

2014 Spring

**“Advanced Physical Metallurgy”
- Bulk Metallic Glasses -**

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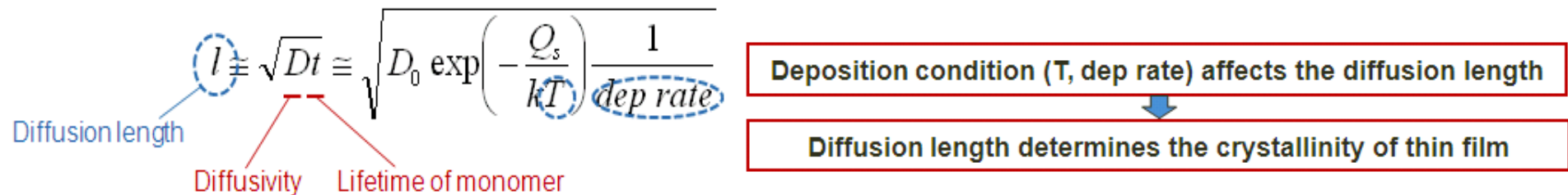
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2.6 Methods to Synthesize Metallic Glasses

2.6.1 Vapor-state Processes: expensive & slow, electronic & magnetic applications

Thermal Evaporation/ Sputtering/ Vapor Chemical Deposition



2.6.2 Liquid-state Processes : Rapid Solidification Process (RSP) 10^{5-6} K/s most ideal way to obtain metallic glasses, especially the bulk variety

Splat Quenching/ Melt-spinning/ Electro Deposition/ Gas Atomization

2.6.3 Solid-state Processes

Mechanical Alloying & Milling/ Hydrogen-induced Amorphization/ Multilayer Amorphization_Solid state diffusional amorphization/
Pressure-induced Amorphization/ Amorphization by Irradiation/ Severe Plastic Deformation_Intense deformation at low temperatures/
Accumulative Roll Bonding (ARB process)

2.7 Bulk Metallic Glasses (BMGs)

- More commonly, metallic glasses with at least a diameter or section thickness of 1 mm are considered “bulk.” (Nowadays researchers tend to consider 10mm as the minimum diameter or section thickness at which a glass is designated bulk.)

2.7.1 Characteristics of Bulk Metallic Glasses

- The alloy systems have a minimum of three components; more commonly the number is much larger and that is why they are frequently referred to as multicomponent alloy systems.
- They can be produced at slow solidification rates, typically 10^3 K s^{-1} or less. The lowest solidification rate at which BMGs have been obtained was reported as 0.067 K s^{-1} , that is, 4 K min^{-1} [61]; a really slow solidification rate indeed!
- BMGs exhibit large section thicknesses or diameters, a minimum of about 1 mm. The largest diameter of a bulk metallic glass rod produced till date is 72 mm in a $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ alloy [62].
- They exhibit a large supercooled liquid region. The difference between the glass transition temperature, T_g , and the crystallization temperature, T_x , that is, $\Delta T_x = T_x - T_g$, is large, usually a few tens of degrees, and the highest reported value so far is 131 K in a $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ alloy [17].

When the as-cast alloy is characterized by XRD techniques, the presence of a broad and diffuse peak is often taken to be evidence for the presence of a glassy phase. This is normally true. But, it should be realized that the technique of XRD is not very sensitive to the presence of a small volume fraction of a crystalline phase in a glassy phase, especially when the crystals are in nanocrystalline condition. Therefore, even if the XRD pattern shows a broad halo, the material may contain a small volume fraction of a crystalline phase dispersed in the glassy matrix. Further, a structure consisting of a glassy phase, or extremely fine grains, or a nanocrystalline material with a small grain size of about <10nm, will all produce a broad and diffuse halo. Therefore, it is always desirable to confirm the lack of crystallinity in the material by conducting (high-resolution) transmission electron microscopy investigations.

2.7.2 The Origins of BMGs

* 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 (Au₈₀Si₂₀)**
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}Cu₆Si_{16.5})**
produced by droplet quenching at Harvard Univ.
by H.S. Chen and D. Turnbull in 1969

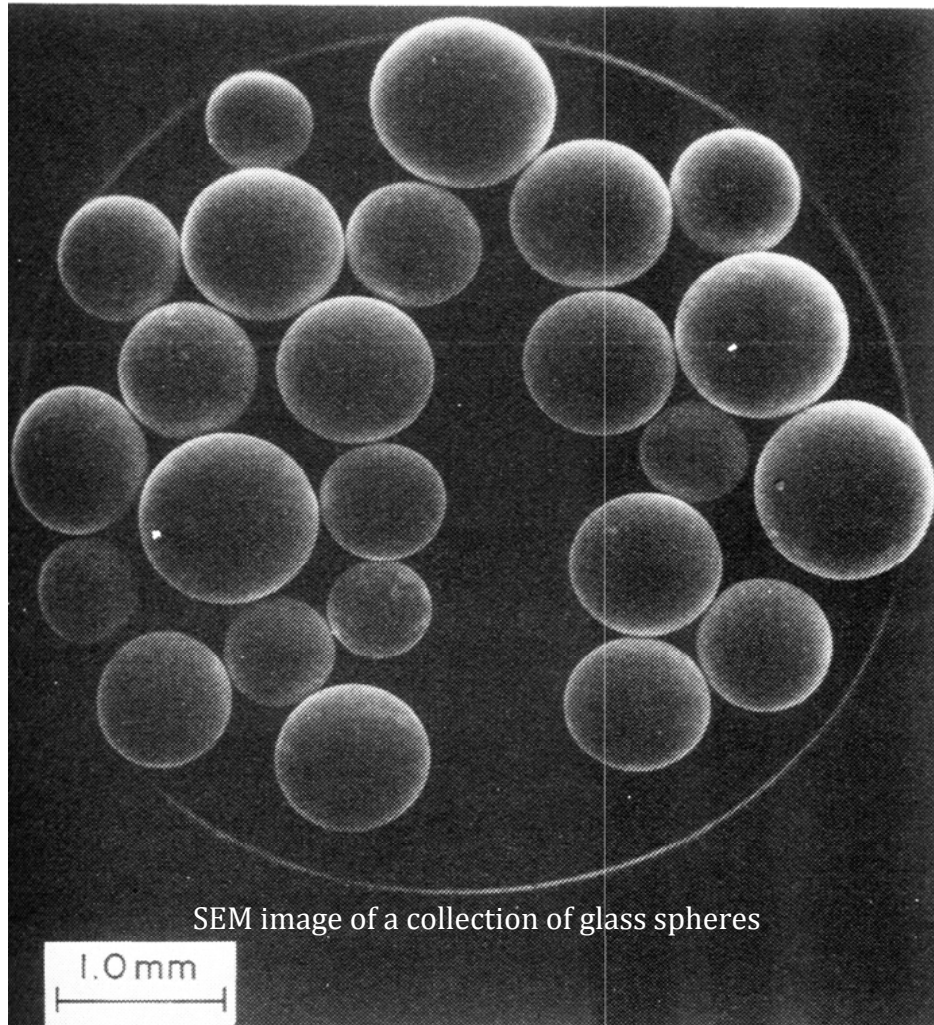
** H.S. Chen and D. Turnbull, Acta Metall. 1969; 17: 1021.*

produced by water quenching of PdTMSi, Pt-Ni-P and Pd-Ni-P system
by H.S. Chen in 1974 (long glassy rods, 1-3 mm in diameter and several centimeters in length)

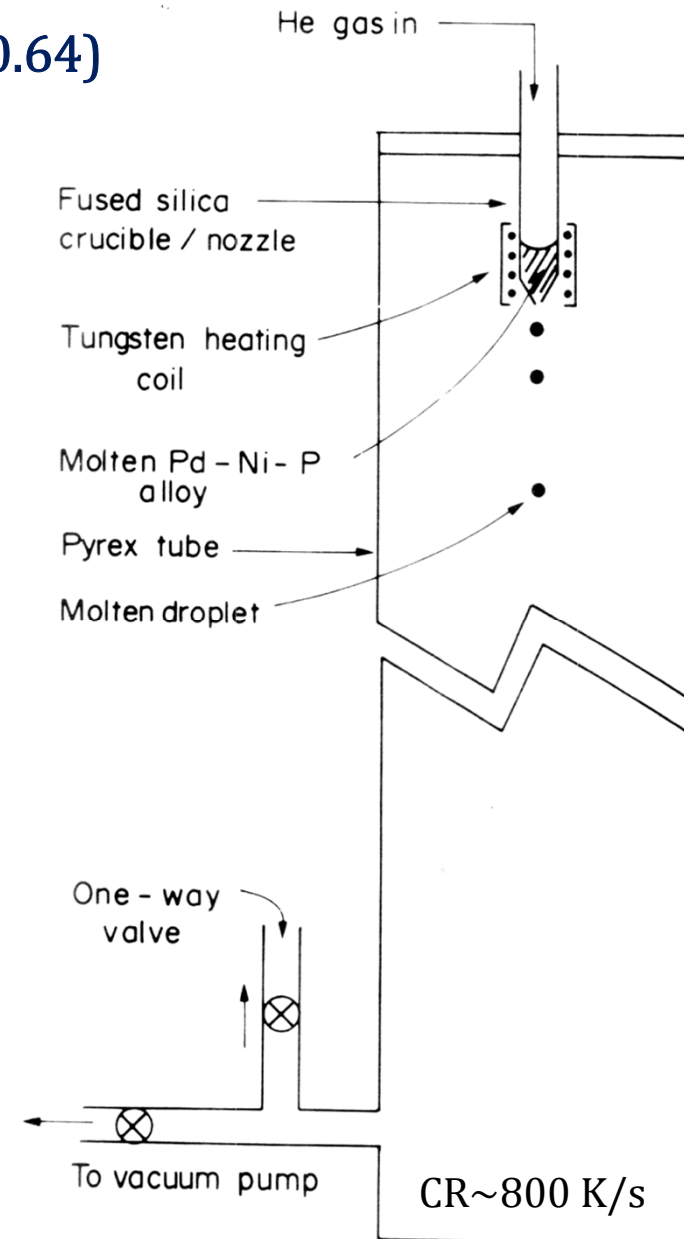
** H.S. Chen, Acta Metall. 1974; 22: 1505*

► **First bulk metallic glass: Pd_{77.5}Cu₆Si_{16.5} (T_{rg}=0.64)**

By droplet quenching (CR~800 K/s)



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



Bulk formation of a metallic glass: Pd₄₀Ni₄₀P₂₀

Alloy Selection: Consideration of T_{rg}

* Pd₈₂Si₁₈ → $T_{rg}=0.6$

- Homogeneous nucleation rate: $>10^5/\text{cm}^3\text{s}$

- Critical cooling rate: $> 800 \text{ K/s}$

* Pd_{77.5}Cu₆Si_{16.5} → $T_{rg}=0.64$

* Pd₄₀Ni₄₀P₂₀ → $T_{rg}=0.67$
 $T_g=590 \text{ K}, T_e = 880 \text{ K}, T_l = 985 \text{ K}$

Suppression of Heterogeneous nucleation

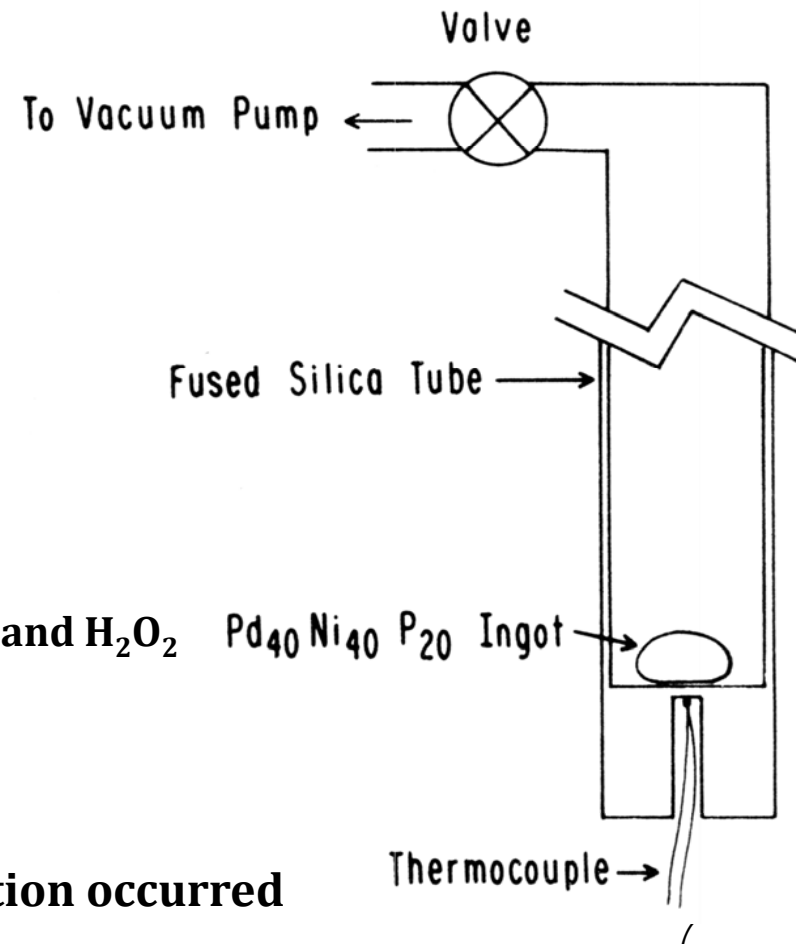
1. **Surface Etching of ingot** in a mixture of HCL and H₂O₂
: elimination of surface heterogeneities

2. **Thermal cycling -5 cycles**

: dissolution of nucleating heterogeneities

→ reduce the temperature at which nucleation occurred

<Schematic diagram of apparatus>



Bulk formation of a metallic glass: Pd₄₀Ni₄₀P₂₀

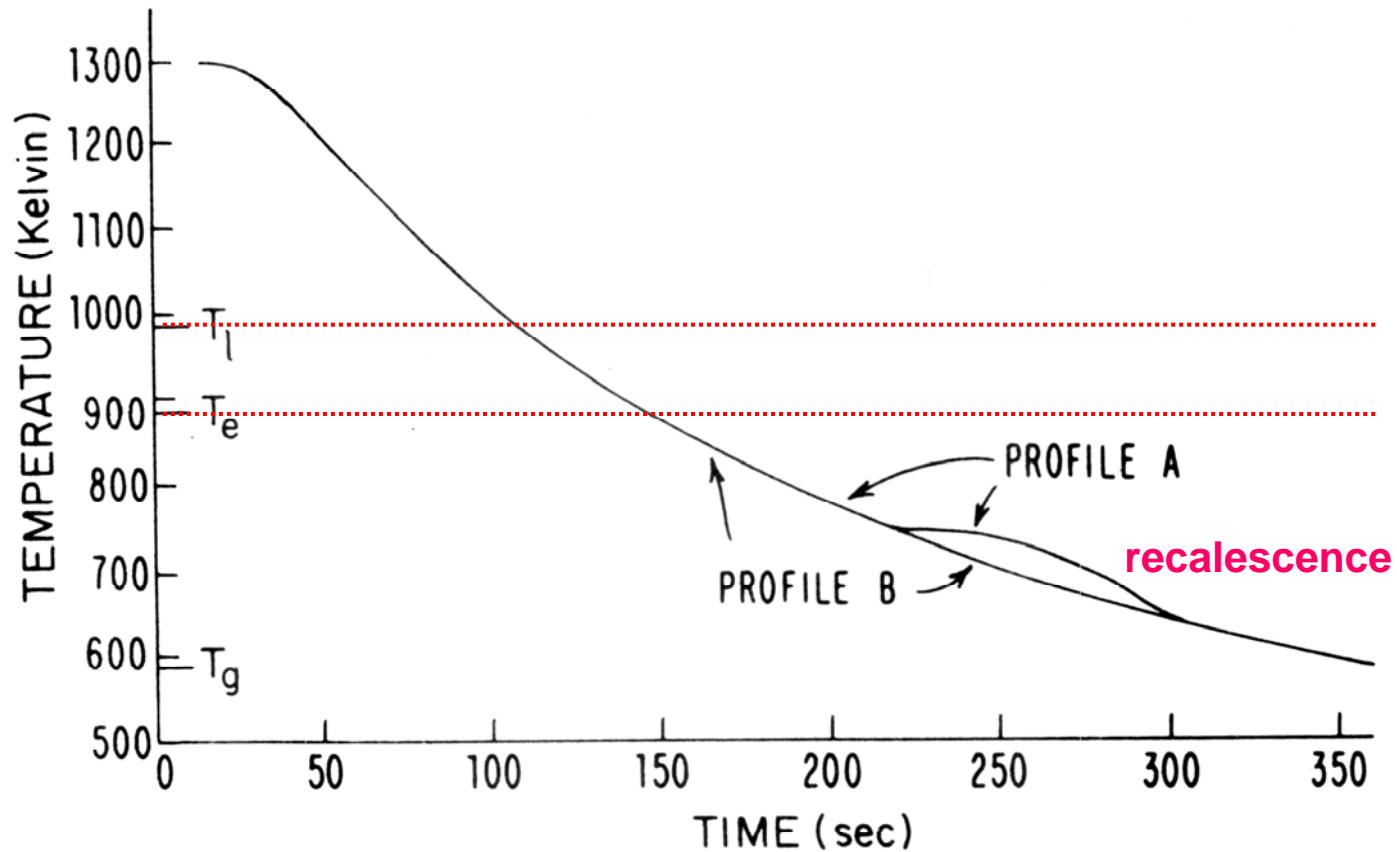


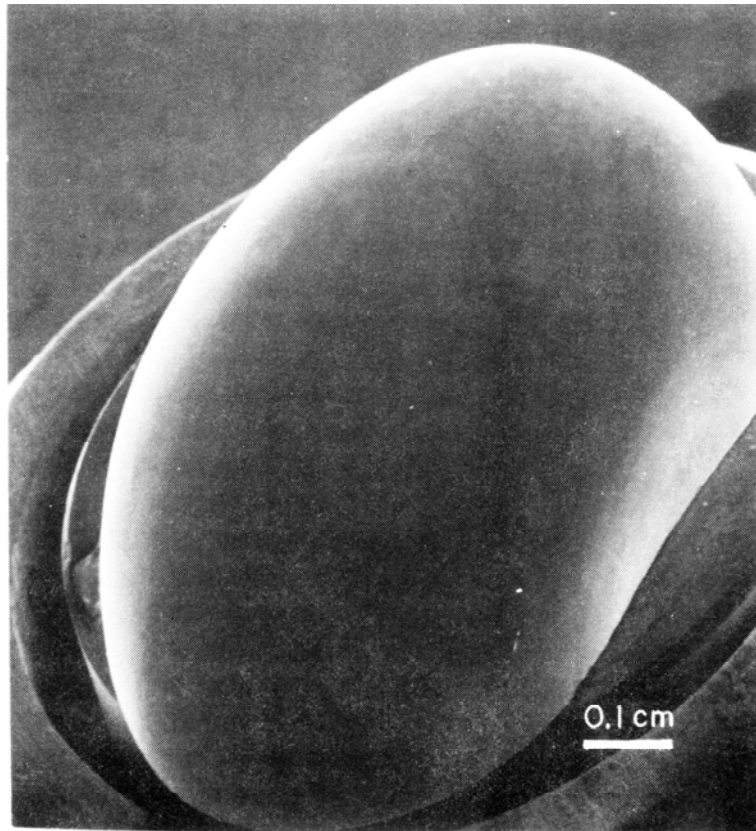
FIG. 2. Superposition of two cooling profiles: A—bulk crystallization which began at 740 K. B—formation of a glassy ingot.

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

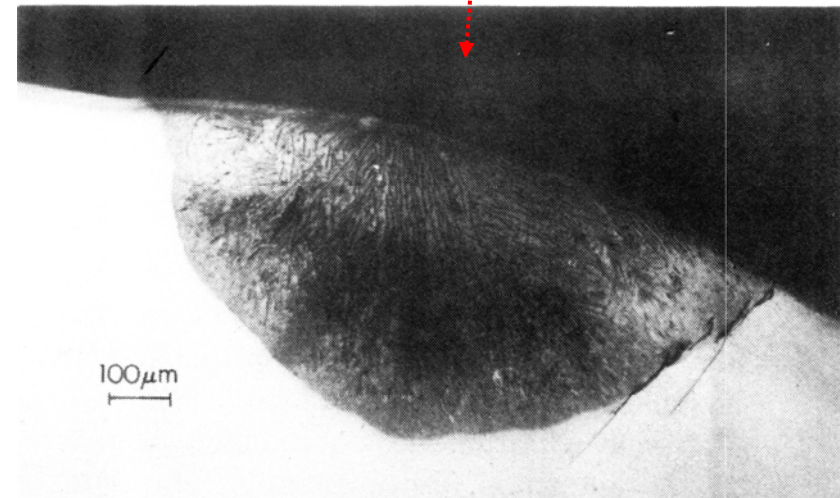
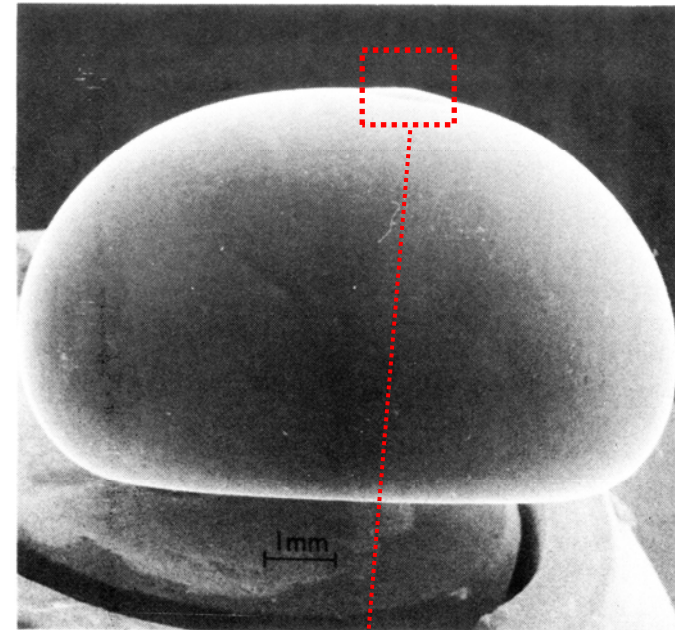
Bulk formation of a metallic glass: Pd₄₀Ni₄₀P₂₀

• Largest ingot

- minimum dimension 0.6 cm and mass of 2.3 g
- Critical cooling rate: ~ 1.4 K/sec.



**Appl. Phys. Lett. 1982; 41: 716.*



OM image of the cross section of a crystalline inclusion showing the eutectic structure

Formation of bulk metallic glass by fluxing

• Heterogeneous nucleation

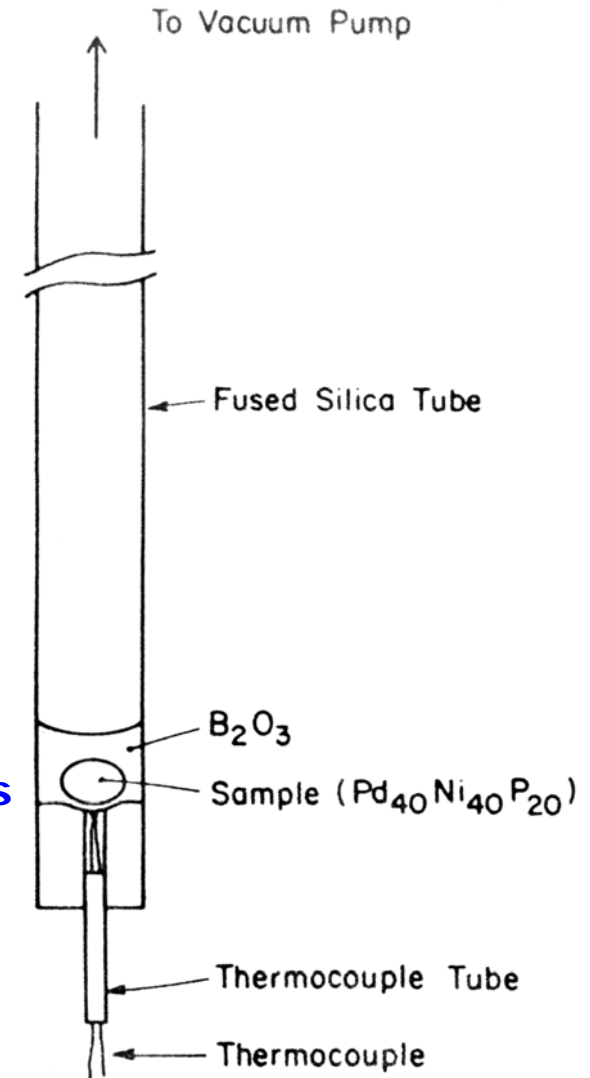
1. Surface oxide layer
2. Container walls
3. Motes in the liquid

→ Suppression

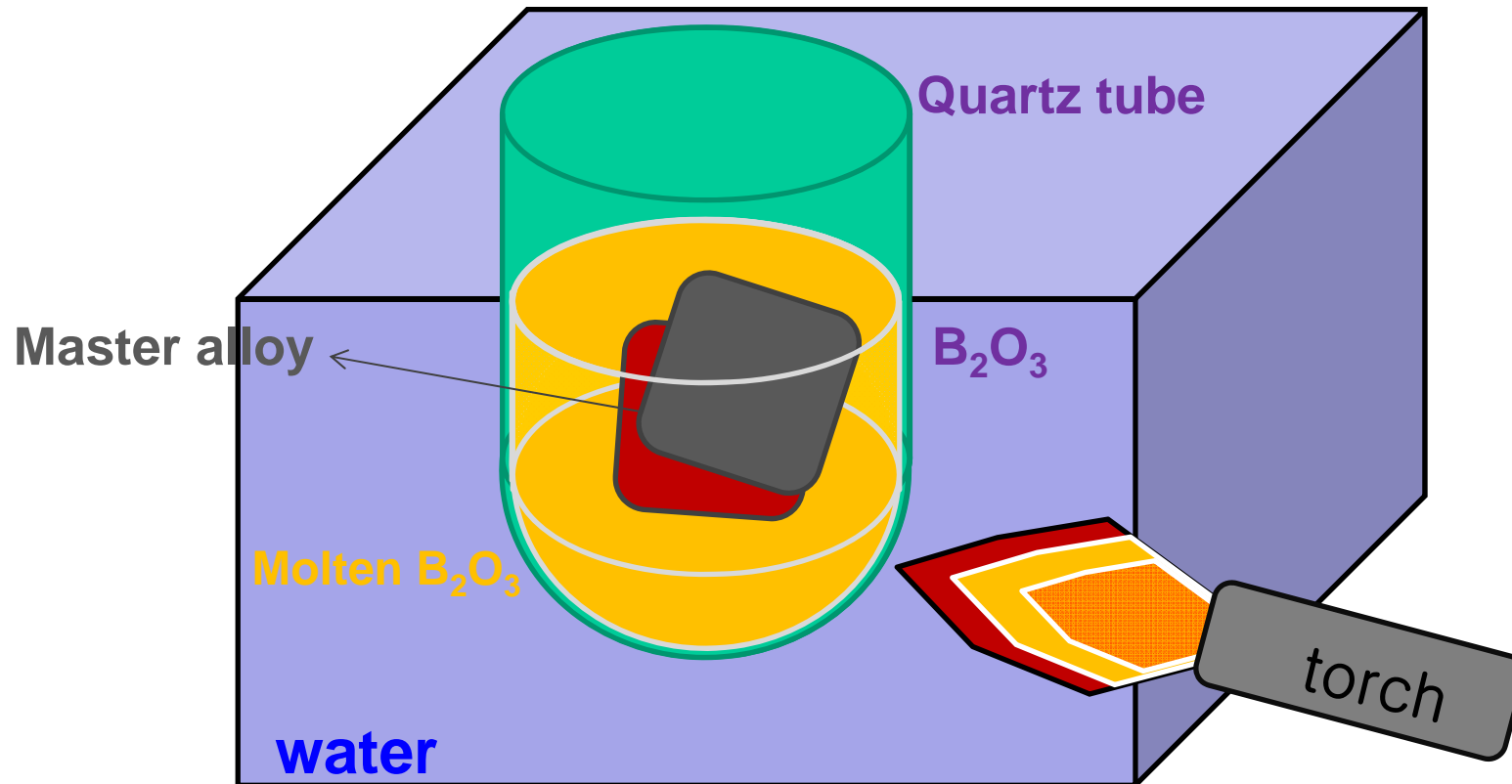
1. **Ingot = Chemical etching**
by dilute aqua regia ($\text{HNO}_3 + \text{HCl}$)
2. **Interior of the vessel = Cleaning**
by hydrofluoric acid
3. **Impurities = Successive heating-cooling cycles**
in a molten oxide flux

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

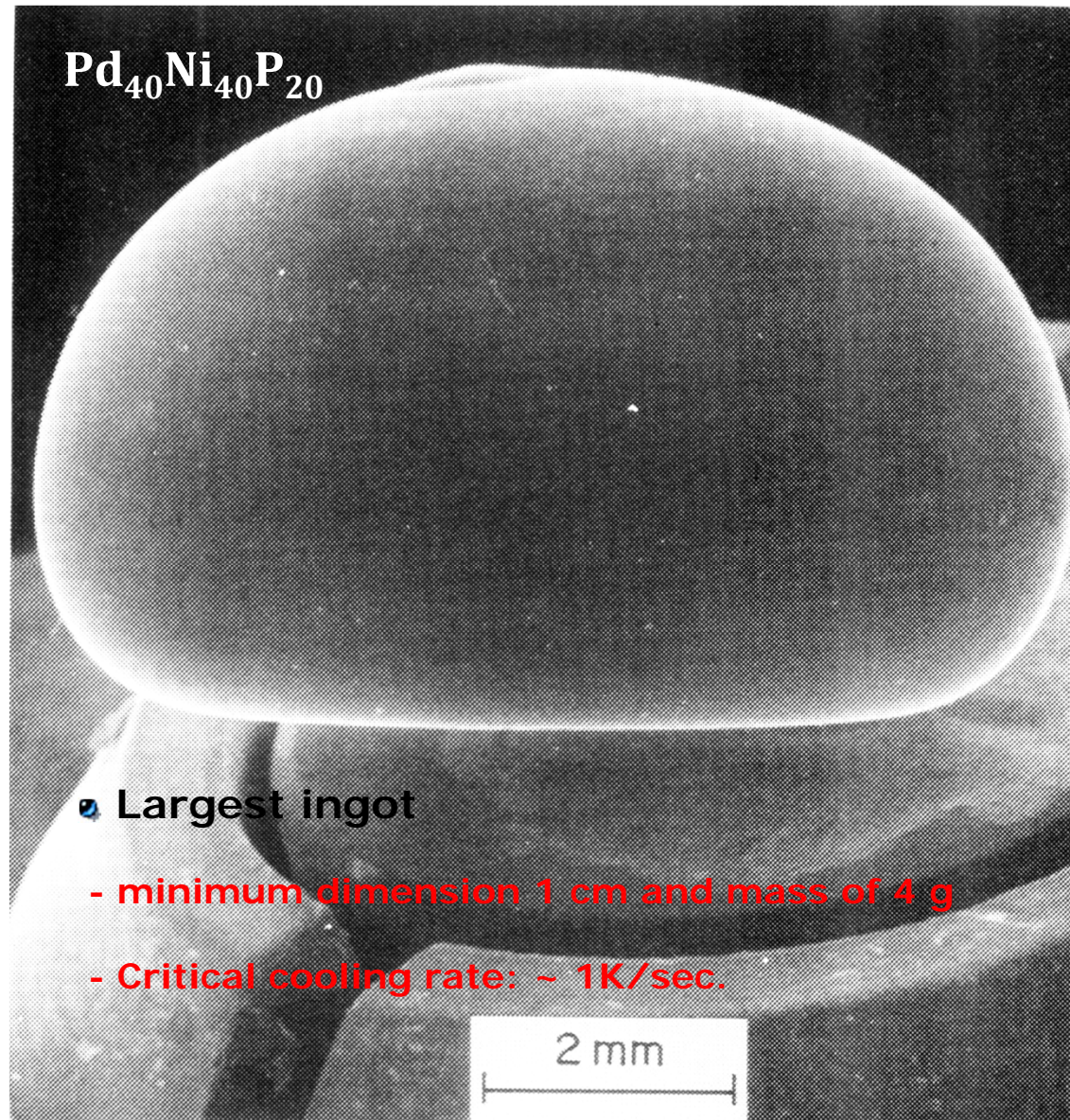


Schematic process of fluxing

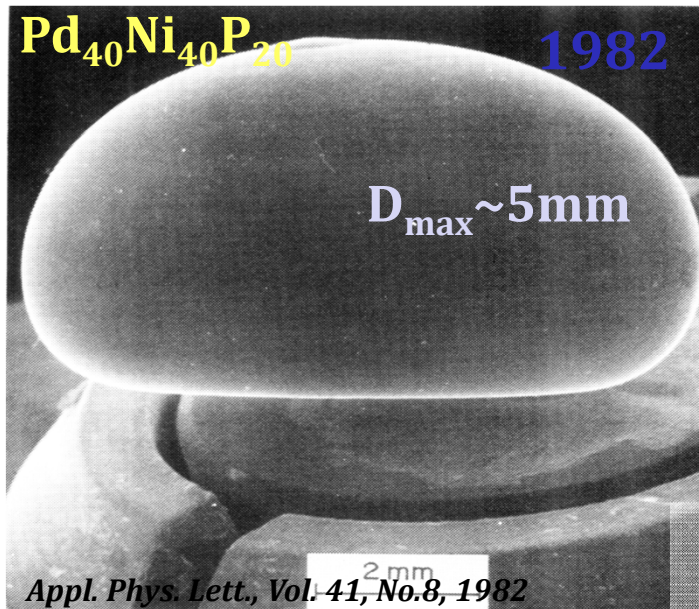


B₂O₃ melting point 723 K, boiling point <40,000 K

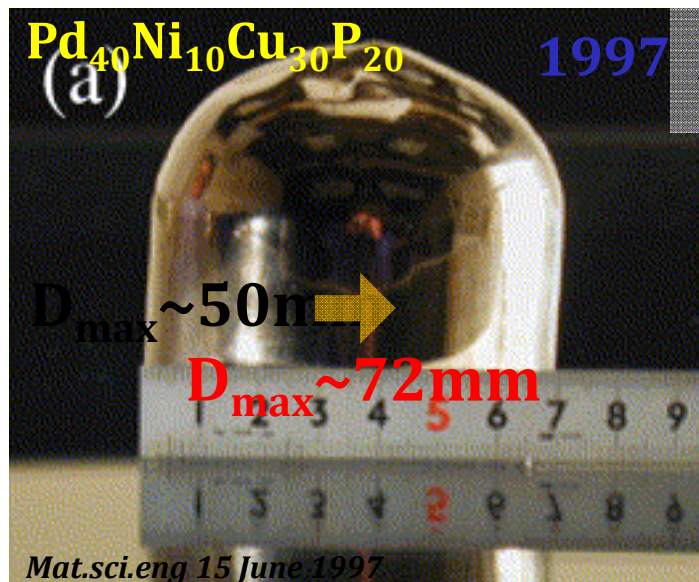
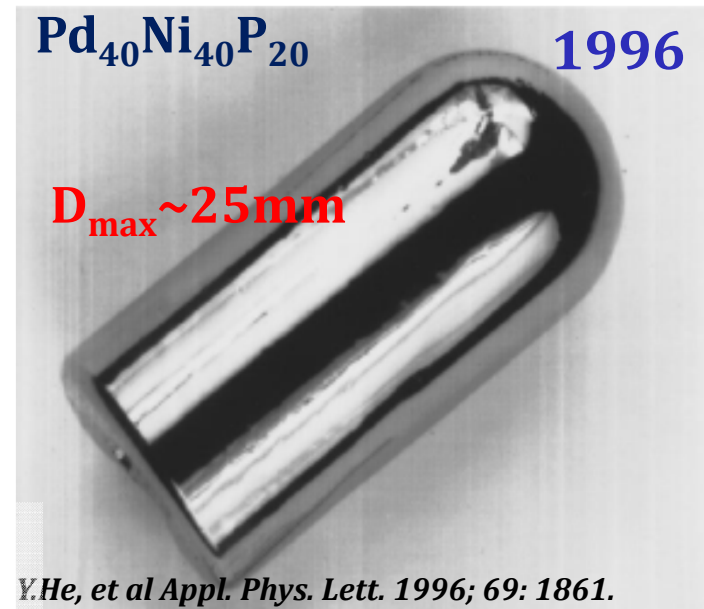
Formation of centimeter-sized BMG by fluxing



Formation of centimeter-sized BMG by fluxing



1984
→
 $D_{\text{max}} \sim 10\text{mm}$

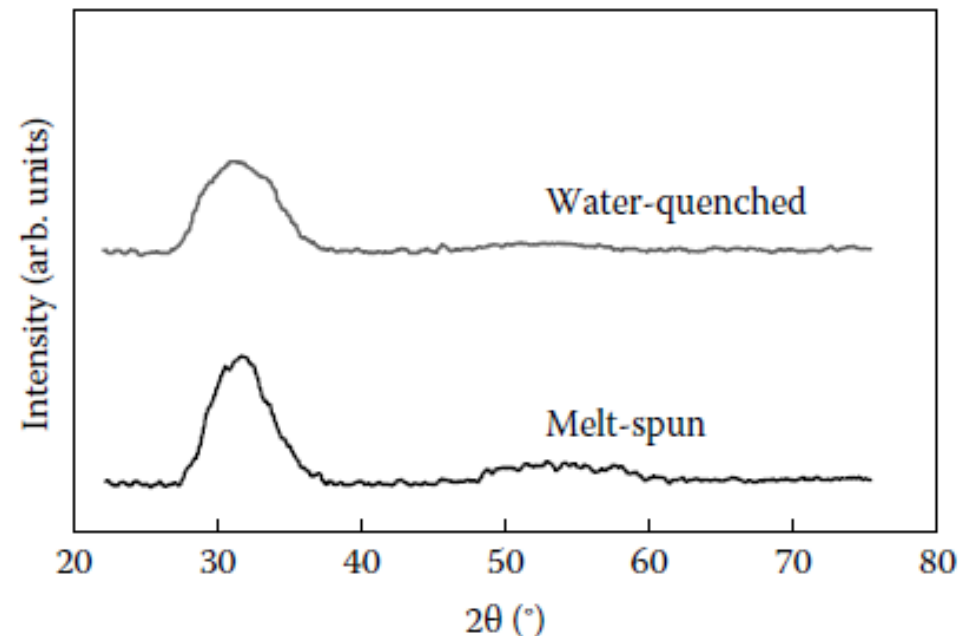


Starting in the late 1980s, the RSP group at Tohoku University in Sendai, Japan, has systematically investigated the glass-forming ability (GFA) of different alloy systems and was able to produce bulk glassy alloys in some of the systems at solidification rates of 10^3 K s^{-1} or lower. A brief account of the development of BMGs at Tohoku University is described below.

Al–La–Ni [67] and Mg–Ni–La [68] glassy alloys were produced in a wide composition range \longrightarrow The ΔT_x values reported were 69K for the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ glass and 58K for the $\text{Mg}_{50}\text{Ni}_{30}\text{La}_{20}$ glass. These ΔT_x values are much larger than those reported for the noble-metal-based glasses, Pd–Ni–P and $\text{Pt}_{60}\text{Ni}_{15}\text{P}_{25}$ (35–40K) reported earlier.

Figure 2.6

X-ray diffraction patterns of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ glassy samples in the water-quenched rod (0.8 mm dia. \rightarrow $D_{\text{max}} = 1.2 \text{ mm}$) and melt-spun ribbon (20 μm) conditions. Note that in both the cases, the diffraction pattern shows only a broad peak and sharp peaks indicative of any crystalline phase are absent. Furthermore, the position of the broad peak is the same in both the samples, suggesting that the glassy phase produced in same in both the cases.



* Inoue A, et al., Mater. Trans. JIM, 30, 722, 1989.

These observations have subsequently been confirmed in a number of other alloy systems and by several researchers. Subsequent to this initial discovery, Peker and Johnson [70] produced a 14 mm diameter fully glassy rod in the composition Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} (most commonly referred to as Vitreloy 1 or Vit 1, and now redesignated as liquid metal or LM-001), and since then there has been an explosion in the research activity in this area all over the world.

A highly processable metallic glass: Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}

A. Peker and W. L. Johnson

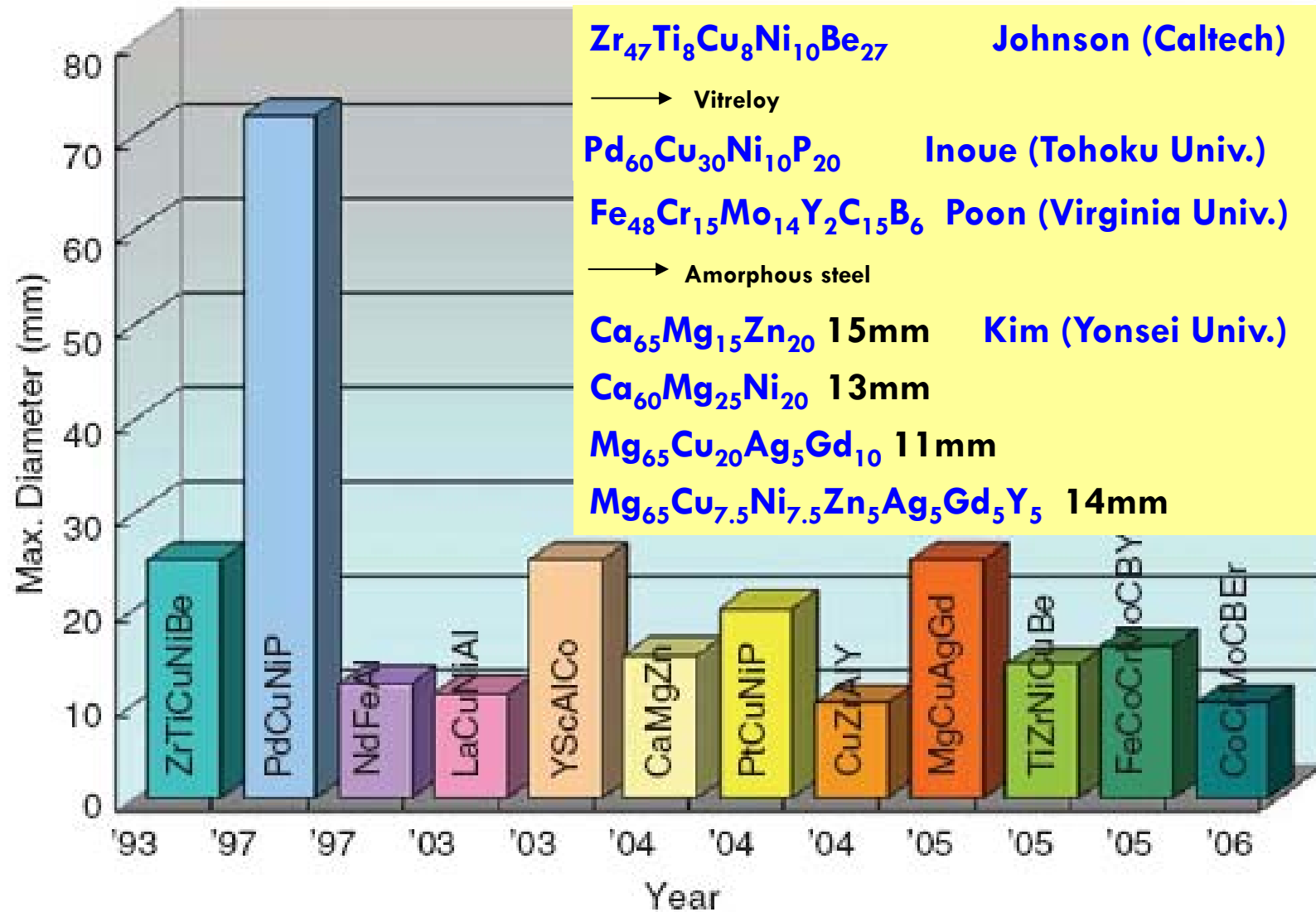
W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California 91125

We report on the properties of one example of a new family of metallic alloys which exhibit excellent glass forming ability. The critical cooling rate to retain the glassy phase is of the order of 10 K/s or less. Large samples in the form of rods ranging up to 14 mm in diameter have been prepared by casting in silica containers.

** [Appl. Phys. Lett. 63: 2342-2344.](#)*

Starting with the initial discovery of the formation of BMGs in the La–Al–Ni system, the Tohoku group has produced a very large number of BMGs in different alloy systems based on Mg, Zr, Ti, Pd, Fe, Co, Ni, and Cu. They have been able to produce several new alloys in the BMG state and also increase the critical (or maximum) diameter of the BMG alloy rods during the last nearly 20 years.

Recent BMGs with critical size ≥ 10 mm



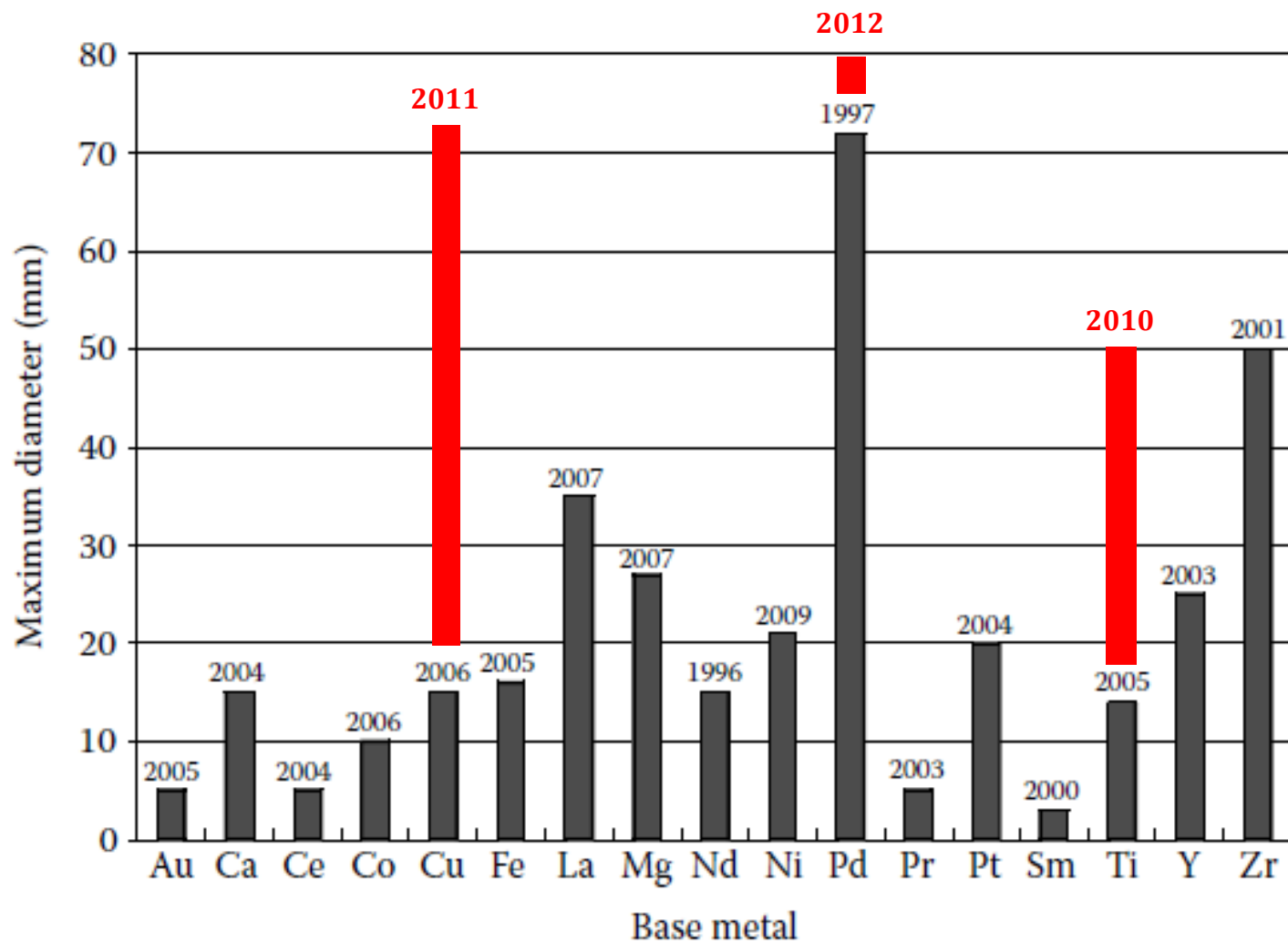


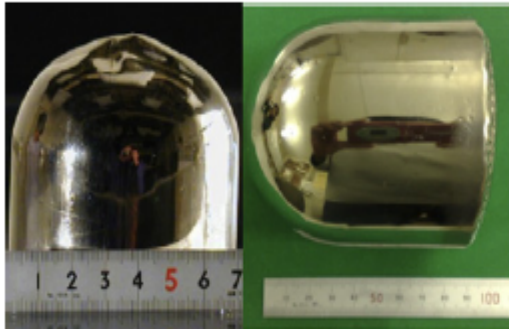
FIGURE 2.7

Maximum diameters of the BMG rods achieved in different alloy systems and the years in which they were discovered.

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

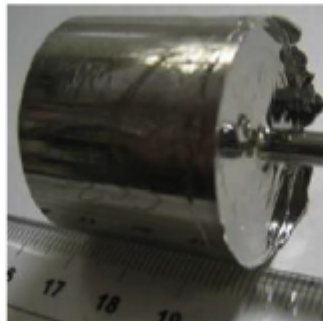
Massy Ingot Shape

(a) Pd-Cu-Ni-P

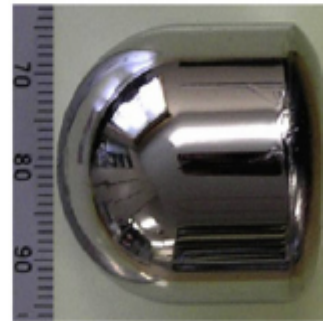


72 ϕ x 75 mm 80 ϕ x 85 mm

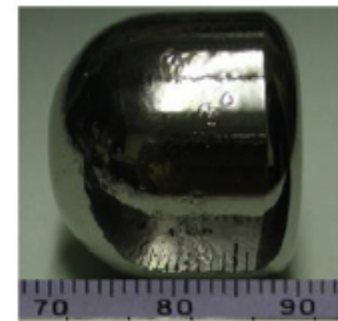
(b) Zr-Al-Ni-Cu



(c) Cu-Zr-Al-Ag

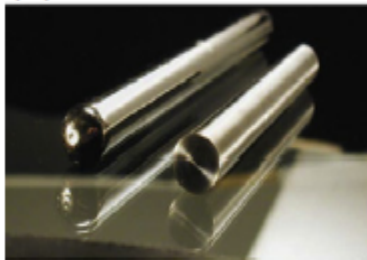


(d) Ni-Pd-P-B



Cylindrical Rods

(e) Pd-Cu-Ni-P

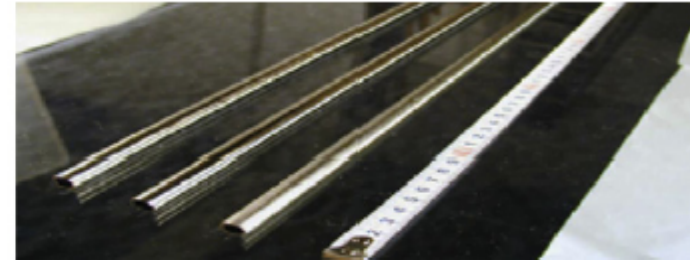


(f) Pt-Pd-Cu-P



Hollow Pipes

(g) Pd-Cu-Ni-P



3. Glass-Forming Ability of Alloys


- Many glasses were produced more or less by trial and error.
→ The ability of a metallic alloy to transform into the glassy state is defined in this chapter as the glass-forming ability (GFA).

3.2 Critical Cooling Rate

If an alloy melt is solidified from a temperature above the liquidus temperature, T_l to below the glass transition temperature, T_g , then the volume fraction of the solid crystalline phase, X formed under non-isothermal crystallization conditions can be given by the equation [8,9]

$$X(T) = \frac{4\pi}{3R^4} \int_{T_l}^{T_g} I(T') \left[\int_{T''}^{T_g} U(T'') dT'' \right]^3 dT' \quad (3.1)$$

where I and U are the steady-state nucleation frequency and crystal growth rate,

$X = 10^{-6}$  $R_c^4 = \frac{4\pi}{3 \times 10^{-6}} \int_{T_l}^{T_g} I(T') \left[\int_{T''}^{T_g} U(T'') dT'' \right]^3 dT' \quad (3.2)$

Since the equations for I and U contain terms like viscosity of the supercooled liquid, η , entropy of fusion, ΔS_f , etc., the critical cooling rate, R_c decreases with increasing η , ΔS_f , and decreasing liquidus temperature, T_l . The best way to experimentally determine R_c is by constructing the time-temperature-transformation (T - T - T) diagrams.

3.2.1 T-T-T Diagrams: isothermal processes

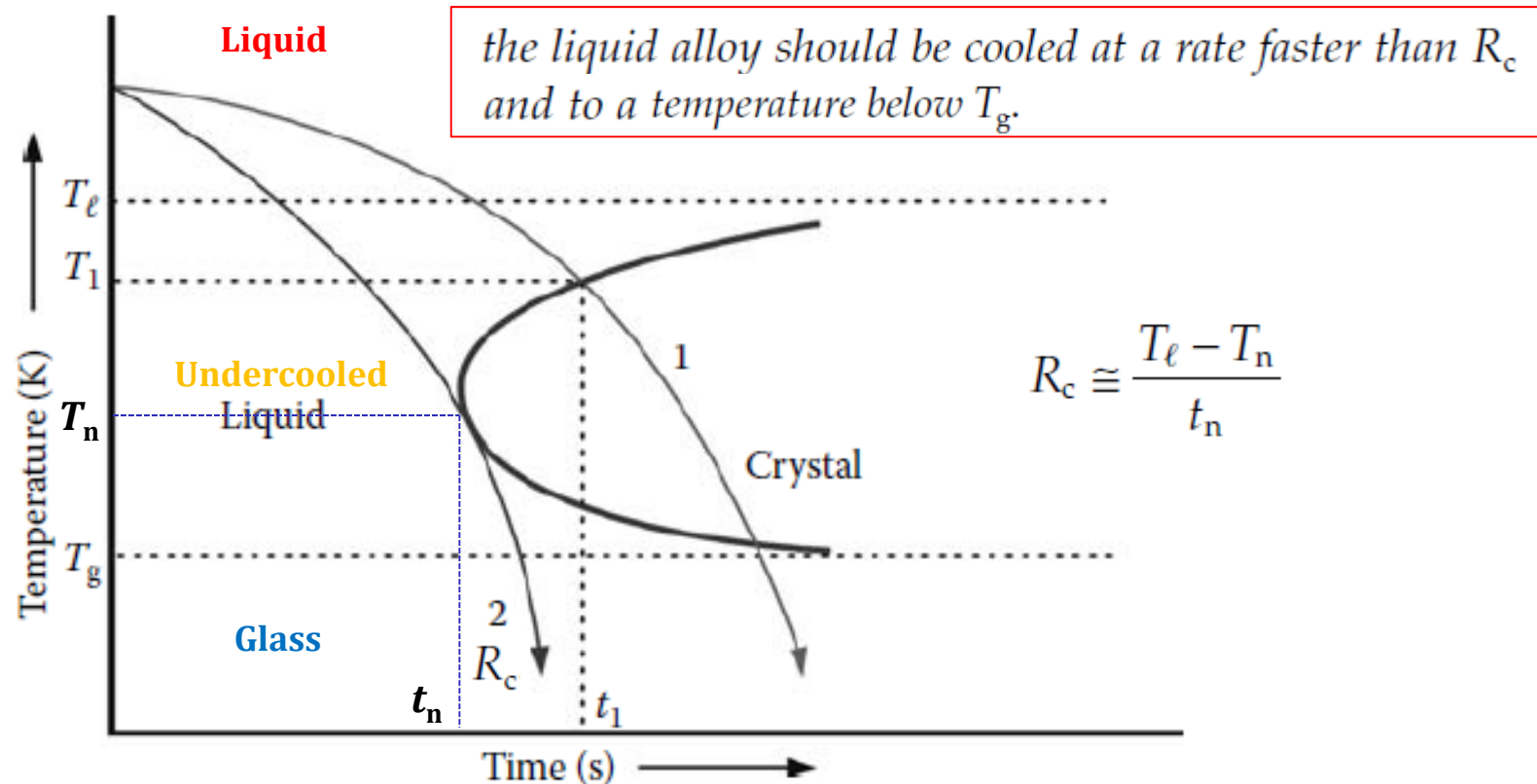


FIGURE 3.1

Schematic time–temperature–transformation (T - T - T) diagram for a hypothetical alloy system. When the liquid alloy is cooled from above the liquidus temperature T_l , at a rate indicated by curve “1,” solidification starts at a temperature T_1 and time t_1 . The resultant product is a crystalline solid. However, if the same liquid alloy is now cooled, again from T_l , at a rate faster than the rate indicated by curve “2,” the liquid will continue to be in the undercooled state, and when cooled below the glass transition temperature T_g , the liquid is “frozen-in” and a glassy phase is formed. The cooling rate represented by curve “2” is referred to as the critical cooling rate, R_c .

R_c vs D_{max} in Ti-Zr-Cu-Ni alloy system

J. Appl. Phys. 78, 1 December 1995

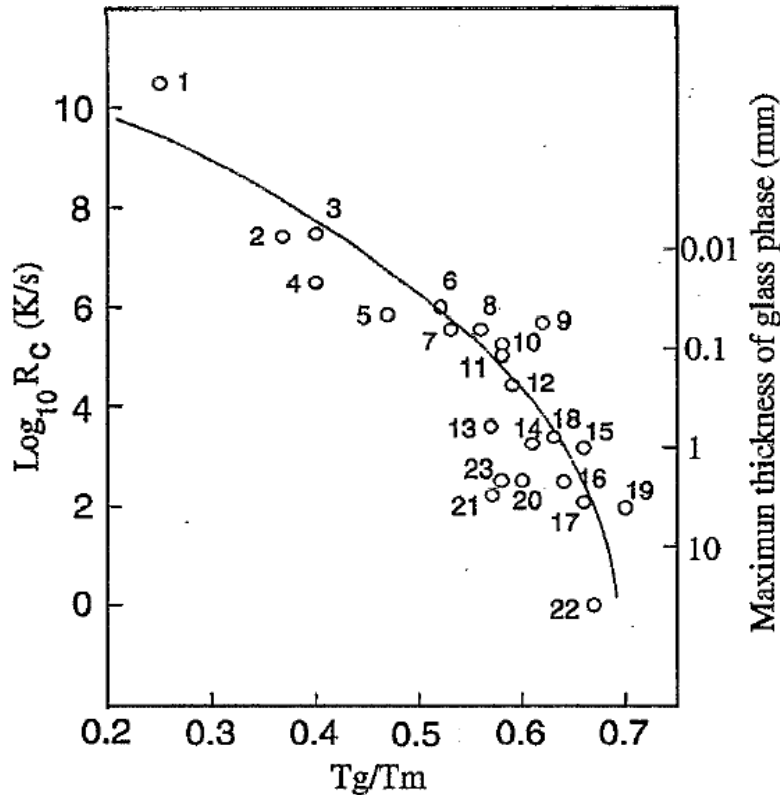


FIG. 1. Critical cooling rates for glass formation and corresponding maximum thickness of glass phase. Key to the alloys: (1) Ni; (2) $Fe_{91}B_9$; (3) $Fe_{89}B_{11}$; (4) Te; (5) $Au_{77.8}Ge_{13.8}Si_{8.4}$; (6) $Fe_{83}B_{17}$; (7) $Fe_{41.5}Ni_{41.5}B_{17}$; (8) $Co_{75}Si_{15}B_{10}$; (9) Ge; (10) $Fe_{79}Si_{10}B_{11}$; (11) $Ni_{75}Si_8B_{17}$; (12) $Fe_{80}P_{13}C_7$; (13) $Pt_{60}Ni_{15}P_{25}$; (14) $Pd_{82}Si_{18}$; (15) $Ni_{62.4}Nb_{37.6}$; (16) $Pd_{77.5}Cu_6Si_{16.5}$; (17) $Pd_{40}Ni_{40}P_{20}$ (above from Ref. 3); (18) $Au_{55}Pb_{22.5}Sb_{22.5}$ (Ref. 6); (19) $La_{55}Al_{25}Ni_{10}Cu_{10}$ (Ref. 7); (20) $Mg_{65}Cu_{25}Y_{10}$ (Ref. 8); (21) $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ (Ref. 9); (22) $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Refs. 4 and 5); (23) $Ti_{34}Zr_{11}Cu_{47}Ni_8$.

Total cooling time $\tau \sim (R^2/\kappa)$

sample dimension (dia. or thickness) : R

initial temperature: T_m

thermal diffusivity : κ

$\kappa = K/C$

thermal conductivity : K

heat capacity per unit volume: C

$$\dot{T} = \frac{dT}{dt} = \frac{(T_m - T_g)}{\tau} = \frac{K(T_m - T_g)}{CR^2}$$

For Ti-Zr-Cu-Ni system,

$T_m - T_g \sim 400K$ $K \sim 0.1W/cm s^{-1}K^{-1}$ $C \sim 4J/cm^3K^{-1}$

$$\dot{T}(K/s) = 10/R^2(cm)$$

3.2.2. Effect of Alloying Elements

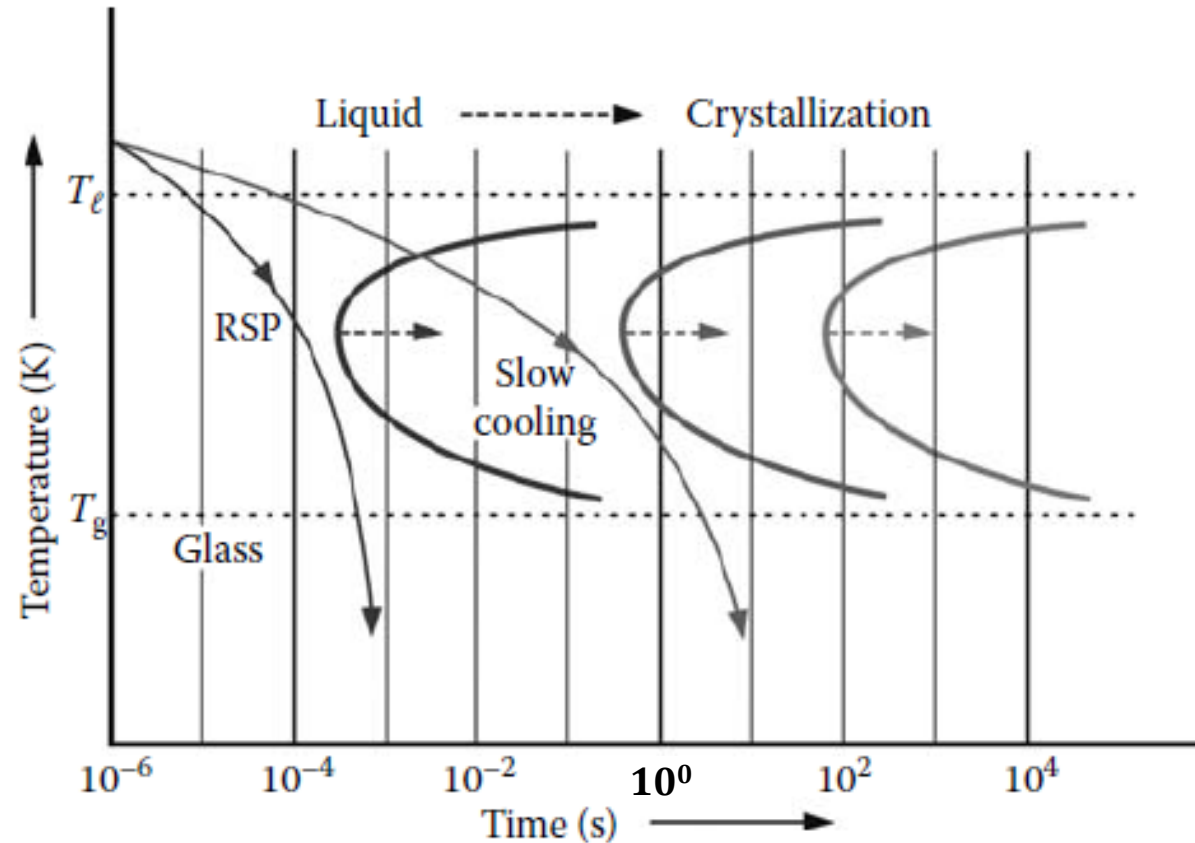


FIGURE 3.2

Position of the T - T - T curves with the addition of a large number of alloying elements. The C-curve shifts to the right with increasing number of alloying elements and consequently, the glassy phase can be synthesized at slow solidification rates. The left-most C-curve represents a typical situation of an alloy system where a glassy phase is obtained by rapid solidification processing (RSP) from the liquid state. The middle C-curve represents an alloy composition where a glassy phase can be obtained by slow cooling. The right-most C-curve represents a situation when an alloy can be very easily produced in a glassy state.

R_c

$> 10^{10-12}$ K/s **10^{4-6} K/s** **10^2 K/s** **1.3×10^{-2} or 0.067 K/s** **10^{-5} to 10^{-4} K/s**
 pure metals binary typically Pd_{37.5}Cu_{32.5}Ni₁₀P₂₀ Oxide glasses
 metallic liquids multicomponent Pd₃₀Pt_{17.5}Cu_{32.5}P₂₀

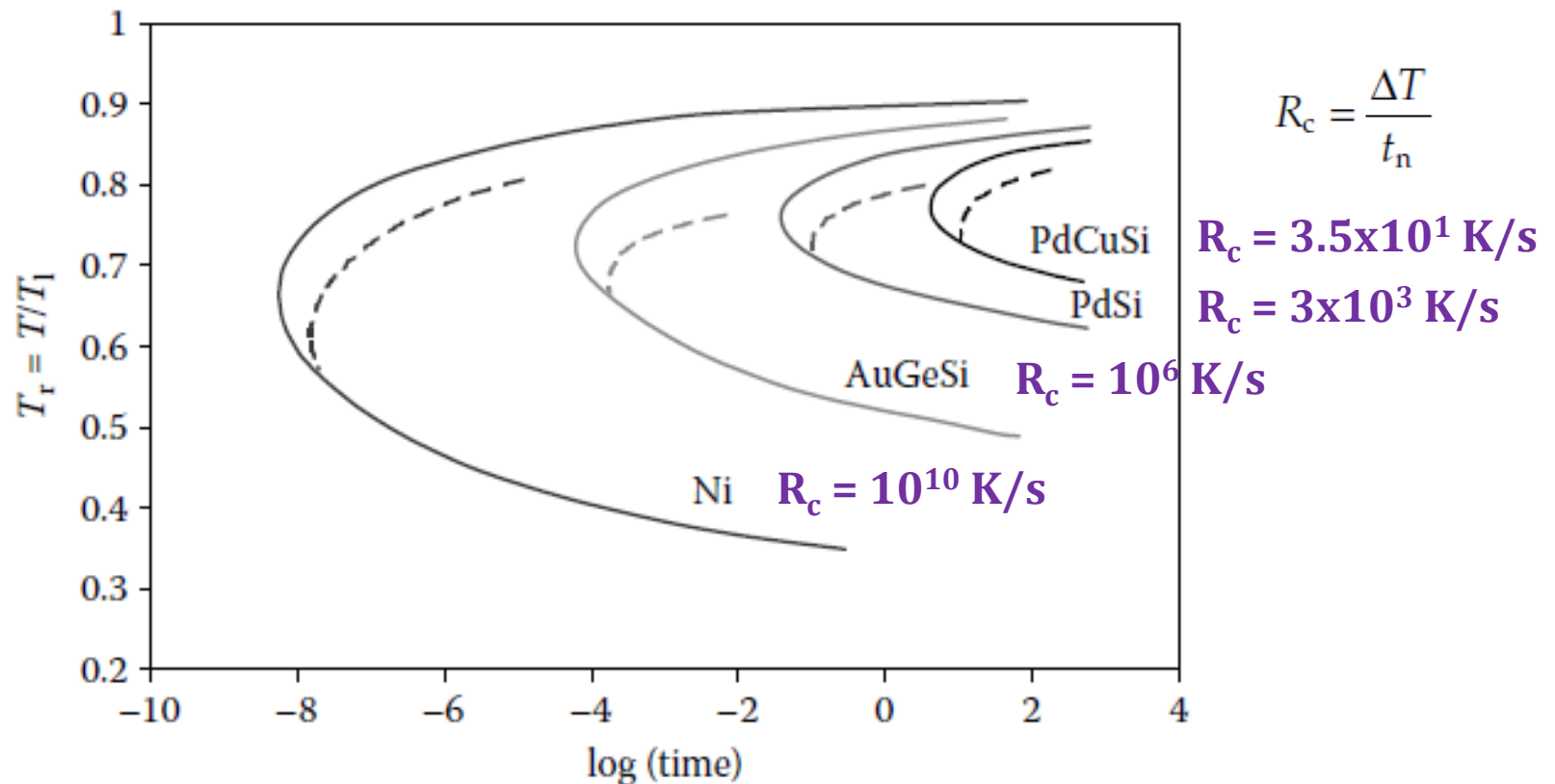


FIGURE 2.3

Time-temperature-transformation (T - T - T) curves (solid lines) and the corresponding continuous cooling transformation curves (dashed lines) for the formation of a small volume fraction for pure metal Ni, and Au₇₈Ge₁₄Si₈, Pd₈₂Si₁₈, and Pd₇₈Cu₆Si₁₆ alloys.

T_{rg}

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1/4

1/2

2/3
