2010 Spring

“Amorphous Materials”

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Ease of glass formation

- Glass forming ability: basically depending on glass transition

  ➡ unsolved mystery ➡ no universal rule: empirical rules

  ➡ still alchemy stage: by trial & error considering various aspects

1. Structure & topology

➡ **(1) Continuous Random Network (CRN)** ⟶ **GFA** ⬆

- Similar Internal energy between C and G in oxide glasses

➡ **(2) Dense random packed structure in metallic glasses**

1) Large atomic size difference: ex) TM - metalloid (M, ex) Boron)

2) Multi-component system (over 3 elements): confusion theory

2. Thermodynamic aspect

Deep eutectic condition

- **High GFA : low free energy** $\Delta G(T)$

for transformation of liquid to crystalline phase

$$\Delta G(T) = \Delta H_f - T\Delta S_f$$

$\Delta G \downarrow \rightarrow \Delta H_f \downarrow$ & $\Delta S_f \uparrow$

Enthalpy of fusion **Entropy of fusion**

- ***The large decrease in T_E is shown to result from a large negative excess free energy of mixing, for which the dominant contribution is the enthalpy.***

- decreasing melting point → less supercooled at T_g

ex) metallic / inorganic system

3. Kinetic aspect

Decrease of nucleation and growth rate $X(t,T) \sim \pi I(T)\mu(T)^3 t^{4/3}$

Glass formation

Retention of liquid phase

Formation of crystalline phases

Thermodynamical point
Small change in free E. (liq.→ cryst.)

Kinetic point
Low nucleation and growth rates

Structural point
Highly packed random structure

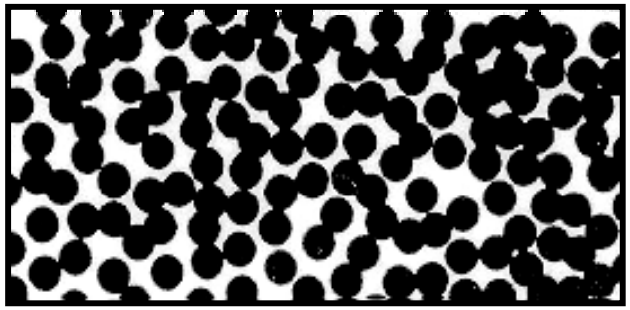
Empirical rules

(1) multi-component alloy system (2) significant difference in atomic size ratios
(3) negative heats of mixing (4) close to a eutectic composition
(5) compositions far from a Laves phase region

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

→ ***High glass-forming ability (GFA)***

Definition of metallic glass



- Non-crystalline metallic solid lacking long-range periodicity of atomic arrangement and showing glass transition.

Bulk metallic glass (BMG)

- Metallic glass having a minimum dimension of 1mm which is equivalent to a critical cooling rate of about 10^3 to 10^4 K/s.

Glass Formation

- Competing process between retention of liquid phase and formation of crystalline phases

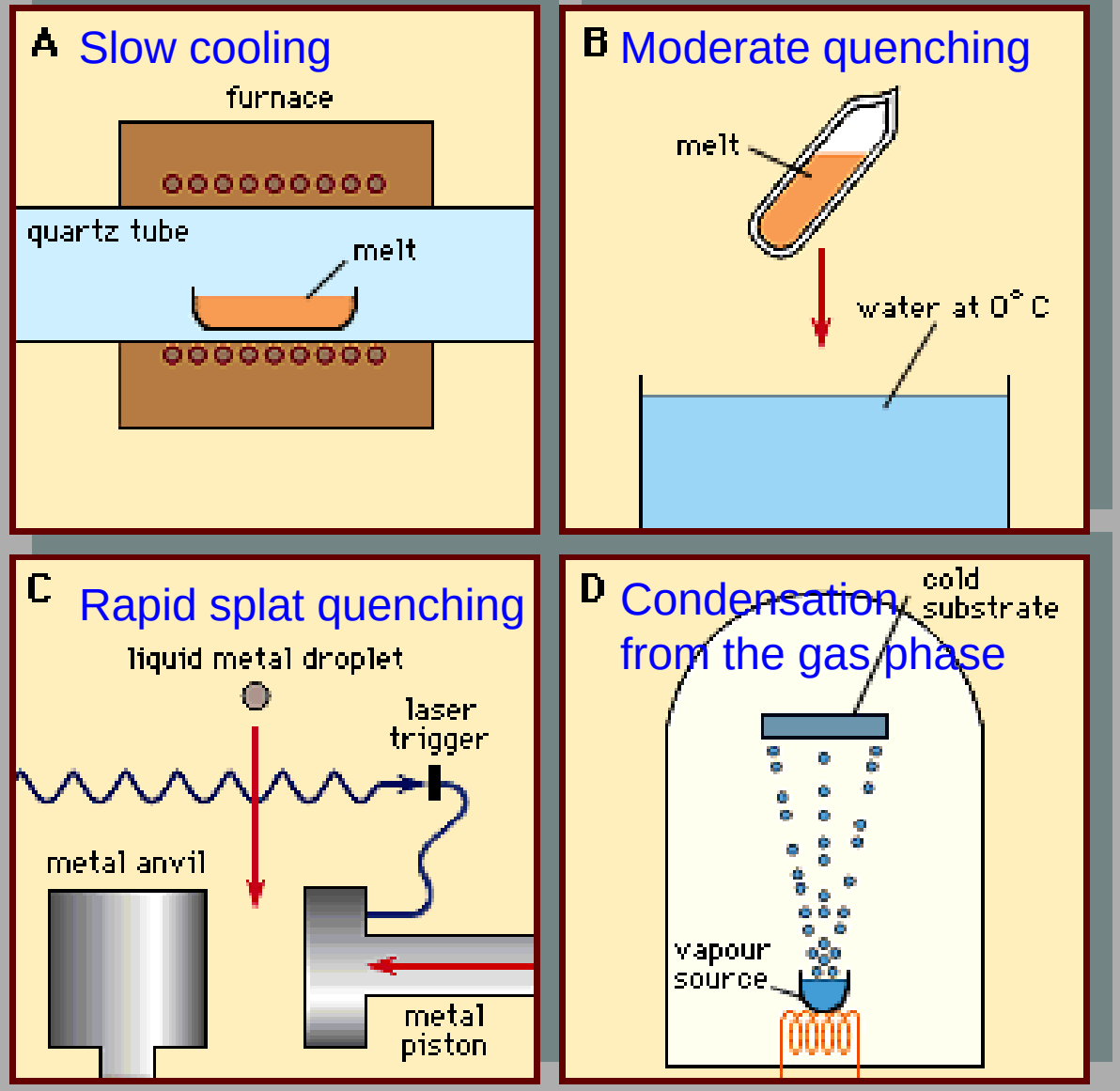
a. Liquid phase stability

- Stability of the liquid in the equilibrium state (i.e. stable state, T_l)
- Stability of the liquid during undercooling (i.e. metastable state, T_g)

b. Resistance to crystallization

- Nucleation and growth of the competing crystalline phases

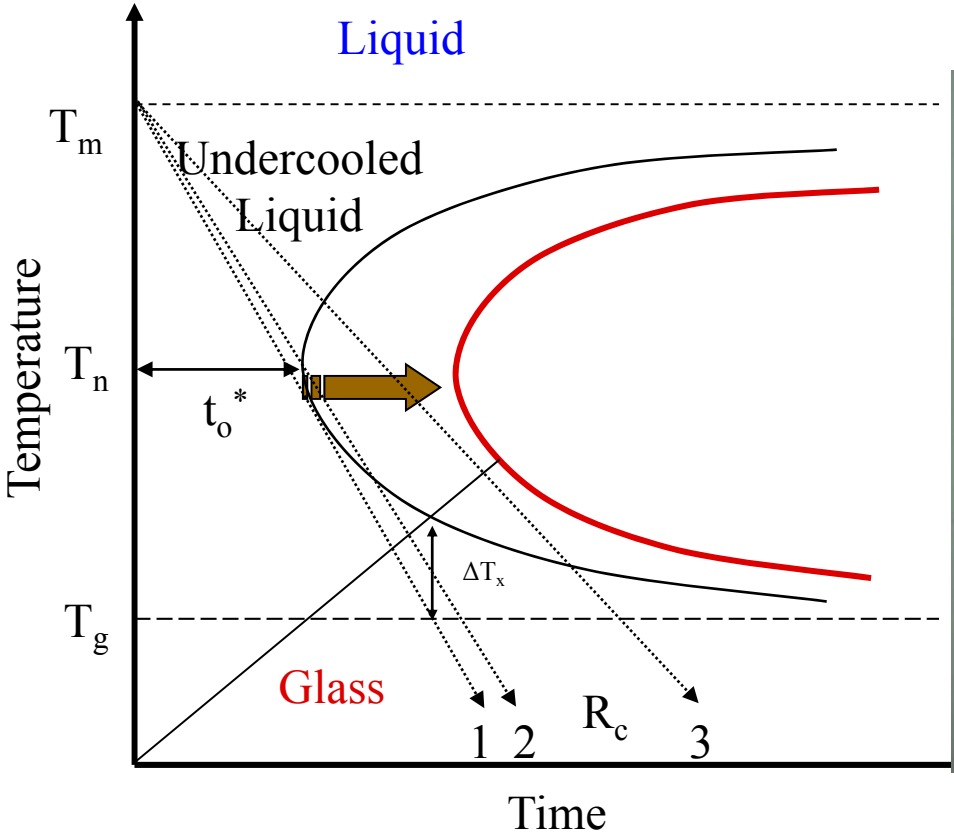
Four methods for preparing amorphous solids

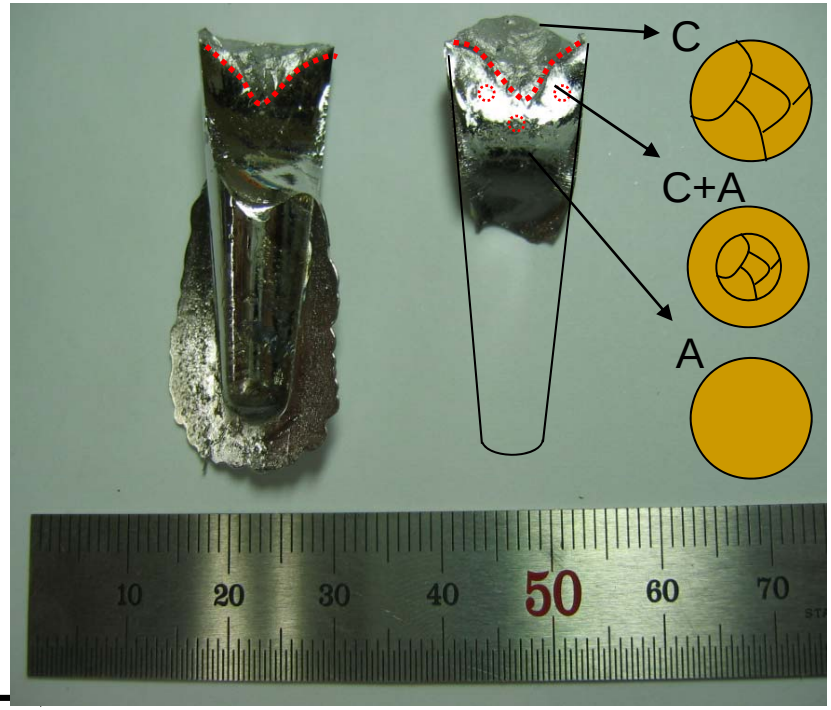


From R. Zallen, The Physics of Amorphous Solids

Critical cooling rate

$$R_c = \frac{T_m - T_n}{t_o^*}$$

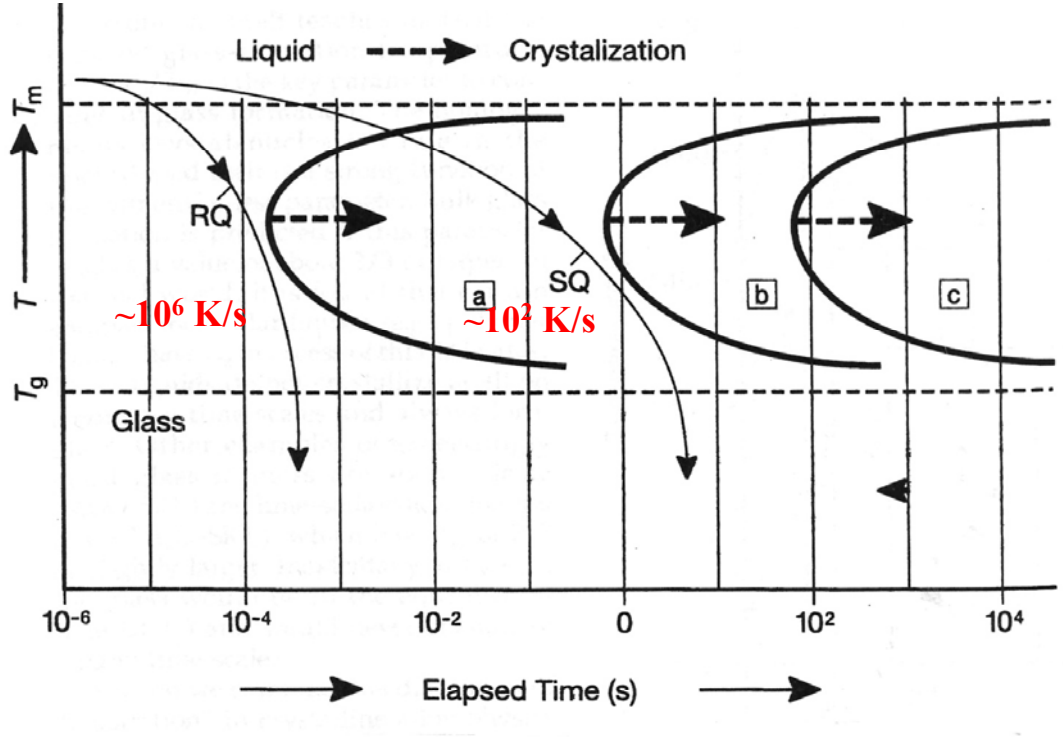




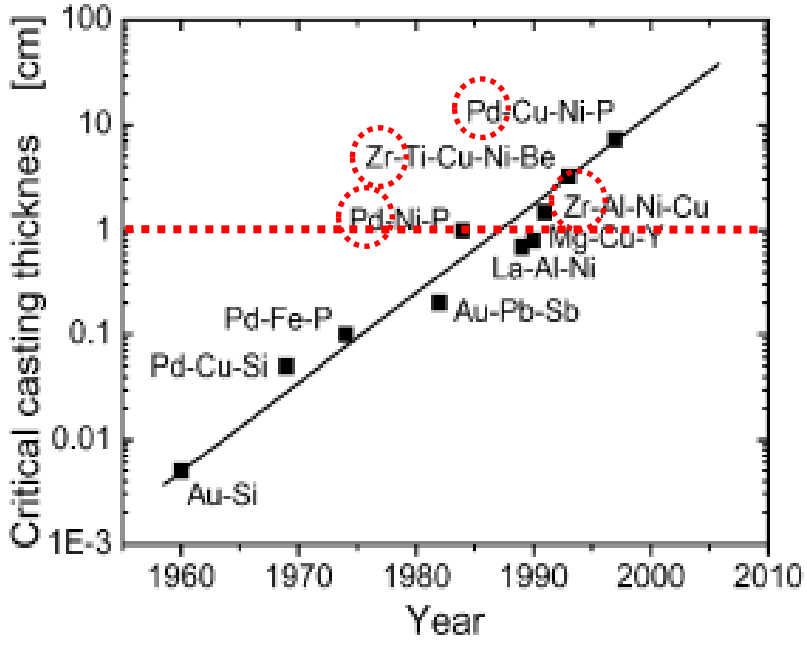
Critical cooling rate is inversely proportional to the diameter of ingot.

Glass forming ability

(a) critical cooling rate, Rc



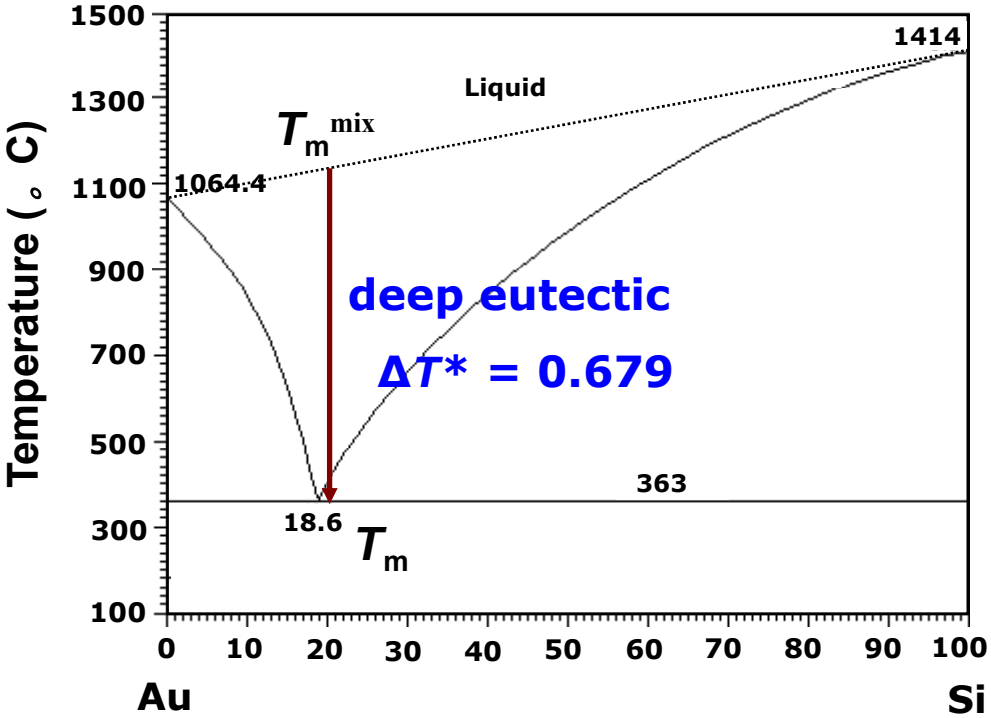
(b) Critical casting thickness, D_{max}



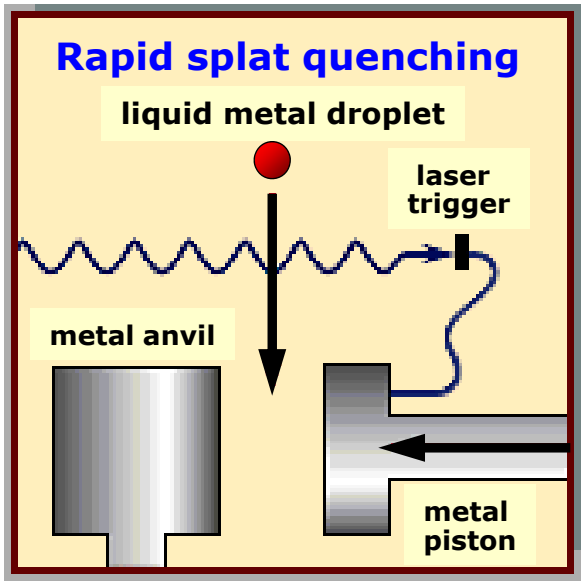
< Schematic TTT diagrams >

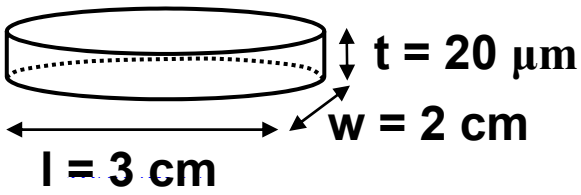
Glass formation: stabilizing the liquid phase

- 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.*

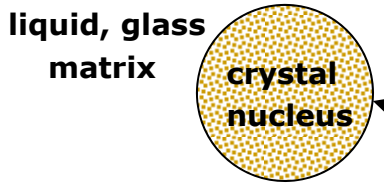




Glass formation: destabilizing the crystalline phase

Crystal nucleation rate (*J*)

- Assuming a spherical shape of the nucleus and a homogeneous manner of the nucleation process



interfacial energy

$$J = \frac{10^{36}}{\eta(T)} \exp\left[-\frac{16\pi}{3kT} \frac{\sigma^3}{(\Delta G_v(T))^2} f(\theta) \right] m^{-3} s^{-1}$$

nucleation events per volume, time

Viscosity

Gibbs free energy difference per volume

(a) first-order approximation (i.e., $\Delta G = \Delta S_m (T_m - T)$; ΔS_m is the entropy of fusion per volume)

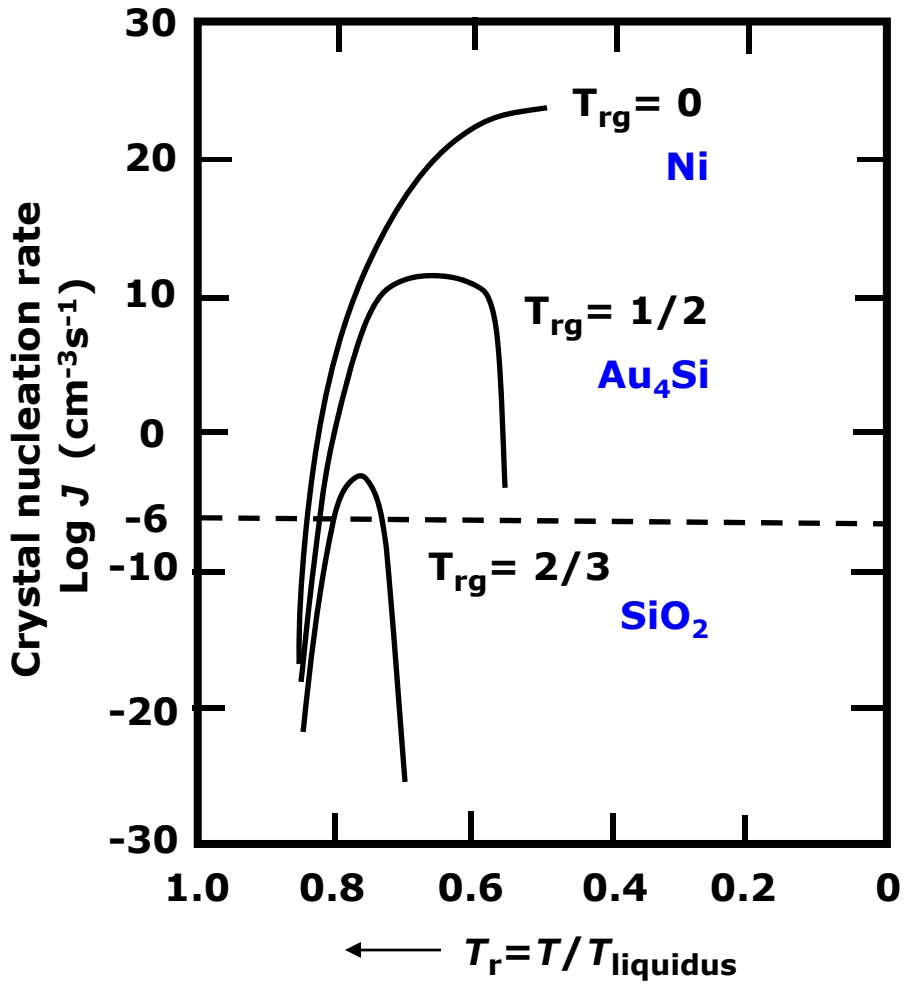
(b) simplified Vogel-Fulcher-Tamman (VFT) equation $\eta = 10^{-3.3} \exp\left(\frac{3.34}{T_r - T_{rg}}\right)$

(c) $T_r = T/T_m$ and $\Delta T_r = (T_m - T)/T_m = 1 - T_r$

Criterion for glass formation

T_{rg} parameter $= T_g / T_m$

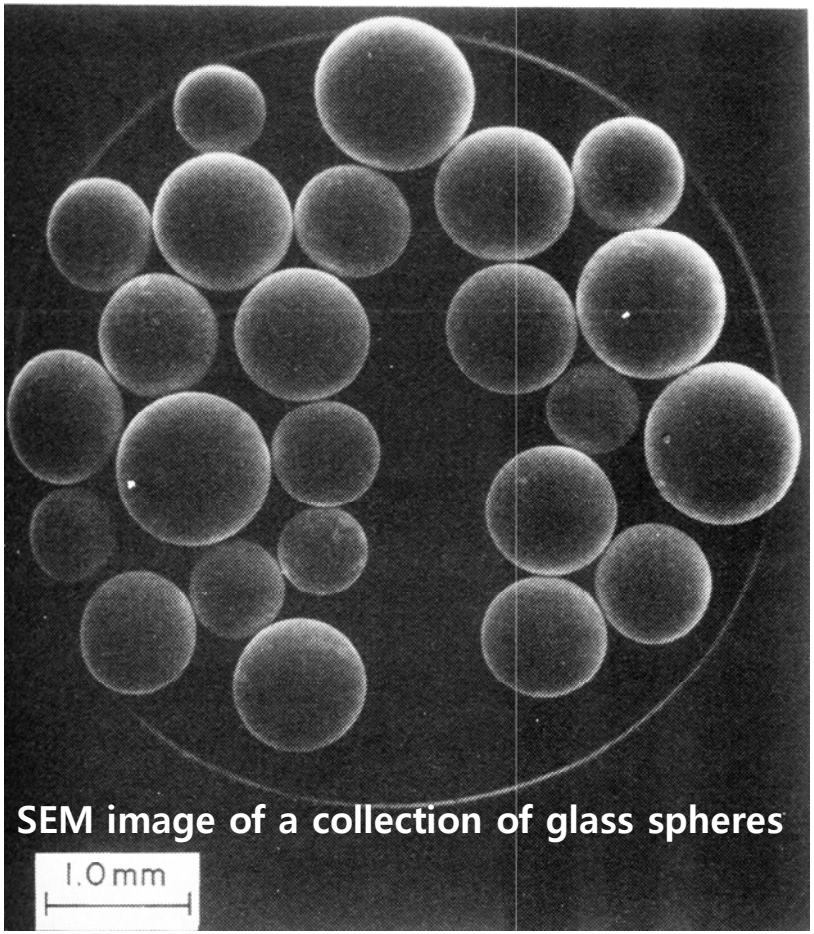
: ability to avoid crystallization during cooling



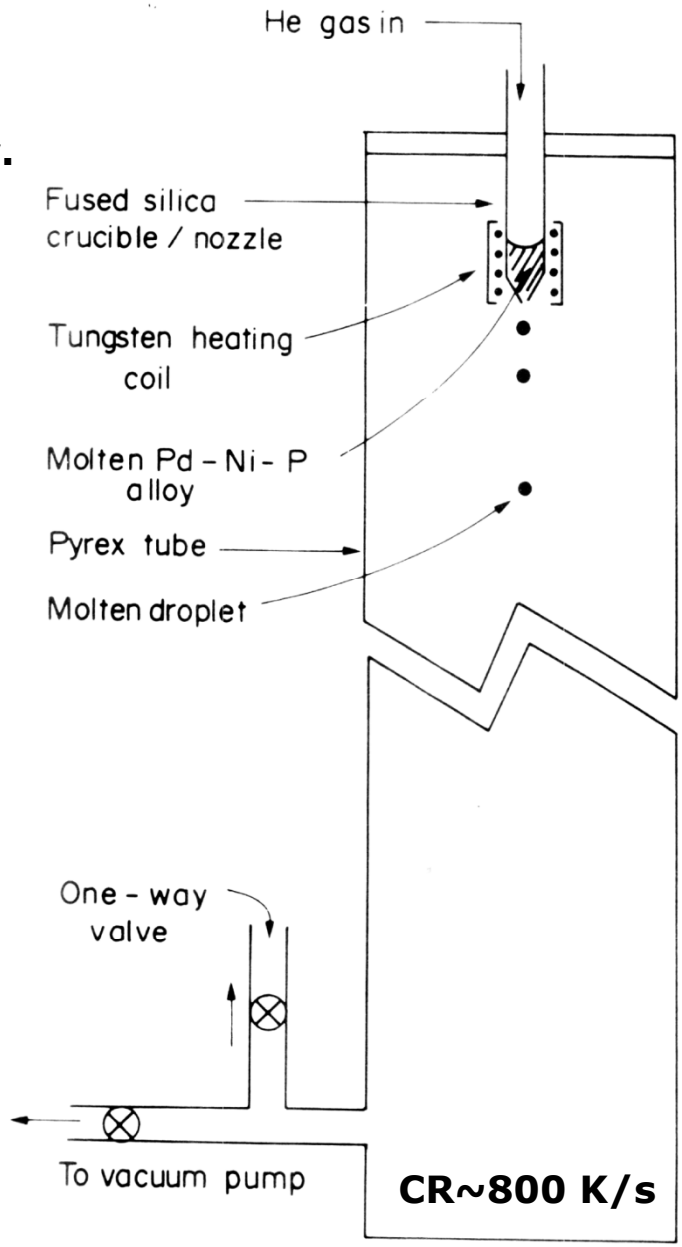
Turnbull, 1959 ff.

Bulk formation of metallic glass

- **First bulk metallic glass $Pd_{77.5}Cu_6Si_{16.5}$ (T_{rg}=0.64)**
  produced by droplet quenching at Harvard Univ. by H.S. Chen and D. Turnbull in 1969



SEM image of a collection of glass spheres



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

Bulk formation of a metallic glass: $Pd_{40}Ni_{40}P_{20}$

- **Alloy Selection: Consideration of T_{rg}**

  * $Pd_{82}Si_{18}$ → T_{rg}=0.6
  - Homogeneous nucleation rate: >10^5/cm^{3}s

  * $Pd_{77.5}Cu_6Si_{16.5}$ → T_{rg}=0.64
  - Critical cooling rate~ 800 K/s

  * $Pd_{40}Ni_{40}P_{20}$ → T_{rg}=0.67
  T_g=590 K, T_e = 880 K, T_l = 985 K

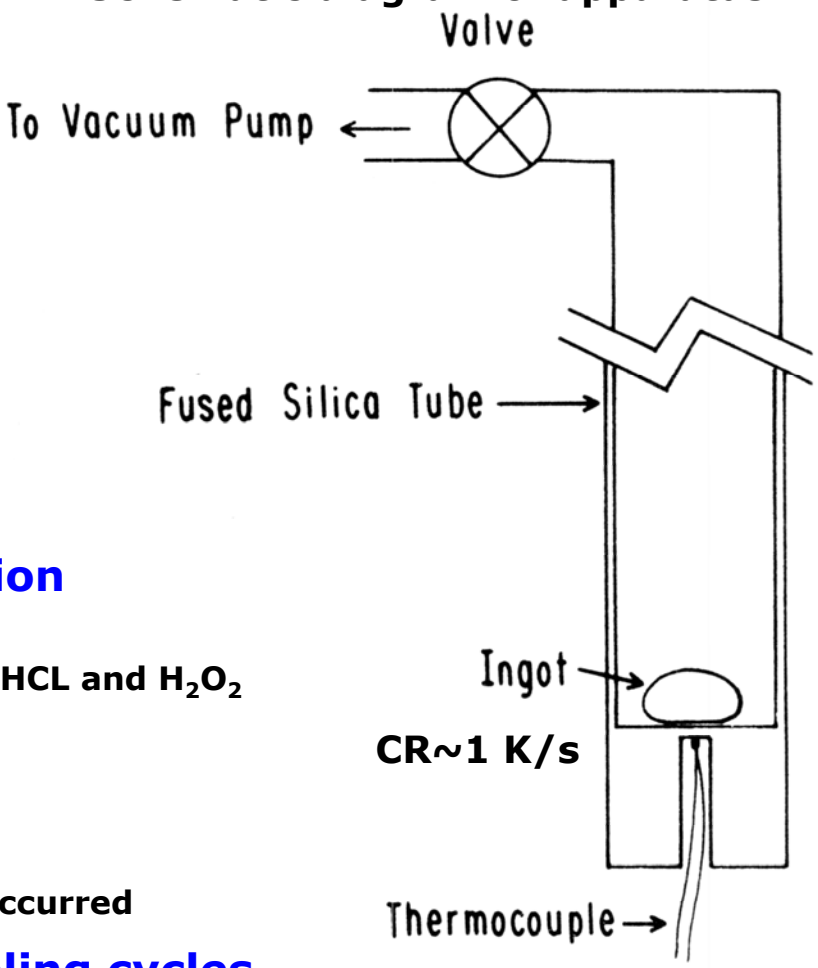
- **Suppression of Heterogeneous nucleation**

  1. **Surface Etching of ingot** in a mixture of HCL and H_2O_2
     : elimination of surface heterogeneities

  2. **Thermal cycling –5 cycles**
     : dissolution of nucleating heterogeneities
     → reduce the temperature at which nucleation occurred

  3. **Impurities = Successive heating-cooling cycles in a molten oxide flux**
     B_2O_3 melting point 723 K, boiling point <40,000 K

<Schematic diagram of apparatus>



Bulk formation of a metallic glass: $Pd_{40}Ni_{40}P_{20}$

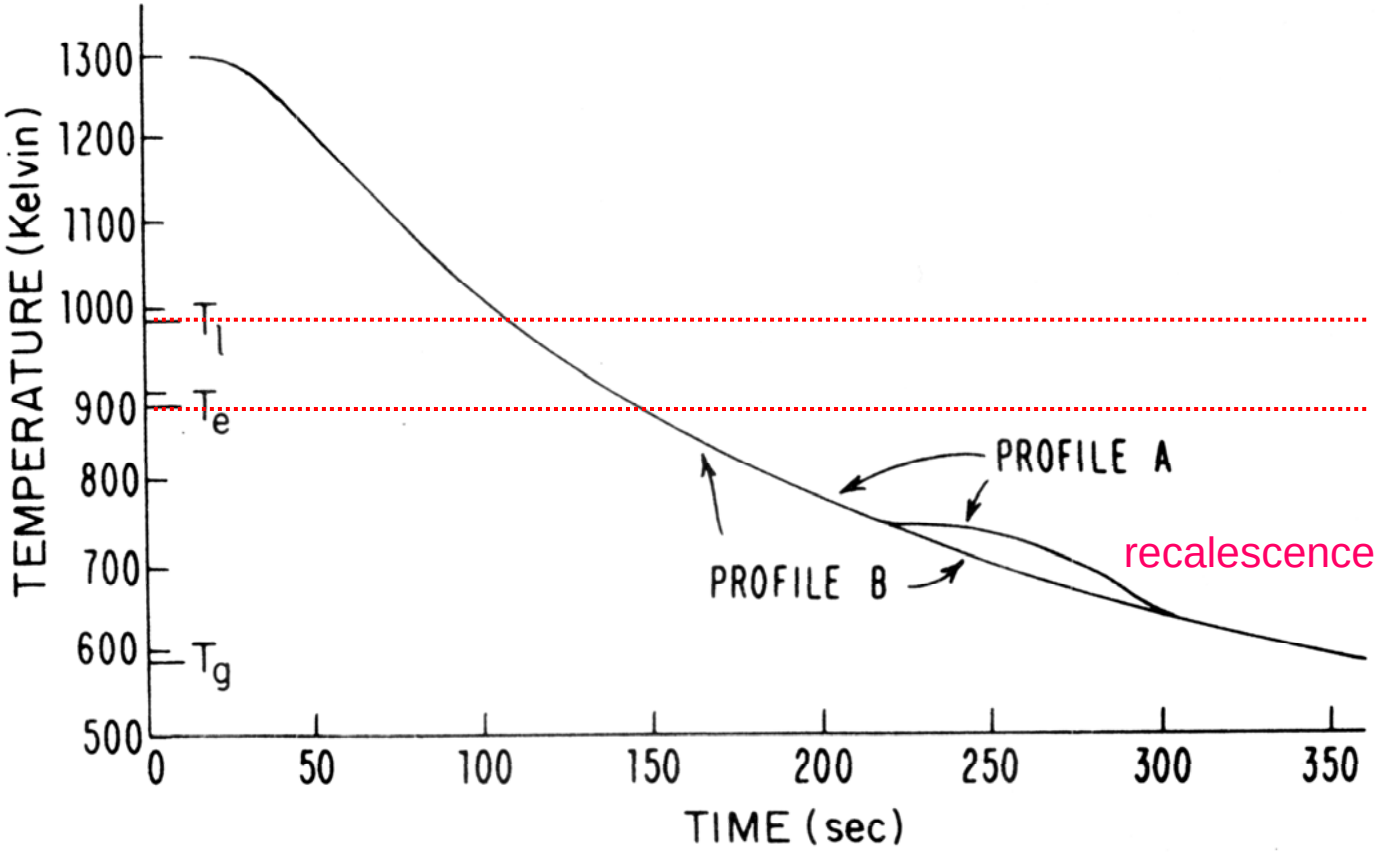
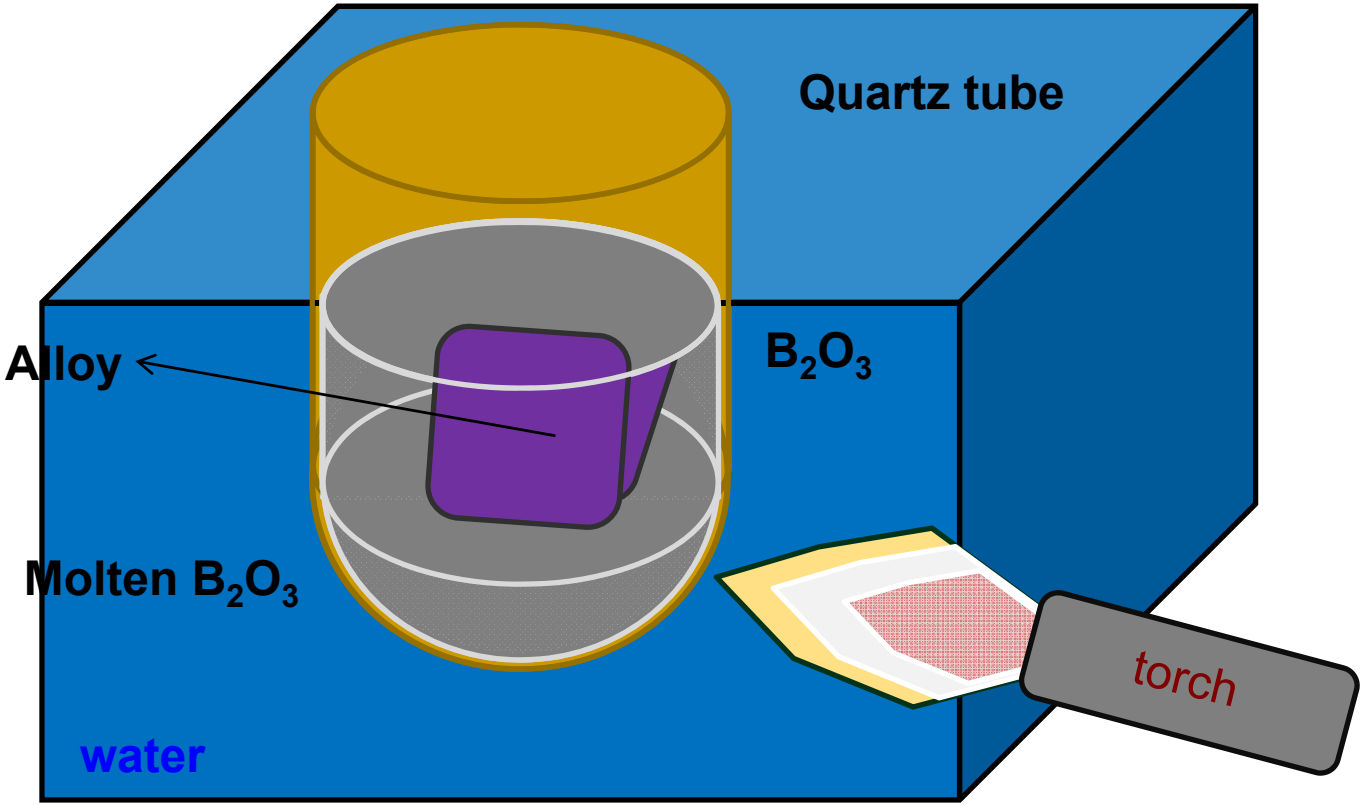


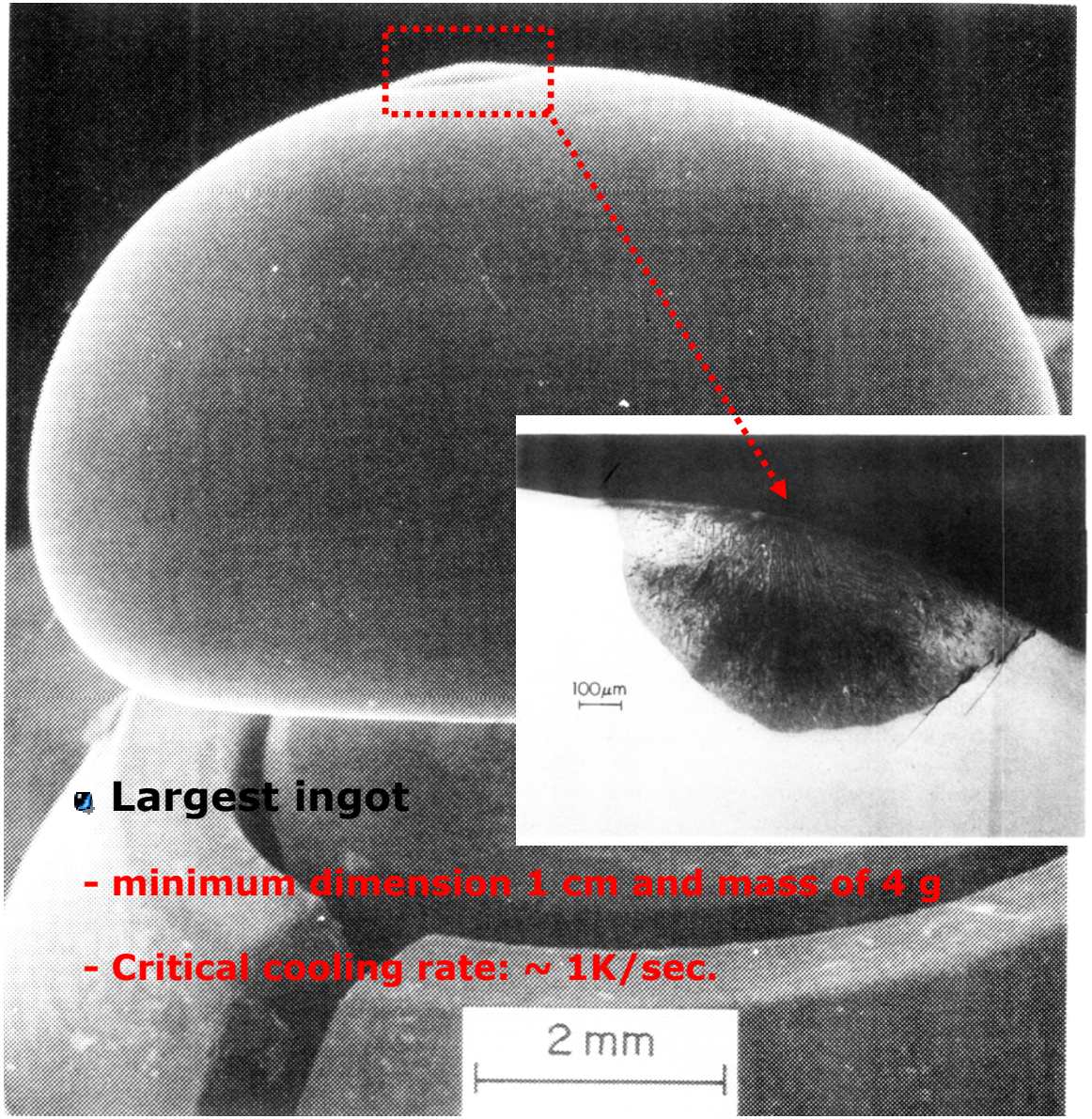
FIG. 2. Superposition of two cooling profiles: A—bulk crystallization which began at 740 K. B—formation of a glassy ingot.

A.J. Drehman, A.L. Greer, D. Turnbull, Appl. Phys. Lett. 1982; 41: 716.

Schematic process for fluxing in BMG



Improvement of glass forming ability by fluxing



- Largest ingot

- minimum dimension 1 cm and mass of 4 g

- Critical cooling rate: ~ 1K/sec.

RQ Distinguished Fellow

Bulk glass formation in the Pd-Ni-P system

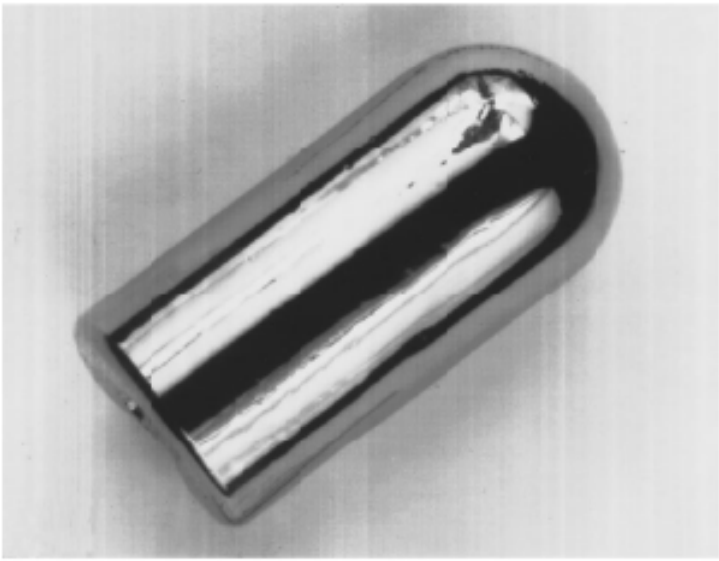
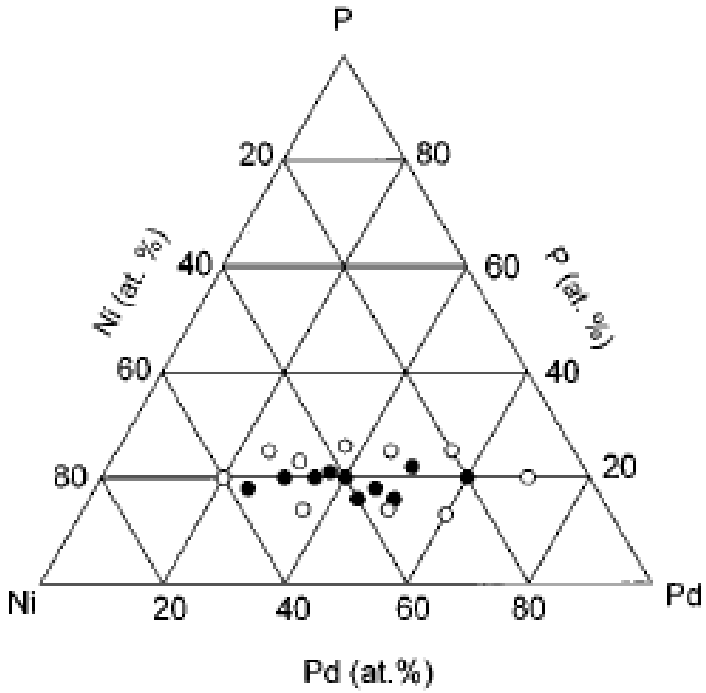


FIG. 1. 300-g ingot of bulk amorphous $Pd_{40}Ni_{40}P_{20}$ rod with 25 mm in diamter prepared by fluxing in B_2O_3 and water quenching.



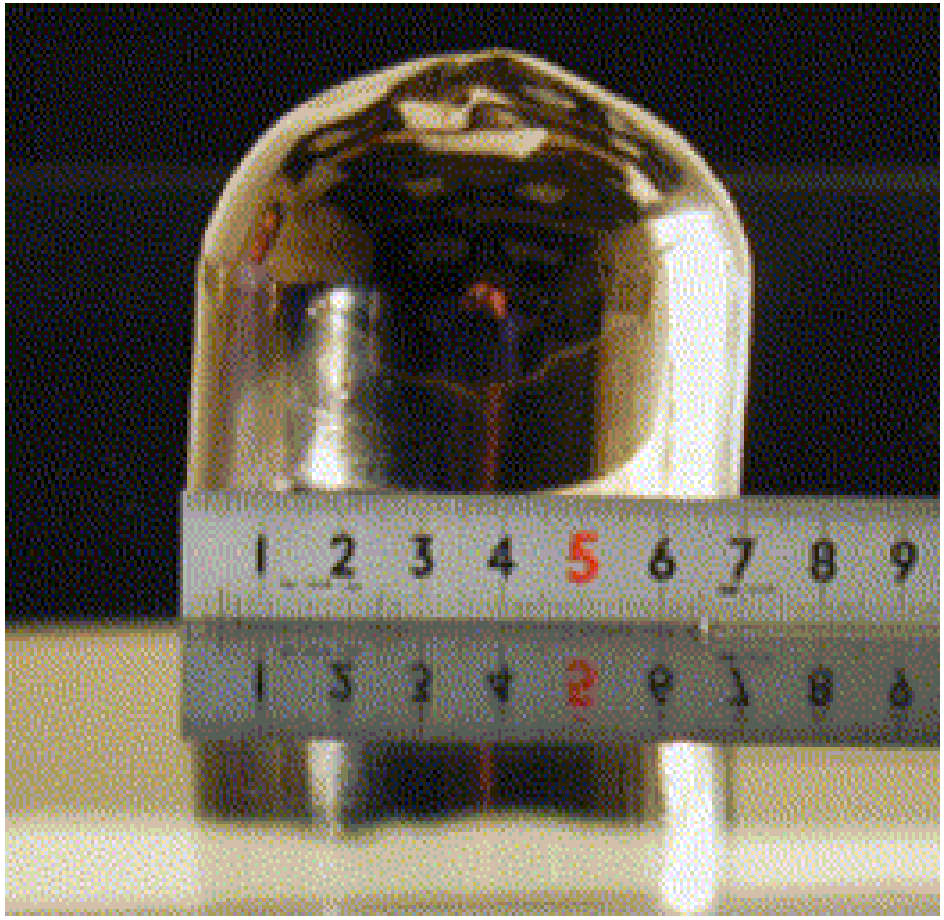
- **Experimental Difference**

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

2. Water quenching : Improvement of cooling rate

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

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



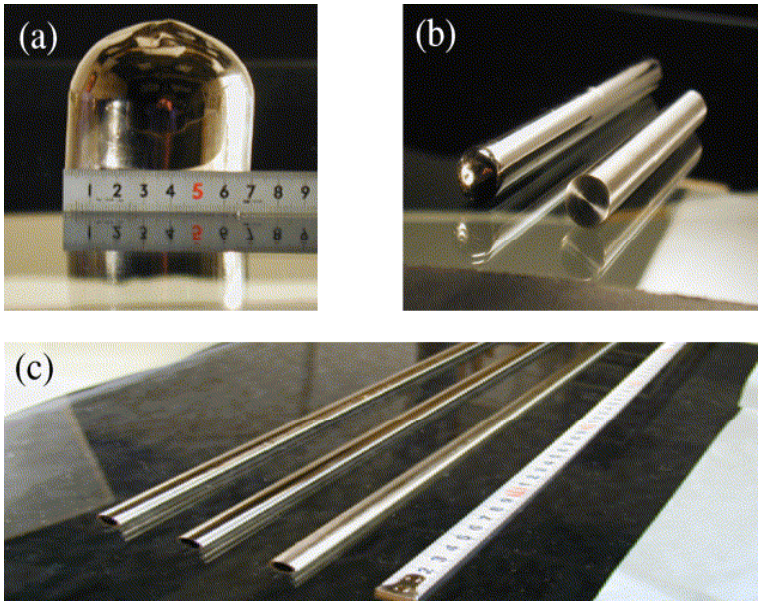
- **Largest ingot**

maximum diameter for glass formation : 72 mm

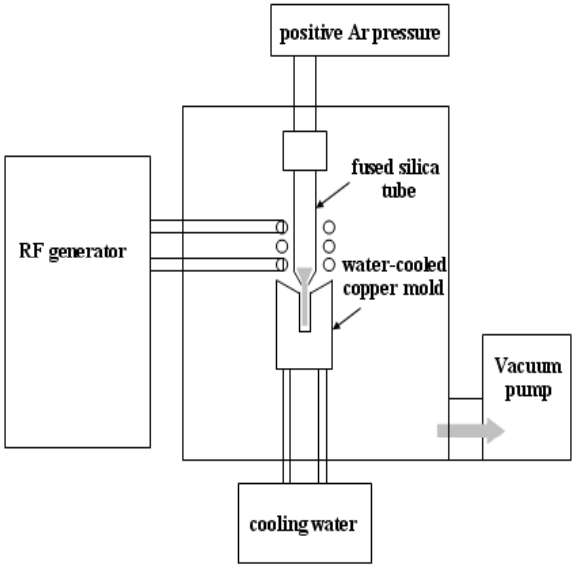
Critical cooling rate: ~ 0.1K/sec.

How to make bulk metallic glasses

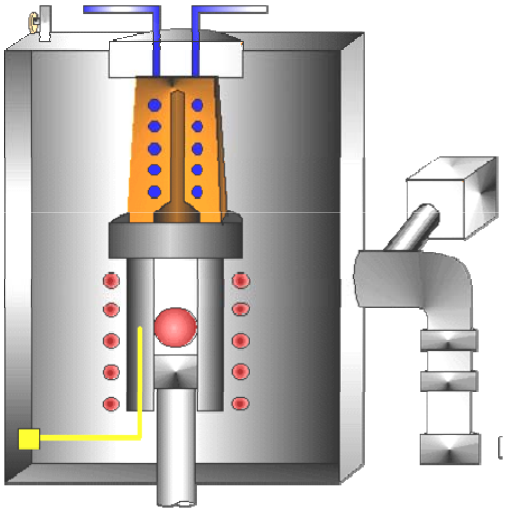
< Casting >



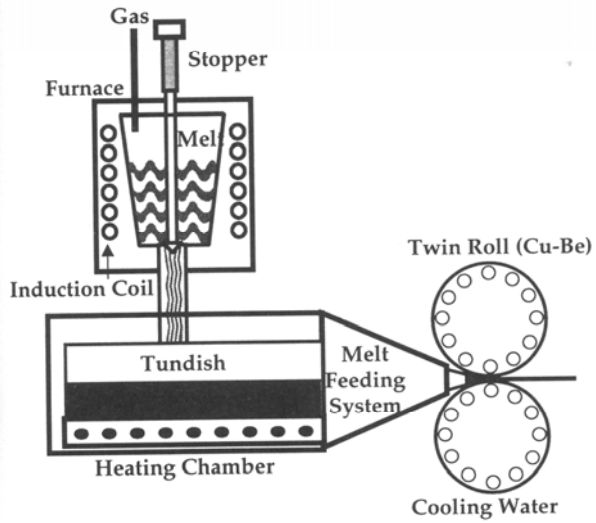
1) Injection casting



2) Squeeze casting



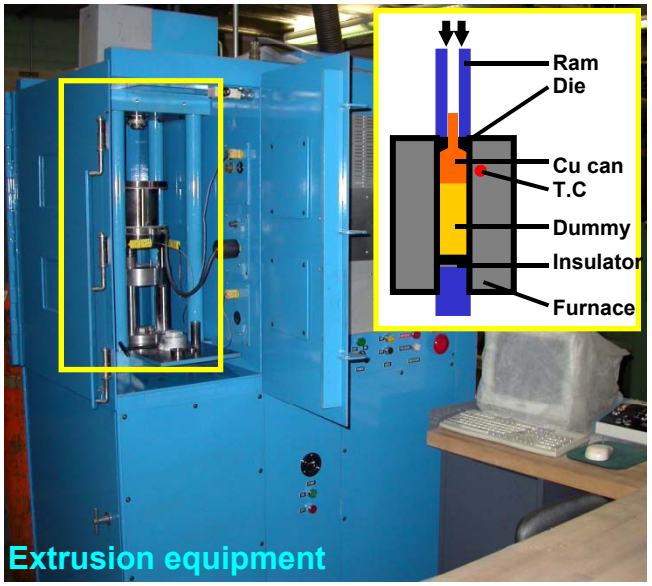
3) Strip casting

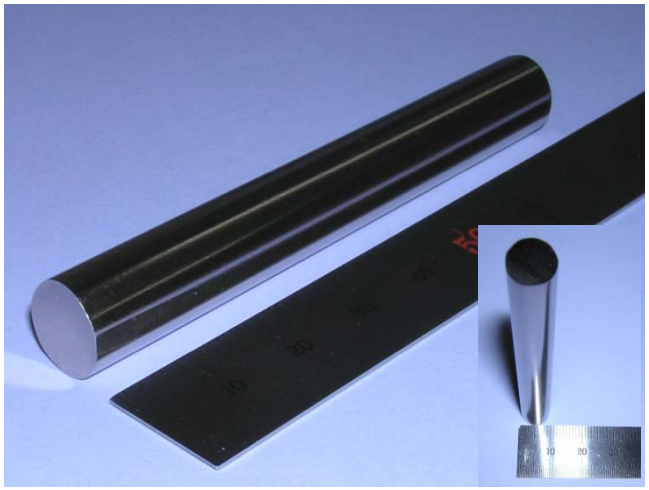


How to make bulk metallic glasses

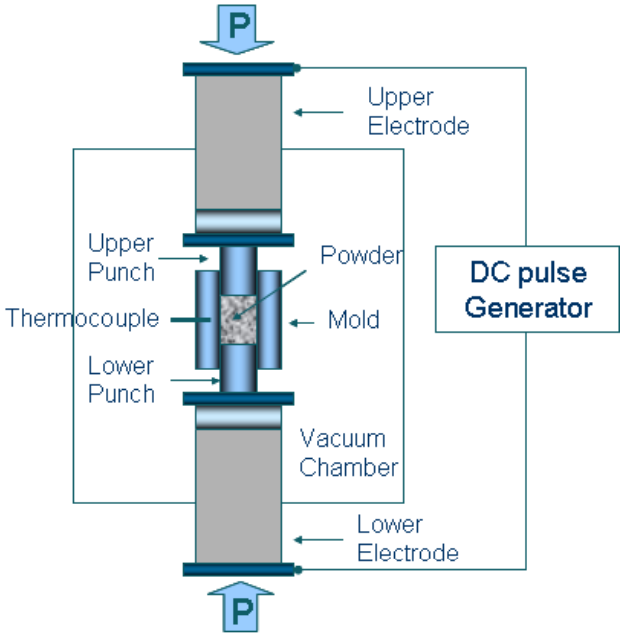
< Powder Metallurgy>

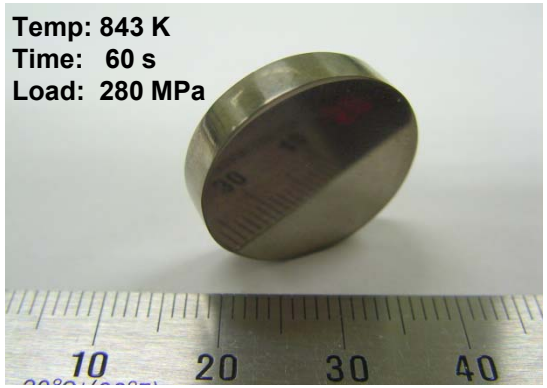
1) Extrusion

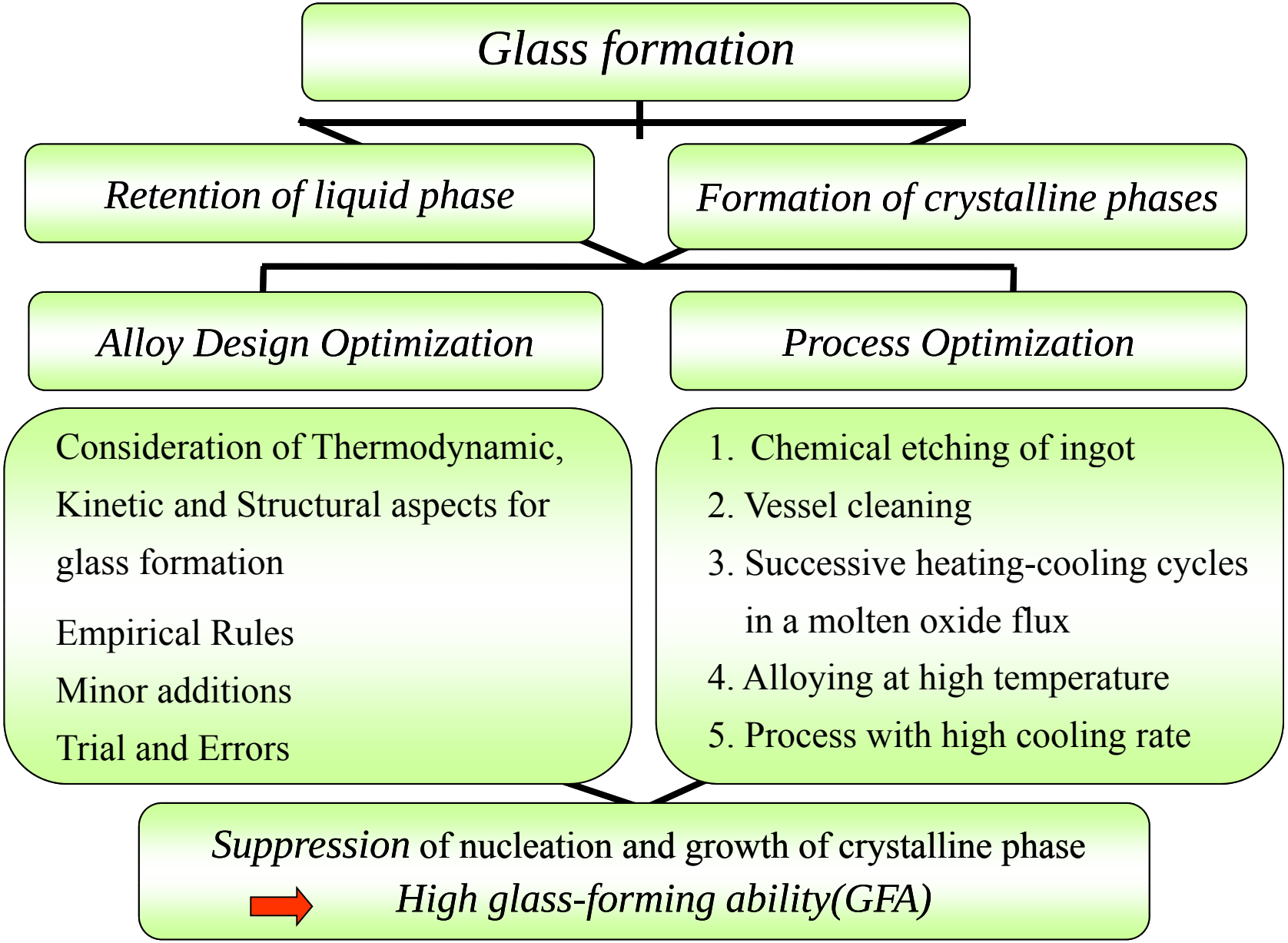




2) Spark Plasma Sintering



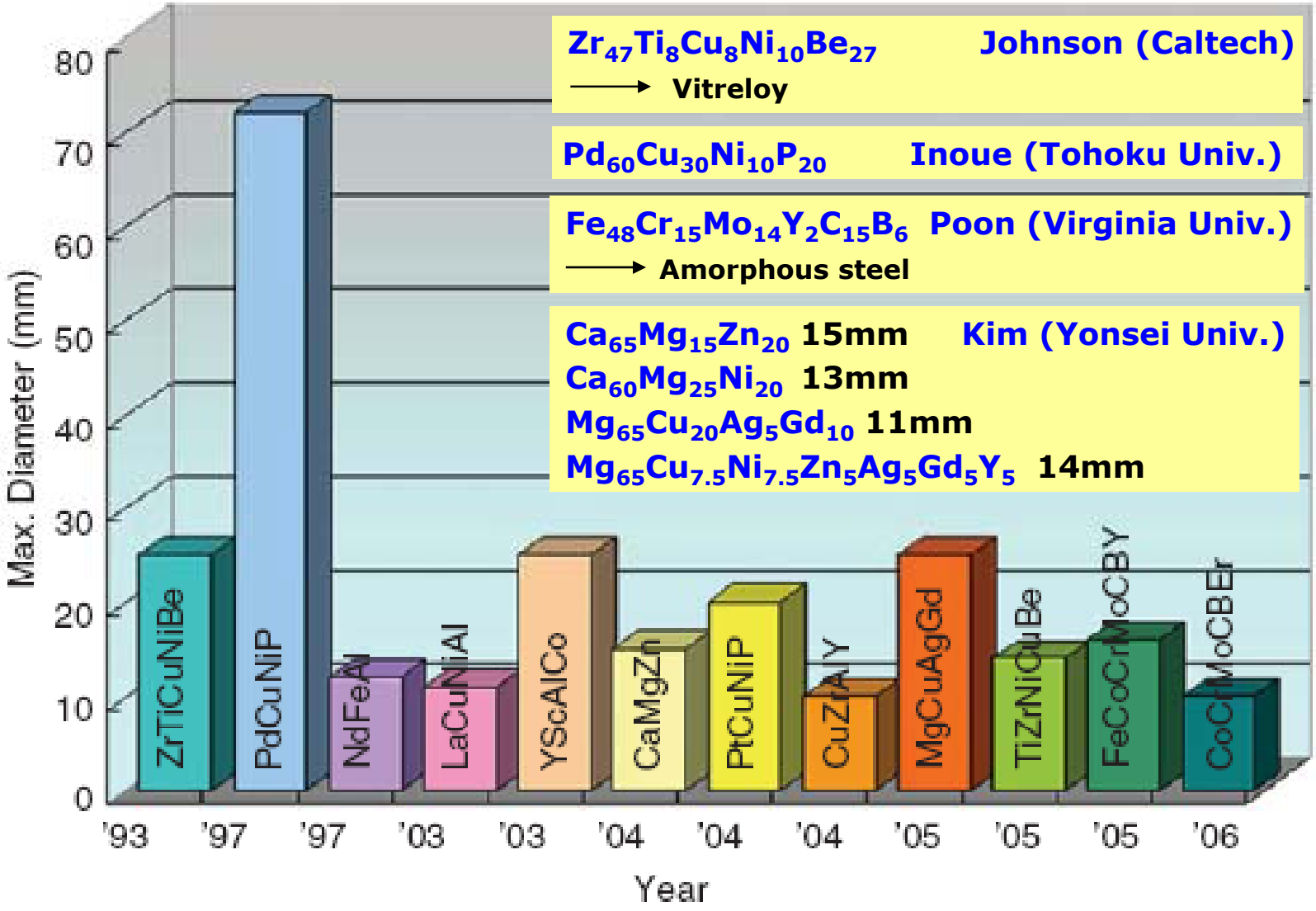



Glass formation
Retention of liquid phase
Formation of crystalline phases
Alloy Design Optimization
Process Optimization
Consideration of Thermodynamic, Kinetic and Structural aspects for glass formation
Empirical Rules
Minor additions
Trial and Errors
1. Chemical etching of ingot
2. Vessel cleaning
3. Successive heating-cooling cycles in a molten oxide flux
4. Alloying at high temperature
5. Process with high cooling rate
Suppression of nucleation and growth of crystalline phase
High glass-forming ability(GFA)

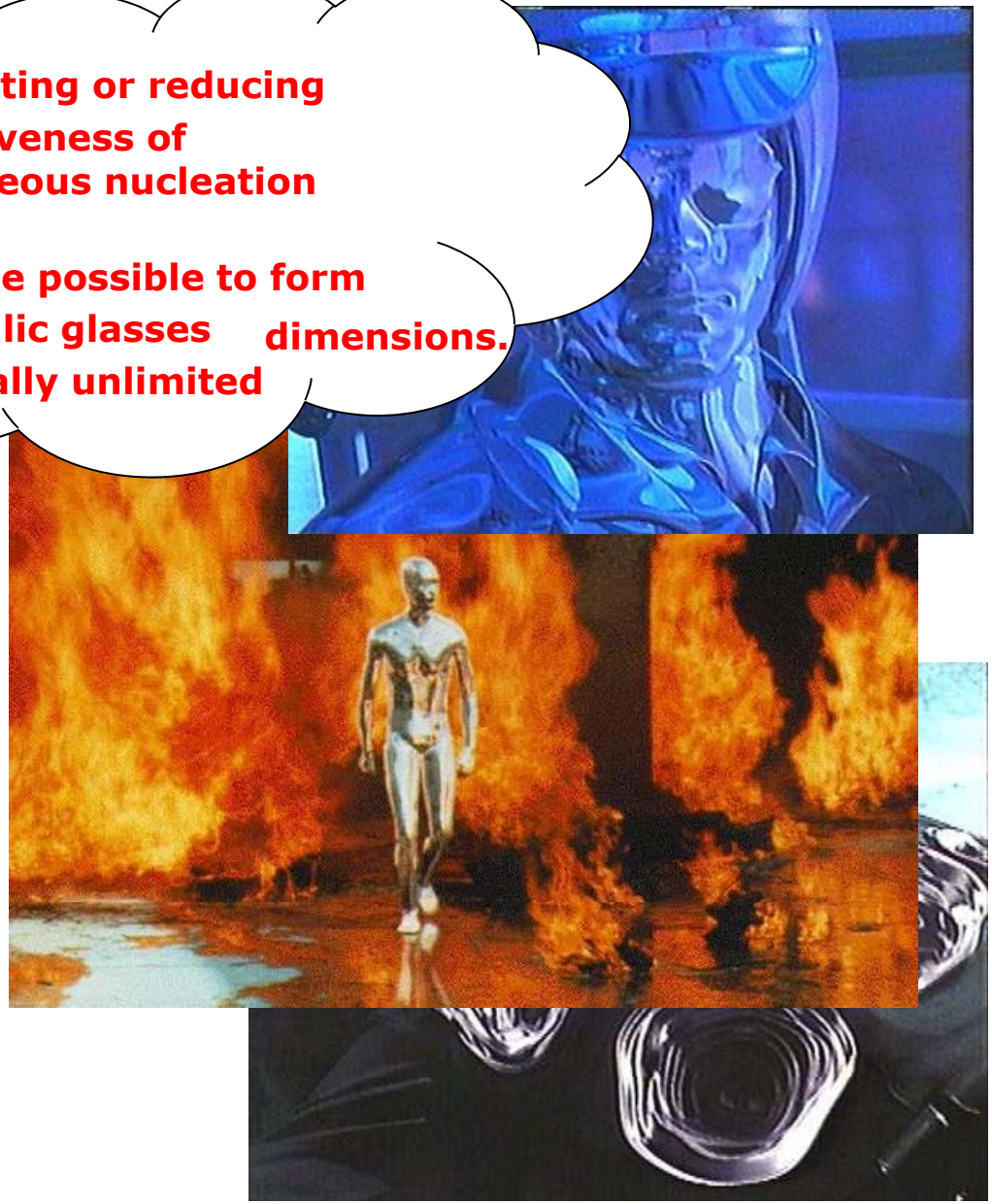
Summaries of BMGs with Critical size ≥ 10 mm

System	Alloy	Critical Size, D_c (mm)	Method	Year
Pd-based	$Pd_{40}Ni_{40}P_{20}$	10	Fluxing	1984
	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	72	Water quenching	1997
Zr-based	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	16	Water quenching	1993
	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	25	Copper mold casting	1996
Cu-based	$Cu_{46}Zr_{42}Al_7Y_5$	10	Copper mold casting	2004
	$Cu_{49}Hf_{42}Al_9$	10	Copper mold casting	2006
RE-based	$Y_{36}Sc_{20}Al_{24}Co_{20}$	25	Water quenching	2003
	$La_{62}Al_{15.7}Cu_{11.15}Ni_{11.15}$	11	Copper mold casting	2003
Mg-based	$Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$	25	Copper mold casting	2005
	$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Y_5Gd_5$	14	Copper mold casting	2005
Fe-based	$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	12	Copper mold casting	2004
	$(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2}C_{15.8}B_{5.9})_{98.5}Y_{1.5}$	12	Copper mold casting	2004
	$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	Copper mold casting	2005
Co-based	$Co_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$	10	Copper mold casting	2006
Ti-based	$Ti_{40}Zr_{25}Cu_{12}Ni_3Be_{20}$	14	Copper mold casting	2005
Ca-based	$Ca_{65}Mg_{15}Zn_{20}$	15	Copper mold casting	2004
Pt-based	$Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$	20	Water quenching	2004

Recent BMGs with critical size ≥ 10 mm



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

At the Cutting Edge of Metals Research

By eliminating or reducing the effectiveness of heterogeneous nucleation sites, it should be possible to form bulk metallic glasses with virtually unlimited dimensions.