2019 Fall

"Advanced Physical Metallurgy"

- Non-equilibrium Solidification -

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Chapter 1. Introduction   Development of New Materials

* Search for new and advanced materials

: addition of alloying elements, microstructural modification and by subjecting the materials to thermal, mechanical, or thermo-mechanical processing methods

→ Completely new materials

“ Stronger, Stiffer, Lighter and Hotter…”

Q1: What kind of new and advanced metallic materials were developed up to now?

: Superalloys, Metallic Glass (1960), Shape Memory Alloys (1963),

Quasi-crystal (1984), Gum Metal (2003), High Entropy Alloy (2004)

Q2: What is the development strategy of completely new materials?

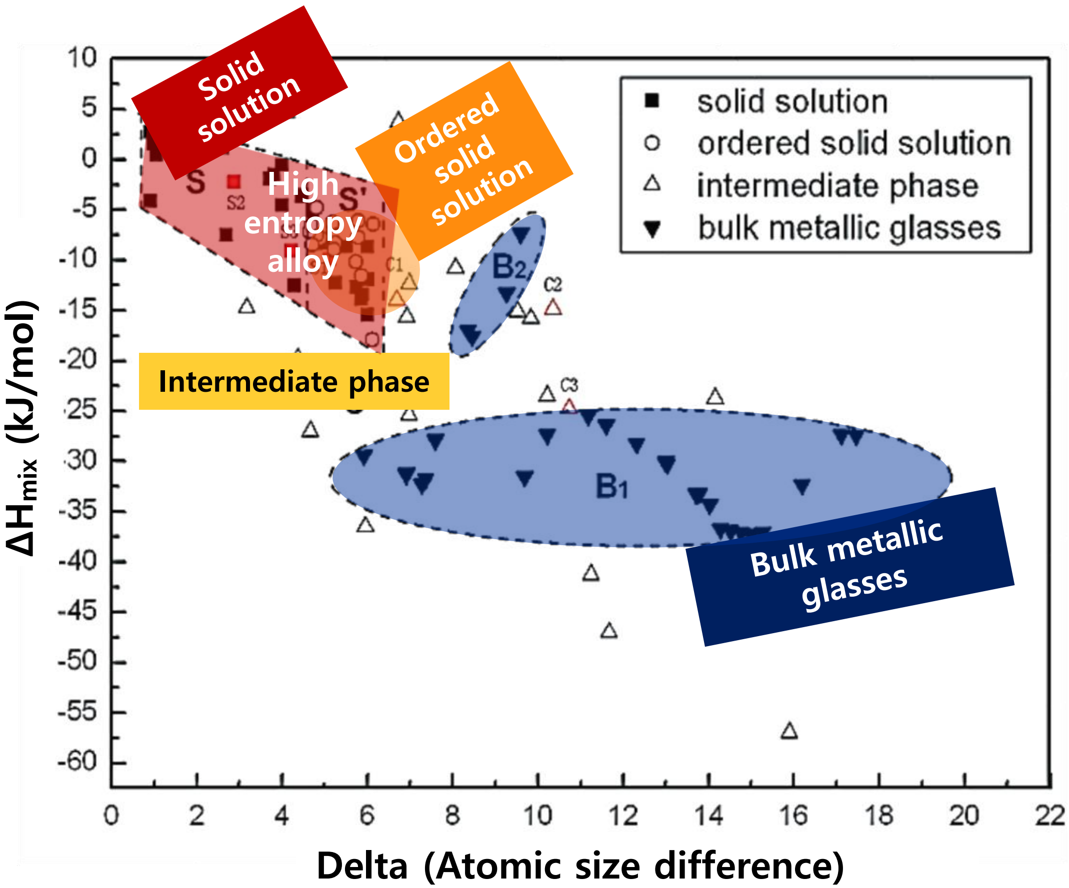
a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

Multi-component system



High entropy alloy (HEA)

- Multi-component systems consisting of more than five elements
- Small difference of atomic size ratio under 12%
- Almost zero value of heats of mixing among the three main constituent elements

Bulk metallic glass (BMG)

- multi-component systems consisting of more than three elements
- Significant difference in atomic size ratios above about 12% among the three constituent elements
- Negative heats of mixing among the three main constituent elements

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Equilibrium conditions → Non-equilibrium conditions

: non-equilibrium processing = "energize and quench" a material

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Condensation from vapor	10^{12}	—	160

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1.3 Rapid Solidification Processing (RSP)

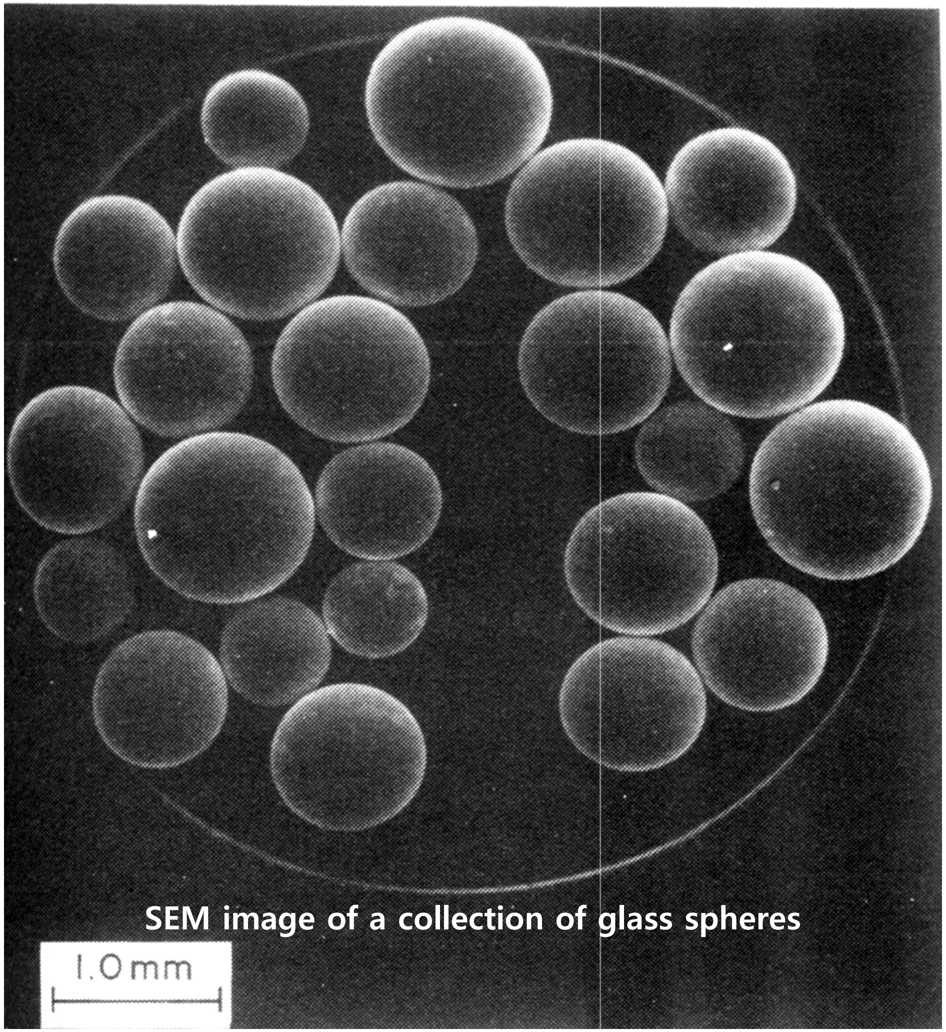
1. *Droplet methods*: In this group of methods, a molten metal is atomized into small droplets, and these are allowed to solidify either in the form of splats (on good thermally conducting substrates, e.g., as in "gun" quenching) or by impinging a cold stream of air or an inert gas against the molten droplets (as, for example, in atomization solidification).
2. *Jet methods*: In these methods, a flowing molten stream of metal is stabilized so that it solidifies as a continuous filament, ribbon, or sheet in contact with a moving chill surface (e.g., chill block melt spinning and its variants).

   A typical solidification rate for a foil of 50 um thickness is about 10^6 K/s.
3. *Surface melting technologies*: These methods involve rapid melting at the surface of a bulk metal followed by high rates of solidification achieved through rapid heat extraction into the unmelted block (laser surface treatments).

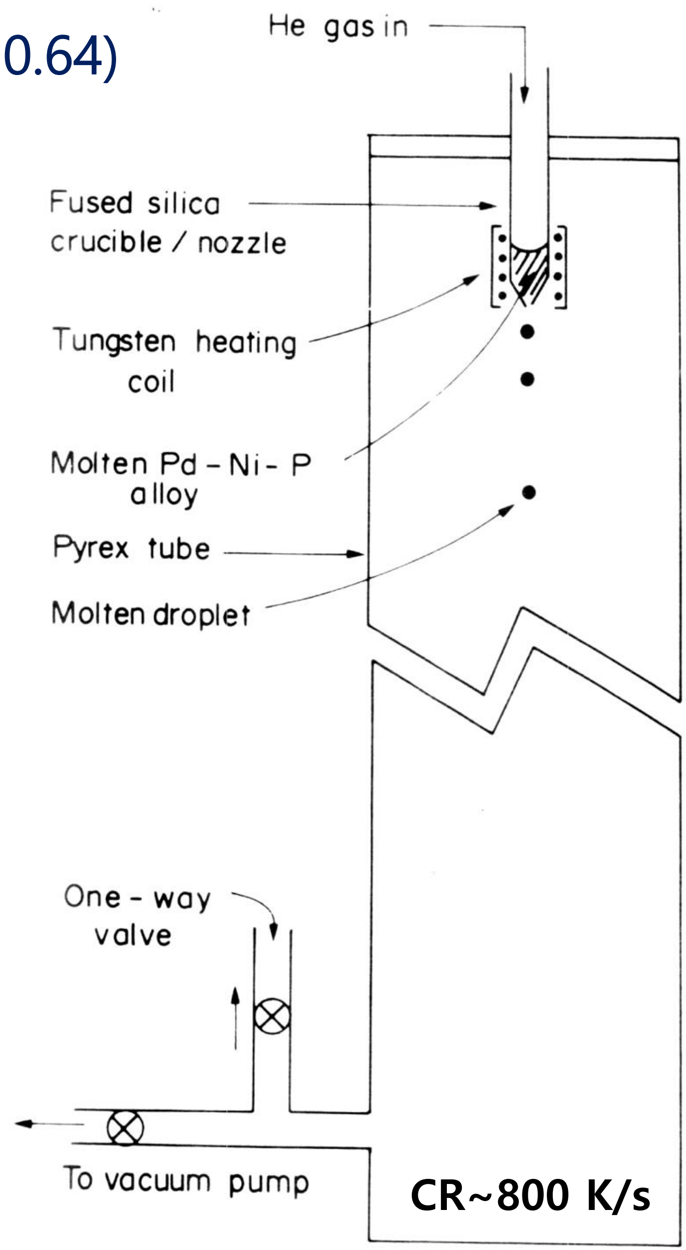
Bulk formation of metallic glass

- First bulk metallic glass: $Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)

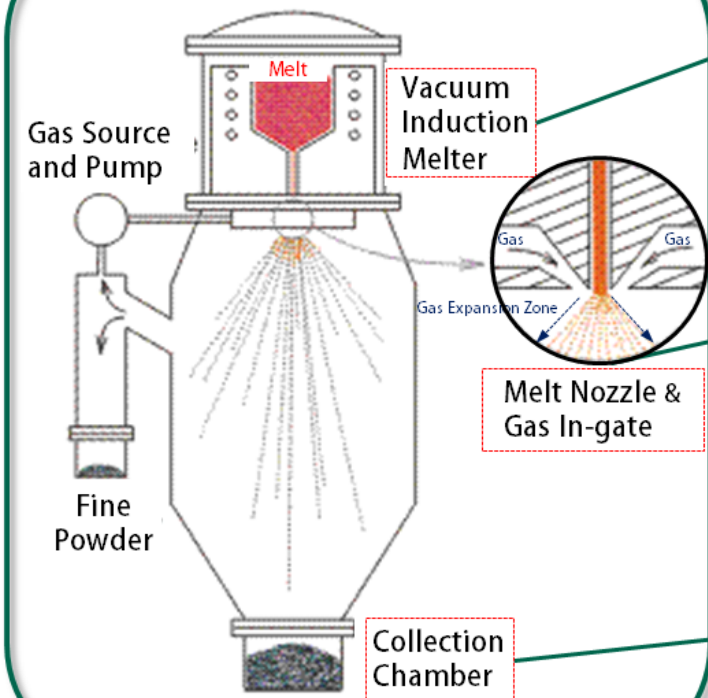
By droplet quenching (CR~800 K/s)

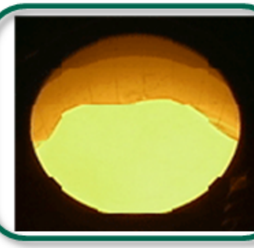


SEM image of a collection of glass spheres



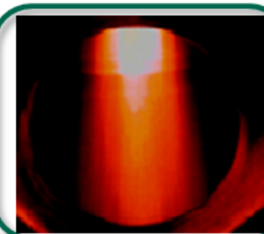
Gas Atomization





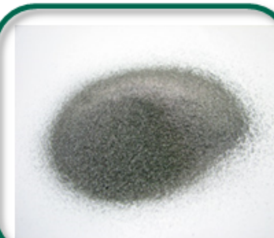
- **Melting Furnace Facility**

  Melting of Metal or Ceramics



- **Melt Nozzle and Gas In-gate**

  A rapidly expanding gas breaks up the liquid stream → thin sheet → ligament → ellipsoid → sphere.



- **Collection Chamber**

  The collection chamber is designed to maximize the yield, minimize contamination, and ease of cleaning.

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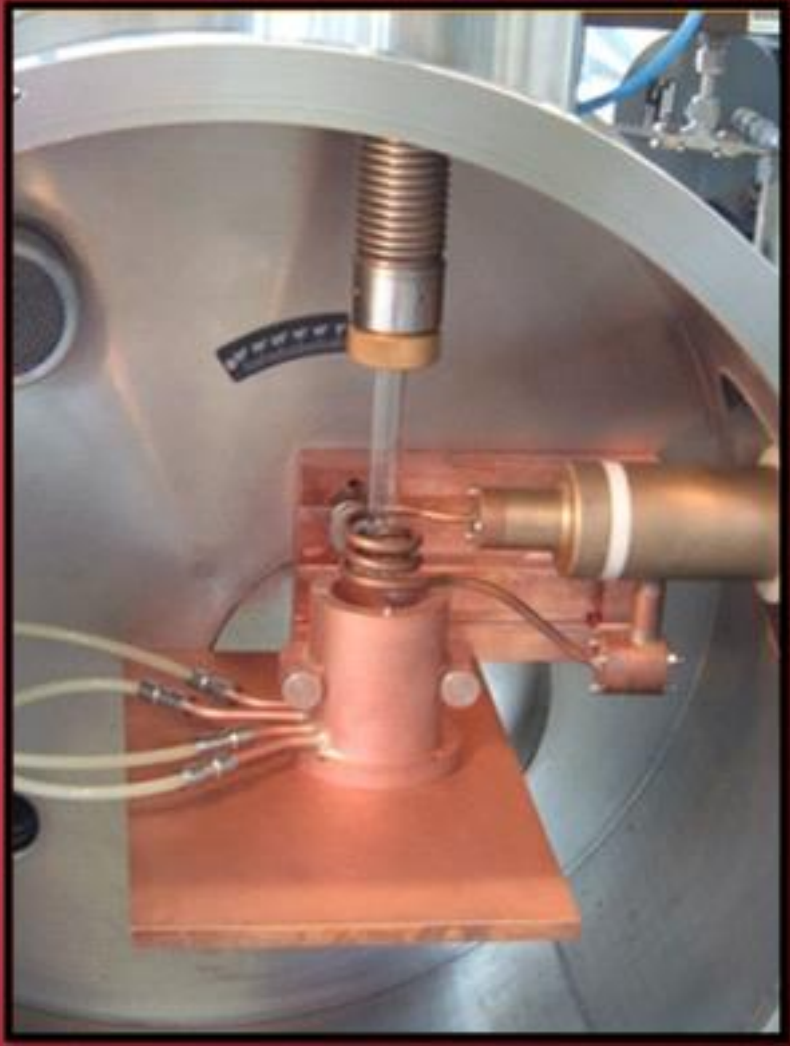
Glass formation : Rapid quenching of liquid phase

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

Bulk sample: rod

Injection casting

- Simple casting method for preparing bulk samples
- Cooling medium : Cu mold with water cooling
- Max. cooling rate for rod sample with
  D=5mm : ~10 K/s
  D=3mm : ~10^2 K/s



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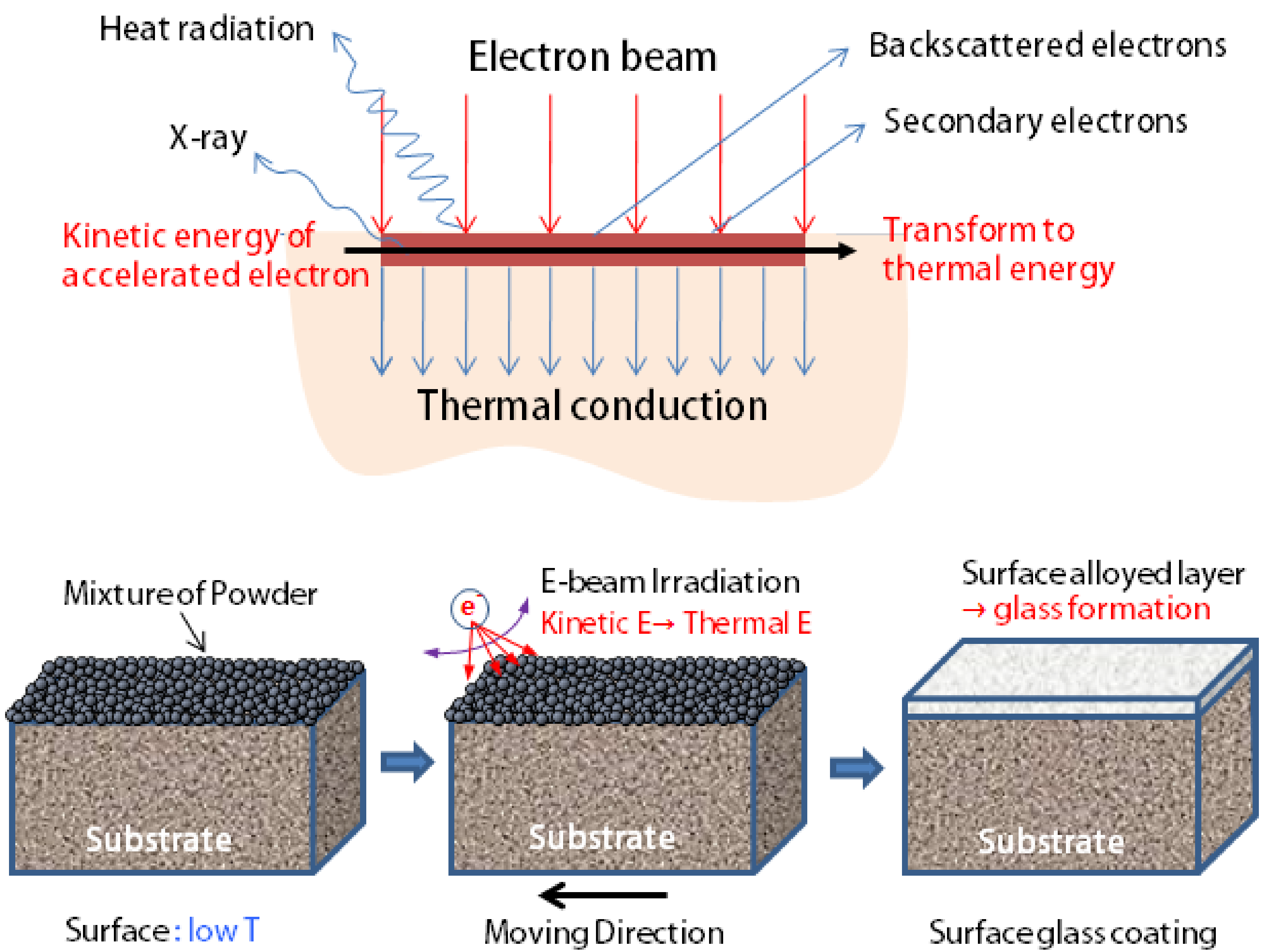

Heat radiation
Electron beam
Backscattered electrons
X-ray
Secondary electrons
Kinetic energy of
accelerated electron
Transform to
thermal energy
Thermal conduction
Mixture of Powder
E-beam Irradiation
Kinetic E→ Thermal E
Surface alloyed layer
→ glass formation
Substrate
Substrate
Substrate
Surface : low T
Moving Direction
Surface glass coating

* Development strategy of completely new materials

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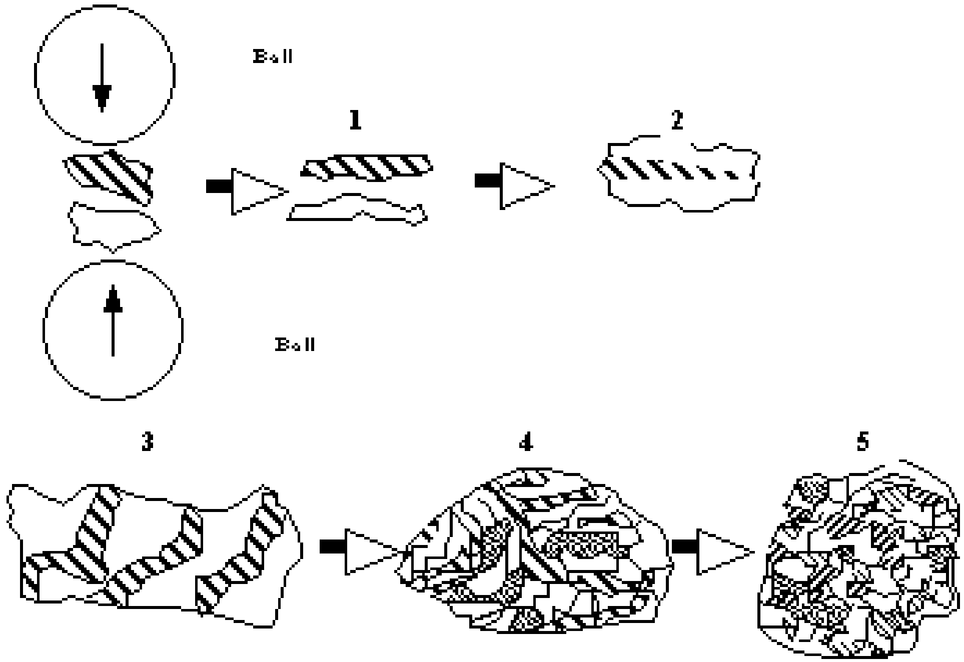
1.4 Mechanical Alloying

Mechanical alloying takes place via repeated plastic deformation, fracturing, and cold welding of powder particles in a high-energy ball mill.

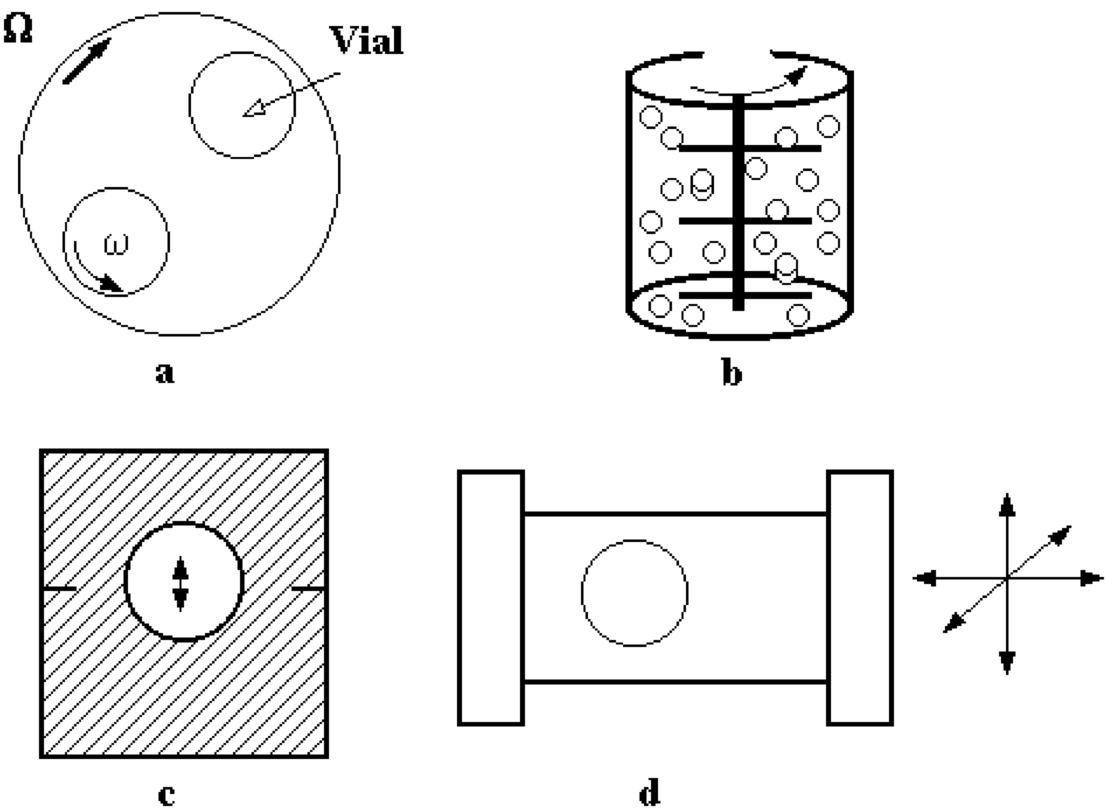
It is a method that can produce extremely small grain size (to below 10 nm), metastable phases (both crystalline and amorphous), and high concentration of lattice defects.

The figure below is a very schematic representation of the process in a mixture of two ductile materials. Notice the formation of layers that get randomized later.



The equipment of mechanical alloying

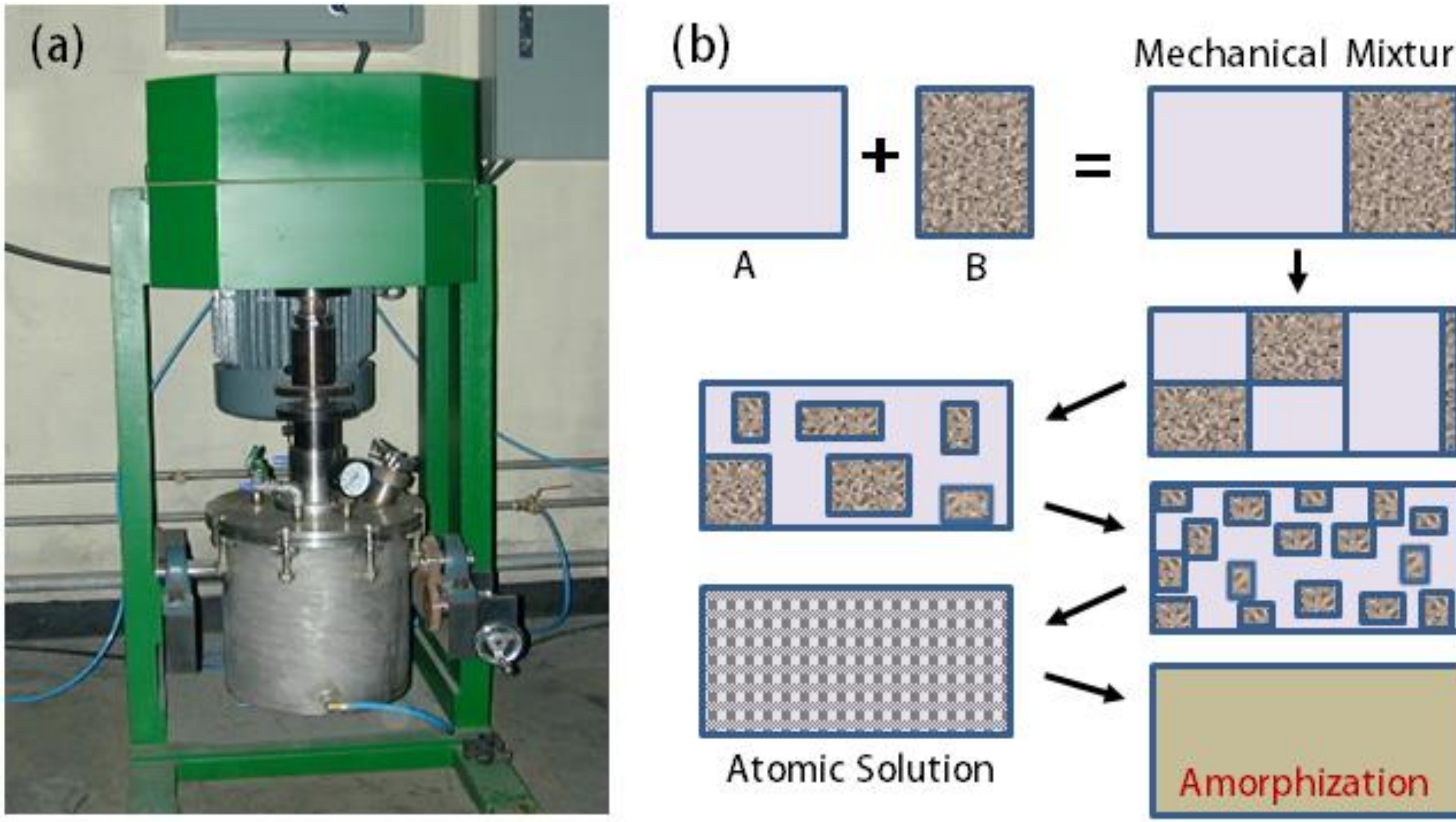
Ball mills produce a mixture of impact and shearing/friction between the balls producing the mixing/alloying needed.



Planetary mills and attritors produce more friction, the dominant form of action in vibratory and shaker mills is impact/compression.

Available mills range from small laboratory versions to large industrial mills.

Mechanical Alloying/ Milling



* Produce equilibrium alloys & non-equilibrium phase

such as supersaturated solid solution, metastable intermediated phases, quasicrsytalline alloys, nanostructured materials and metallic glasses

starting from blended elemental powders at low temperature

→ Thin lamella + small rise in the temperature

→ increased diffusivity (due to the presence of a high concentration of crystal defects)

→ allows the blended elemental particles to alloy with each other at room or near-room temperature

→ a variety of constitutional and microstructural changes

: In fact, all the non-equlibrium effects achieved by RSP of metallic melts have also been achieved in mechanically alloyed powders.

→ <u>consolidated to full density by conventional or advanced methods</u>

such as vacuum hot pressing, hot extrusion, hot isostatic pressing, or shock consolidation, or combinations of these and <u>obtain bulk samples</u>

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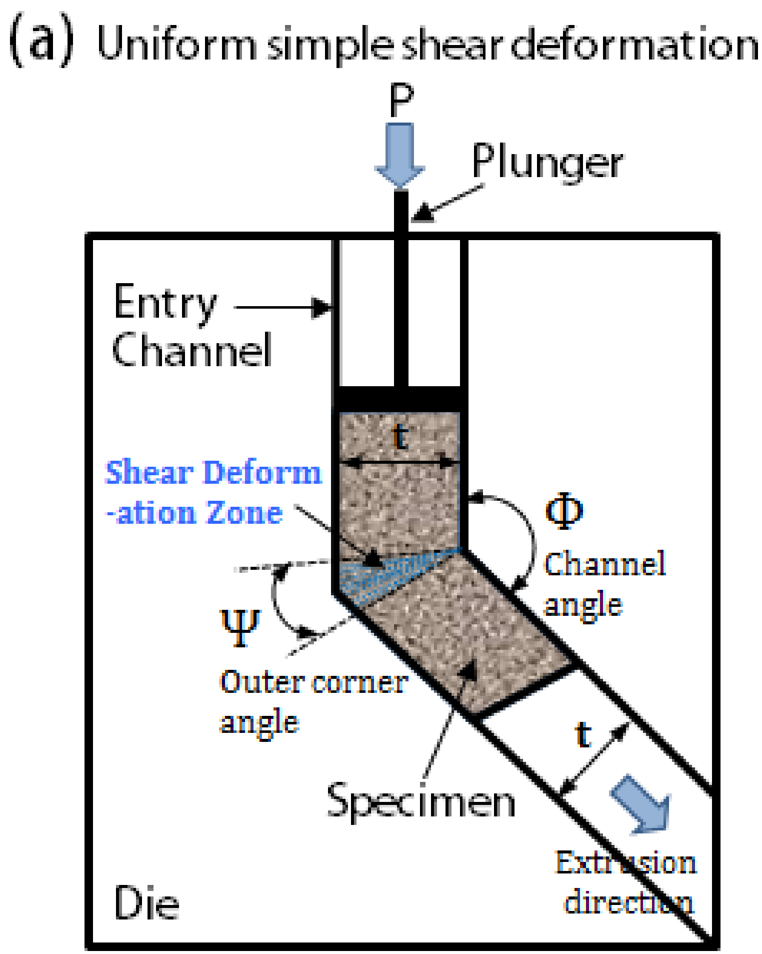
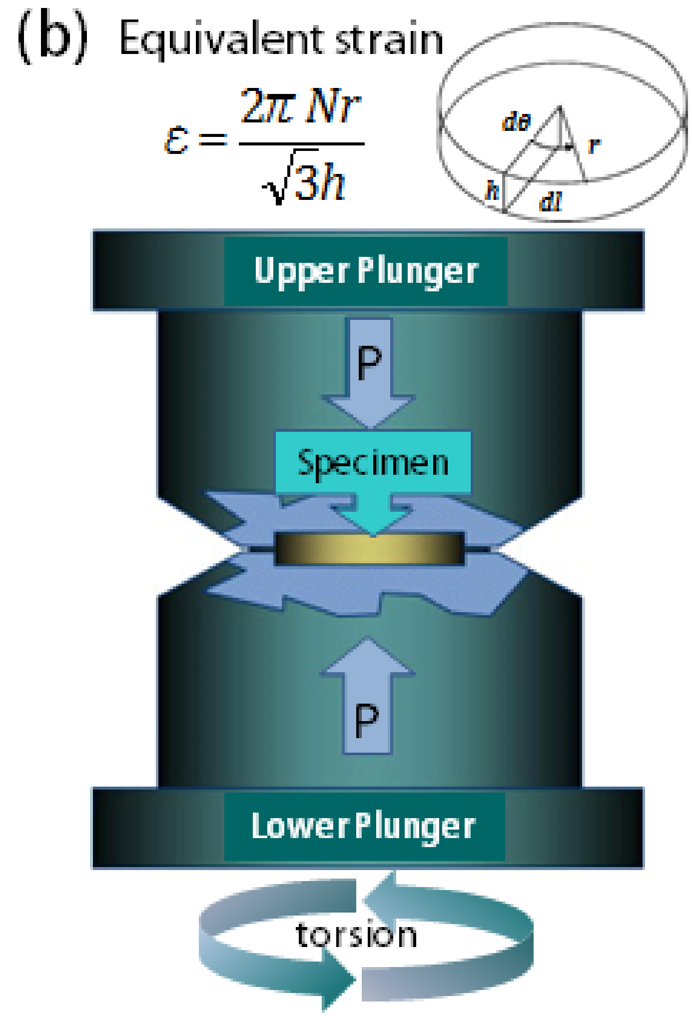
* Severe Plastic Deformation:

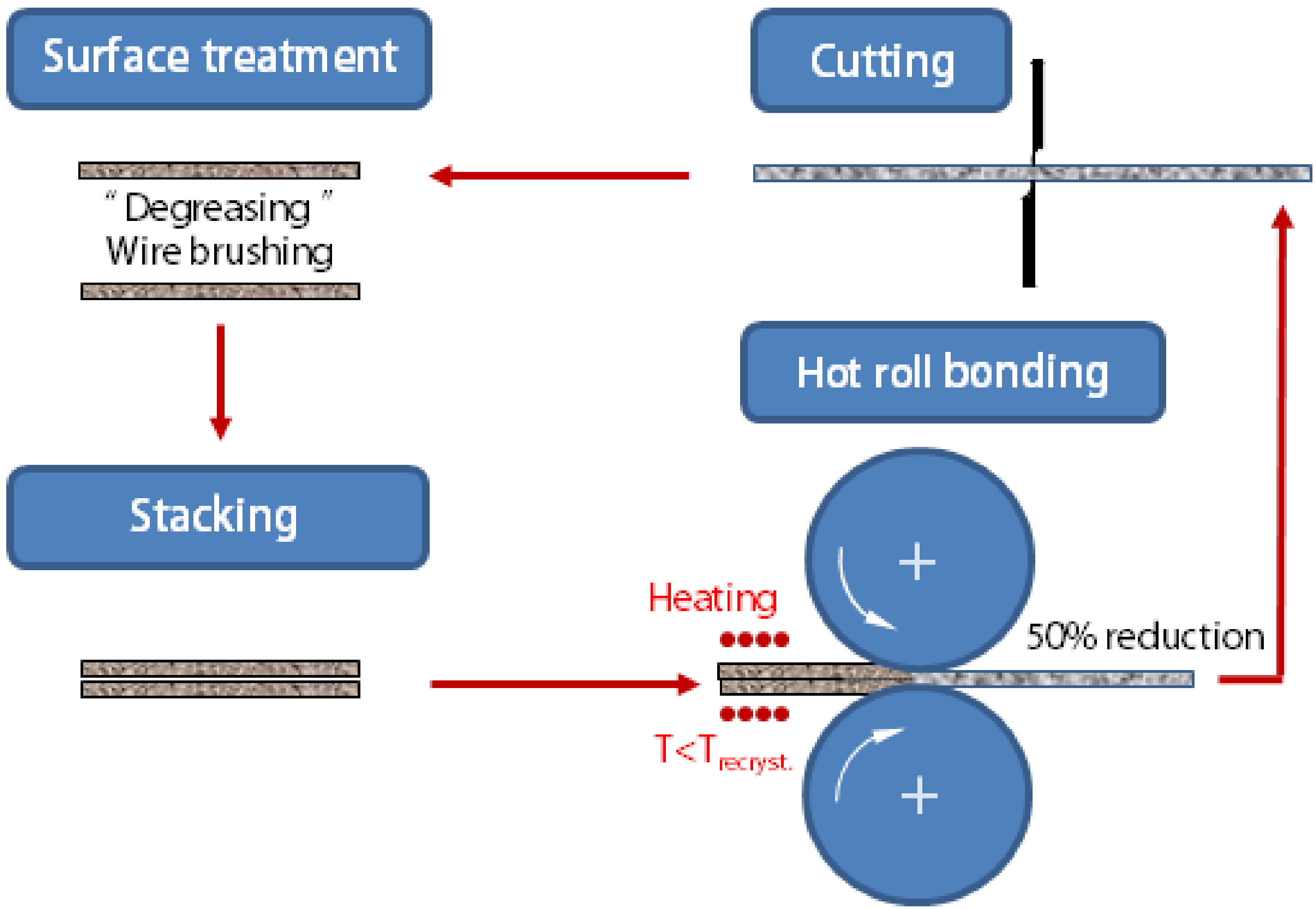
Equal channel angular pressing, ECAP



High-pressure torsion



* Accumulative Rolling Bonding



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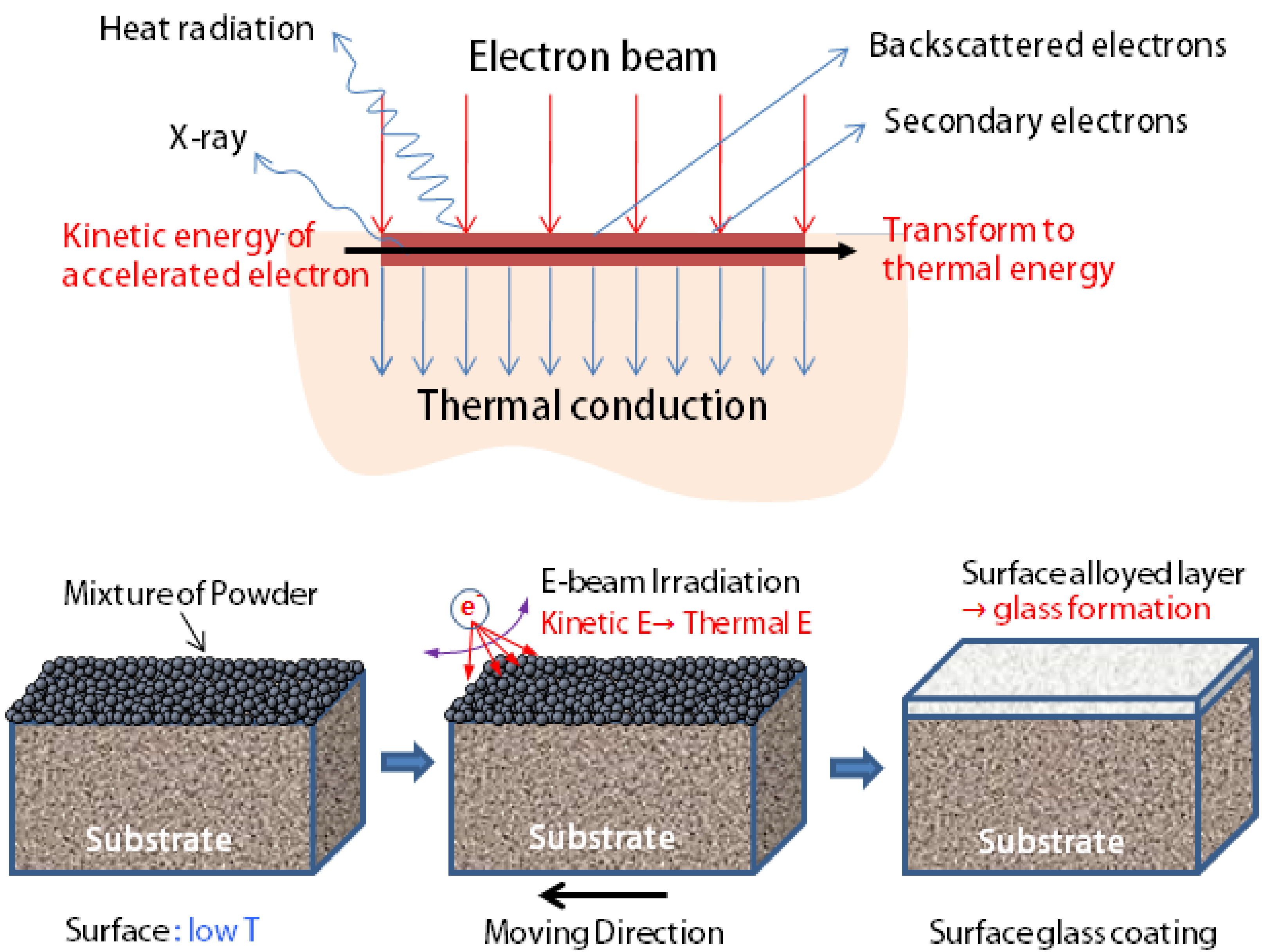
Heat radiation
Electron beam
Backscattered electrons
X-ray
Secondary electrons
Kinetic energy of
accelerated electron
Transform to
thermal energy
Thermal conduction
Mixture of Powder
E-beam Irradiation
Kinetic E→ Thermal E
Surface alloyed layer
→ glass formation
Substrate
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Surface : low T
Moving Direction
Surface glass coating

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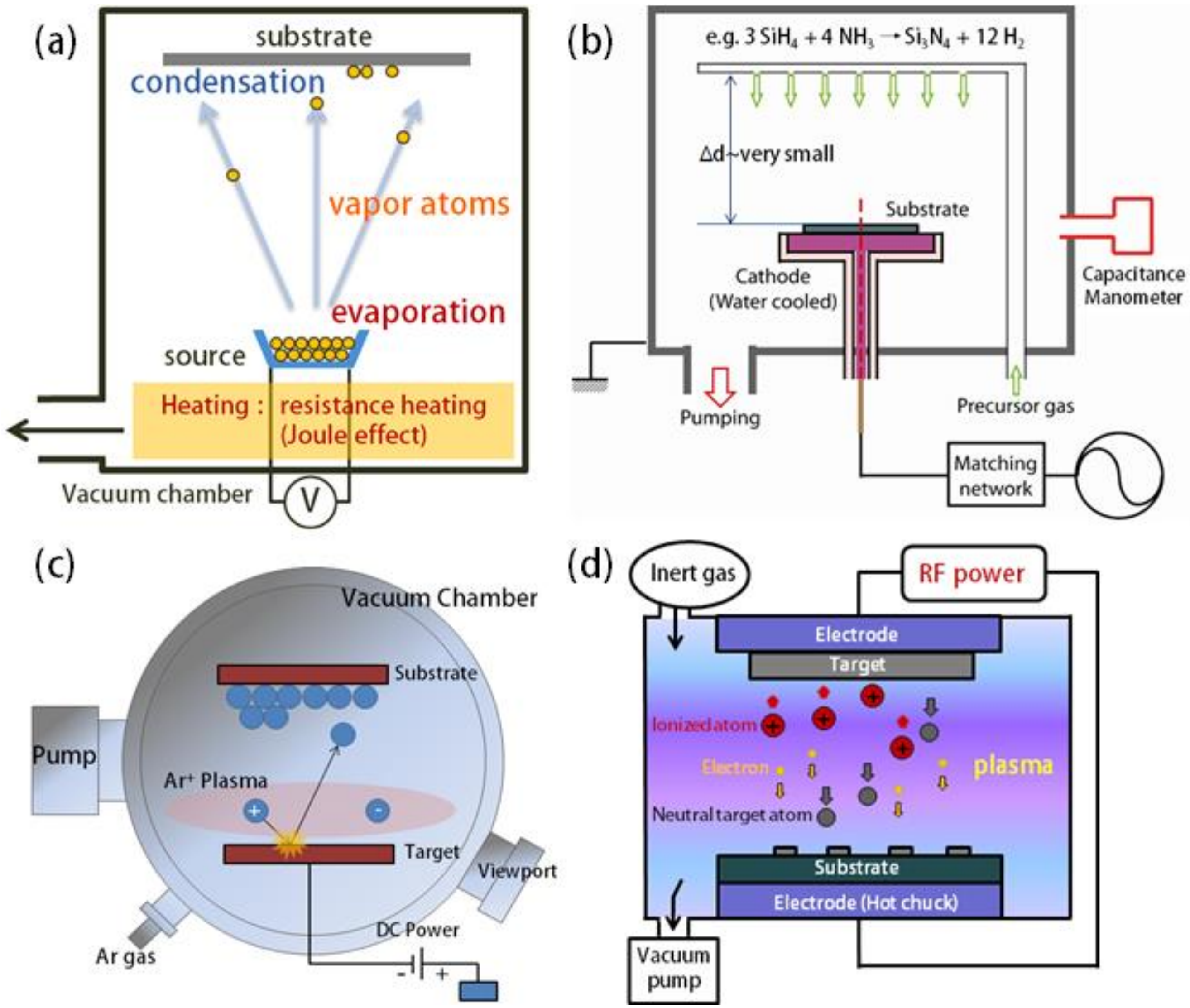
Chemical vapor deposition Sputtering



Electron beam evaporation Ion implantation

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Bulk Metallic Glass

What is an Amorphous Materials?

- ***Amorphous*** **– from the Greek for "without form"**
  not to materials that have no shape,
  but rather to materials with no particular structure

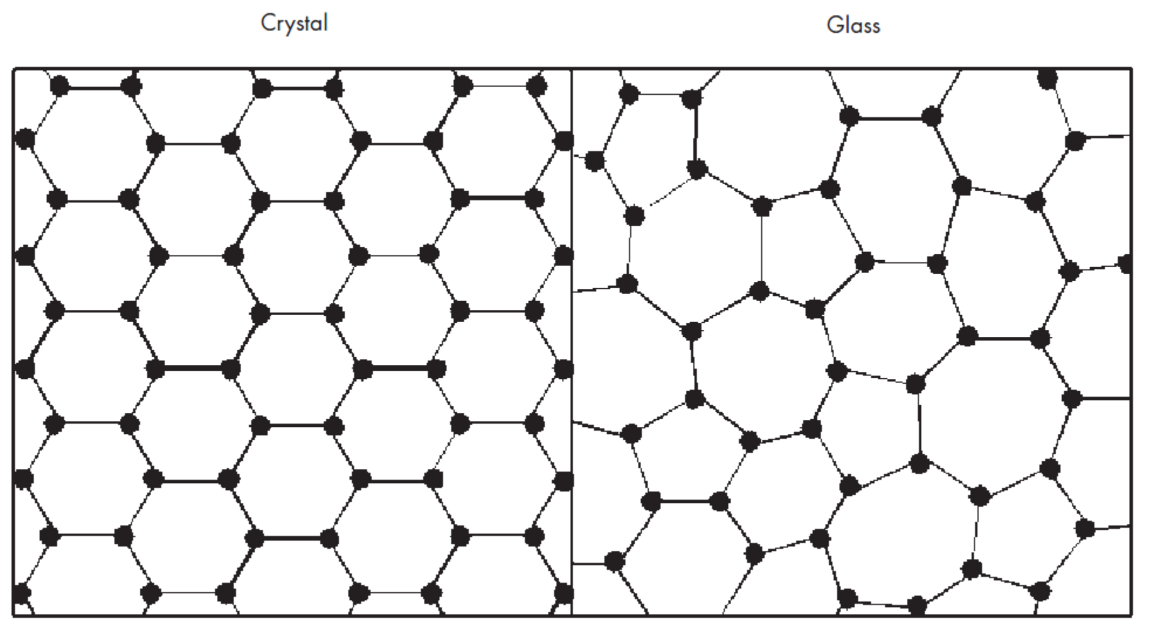


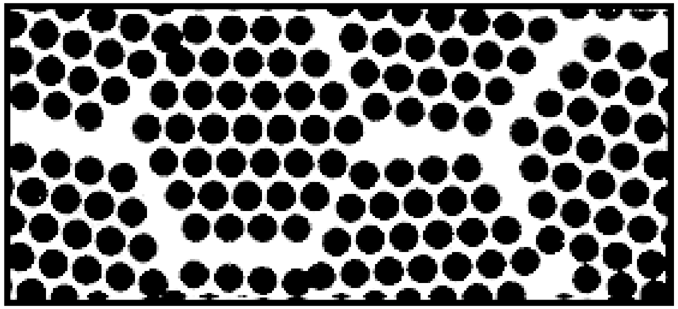
Figure 1. **Schematic Illustration of the Structures of Crystals and Glasses.**

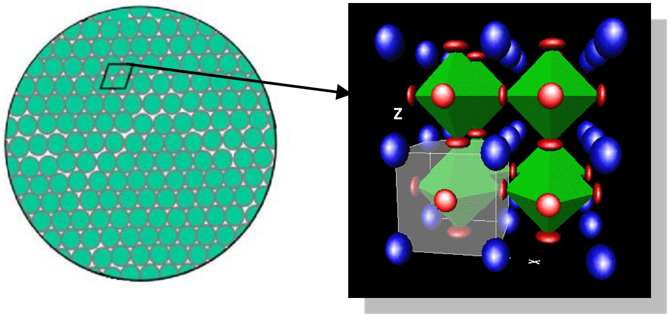
closely packed and chemically bonded solid
~ elastic response to shear stress

2.2 Distinction between crystals and glasses

Structure of crystals, liquids and glasses

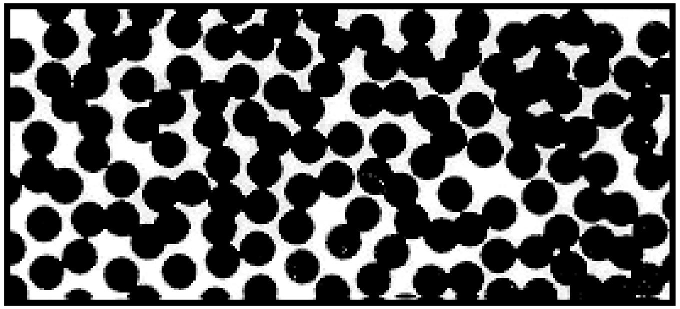
Crystals

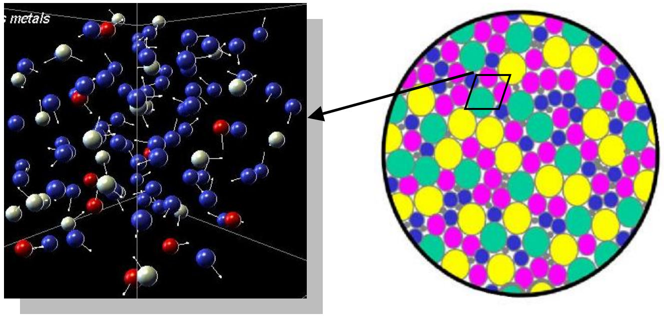




- **periodic**
- **grain boundaries**

Liquids, glasses





- **amorphous = non-periodic**
- **no grain boundaries**

* Each atom in the noncrystalline solid will have different nearest neighbors and CNs. But, it can be safely sated that the nearest neighbor distances are longer and the CNs smaller in a noncrsytalline solid in comparison to its crystal counterpart.

X-ray or Neutron results

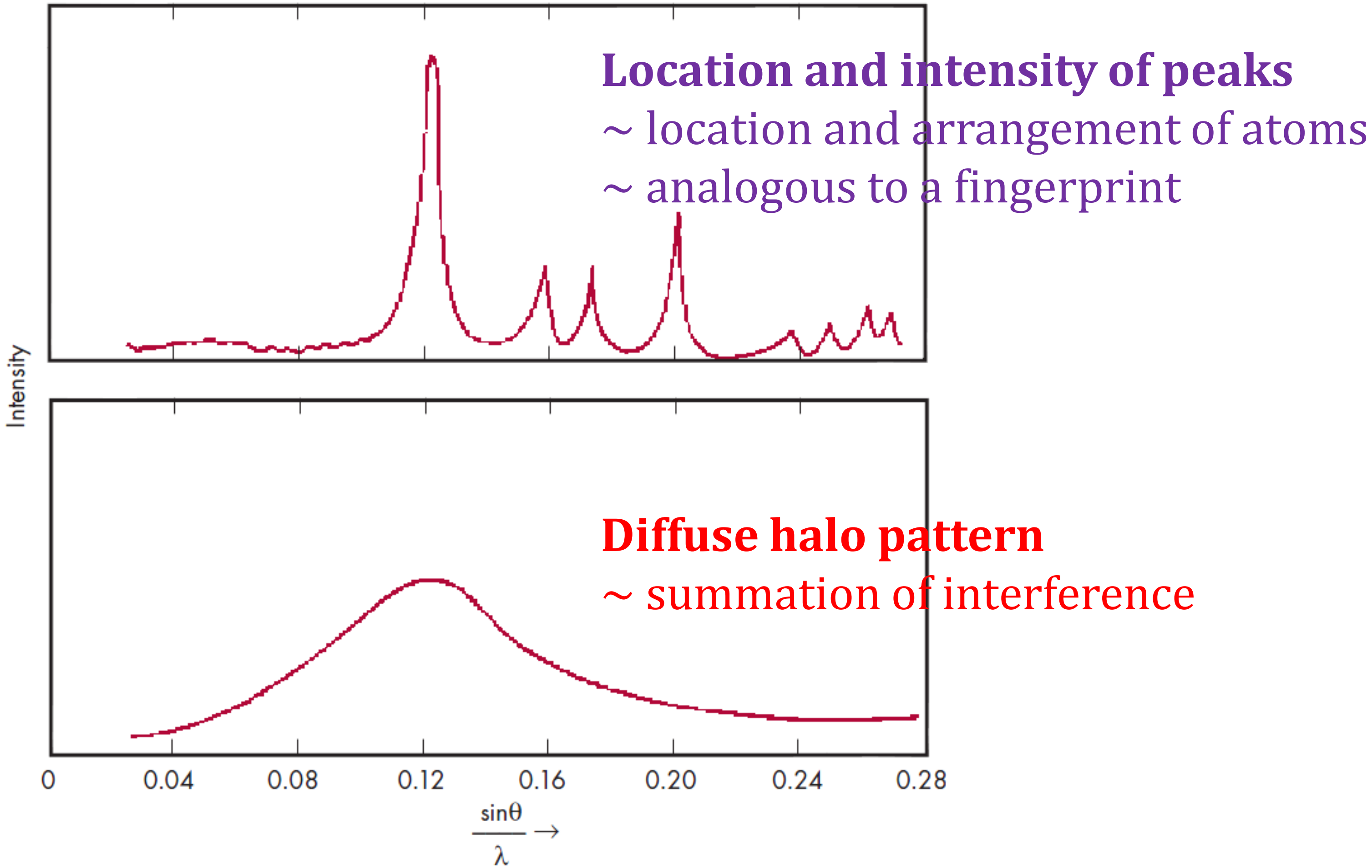
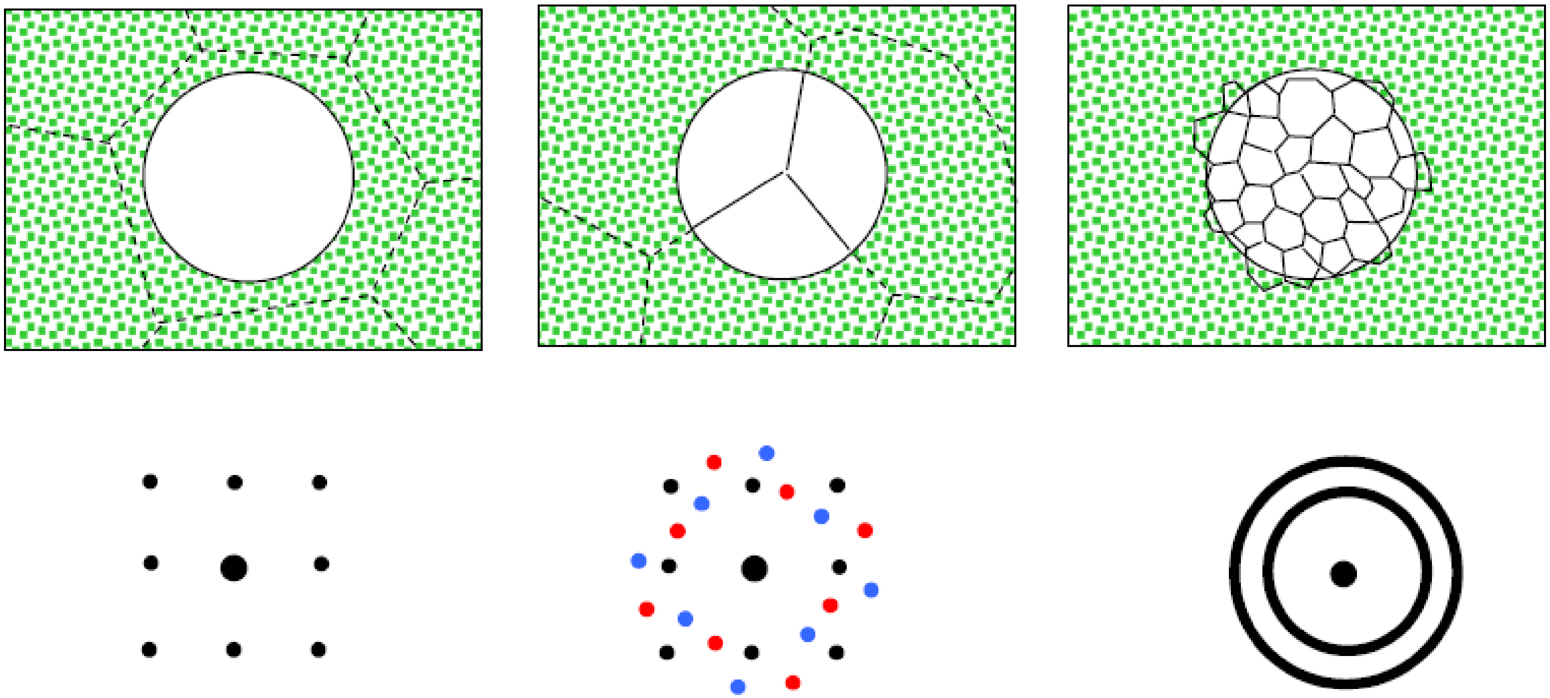


Figure 3. Characteristic Diffraction Patterns from Crystalline Material (Top) and Amorphous Material (Bottom).

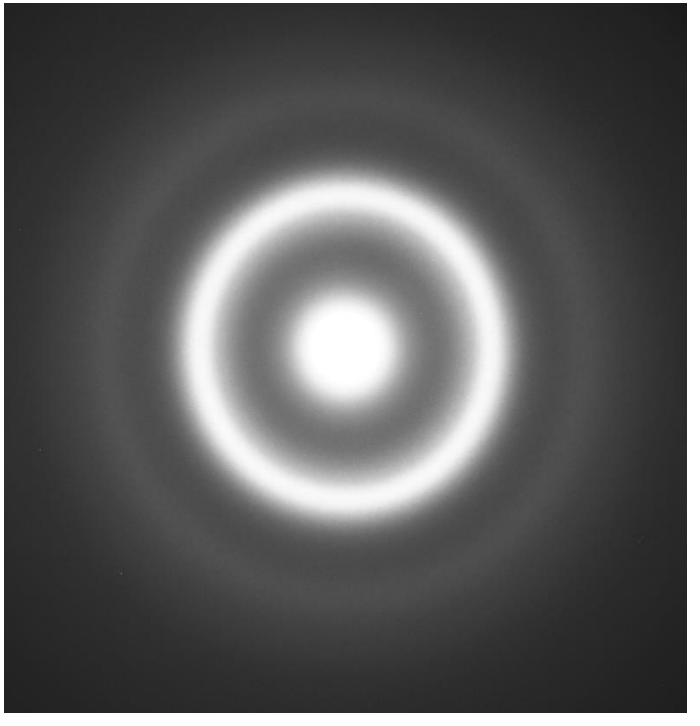
Electron Diffraction Pattern--Spot to Ring



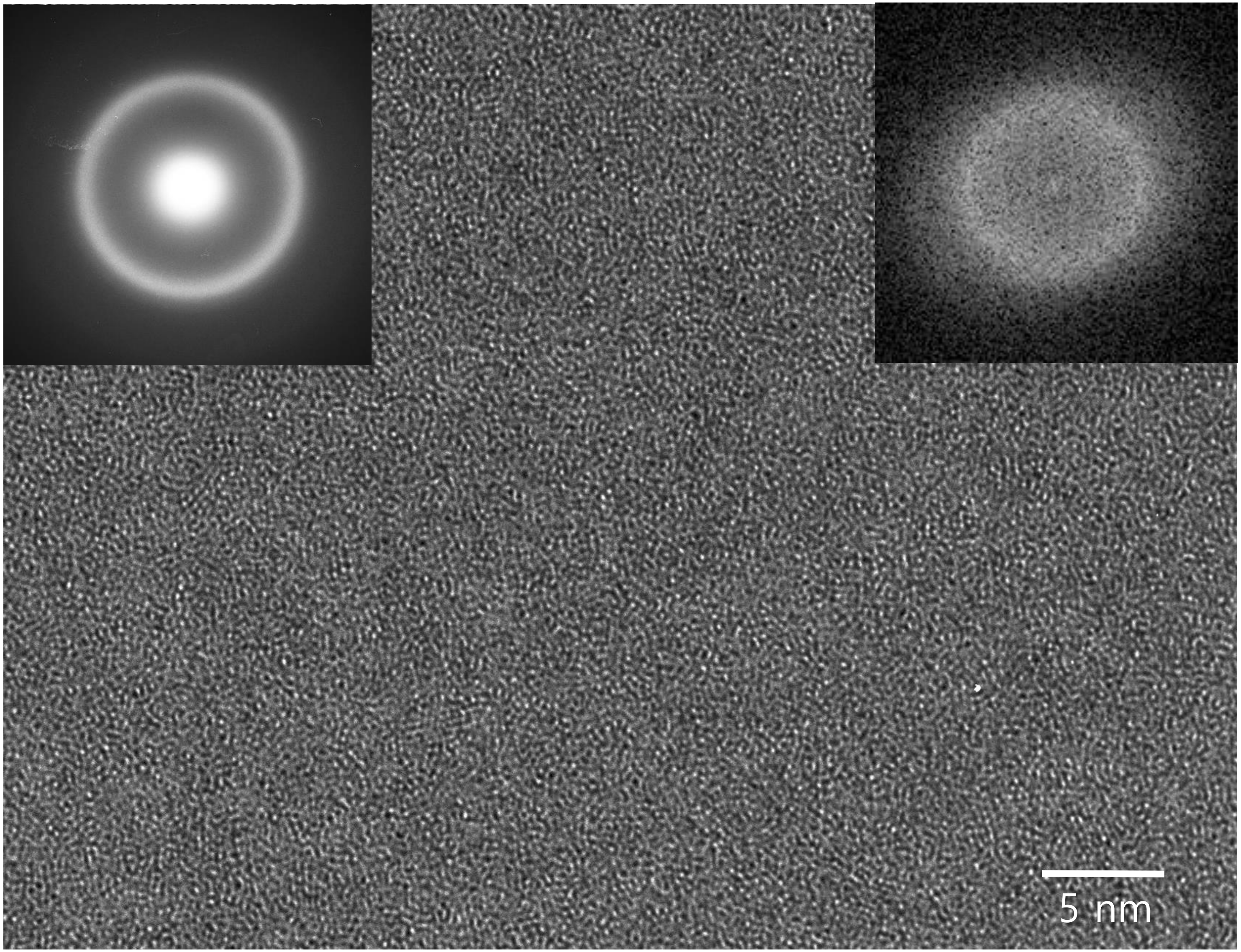
(a) (b) (c)

Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film



TEM results_Zr-based BMGs

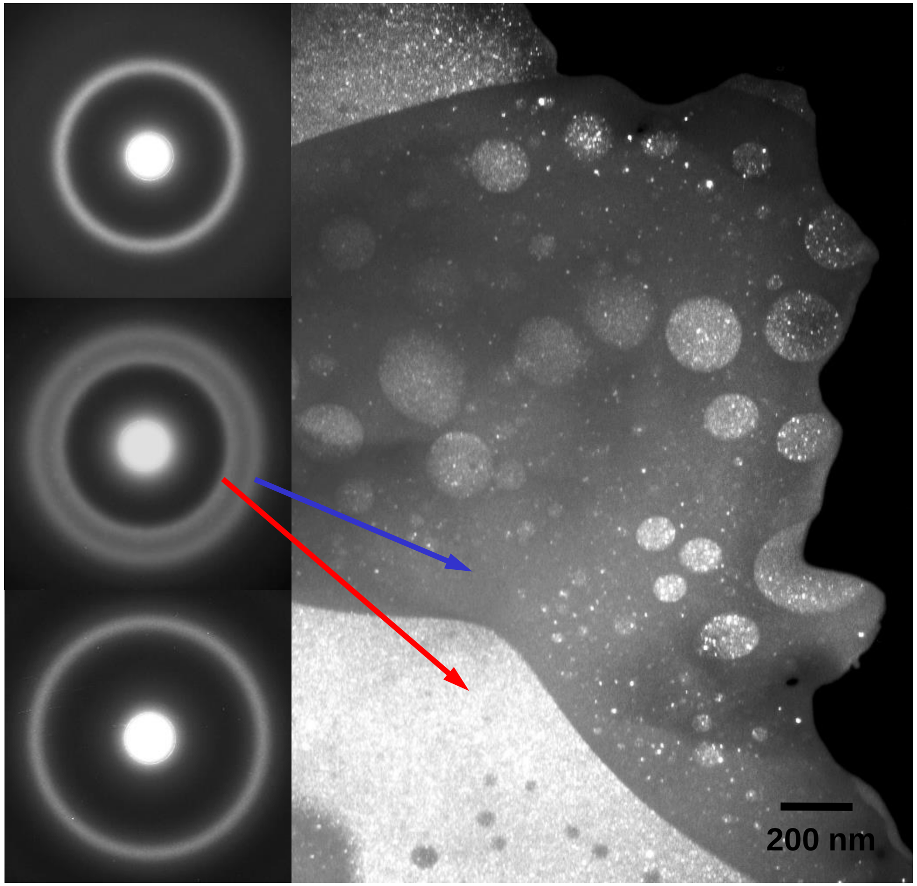


TEM results for $Nd_{30}Zr_{30}Al_{10}Co_{30}$ alloy

$Nd_{60}Al_{10}Co_{30}$
2.91 Å

$Nd_{30}Zr_{30}Al_{10}Co_{30}$
2.37 Å, 2.99 Å

$Zr_{60}Al_{10}Co_{30}$
2.40 Å



SADP and Dark-field TEM image

Classification of materials with structure

Perfect crystal → ***disorder*** → ***quasicrystal*** → ***amorphous***

: ***unit cell***

: ***underlying perfect crystalline lattice***

(a), (b), (c), (d)

Spin disorder **Vibrational disorder**

ex) *icosahedral phase*

: ***no topological ordering***

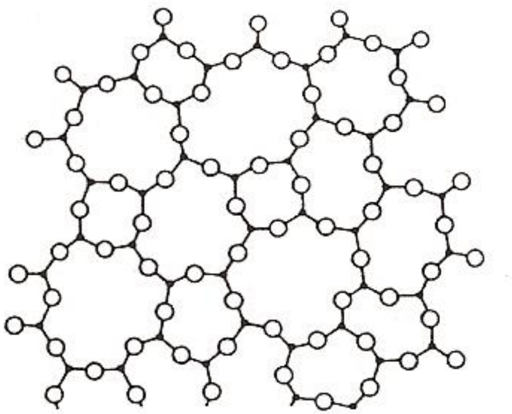
ex) *icosahedral glass*

(a) Topological disorder : various defects

(c) Substitutional disorder: Solid solution vs intermetallic compounds

⇨ **Hume-Rothery Empirical Rules for Alloys**

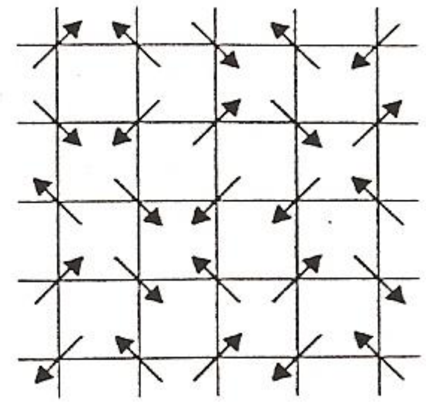
* Four types of disorder



a) Topological (or geometric) disorder

: no translational order at all

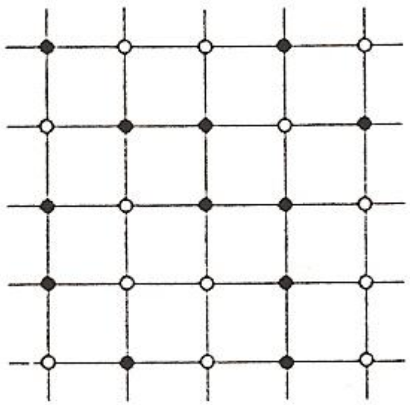
: but some degree of short range ordering



b) Spin disorder

: spin (or magnetic moment) exhibits random orientation.

: underlying perfect crystalline lattice

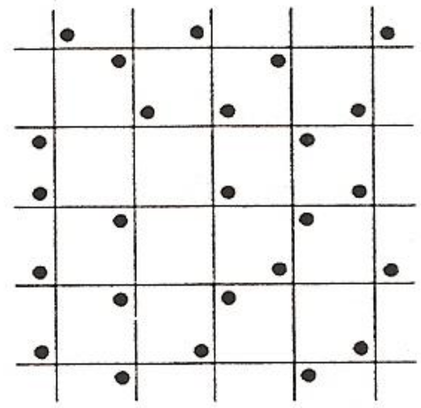


c) Substitutional disorder

: metallic alloy

: solid solution

: underlering perfect crystalline lattice



d) Vibrational disorder

at any finite temperature the random motion of atoms about their equilibrium position destroys the perfect periodicity

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: *unit cell*

: *underlying perfect crystalline lattice*

(a), (b), (c), (d)

Spin disorder   Vibrational disorder

ex) *icosahedral phase*

: *no topological ordering*

ex) *icosahedral glass*

(a) Topological disorder : various defects

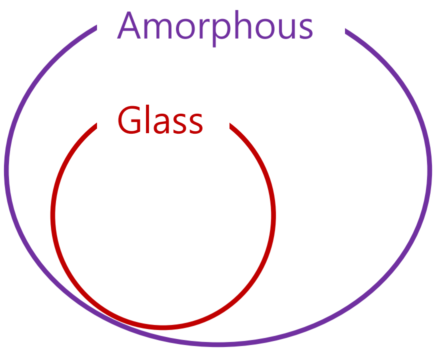
(c) Substitutional disorder: Solid solution vs intermetallic compounds

➡ Hume-Rothery Empirical Rules for Alloys

2.3 differences between Amorphous Alloys and Metallic Glasses

Non-crystalline solid : Amorphous solid vs Glass

Glass is any noncrystalline solid obtained by continuous cooling from the liquid state, and *amorphous solid* is any noncrystalline material obtained by any other method, except by continuous cooling from the liquid state.



* presence of a glass transition temperature, T_g

Exception: In the case of bulk metallic glasses (BMGs), there is usually a large supercooled liquid region, $\Delta T_x = T_x - T_g$, and in such cases it is relatively easy to locate the T_g. But, there are instances even in the case of BMGs, which exhibit a very large ΔT_x value, but the presence of T_g could not be clearly identified. For example, an $Nd_{70}Fe_{20}Al_{10}$ ternary alloy melt could be cast into a 7 mm diameter glassy rod, but the DSC curves did not indicate the presence of a T_g [14].

Angell [15] mentions that the presence of T_g is not essential for a material to be called a glass!

Fundamentals of the Glass Transition

If liquid is cooled, two events can occur.

1) Crystallization (solidification at $T_{m.p.}$)

2) Undercooled below $T_{m.p.}$ (supercooled) ➡ More viscous ➡ Glass

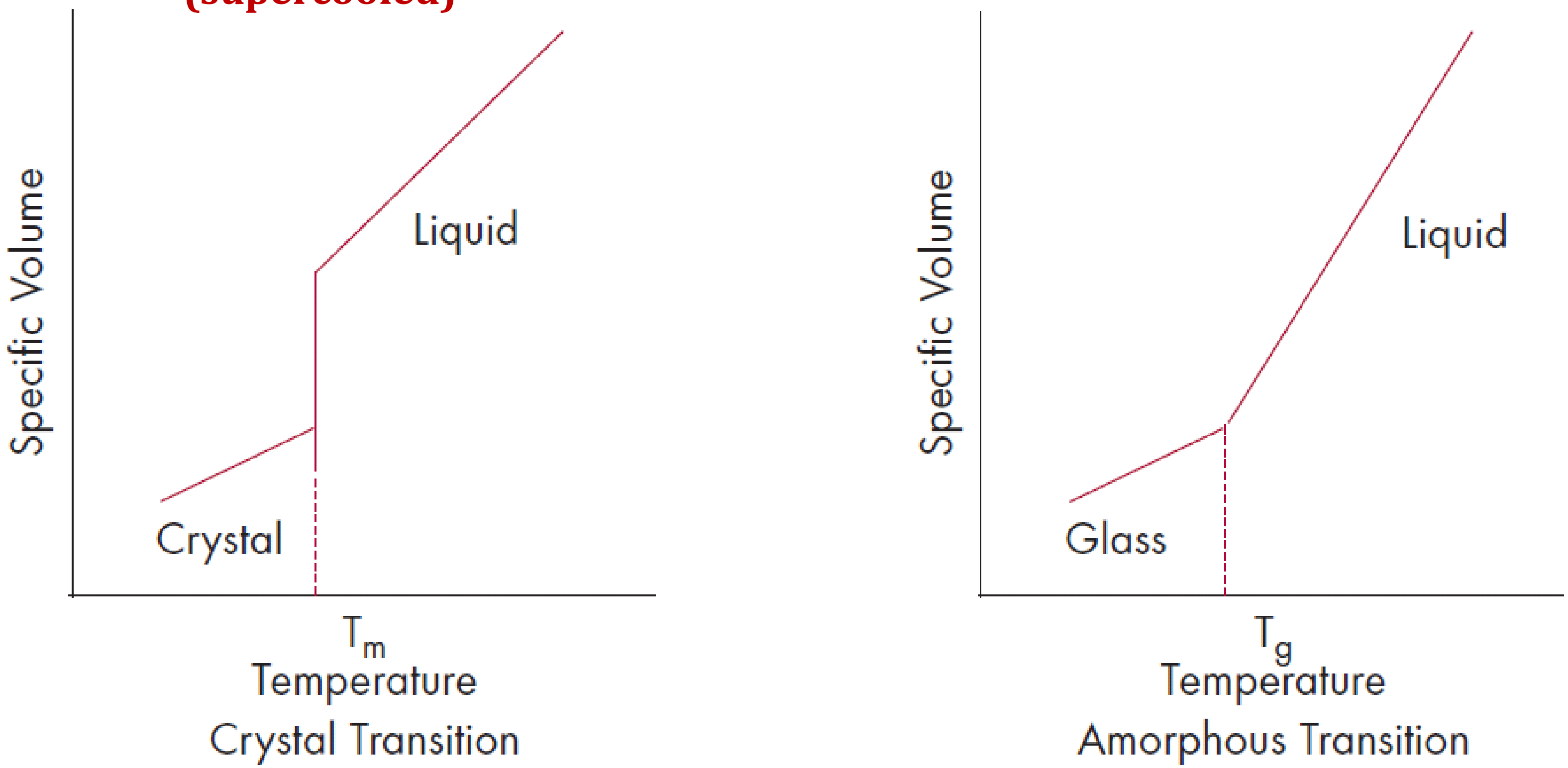


Figure 4. **Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).**

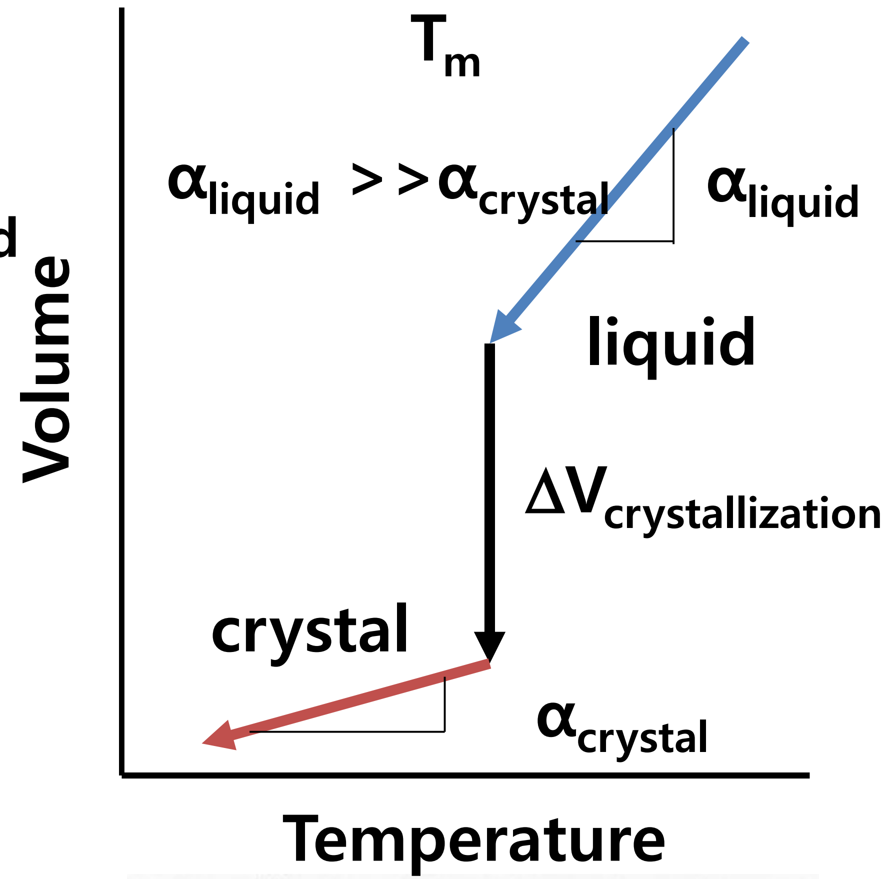
Fundamentals of the Glass Transition

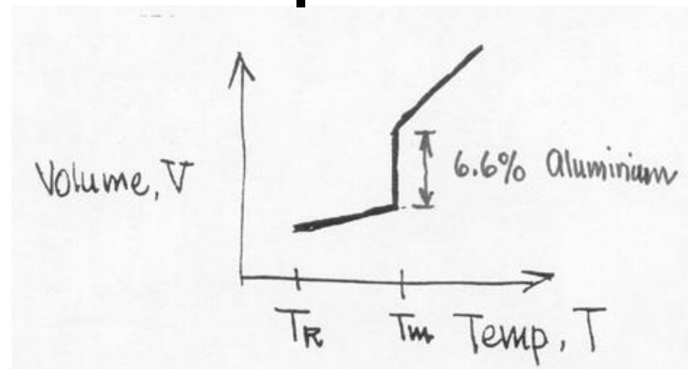
- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at T_m
  - Structures are thermodynamically controlled and described by the
  - Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2, for example

- **The Glass Transition is a Kinetic Transition**
  - Continuous changes in structure and properties near T_g
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

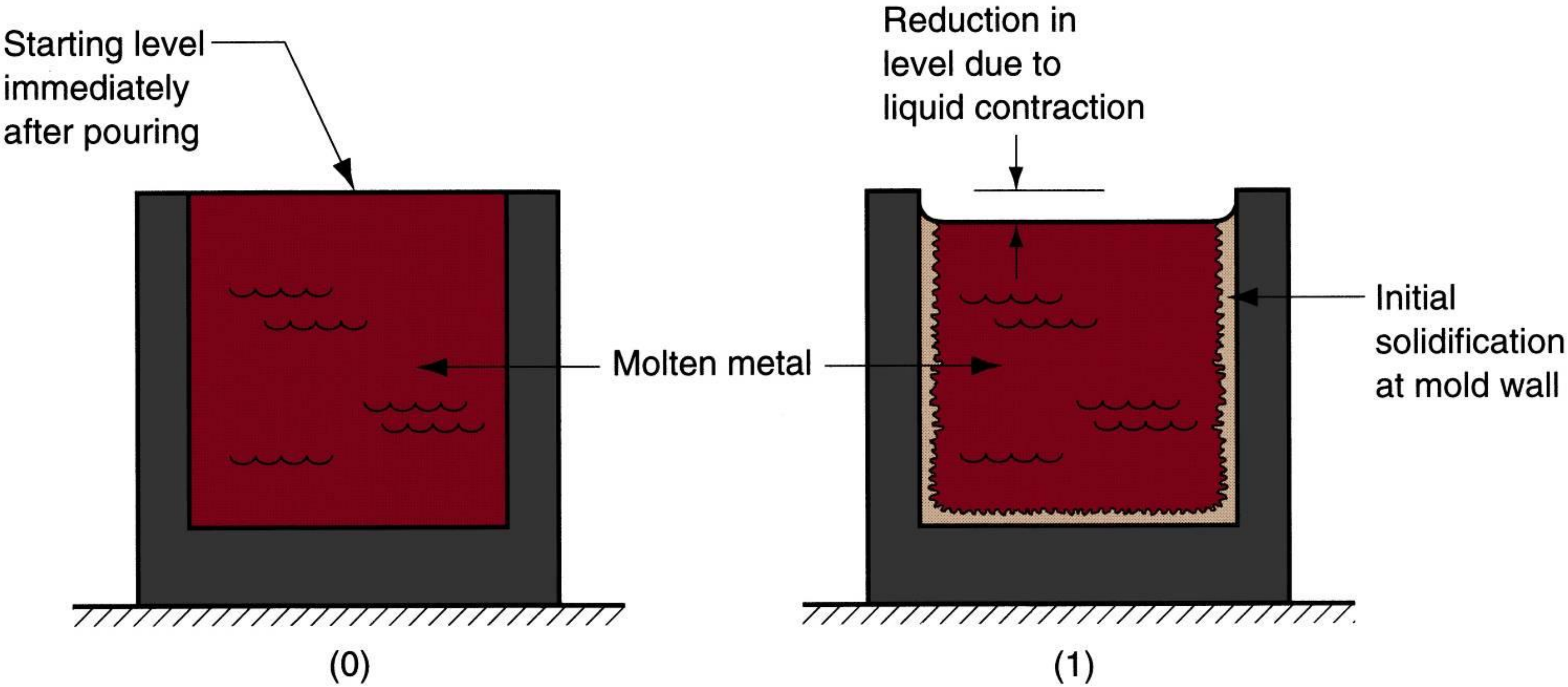
Crystallization is Controlled by Thermodynamics

- 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



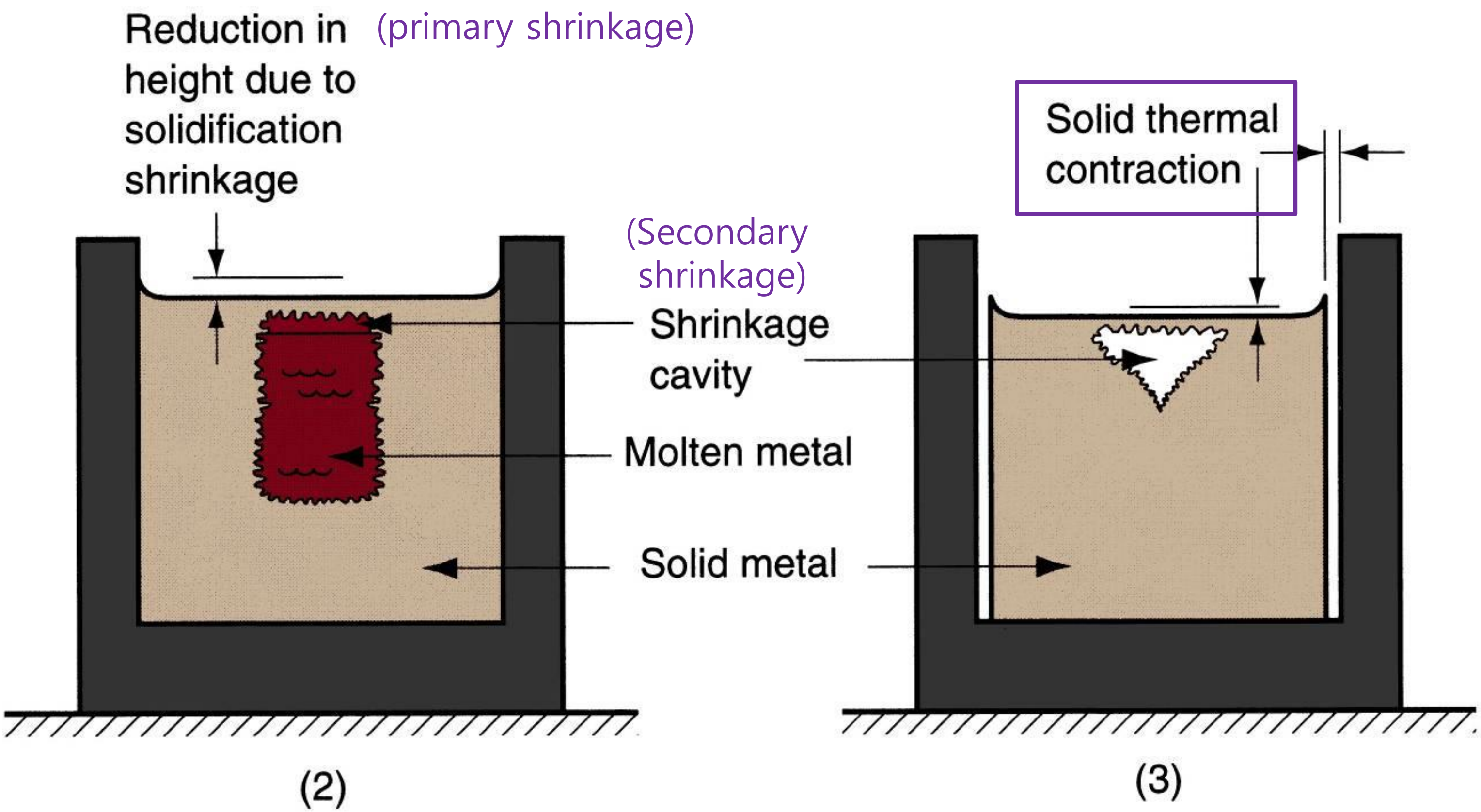


Shrinkage in Solidification and Cooling



* 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).

* Formation of Voids during solidification

Central shrinkage:

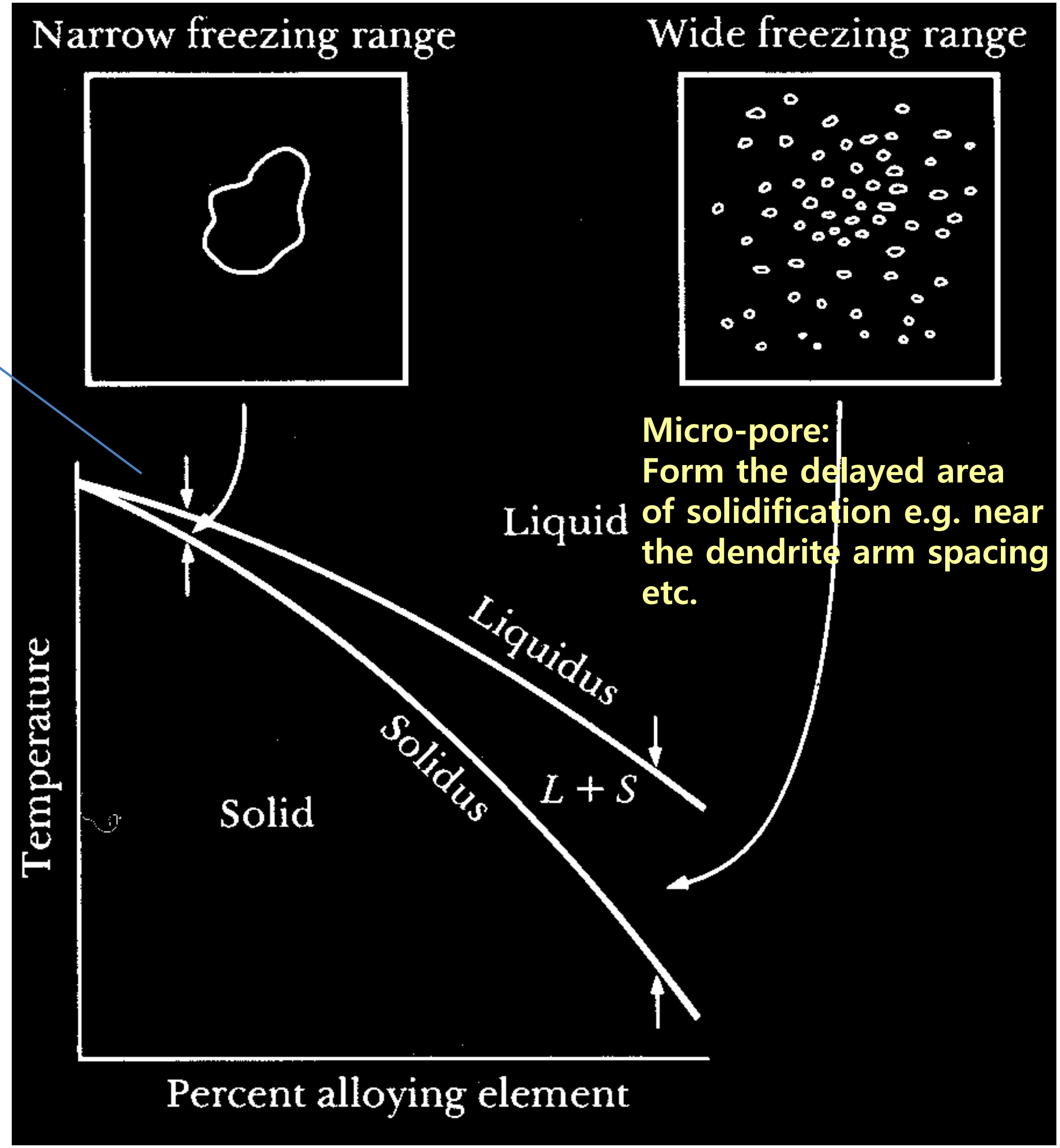
조성 변화가 크지 않은 주물의 응고 시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

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: H_2O (10%), Si (20%), Ge**

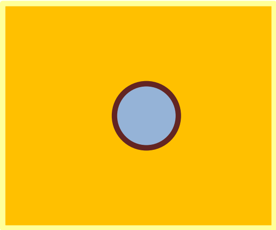
ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

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

→ precipitation of graphite during solidification reduces shrinkage.

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid T_m Undercooled Liquid Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

vapor

Melting: Liquid ← Solid

In general, wetting angle = 0 ⇨ No superheating required!

Homogeneous Nucleation

Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

$\Delta G = \Delta H - T\Delta S$

L : $\Delta H = H^L - H^S$

(Latent heat)

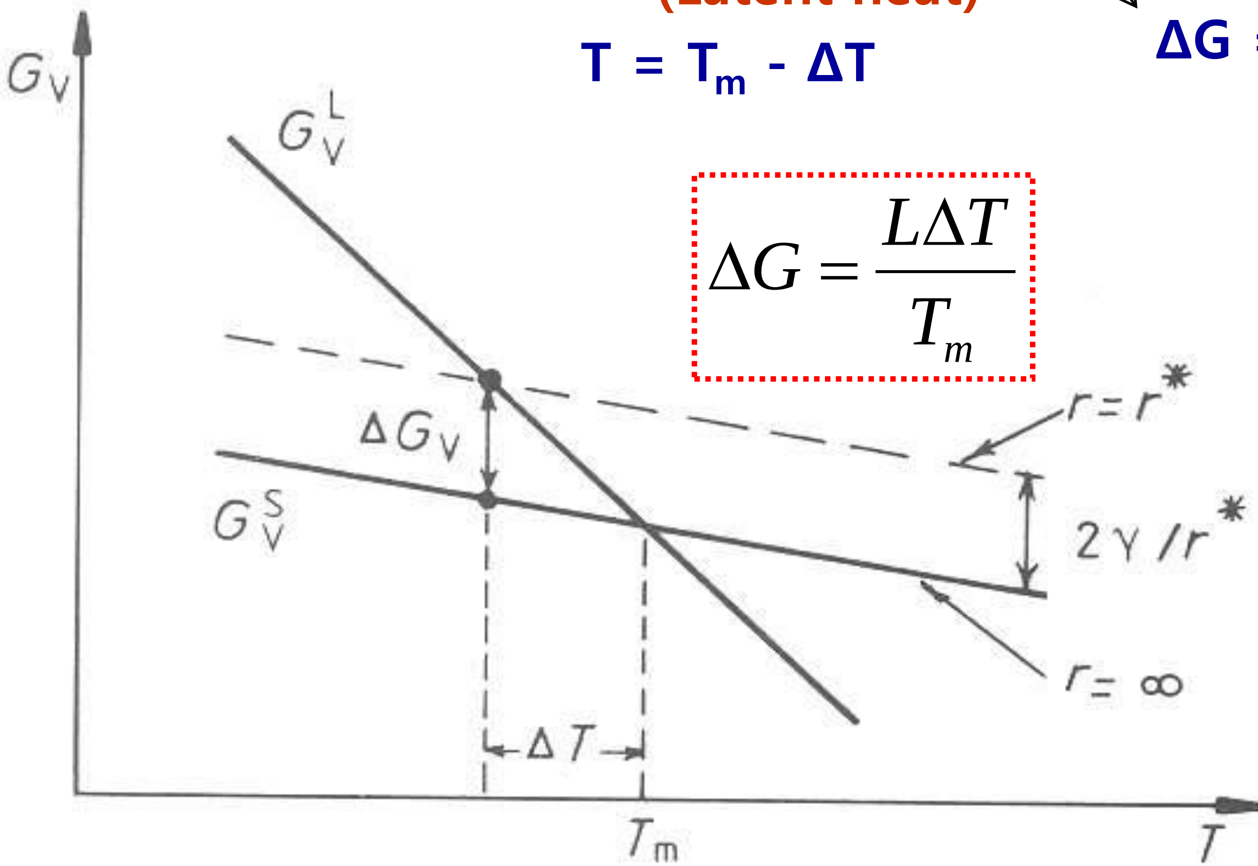
$T = T_m - \Delta T$

$\Delta G = 0 = \Delta H - T_m \Delta S$

$\Delta S = \Delta H / T_m = L / T_m$

$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

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



,

*** Quasi-chemical approach** $\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$

- Solid: force between pairs of atoms

→ vaporize: break all "pairwise" bonds

For, example: Copper (Cu)

Vaporization **Melting**

Heat of vaporization 80 Kcal/mole vs Heat of fusion 3.1 Kcal/mole

25 times → 1/25 broken

Melting: each bond is replaced by <u>one with 4 percent less E</u>,

although bond energy of liquid is changed by the positions.

→ Heat of fusion during melting: need to generate weaker liquid bonds

4.1.4. Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Why?

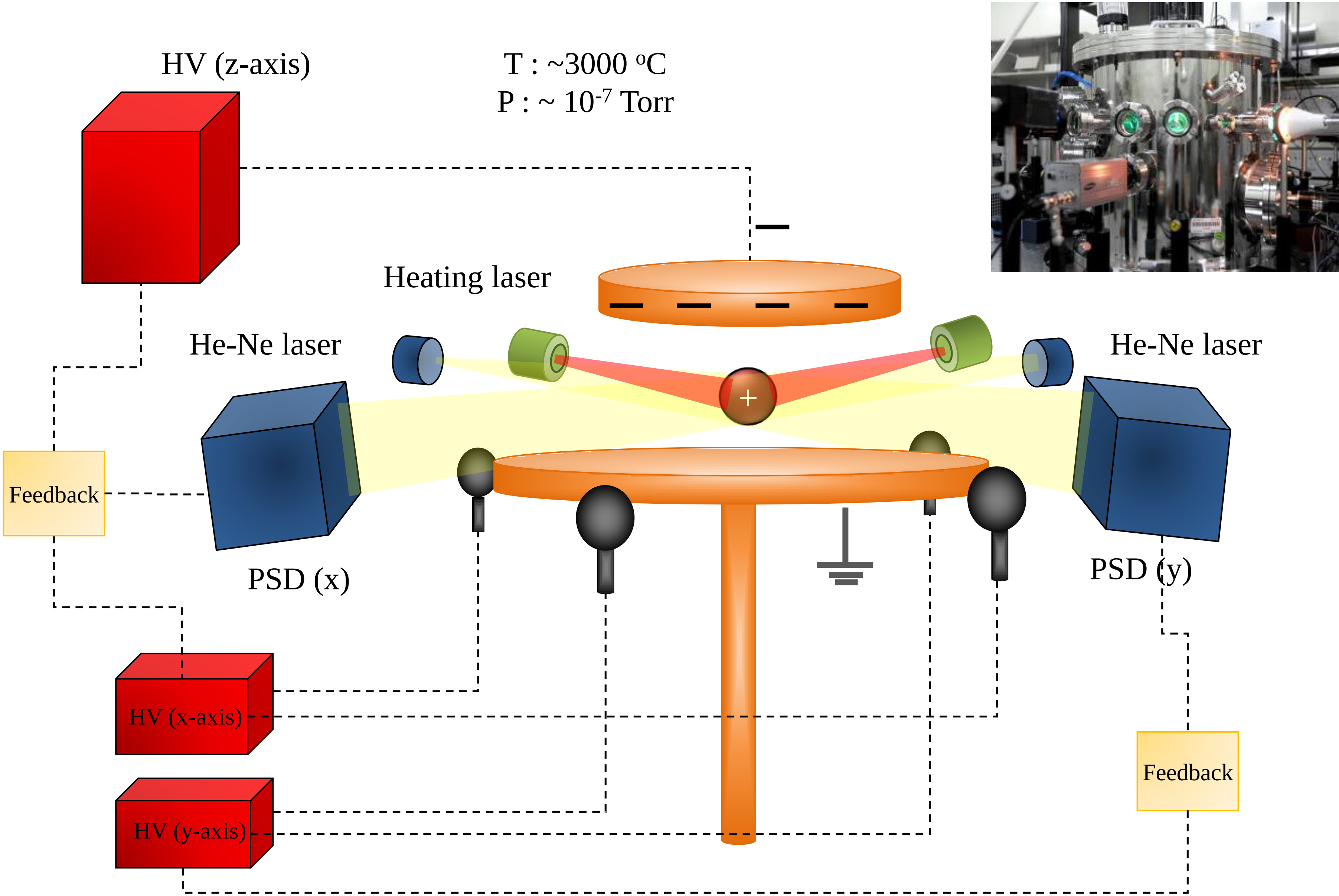
개념적으로 생각해보면

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ (commonly)

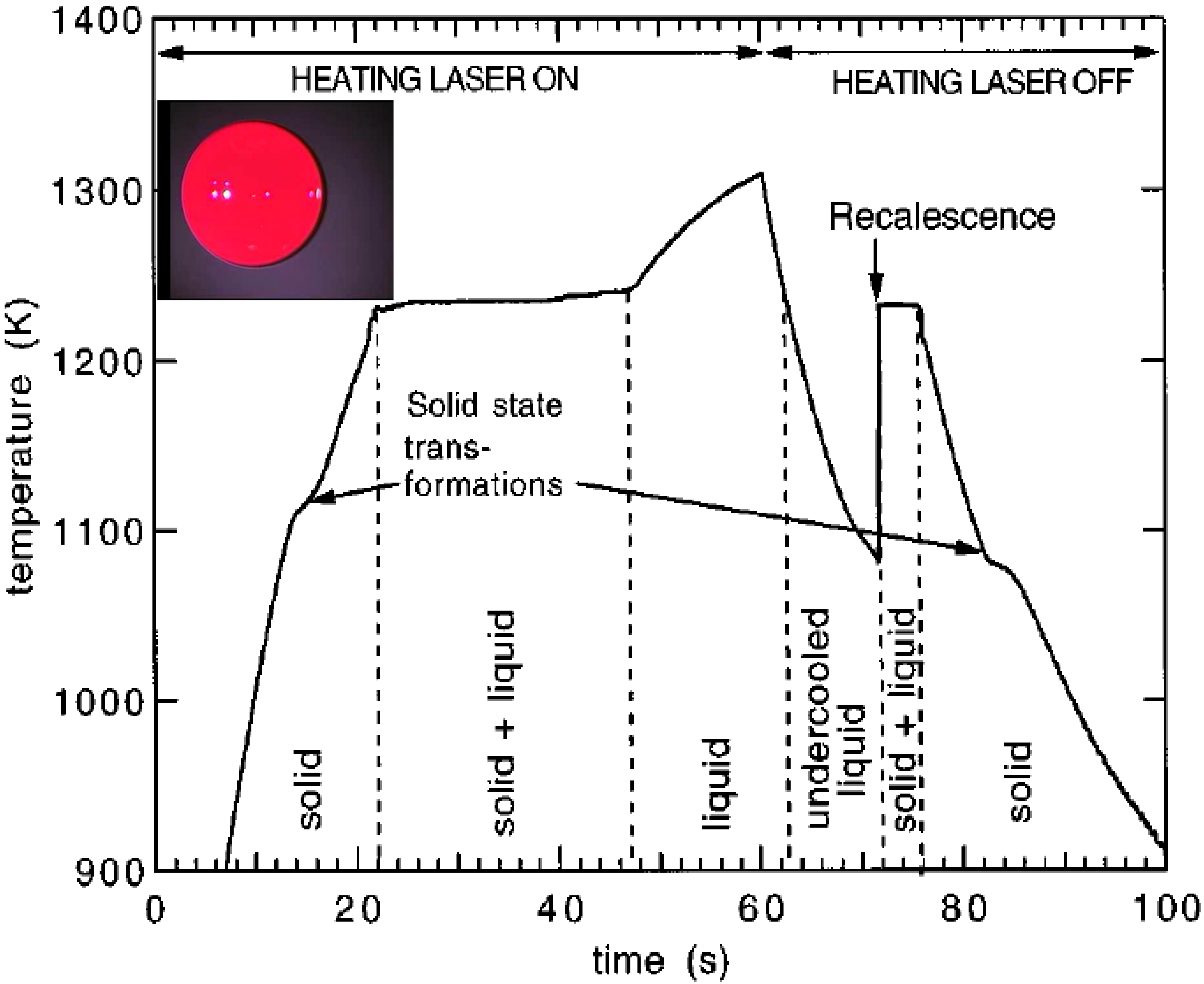
Solid -> liquid 로 원자 떼어내는 데 드는 힘	+	Liquid-> Vapor 로 원자 떼어내는 데 드는 힘	<	Solid-> Vapor 로 원자 떼어내는 데 드는 힘

In general, wetting angle = 0 ⇨ No superheating required!

Electrostatic levitation in KRISS



KRISS material : Dr. G.W.Lee



HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state
trans-
formations
solid
solid + liquid
liquid
undercooled
liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

* Comparison between experiment and theory

Most metal ΔT_N < several K

but Turnbull and his coworker ΔT_N → larger (~several hundreds K)

by formation of large number of very small drops

Table 3.1. Relationship between Maximum Supercooling, Solid-Liquid Interfacial Energy and Heat of Fusion[a]

Metal	Interfacial Energy σ (ergs/cm²)	σ_g (cal/mole)	σ_g/L	ΔT_{MAX} (deg)
Mercury	24.4	296	0.53	77
Gallium	55.9	581	0.44	76
Tin	54.5	720	0.42	118
Bismuth	54.4	825	0.33	90
Lead	33.3	479	0.39	80
Antimony	101	1430	0.30	135
Germanium	181	2120	0.35	227
Silver	126	1240	0.46	227
Gold	132	1320	0.44	230
Copper	177	1360	0.44	236
Manganese	206	1660	0.48	308
Nickel	255	1860	0.44	319
Cobalt	234	1800	0.49	330
Iron	204	1580	0.45	295
Palladium	209	1850	0.45	332
Platinum	240	2140	0.45	370

[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

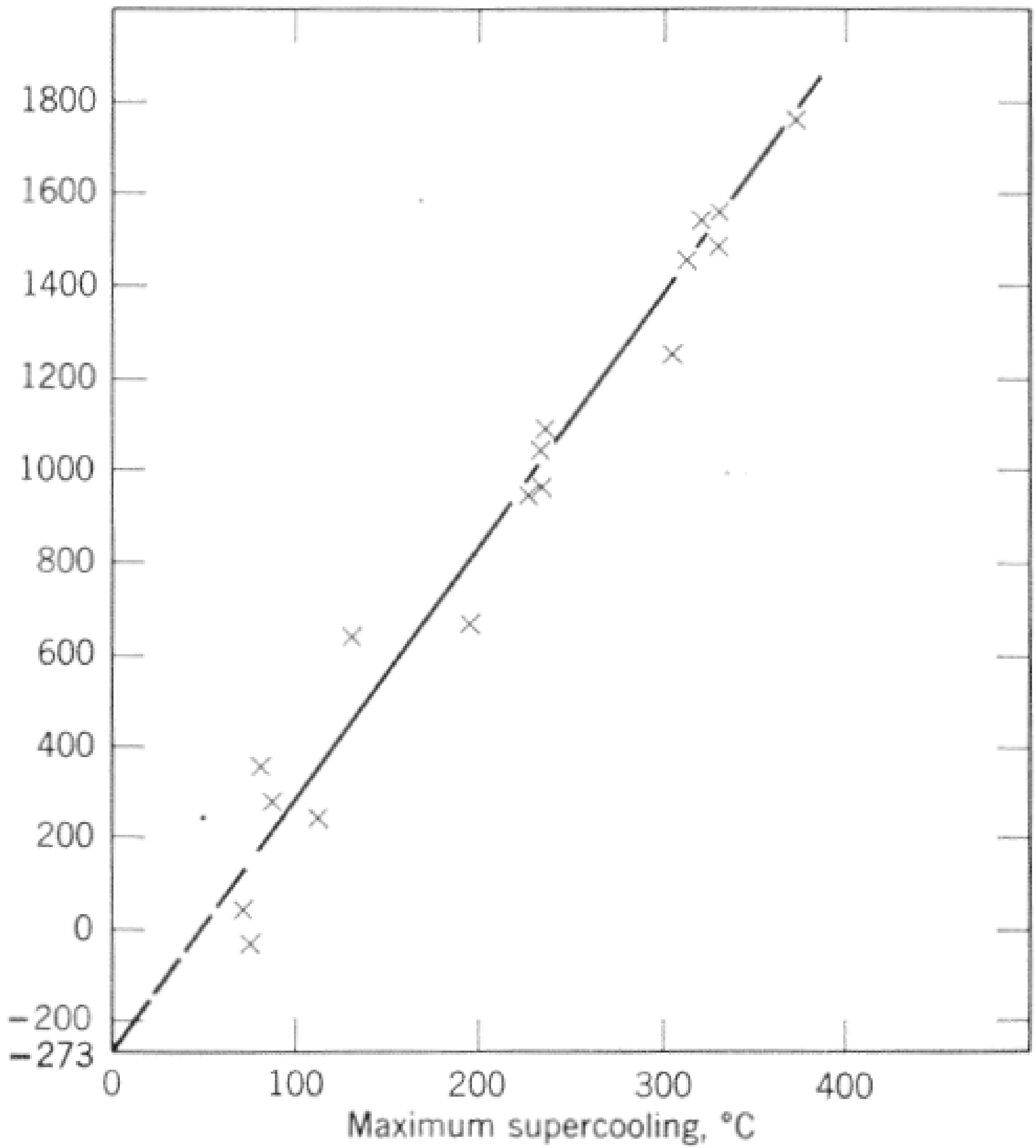
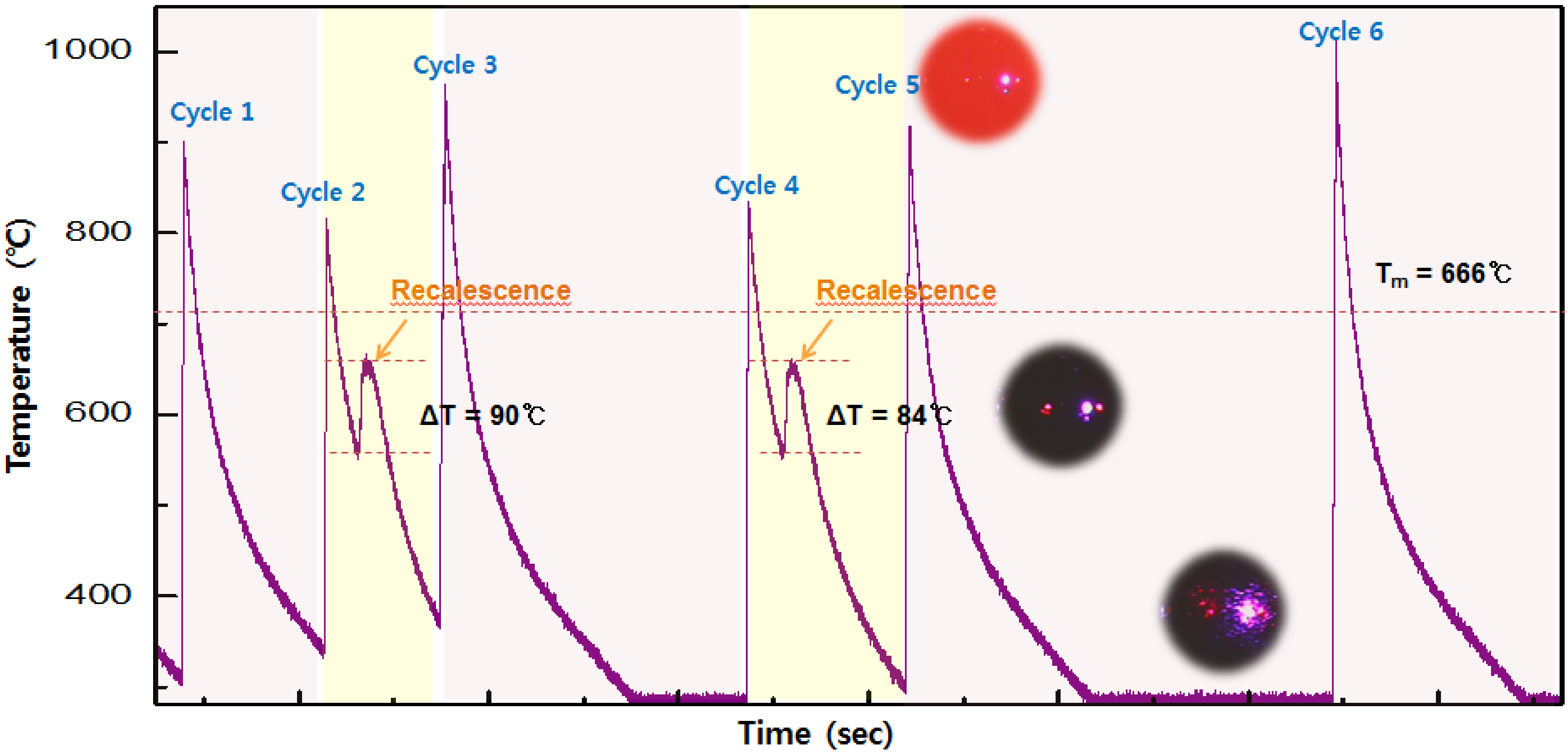
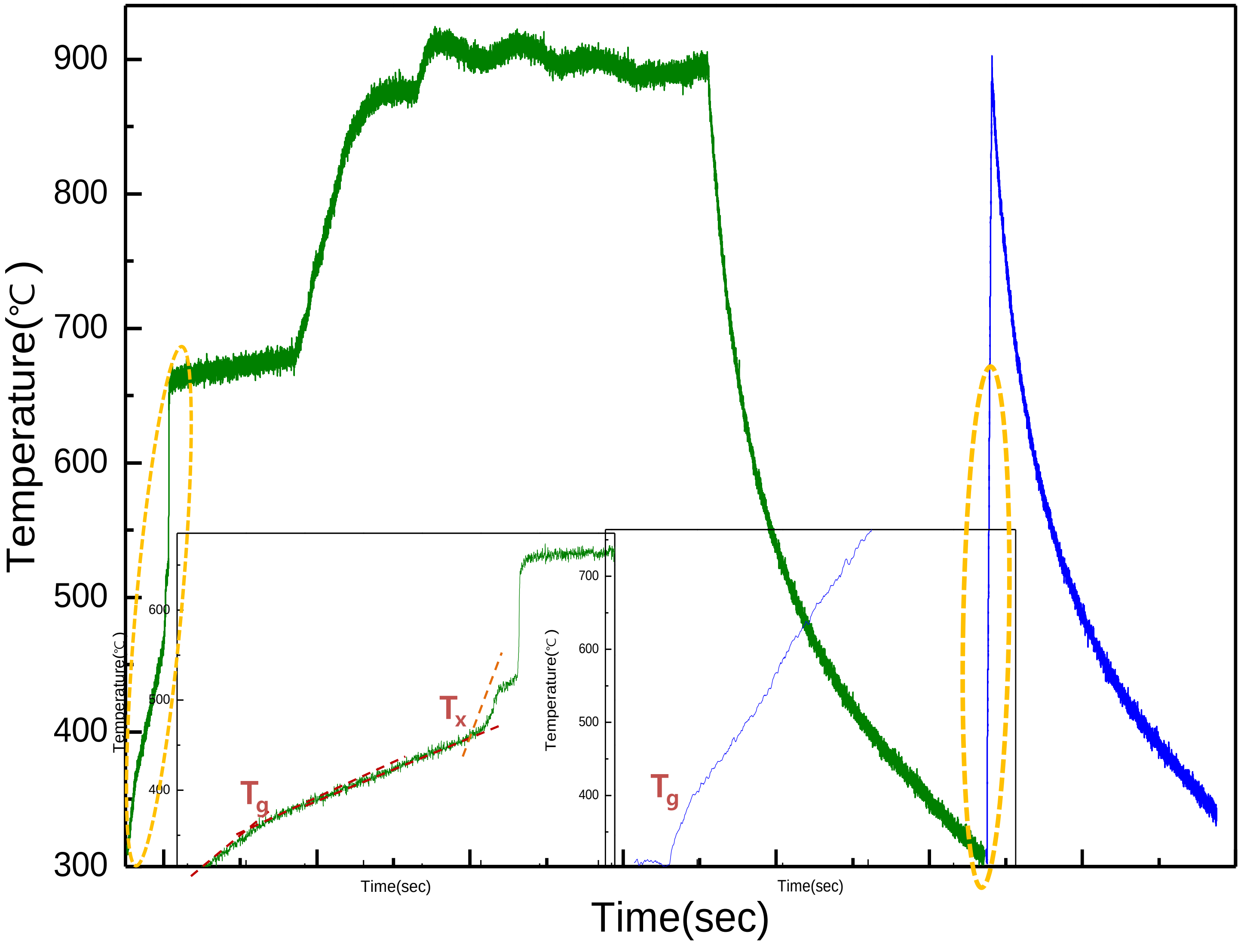


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

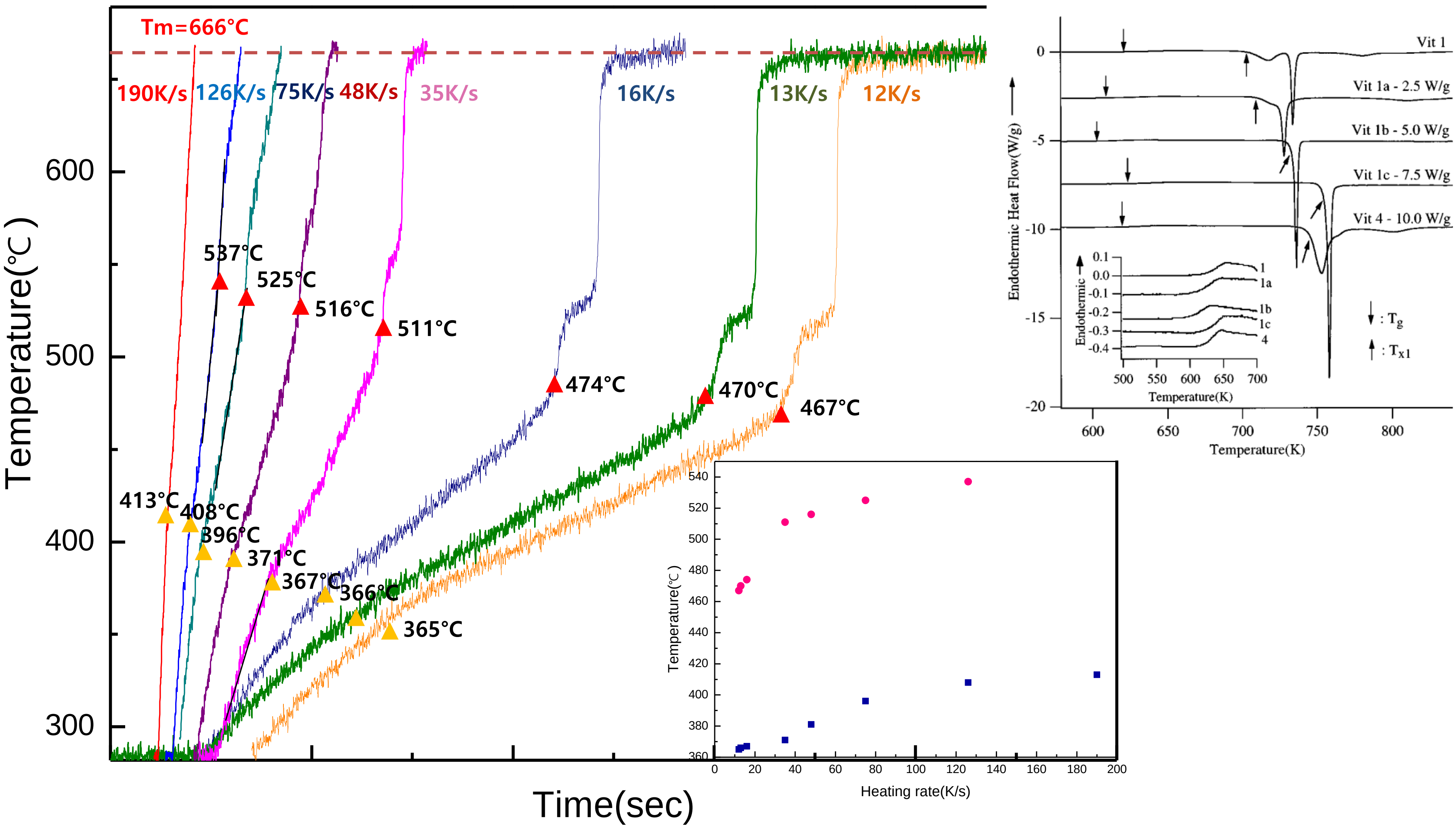
Cyclic cooling curves in ESL





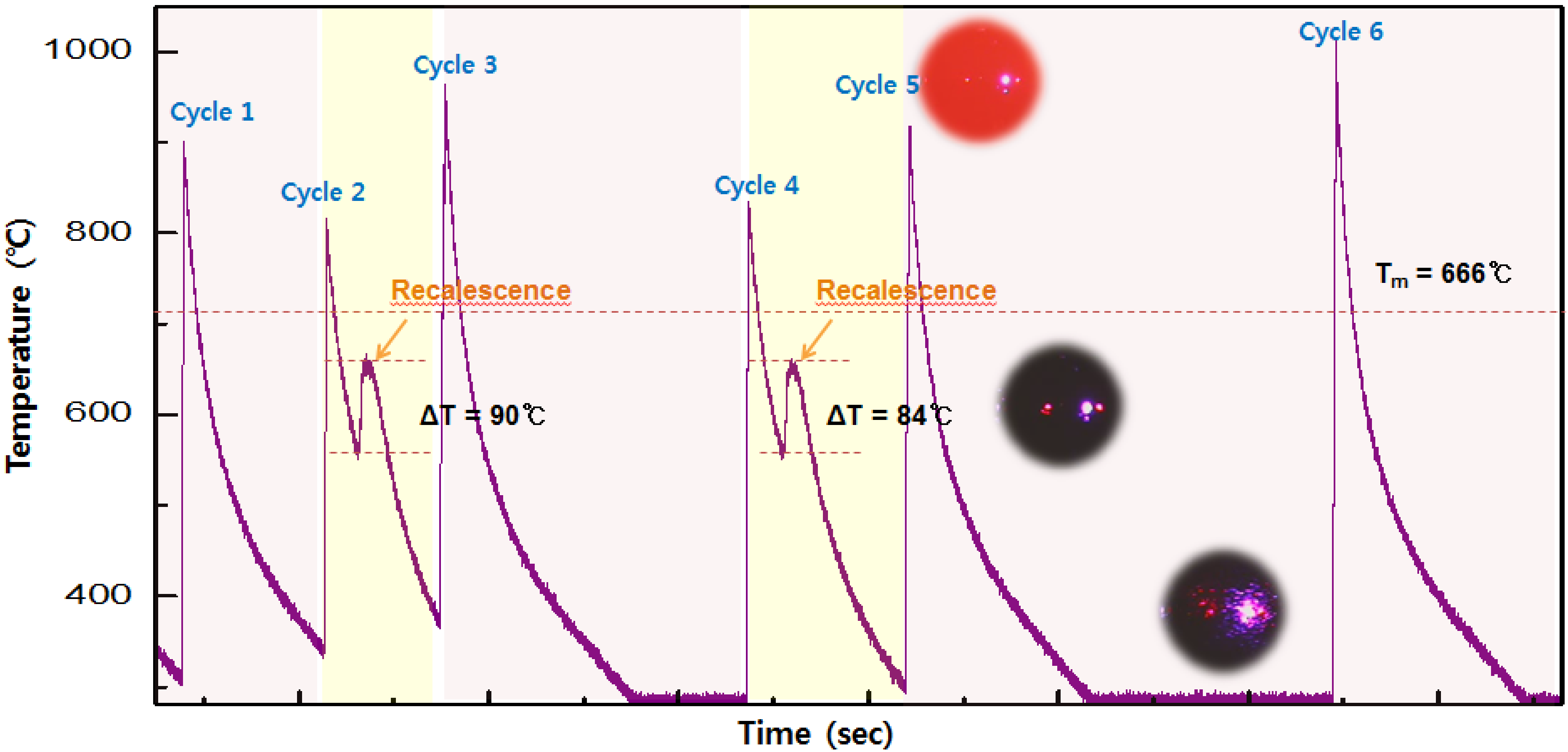
Temperature(℃)
900
800
700
600
500
400
300
Time(sec)
Temperature(℃)
600
500
400
T_g
T_x
Time(sec)
Temperature(℃)
700
600
500
400
T_g
Time(sec)

VIT 1



Tm=666°C
190K/s
126K/s
75K/s
48K/s
35K/s
16K/s
13K/s
12K/s
537°C
525°C
516°C
511°C
474°C
470°C
467°C
413°C
408°C
396°C
371°C
367°C
366°C
365°C
Temperature(℃)
Time(sec)
Vit 1
Vit 1a - 2.5 W/g
Vit 1b - 5.0 W/g
Vit 1c - 7.5 W/g
Vit 4 - 10.0 W/g
Endothermic Heat Flow(W/g)
Endothermic
Temperature(K)
: T_g
: T_{x1}
Temperature(℃)
Heating rate(K/s)

Cyclic cooling curves in ESL



Fundamentals of the Glass Transition

If liquid is cooled, two events can occur.

1) Crystallization (solidification at $T_{m.p.}$)

2) Undercooled below $T_{m.p.}$ (supercooled) → More viscous → Glass

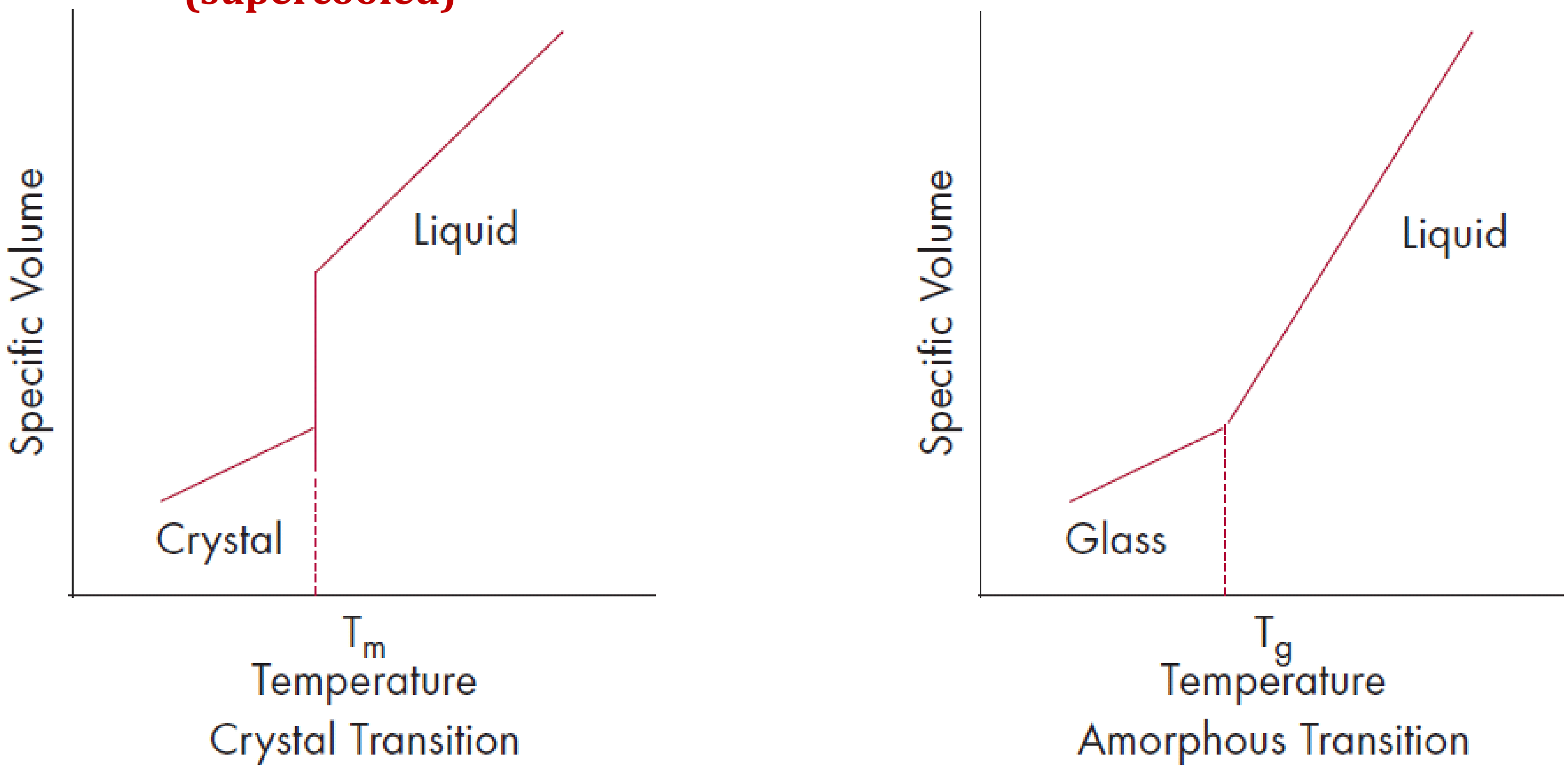


Figure 4. **Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).**

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