2009 spring

Advanced Physical Metallurgy

"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**

- decreasing melting point → less supercooled at T_g

ex) metallic / inorganic system

- ***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.***

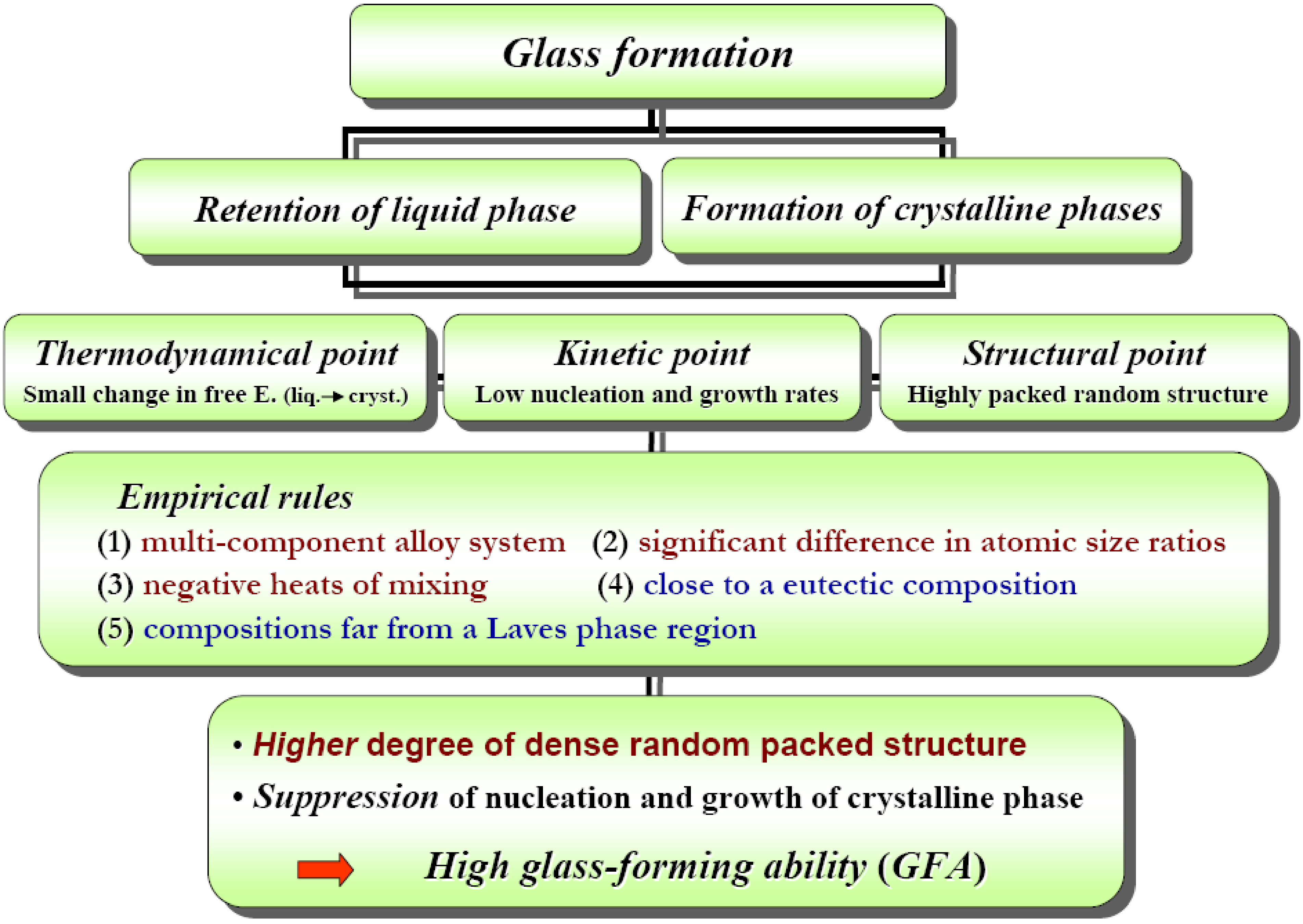
- **deep eutectic** → H^E ↓ → **Occurrence of Short range ordering**
  at liquid state, amorphous state
  → **Increase A-B bonding**

∴ **Occurrence of SRO at eutectic composition (especially deep eutectic)**

Ex) eut. comp. in TM-metalloid system- TM: Metalloid → 6 : 1 or 5 : 1
most frequent ratio

3. Kinetic aspect

➡ **Decrease of nucleation and growth rate**


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)

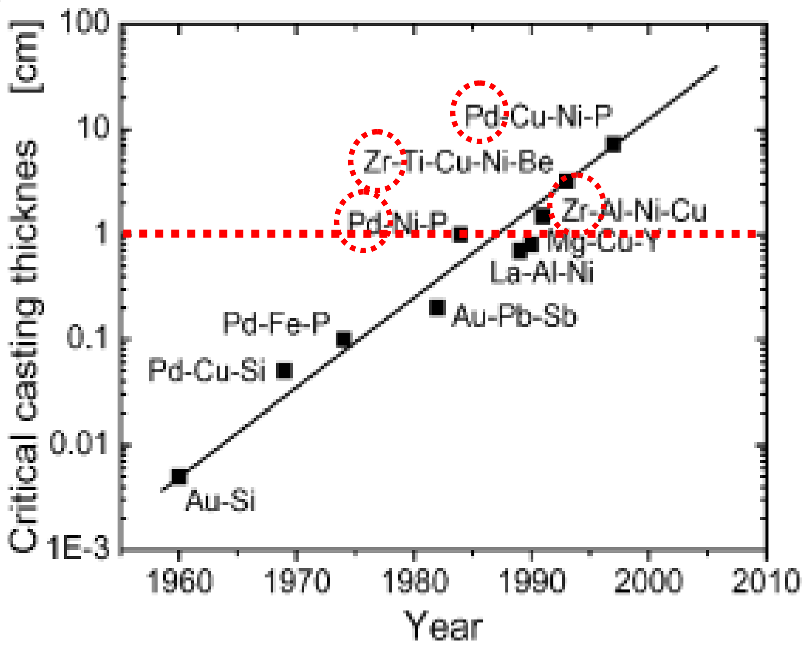
Glass forming ability

(a) critical cooling rate, Rc

(b) Critical casting thickness, D_{max}

~10^6 K/s

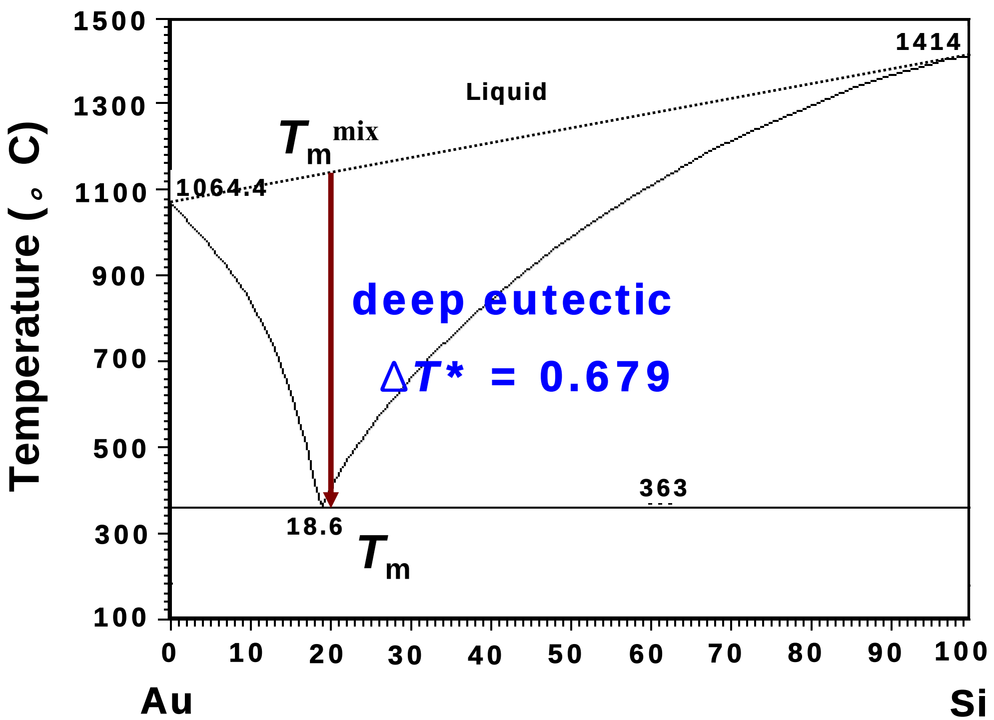
~10^2 K/s



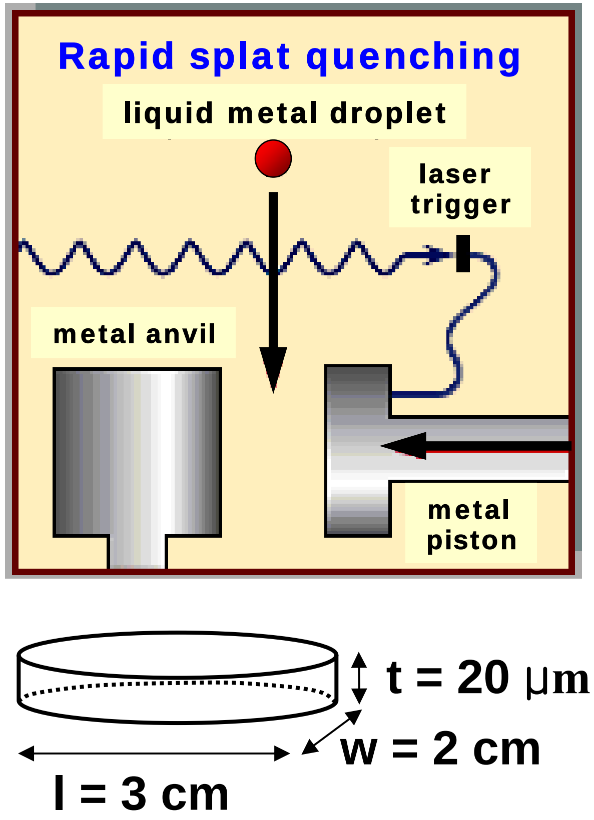
< Schematic TTT diagrams >

Glass formation: stabilizing the liquid phase

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



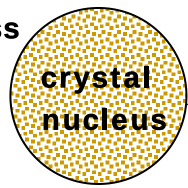
W. Klement, R.H. Willens, P. Duwez, Nature 1960; **187**: 869.



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)

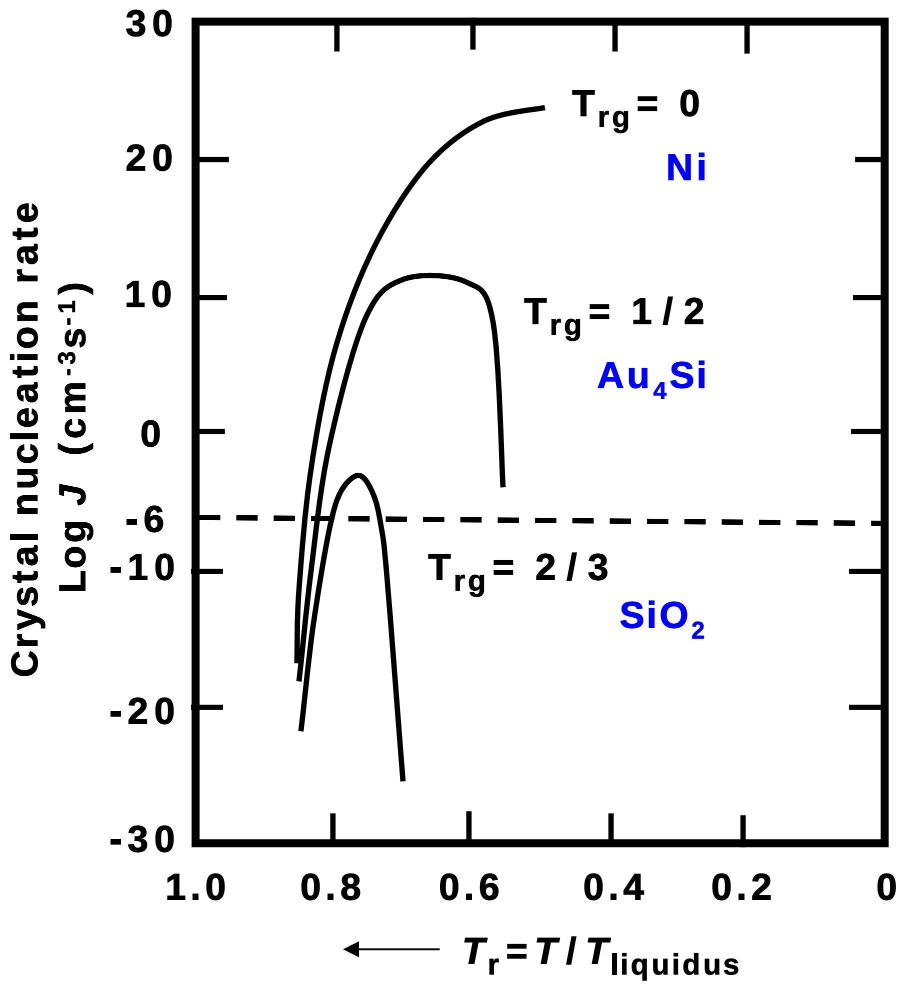
(b) simplified Vogel-Fulcher-Tamman (VFT) equation $\eta = 10^{-3.3} \exp\left(\frac{3.34}{T_r - T_{rg}}\right)$

(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** $= T_g / T_m$

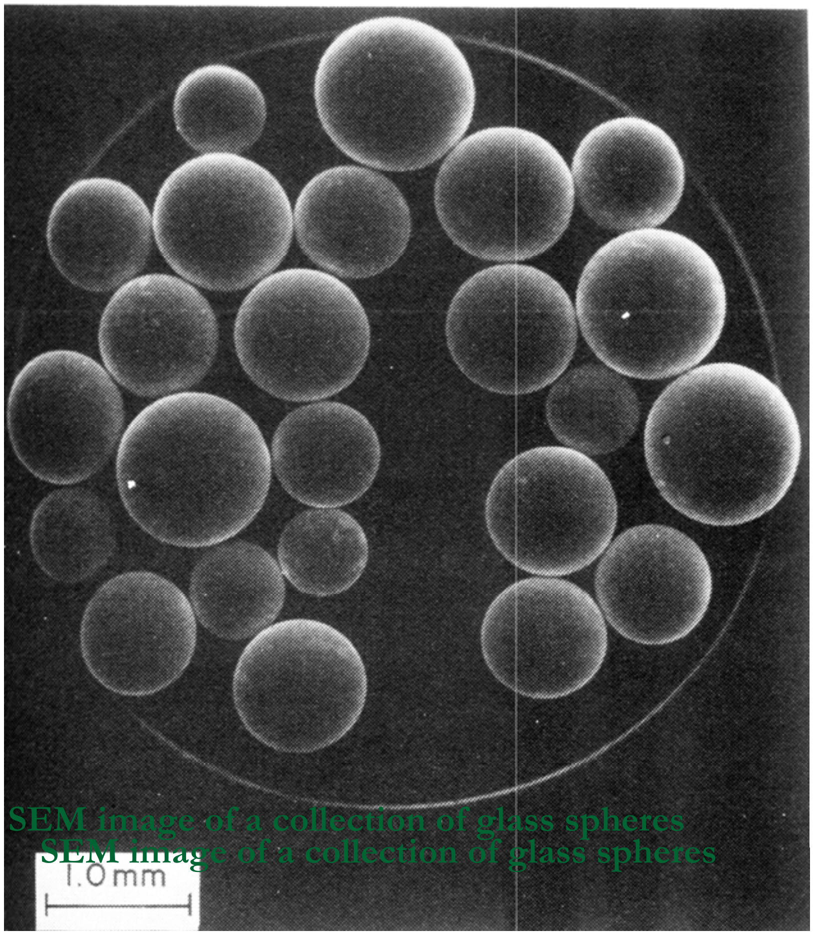
: ability to avoid crystallization during cooling



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
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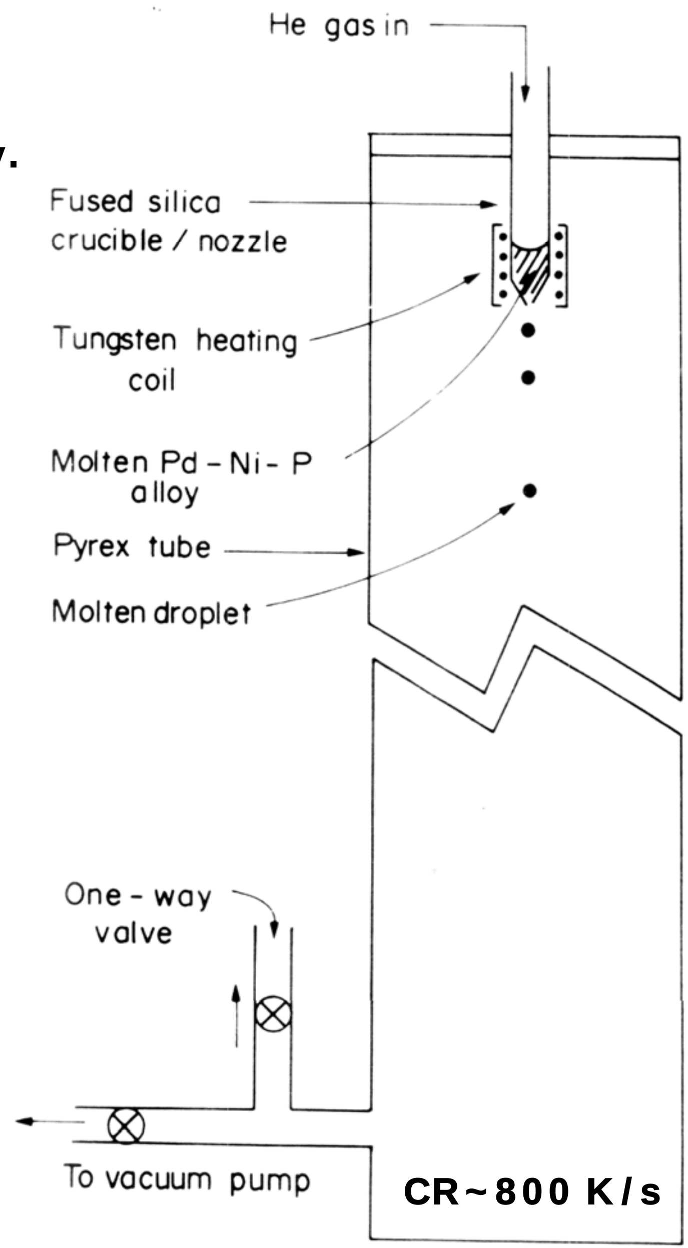


CR~800 K/s

* *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: $>10^5/cm^3s$

  * $Pd_{77.5}Cu_6Si_{16.5}$ ➡ $T_{rg}=0.64$
  - 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

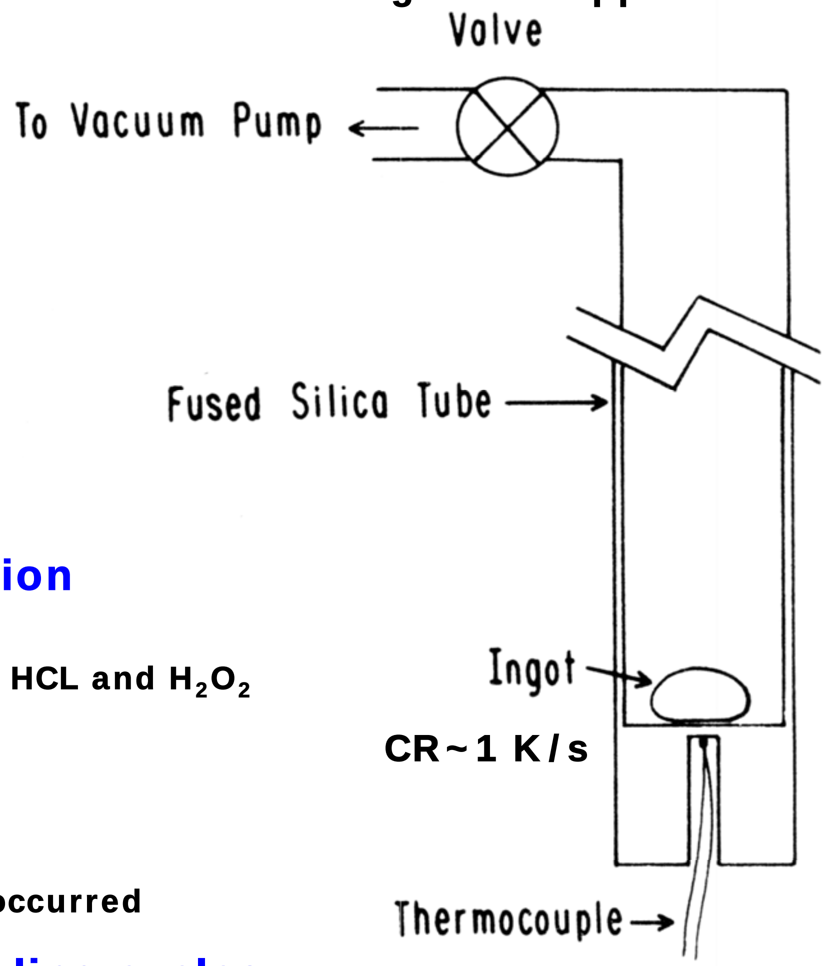
- **Suppression of Heterogeneous nucleation**

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

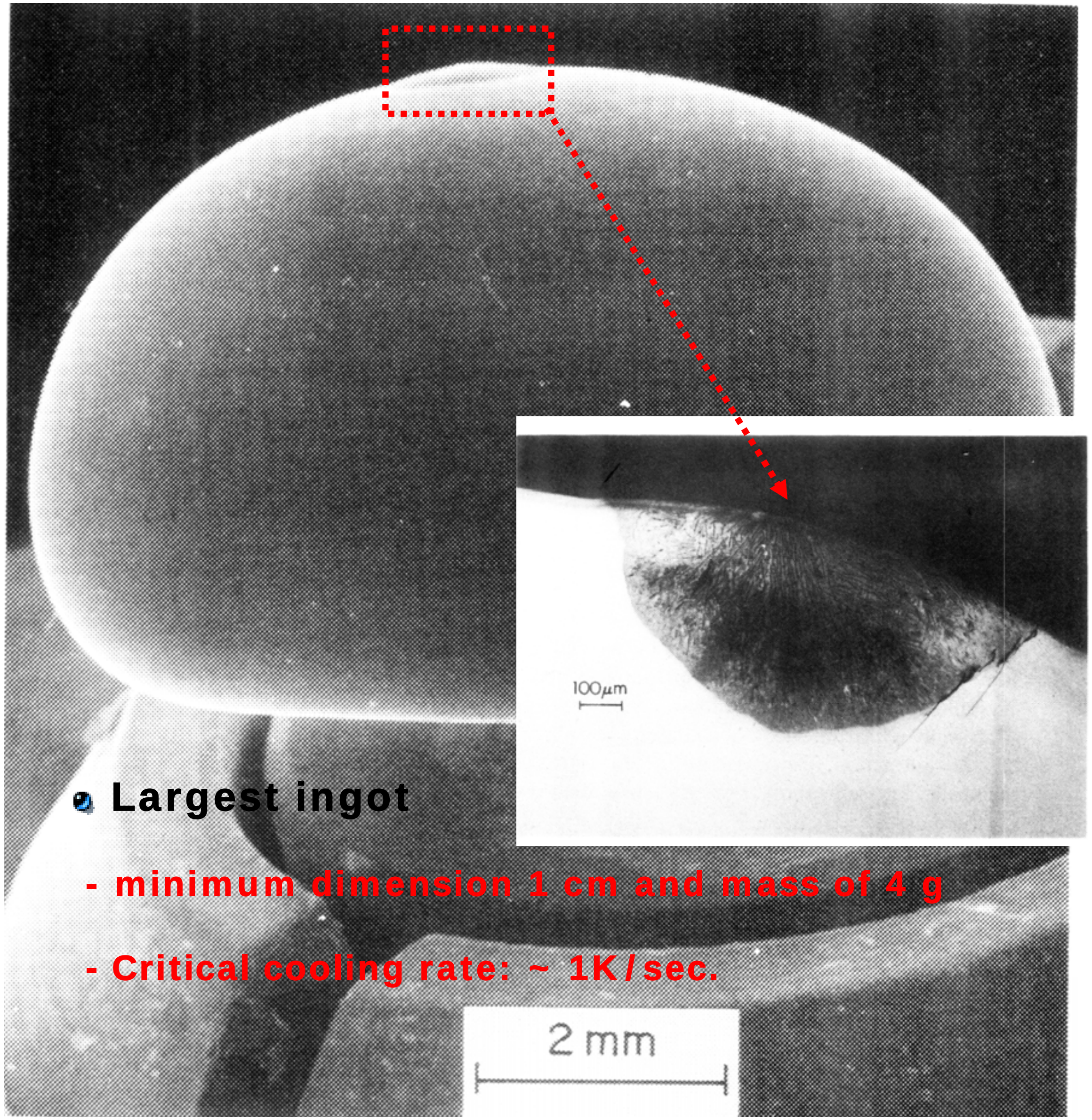
  2. **Thermal cycling –5 cycles**
     : dissolution of nucleating heterogeneities
     ⟶ reduce the temperature at which nucleation occurred

  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>



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

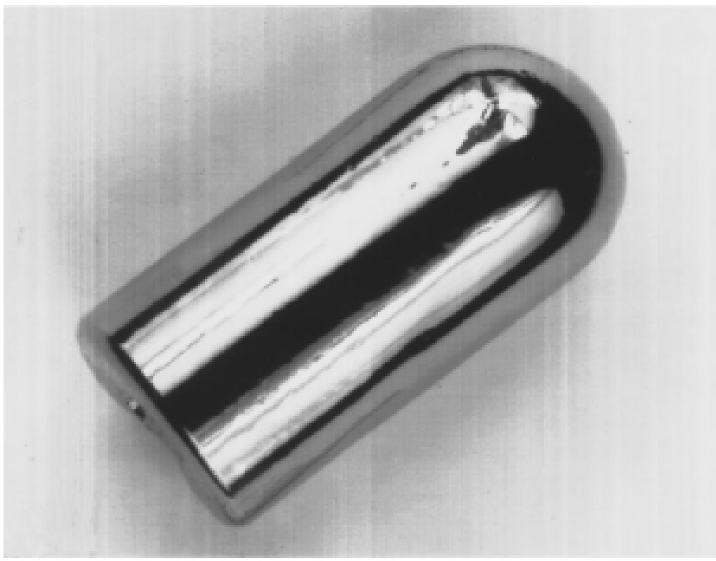
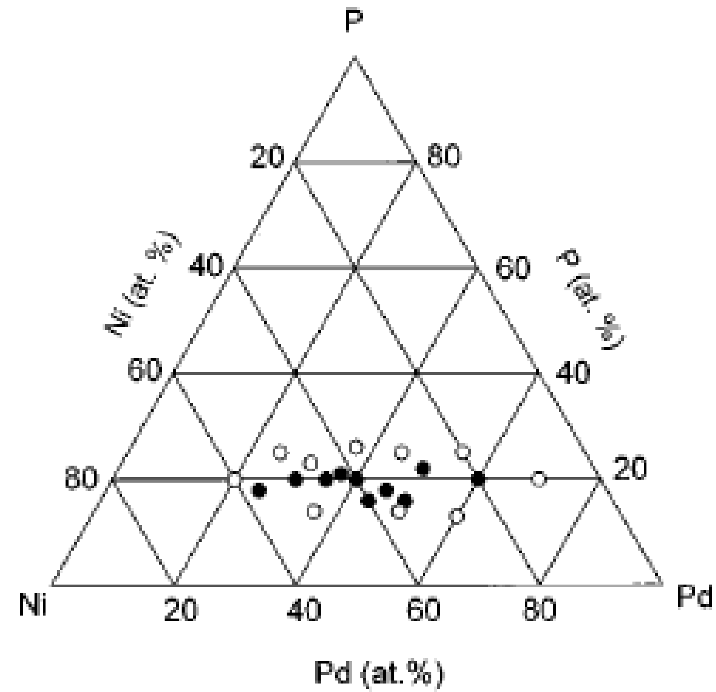


FIG. 1. 300-g ingot of bulk amorphous $Pd_{40}Ni_{40}P_{20}$ rod with 25 mm in diamter prepared by fluxing in B_2O_3 and water quenching.



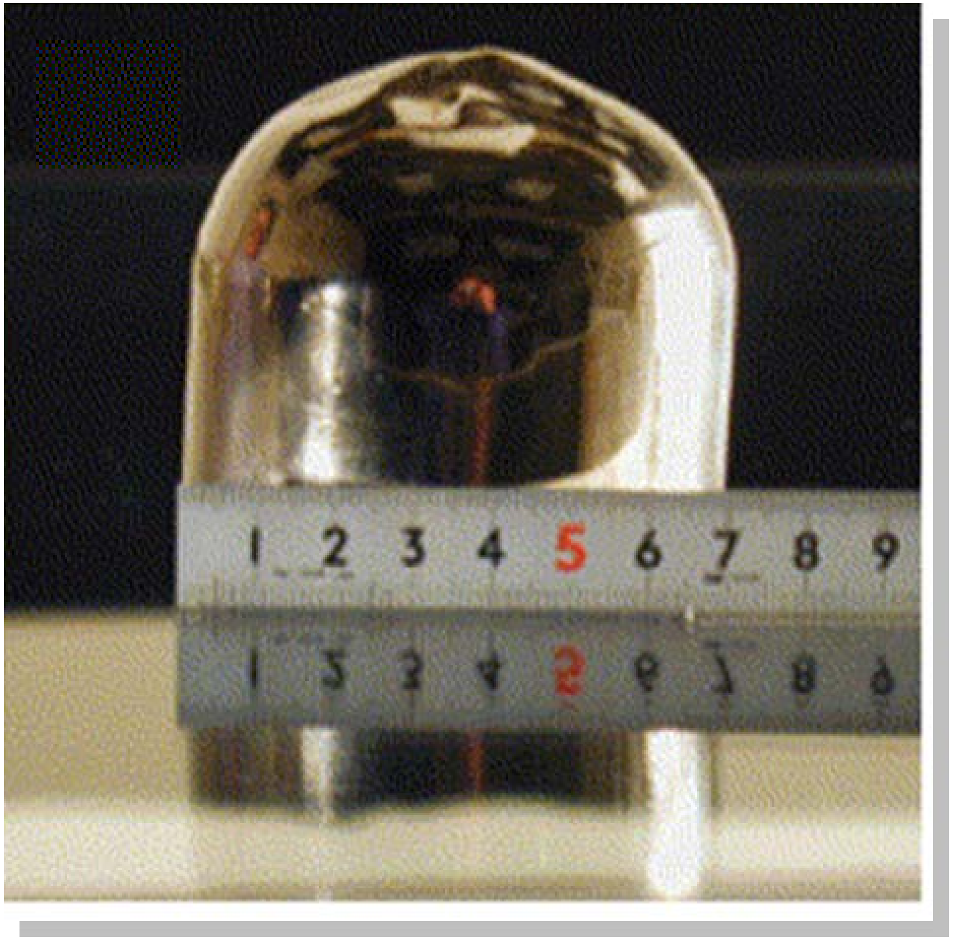
- **Experimental Difference**

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



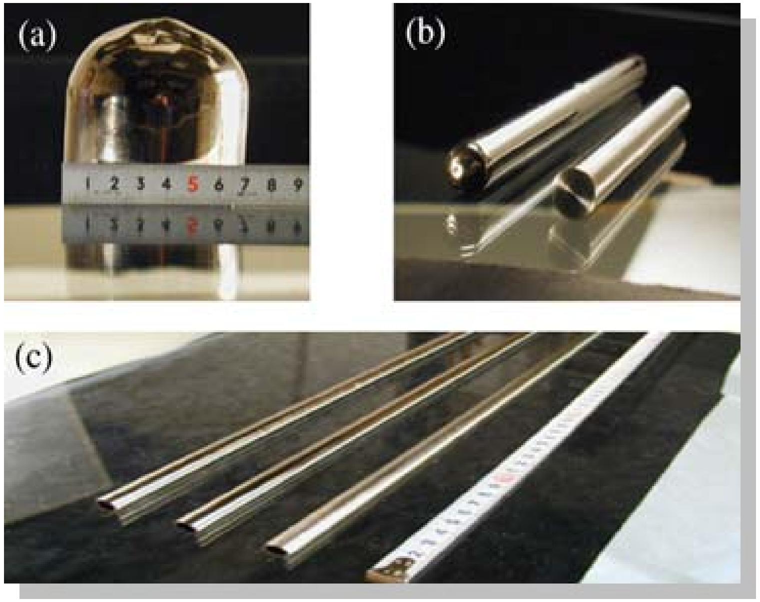
- **Largest ingot**

maximum diameter for glass formation : 72 mm

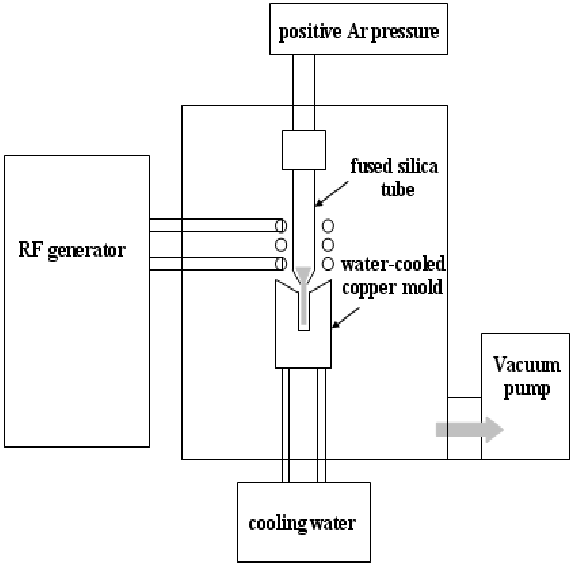
Critical cooling rate: ~ 0.1K/sec.

How to make bulk metallic glasses

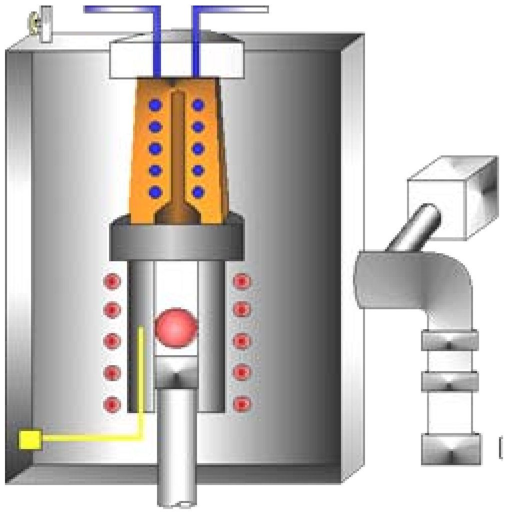
< Casting >



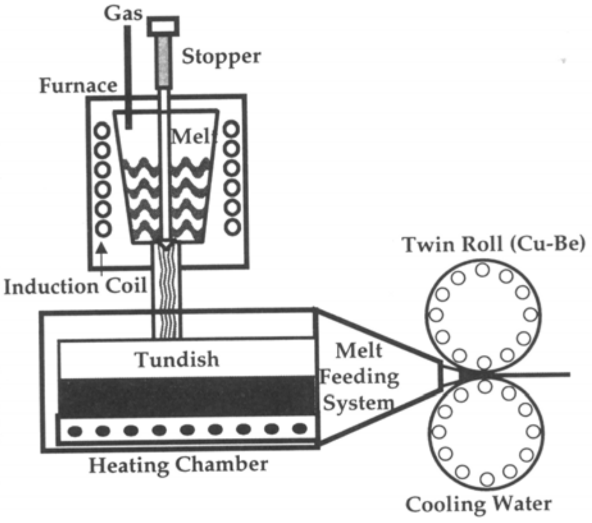
1) Injection casting



2) Squeeze casting



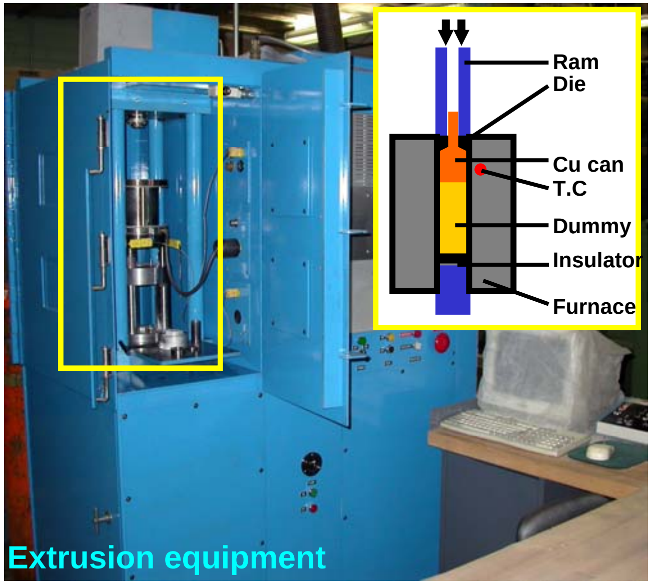
3) Strip casting

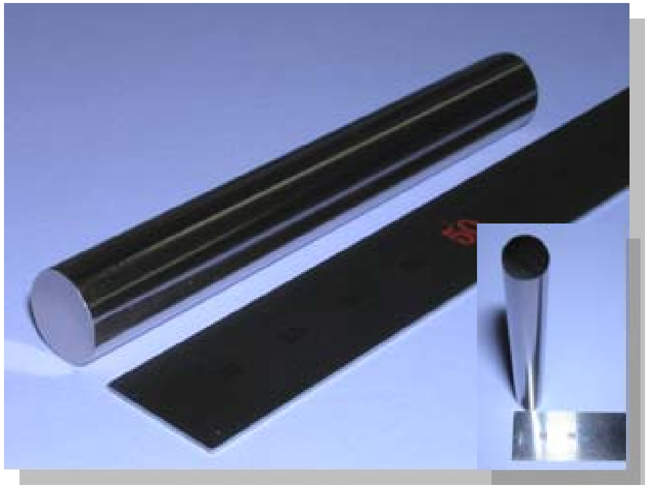


How to make bulk metallic glasses

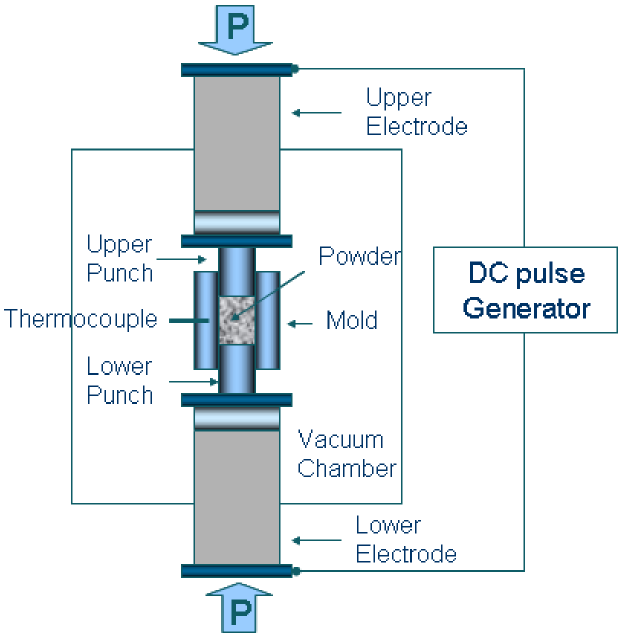
< Powder Metallurgy>

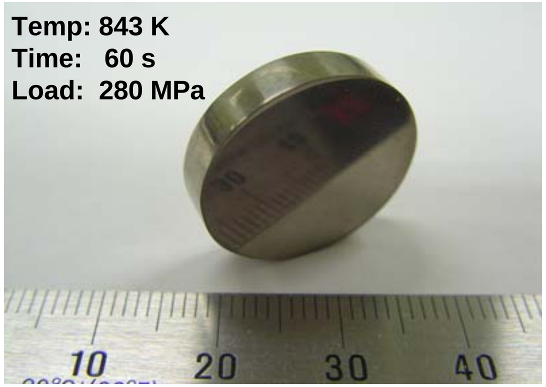
1) Extrusion



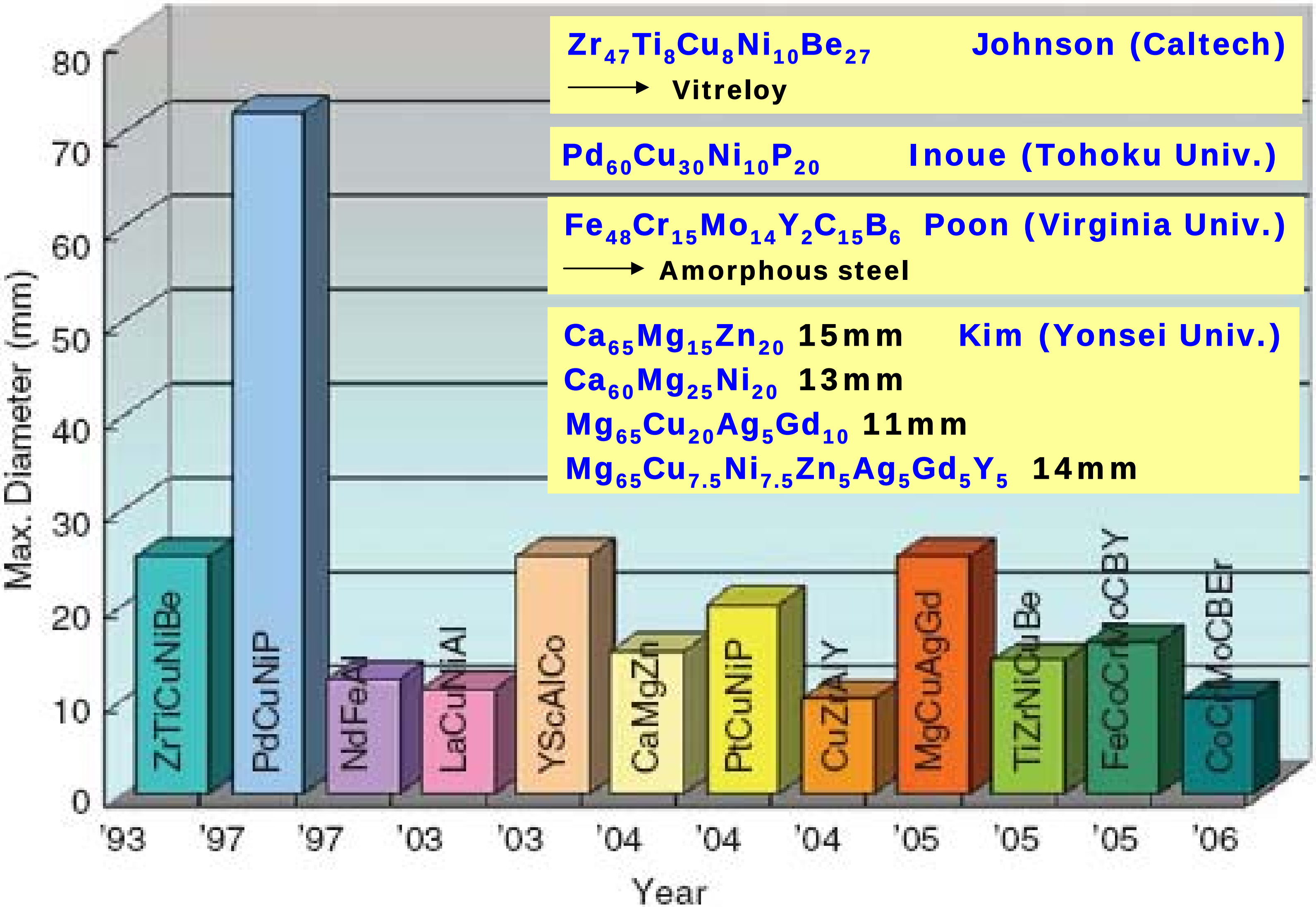


2) Spark Plasma Sintering





Recent BMGs with critical size ≥ 10 mm



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

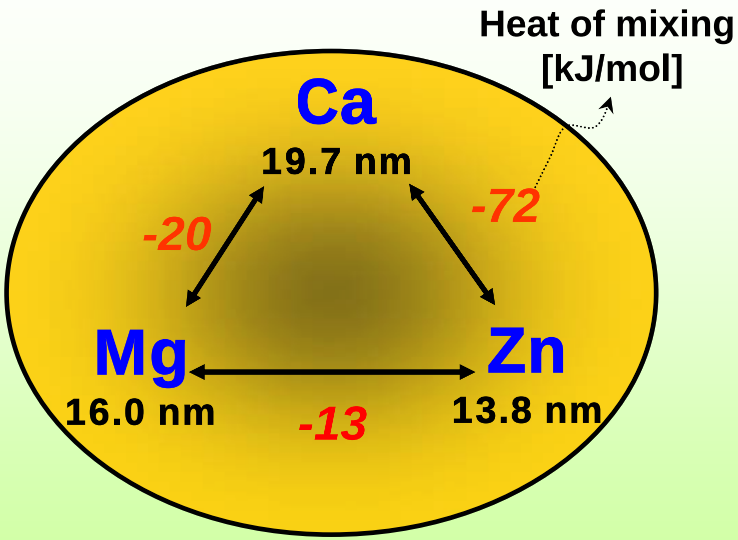
At the Cutting Edge of Metals Research

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

Alloy design and new BMG development

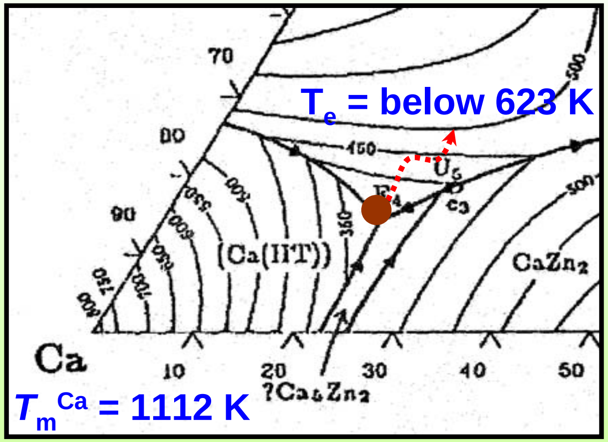
Ca-Mg-Zn alloy system

● **Dense packed structure**



- Large difference in atomic size
- Large negative heat of mixing

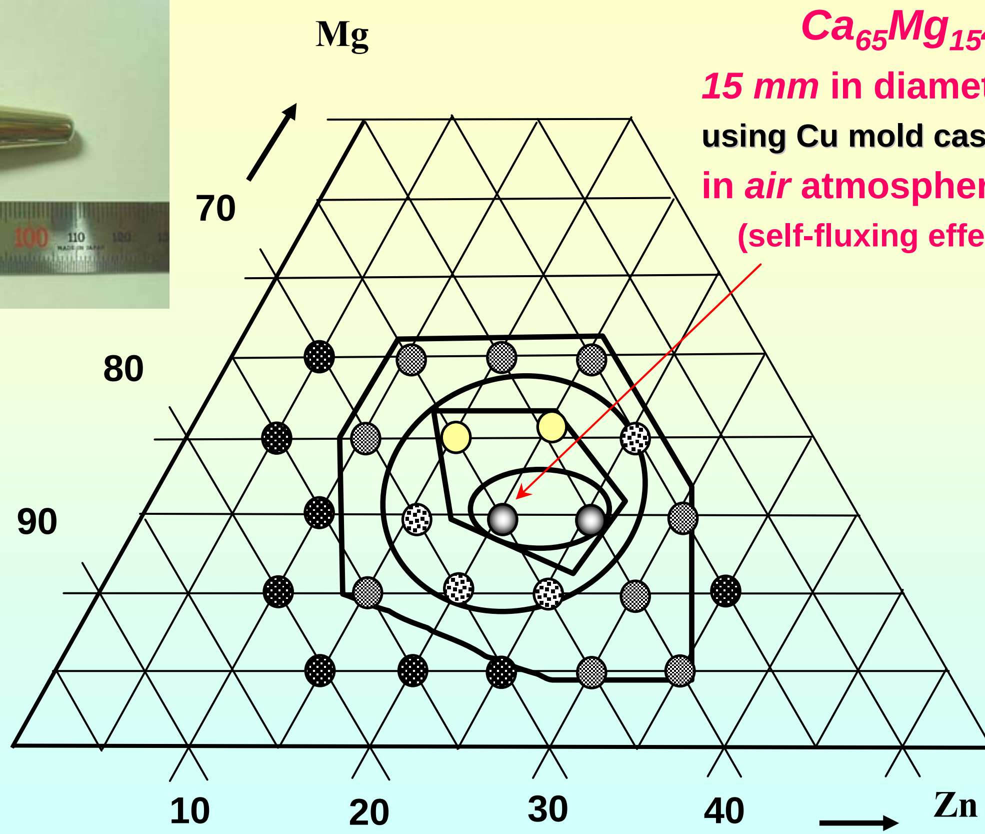
● **Decrease of melting temp.**



Deep eutectic condition

$T_e / T_m^{Ca} = 0.560$

Ca-Mg-Zn alloy system



$Ca_{65}Mg_{15}Zn_{20}$

15 mm in diameter sample

using Cu mold casting method

in *air* atmosphere

(self-fluxing effect by Ca)

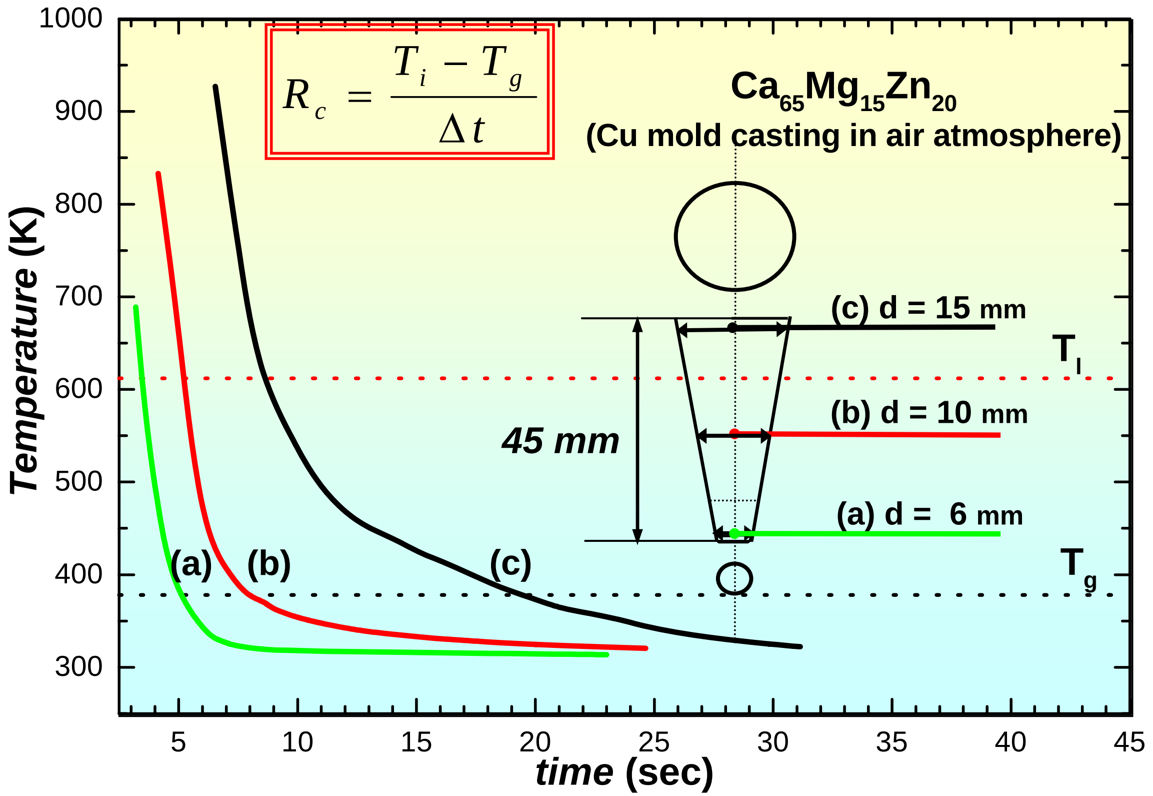
Maximum diameter for glass formation in Ca-rich Ca-Mg-Zn alloy system

over 10mm *over 7mm* *over 3mm* *over 1mm* *below 1mm*

* J. Mater. Res. 19, 685 (2004)
* Mater. Sci. Forum 475-479, 3415 (2005)

Measurement and calculation of R_c in $Ca_{65}Mg_{15}Zn_{20}$ alloy system

* Cooling curves measured at the center of the three transverse cross sections



(a) bottom position : 149 K/s **(b) middle position : 93 K/s** **(c) top position : 20 K/s**

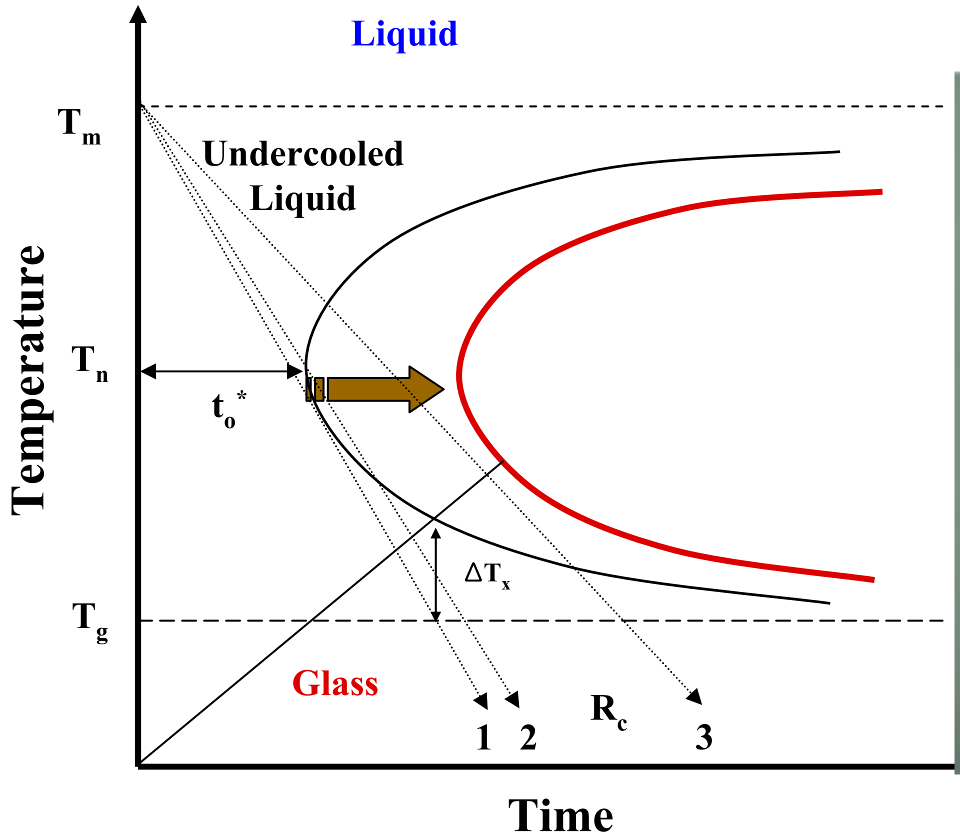
⇒ **Critical cooling rate for glass formation calculated from CCT and CHT curves is in good agreement with measured value.**

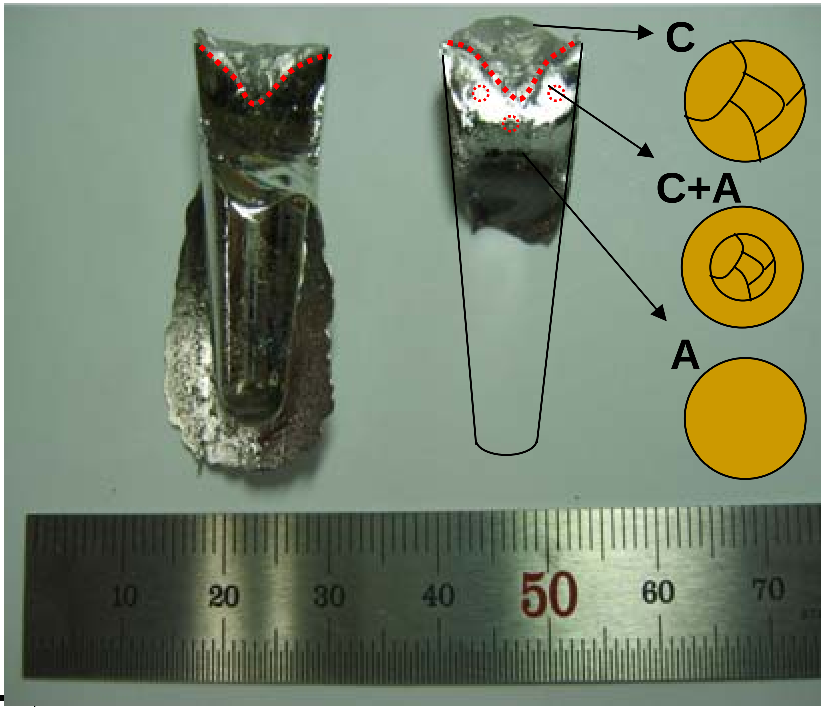
* Trans. Indian Inst. Met. 58, 739 (2005)
* Met. Mater. –Int. 11, 1 (2005)

Formation of Bulk Metallic Glass

Critical cooling rate

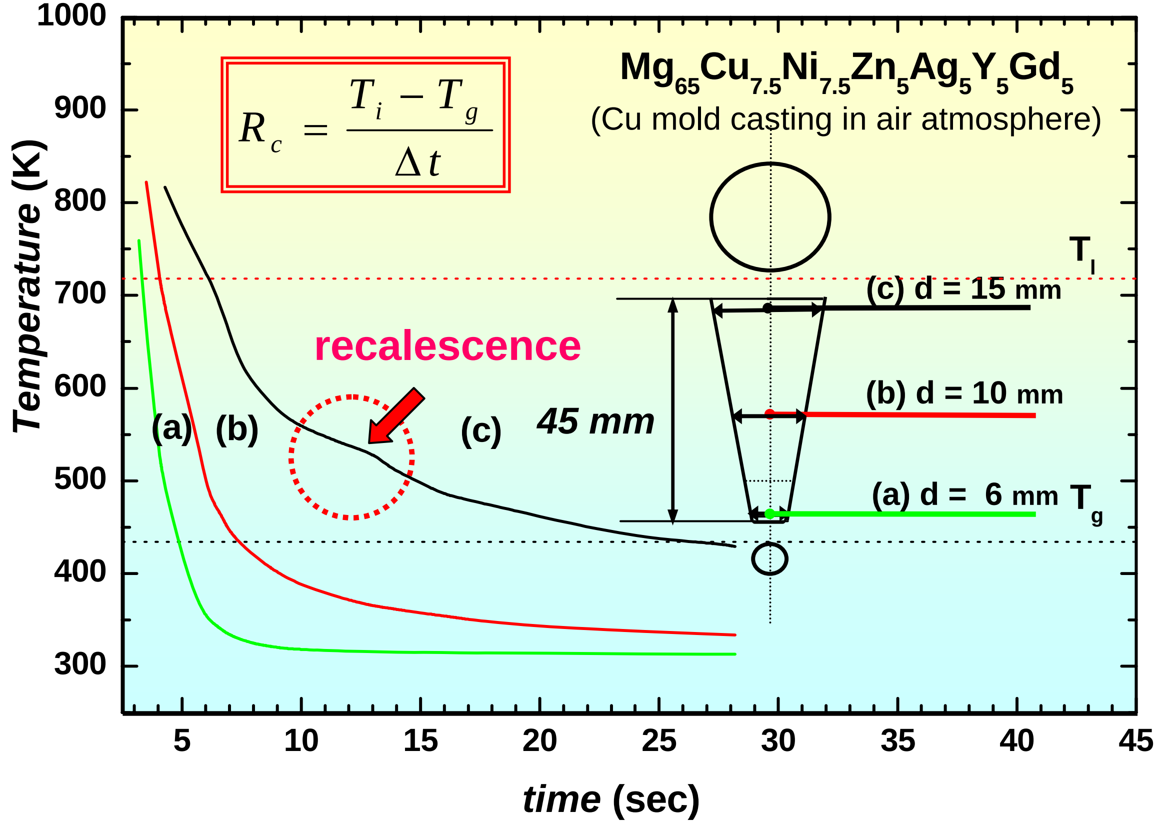
$$R_c = \frac{T_m - T_n}{t_o^*}$$





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

Measurement of R_c in Mg BMG (D_{max}=14 mm)



top position : recalescence

middle position : 64K/s

bottom position : 137 K/s

*** Cooling curves measured at the center of the three transverse cross sections**