2018 Spring

"Advanced Physical Metallurgy"
- Bulk Metallic Glasses -

05.09.2018

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• Amorphous vs Nanocrystalline

1) Microstructural observation

XRD, (HR)TEM, EXAFS …

2) Thermal analysis

DSC (Differential Scanning Calorimetry)

: Measure heat absorbed or liberated during heating or cooling

cf) - glass → nucleation & growth

(perfect random)

- *local clustering*: quenched-in nuclei → *only growth*
- *Nanocrystalline → growth*

→ **local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.**

: *Characterization of structure by pair distribution function*

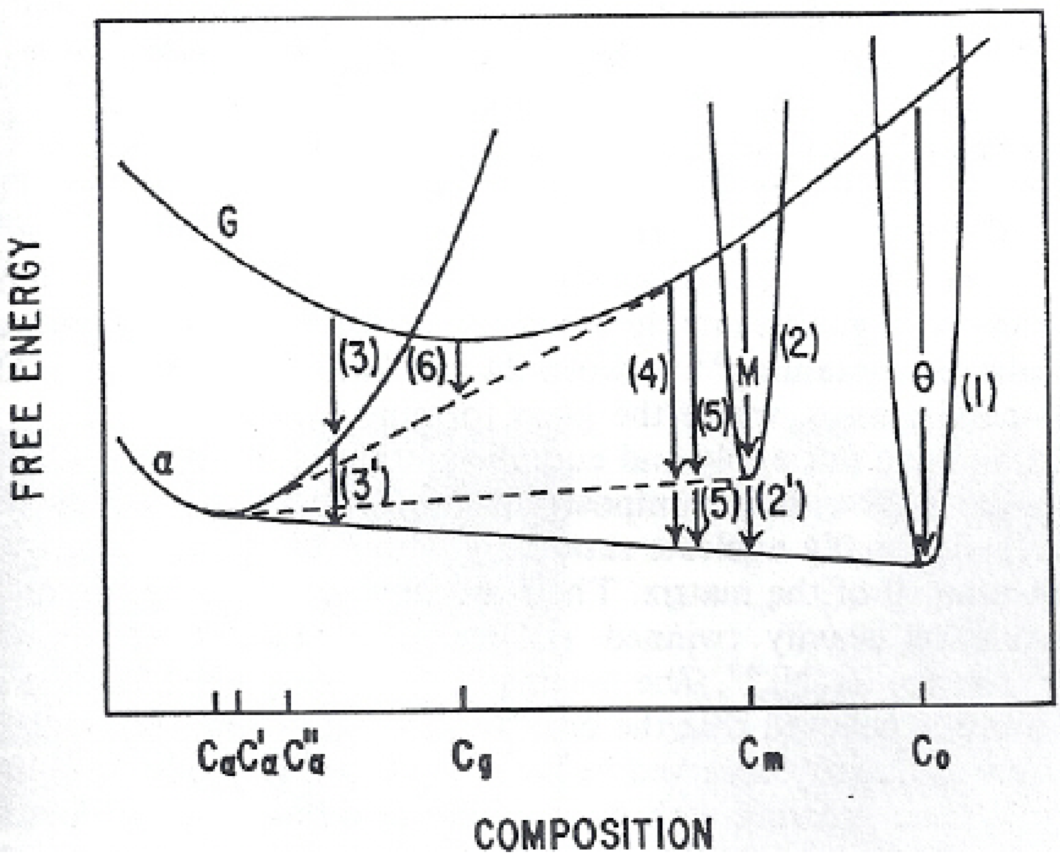
3) Intensive Structural Analysis: *radial distribution function*

THERMODYNAMICS OF CRYSTALLIZATION

Crystallization Behaviors in Metallic Glass

Metallic glasses crystallize by a nucleation and growth process.

The driving force is the free energy difference between the glass and the appropriate crystalline phase. → (Free energy vs. Composition diagram)



Crystallization mechanisms

1. **Polymorphous Crystallization** of the glass to a crystalline phase of the **same composition**.
2. **Eutectic Crystallization**
3. **Primary Crystallization** of supersaturated solid solution

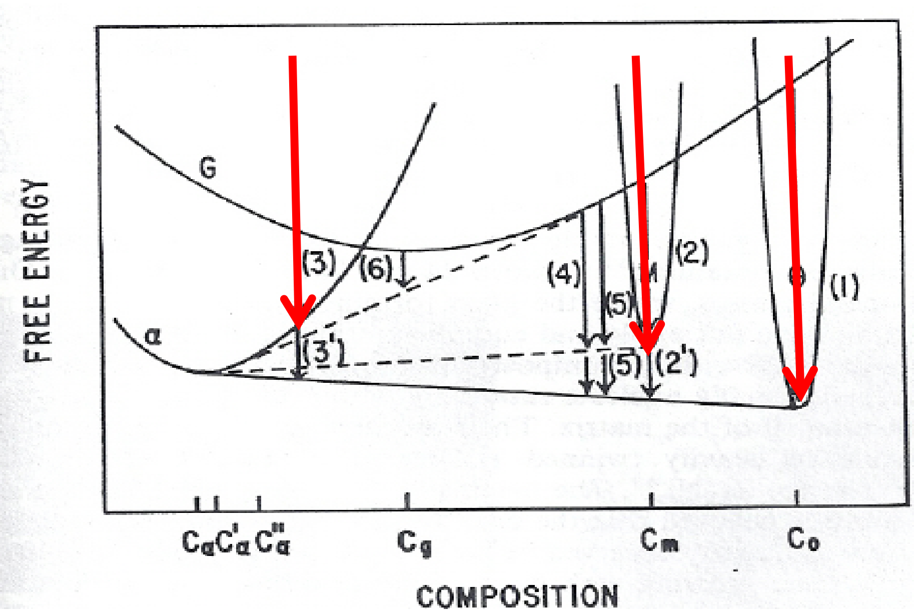
G: Glass

α : Solid solution (Crystalline phase)

θ : Intermetallic phase

M: metastable phase

1. Polymorphous Crystallization: single crystalline phase without any change in composition

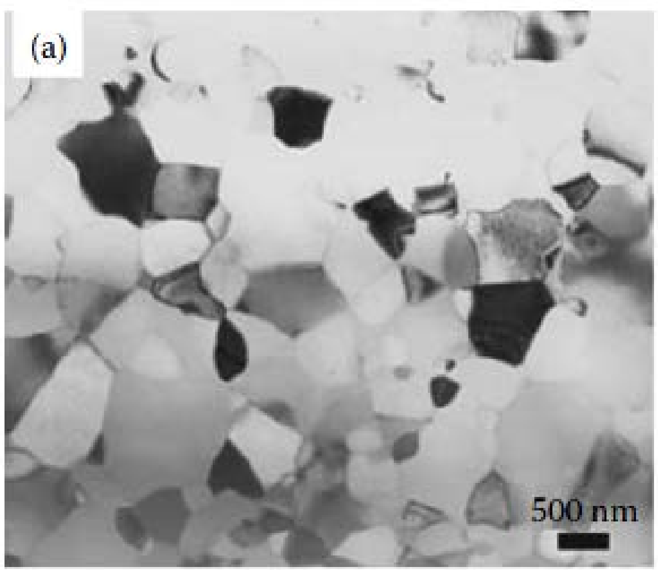


Growth rates and morphologies

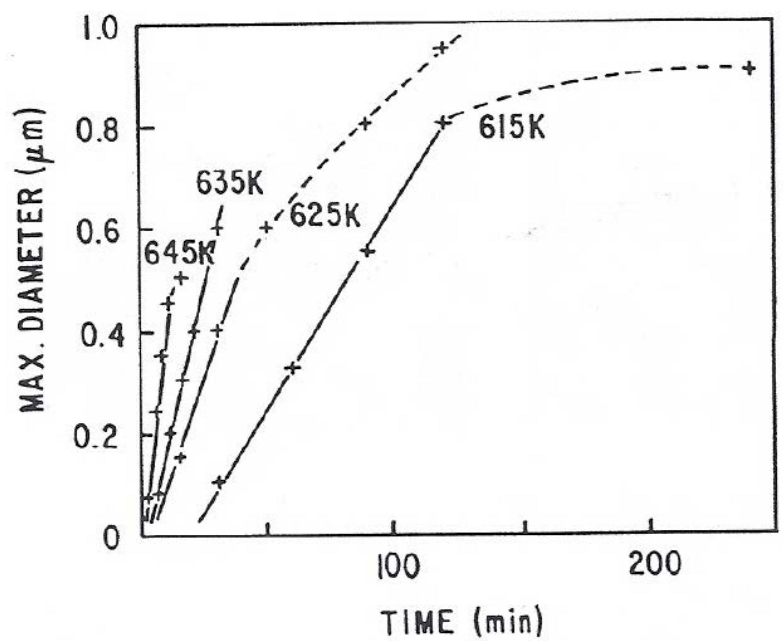
$$u = a_0 v_0 \left\{ \exp\left[\frac{-\Delta F_a}{kT}\right] \right\} \left\{ 1 - \exp\left[\frac{-\Delta F_v}{kT}\right] \right\}$$

ΔF_a= activation energy for an atom to leave the matrix and attach itself to the growing phase

ΔF_v=The molar free energy difference btw C and G



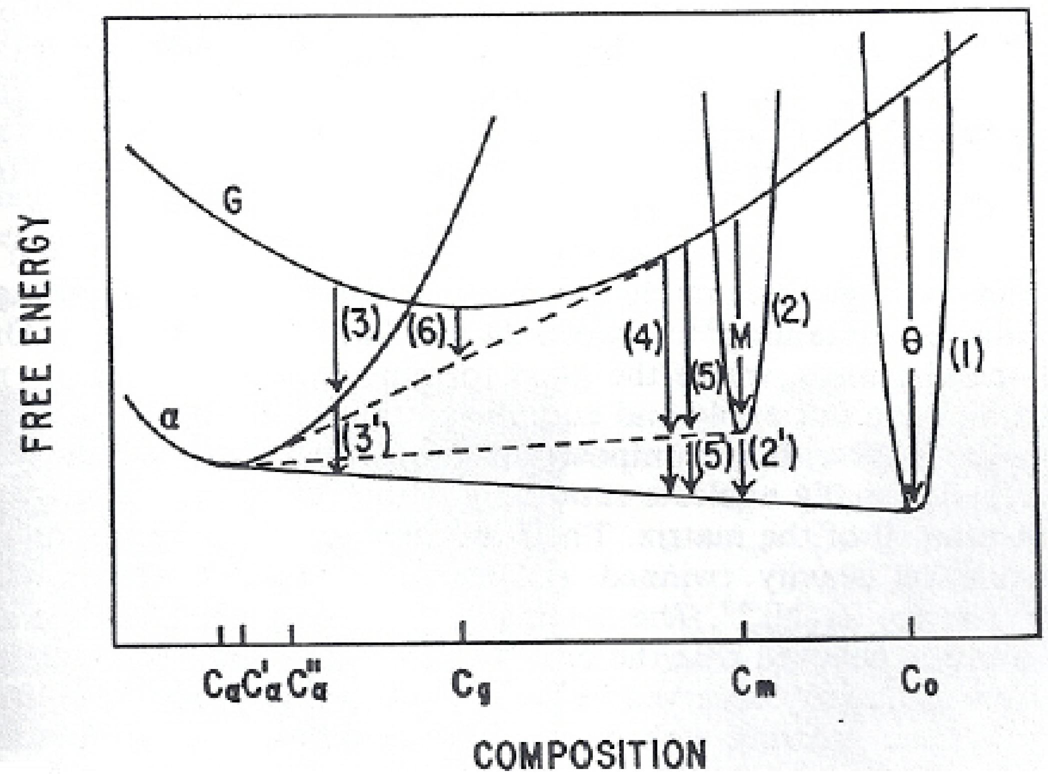
Polymorphous crystallization in a $Ti_{50}Ni_{25}Cu_{25}$ BMG alloy on annealing for 28 min at 709 K.

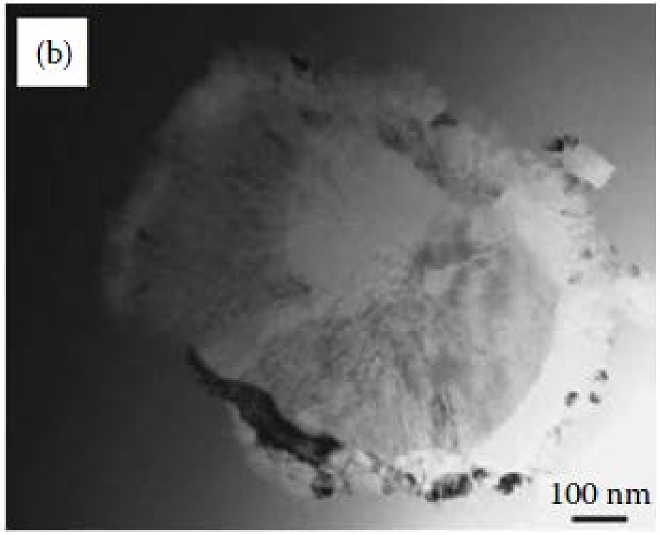


Growth kinetics of Zr_2Ni crystals in glass of same composition. The broken lines indicate crystal impingement.

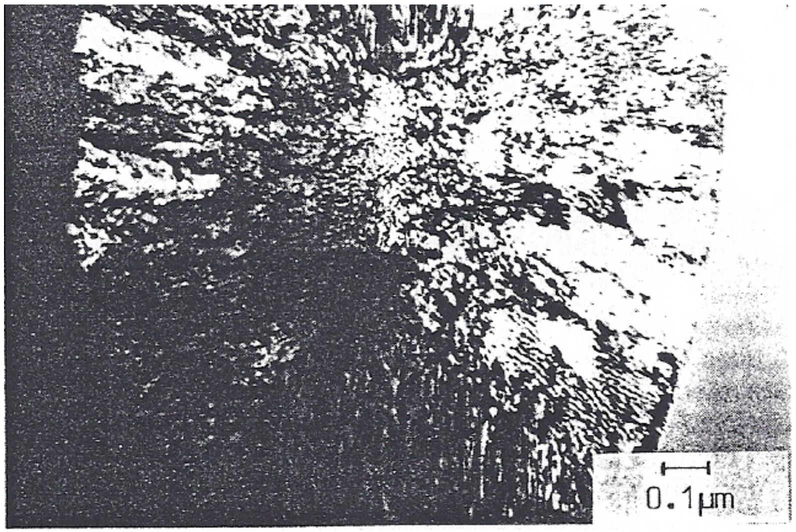
2. Eutectic Crystallization

- Largest driving force
- can occur in the whole concentration range between the stable or metastable phases (Even though the whole transformation takes place in the solid state and therefore it should be more appropriately called a eutectoid crystallization, the term "eutectic" has come to stay, presumably because the stating material (the glass) is more liquid-like.)



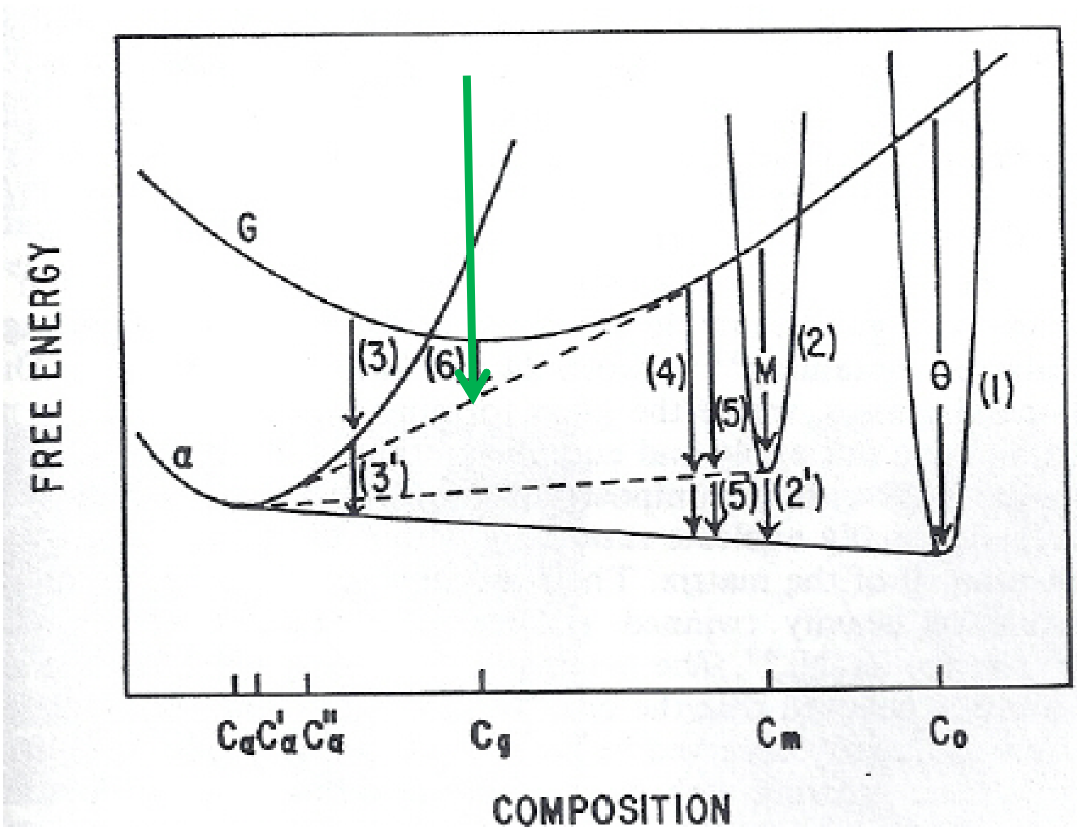


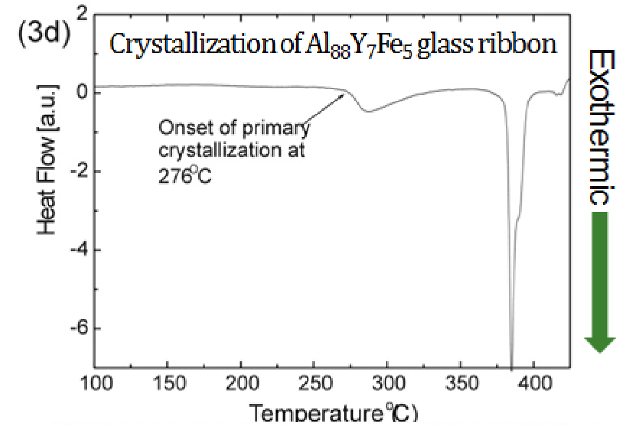
Eutectic crystallization in $Zr_{62.5}Cu_{22.5}Al_{10}Fe_5$ glassy alloy annealed for 10 min. at 713K.

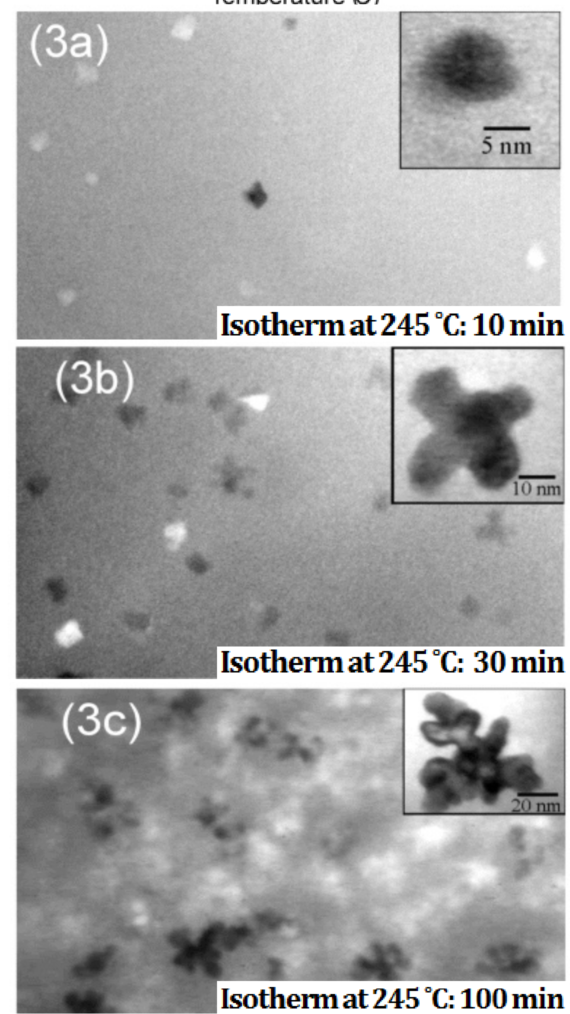


Barrel shaped eutectic crystal in $Fe_{40}Ni_{40}P_{14}B_6$ annealed for 13 min. at 385℃

3. Primary Crystallization







- Forms first from the glass phase

- Supersaturated solid solution

- Since the concentration of the solute in the α-Fe phase is lower than that in the glassy phase, the solute (boron) atoms are rejected into the glassy phase and consequently the remaining glass phase becomes enriched in B until further crystallization is stopped.

5.5. Thermal Stability of Metallic Glasses

(a) Variation of T_g and T_x in the $Zr_{65}Al_xCu_{35-x}$ (x=0, 7.5, 20) alloys

Single exothermic peak

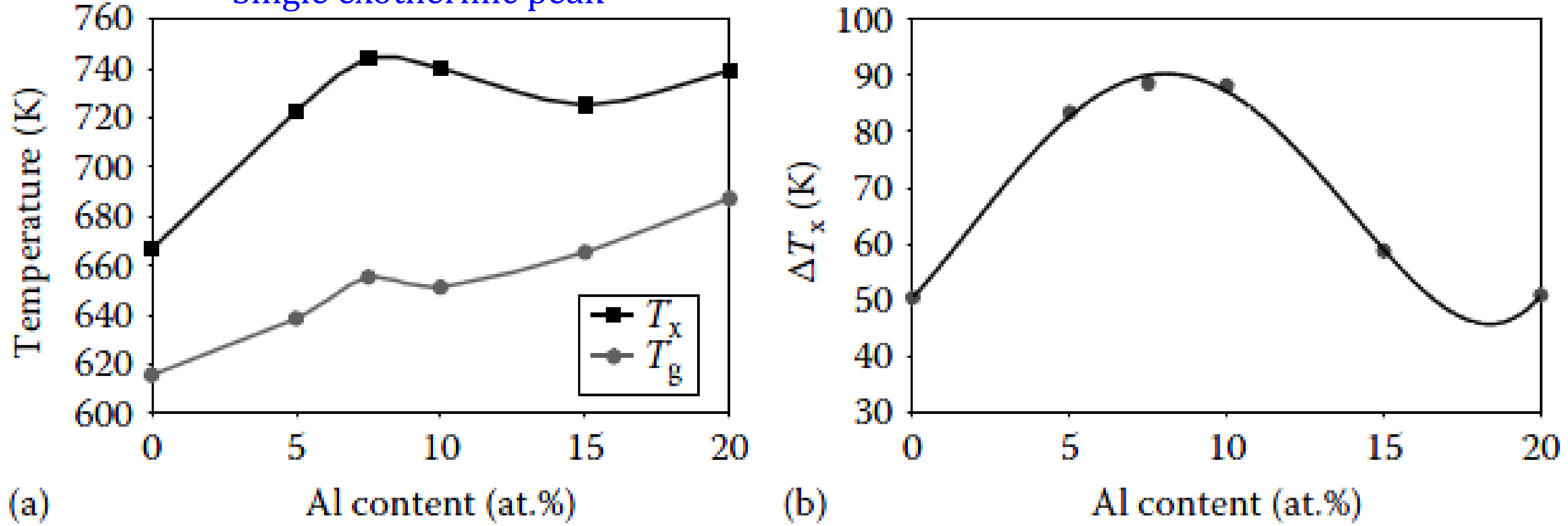
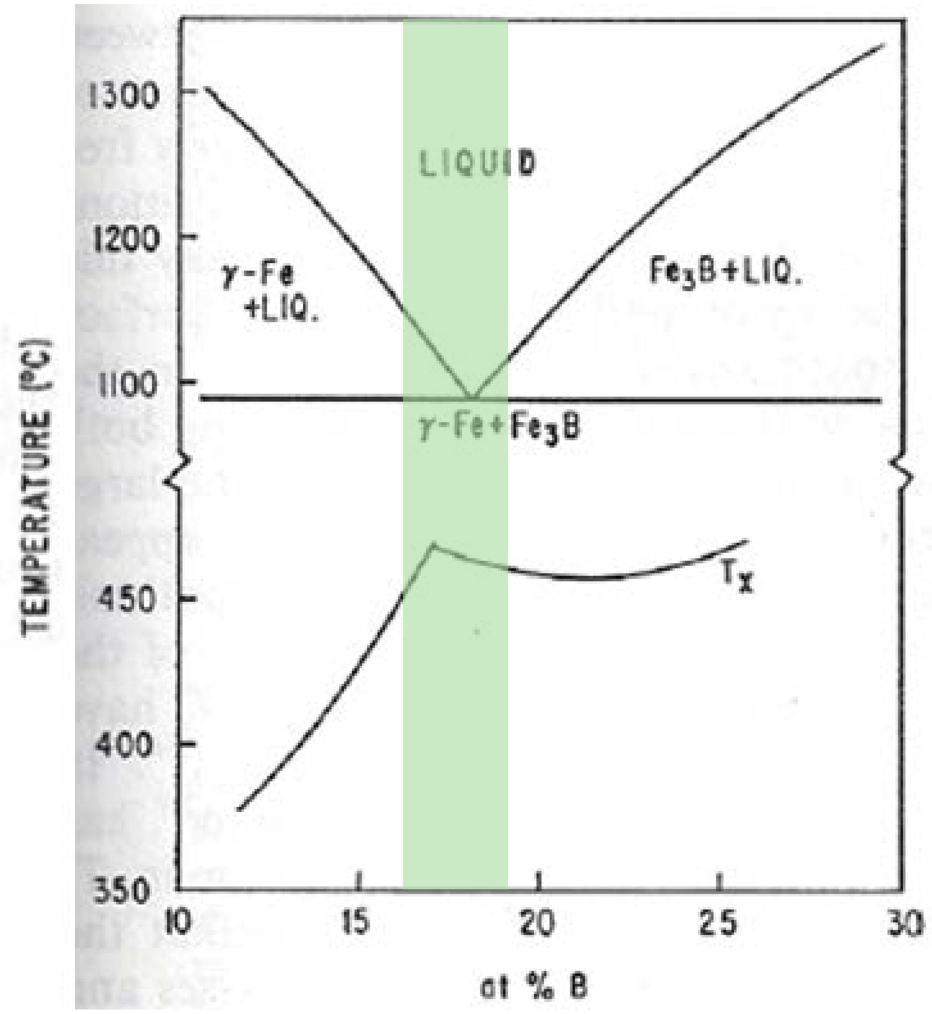


FIGURE 5.7
Variation of (a) T_g and T_x temperatures, and (b) the width of the supercooled liquid region ΔT_x (= $T_x - T_g$), with Al content in the $Zr_{65}Al_xCu_{35-x}$ glassy alloys. (Reprinted from Inoue, A. et al., *Mater. Sci. Eng. A*, 178, 255, 1994. With permission.)

5.6. Crystallization Temperatures and Their Compositional Dependence

Compositional dependence.



In many binary

Metal-Metalloid glass (Fe-B)

T_x is a maximum near the eutectic composition

→ The same does not appear to be the case in all-metallic glasses

Metal-Metal glass (Ni-Zr)

A monotonic decrease of T_x with increasing Zr content despite the existence in two eutectics

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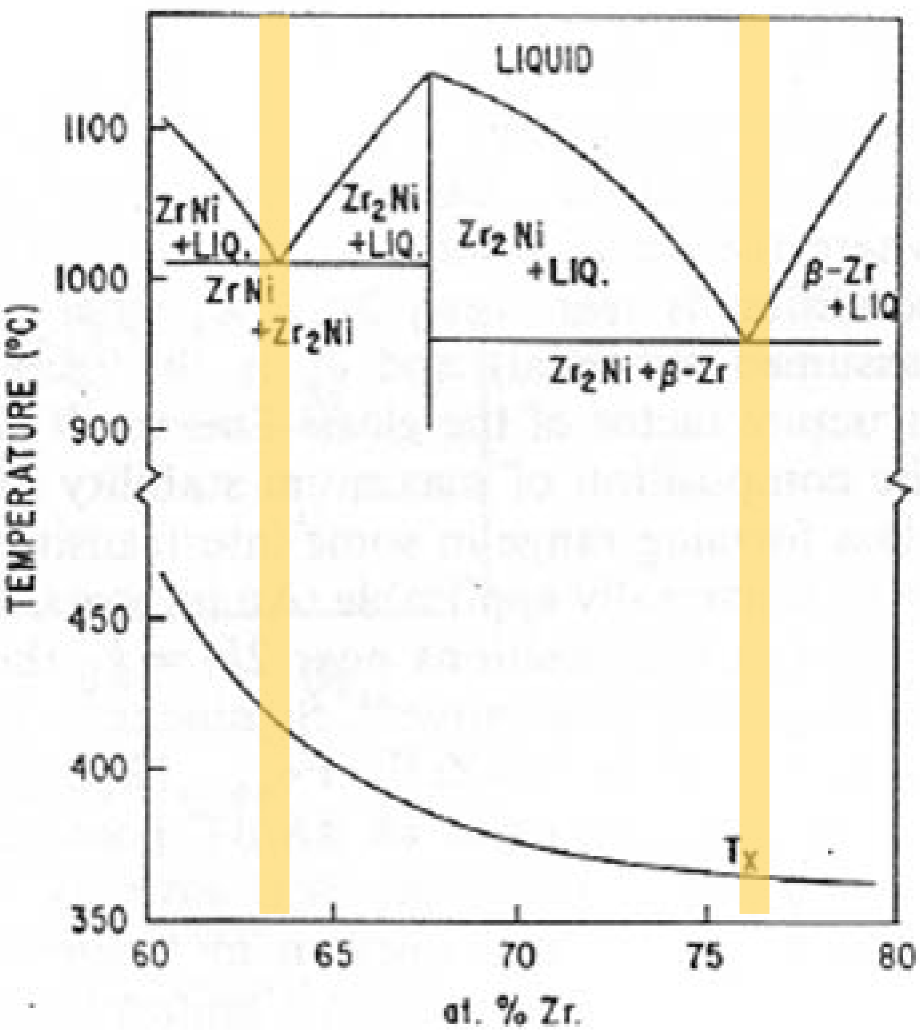


In many binary

Metal-Metalloid glass (Fe-B)

Tx is a maximum near the eutectic composition

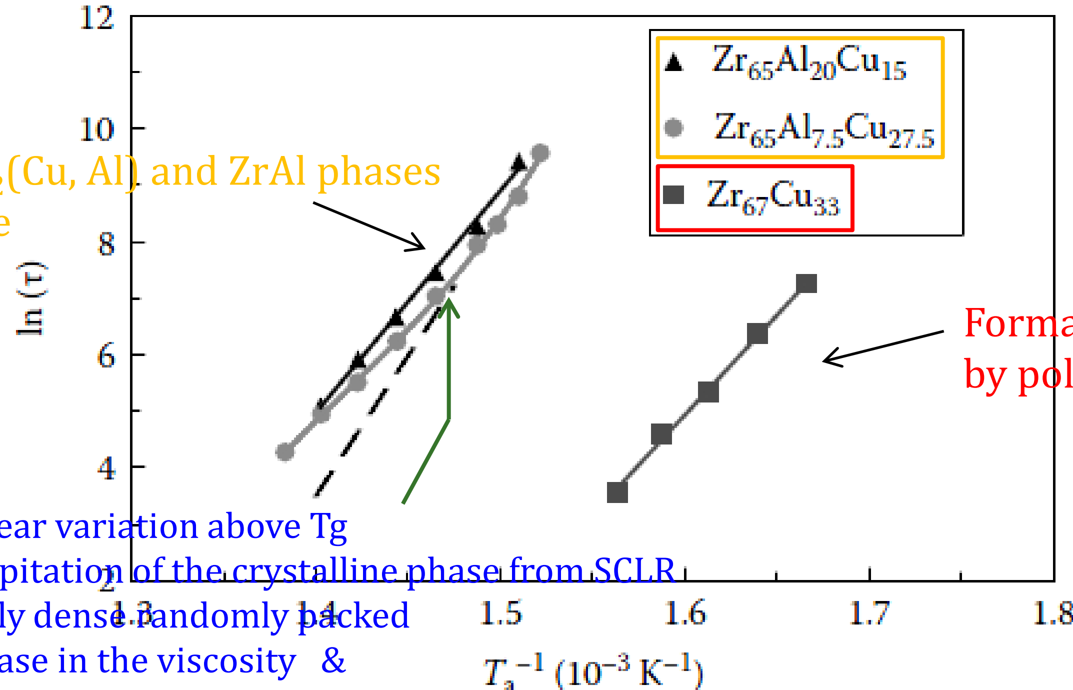
→ The same does not appear to be the case in all-metallic glasses

Metal-Metal glass (Ni-Zr)

A monotonic decrease of T_x with increasing Zr content despite the existence in two eutectics

5.5. Thermal Stability of Metallic Glasses

(b) Arrhenius plot of the incubation time for the precipitation of crystalline phases (τ) in the $Zr_{65}Al_xCu_{35-x}$ (x=0, 7.5, 20) alloys



$$\tau \propto \frac{T\eta}{(T_\ell - T)^2}$$

Formation of Zr_2(Cu, Al) and ZrAl phases by eutectic mode

Formation of Zr_2Cu phase by polymorphous mode

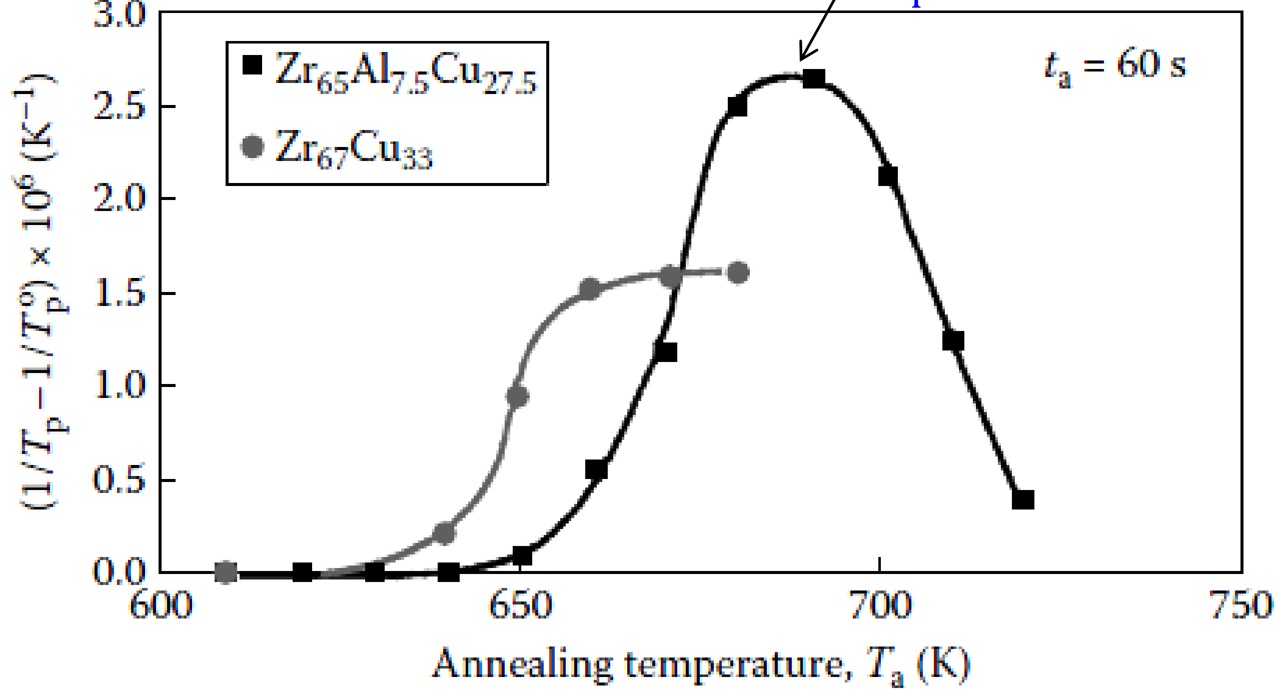
Shifted from the linear variation above Tg
→ suppressed precipitation of the crystalline phase from SCLR due to possess highly dense randomly packed structures → increase in the viscosity & difficult to have long-range diffusion → increased width of SCLR

FIGURE 5.8
Arrhenius plot of the incubation time, τ for the precipitation of crystalline phases in the binary $Zr_{67}Cu_{33}$, and ternary $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{20}Cu_{15}$ alloys. Note the deviation of τ to the positive side of the linear variation (to higher temperatures) only for the ternary $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy, signifying the delayed crystallization in the alloy with 7.5 at.% Al. Such a deviation is not observed for the other alloys. (Reprinted from Inoue, A. et al., *Mater. Sci. Eng. A*, 178, 255, 1994. With permission.)

(C) Annealing up to T_a at a heating rate of 0.17 K/s (10K/min), annealed there for 60s
→ measure peak temperatures for the nucleation and growth reactions of the crystalline phases in the $Zr_{65}Al_xCu_{35-x}$ (x=0, 7.5) alloys

* Difference in the reciprocals of the Tp between the Pre-annealed and as-quenched samples

688 K, correspond to the peak temp. of the nucleation event of a crystalline phase formation



* Measure Tx at a very high heating rate of 5.33 K/s (320 K/min) = corresponding to the maximum growth rates, that is growth temperature
  - Zr67Cu33: Just above the maximum temp of 670 K/ difference ~ very small
  - Zr65Al7.5Cu27.5: the difference btw max nucleation and max growth temp. ~143K, resulting in enhanced resistance to crystallization (high thermal stability)
* Heating rate ↑ – not significantly increase the grain size in Zr67Cu33 ↔ considerably large grain size in Zr65Al7.5Cu27.5 due to the presence of fewer nuclei

5.7. Annealing of Bulk Metallic Glasses: SR → SCLR (& PS) → Crystallization

Figure 5.11 Different pathways for a metallic glass to crystallize into the equilibrium phases