2015 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↓ → 조성적 과냉영역 증가
Cell 선단의 피라미드형상/ 가지들의 square array/ Dendrite 성장방향쪽으로 성장방향 변화

성장하는 crystal로 부터 발생한 잠열을 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, inversegregation, coring and intercrystalline segregation, gravity segregation

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 $(T_S' = 0)$

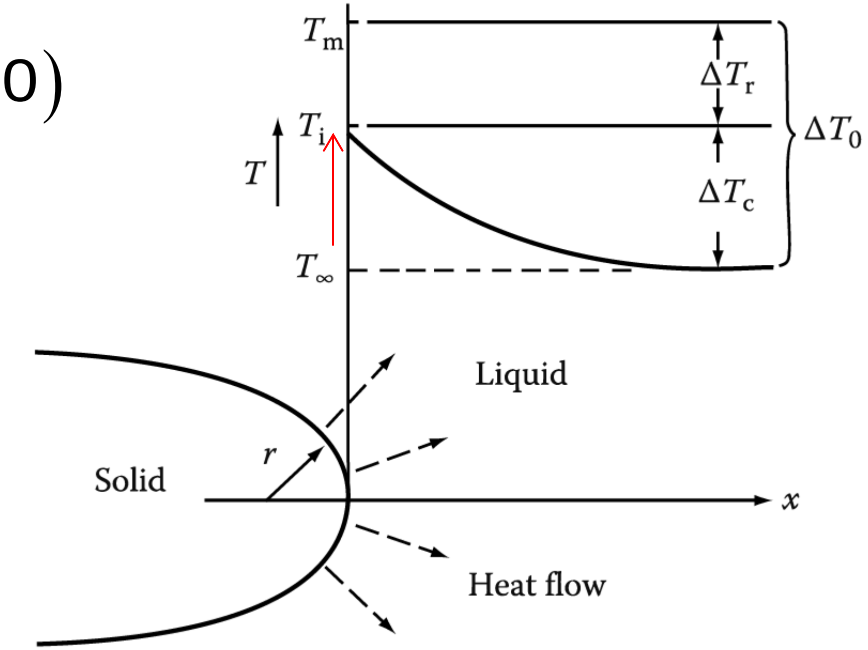
From $K_S T_S' = K_L T_L' + v L_V$

$$\text{If } T_S' = 0, \boxed{v = \frac{-K_L T_L'}{L_V}}$$

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

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

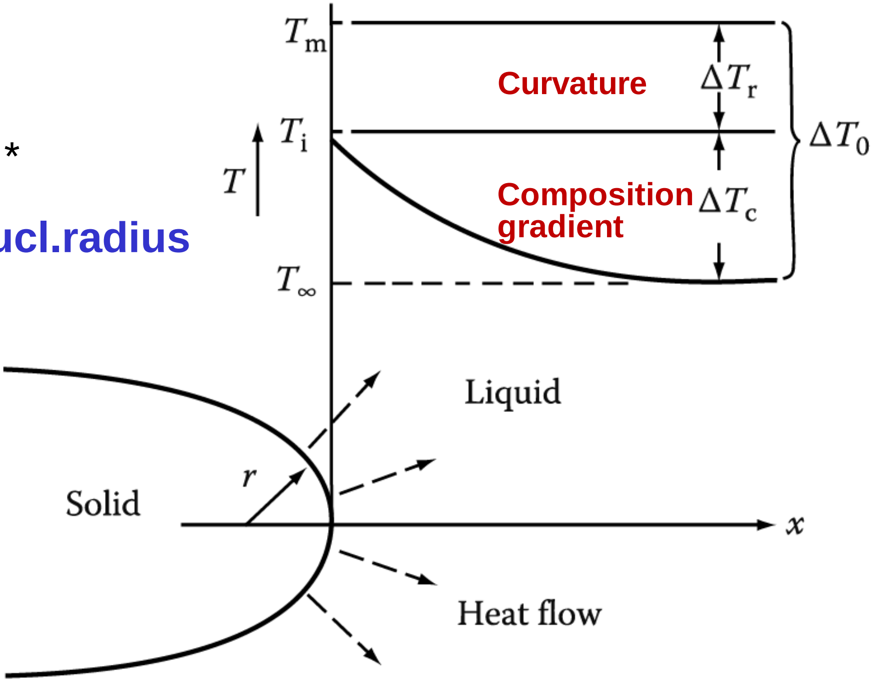
Minimum possible radius (r)?

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

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 ΔT_r *by* r, r^* *and* ΔT_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*

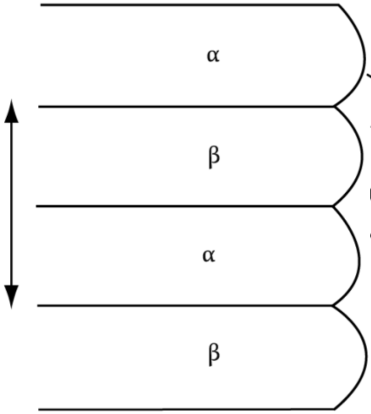
as $r \rightarrow \infty$ *due to slower heat condution*

Maximum velocity?

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

Eutectic Solidification (Kinetics)

: ΔT→ 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**

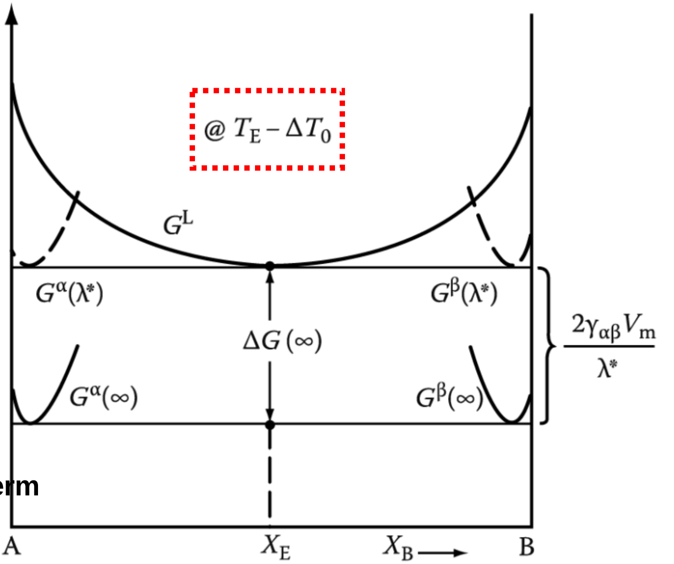
For an interlamellar spacing, λ, there is a total of (2/ λ) m² of α/β interface per m³ of eutectic.

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

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

Molar volume

Driving force for nucleation = Total interfacial E of eutectic phase



For very large values of λ, interfacial E~ 0

Total undercooling

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

No interface (ideal case)

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

With interface (real case)

Interfacial E term

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

a) All **ΔT→ use for interface formation=** min. **λ**

What would be the minimum λ?

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

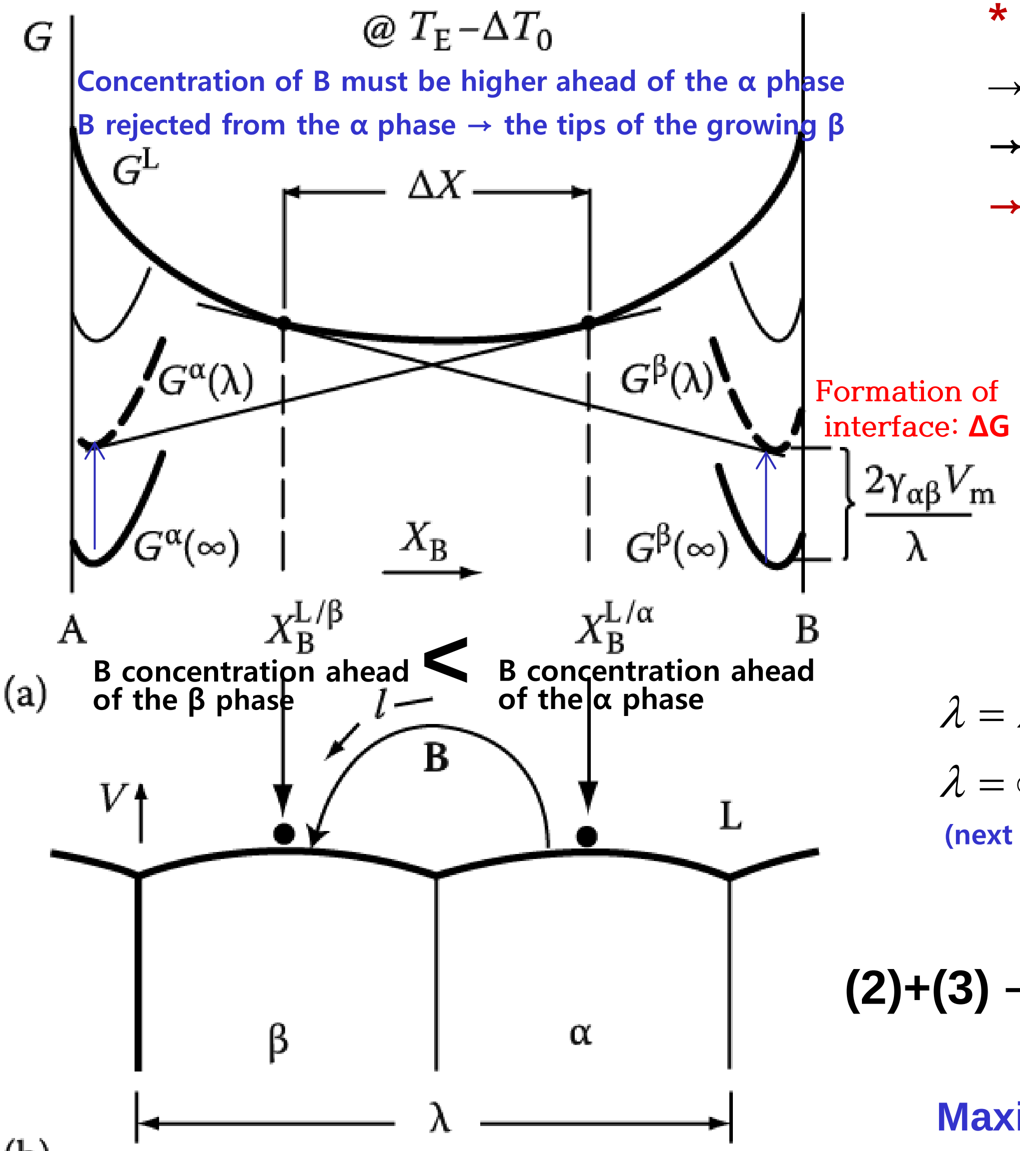
최소 층상 간격

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

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

2) At λ= (∞>) λ (>λ*),

If ∞> λ > λ*, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. → $X_B^{L/\alpha} > X_B^{L/\beta}$



Concentration of B must be higher ahead of the α phase

B rejected from the α phase → the tips of the growing β

Formation of interface: ΔG

B concentration ahead of the β phase

B concentration ahead of the α phase

* Eutectic growth rate, *v*

→ if α/L and β/L interfaces are highly mobile

→ proportional to flux of solute through liquid

→ diffusion controlled process

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

$\propto$ 1/effective diffusion distance.. 1/λ

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

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

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

(next page)

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

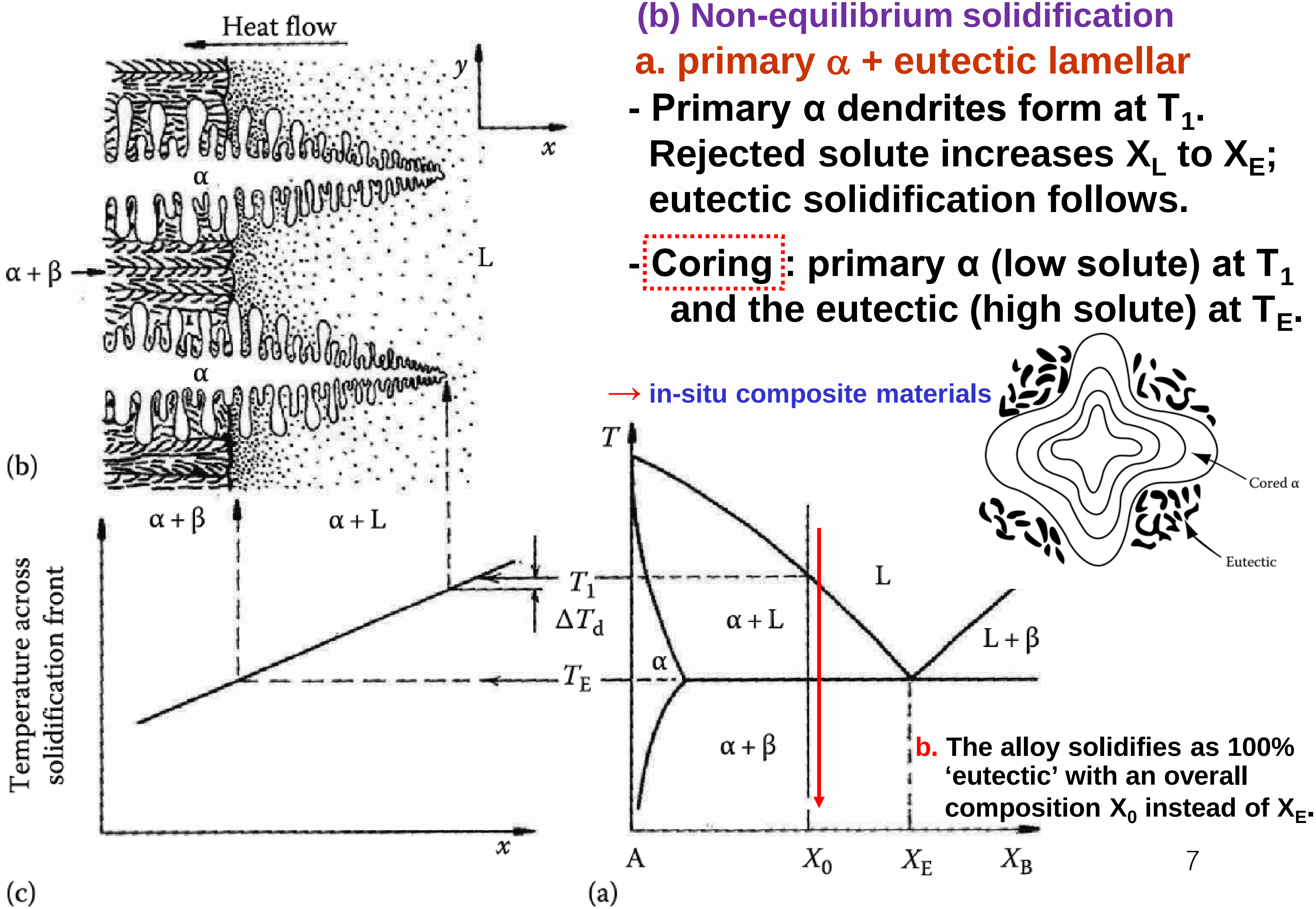
$$\Delta X_0 \propto \Delta T_0 \qquad \textbf{(3)}$$

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

Maximum growth rate at a fixed ΔT_0 → $\boxed{\lambda = 2\lambda^*}$

Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case λ* < λ < ∞, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

4.3.3 Off-eutectic Solidification



(b) Non-equilibrium solidification

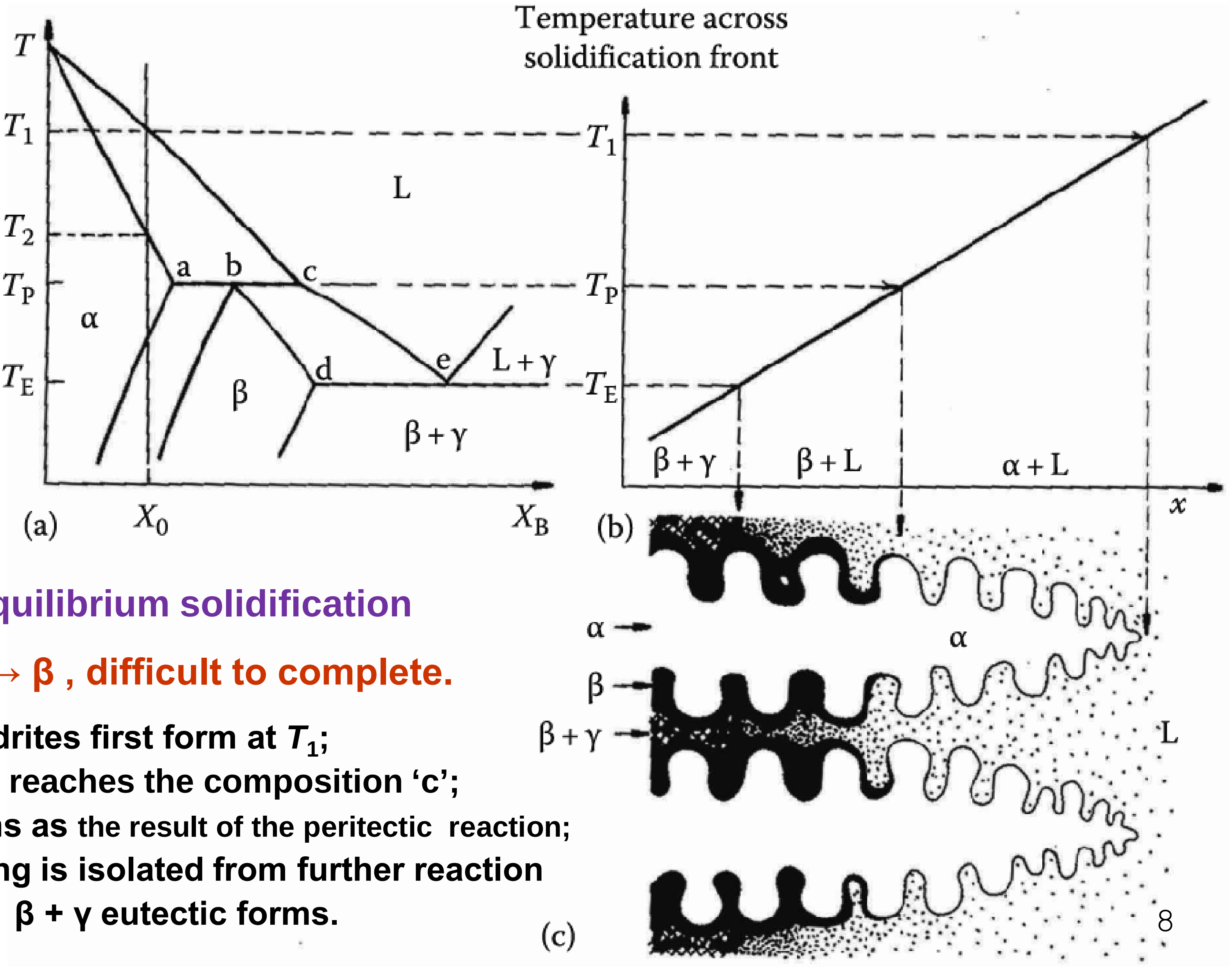
a. primary α + eutectic lamellar

- 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.

4.3.4 Peritectic Solidification



(b) Non-equilibrium 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.

4.4 Solidification of Ingots and Castings

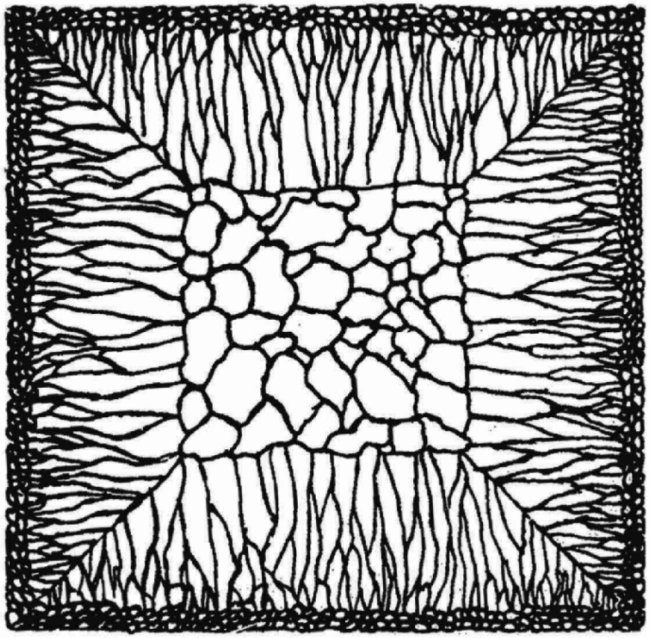
a lump of metal, usually shaped like a brick.

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.**

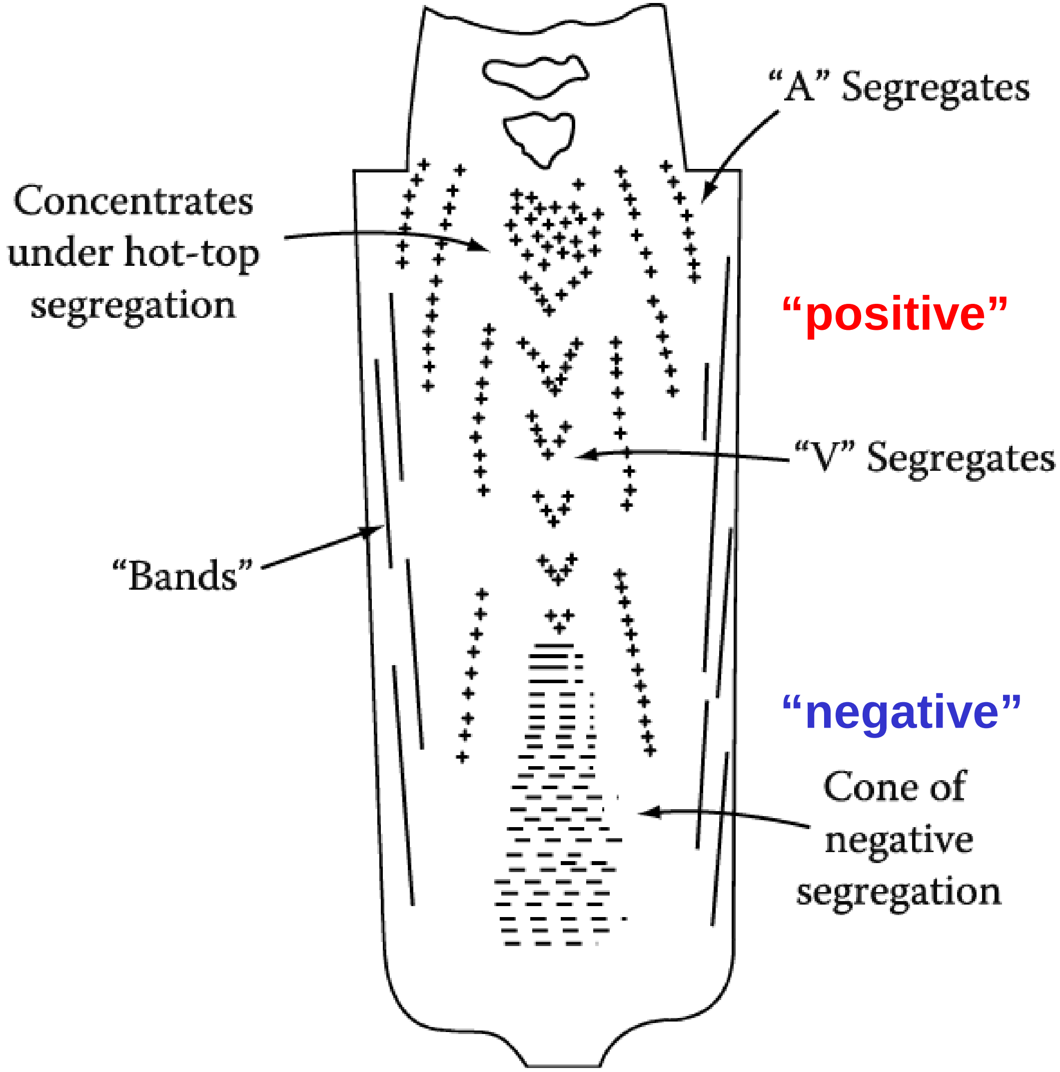
1) **If the pouring temp. is low**: liquid~ rapidly cooled below the liquidus temp. → **big-bang nucleation** → **entirely equiaxed ingot structure**, no columnar zone

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**

* Segregation: undesiable ~ deleterious effects on mechanical properties

→ subsequent homogenization heat treatment, but diffusion in the solid far to slow

→ good control of the solidification process



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)

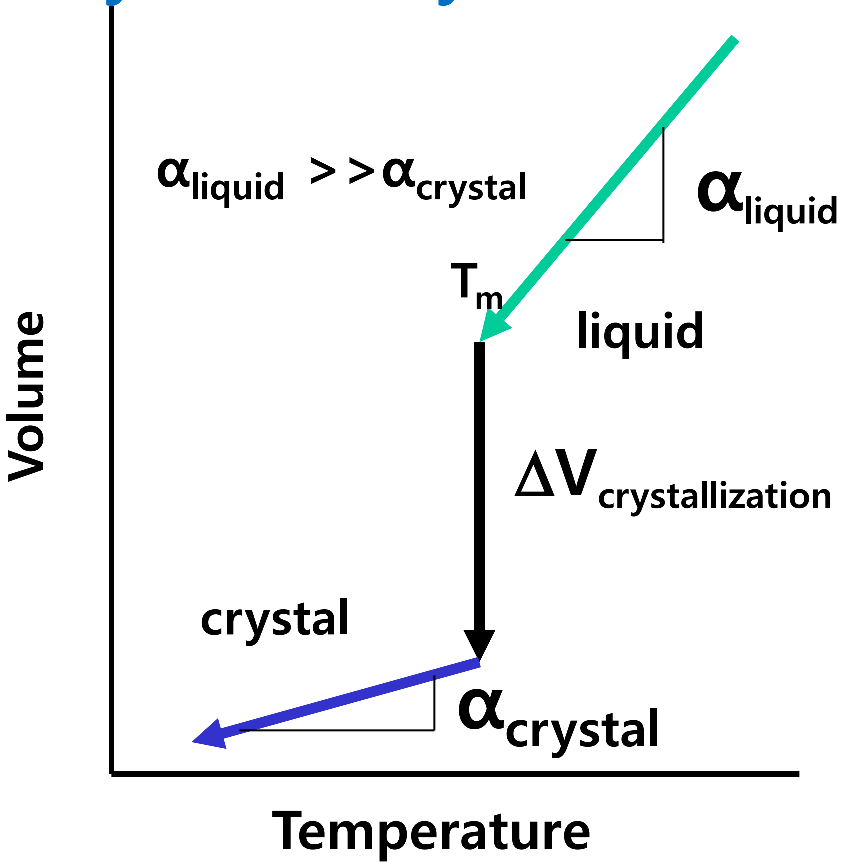
Negative segregation: The solid is usually denser than the liquid and sinks carrying with it less solute (초기응고고상)than the bulk composition (assuming k<1). This can, therefore, lead to a region of negative segregation near the bottom of the ingot. ((b) Gravity effects)

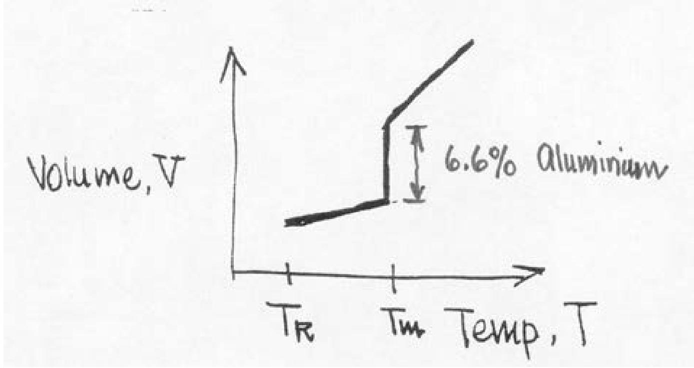
Fig. 4.43 Segregation pattern in a large killed steel ingot. + positive, - negative segregation. (After M.C. Flemings, Scandinavian Journal of Metallurgy 5 (1976) 1.)

(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

- 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

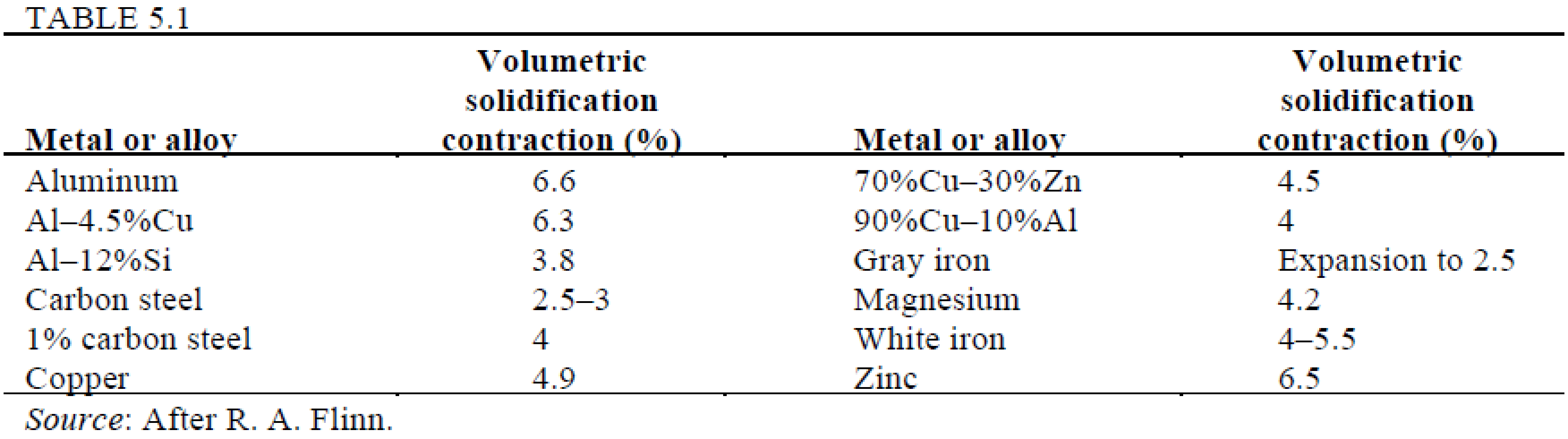


TABLE 5.1

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**

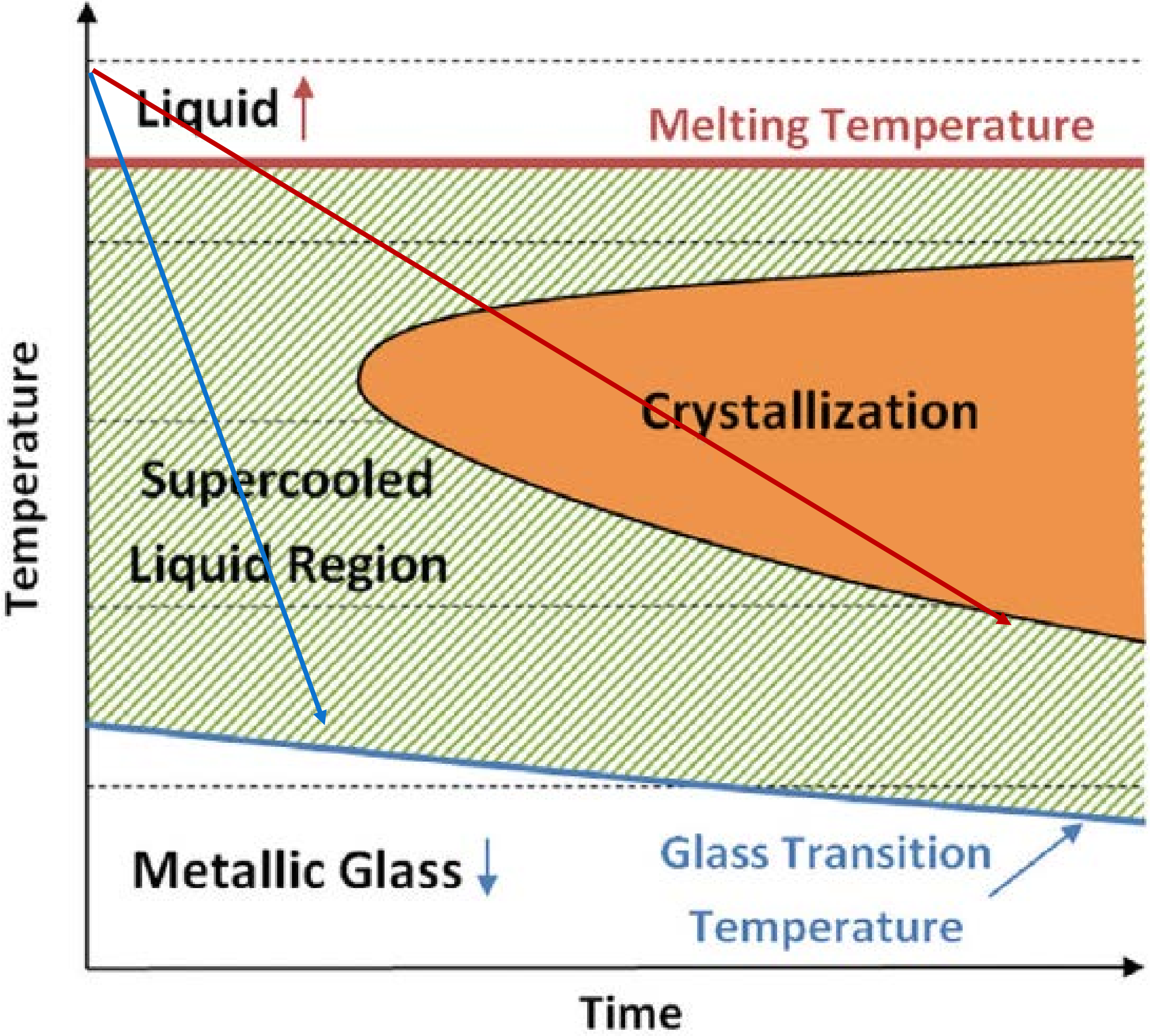
ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

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

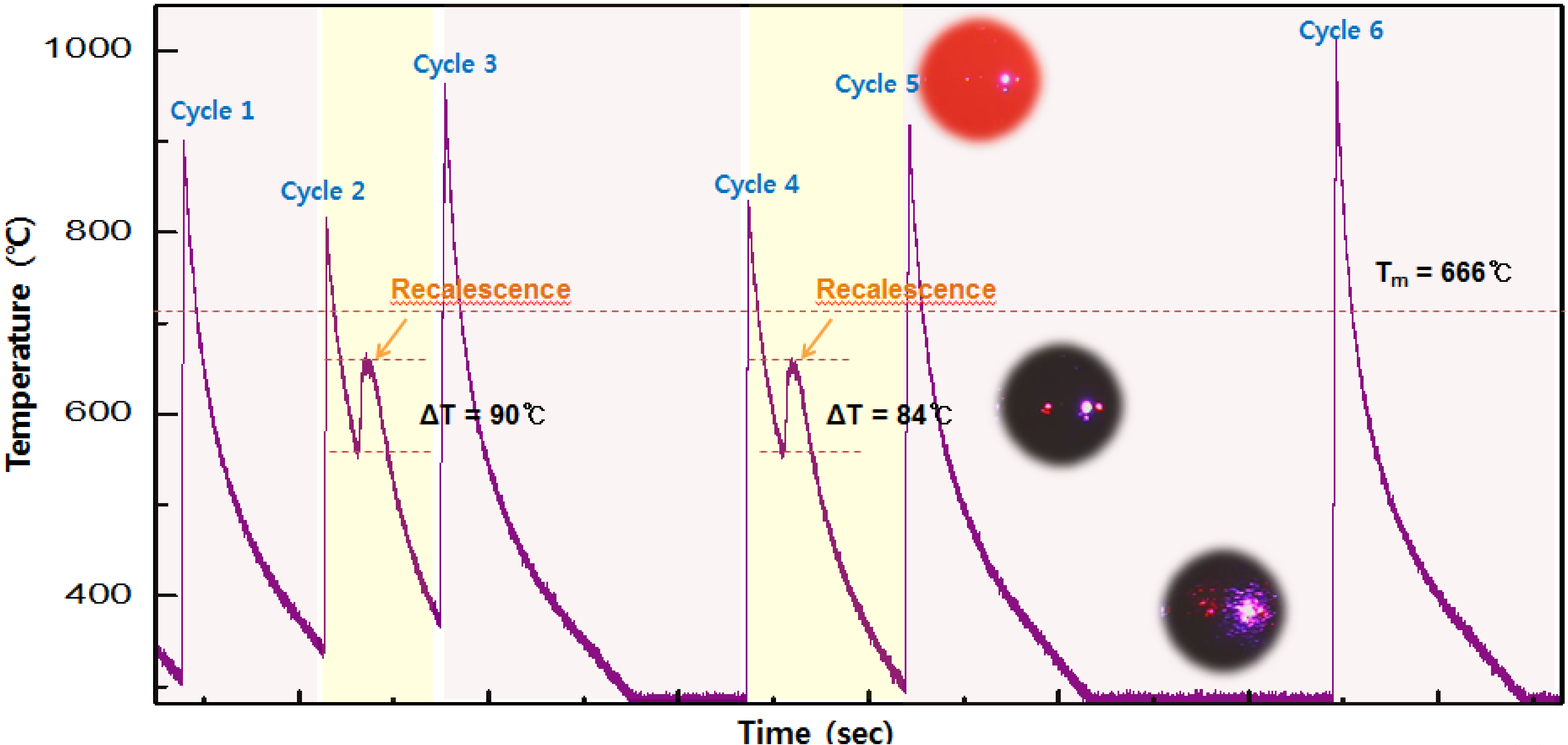
→ precipitation of graphite during solidification reduces shrinkage.

Q: Glass formation?

Time-Temperature-Transformation diagram



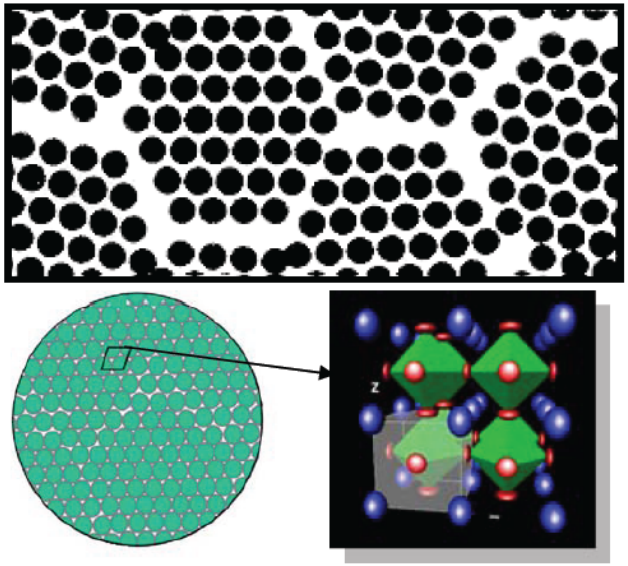
Electrostatic Levitation: cooling curve of Vitreloy 1 system



at KRISS

Structure of Crystals, Liquids and Glasses

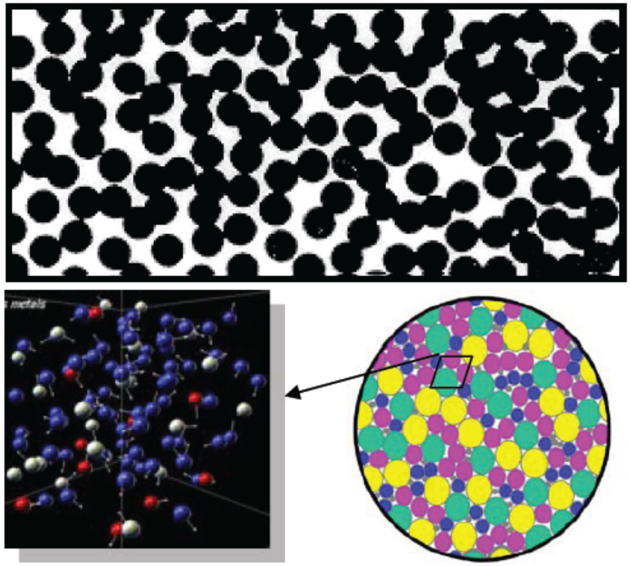
Crystals



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

- **grain boundaries**

Liquids, glasses

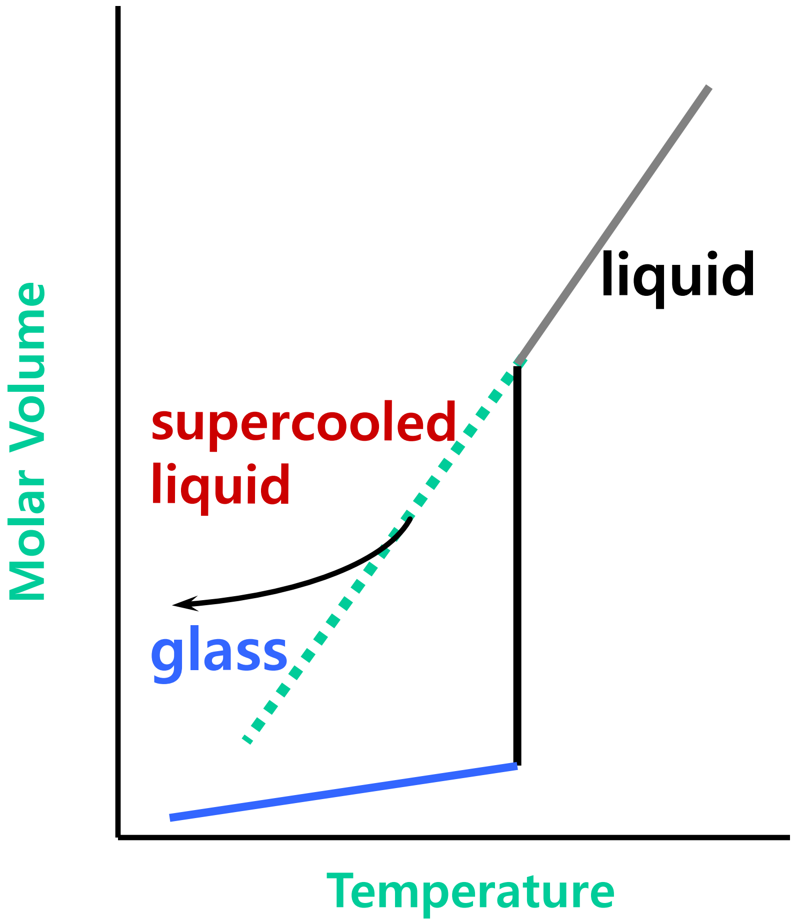


nearly random = non-periodic

- **no grain boundaries**

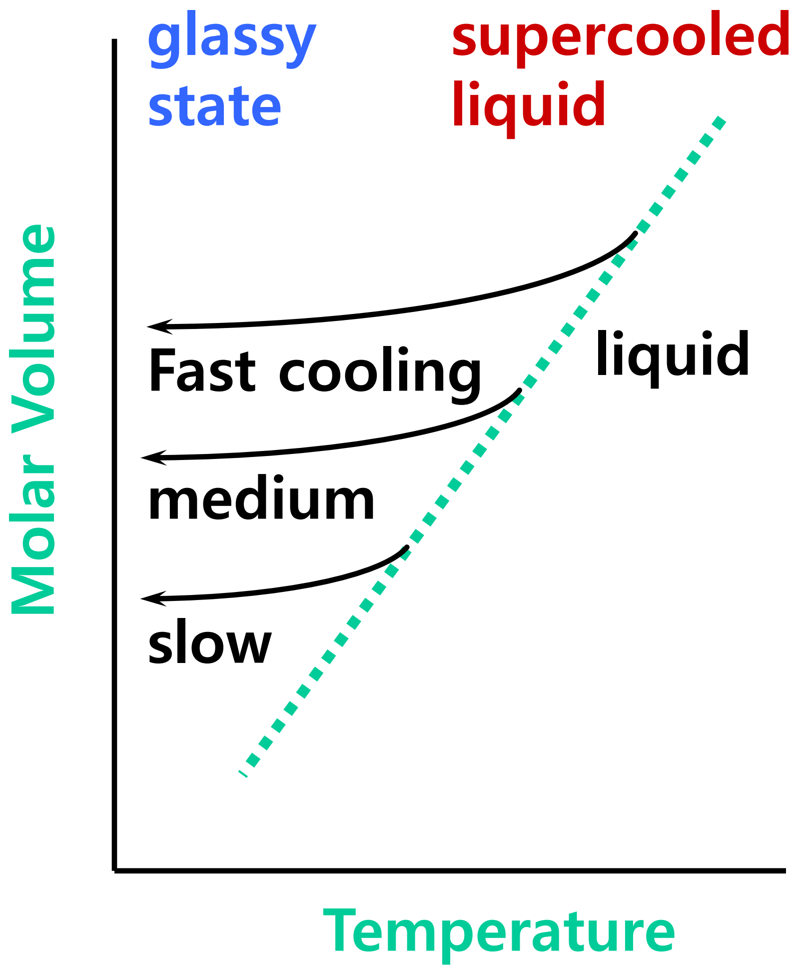
Glass Formation is Controlled by Kinetics

- 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



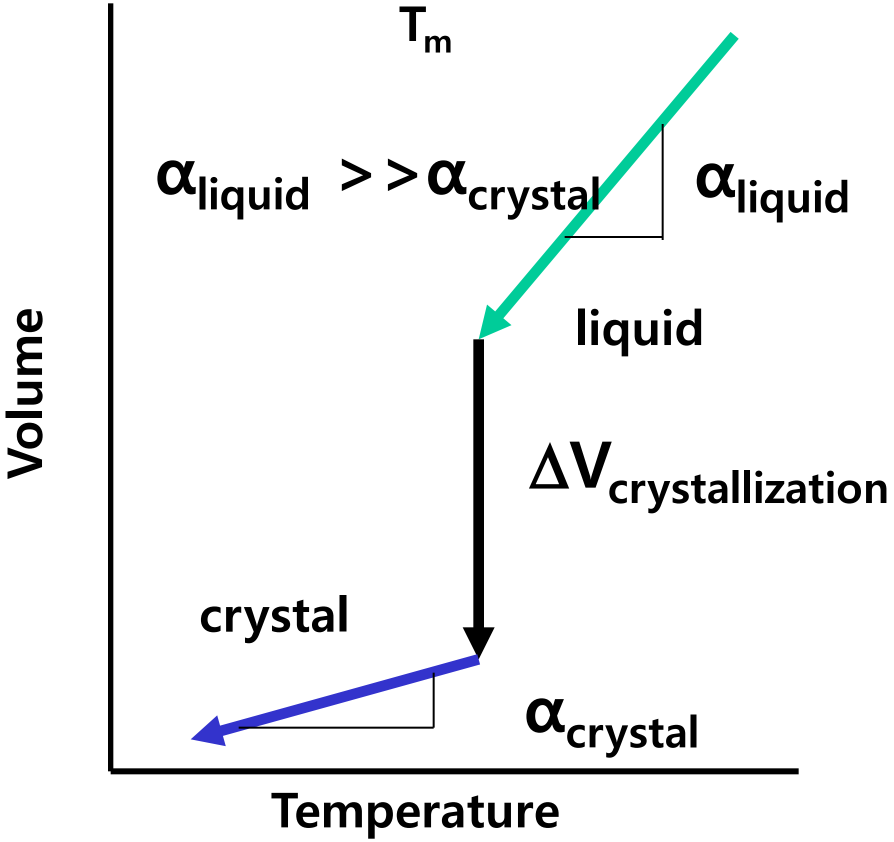
The Cooling Rate Affects the Properties of Glass

- 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

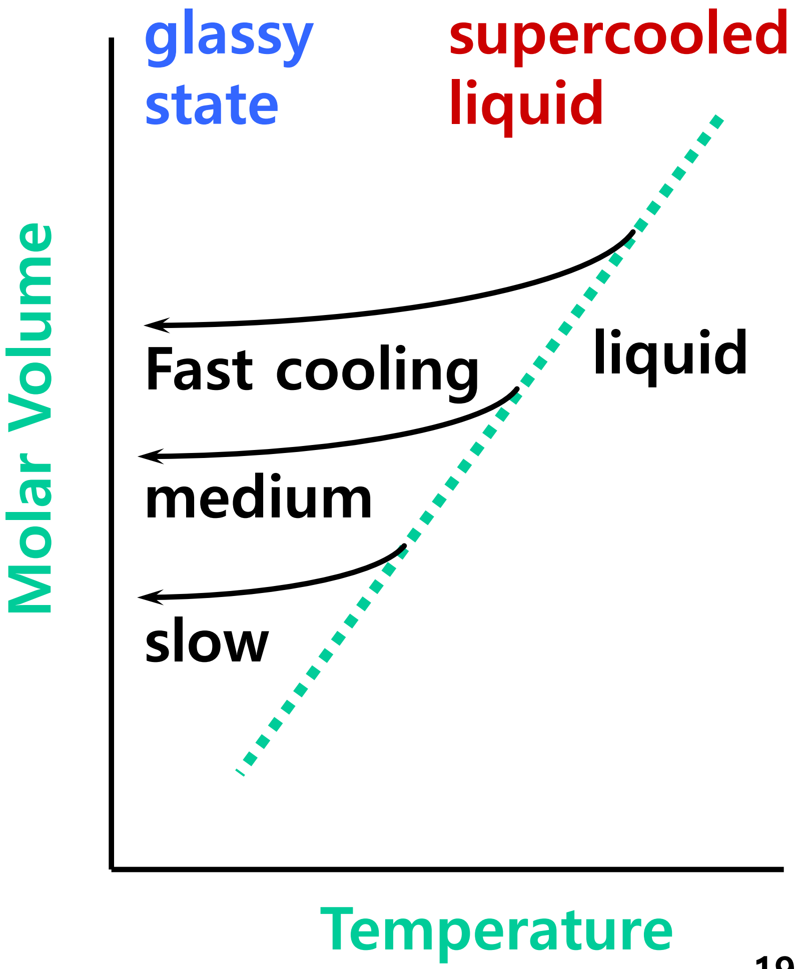


Fundamentals of the Glass Transition

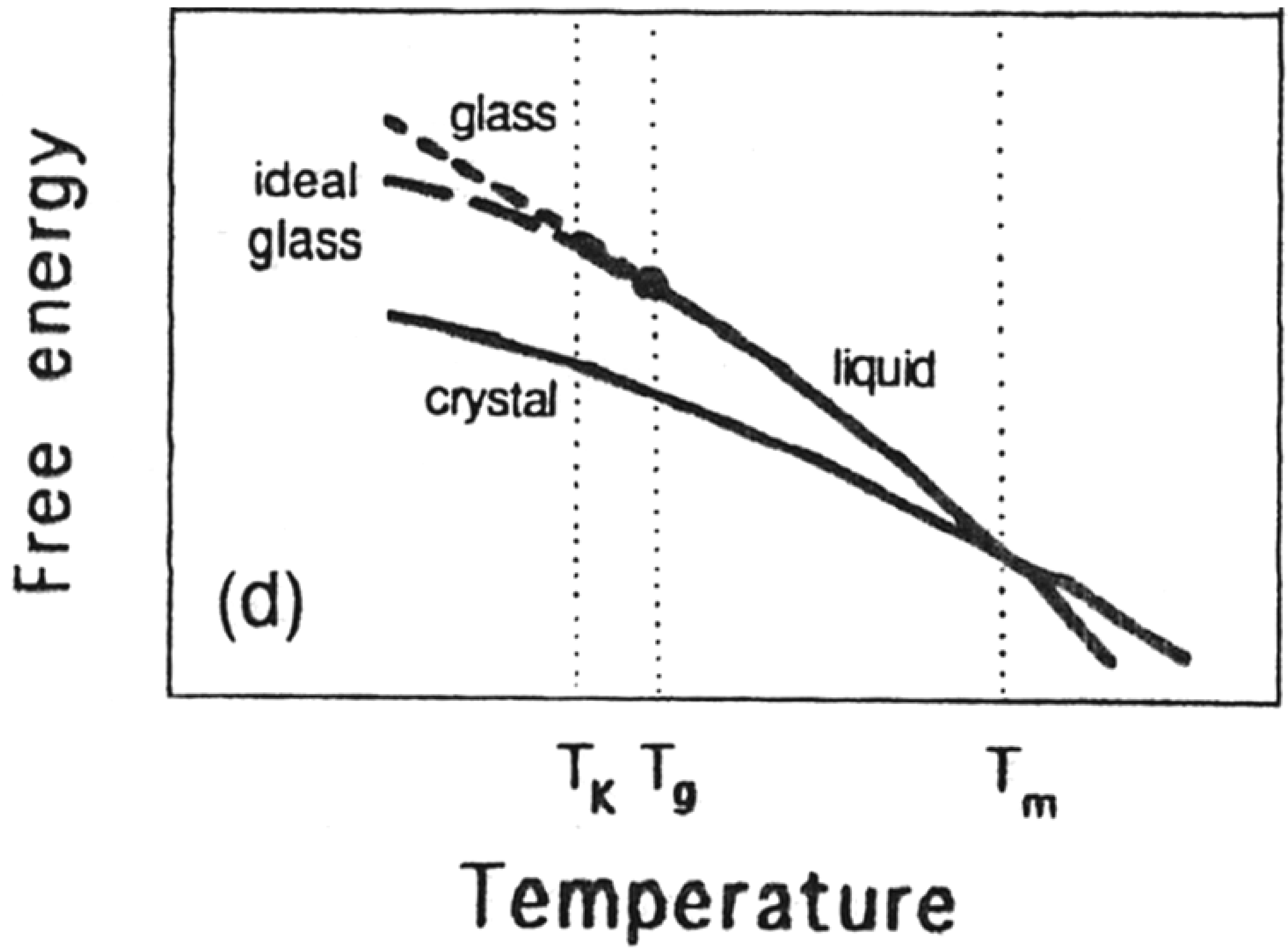
- Melting and Crystallization are Thermodynamic Transitions

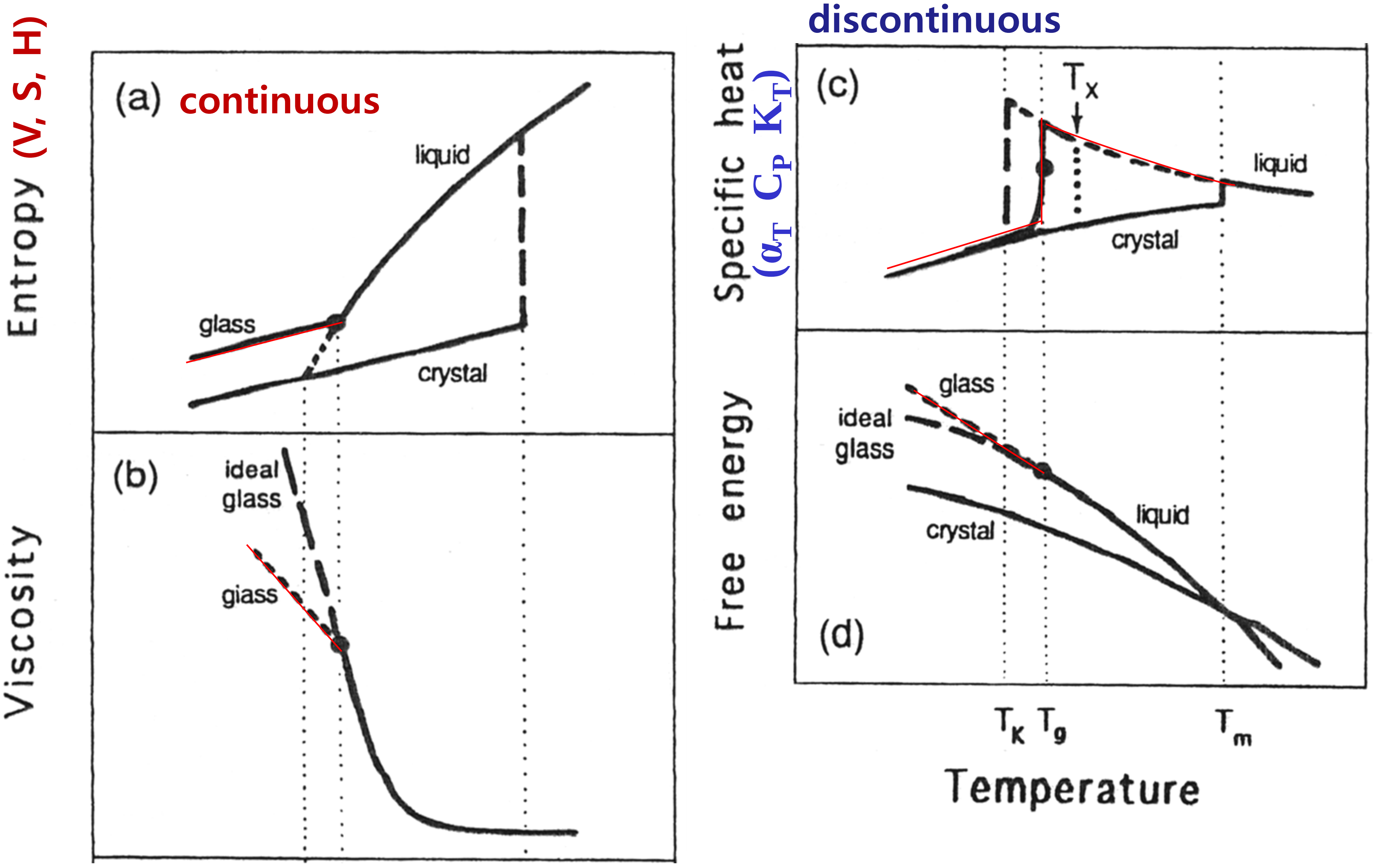


- The Glass Transition is a Kinetic Transition



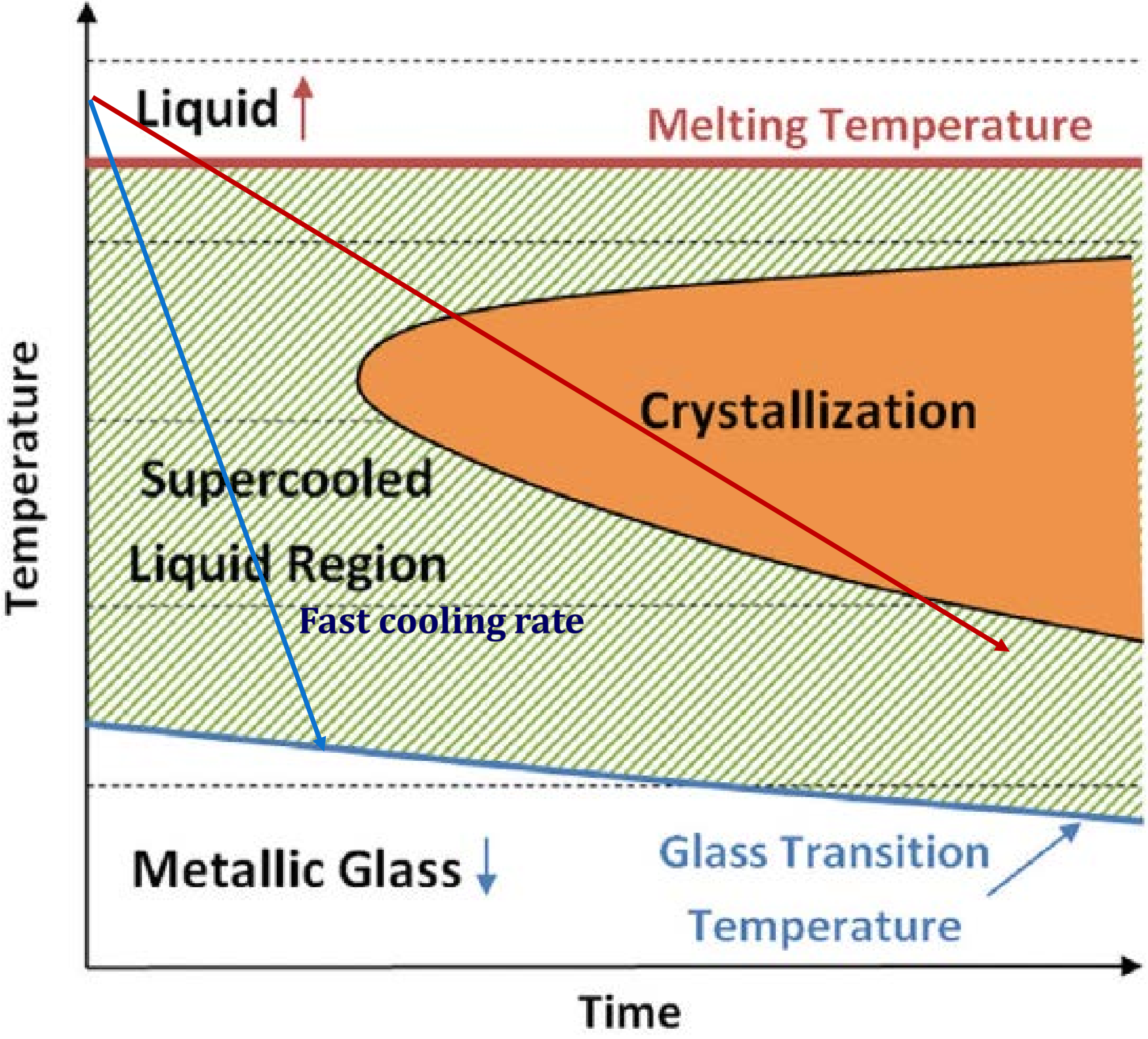
Schematic of the glass transition showing the effects of temperature on free energy





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

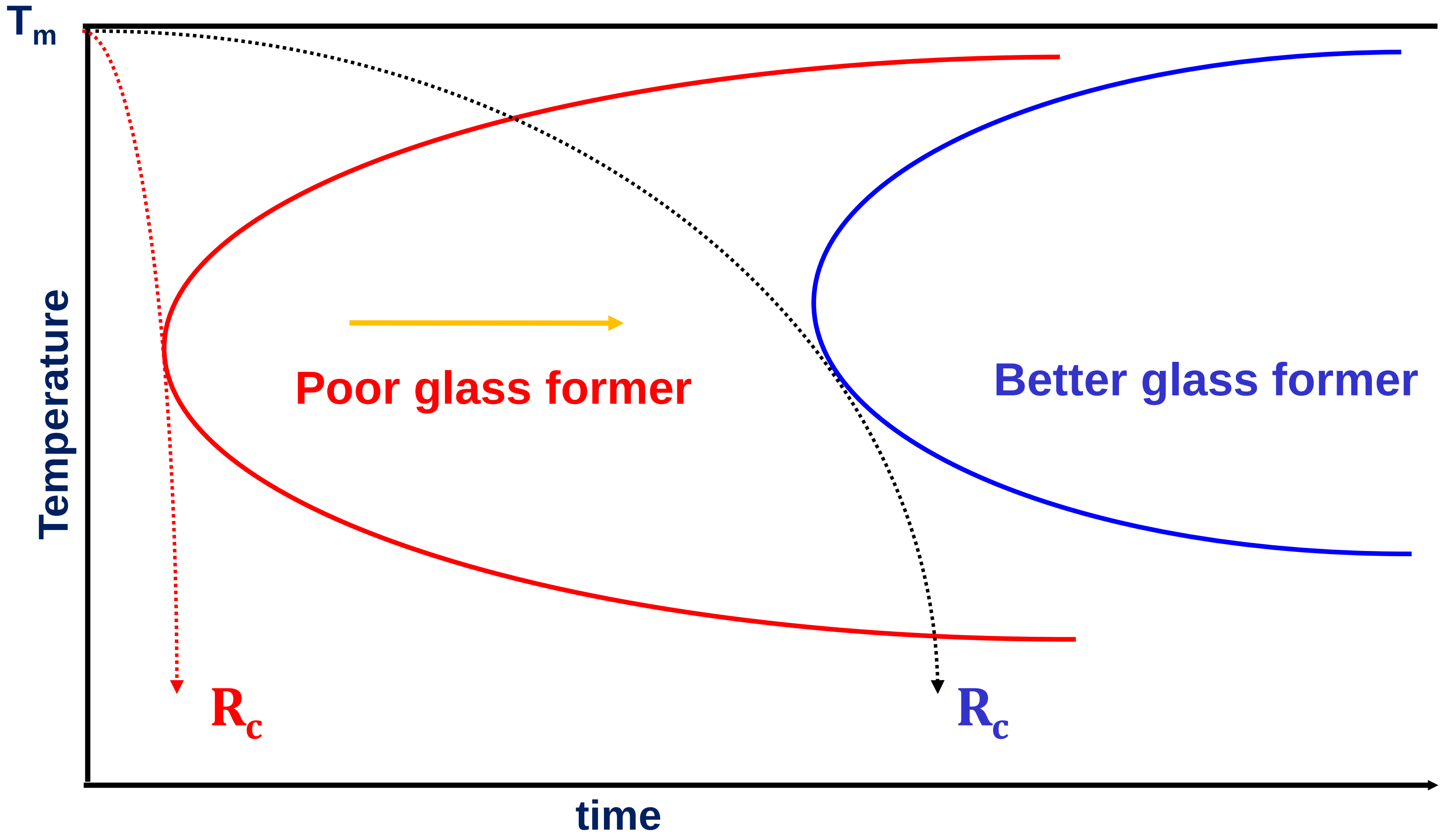


Glass formation : (2) Better Glass Former

GFA

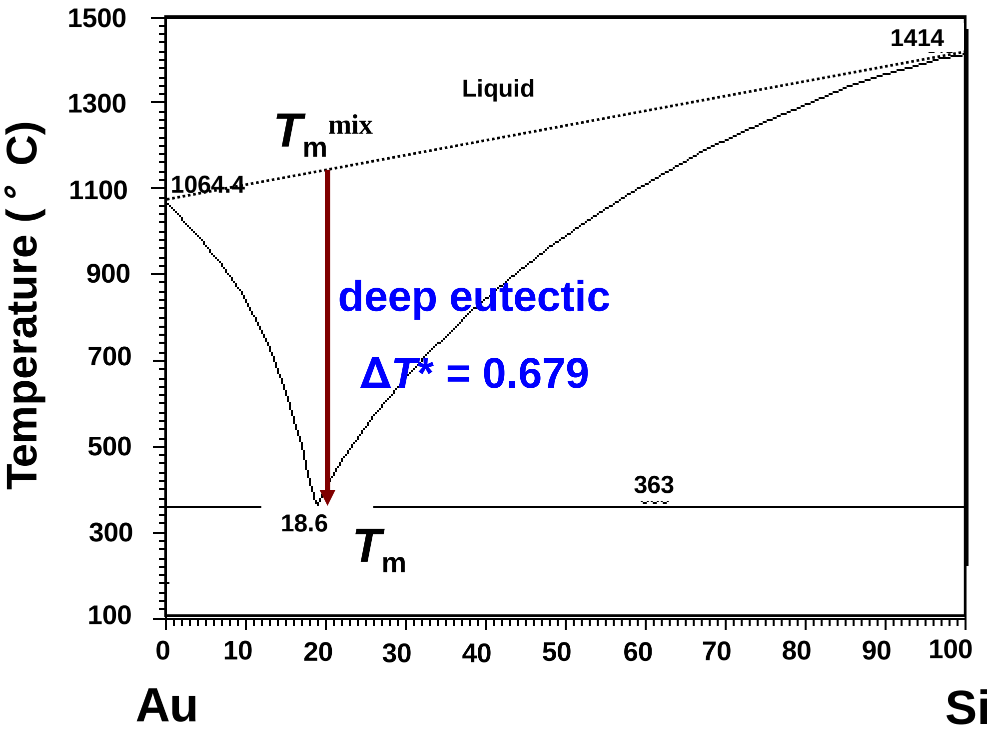
$$R_c = \frac{\Delta T}{t_n}$$

undercooled liquid → crystalline

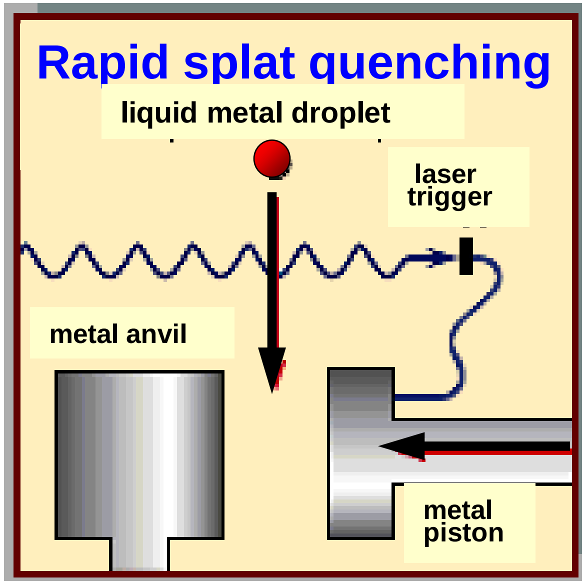


Glass formation : stabilizing the liquid phase

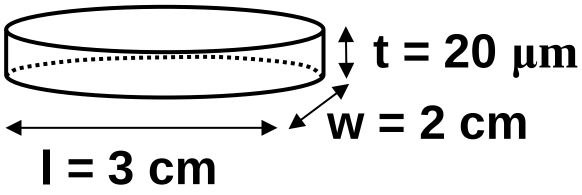
- First metallic glass ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1960.



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



Rapid splat quenching



t = 20 μm

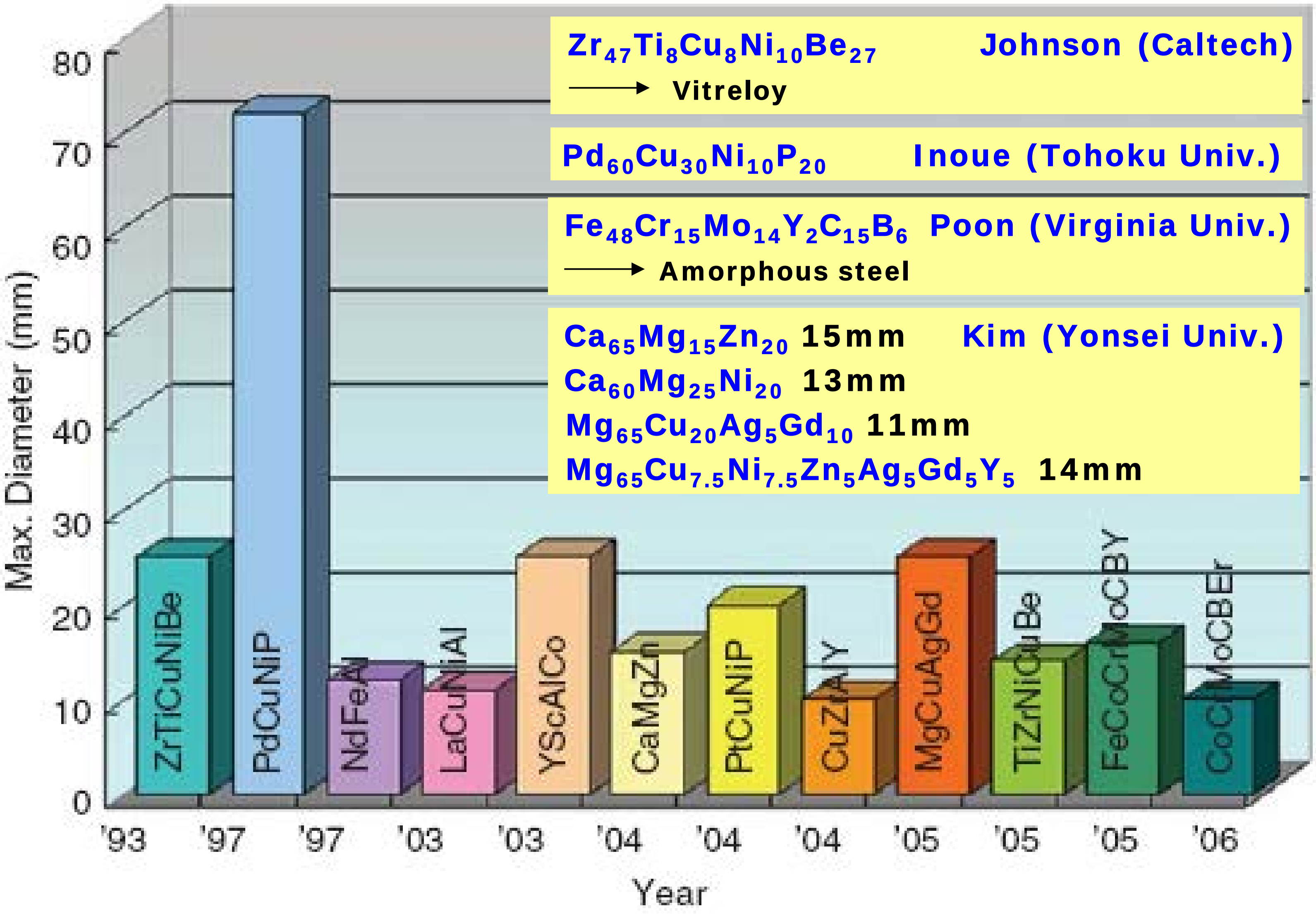
w = 2 cm

l = 3 cm

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

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

Recent BMGs with critical size ≥ 10 mm



$Zr_{47}Ti_8Cu_8Ni_{10}Be_{27}$ 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.

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

Massy Ingot Shape

(a) Pd-Cu-Ni-P

72ϕx 75 mm 80ϕx 85 mm

(b) Zr-Al-Ni-Cu

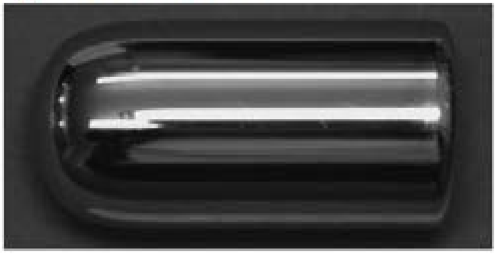
(c) Cu-Zr-Al-Ag

(d) Ni-Pd-P-B

Cylindrical Rods

(e) Pd-Cu-Ni-P

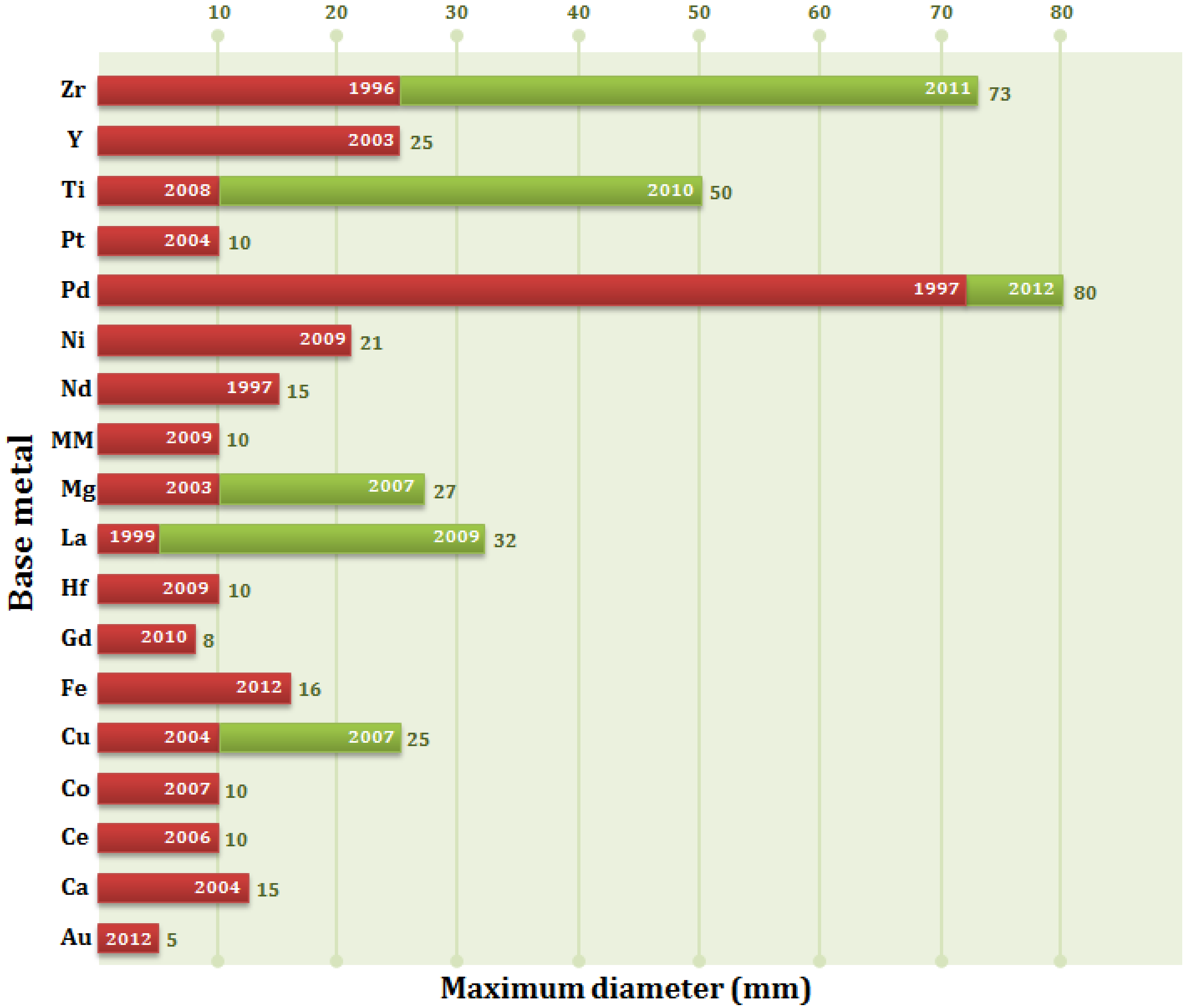
(f) Pt-Pd-Cu-P



Hollow Pipes

(g) Pd-Cu-Ni-P

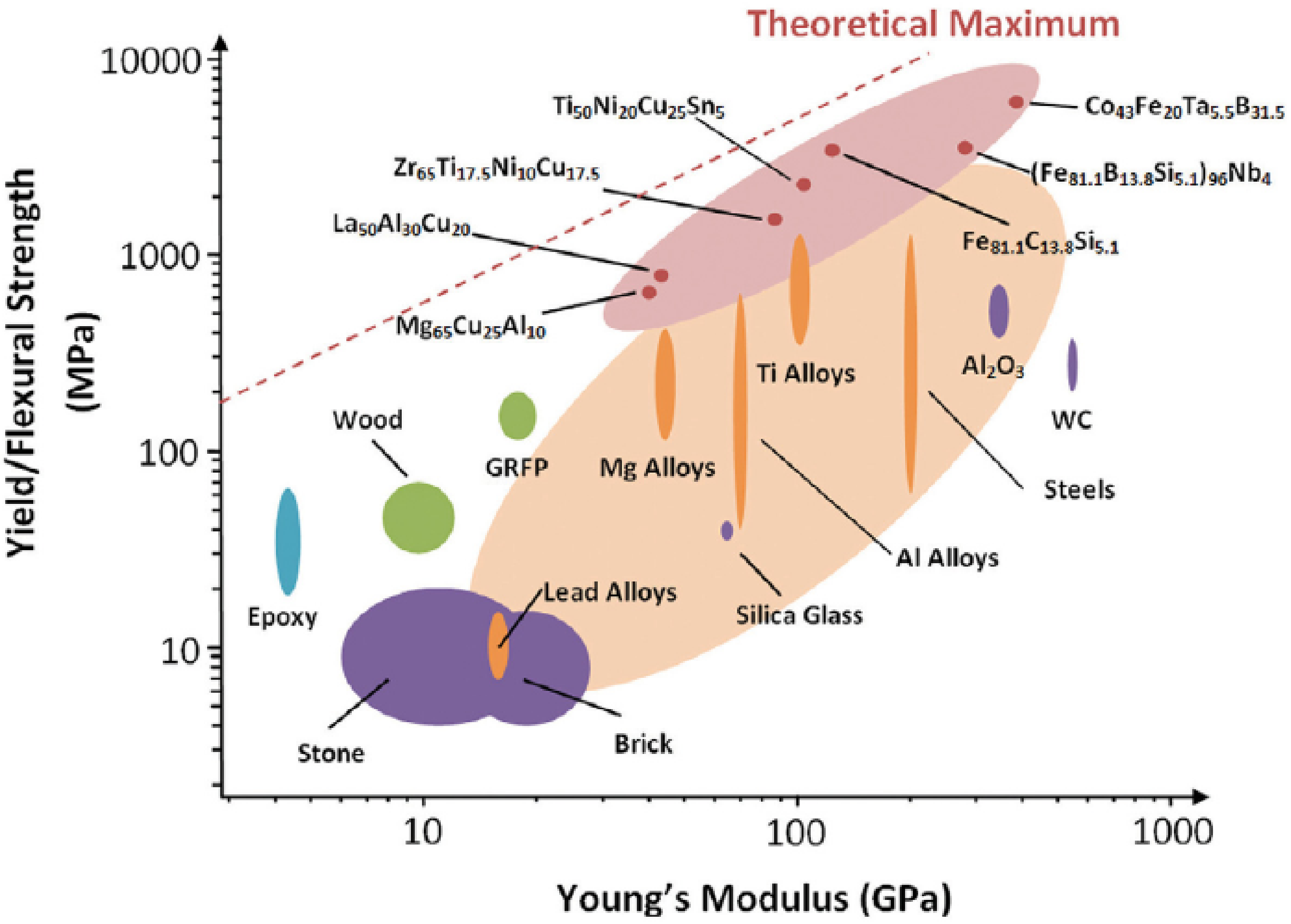
Recent BMGs with critical size ≥ 10 mm



Q: BMG = The 3rd Revolution in Materials?

The 3rd Revolution in Materials

1. High strength of BMGs



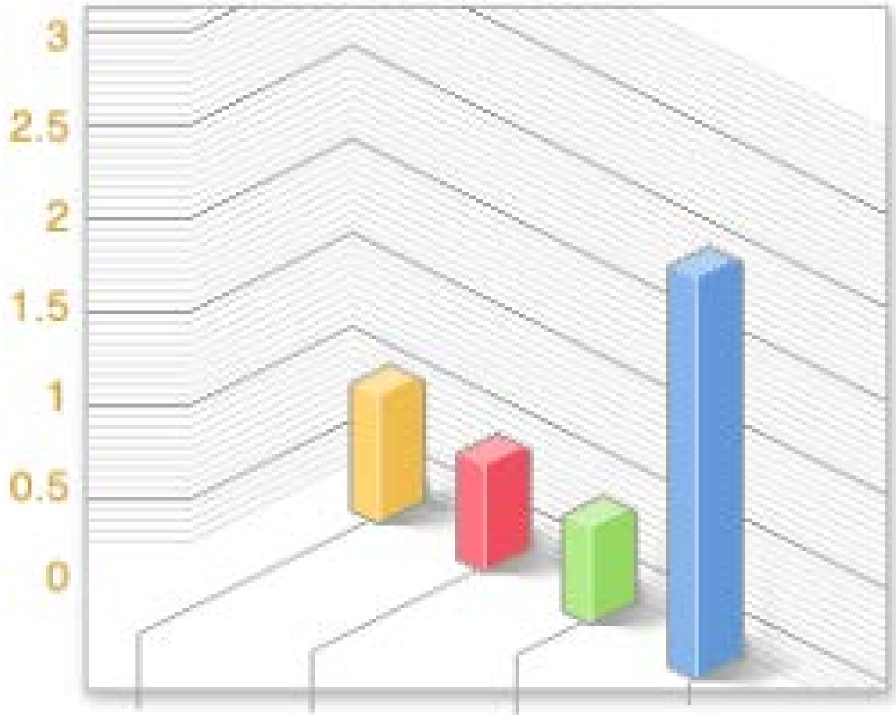
High fracture strength over 5 GPa in Fe-based BMGs

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

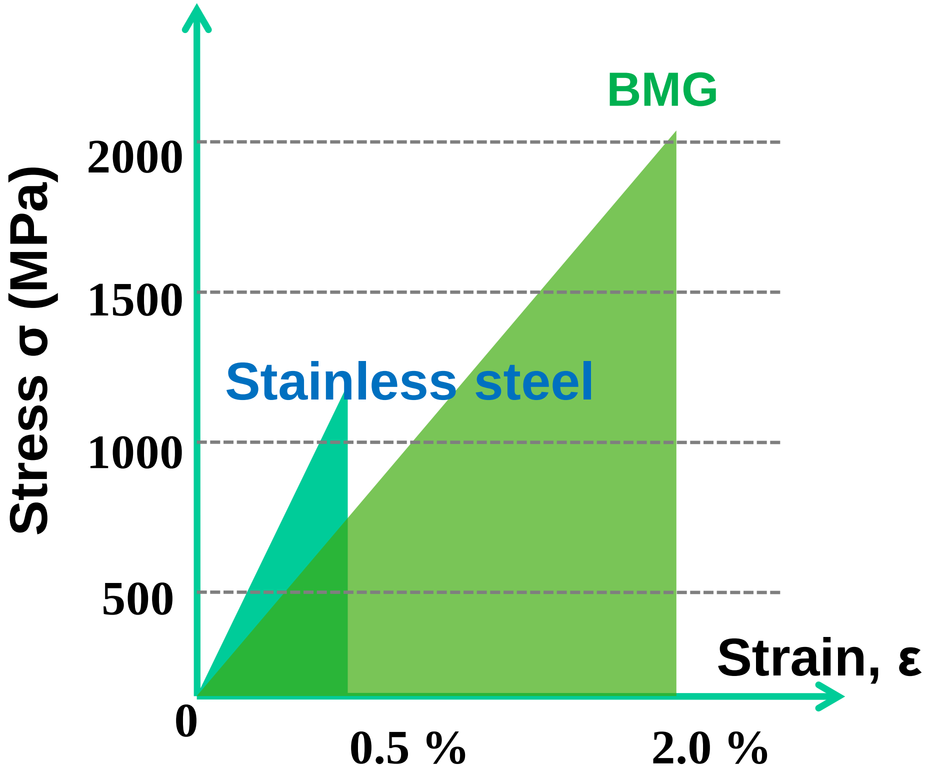
2. Large elastic strain limit of BMGs

Elastic Strain Limit

[as % of Original Shape]

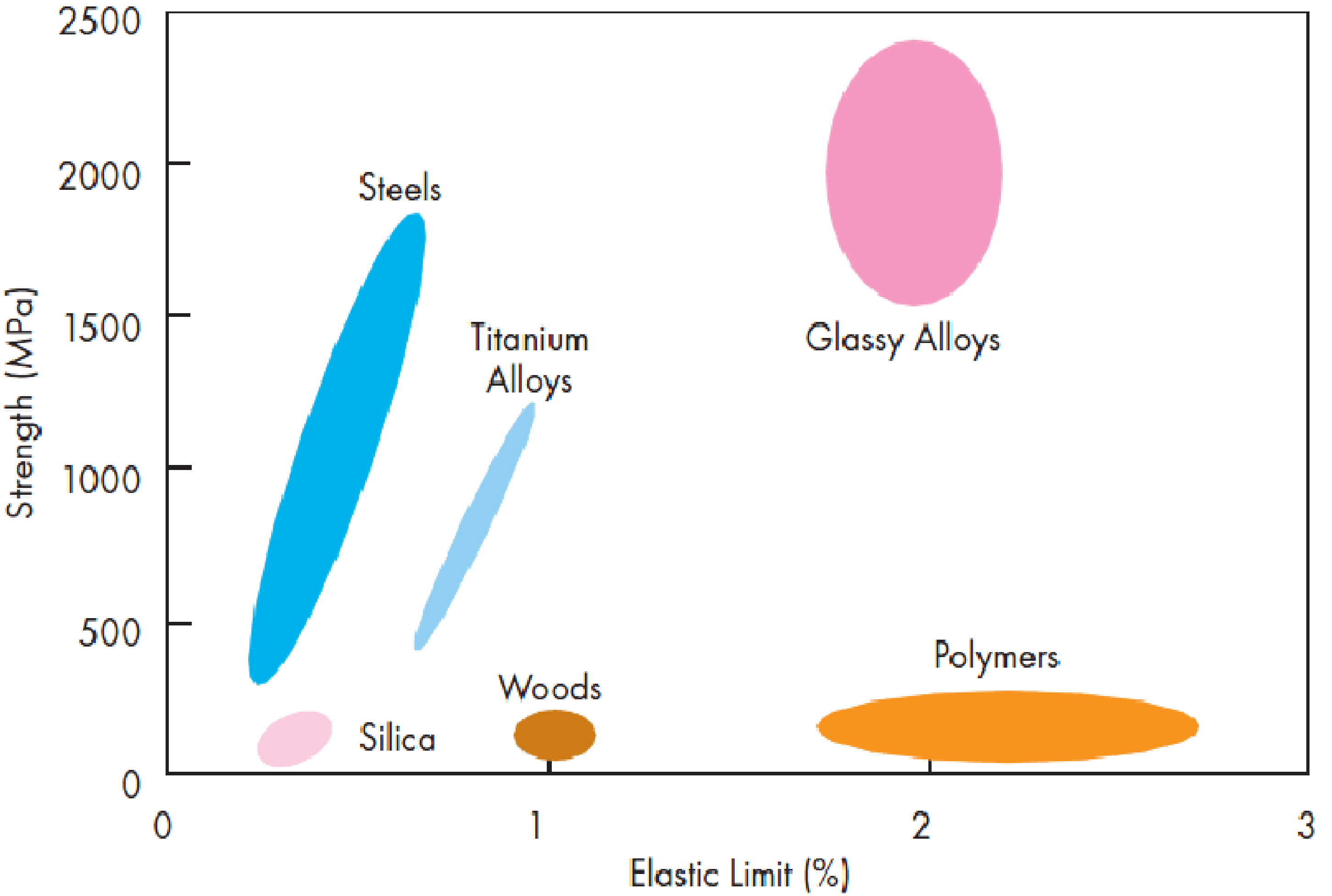


Stress-Strain Curve



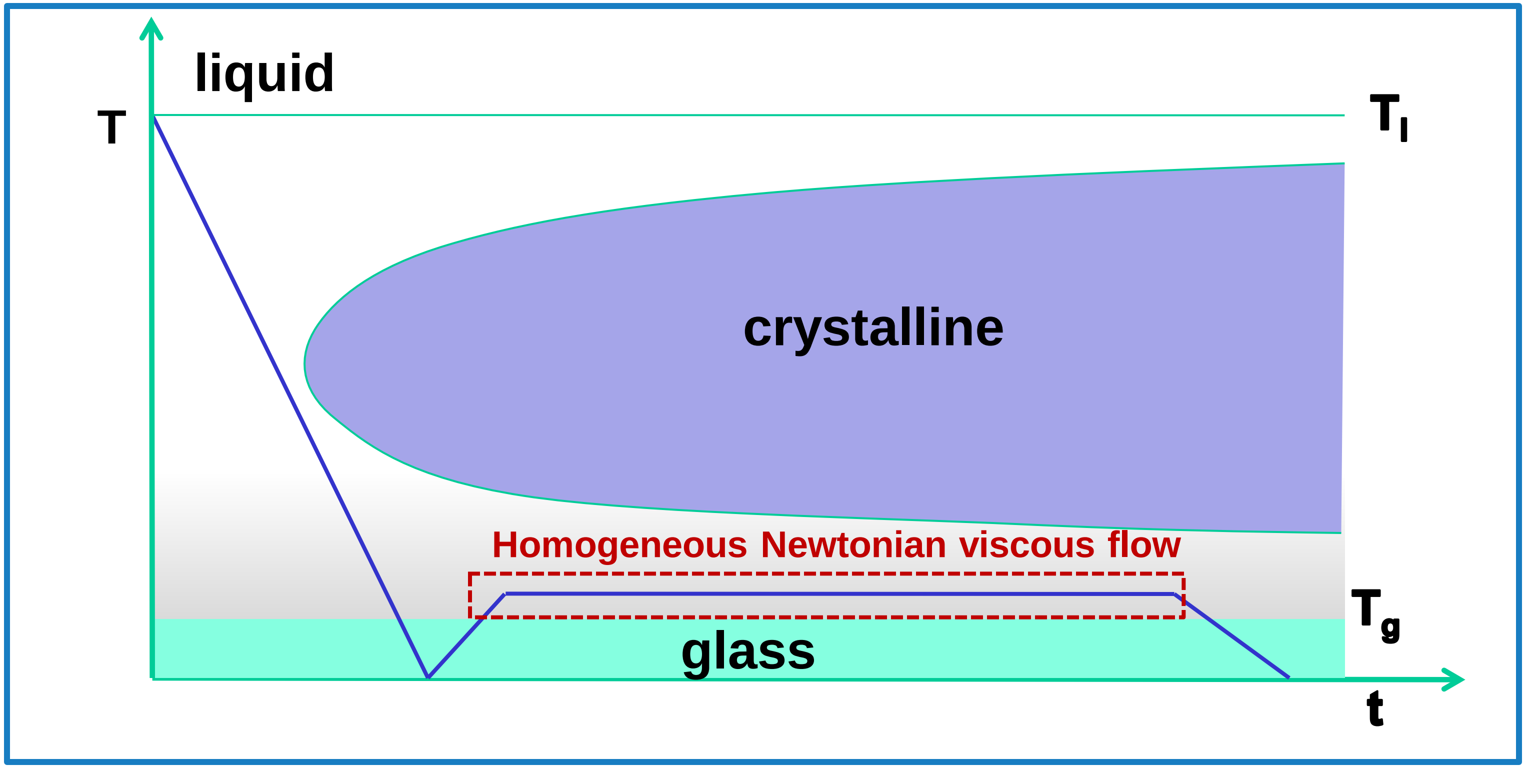
2. Large elastic strain limit of BMGs

Metallic Glasses Offer a Unique Combination of “High Strength” and “High Elastic Limit”



3. Processing metals as efficiently as plastics

* Thermoplastic forming in SCLR

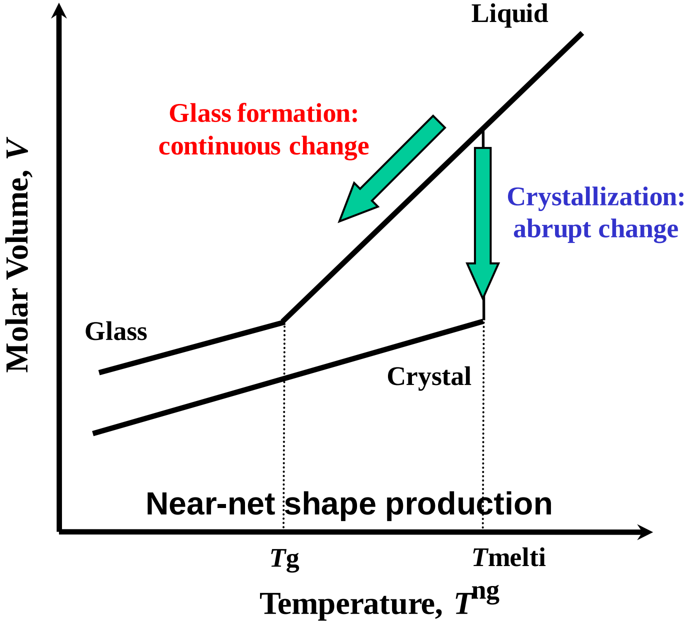


Metallic glass can be processed like plastics by homogeneous Newtonian viscous flow in supercooled liquid region (SCLR).

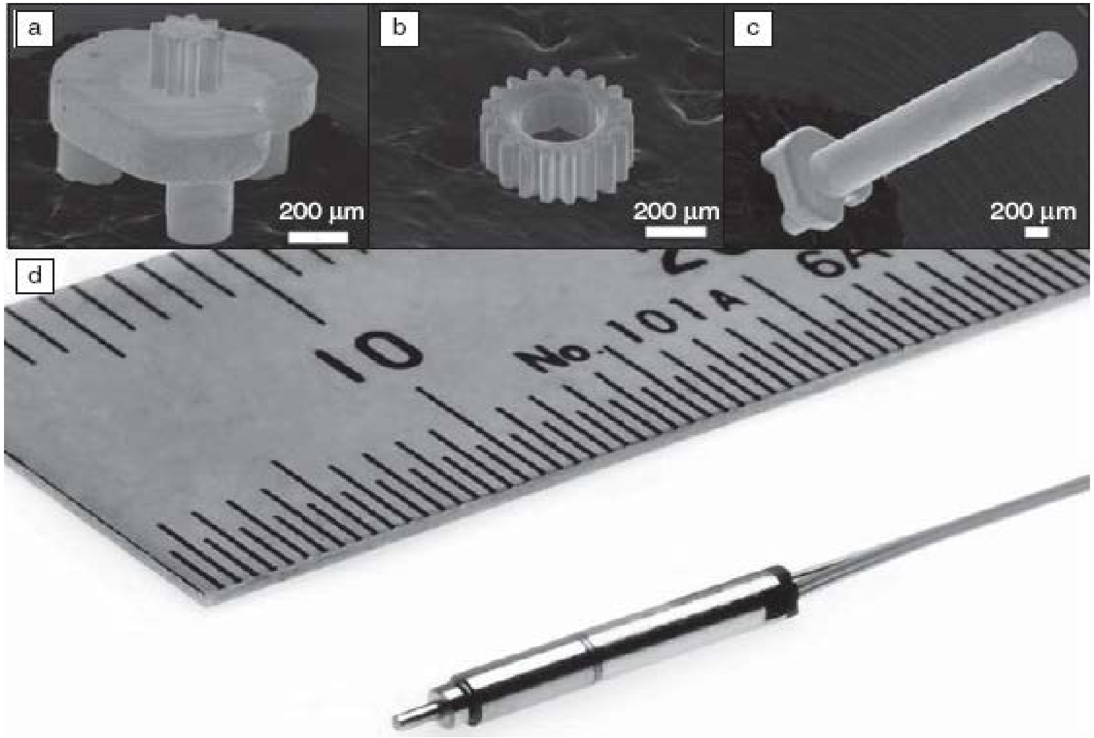
➡ **Possible to deform thin and uniform in SCLR**

3. Processing metals as efficiently as plastics

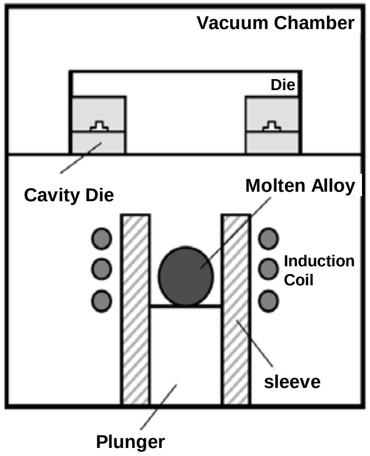
(a) Micro-casting



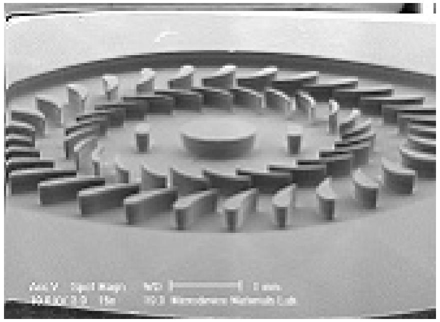
Near-net shape production

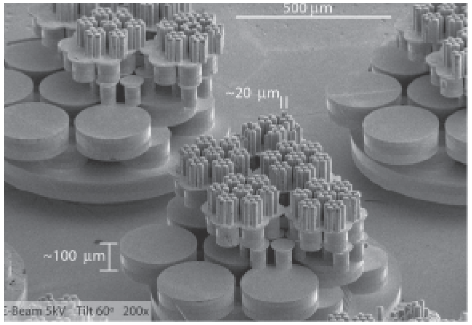


Precision Gears for Micro-motors



Precision die casting

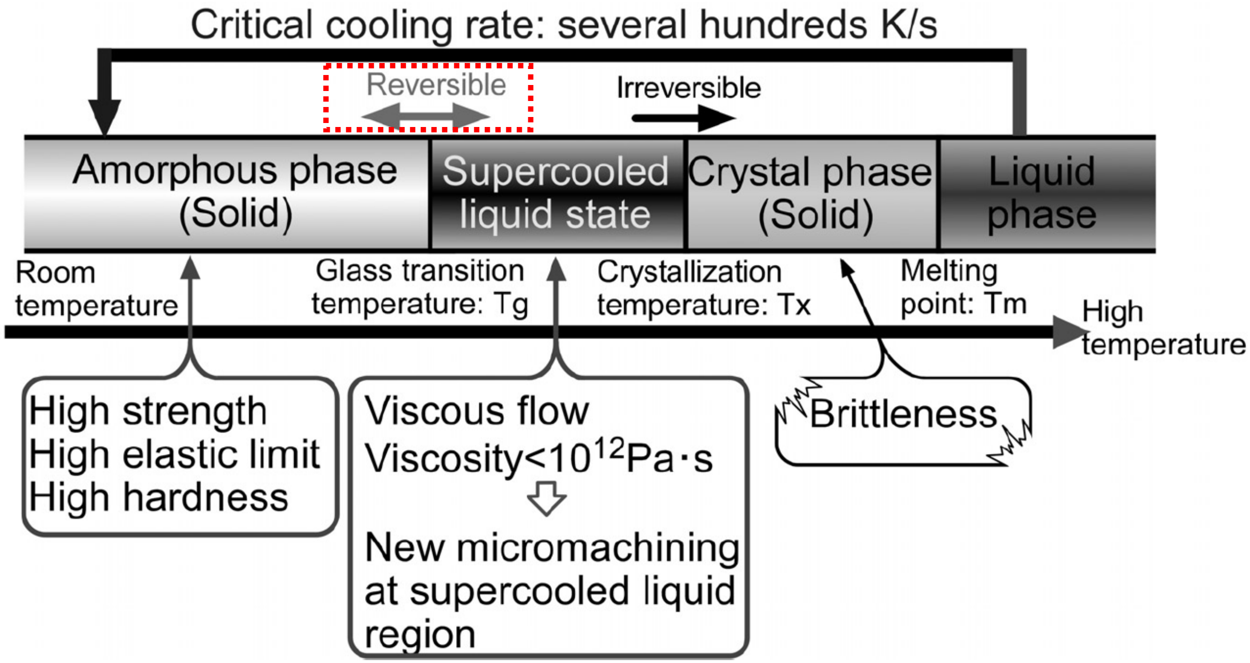




MRS BULLETIN ***32*** *(2007)654.*

3. Processing metals as efficiently as plastics

(b) Micro-forming



Critical cooling rate: several hundreds K/s

Reversible

Irreversible

Amorphous phase (Solid)

Supercooled liquid state

Crystal phase (Solid)

Liquid phase

Room temperature

Glass transition temperature: Tg

Crystallization temperature: Tx

Melting point: Tm

High temperature

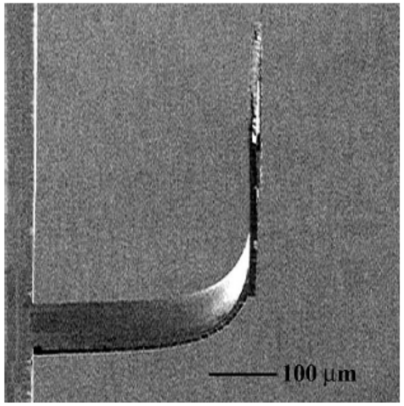
High strength
High elastic limit
High hardness

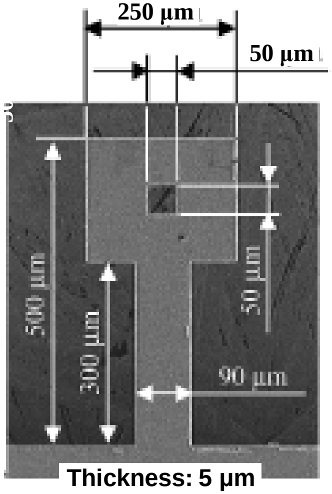
Viscous flow
Viscosity<10^{12}Pa·s
⇩
New micromachining at supercooled liquid region

Brittleness

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

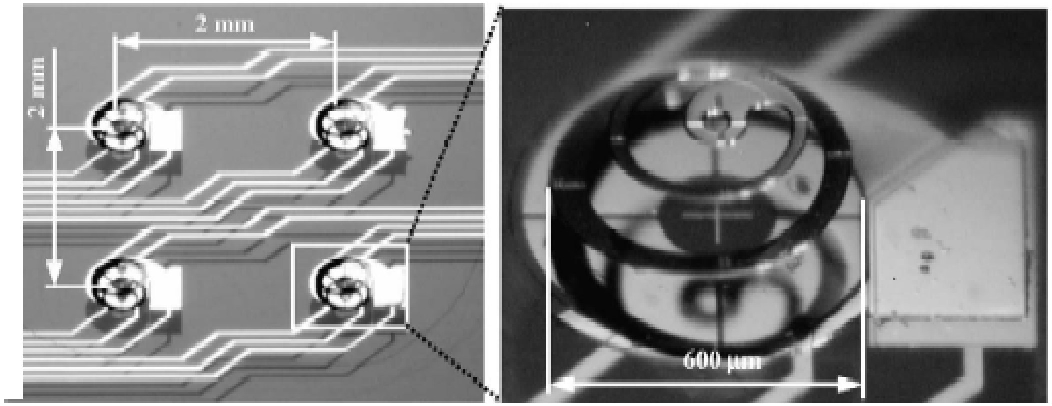
Micro-cantilever





Thickness: 5 µm

Integrated conical spring linear actuator



3. Processing metals as efficiently as plastics

*** Thermoplastic forming in SCLR**

$Mg_{65}Cu_{25}Gd_{10}$ 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**

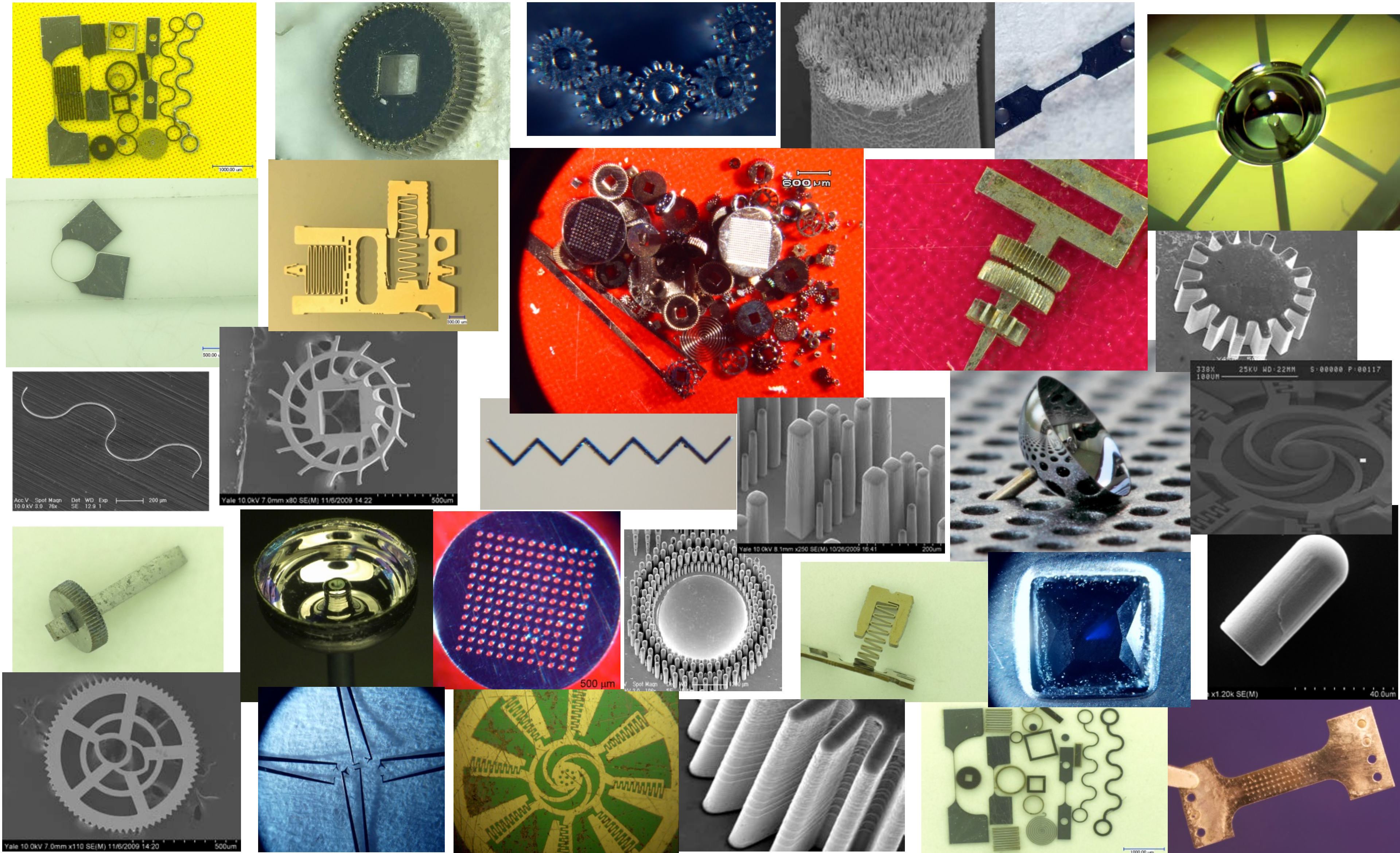
  ↳ **Ideal for small expensive IT equipment manufacturing**

www.MaterialsViews.com

www.advmat.de

Processing of Bulk Metallic Glass

Adv. Mater. **2009**, *21*, 1–32



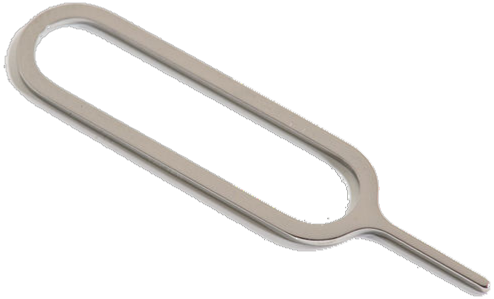
“Yale professor makes the case for Supercool Metals”

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

High performance Liquidmetal® alloy phone case.

Apple is using Liquidmetal for…



USIM ejector (iphone 4)

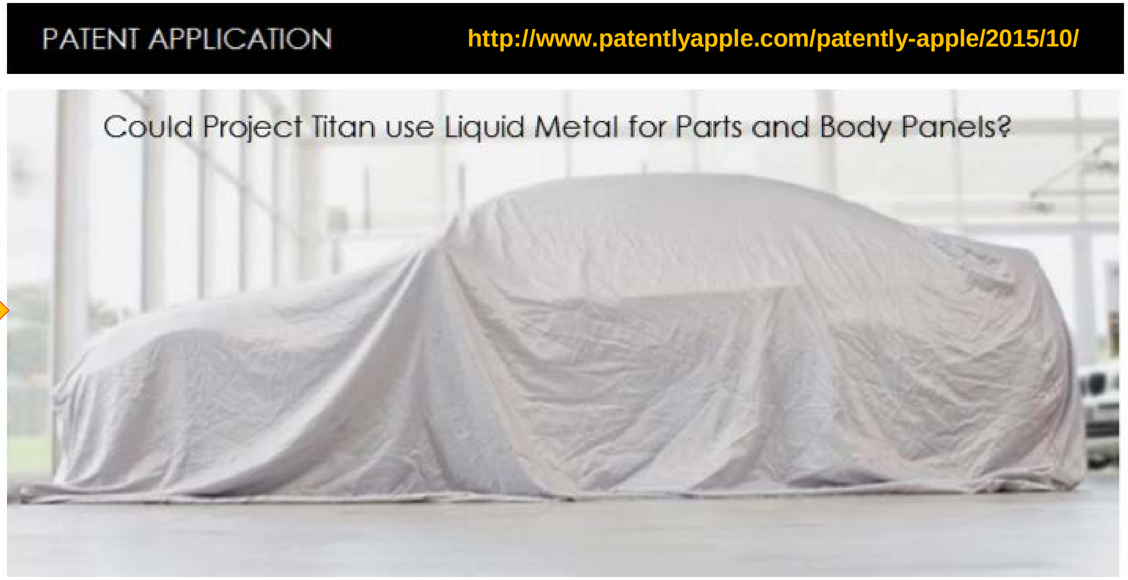
Enclosure / Antenna

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.

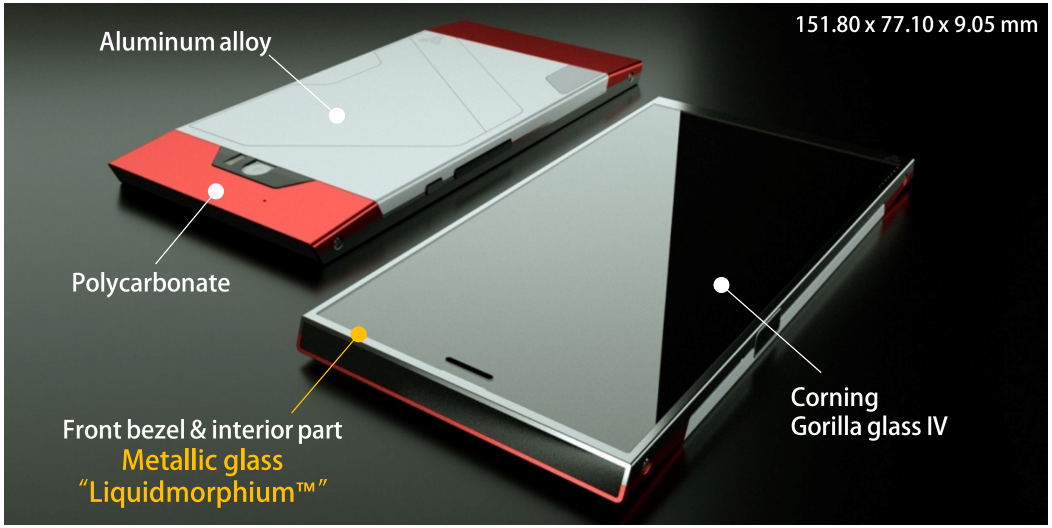
First smart phone with BMG exterior

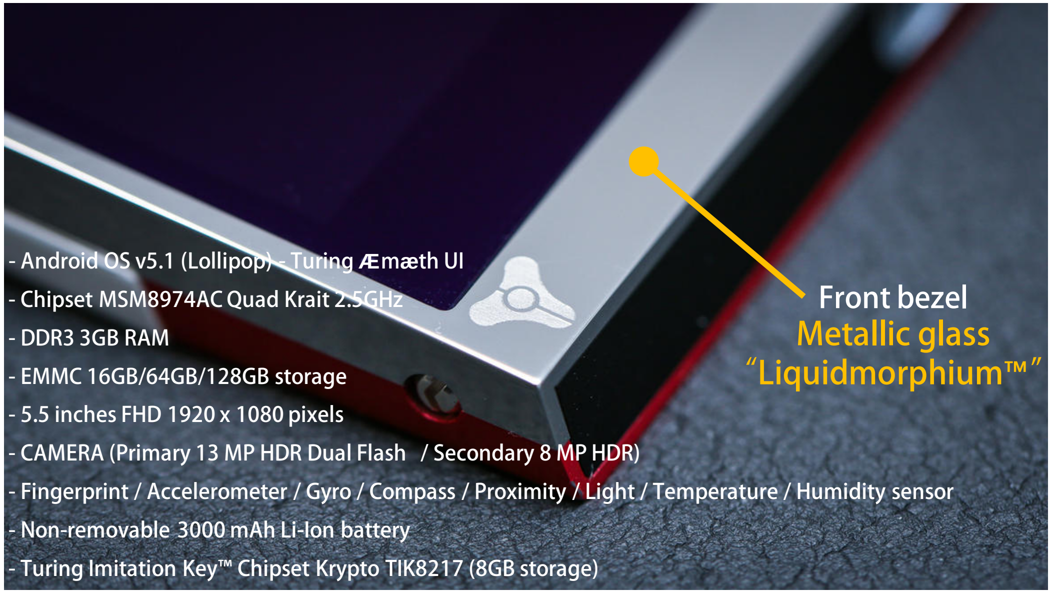
Turing phone

by Turing Robotics Industries (UK)

with

Metallic glass
“Liquidmorphium™”





- Android OS v5.1 (Lollipop) - Turing Æmæth UI
- Chipset MSM8974AC Quad Krait 2.5GHz
- DDR3 3GB RAM
- EMMC 16GB/64GB/128GB storage
- 5.5 inches FHD 1920 x 1080 pixels
- CAMERA (Primary 13 MP HDR Dual Flash / Secondary 8 MP HDR)
- Fingerprint / Accelerometer / Gyro / Compass / Proximity / Light / Temperature / Humidity sensor
- Non-removable 3000 mAh Li-Ion battery
- Turing Imitation Key™ Chipset Krypto TIK8217 (8GB storage)

“Unhackable”

“Waterproof”

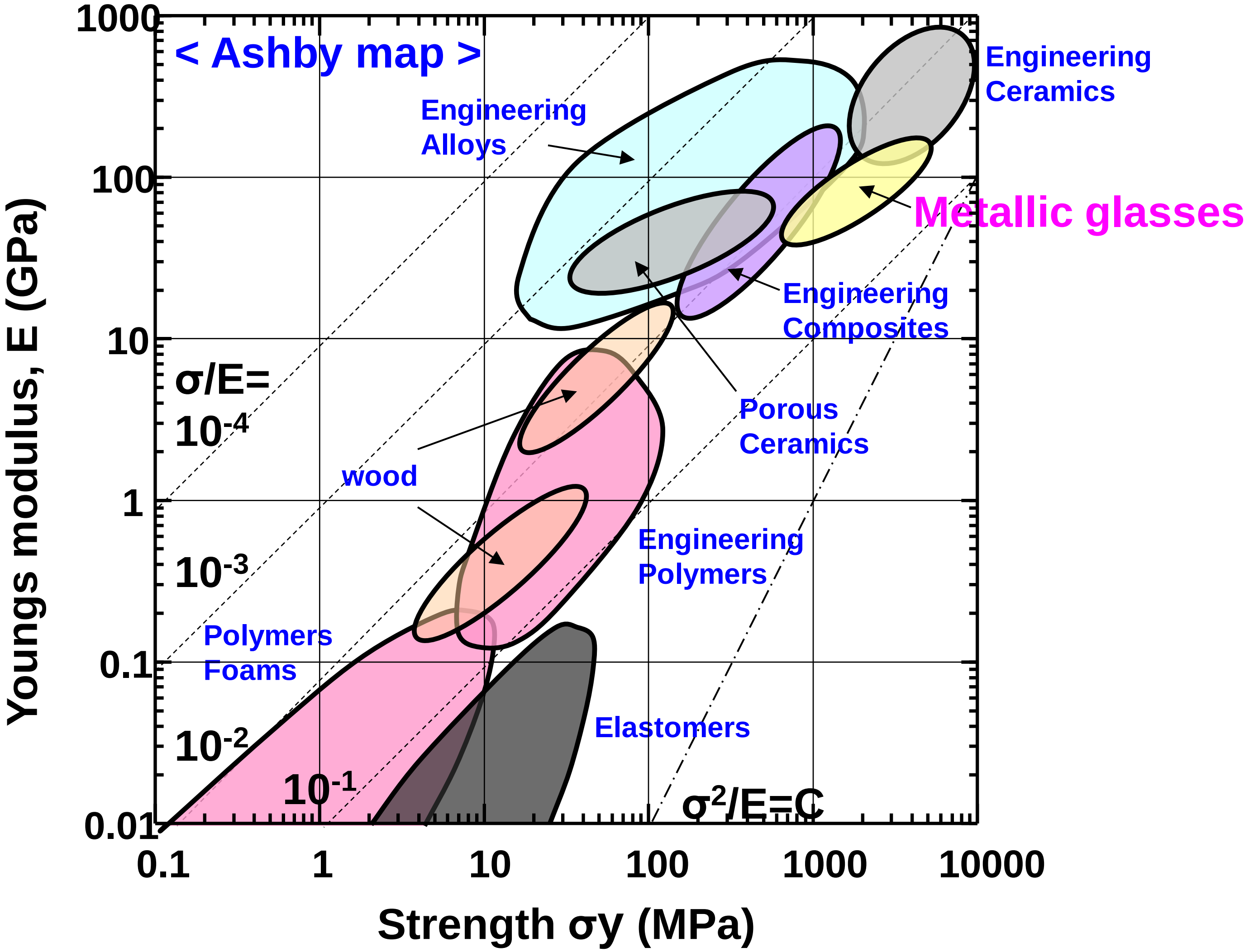
+

“Unbreakable”

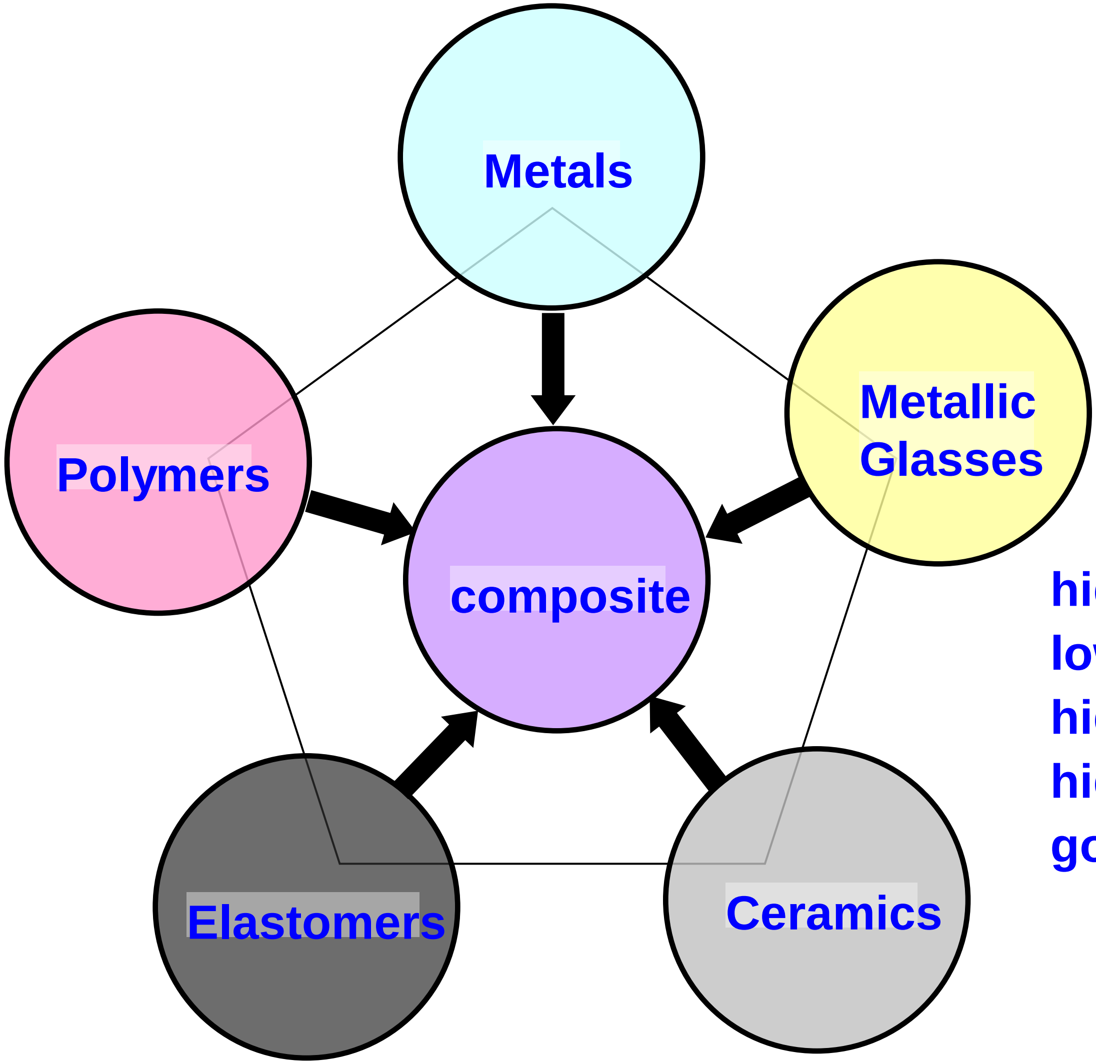
The Turing Phone is built with a pioneering material called Liquidmorphium™, an amorphous “liquid metal” alloy tougher than either titanium or steel - so what’s in your hand is as strong as your privacy protection.

from https://www.turingphone.com/

A new menu of engineering materials



A new menu of engineering materials



Metals

Polymers

composite

Metallic Glasses

Elastomers

Ceramics

High GFA

High plasticity

higher strength

lower Young’s modulus

high hardness

high corrosion resistance

good deformability

⋮

Skip section 4.5 and 4.8 in the text book

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

until 28th November (before class)

Good Luck!!