2010 Spring

"Amorphous Materials"

03.25.2010

Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for today's class

- **Preparation of amorphous materials**

Sputtering — Surface coating

Chemical vapor deposition

Thermal evaporation

Pulsed laser deposition

electrolytic deposition

Droplet quenching — Bulk type : sphere, rod, plate

Water quenching

Injection casting — **Suction casting**

Squeeze casting — **Strip casting**

Centrifugal casting

Gas atomization — powder

Melt-spinning — thin film

Splat quenching — thin plate

Irradiation

Pressure-induced amorphization

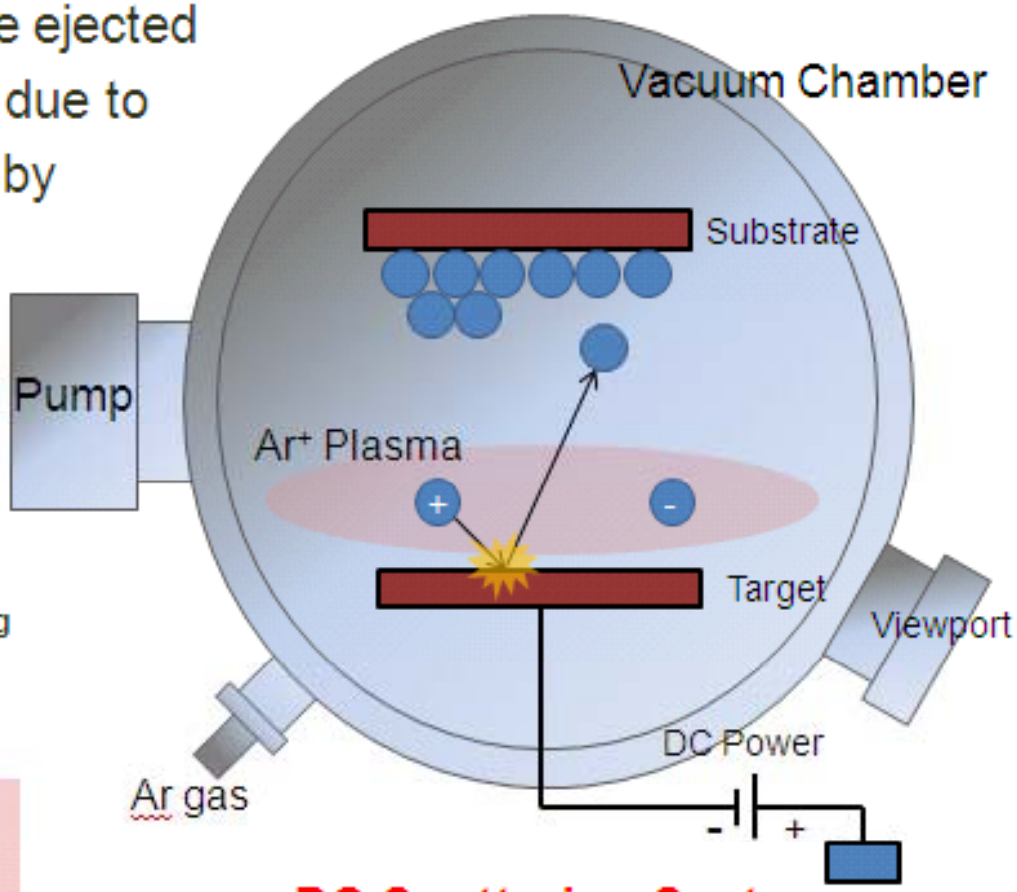
Solid-state diffusional amorphization

Computer simulation

What is Sputtering?

- **Sputtering** is a common method for **thin film deposition.**
- Process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic particles.
- Ejected atoms are deposited on the substrate, form thin film.

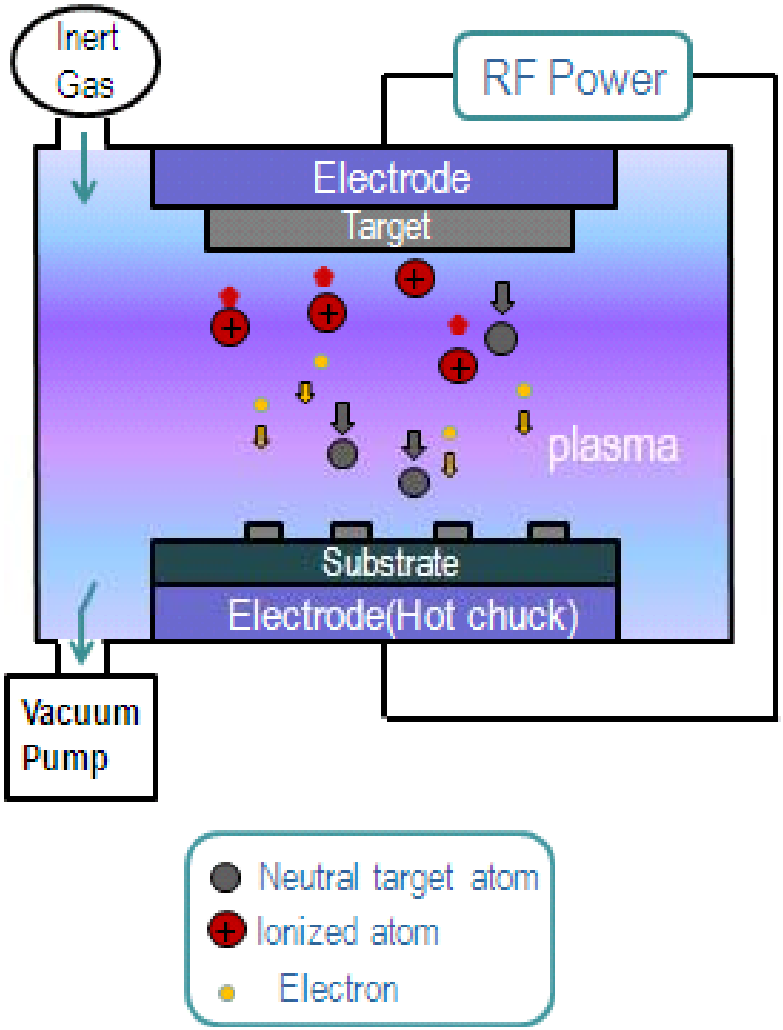
Ref. http://en.wikipedia.org/wiki/Sputtering



DC Sputtering System

Vacuum : evaporated particles can travel directly to the substrate

Radio Frequency Sputtering



✓ DC vs RF

	DC Sputter	RF Sputter
Deposition rate	faster	slower
Inert Gas Pressure	Higher	lower
Dep.material	Metal	Metal, Insulator, oxide
ETC		Improve plasma handling.

✓ Controlling Temperature of Chuck

Cooling rate of the thin film can be modulated.

⬇

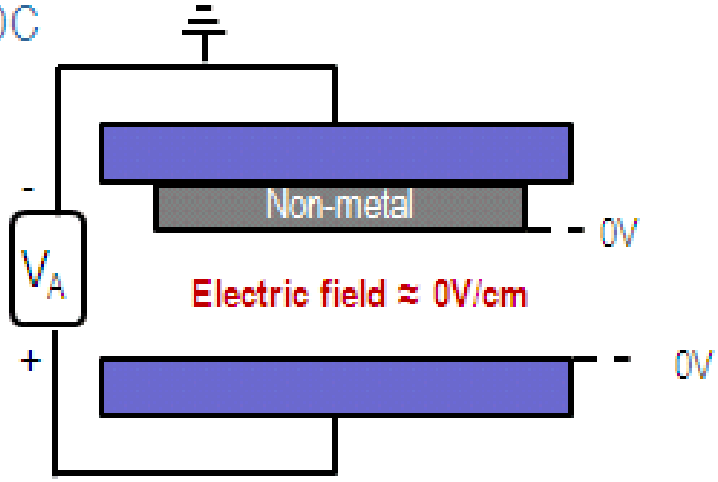
Some of materials can formed to amorphous state.

Ex) Crystallinity of ZnO $\propto \dfrac{1}{\text{Chuck temp}}$

Radio Frequency Sputtering

✓ Principle of non-metal deposition using RF sputter

- DC

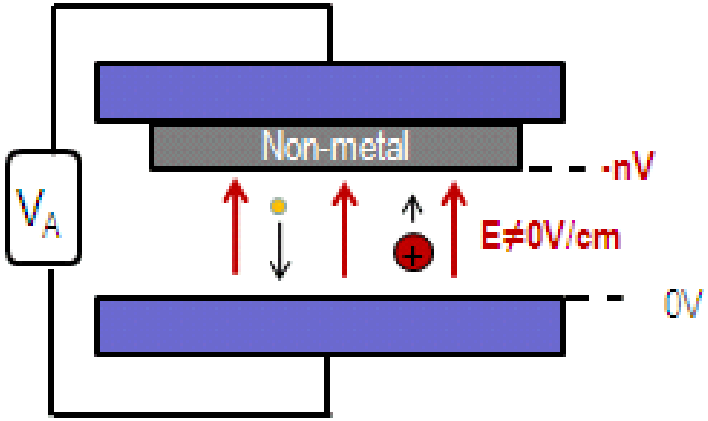


$$\Delta Q = C\Delta V$$

Voltage drop in Target

$\Delta V \approx -V_A$

- RF



1. Alternating current
   → prevent charge buildup in Target

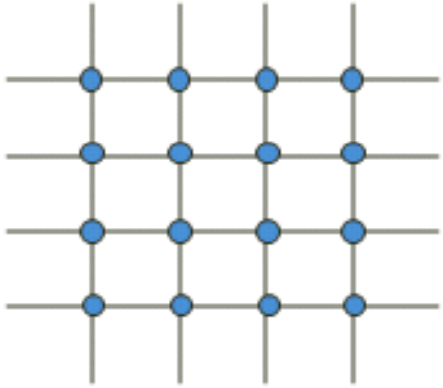
   $\Delta V \approx 0V$

2. Mobility Difference btw Positive ion & electron
   → negative potential at target surface

Formation of Amorphous Thin Film

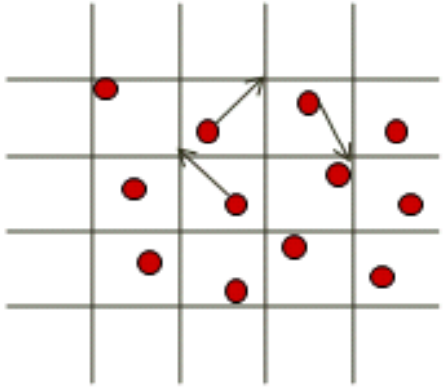
Calculation of Diffusion Length

Crystalline



Enough time for locating at right position

Amorphous



Not enough time for locating at right position

$$l \cong \sqrt{Dt} \cong \sqrt{D_0 \exp\left(-\frac{Q_s}{kT}\right)\frac{1}{dep\ rate}}$$

Diffusion length

Diffusivity

Lifetime of monomer

Deposition condition (T, dep rate) affects the diffusion length

↓

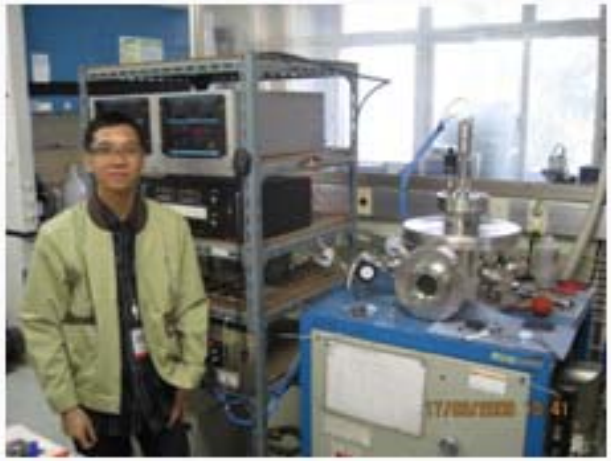
Diffusion length determines the crystallinity of thin film

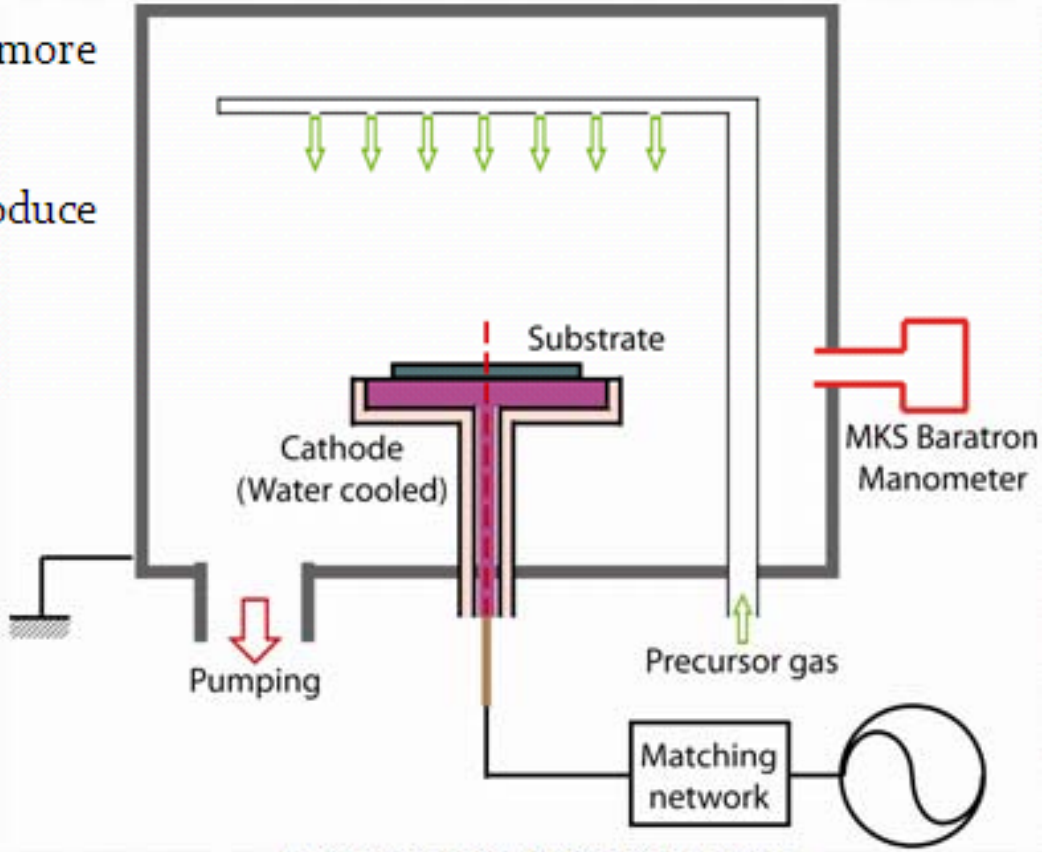
Ref. Prof. Kibum Kim's lecture

Surface coating

Principles of CVD

- Substrate is exposed to one or more volatile precursors.
- Precursors will react and/or decompose on substrate to produce the desire deposit.





A schematic of r.f.PACVD coating chamber.

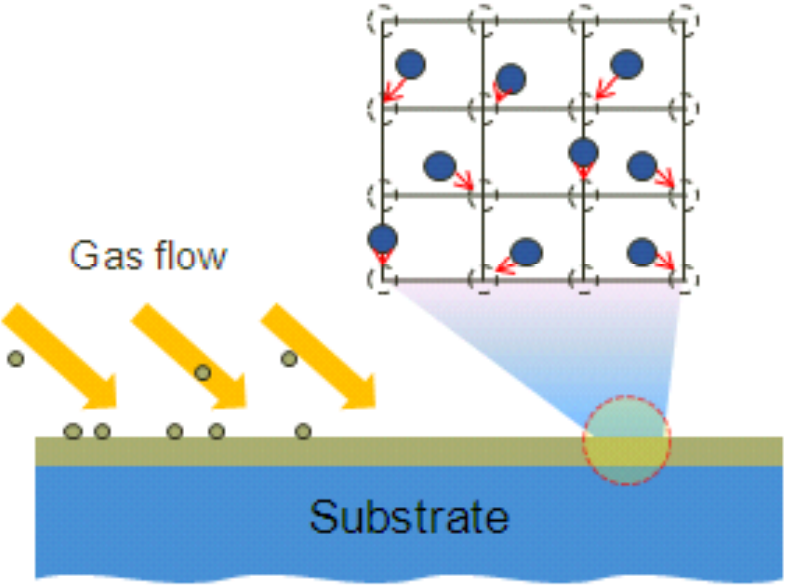
- Base and deposition pressure: 10^{-6} and 10^{-2} Torr
- Bias voltage: -400 to -800V
- Deposition temp. : RT

Surface coating

- PECVD (Plasma Enhanced CVD)
- LPCVD (Low Pressure CVD)
- APCVD (Atmospheric Pressure CVD)
- UHVCVD (Ultra-high vacuum CVD)
- DLICVD (Direct liquid injection CVD)
- AACVD (Aerosol-assisted CVD)
- MPCVD (Microwave Plasma CVD)
- ALCVD (Atomic Layer CVD)
- Laser CVD

Formation of amorphous

- Amorphous forming ability is depends on diffusion length
- Diffusion length $\propto \sqrt{Dt}$
- Deposit process is commonly forming amorphous because of low temperature and rapid growth rate
- CVD process is progressed at little high temperature, so metal do not forming amorphous generally



Low temperature, short time

↓

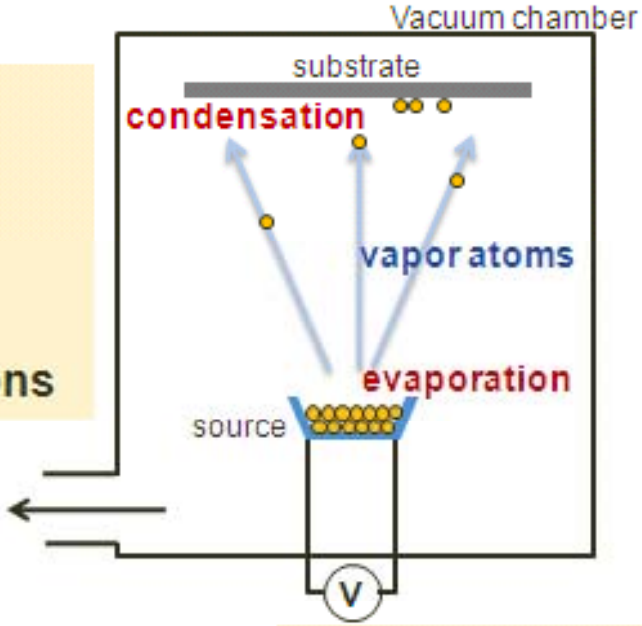
Amorphous

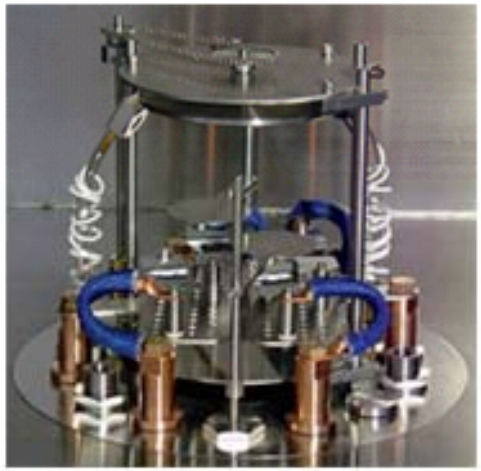
Thermal Evaporation

- Thermal evaporation is a common method for thin film deposition.
- The source material is **evaporated** from a source by heating in a **vacuum**.
- The evaporated material is then **condensed** on the substrate.

Vacuum : evaporated particles can travel directly to the substrate

Mean free path :
~ chamber dimensions





Heating : resistance heating (Joule effect)

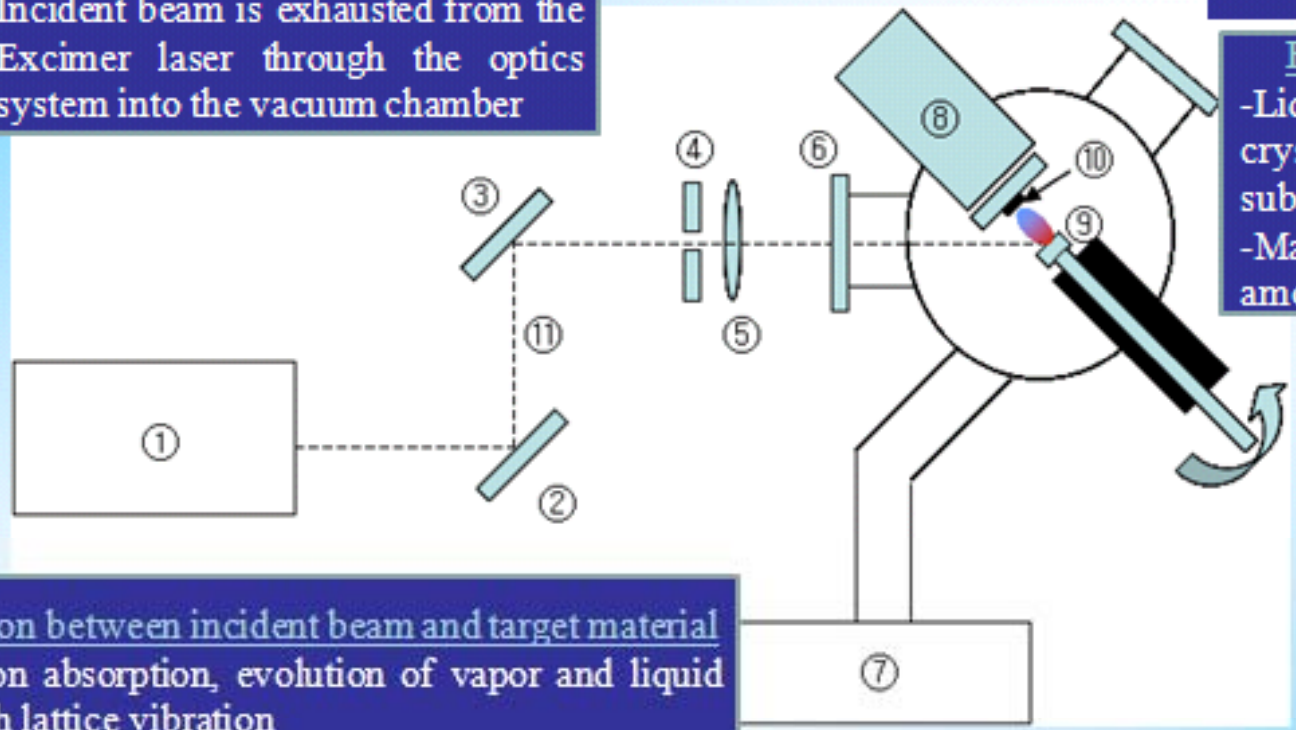
Surface coating

Pulsed Laser Deposition
- What is it?

1. Incident beam is exhausted from the Excimer laser through the optics system into the vacuum chamber

2. Collision between incident beam and target material
- Photon absorption, evolution of vapor and liquid through lattice vibration

3. Film deposition
-Liquid and vapor crystallization on the substrate
-May be crystalline or amorphous



1. Excimer Laser 2, 3. Optical Mirrors 4. Aperture(slit) 5. Focal lens
6. Chamber window 7. Turbo pump 8. Holder heating machine
9. Target material 10. Substrate and substrate holder 11. Laser path

Basic Concept of Electrolytic Deposition

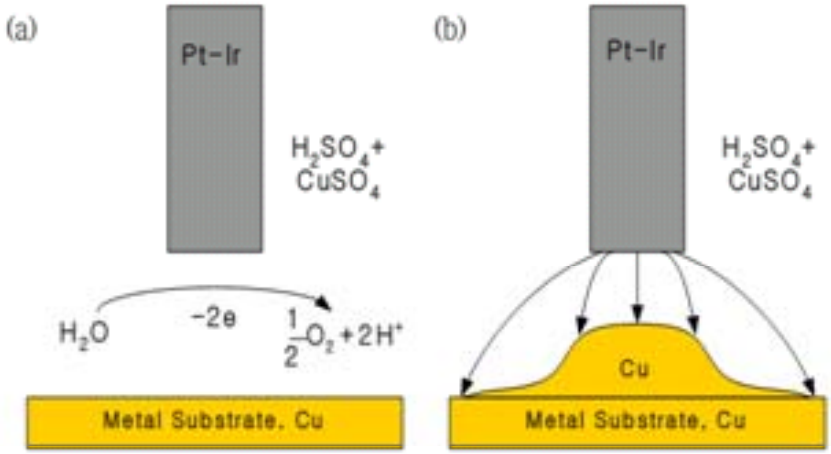


Fig. 1 Schematic diagram of electrochemical reaction at (a) micro electrode and (b) substrate

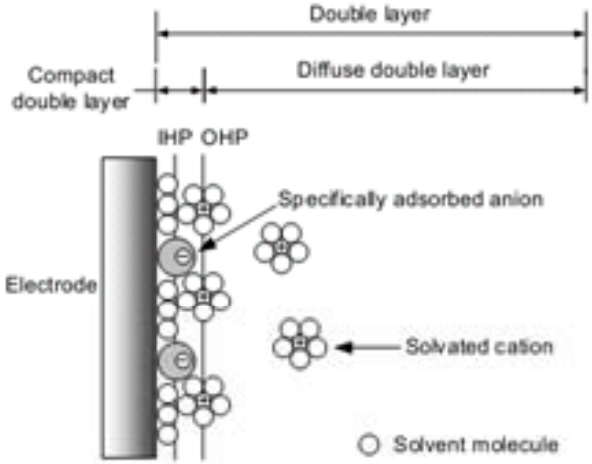


Fig. 2 Electrical double layer

Schematic Diagram of Electrolytic Deposition

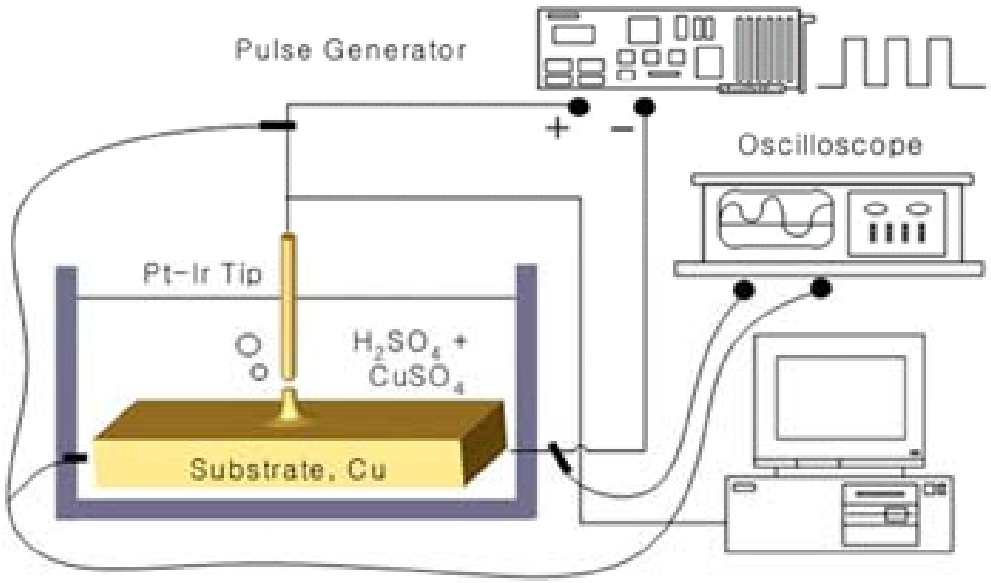


Fig. 4 Schematic diagram of experimental setup

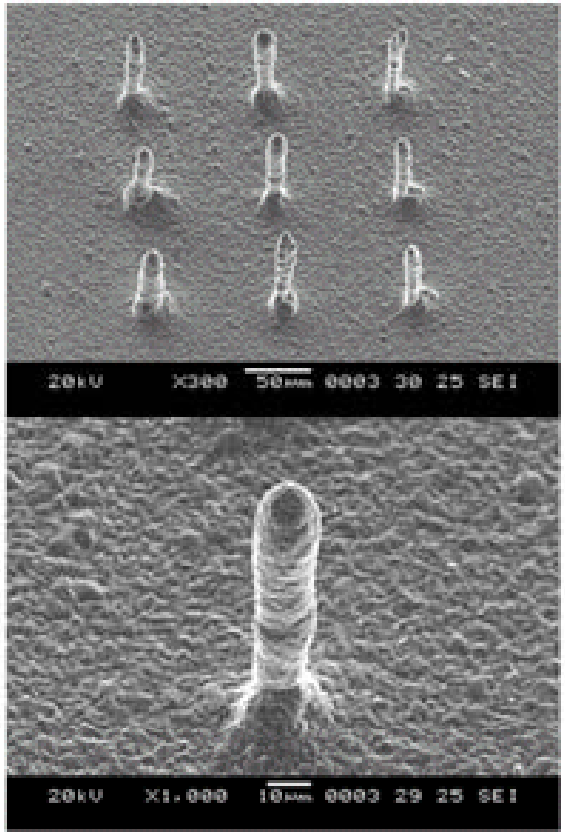
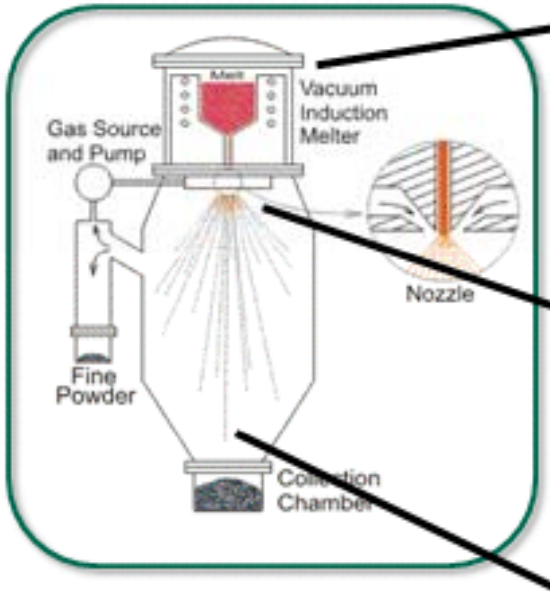


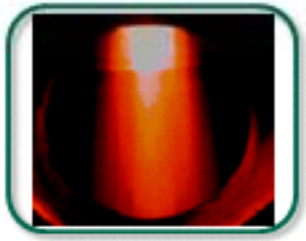
Fig. 15 Column array with 3.5 V, 350 ns/ 1 μs

Gas Atomization

Components of Atomizer



- **Furnace**
  Melting Metal or Ceramics



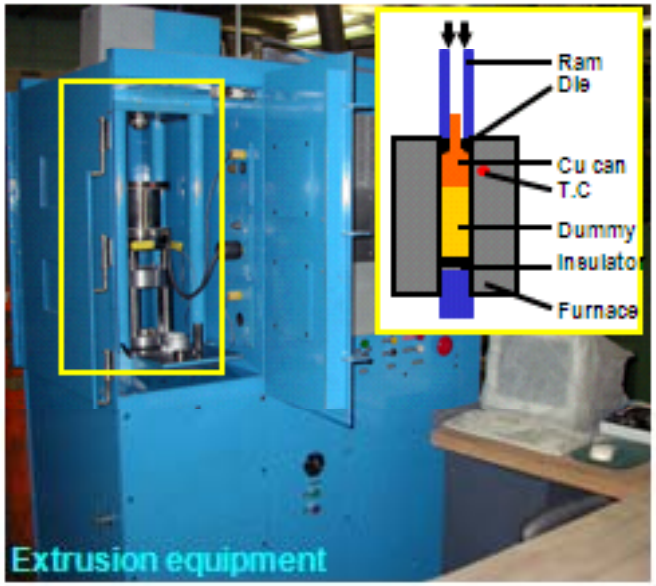
- **Pump and Spray Nozzle**
  Inert gas flows out with breaking bulk liquid.

- **Chamber**
  Powder is Stored in a chamber.

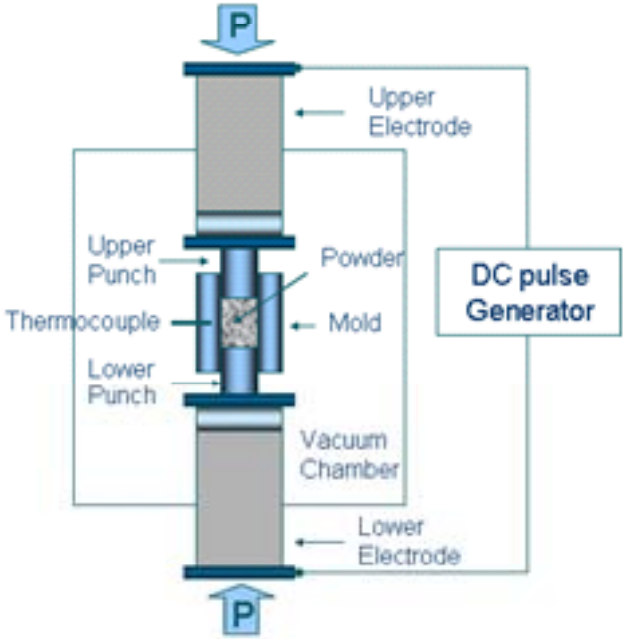
Powder to BMG

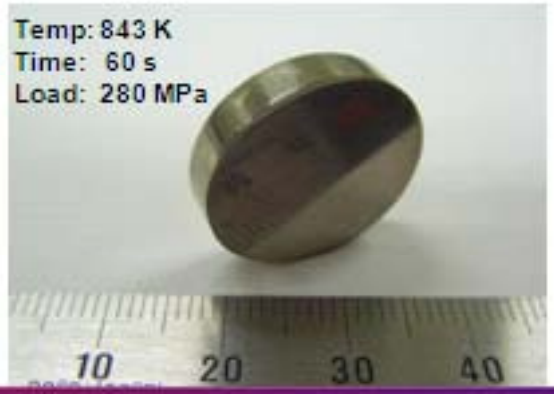
Powder ➡ bulk metallic glasses

1) Extrusion



2) Spark Plasma Sintering

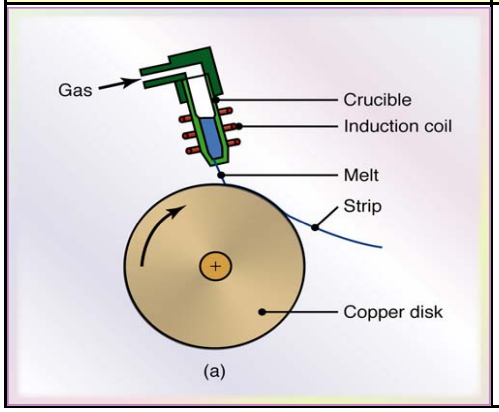
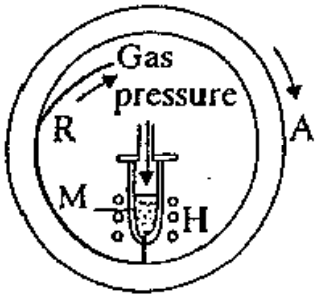
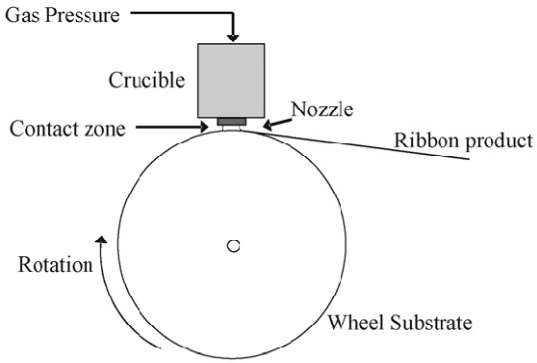
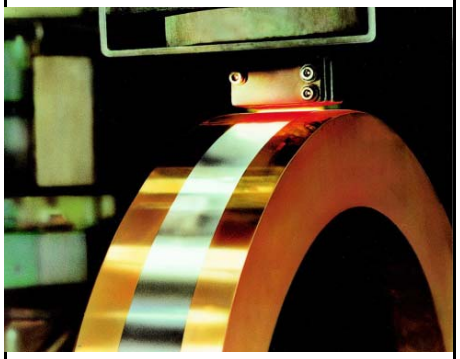




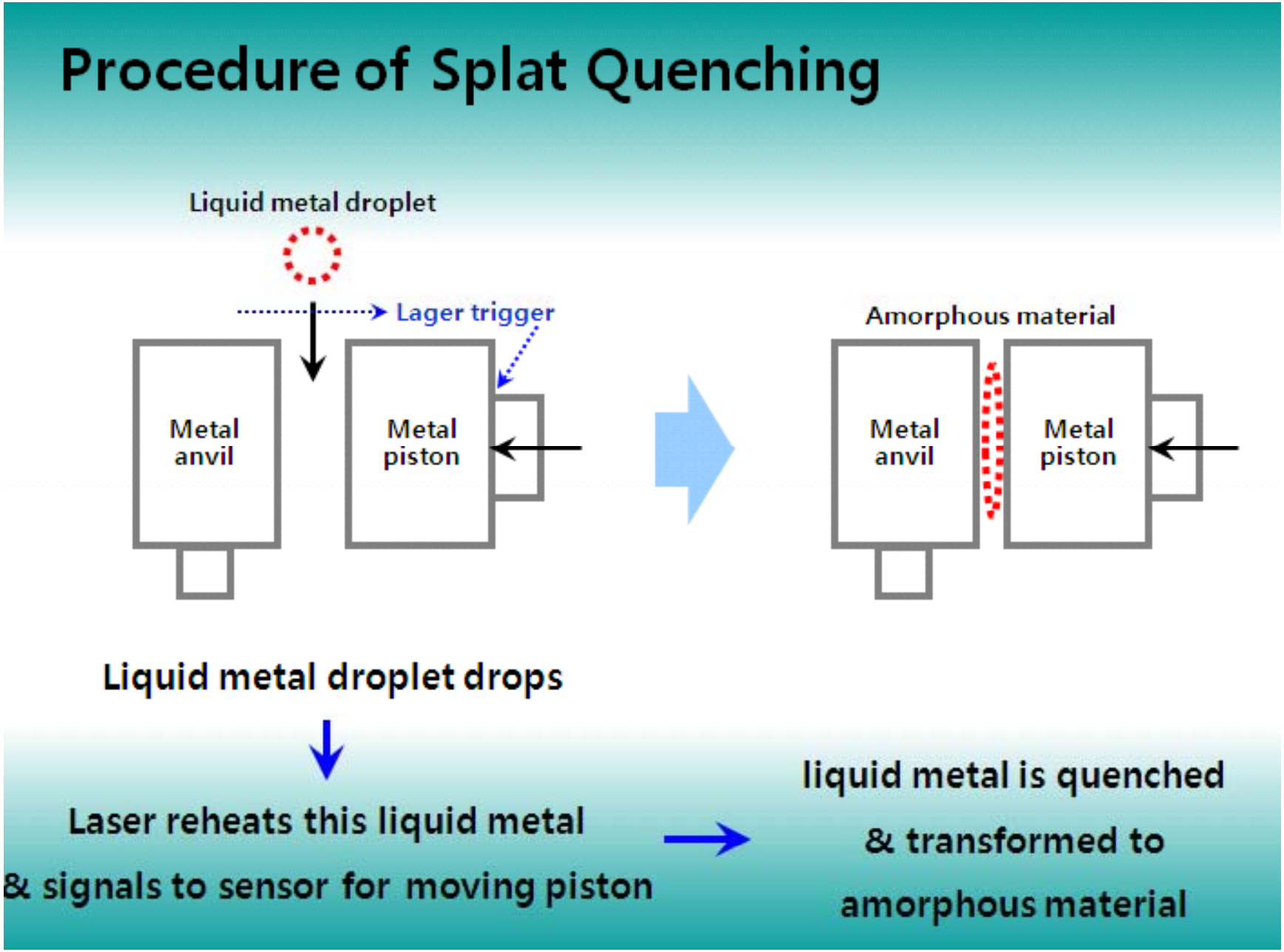
▣ Brief Definition of Melt Spinning

A jet of liquid metal is ejected from a nozzle and impinges on the surface of a rotating substrate, where a thin layer is formed from a melt puddle and rapidly solidifies as a continuous ribbon.

▣ Several Types of Melt Spinning Method

Free Jet Melt spinning (FJMS)		Planar Flow Melt spinning (PFMS)	Example (PFMS, Siemens)
Outside of Wheel	Inside of Wheel		
			

Thin disk


Procedure of Splat Quenching
Liquid metal droplet
Lager trigger
Metal anvil
Metal piston
Amorphous material
Metal anvil
Metal piston
Liquid metal droplet drops
Laser reheats this liquid metal
& signals to sensor for moving piston
liquid metal is quenched
& transformed to
amorphous material

History of Metallic Glasses

- First amorphous metal produced by evaporation in 1934.

  *j. Kramer, Annalen der Phys. 1934; 19: 37.

- First amorphous alloy(CoP or NiP alloy) produced by electro-deposition in 1950.

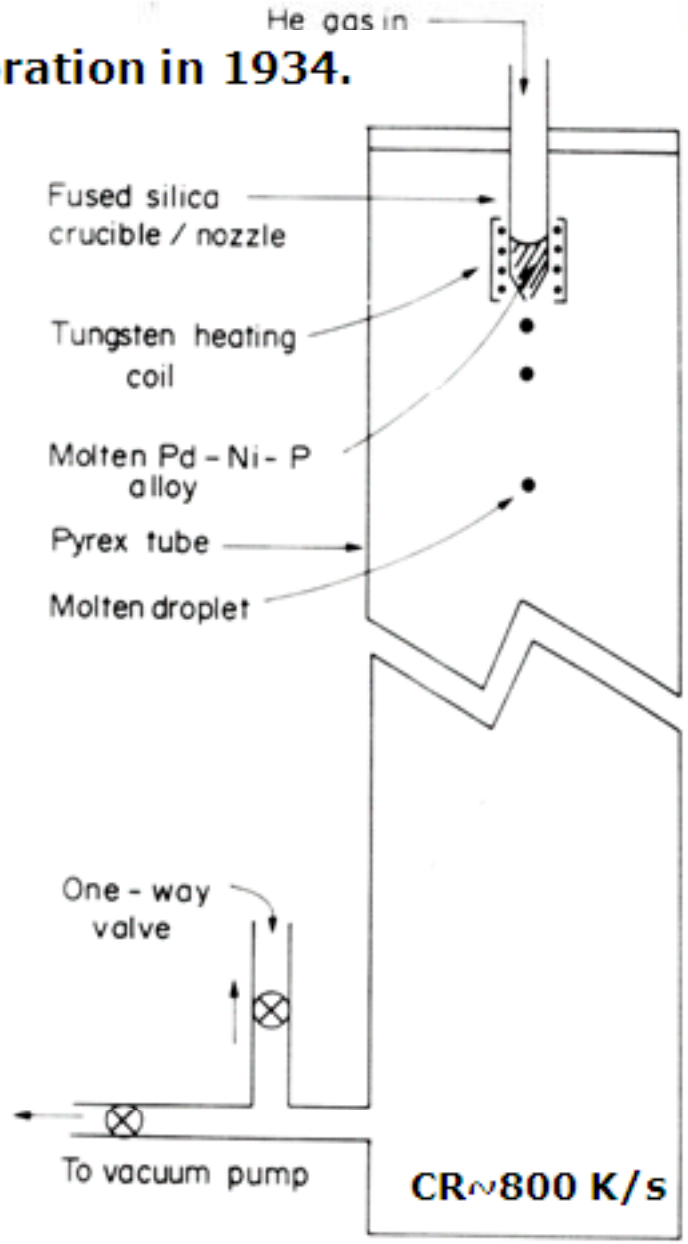
  *A. Brenner, D.E. Couch, E.K. Williams, J. Res. Nat. Bur. Stand. 1950: 44; 109.

- First metallic glass ($Au_{80}Si_{20}$) produced by splat quenching at Caltech by Pol Duwez in 1957.

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

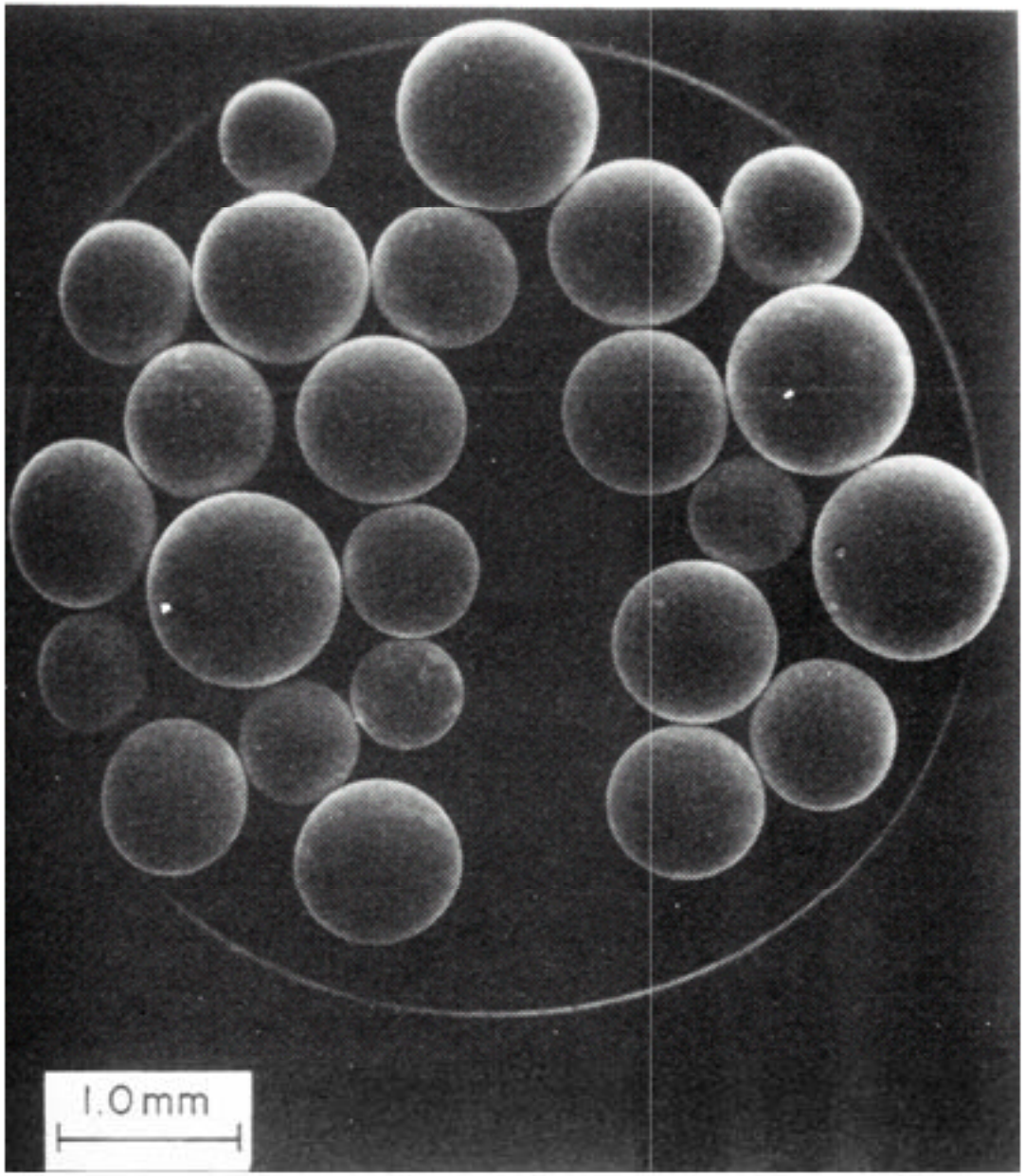
- First bulk metallic glass ($Pd_{77.5}Cu_6Si_{16.5}$) produced by droplet quenching at Harvard Univ. by H.S. Chen and D. Turnbull in 1969

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



SEM image of a collection of glass spheres after droplet quenching

sphere



Bulk sample

Water Quenching

Quenching by plunging the bottom of the Pt container in a water bath

MAB (MgO-Al_2O_3-B_2O_3) glasses

Bulk sample

Fluxing & Water quenching

Making alloying metals

Melting & making alloy

Water removal in B2O3

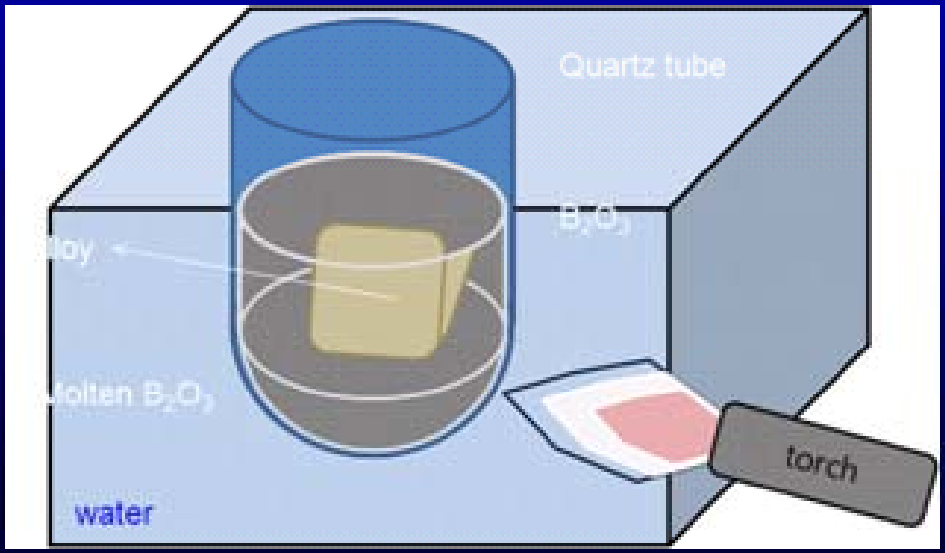
Flux Preheating

Purifying

Repeat of heating & cooling

Quenching

Water quenching



Formation of bulk metallic glass by fluxing

- **Heterogeneous nucleation**

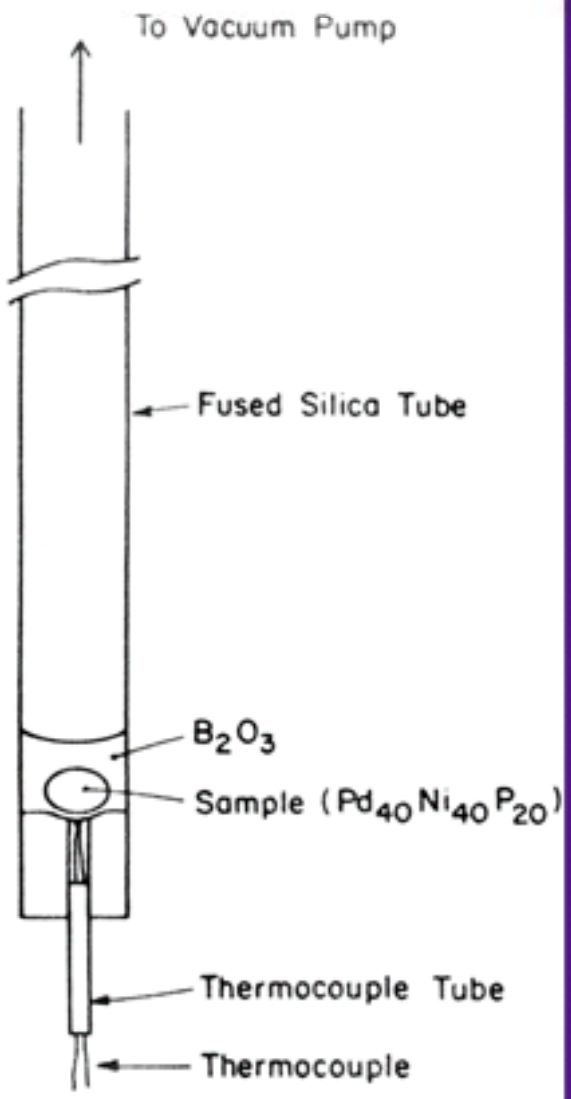
  1. Surface oxide layer
  2. Container walls
  3. Motes in the liquid

→ **Suppression**

1. Ingot = Chemical etching
   by dilute aqua regia (HNO3 + HCl)
2. Interior of the vessel = Cleaning
   by hydrofluoric acid
3. Impurities = Successive heating-cooling cycles
   in a molten oxide flux

B_2O_3 melting point 723 K, boiling point <40,000 K

After gravity segregation to the oxide-metal interface most heterophase impurities presumably are dissolved or deactivated (e.g., by being wet) by the molten oxide



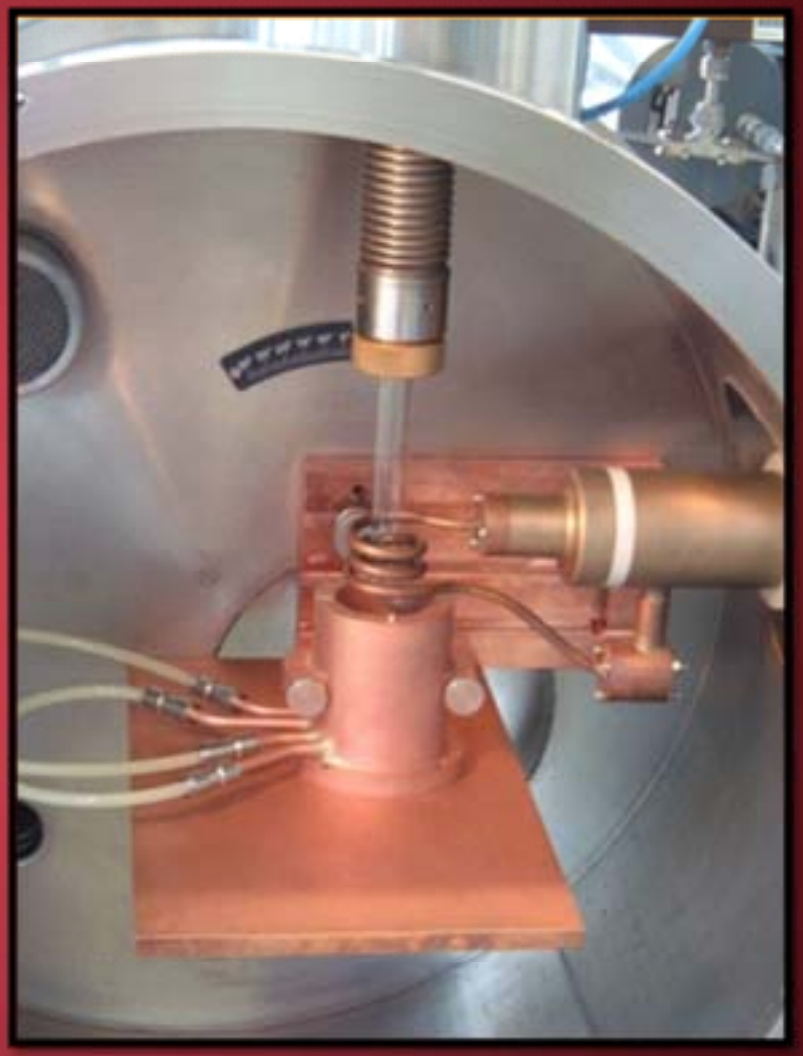
Bulk sample: rod

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



Bulk sample: rod

Suction Casting Method

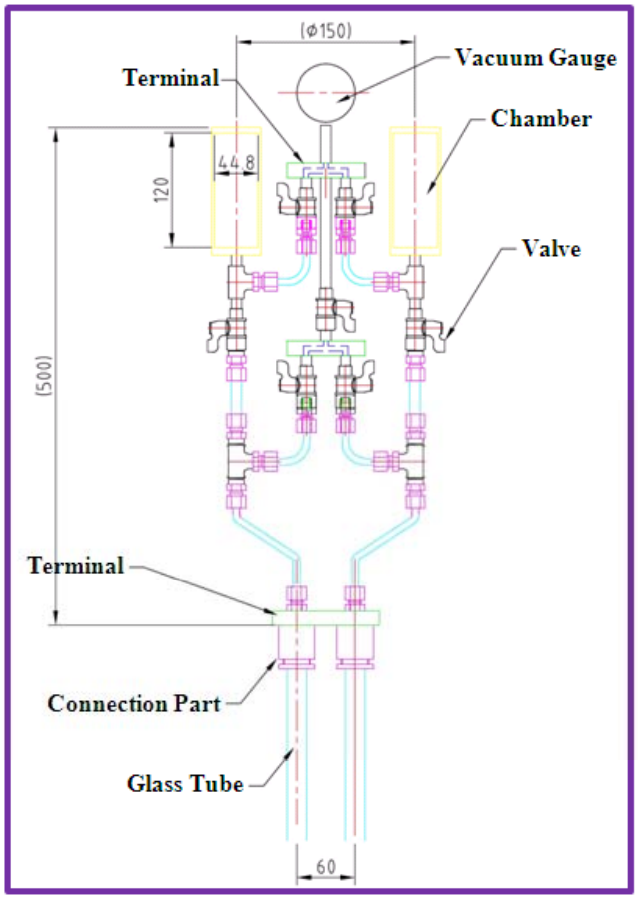
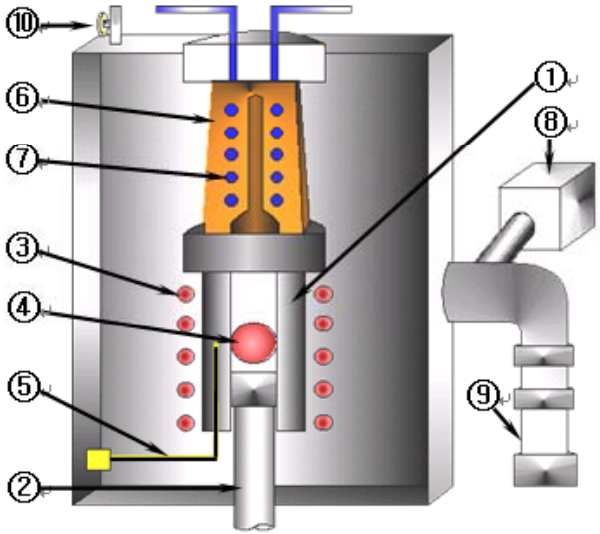


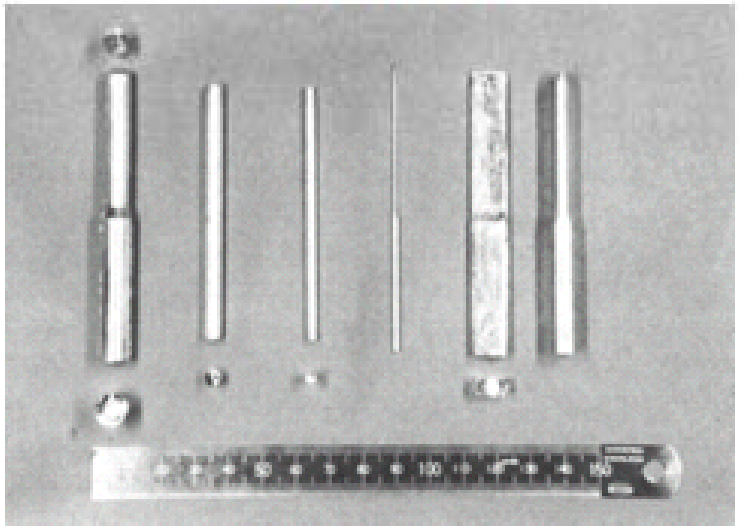
Fig. 6. Photograph of the as-cast specimens of (from left to right):
(a) suction cast 12X1X~70 mm^3 plate,
(b) drop cast 6.4X~70 mm^2 cylinder,
(c) suction cast 3 mm diamX~70 mm cylinder.

High Pressure Die Casting Method: Squeeze casting



①	Graphite crucible	⑥	Copper mold
②	Plunger	⑦	Water cooling
③	Induction coil	⑧	Rotary pump
④	Molten alloy	⑨	Diffusion pump
⑤	Thermocouple	⑩	Evacuation valve

$Mg_{65}Cu_{25}Y_{10}$

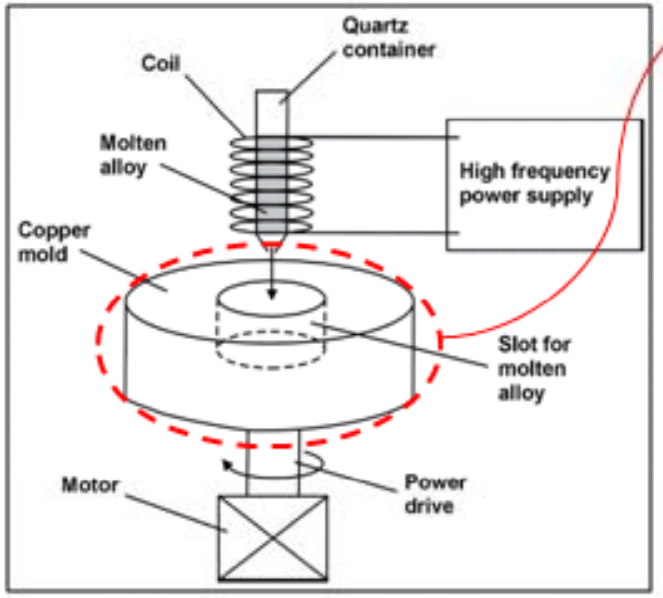


Product

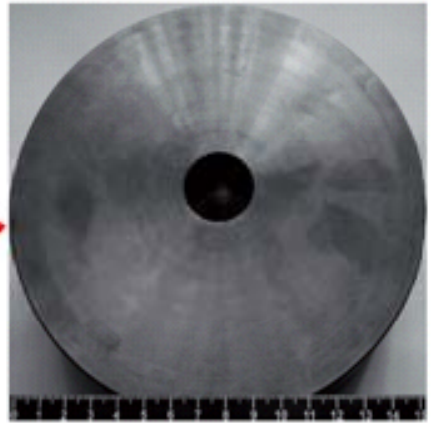
A. Inoue *et al.*, MSE(A), Vol.173 (1993) pp.1-8

Bulk sample: tube

Centrifugal Casting Method

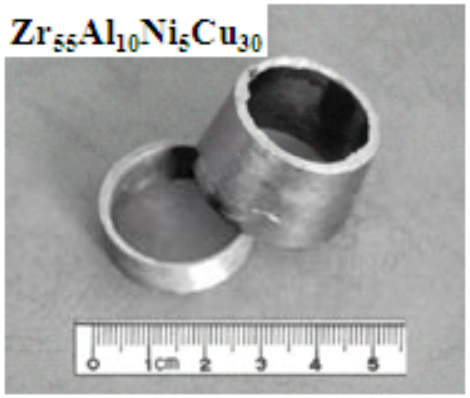


Schematic Diagram

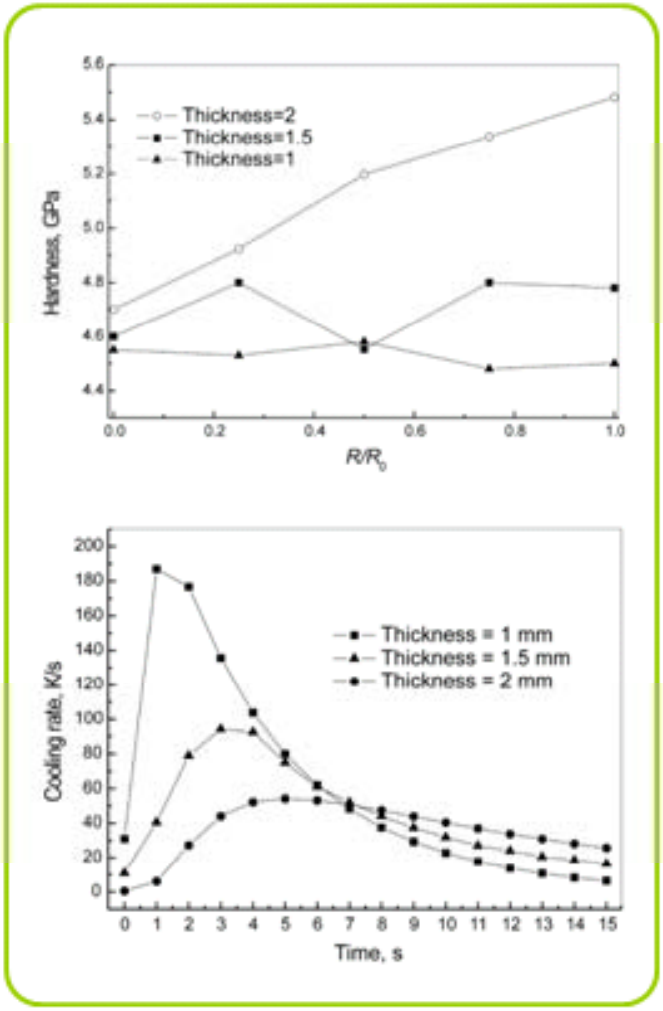


Copper Mold

$Zr_{55}Al_{10}Ni_5Cu_{30}$



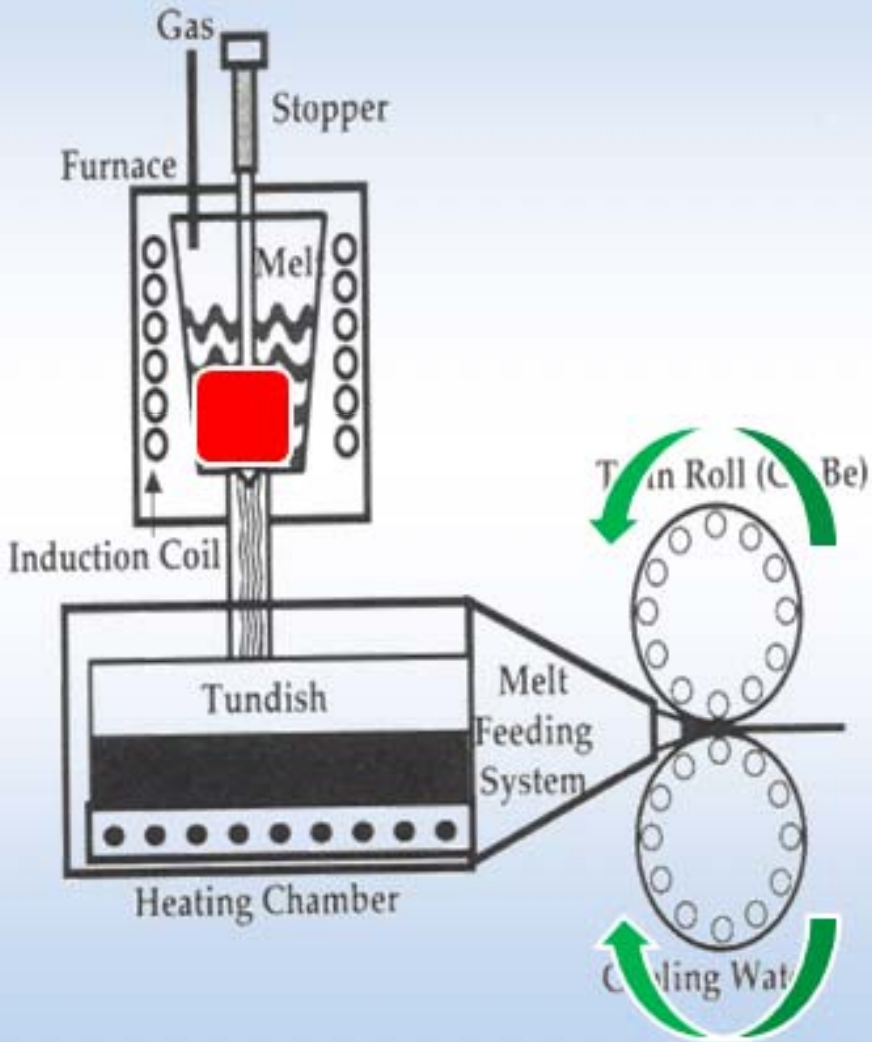
Product



R. Nowosielski *et al.*, J. Ach. in Mater. Man. Eng., Vol.20 (2007) pp.487-490
Q. Zhang *et al.*, Intermetallics Vol.10 (2002) pp.1197-1201

Bulk sample: Plate

Strip casting of amorphous alloys



Developed in Postech, 2004

Thickness : 1 to 4 mm

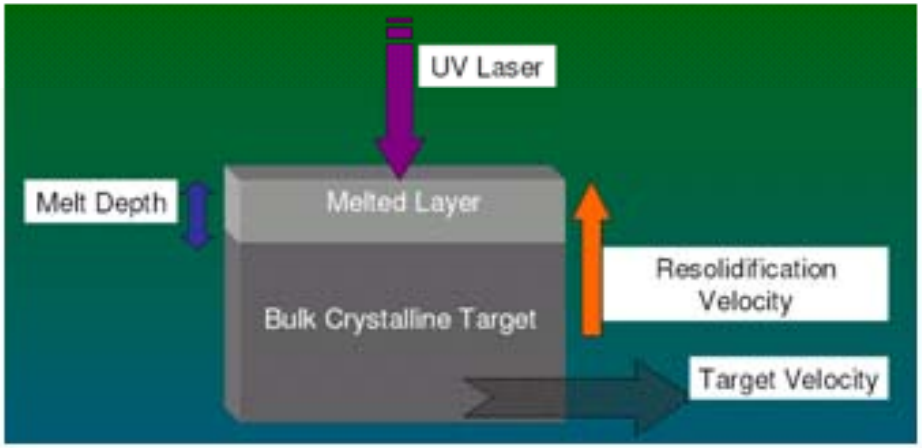
Amorphous alloy or
Amorphous + Crystalline Composites

Preparation of amorphous materials by irradiation

Two kinds of irradiation effects

- Laser/electron irradiation:

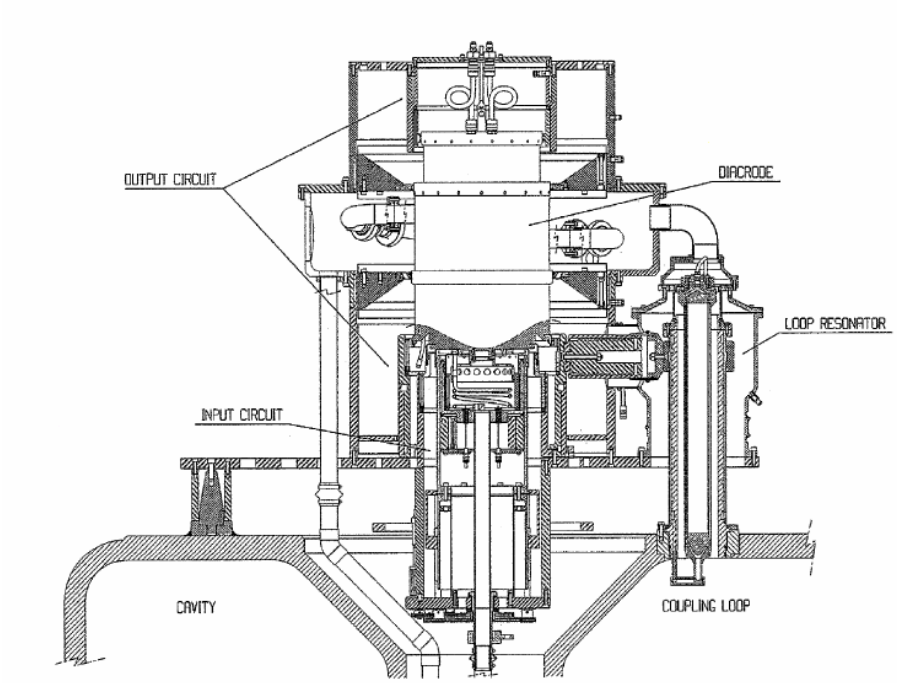
Small area melting → cooling → amorphous layer/crystalline

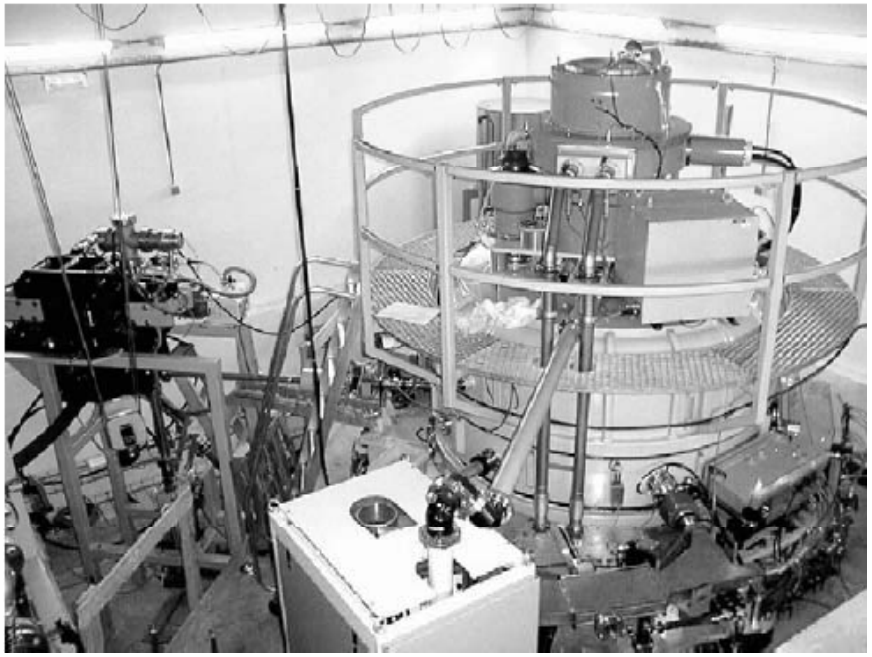


- Neutron and heavy ion irradiation:

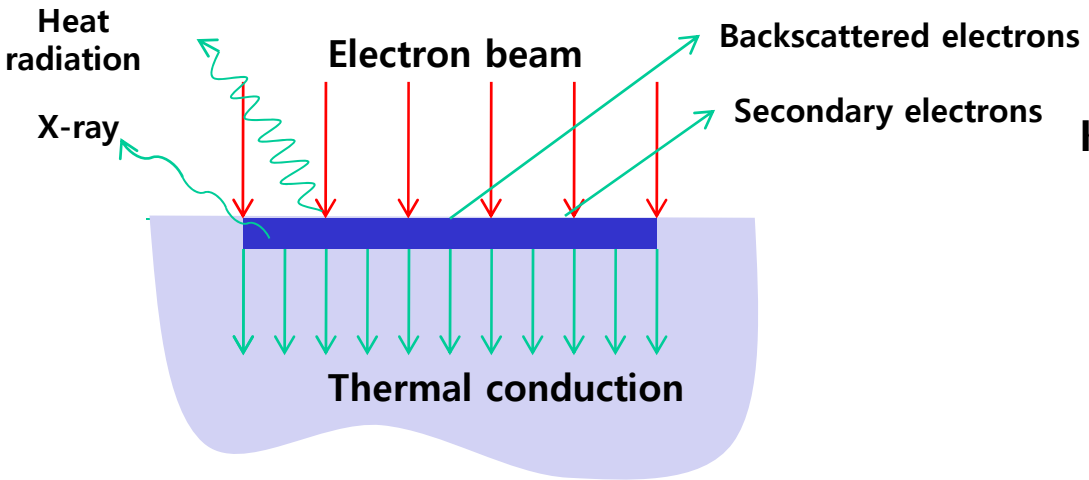
Atomic displacement → recovery → amorphous phase

The schematic diagram of High Energy Electron beam accelerator





TT1000 prototype picture

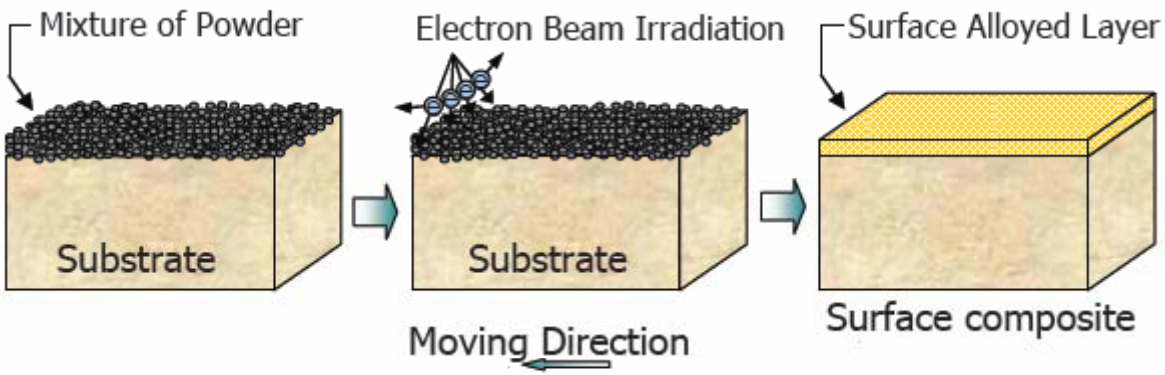


Kinetic energy of accelerated electron

↓ Collided with electrons of materials

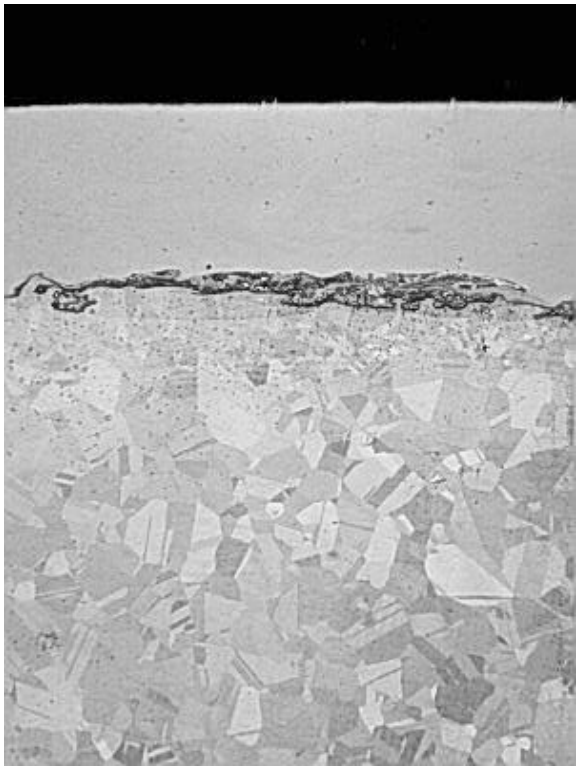
To transform thermal energy

The making method of amorphous materials by Irradiation



❖ Electron beam irradiation is heating the mixture of powder.

❖ The temperature of substrate is so low that surface is super-cooling.



Surface : Amorphous alloy

Surface gloss, Hardness, corrosion resistance,

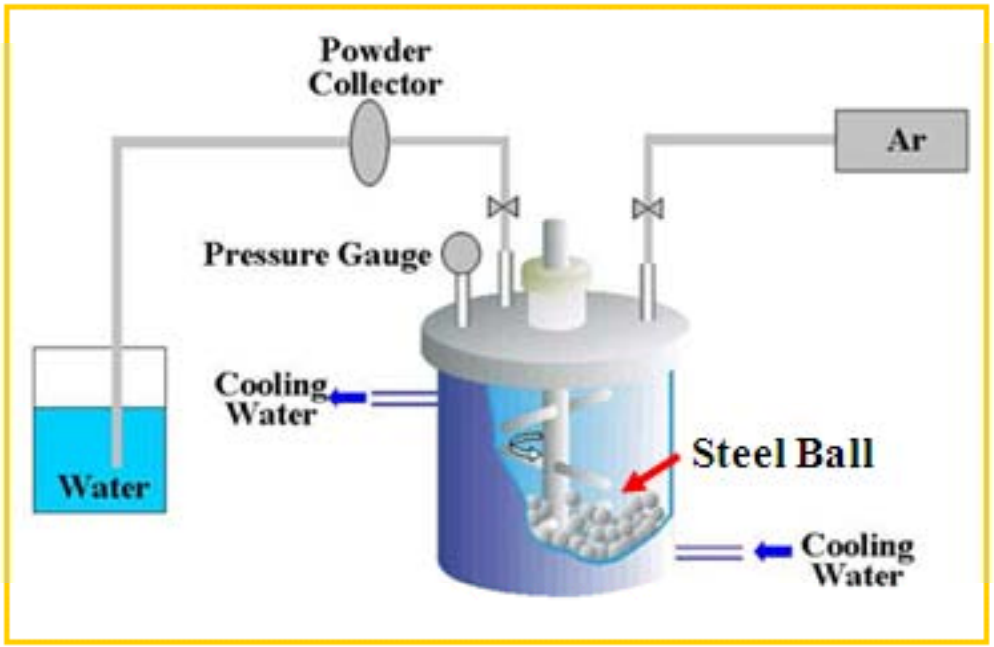
Substrate : Cu(or Ti, Fe) alloy

Ductility, limited size of amorphous materials,

It is possible to make mass production and reduce weight

Pressure induced amorphization

Schematic Diagram of Mechanical Alloying Process

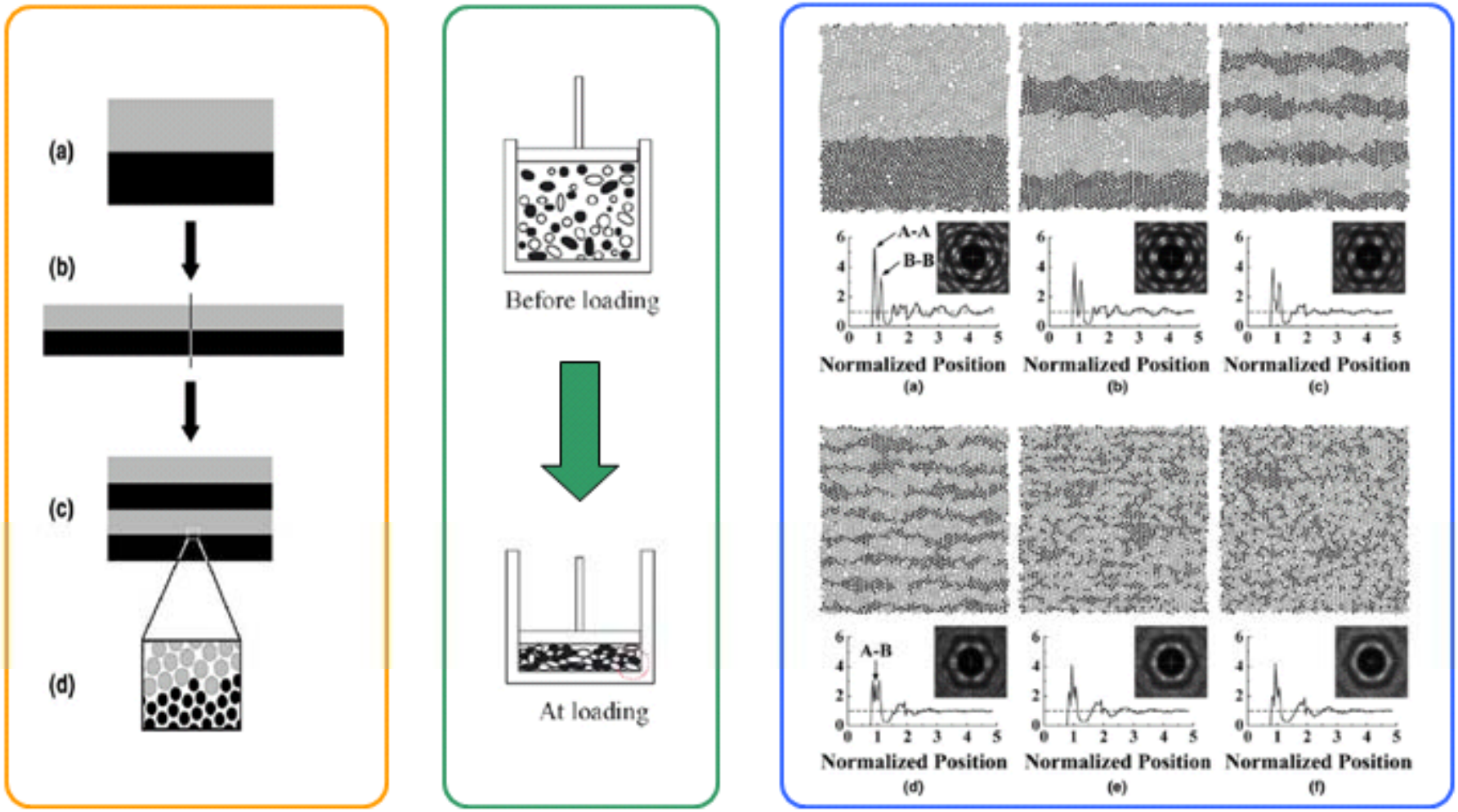


- Increased Solid Solubility Limit
- Easy to Control the Microstructure
- Easy to Fabricate Non-Equilibrium and Nano Phase
- Homogeneous Distribution of Fine Strengthener
- Excellent Mechanical Properties

Attritor

Pressure induced amorphization

Amorphization during Mechanical Alloying

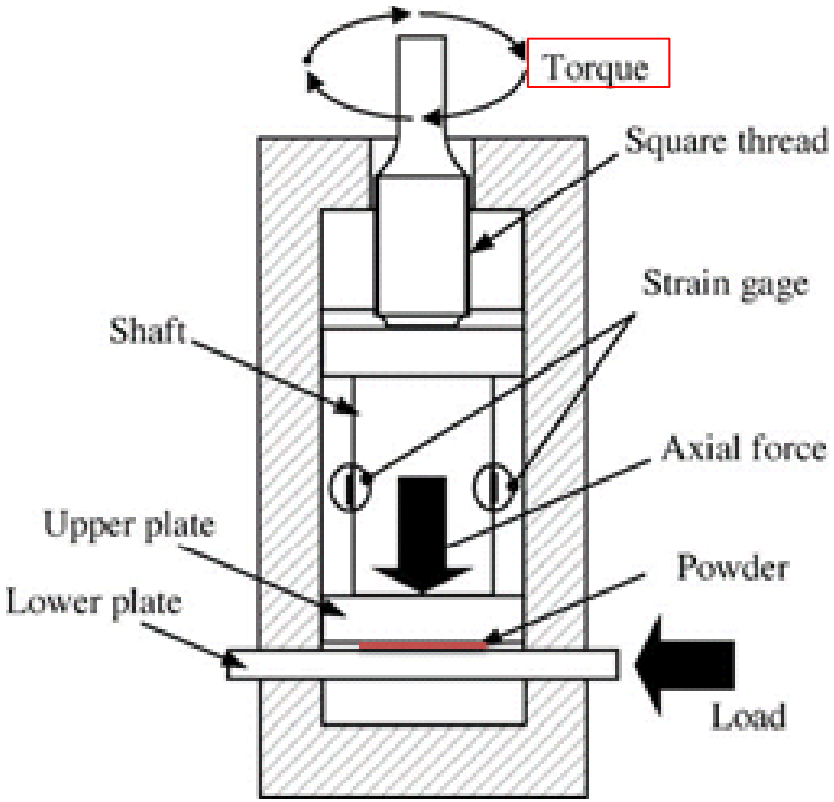


A. C. Lund and C. A. Schuh, Acta Mater. Vol. 52 (2004)

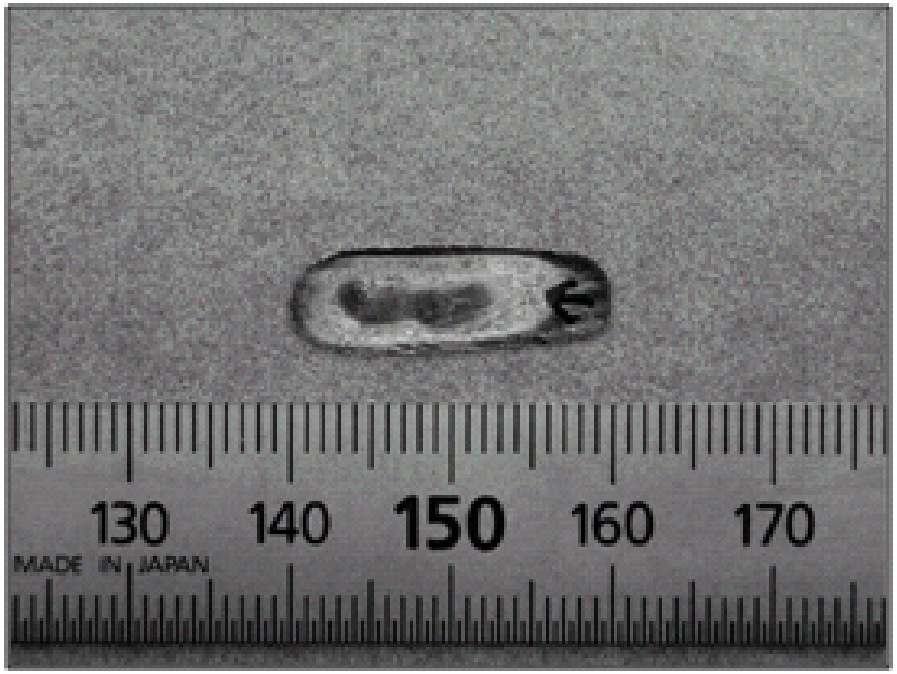
Pressure induced amorphization

Compression Shearing Method – at room temp.

- Axial compression pressure : 100kN
- Lower steel plate : 3mm normal to the axial
- Applied shear stress : 877MPa



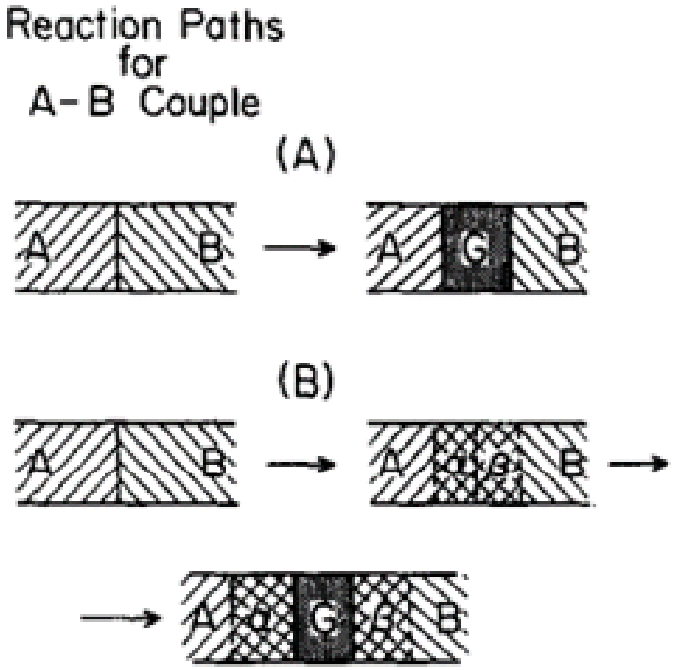
$Nd_{15}Fe_{77}B_8$ (Thickness : 1.0mm)



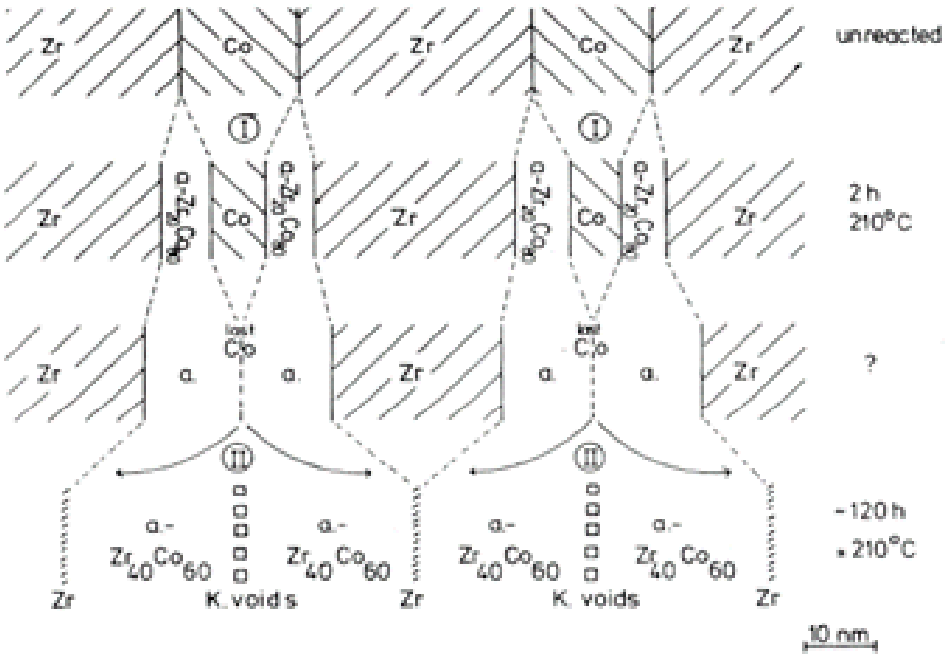
T. Saito et al., Journal of alloys and Compounds 396 (2005) 208-211

Solid-State Diffusional Amorphization

Schematic Diagram



Example (Co-Zr)



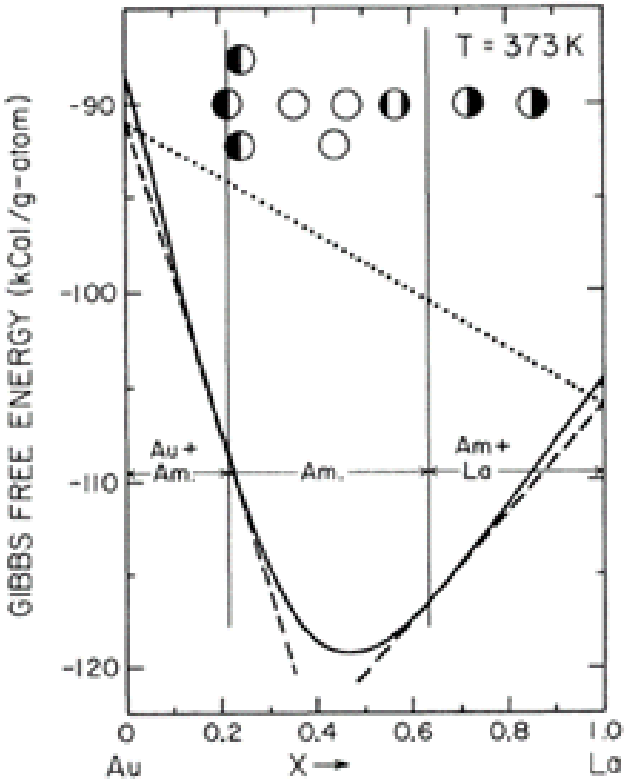
(A) Direct nucleation of the amorphous phase

(B) Substantial mutual dissolution of the parent metals leading to unstable solid solutions

Two Main Attributes

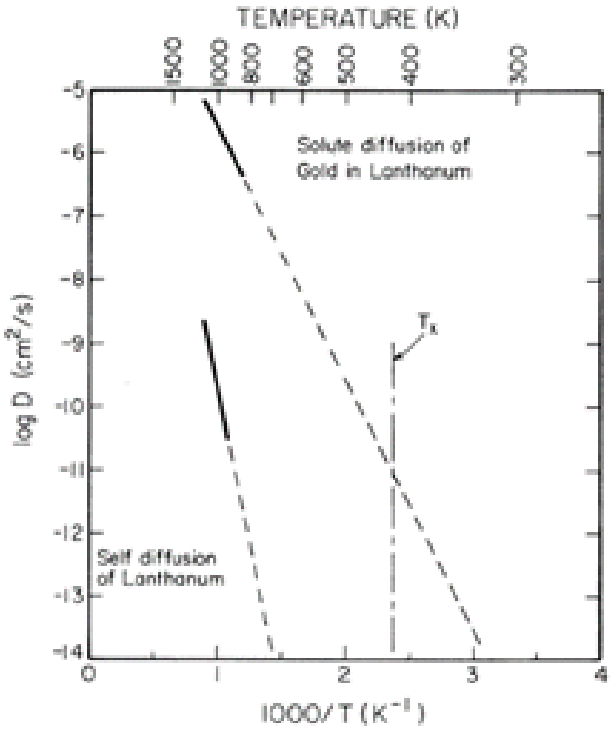
- **A strong thermodynamic driving force**

i.e. a large negative heat of mixing

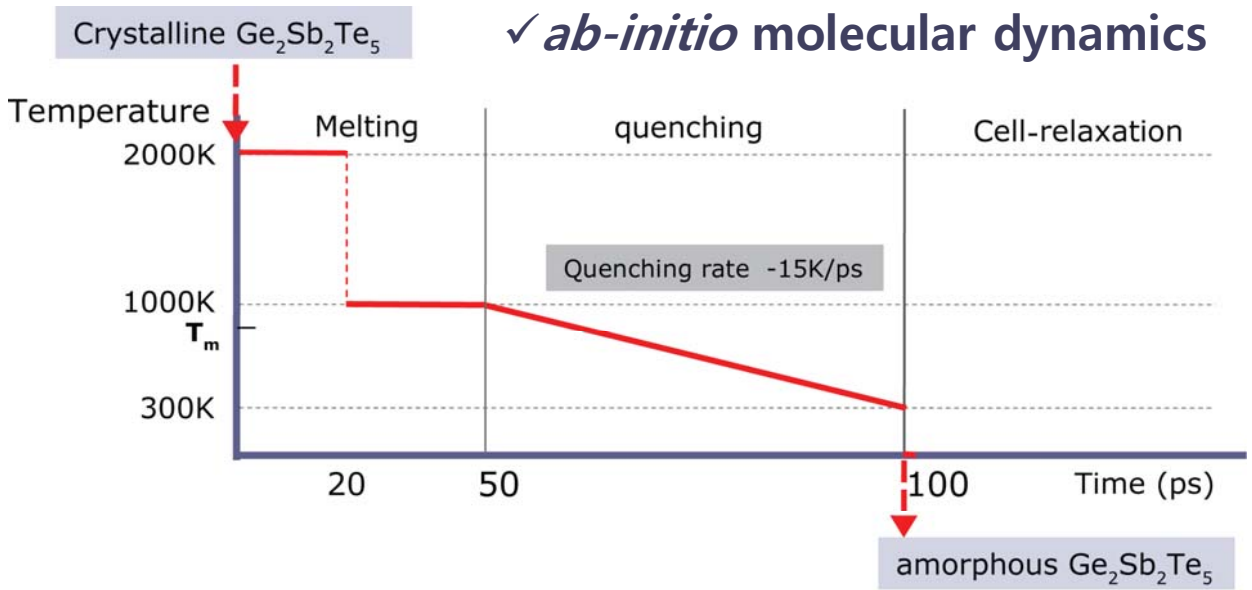


- **Diffusional asymmetry**

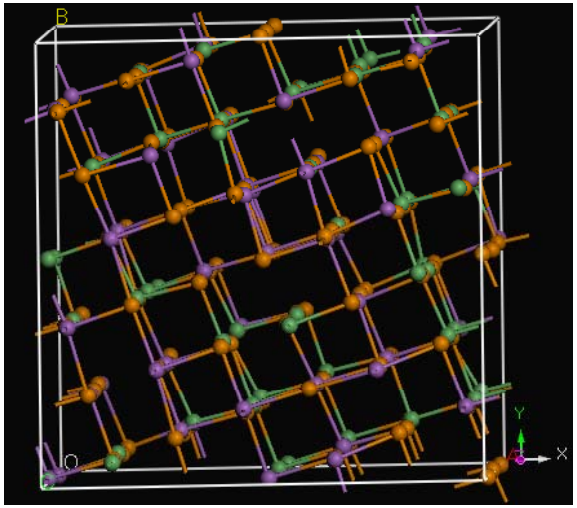
i.e. one element diffuses anomalously fast in the other, but not vice versa



Simulation of amorphous structures

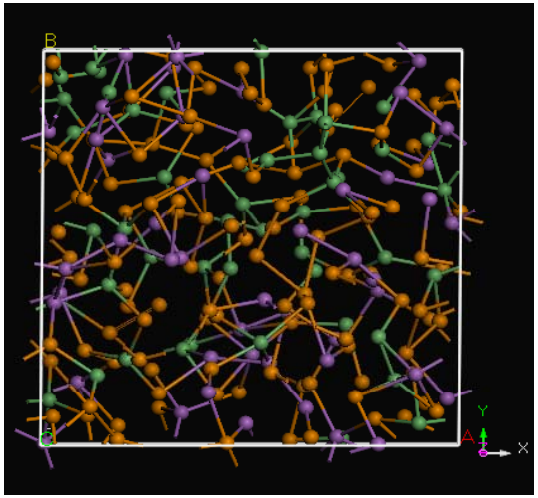


CRYSTAL



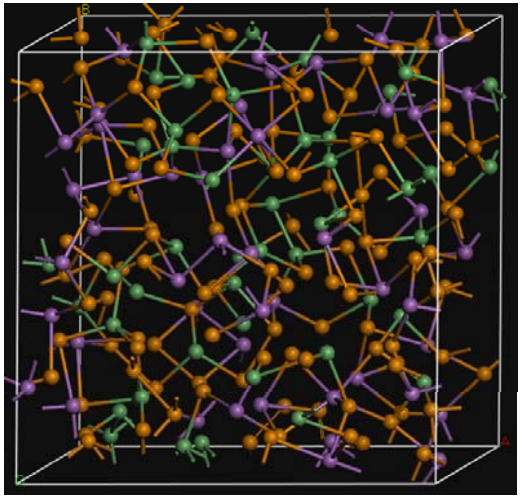
Melting @ 2000K

LIQUID



Quenching to 300K

AMORPHOUS



Ge Sb Te