2010 Spring

“Amorphous Materials”

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Eun Soo Park

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

Ease of glass formation: high glass forming ability

- 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 aspect

- Internal energy : mainly considered in oxide glasses

➡ Depends on the bonding types and arrangements of constituent element

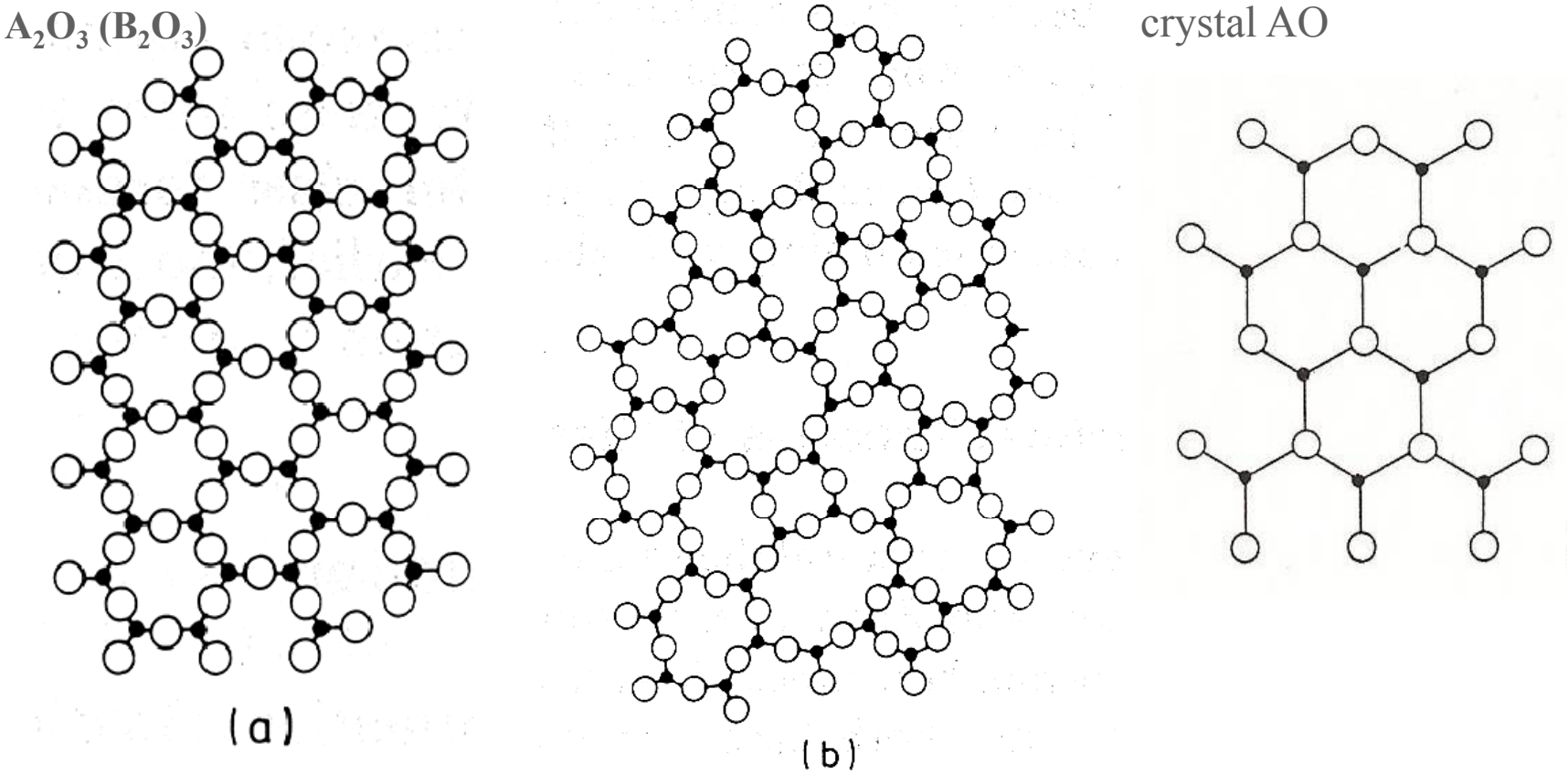
➡ similar types and arrangements of atomic bonding in crystal and amorphous (=similar atomic structure)

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

1. Structure & topology aspect: **(1) CRN**

Oxygen is shared **by two AO_3 triangles** **by three AO_3 triangles**

A_2O_3 (B_2O_3) crystal AO



Small gap of internal energy between crystal and glass

→ GFA ↑

Energy for orientation change is relatively large.

→ GFA ↓

(2) Randomly dense packed structure → ex) metallic glasses

1) Atomic size difference: TM – metalloid (M, ex) Boron)

→ M is located at interstitial site of random packed structure of TM.

→ denser ⇨ by increasing resistivity of crystallization, GFA ⬆

→ Ex) Fe-B: tetrahedron with B on the center position

1) interstitial site, B= simple atomic topology

2) skeleton structure

3) bonding nature: close to covalent bonding

Large size mismatch

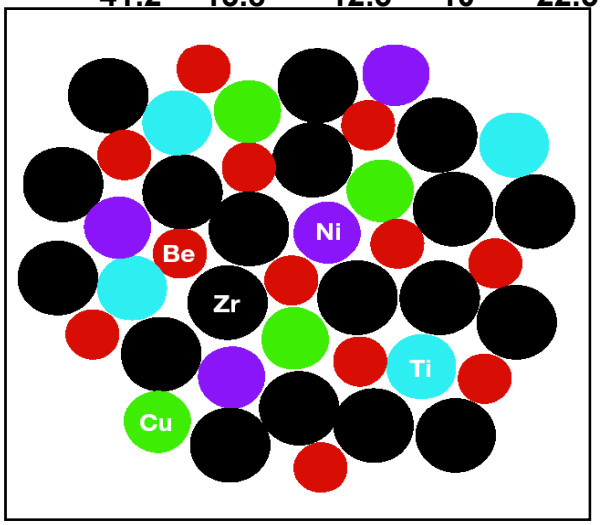
between the components

(destabilization of the crystalline phases)

⇨ **Randomly dense packed structure**

→ GFA ⬆

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$



Tang et al., Nature 402, 160 (1999)

2) min. solute content, C_B*: empirical rule

By Egami & Waseda: in A-B binary system

$$C_B^{min}\left|\frac{(v_B - v_A)}{v_A}\right| = C_B^{min}\left|\left(\frac{r_B}{r_A}\right)^3 - 1\right| \approx 0.1$$

Lower limitation of overall atomic mismatch

(Here, v: atomic volume, A: matrix, B: solute)

minimum concentration of B for glass formation → **Inversely proportional to atomic volume mismatch**

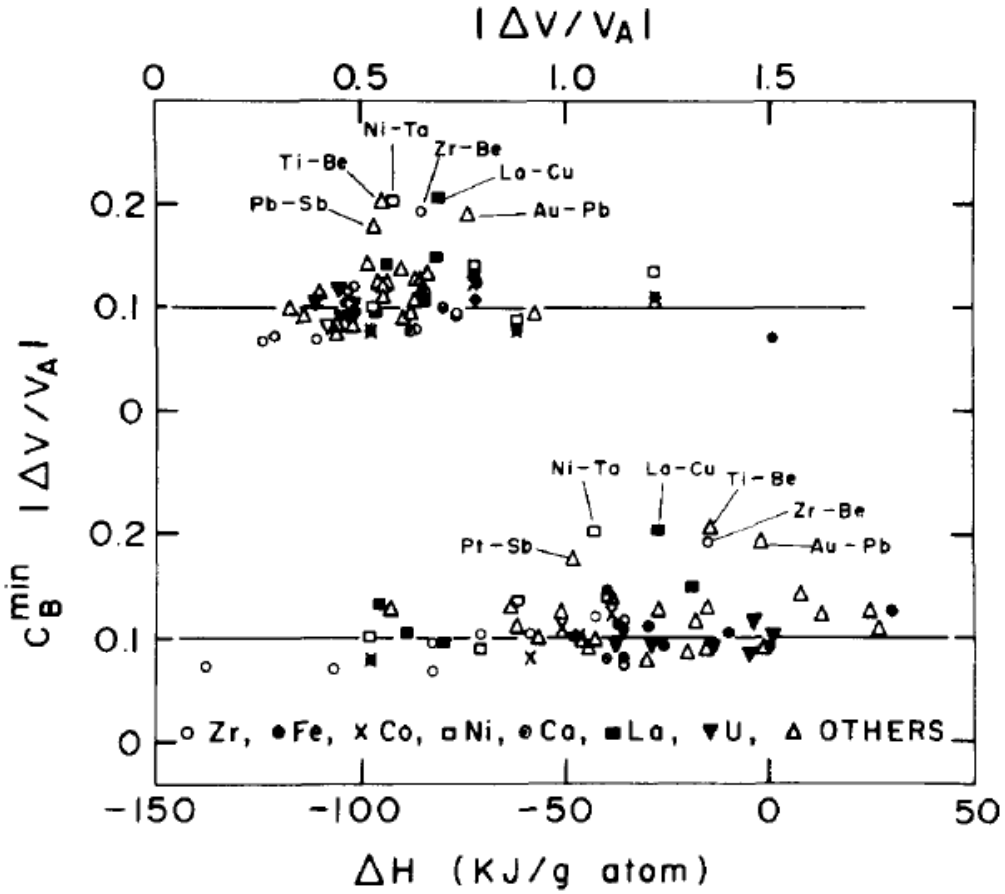


Fig. 1. Relation between $|\lambda_0| = C_B^{min}\,|\Delta v/v_A|$, and $|\Delta v/v_A|$ and ΔH, for 66 binary systems which can be vitrified by liquid quenching.

1. Structure & topology aspect (atomic arrangement)

- **Effect of atomic size difference can be represented as follows;**

$$P = C_B \left| \frac{v_B - v_A}{v_A} \right| + C_C \left| \frac{v_C - v_A}{v_A} \right|$$

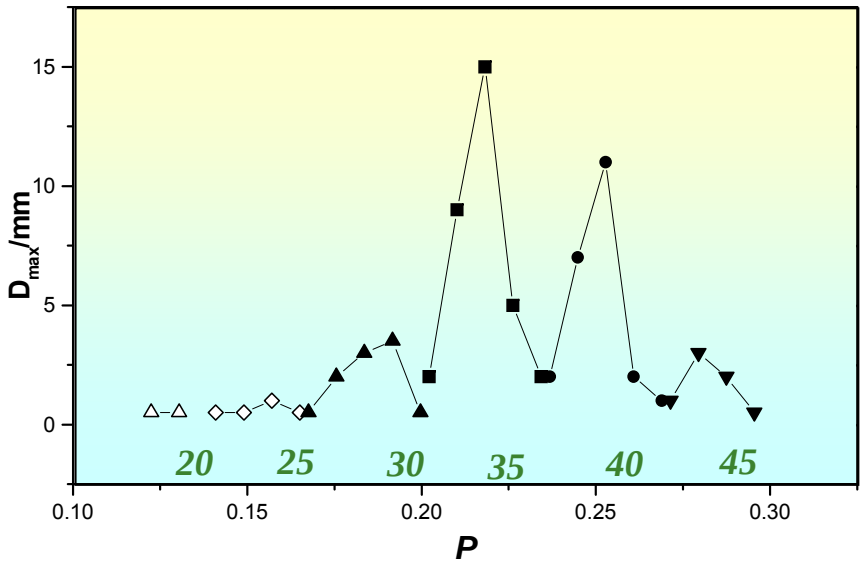
Where, C_i(i=A,B,C) = solute, v_i = content atomic volume

$$P' = \frac{C_B}{C_B + C_C} \left| \frac{v_B - v_A}{v_A} \right| + \frac{C_C}{C_B + C_C} \left| \frac{v_C - v_A}{v_A} \right|$$

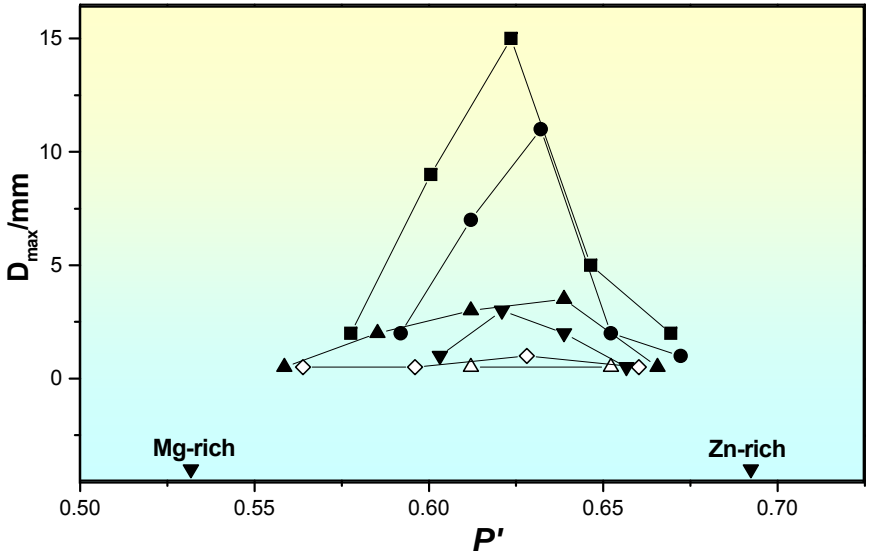
; effective atomic mismatch per solute atom

by dividing by the total amount of solute contents

Ca-Mg-Zn alloy system



Similar trend of D_{max} with P



Maximum D_{max} at P' ~ 0.625

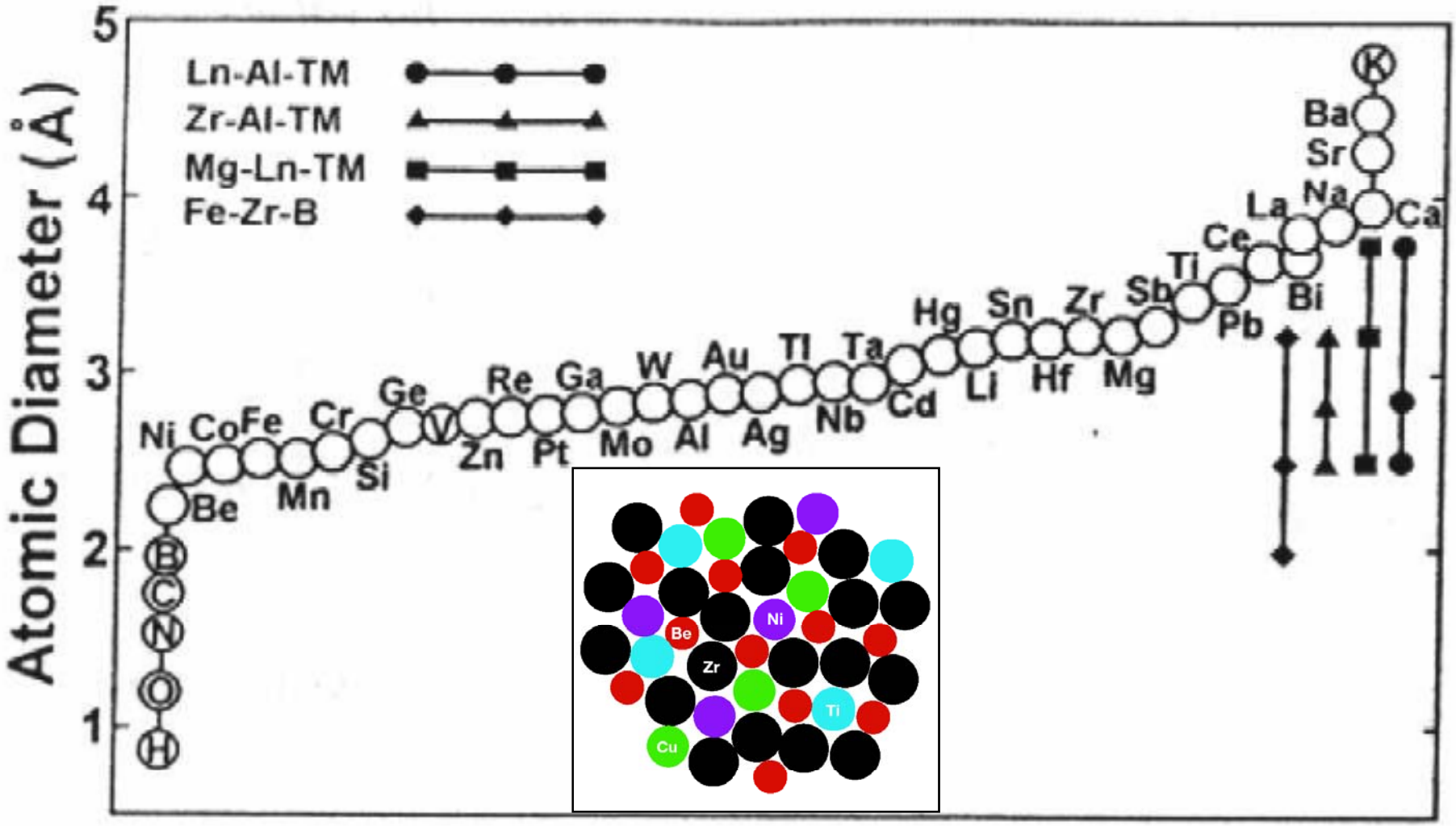
- *Metall. & Mater. Trans. A*, 32A, 200 (2001)

Upper limitation of effective atomic mismatch

3) Multi-component system (over 3 elements)

with large atomic size difference : confusion theory

➡ packing density ⬆ ➡ dense random packed structure



< significant difference in atomic size ratios >

2. Thermodynamic aspect

- **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**

$\Delta S_f \uparrow$: proportional to the number of microscopic states

Entropy of fusion

Multi-component alloy systems **containing more than 3 elements**

causes an increase in the degree of dense random packing

$\Delta H_f \downarrow$ Large negative enthalpy of mixing **among constituent elements**

Enthalpy of fusion

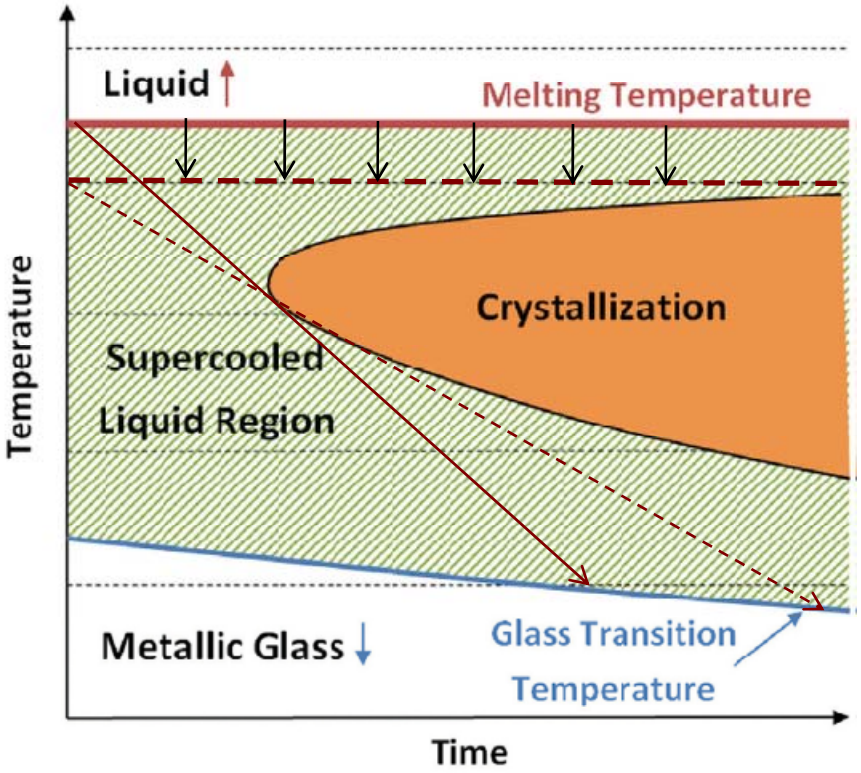
* **The free energy at a constant temperature also decreases in the cases of low chemical potential caused by low enthalpy and high reduced glass transition temperature (=T_l/T_g) and high interface energy between liquid and solid phase.**

2. Thermodynamic aspect

ΔH_f ⬇ → deep eutectic condition: increase stability of stable liquid (=T_l/T_g ↑)

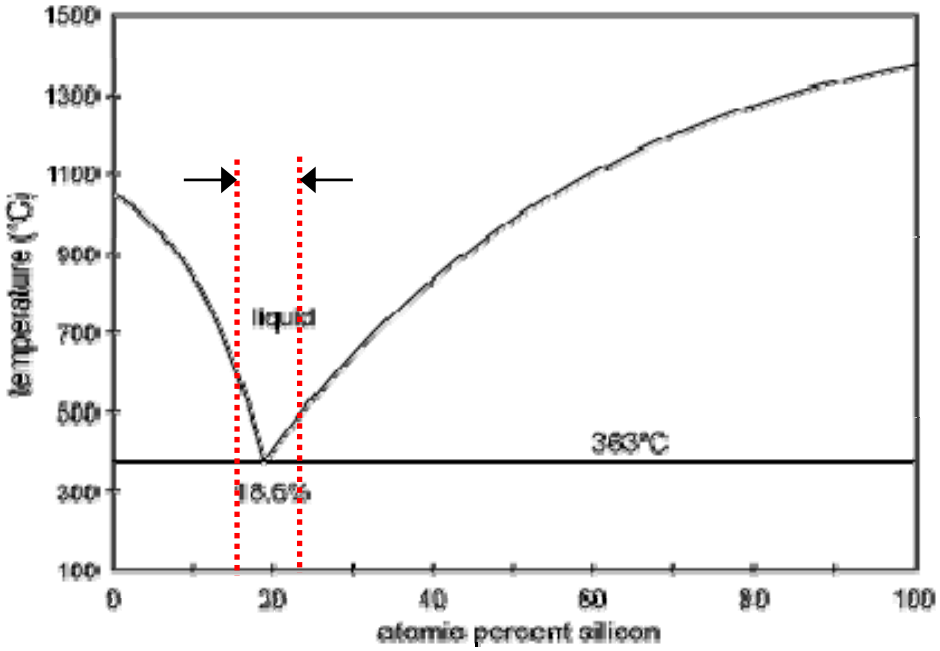
- decreasing melting point → less supercooled at T_g → **$\Delta G = G^{liq} - G^{cryst}$** ⬇

ex) metallic / inorganic system

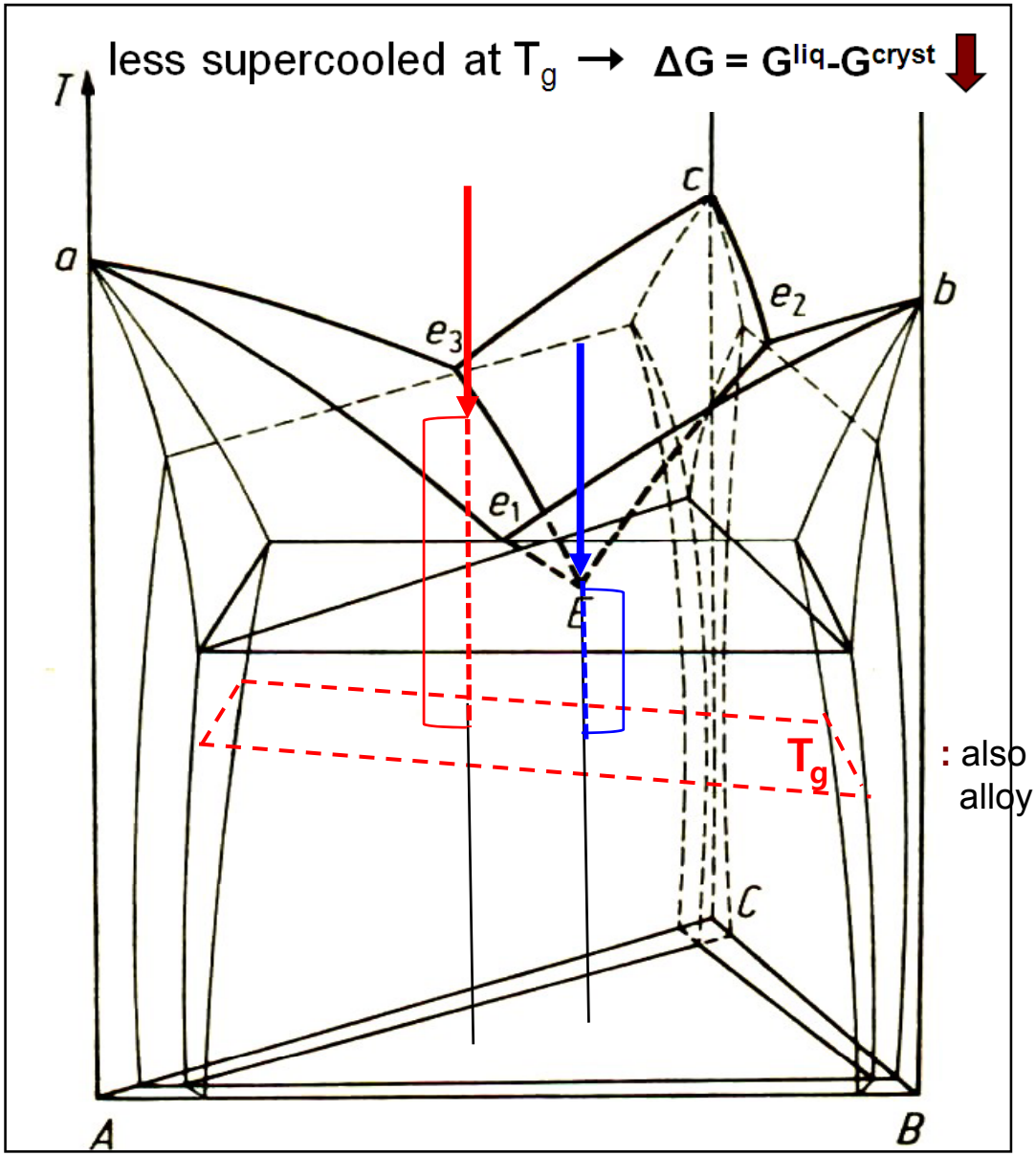


Glass forming region:

Compositions near the eutectic



Multi-component **eutectic alloys** with strong **negative heat of mixing**

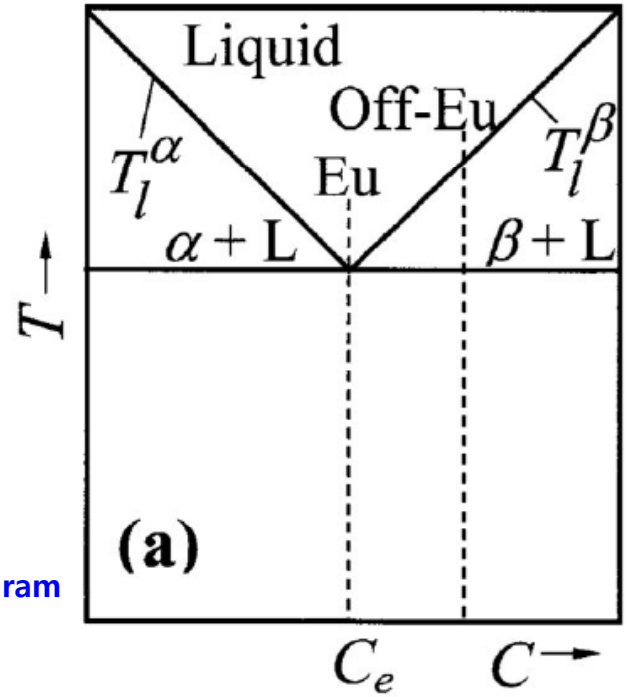


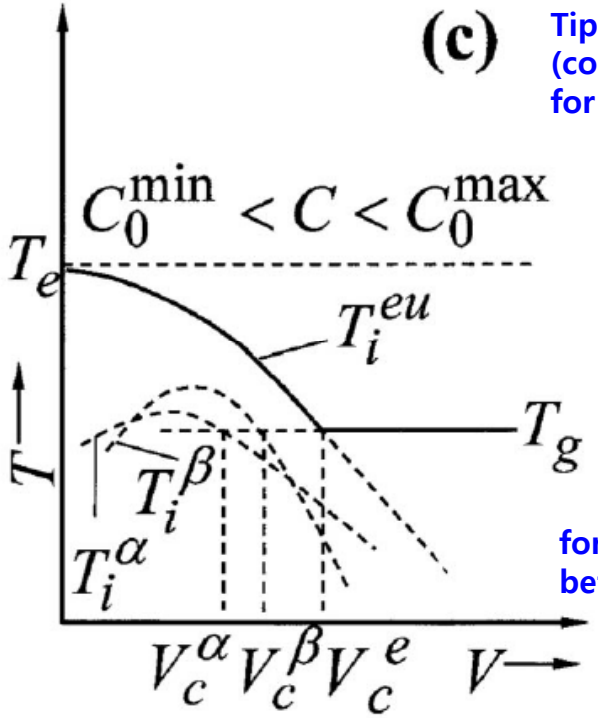
: also changes depending on alloy composition

P. Haasen, Physical Metallurgy 3rd ed

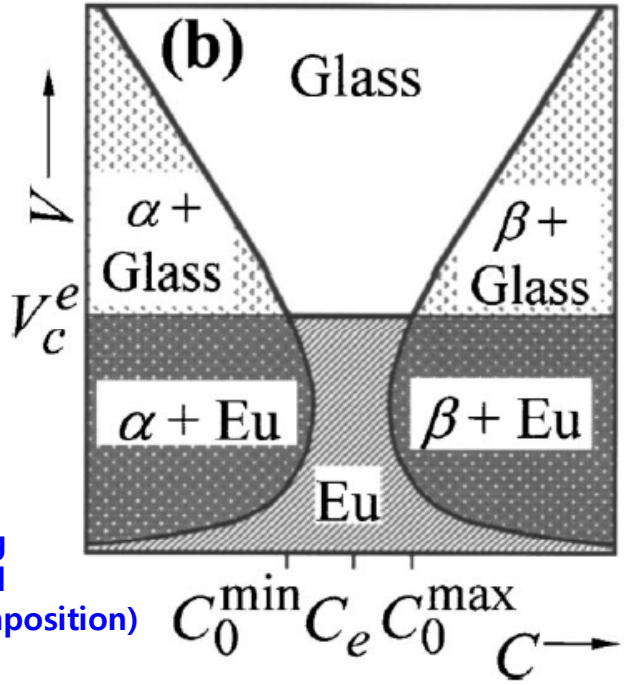
Tip temp.-growth rate (cooling rate) relationship for eutectic, dendritic α, β

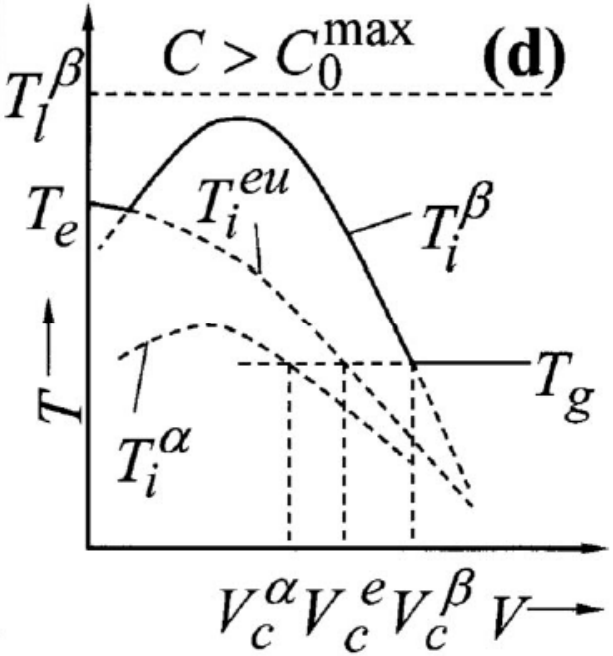
Part of a regular Eutectic phase diagram





for alloy composition between C_0^{min} and C_0^{max}



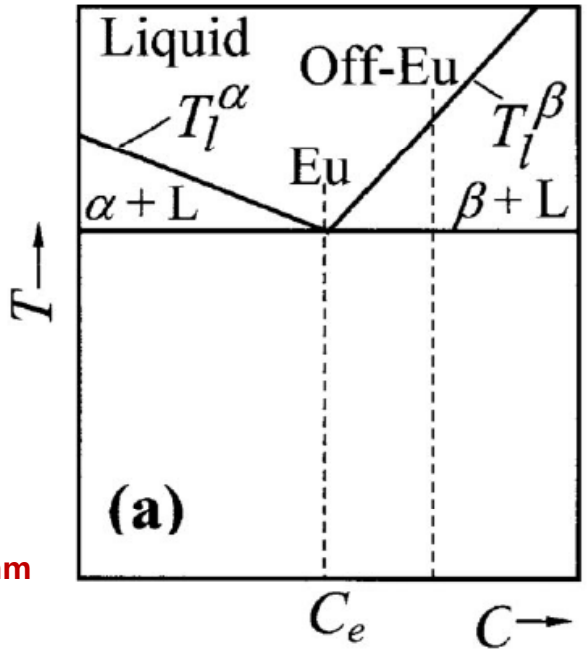


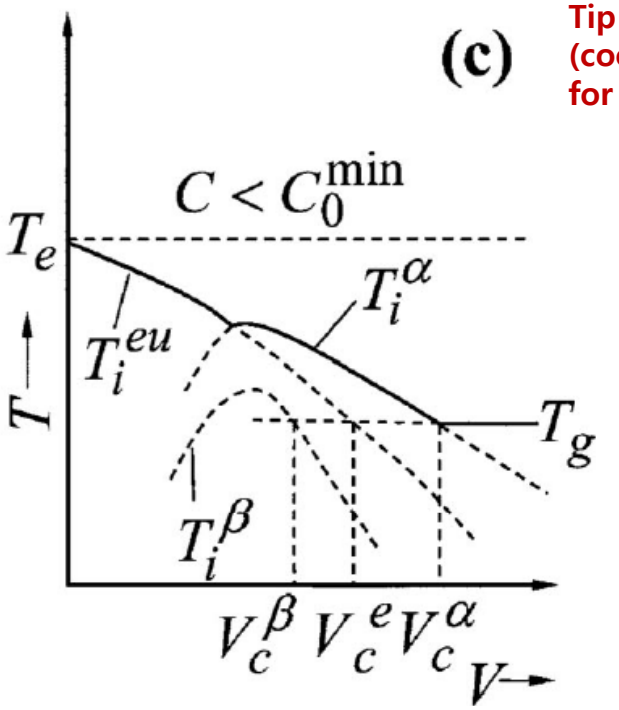
Glass-forming and Composite-forming Zones (symmetrical about eutectic composition)

for alloy composition of $C > C_0^{max}$

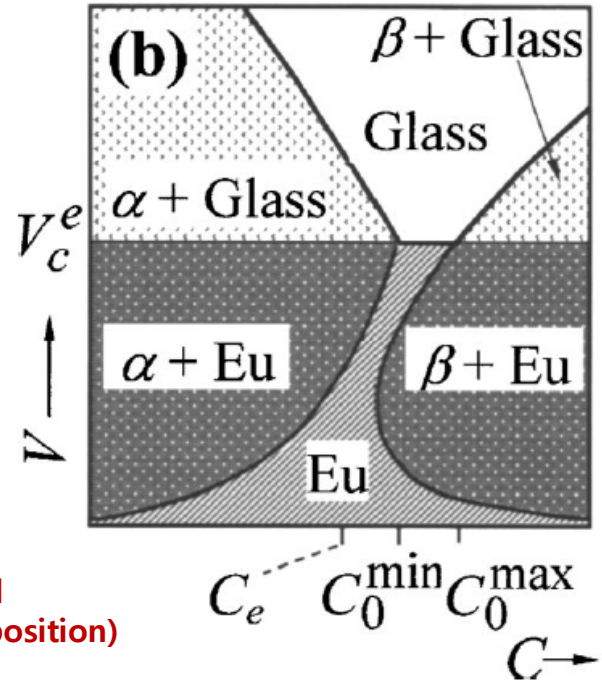
Tip temp.-growth rate (cooling rate) relationship for eutectic, dendritic α, β

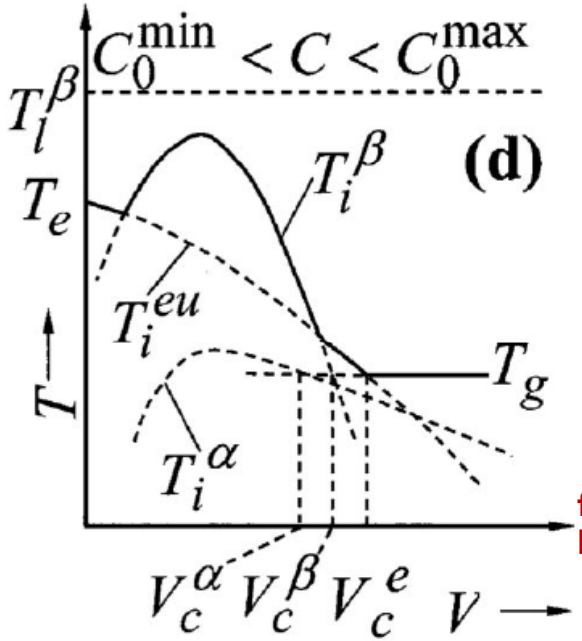
Part of a irregular eutectic phase diagram





for alloy composition of $C < C_0^{min}$



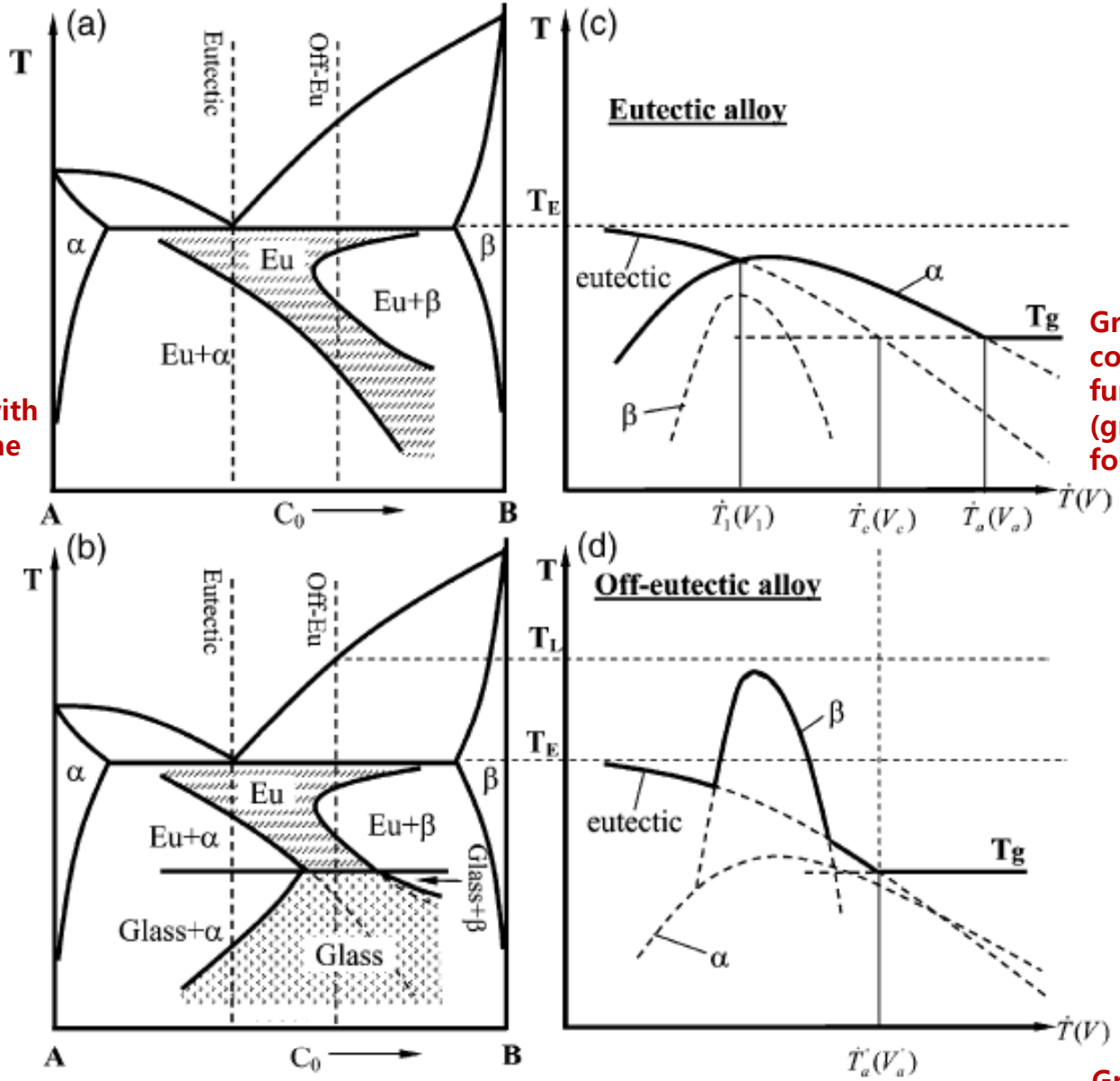


for alloy composition between $C_0^{min} < C < C_0^{max}$

Glass-forming and Composite-forming Zones (asymmetrical about eutectic composition)

Schematic diagram showing skewed eutectic coupled zone and its relation to the glass-forming ability

A eutectic system with skewed coupled zone



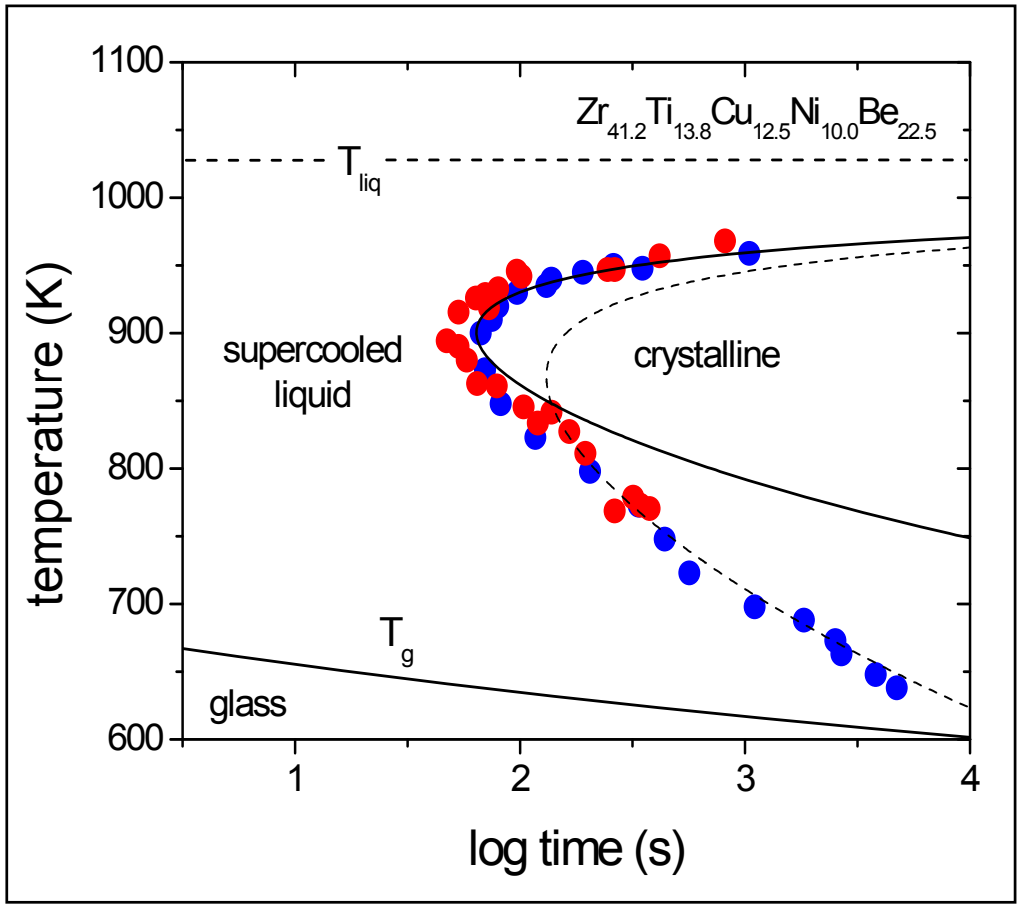
Growth temp. of the constituents as a function of cooling rate (growth rate) for the eutectic alloy

Glass forming and composite forming regions related to the skewed coupled zone

Growth temp. of the constituents as a function of CR (GR) for an off-eutectic alloy

3. Kinetic aspect ➡ Decrease of nucleation and growth rate

Crystallization kinetics



A. Masuhr et al. PRL, 2290 (1999)
R. Busch, JOM 52 (7), 39 (2000)

Nucleation rate:

$I_s(T)=A\cdot D_{eff}\cdot\exp(-\Delta G^*/kT)$

with: $D_{eff}\propto 1/\eta$, $\Delta G^*=16\pi\sigma^3/3\Delta G^2$

Growth velocity:

$u(T)=f\cdot l^{-1}\cdot D_{eff}\,[1-\exp(\nu_m\cdot\Delta G/kT)]$

$$X(t,T)\sim\pi I(T)\mu(T)^3 t^4/3$$

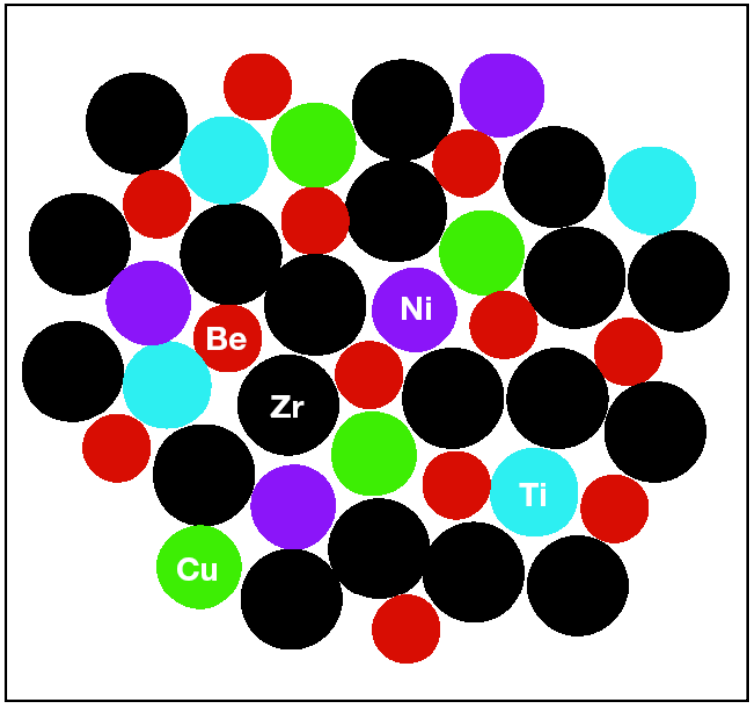
Crystallization time:

$$t_x=\left(\frac{3x}{\pi I_s u^3}\right)^{\frac{1}{4}} \rightarrow t_x\propto\eta$$

Important for high glass forming ability:

Bulk metallic glass forming liquids:

- ***multi-component eutectic alloys with large atomic size mismatch***
- ***high packing density and small free volume (short range order, SRO)***



Tang et al., Nature 402, 160 (1999)

⇒ Melt energetically close to crystal

+

⇒ Slow kinetics (high viscosity)

⇒ slow crystallization

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)***