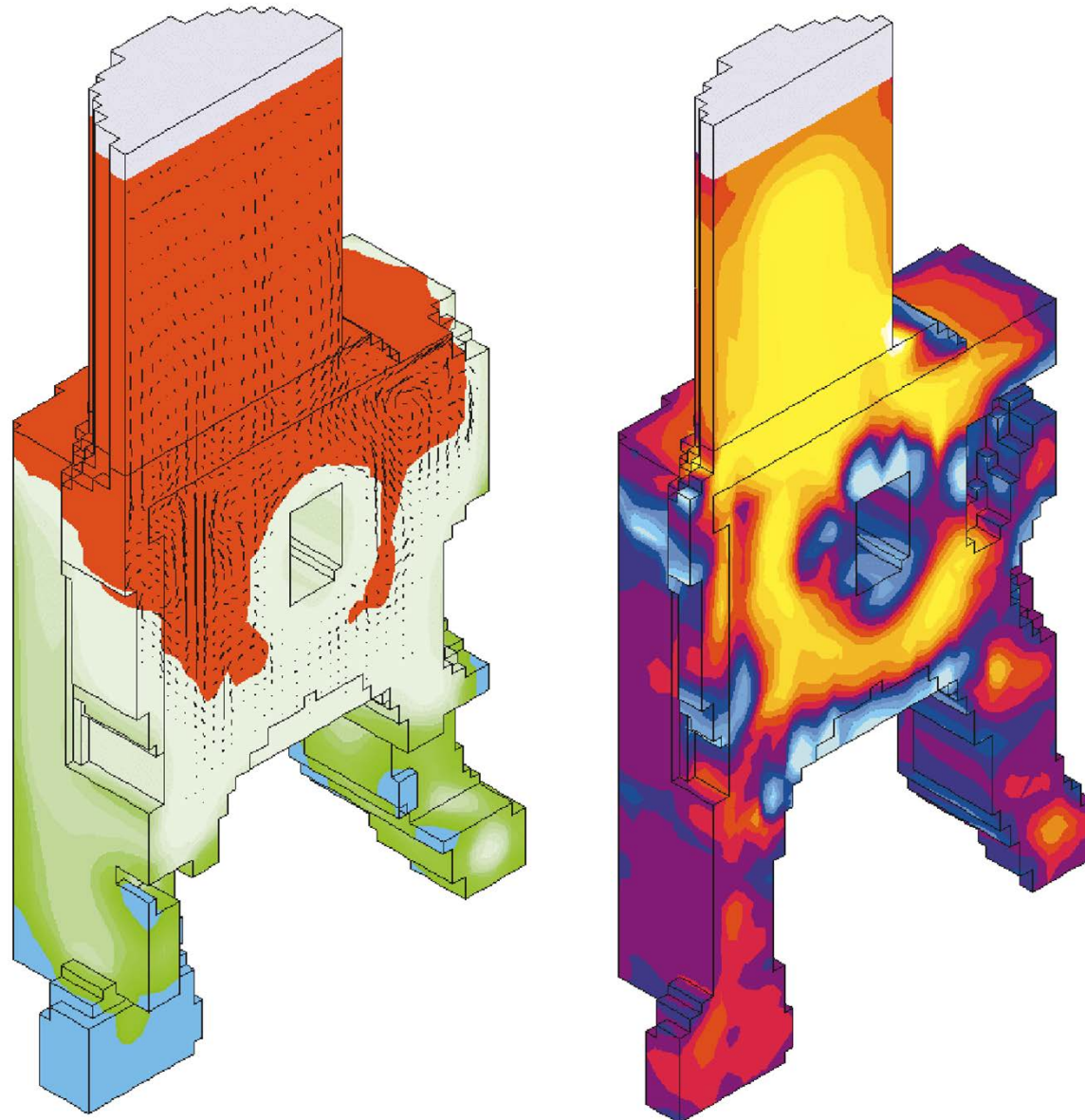


Fig.

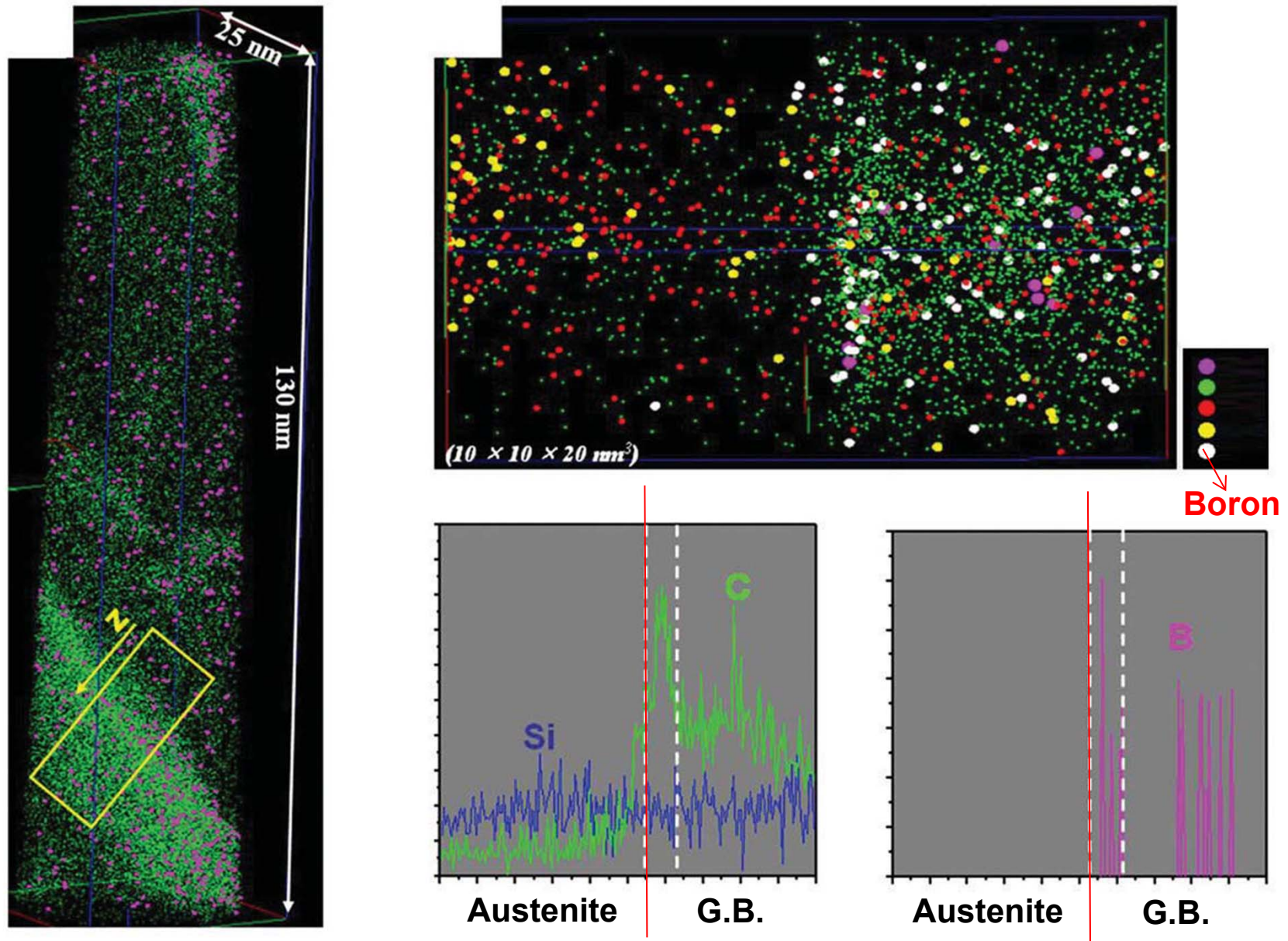
Freckles in a single-crystal nickel-based superalloy prototype blade (left) and close-up of a single freckle (right) (courtesy of A. F. Giamei, United Technologies Research Center).



Fig.

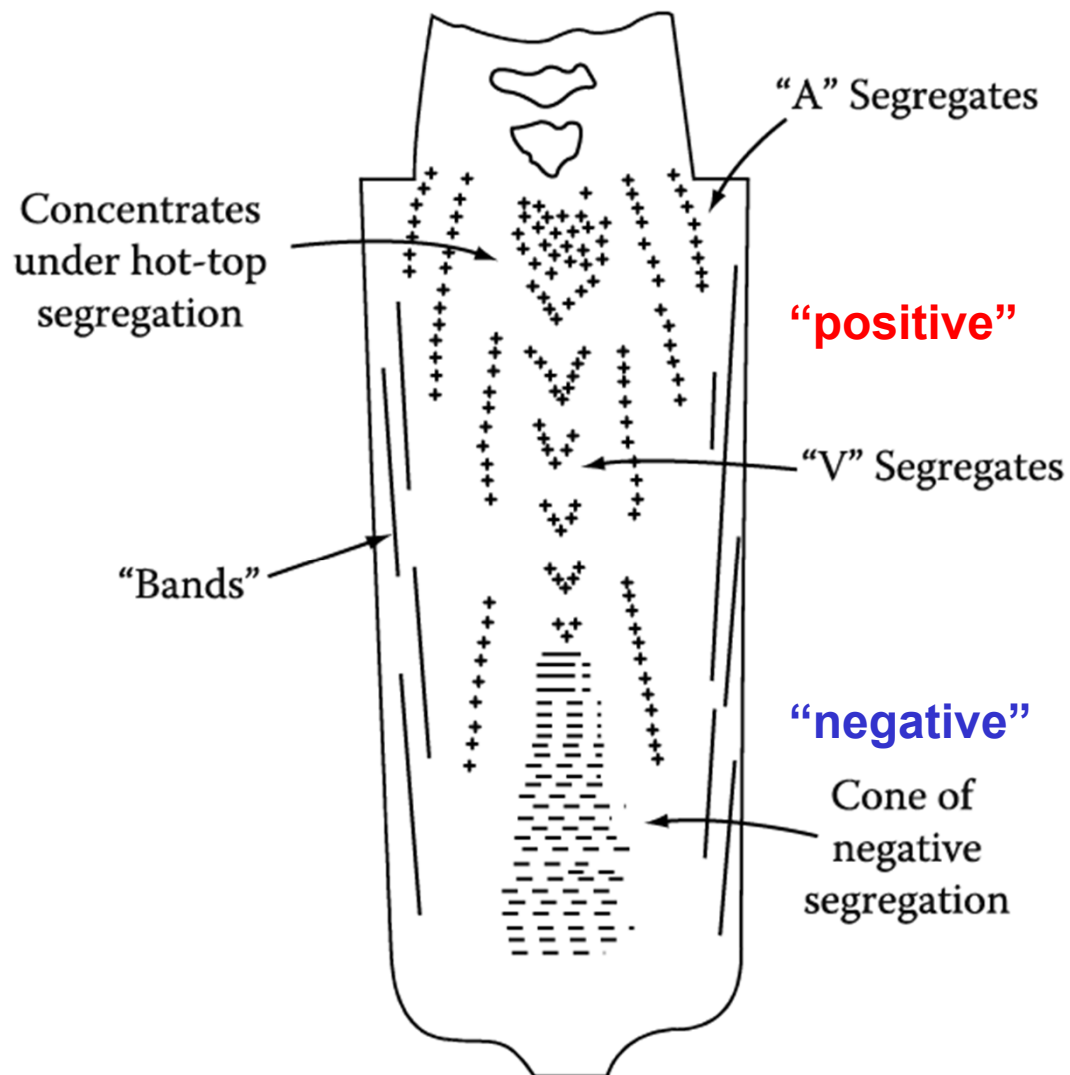
Sulfur print showing centerline segregation in a continuously cast steel slab (courtesy of IPSCO Inc.).





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**²⁵

- * **Segregation:** undesirable ~ deleterious effects on mechanical properties
 - subsequent **homogenization heat treatment**, but diffusion in the solid far too slow
 - **good control of the solidification process**



Inverse segregation (역편석): 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 (초기응고고상) 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)**

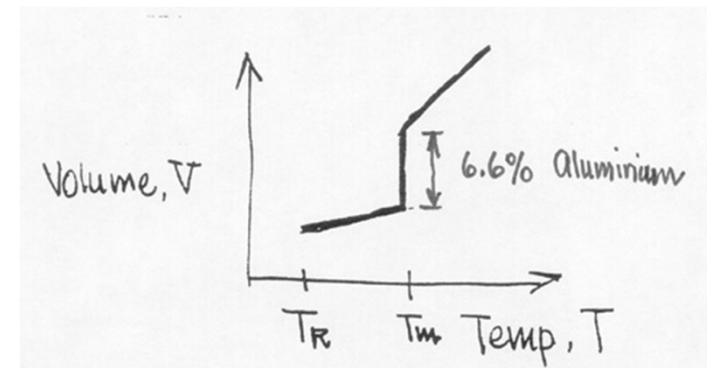
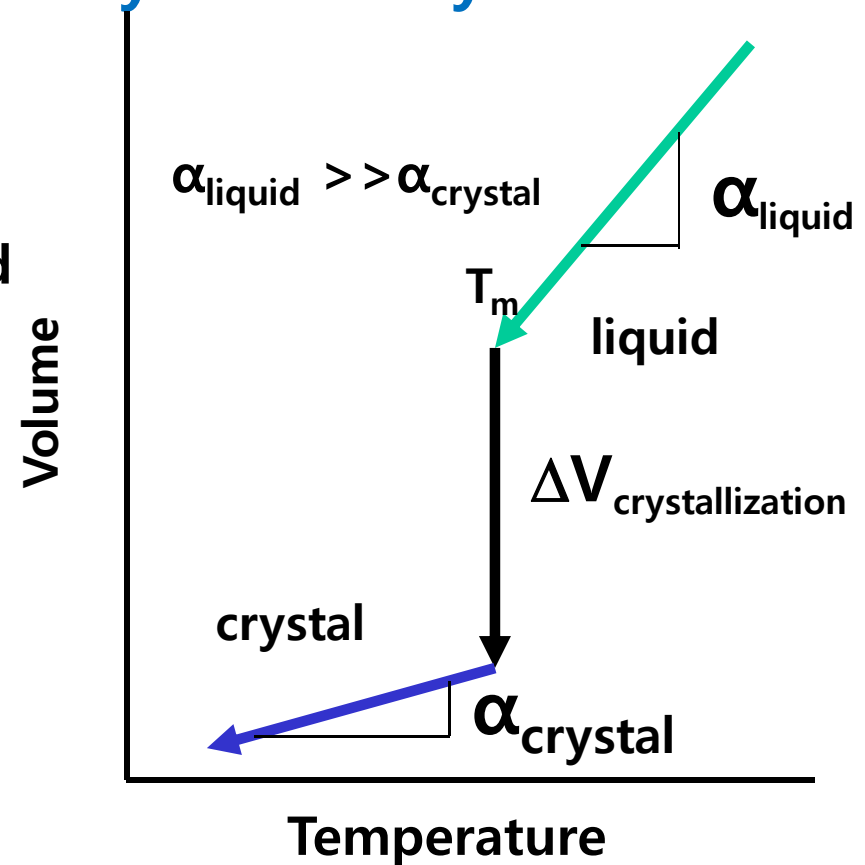
Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.) 26

Q: Shrinkage in Solidification and Cooling?

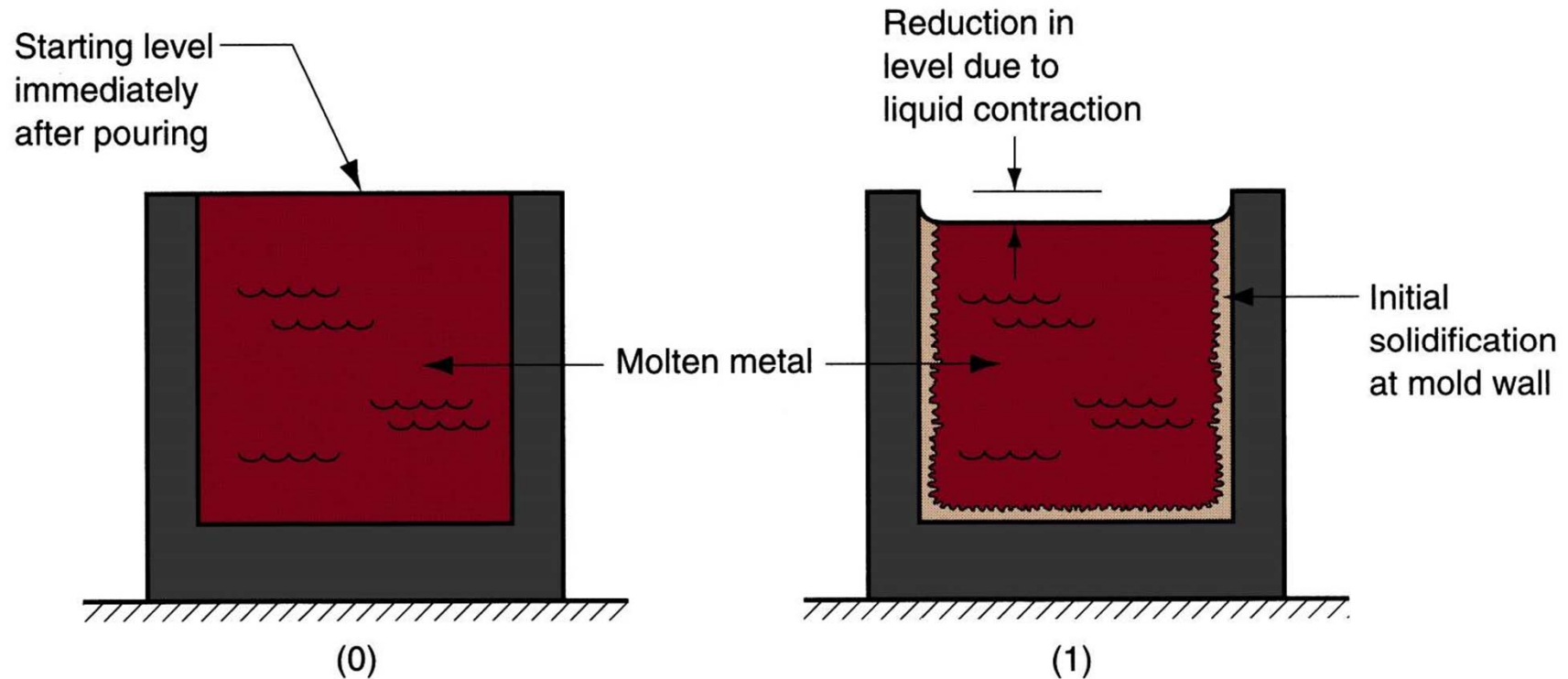
(b) Shrinkage

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**

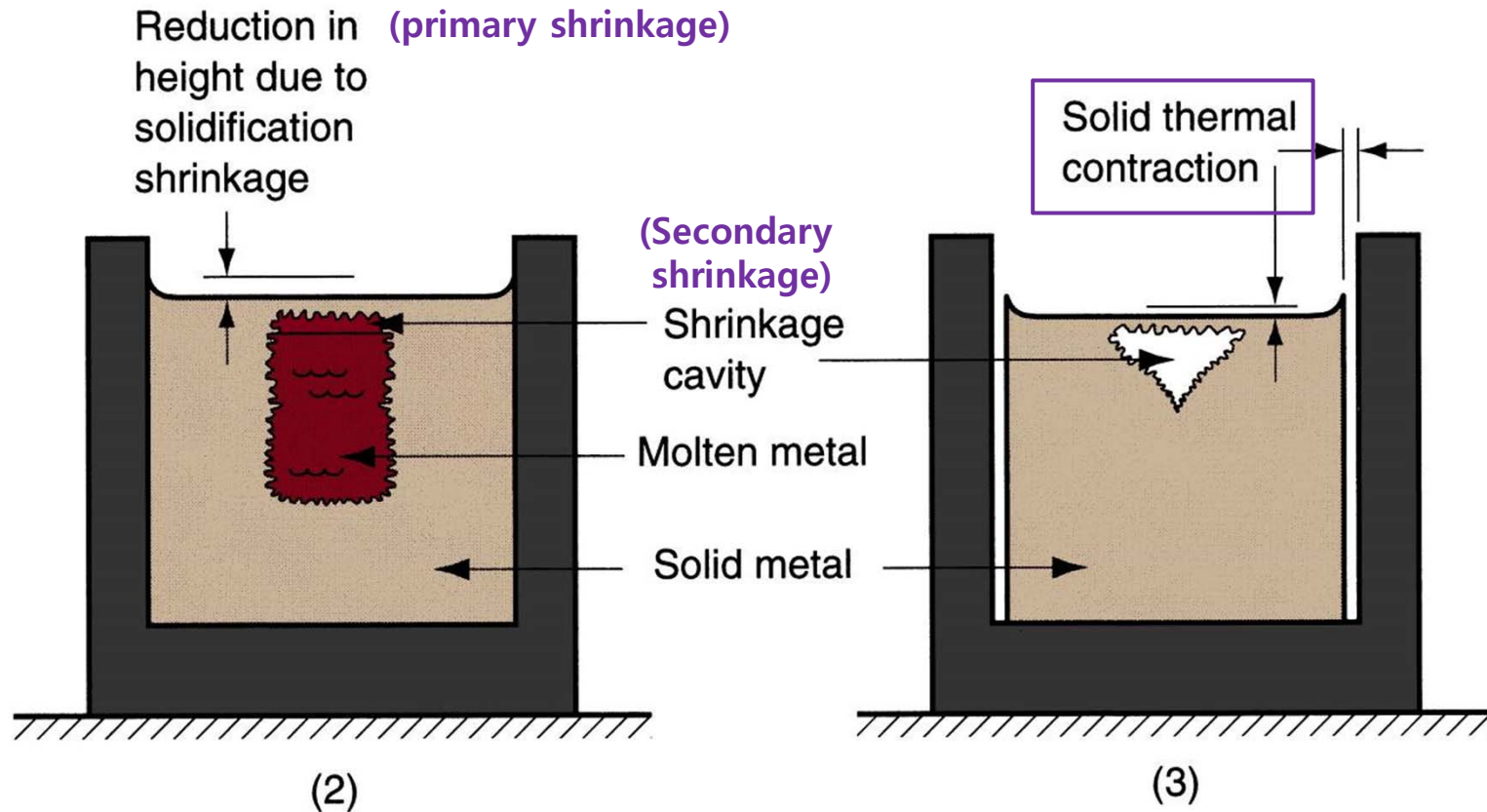


Shrinkage in Solidification and Cooling



- * 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) 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).

Shrinkage effect

* Formation of Voids during solidification

Central shrinkage:

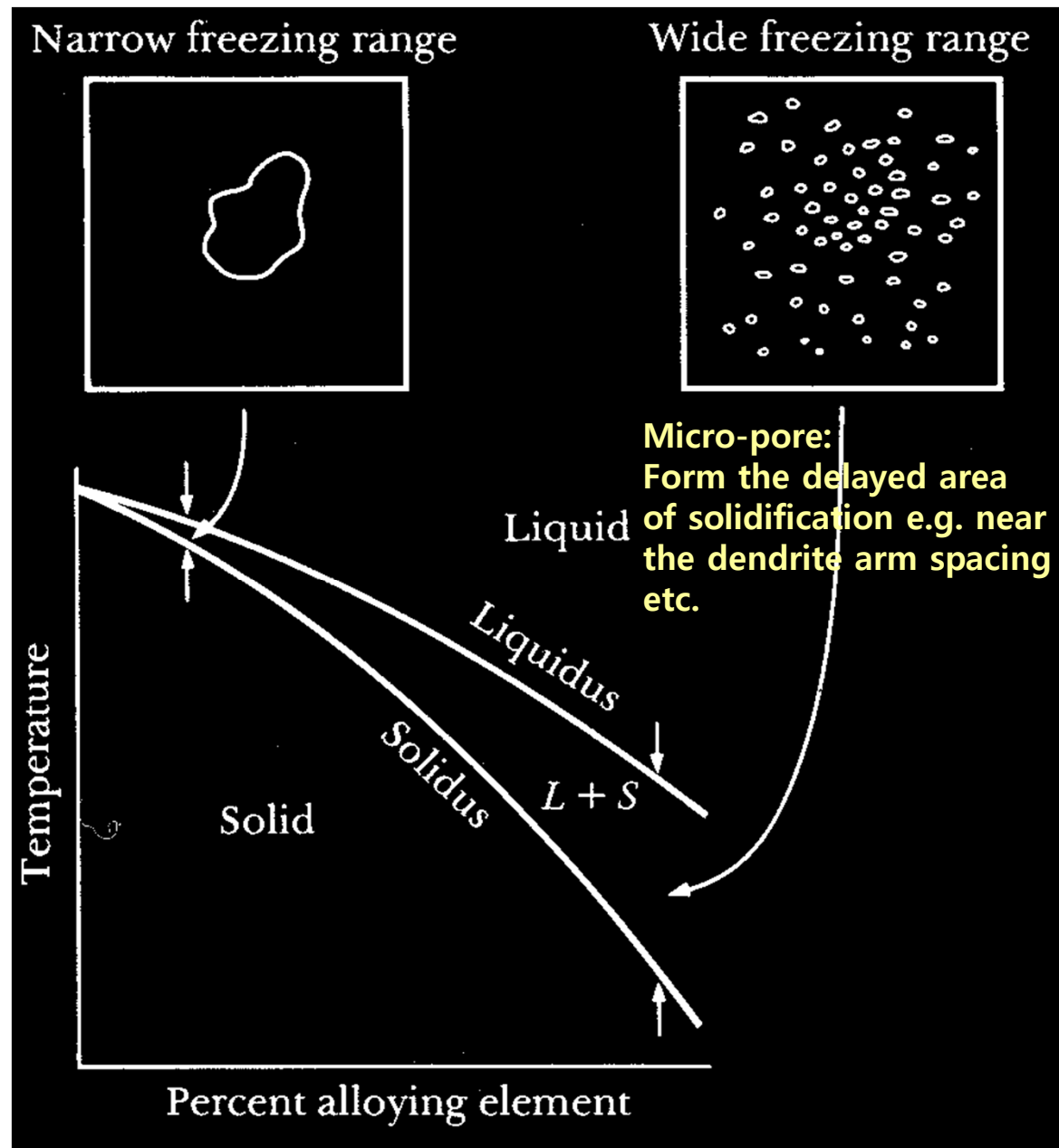
조성 변화가 크지 않은 주물의 응고 시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

Dispersed Micro-Pore:

상당히 넓은 범위에 분산된 미소기공

외부수축 (몰드 주위) 및 1차수축공 (표면) 을 제외하면, 이러한 수축공 결함은 주로 기포 결함임

기포 내에는 철합금에서는 CO, 질소, 산소, 수소 등이, 동합금에서는 수소, 산소, 알루미늄 합금에서는 수소 등의 가스가 존재



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: H₂O (10%), Si (20%), Ge**

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

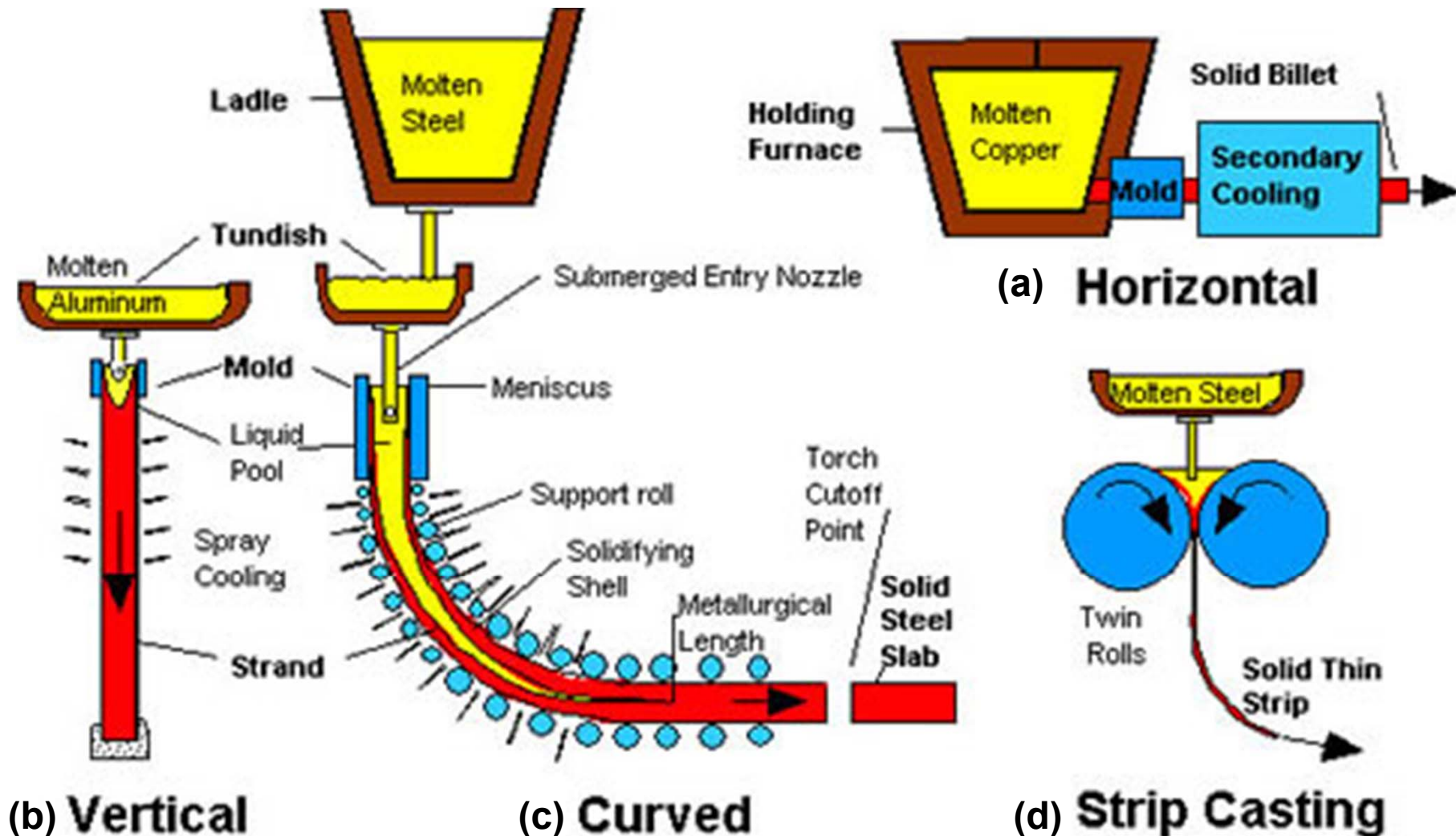
Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

→ precipitation of graphite during solidification reduces shrinkage.

Q: What is continuous casting?

4.4.3 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)



“Dynamic process: importance of isotherm distribution”

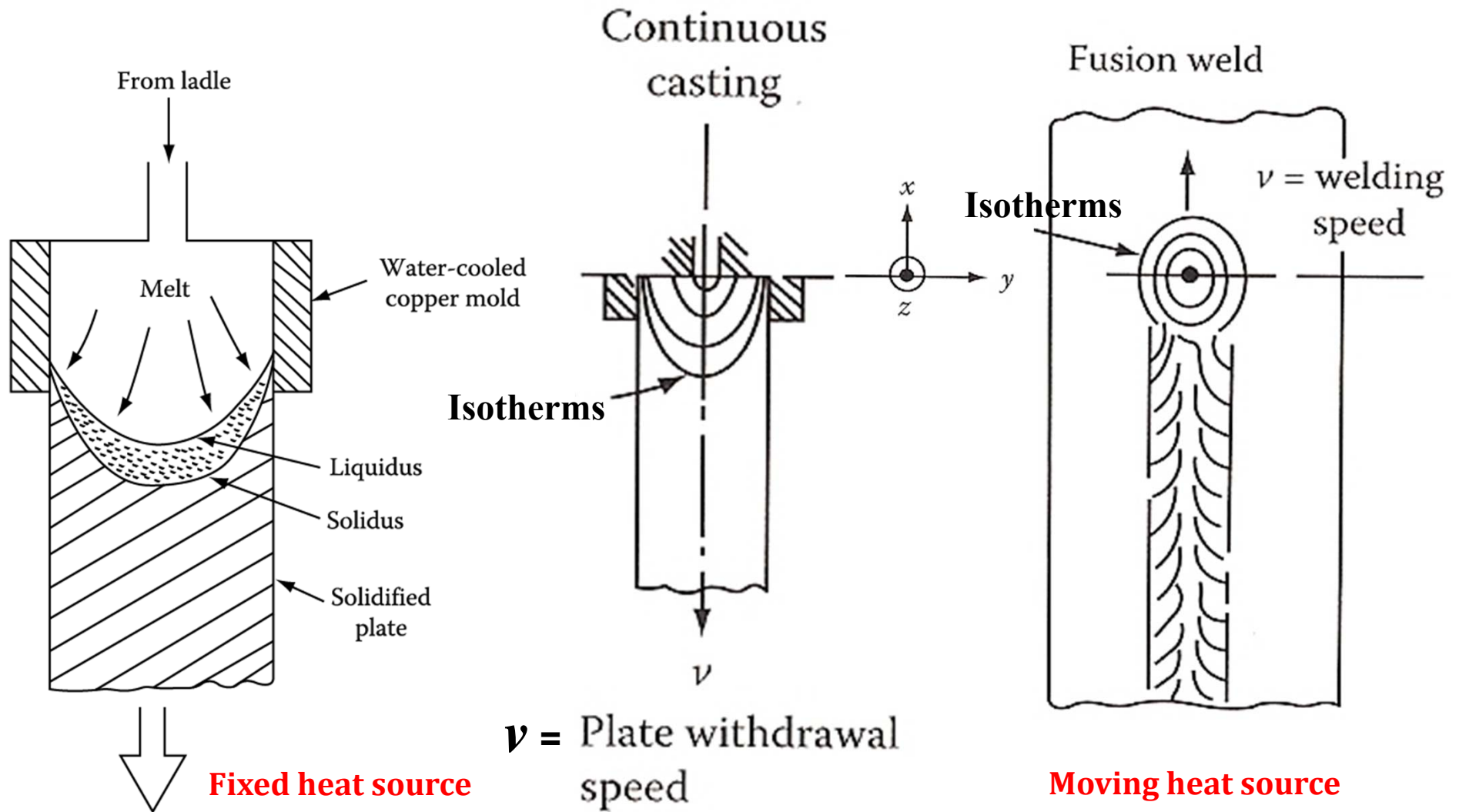


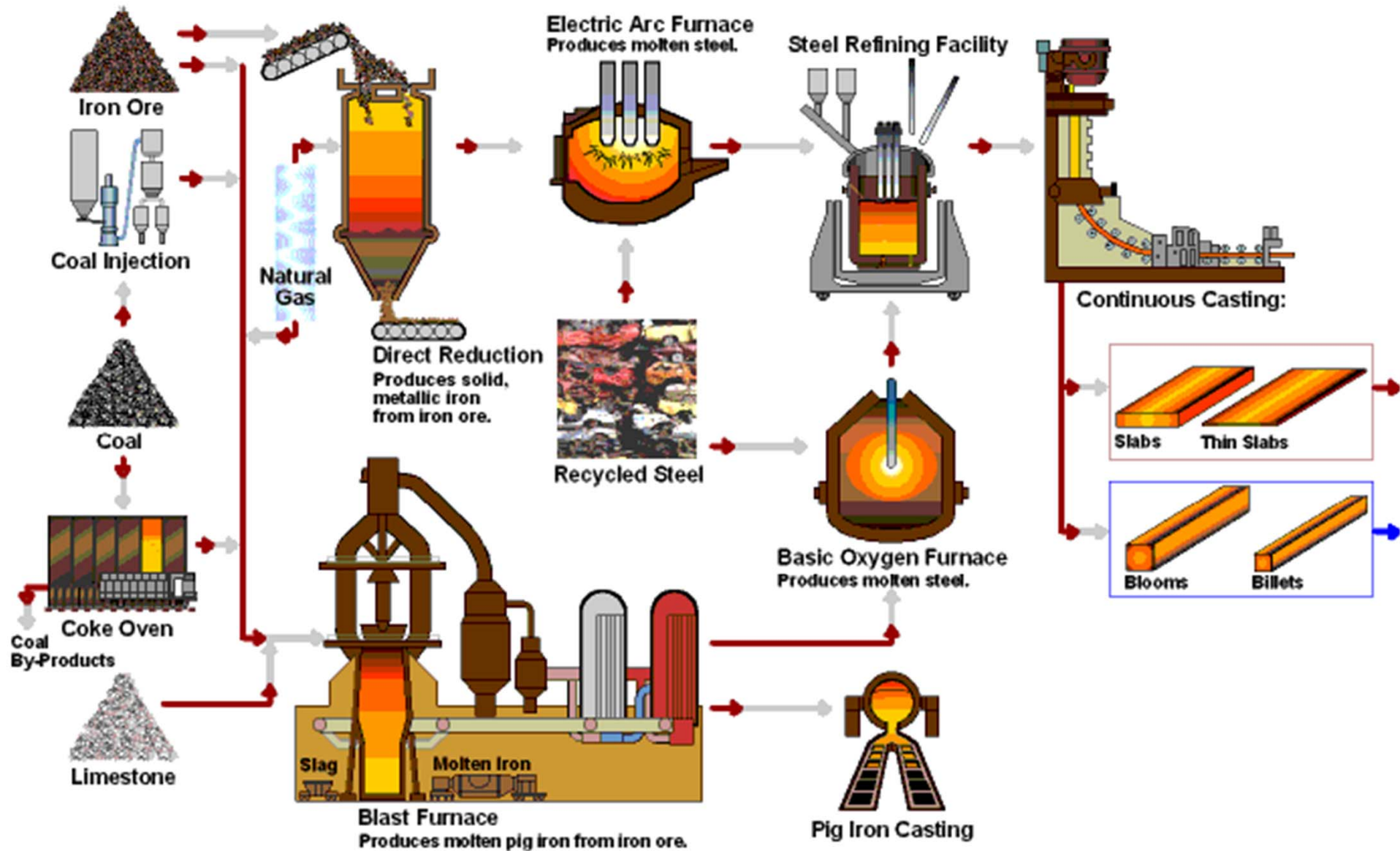
Fig. 4.44 Schematic illustration of a continuous casting process

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

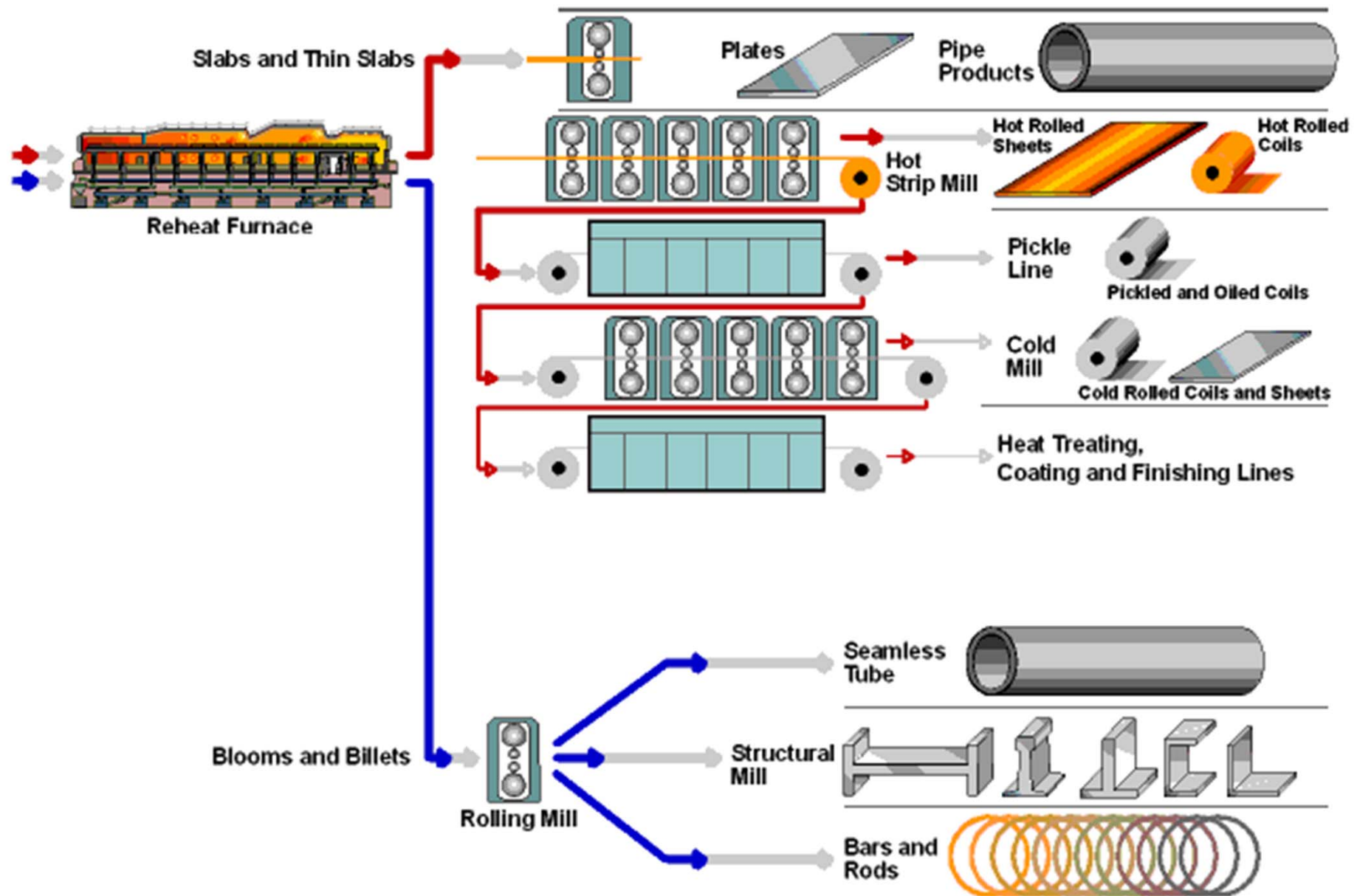
4.4.3 continuous casting



4.4.3 continuous casting



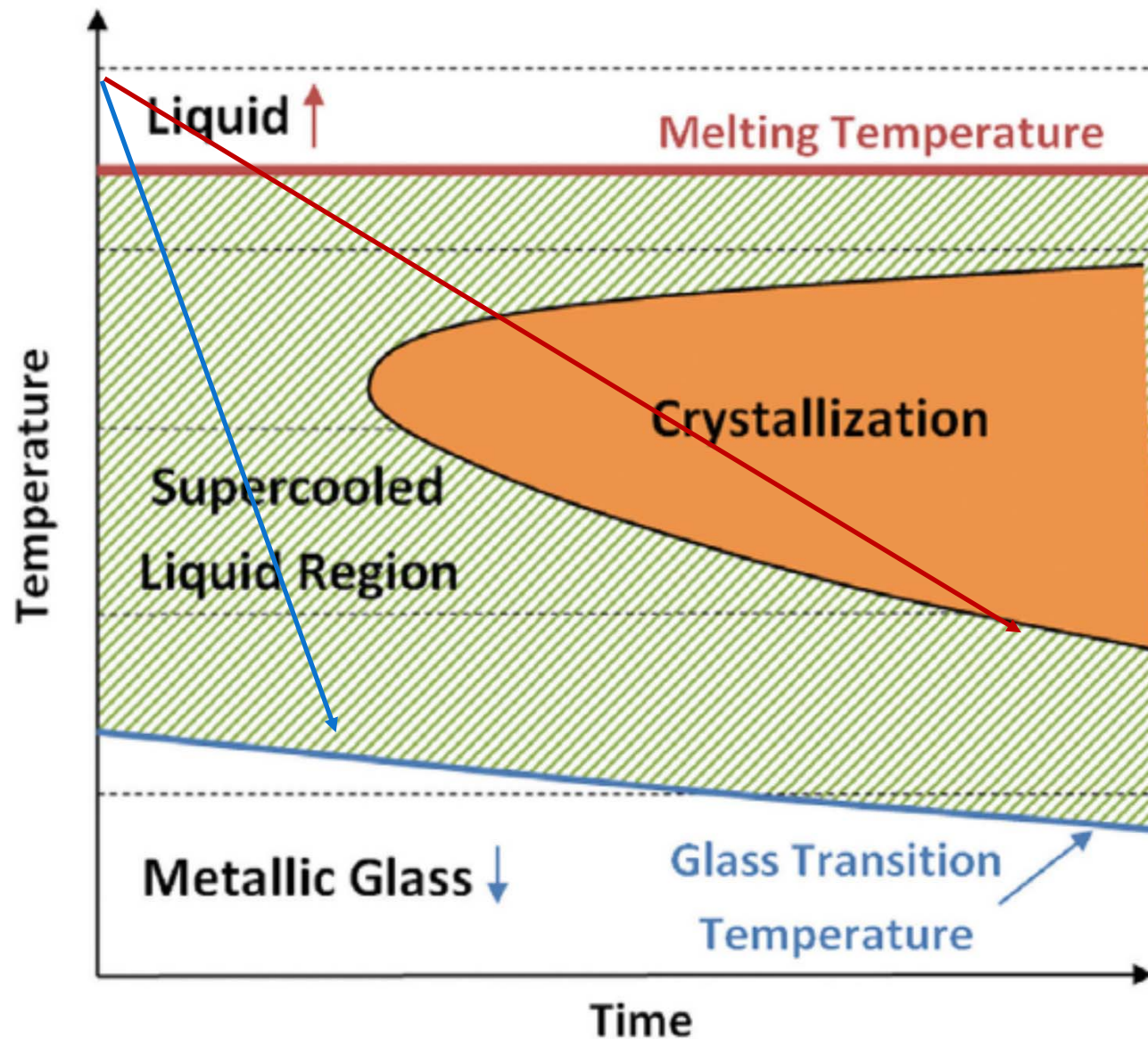
4.4.3 continuous casting



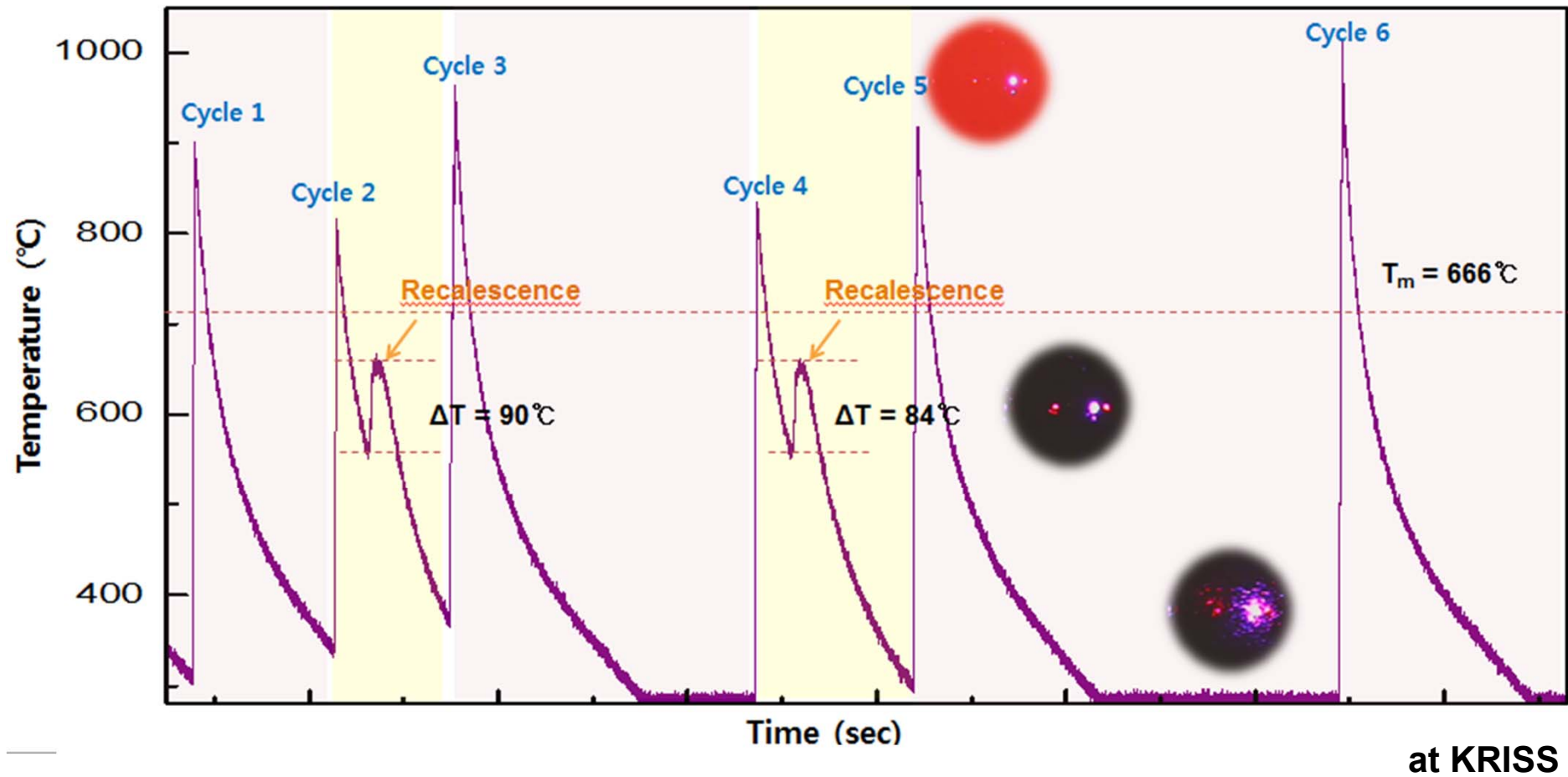
Q: Glass formation?

4.6 Solidification during Quenching from the Melt

Time-Temperature-Transformation diagram

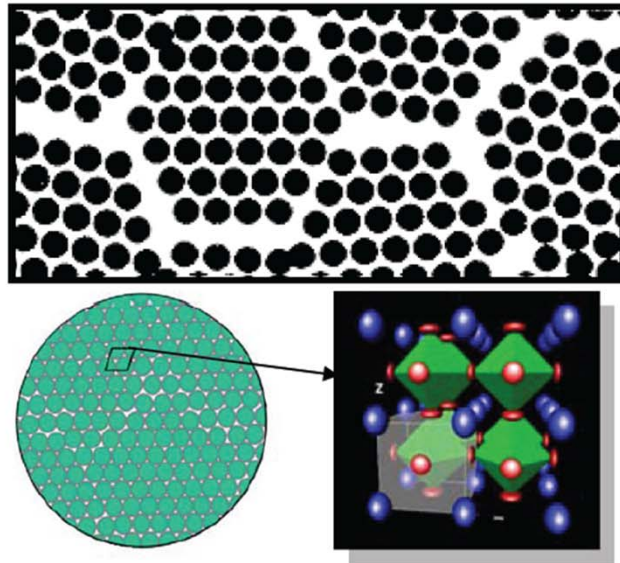


Electrostatic Levitation: cooling curve of Vitreloy 1 system



Structure of Crystals, Liquids and Glasses

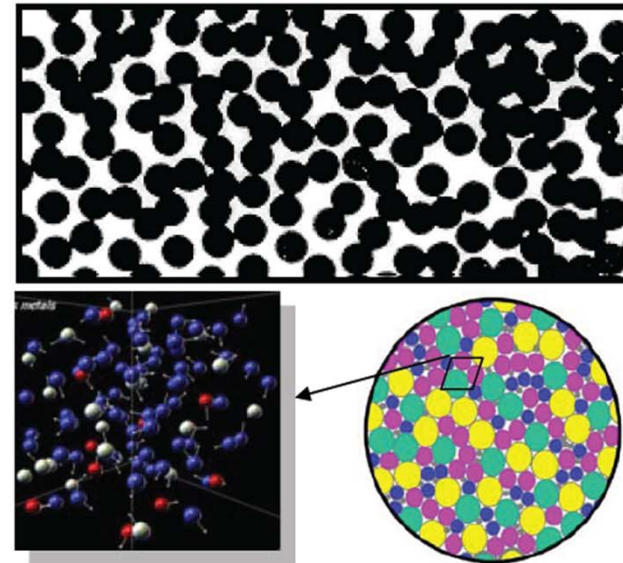
Crystals



Building block: arranged in orderly,
3-dimensional,
periodic array

- grain boundaries

Liquids, glasses

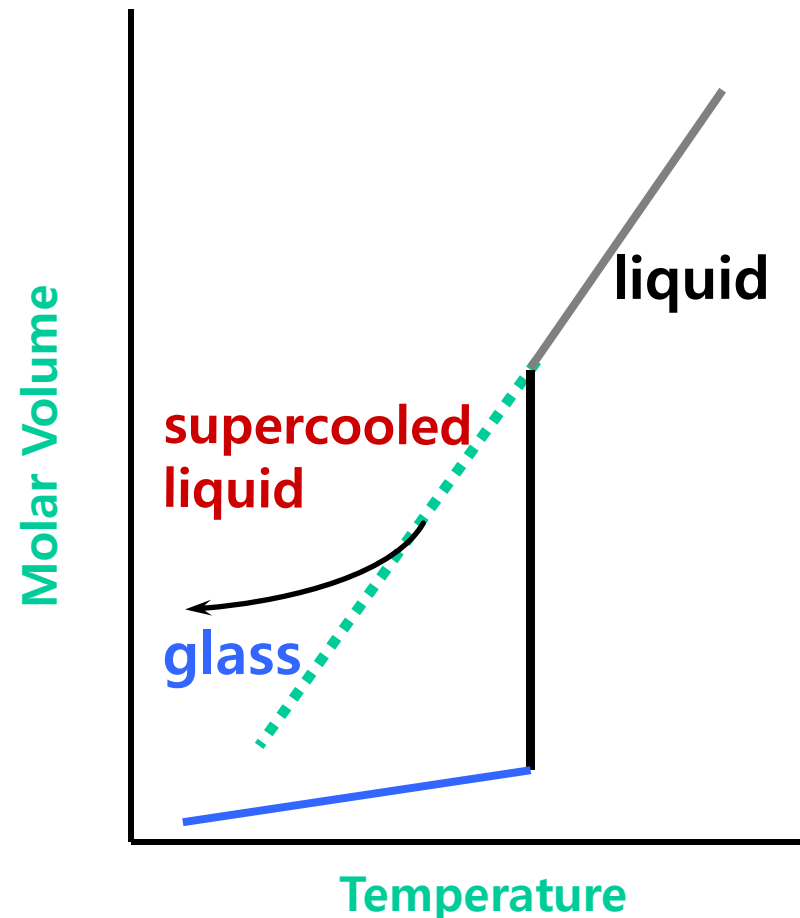


nearly random = non-periodic

- no grain boundaries

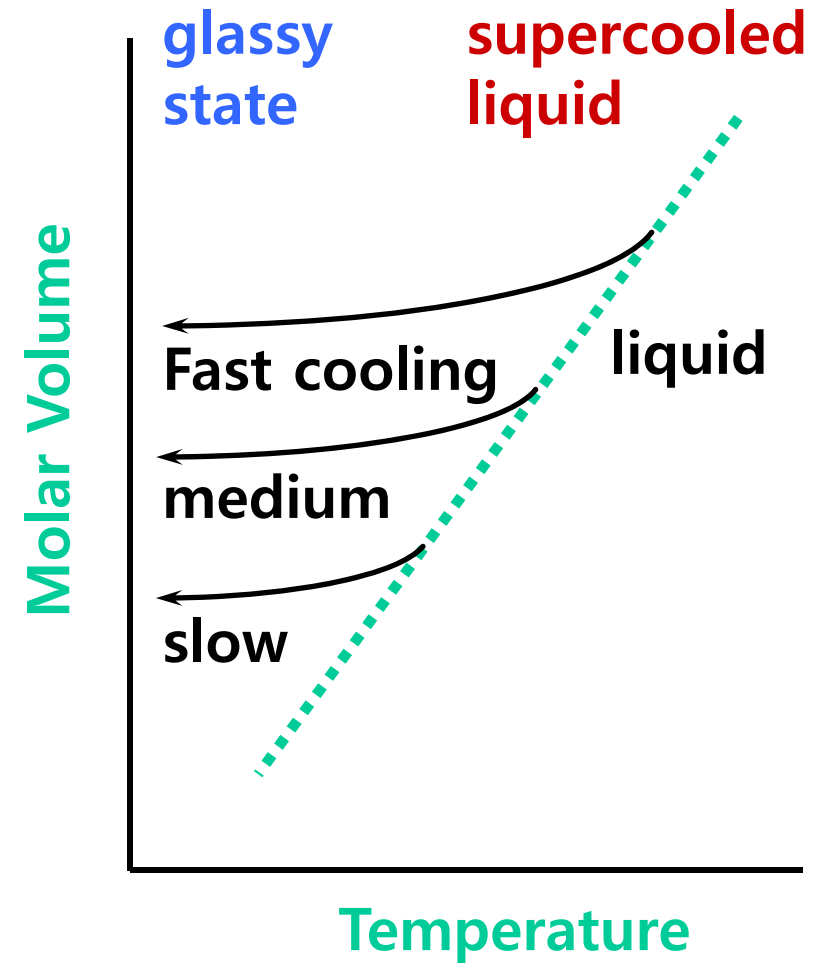
Glass Formation is Controlled by Kinetics

- Glass forming liquids are those that are able to “**by-pass**” the **melting point, T_m**
- Liquid may have a **high viscosity** that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does **not have enough time to crystallize**
- Two time scales are present
 - “**Internal**” **time scale** controlled by the viscosity (bonding) of the liquid
 - “**External**” **timescale** controlled by the cooling rate of the liquid



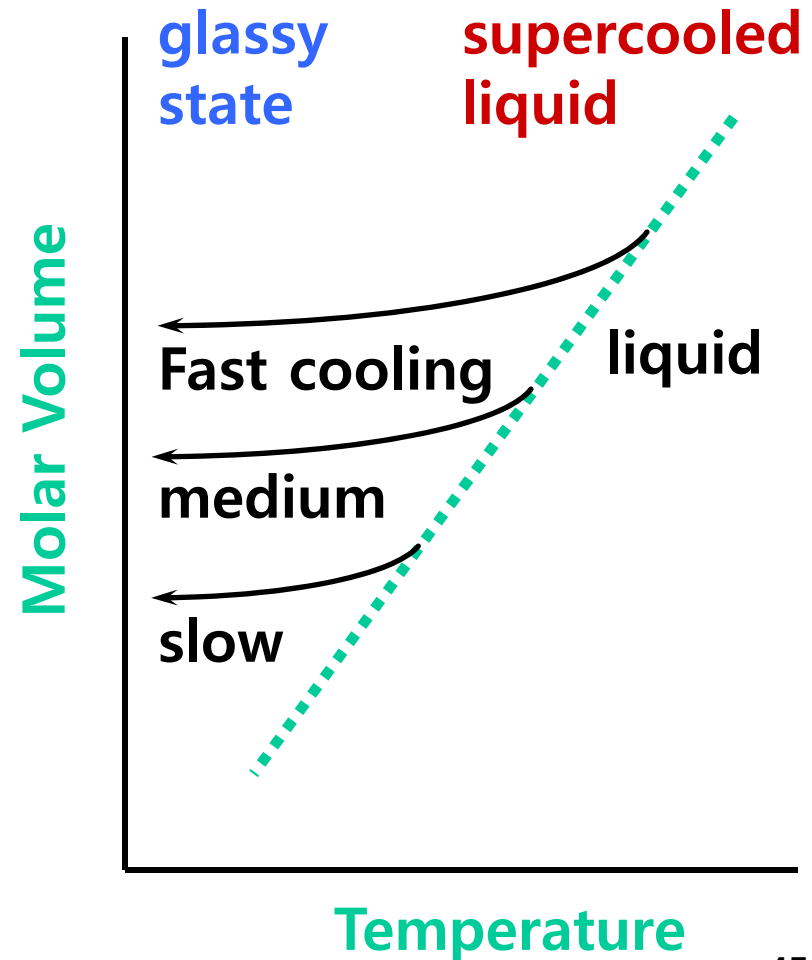
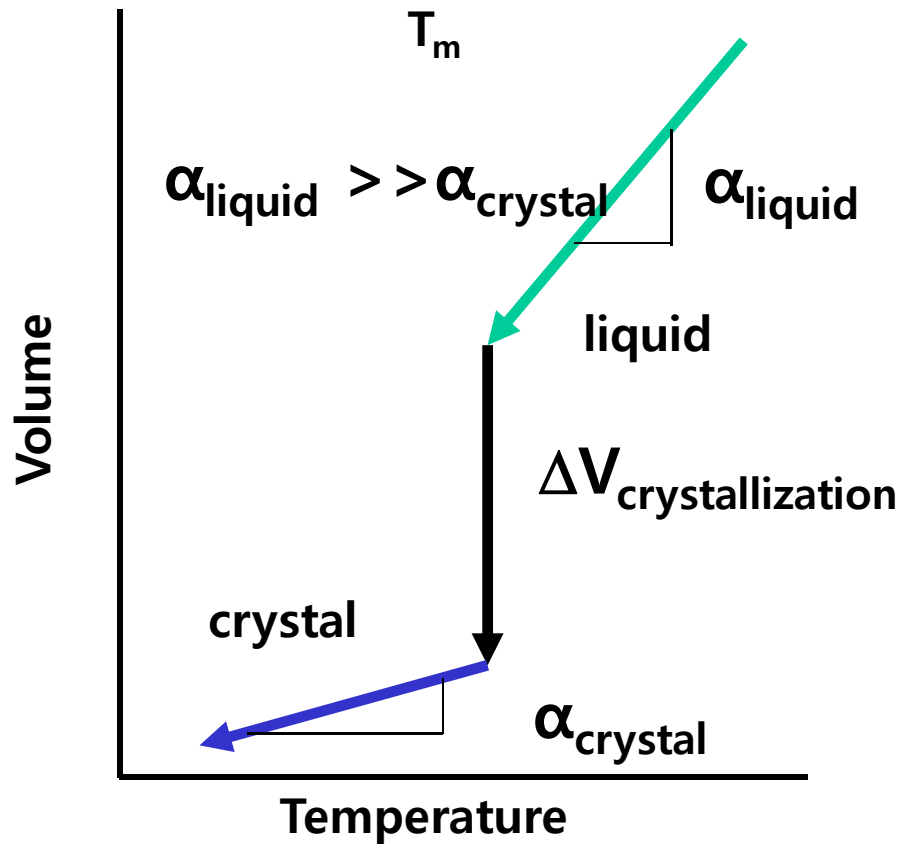
The Cooling Rate Affects the Properties of Glass

- **Faster cooling** freezes in the glass at a **higher temperature**
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- **Slower cooling** freezes in the glass at a **lower temperature**
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature

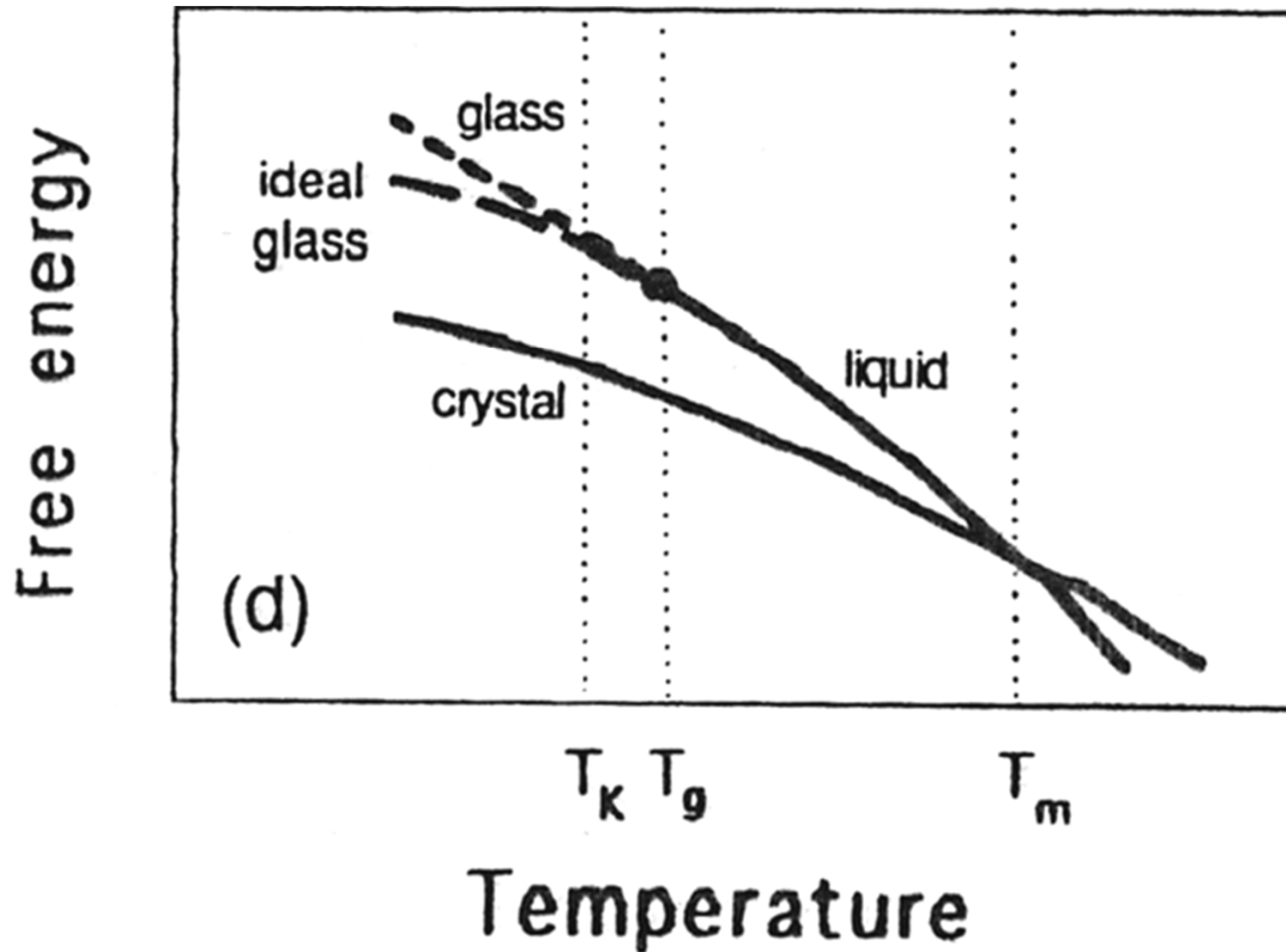


Fundamentals of the Glass Transition

- Melting and Crystallization are **Thermodynamic Transitions**
- The Glass Transition is a **Kinetic Transition**

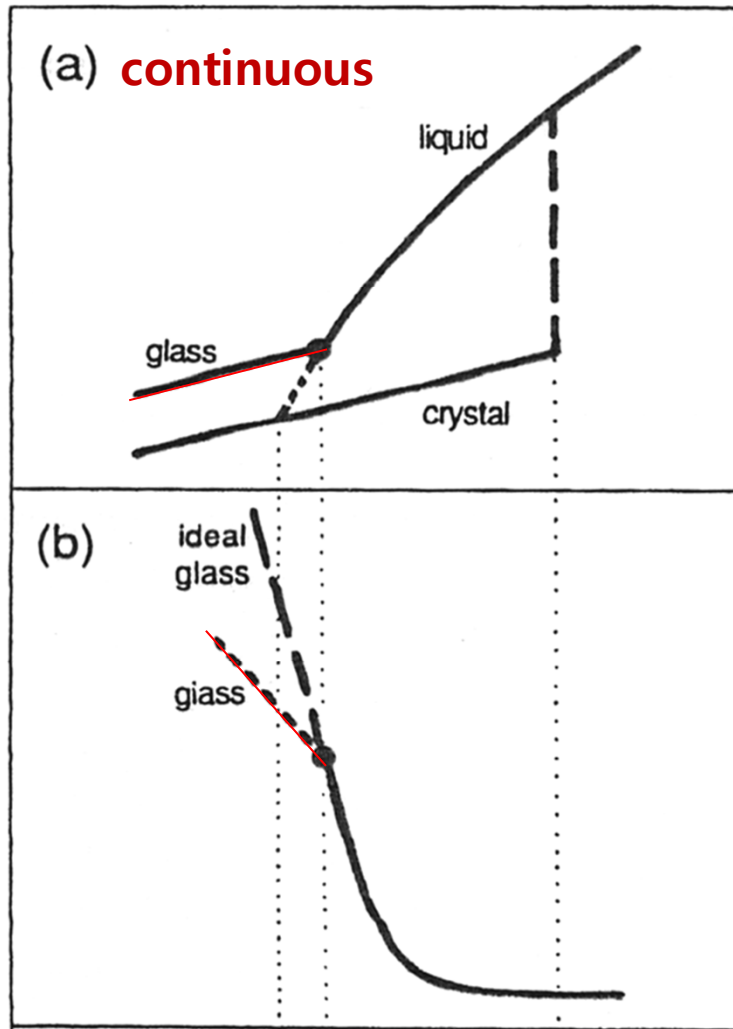


Schematic of the glass transition showing the effects of temperature on free energy



Entropy (V, S, H)

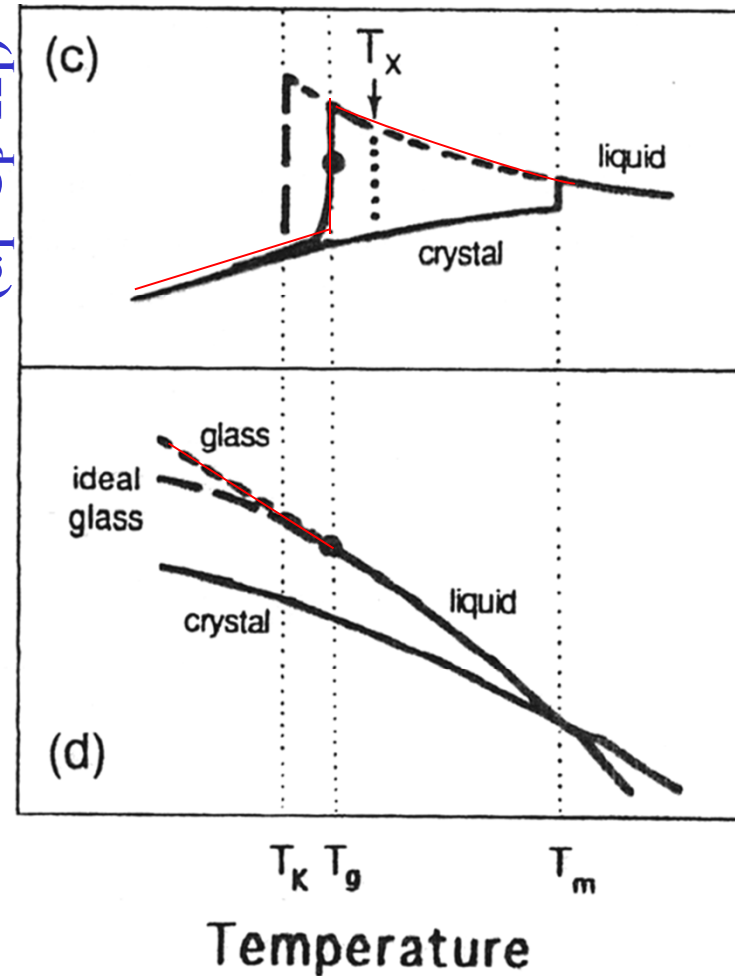
Viscosity



discontinuous

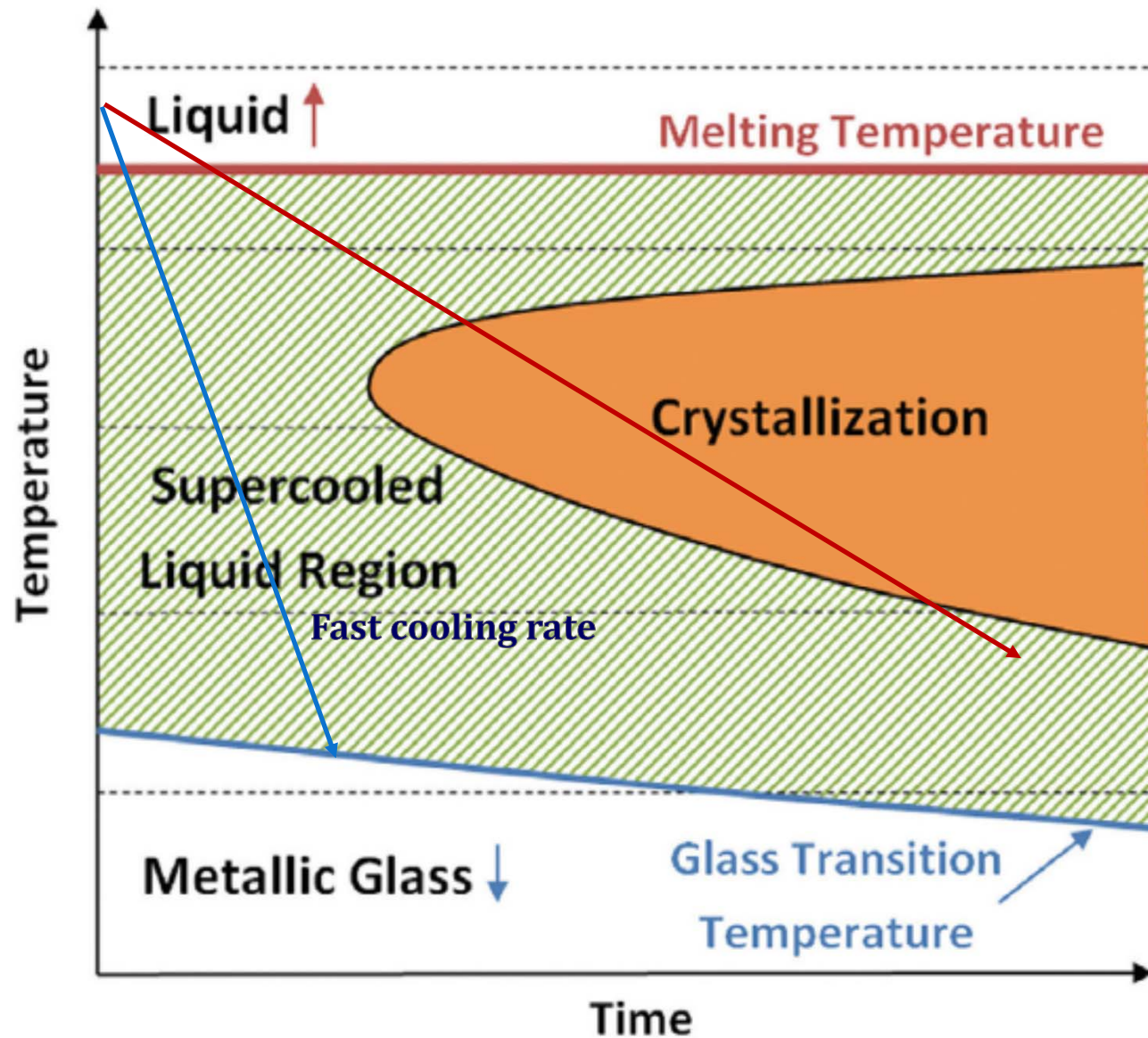
Specific heat
($\alpha_T C_p K_T$)

Free energy



Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Glass formation : (1) Fast Cooling

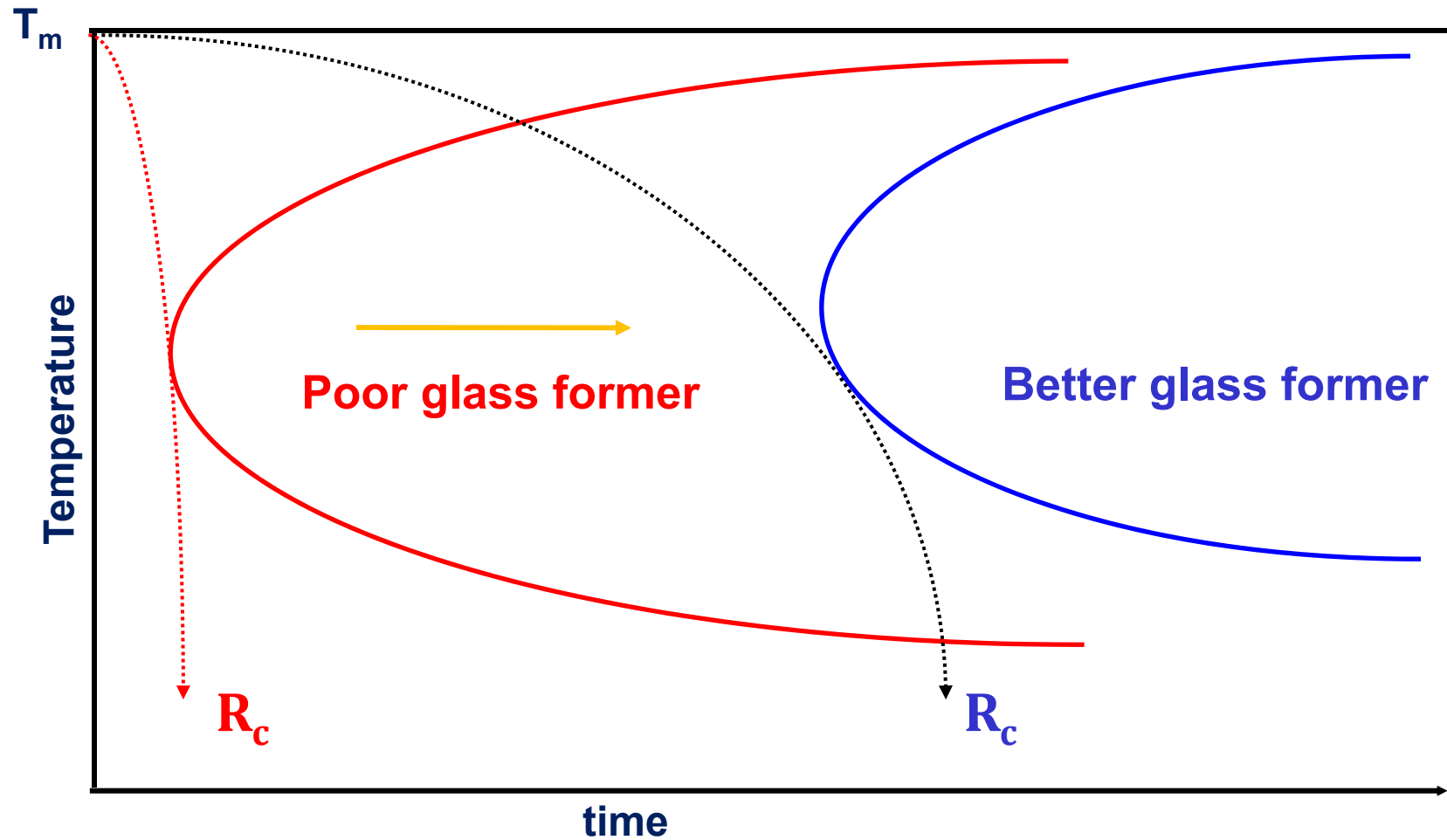


Glass formation : (2) Better Glass Former

GFA

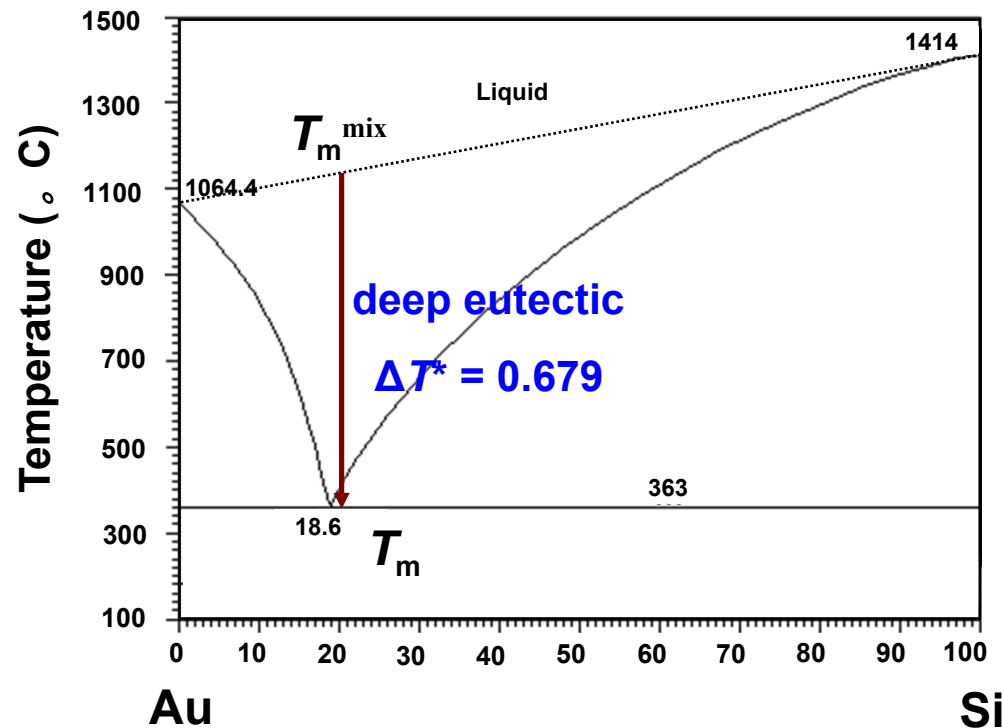
$$R_c = \frac{\Delta T}{t_n}$$

undercooled liquid \rightarrow crystalline

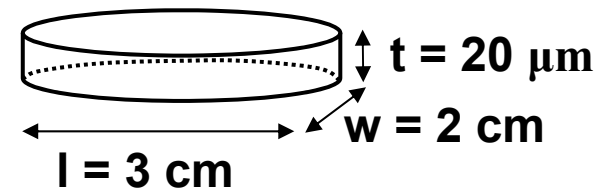
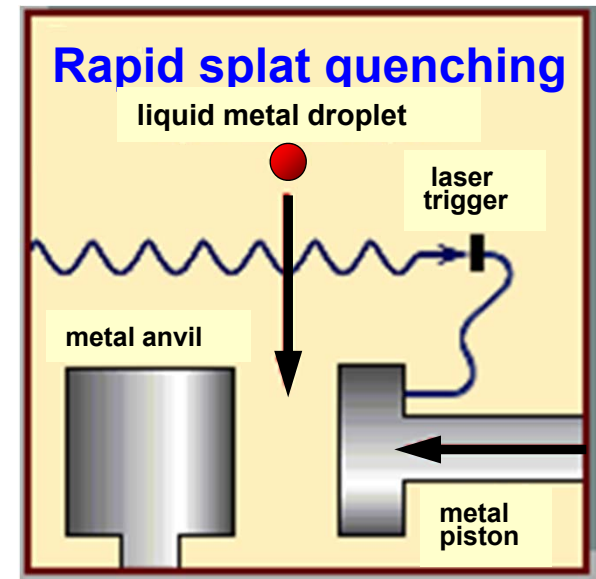


Glass formation : stabilizing the liquid phase

- First **metallic glass** ($\text{Au}_{80}\text{Si}_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.

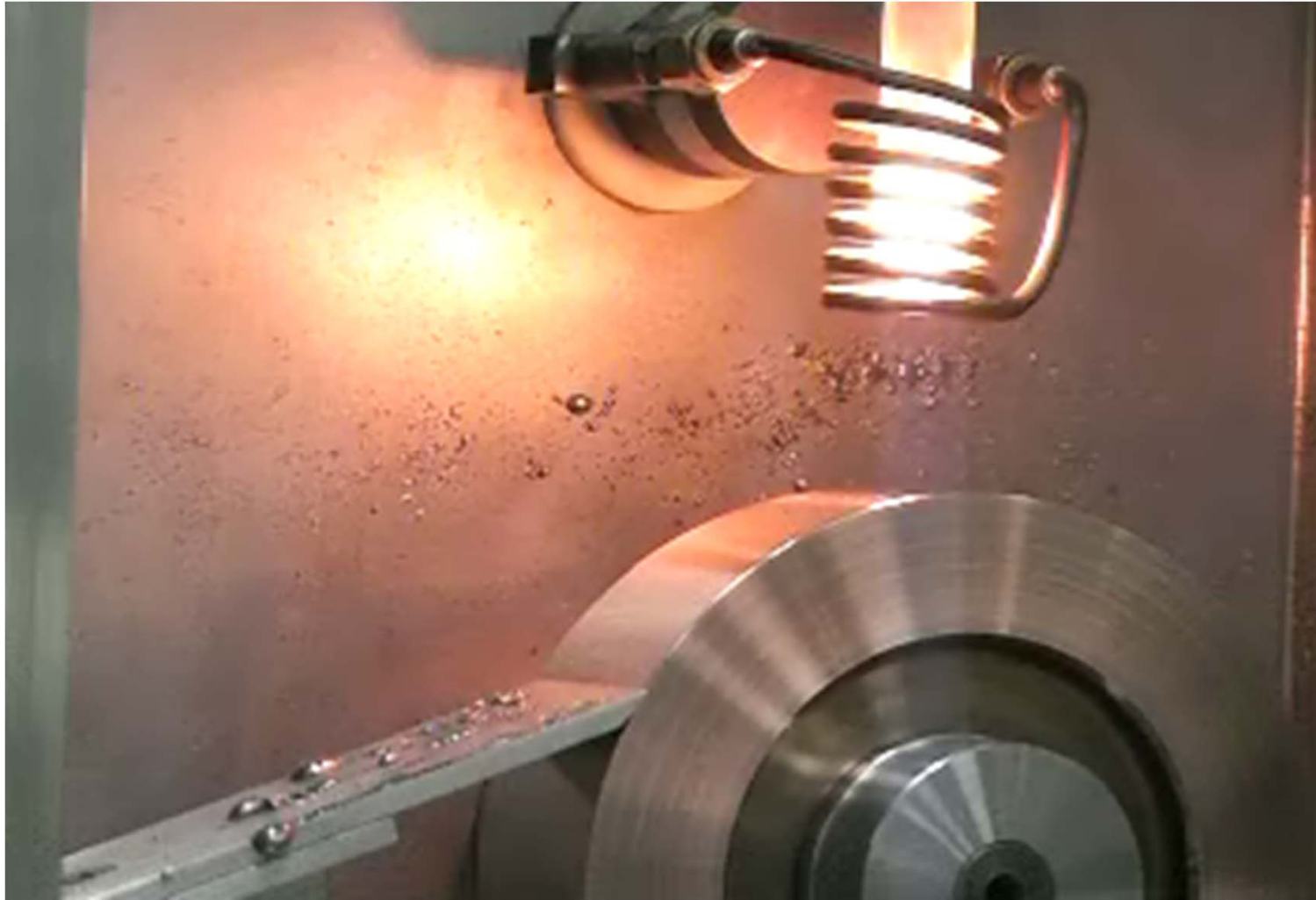


W. Klement, R.H. Willens, P. Duwez, Nature 1960; 187: 869.

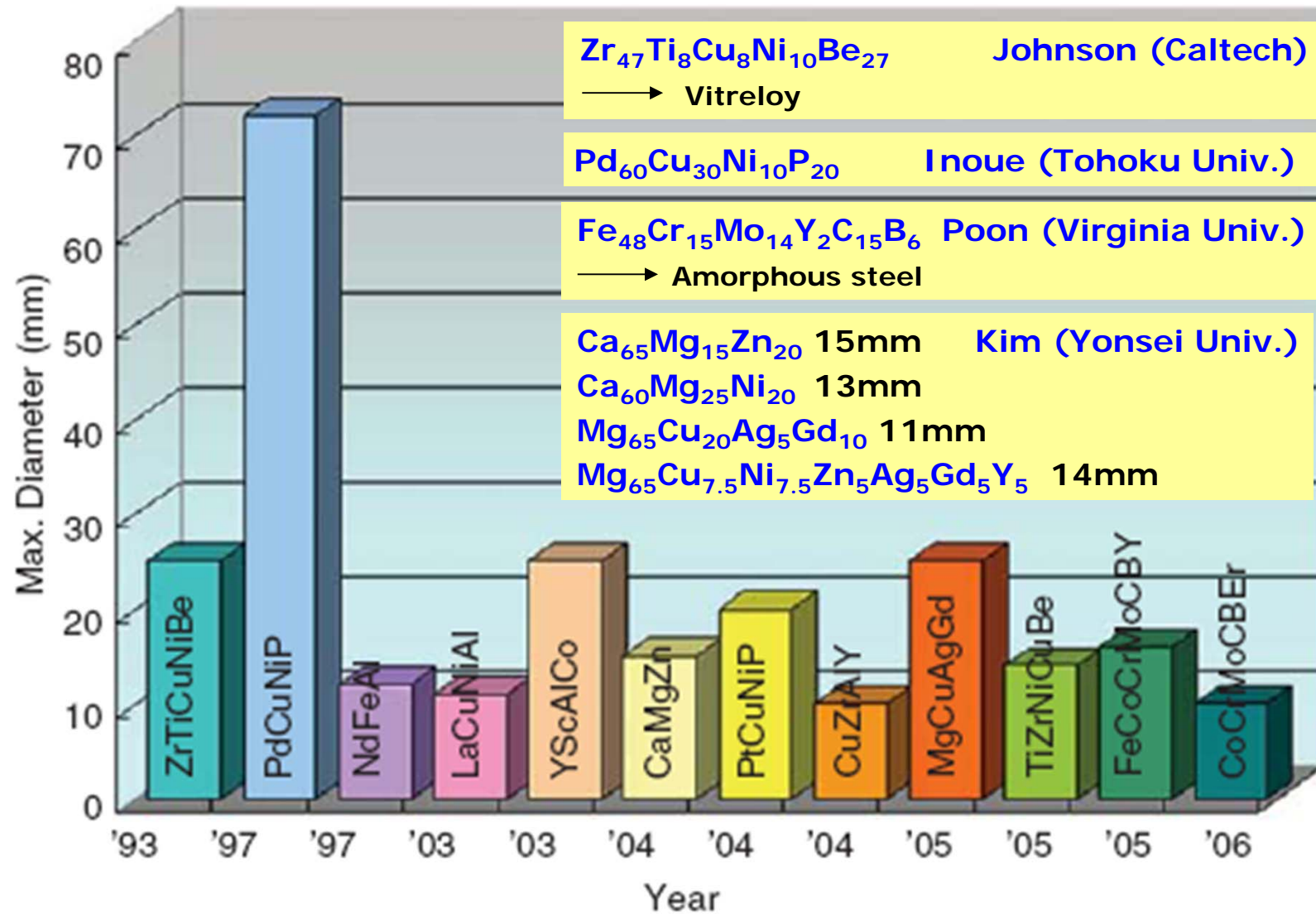


Glass formation: Rapid quenching ($\sim 10^{5-6}$ K/s) of liquid phase

1969 Ribbon type with long length using melt spinner : FePC, FeNiPB alloy



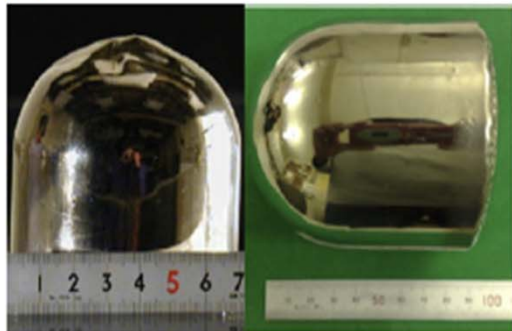
Recent BMGs with critical size ≥ 10 mm



Bulk glass formation in the Pd-/Ni-/Cu-/Zr- element system

Massy Ingot Shape

(a) Pd-Cu-Ni-P



72 ϕ x 75 mm 80 ϕ x 85 mm

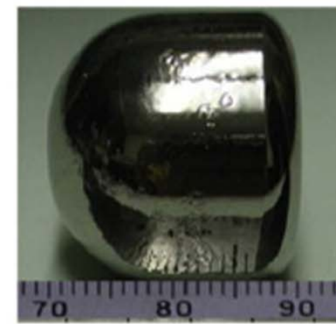
(b) Zr-Al-Ni-Cu



(c) Cu-Zr-Al-Ag

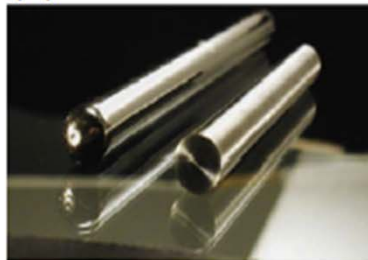


(d) Ni-Pd-P-B



Cylindrical Rods

(e) Pd-Cu-Ni-P

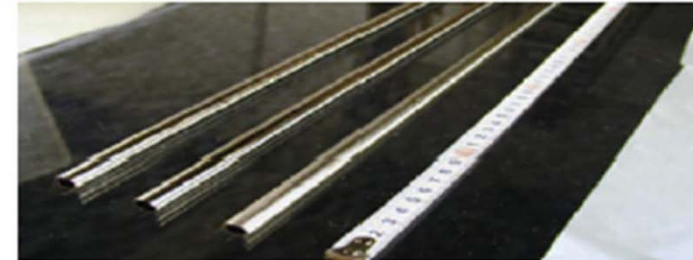


(f) Pt-Pd-Cu-P

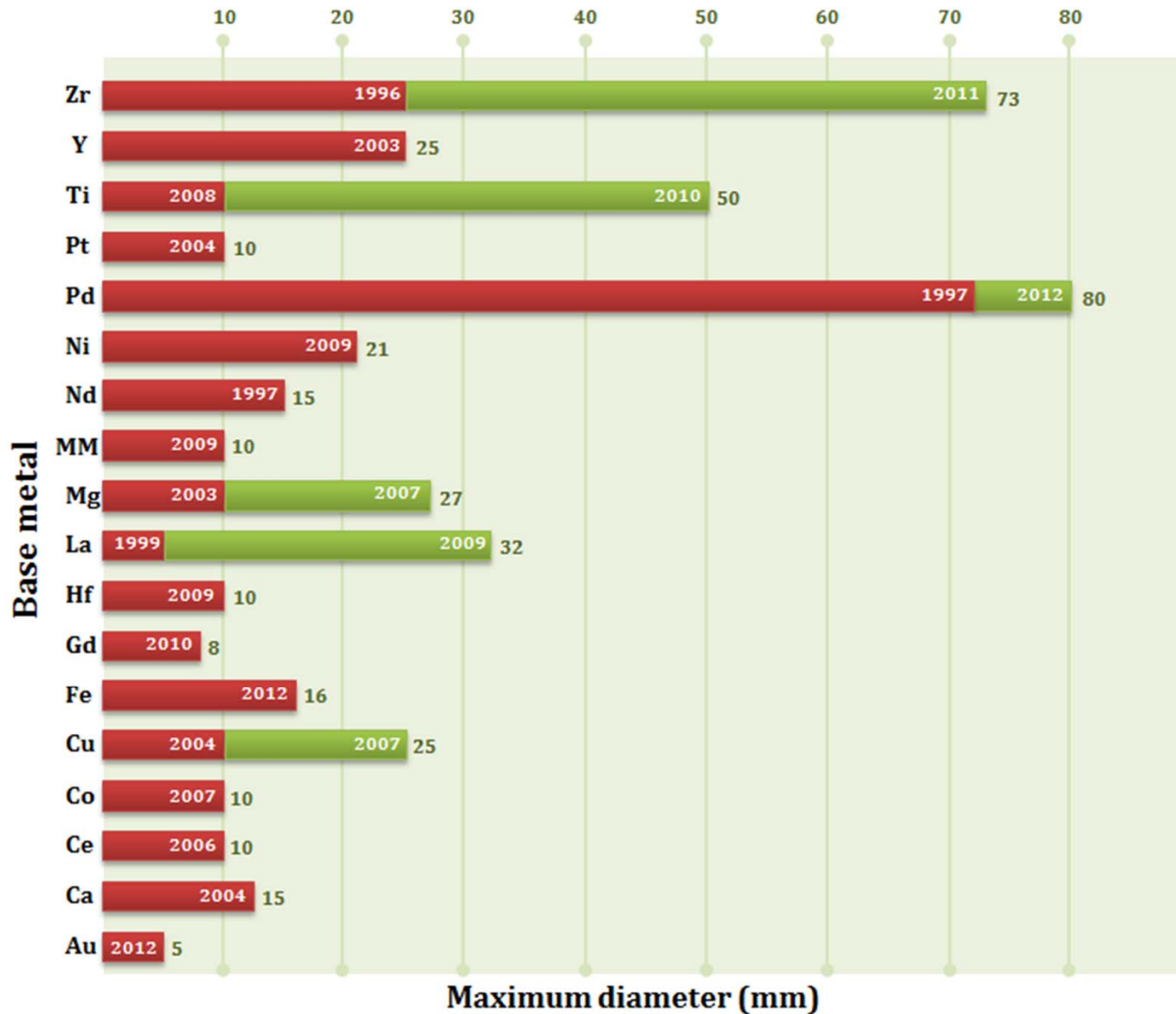


Hollow Pipes

(g) Pd-Cu-Ni-P

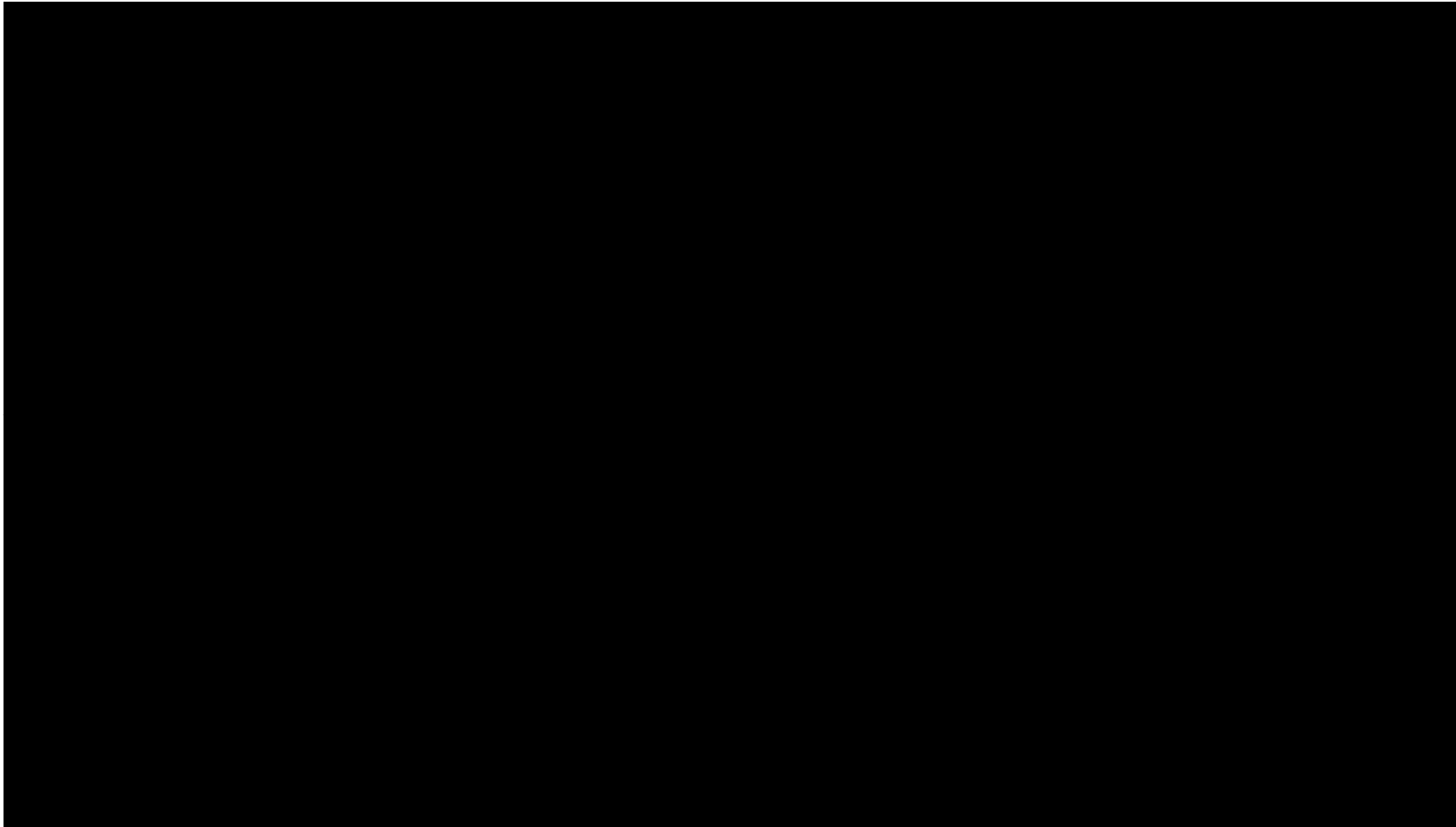


Recent BMGs with critical size ≥ 10 mm

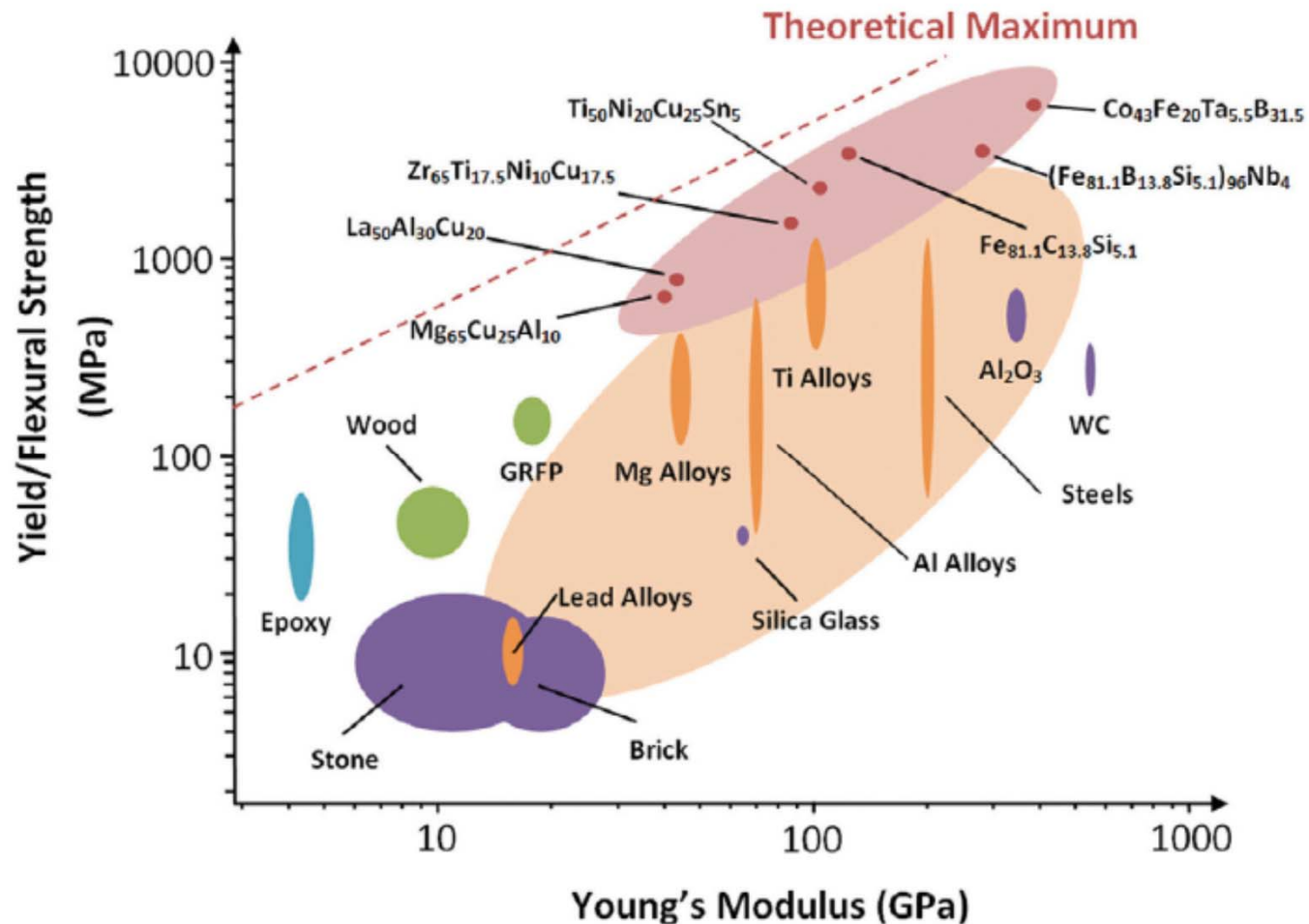


Q: BMG = The 3rd Revolution in Materials?

The 3rd Revolution in Materials



1. High strength of BMGs



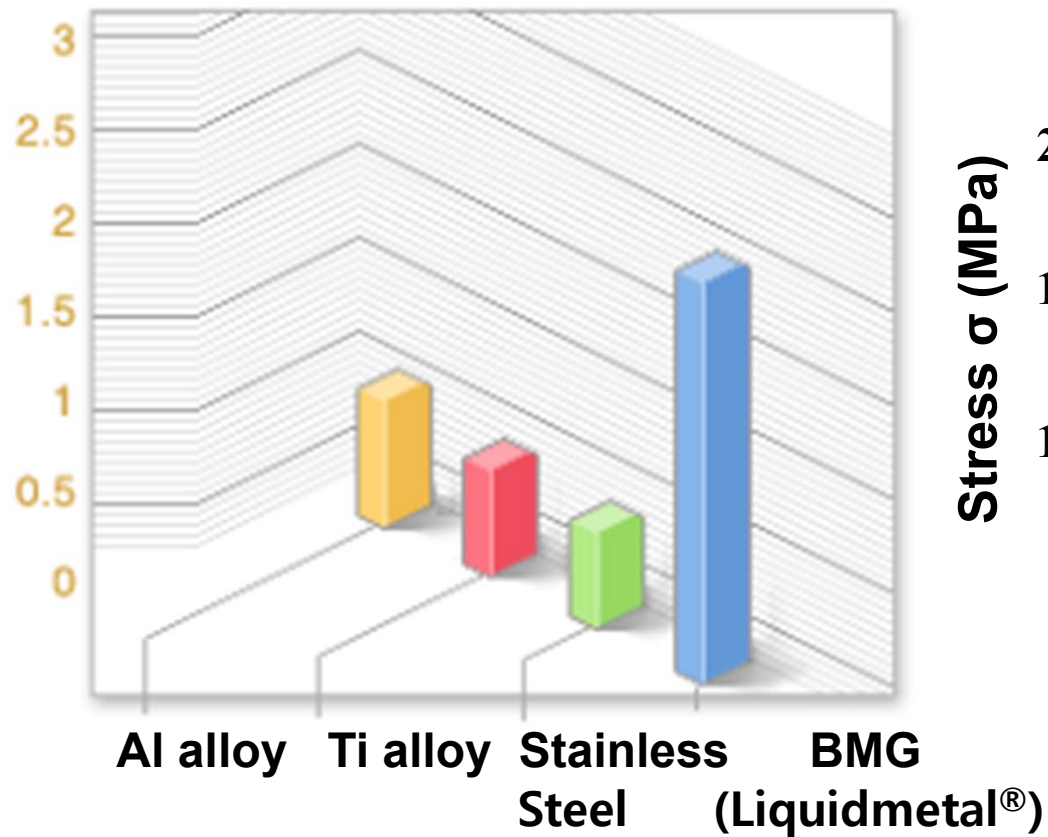
High fracture strength over 5 GPa in Fe-based BMGs

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

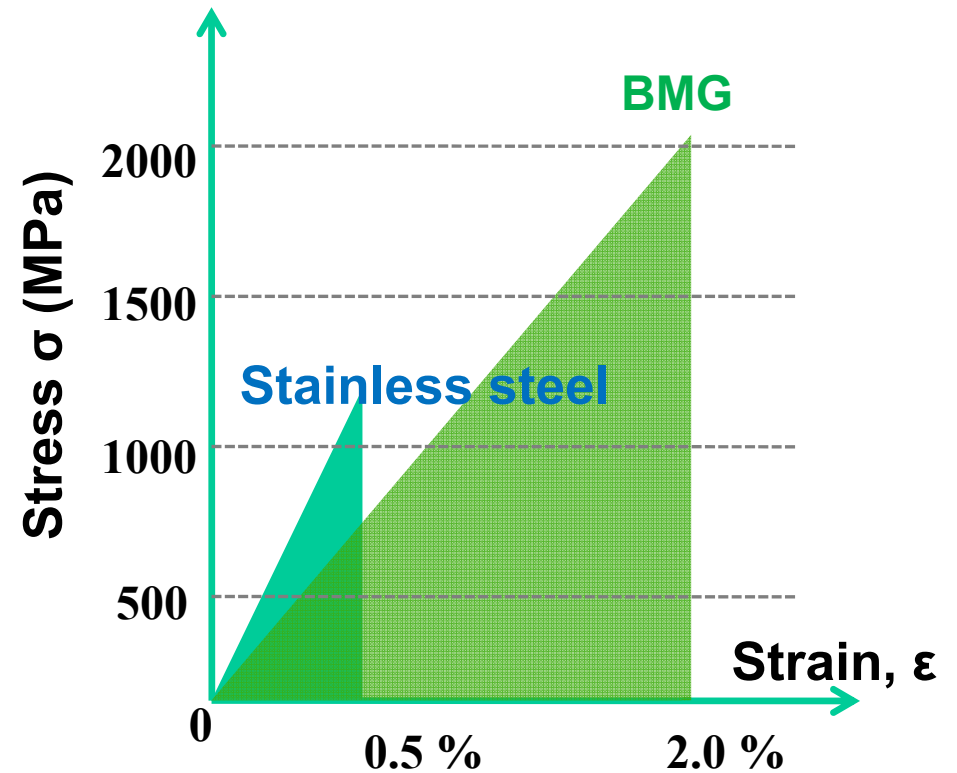
2. Large elastic strain limit of BMGs

Elastic Strain Limit

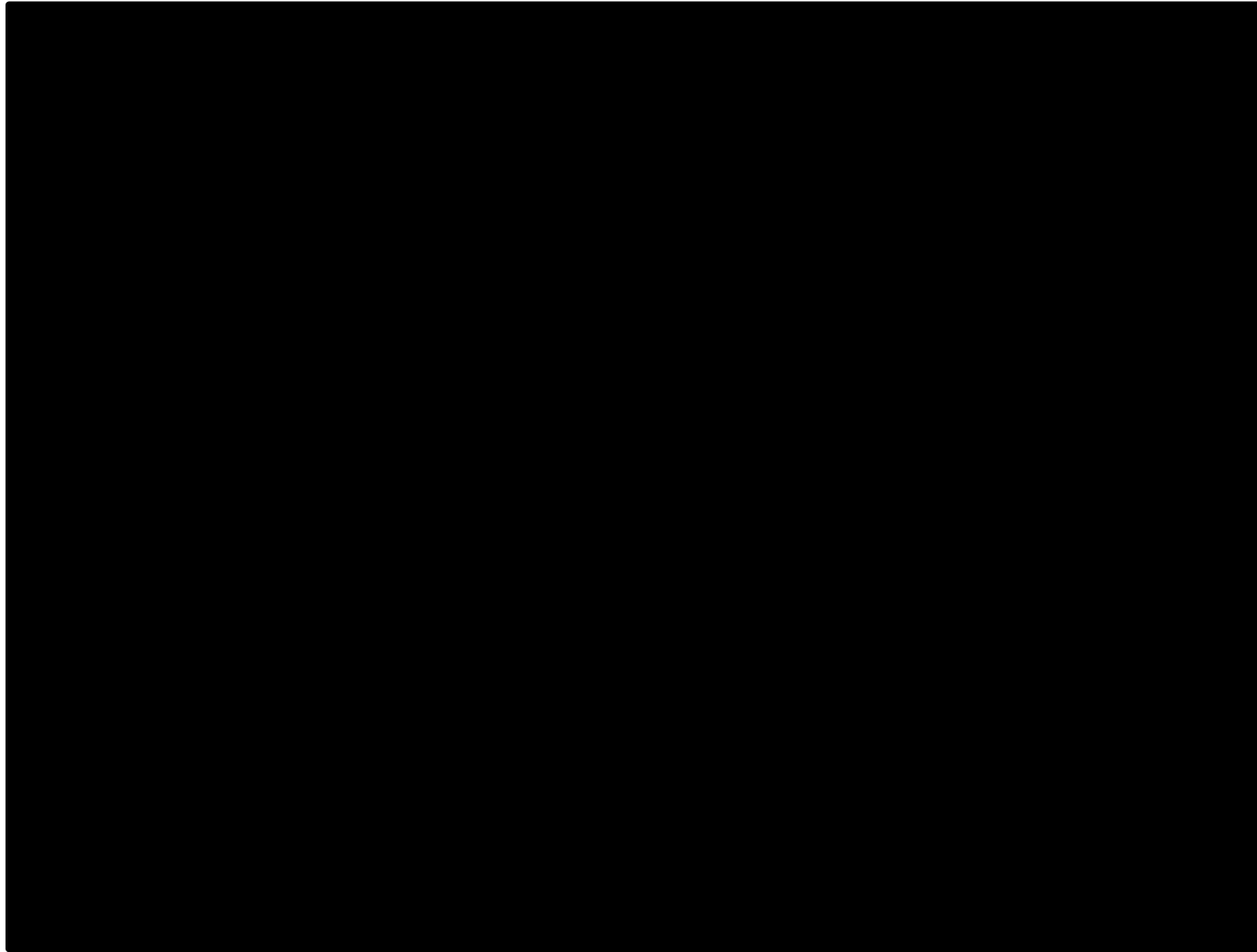
[as % of Original Shape]



Stress-Strain Curve

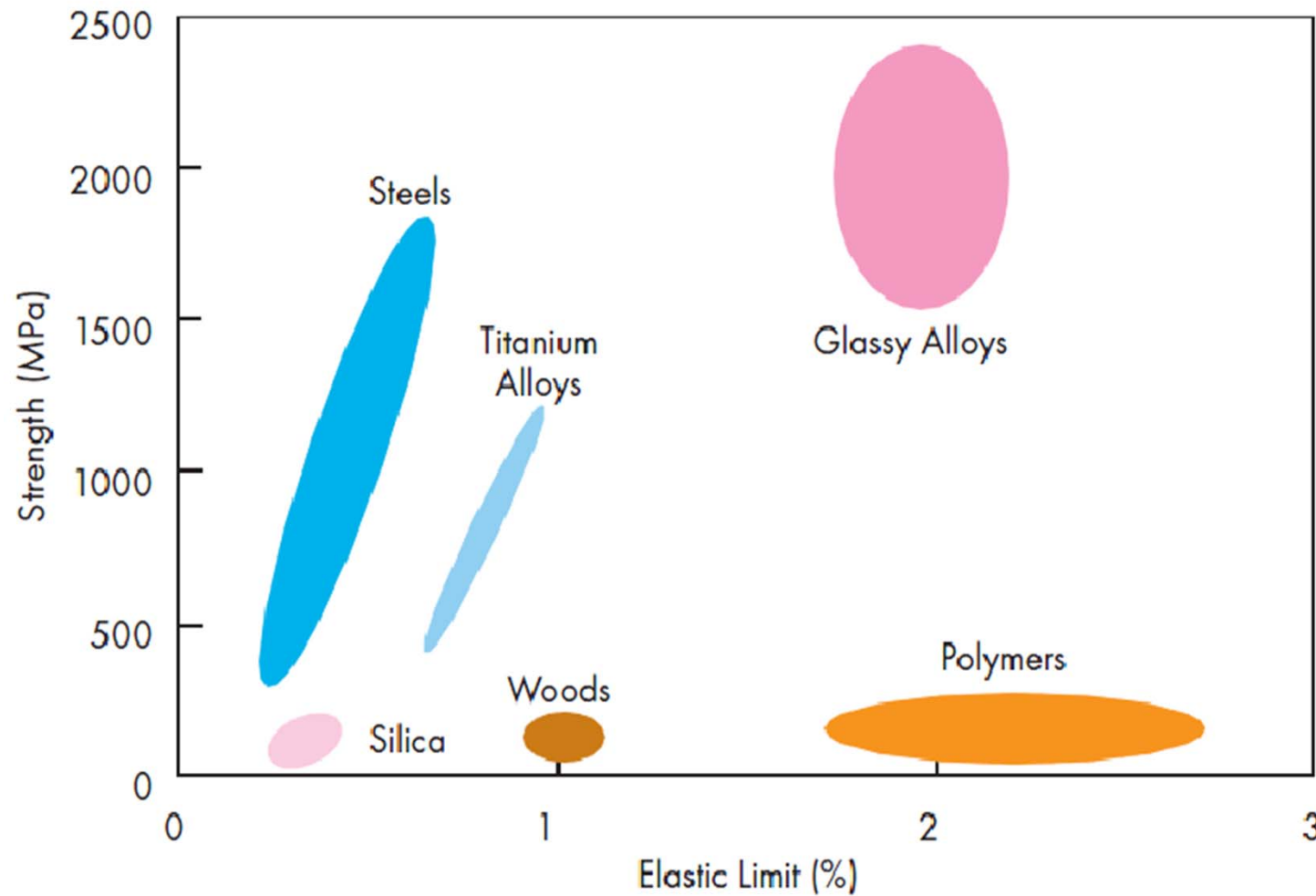


2. Large elastic strain limit of BMGs



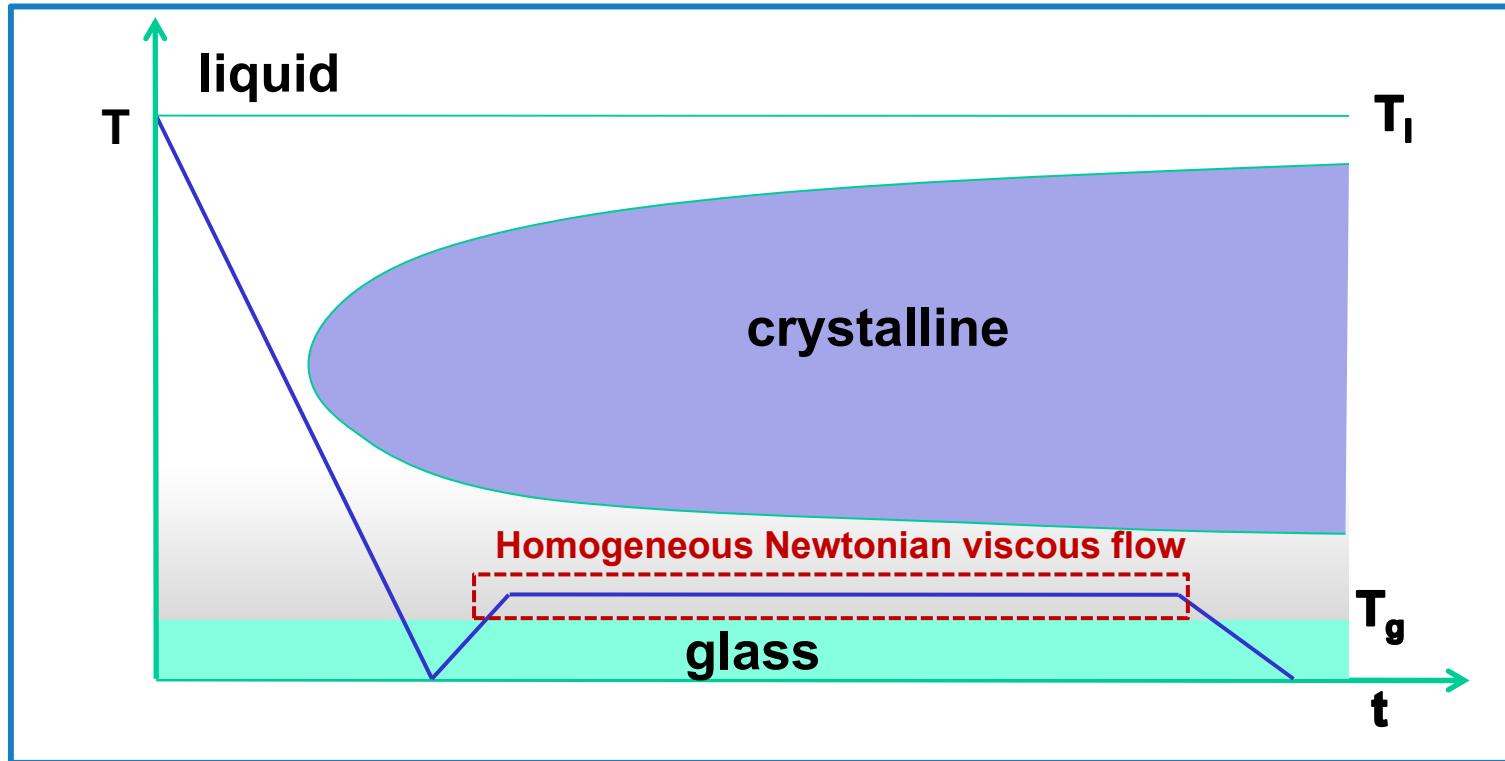
Metallic Glasses Offer

a Unique Combination of “High Strength” and “High Elastic Limit”



3. Processing metals as efficiently as plastics

* Thermoplastic forming in SCLR

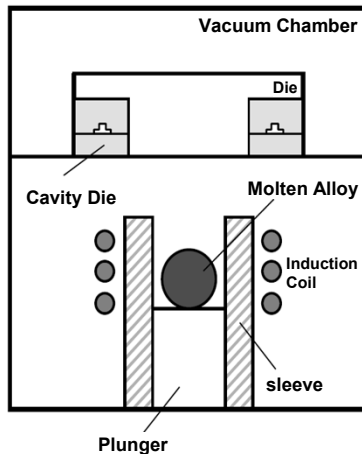
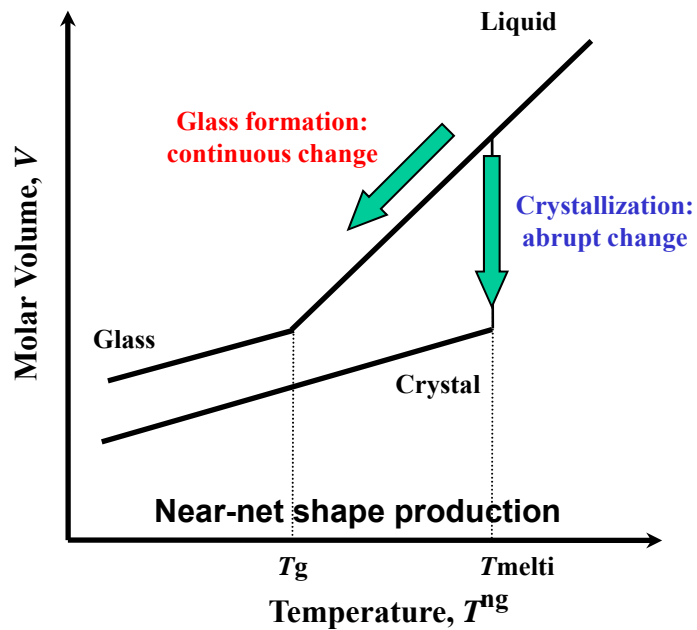


Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

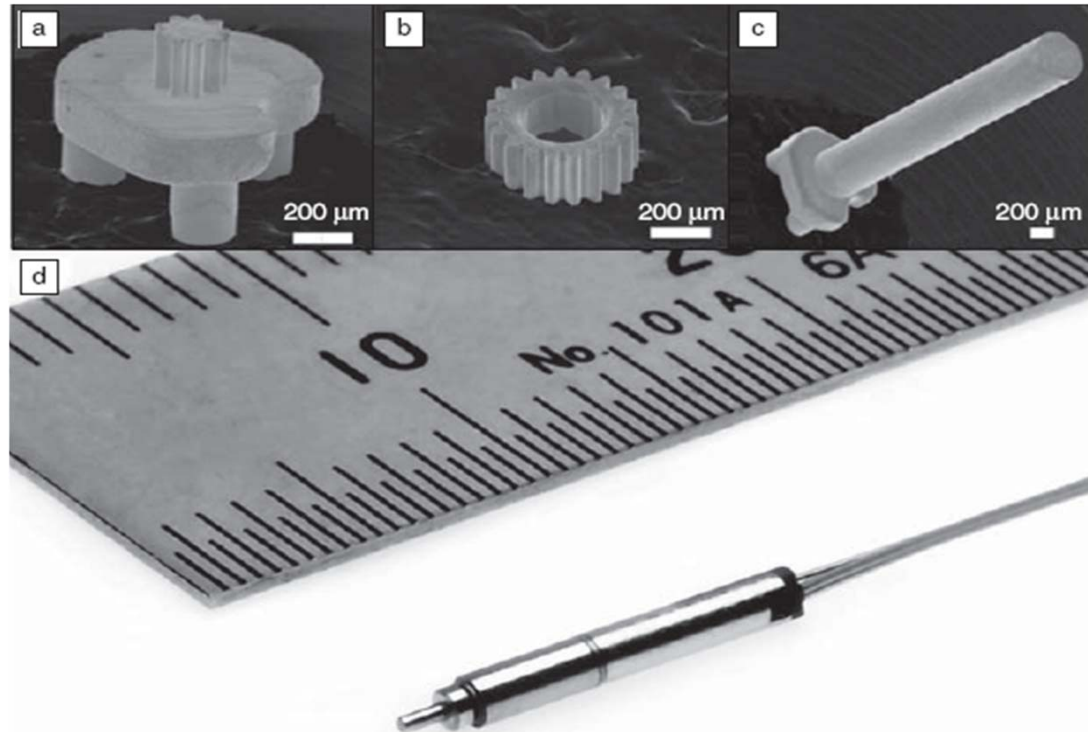
➡ Possible to deform thin and uniform in SCLR

3. Processing metals as efficiently as plastics

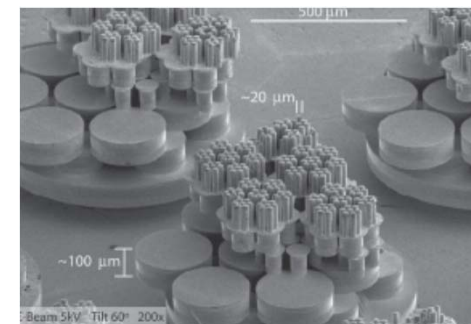
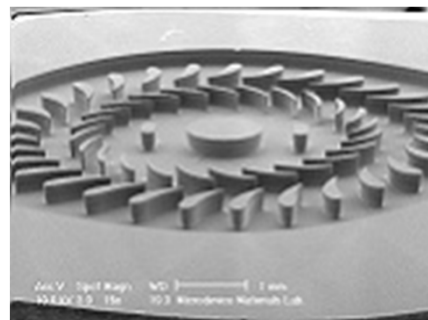
(a) Micro-casting



Precision die casting



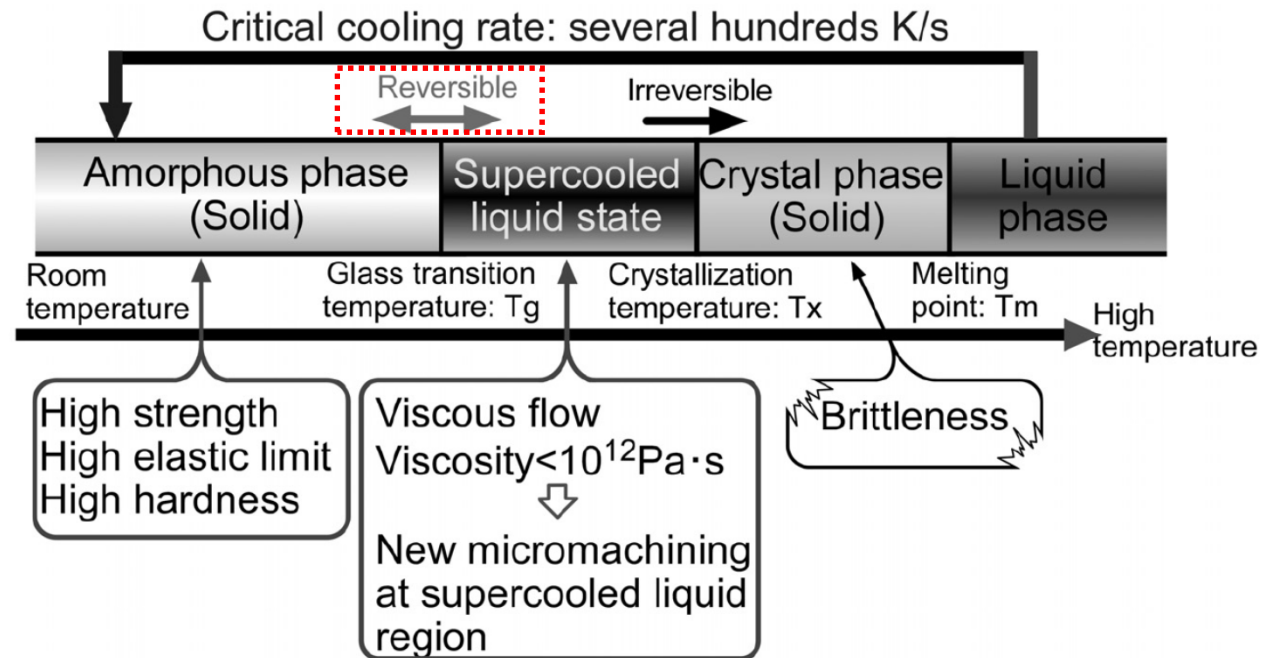
Precision Gears for Micro-motors



MRS BULLETIN 32 (2007)654.

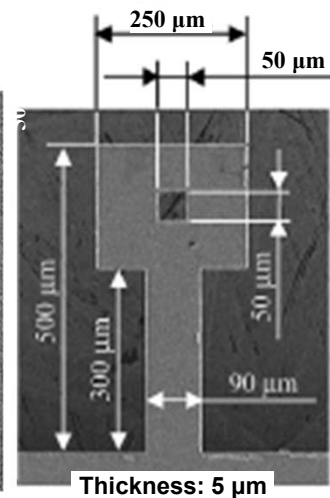
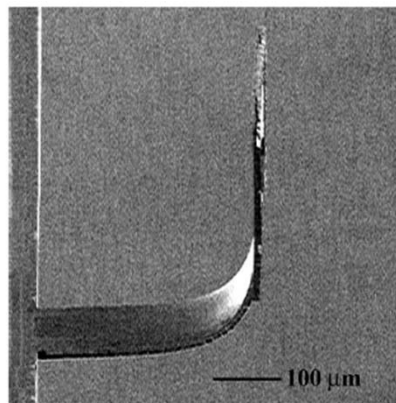
3. Processing metals as efficiently as plastics

(b) Micro-forming

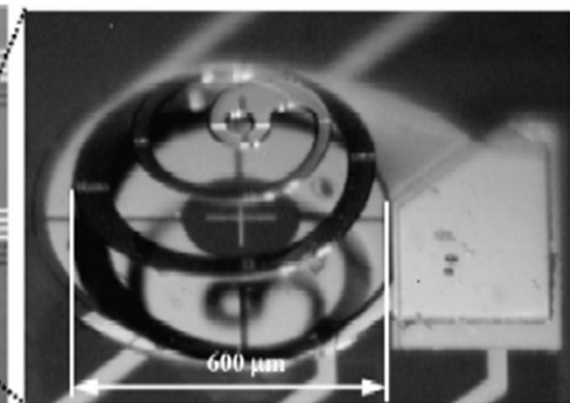
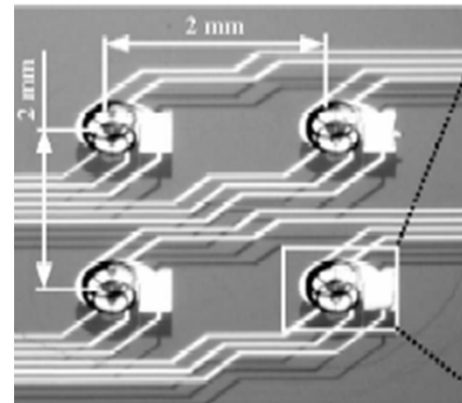


Micro-forming of three-dimensional microstructures from thin-film metallic glass

Micro-cantilever



Integrated conical spring linear actuator



3. Processing metals as efficiently as plastics

* Thermoplastic forming in SCLR

$\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ metallic glass ribbon



► Drawing sample at 220°C → Elongation over 1100%

3. Processing metals as efficiently as plastics

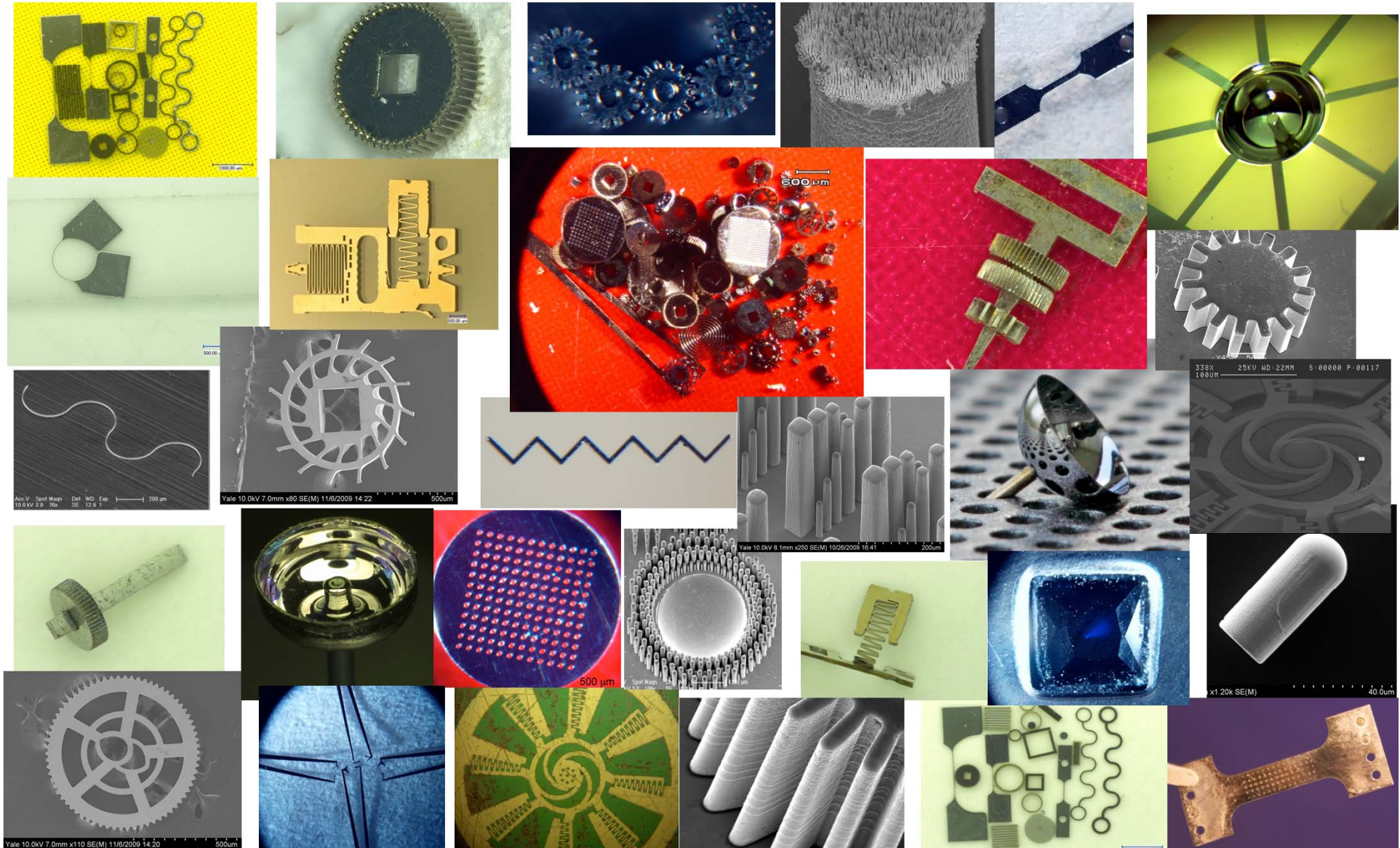


Seamaster Planet Ocean Liquidmetal® Limited Edition

- ▶ **Superior thermo-plastic formability**
 - : possible to fabricate complex structure without joints
 - ↳ **Multistep processing can be solved by simple casting**
 - ↳ **Ideal for small expensive IT equipment manufacturing**

Processing of Bulk Metallic Glass

Adv. Mater. 2009, 21, 1–32



“Yale professor makes the case for Supercool Metals”



According to Yale researcher Jan Schroers, This material is 50 times harder than plastic, nearly 10 times harder than aluminum and almost three times the hardness of steel."



Apple buys exclusive right for Liquidmetal

Apple is using Liquidmetal for...



USIM ejector (iphone 4)



Enclosure / Antenna

Apple continuing work on Liquidmetal casting techniques...

October 29, 2015

Two New Liquid Metal Inventions Published Today Cover Every Current Apple Product and even Complete Car Panels



Liquidmetal™ in
NEXT iPhone?



PATENT APPLICATION

<http://www.patentlyapple.com/patently-apple/2015/10/>

Could Project Titan use Liquid Metal for Parts and Body Panels?



Apple's patents cover the use of liquid metal in every imaginable Apple product and even hints that the process described in these inventions could produce **complete car panels**. That makes you wonder if Apple's Project Titan will be able to take advantage of the liquid metal process for car parts and beyond.

First smart phone with BMG exterior

Turing phone
by Turing Robotics Industries (UK)
with
Metallic glass
“Liquidmorphium™”



“Unhackable”
“Waterproof”

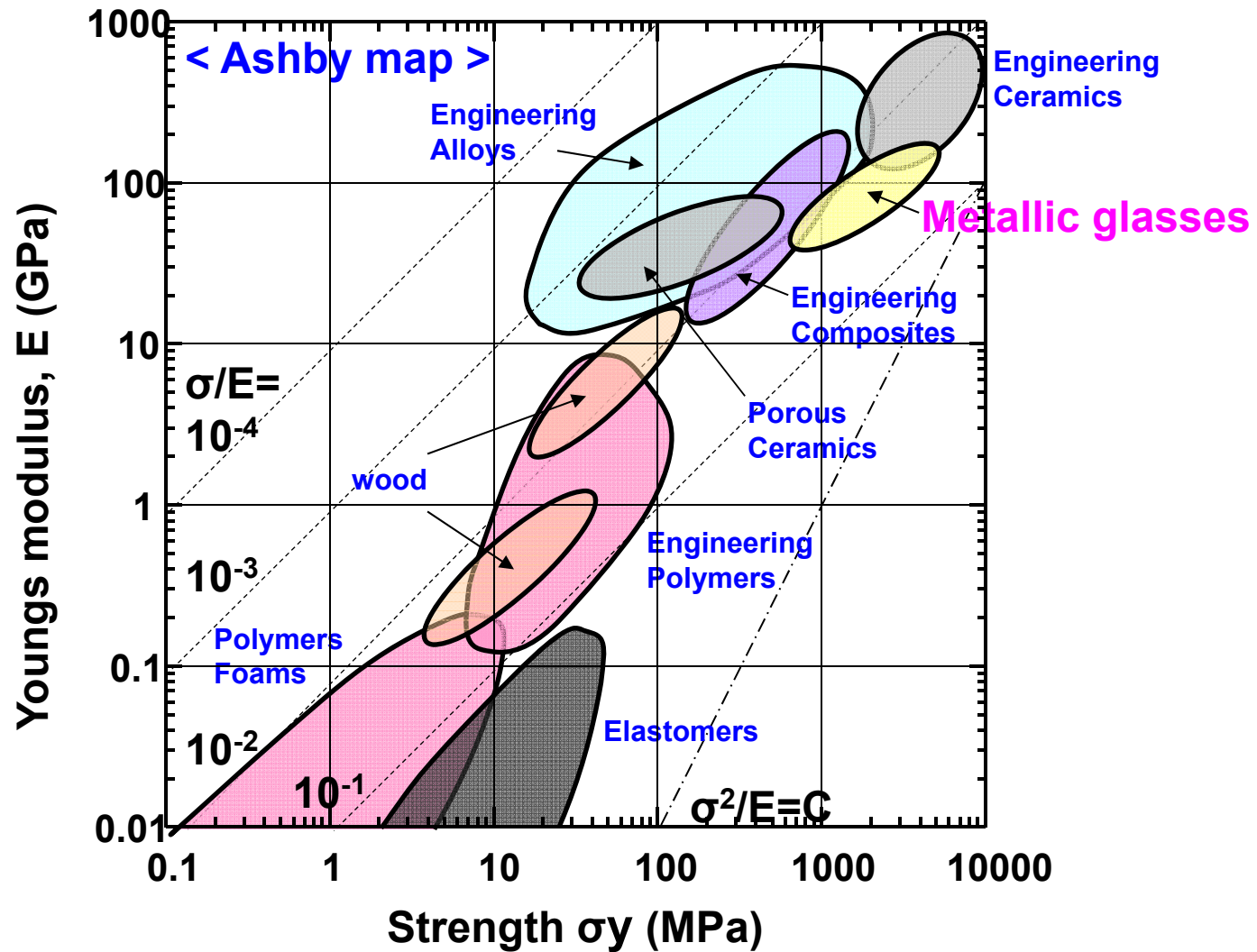
+

“Unbreakable”

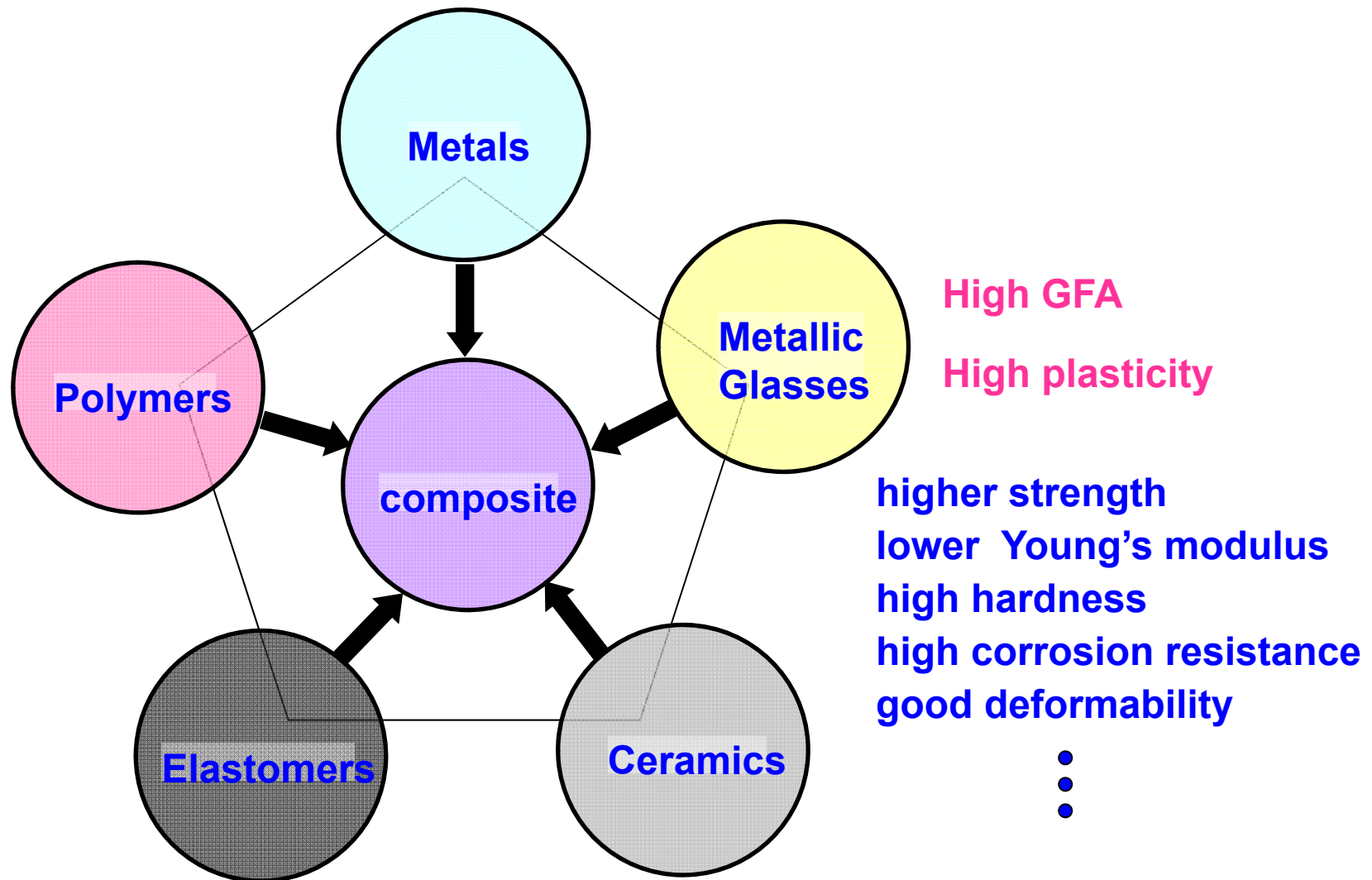
The Turing Phone is built with a pioneering material called Liquidmorphium™, an amorphous “liquid metal” alloy tougher than either titanium or steel - so what’s in your hand is as strong as your privacy protection.

from <https://www.turingphone.com/>

A new menu of engineering materials



A new menu of engineering materials



Skip section 4.5 and 4.8 in the text book

*** Homework 4 : Exercises 4 (pages 257-259)**

until 4th December (before class)

Good Luck!!