2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

05. 13. 2009

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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

- Internal energy : mainly considered in oxide glasses

➡ Depends on the bonding types and arrangements of constituent element

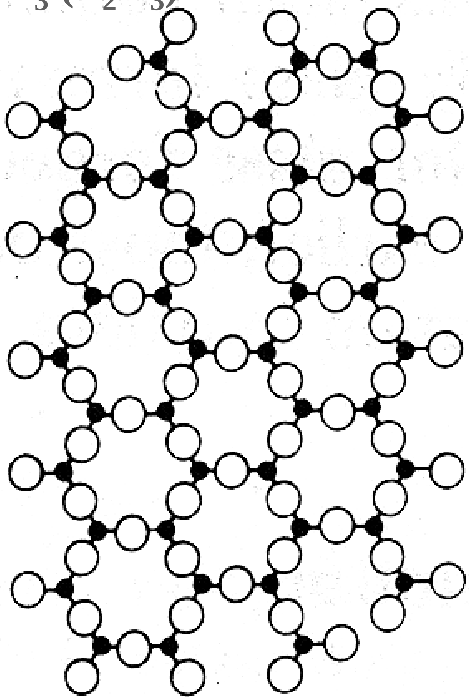
➡ similar types and arrangements of atomic bonding in crystal and amorphous (=similar atomic structure)

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

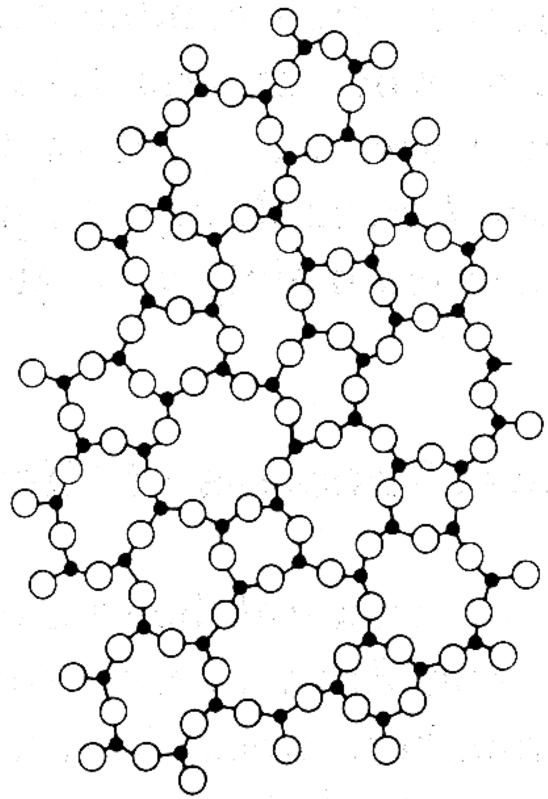
1. Structure & topology: CRN

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

A_2O_3 (B_2O_3)

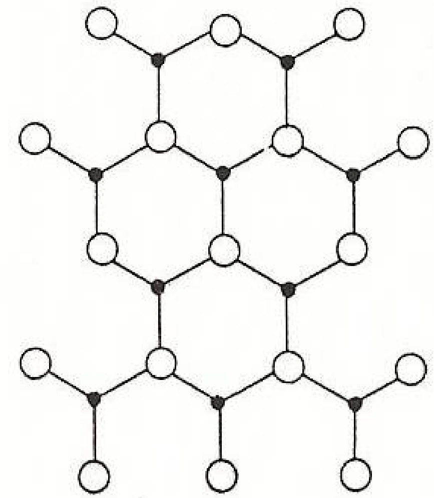


(a)



(b)

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 in 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

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

By Egami & Waseda: in A-B binary system

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

ν: atomic volume
A: matrix, B: solute

minimum concentration of B for glass formation

→ Inversely proportional to atomic volume mismatch

3) Multi-component system (over 3 elements)

with large atomic size difference : confusion theory

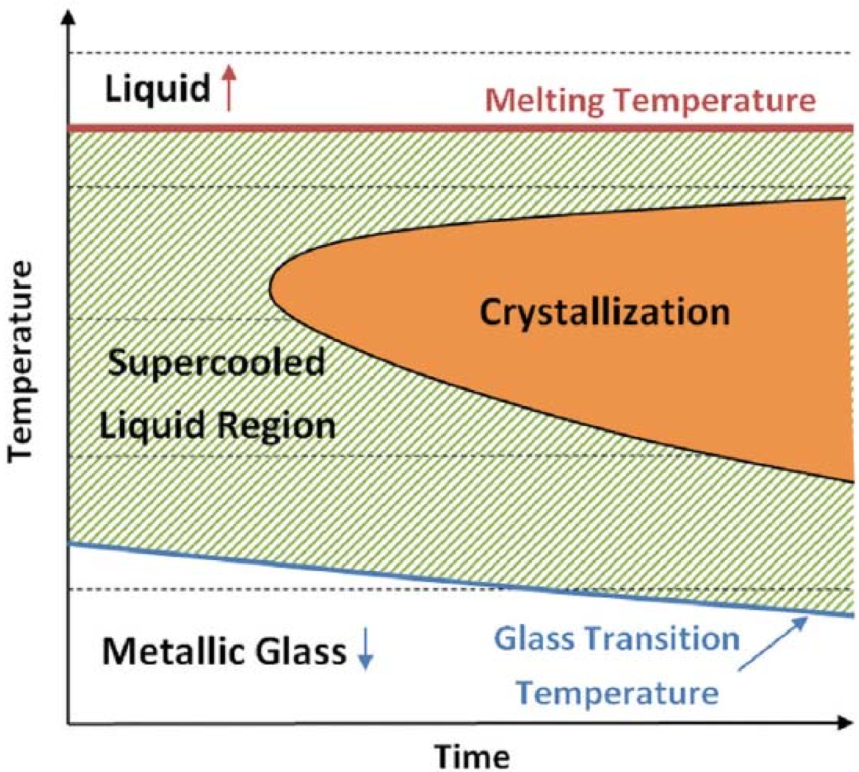
⇨ packing density ⬆ ⇨ dense random packed structure

2. Thermodynamic aspect

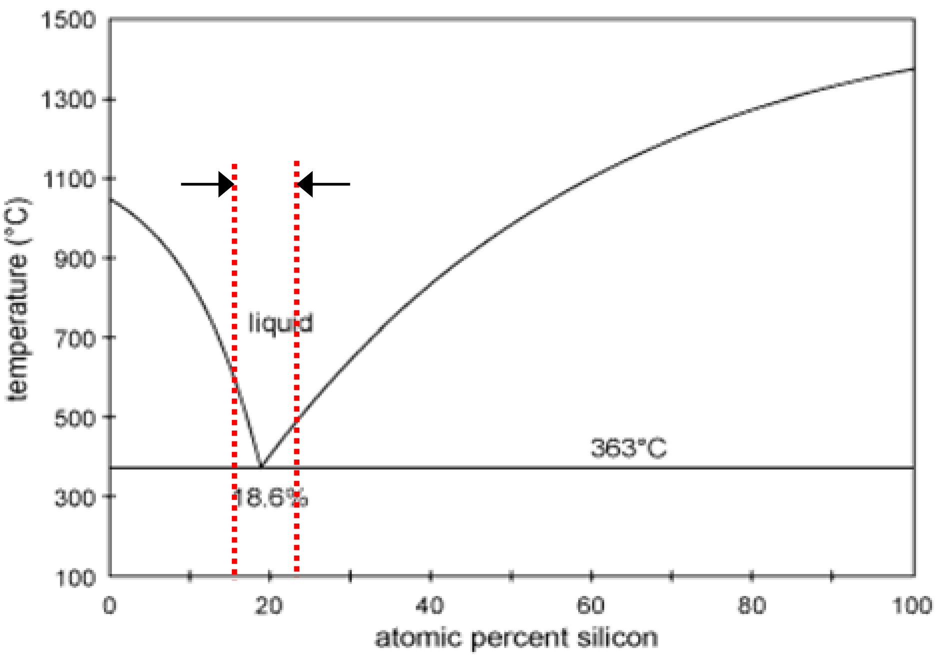
1) deep eutectic condition

- decreasing melting point → less supercooled at T_g

ex) metallic / inorganic system



Glass forming region:
Compositions near the eutectic



2. Thermodynamic aspect

- ***How much can decrease the eutectic temperature at real state rather than that at ideal state?***

- ***Main points***

1) If the liquid has large negative heat of mixing, the eutectic temperature at real state decreases than that at ideal state.

2) Eutectic composition depends on the magnitude of free energy for solid formation of A and B.

→ The composition is not changed by other special properties of liquid.

3) Excess entropy of mixing at high temperature is positive.

With decreasing the temperature, the value changes negative near eutectic temperature.

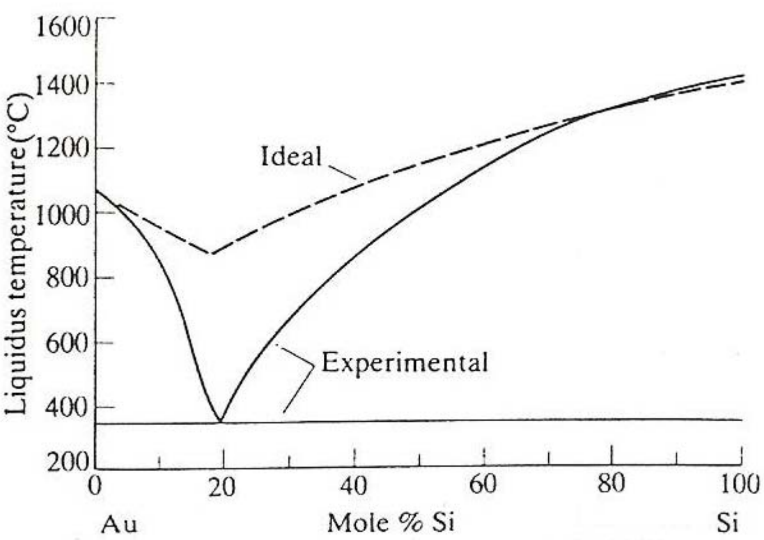
→ This phenomena is not matched to decrease eutectic temperature.

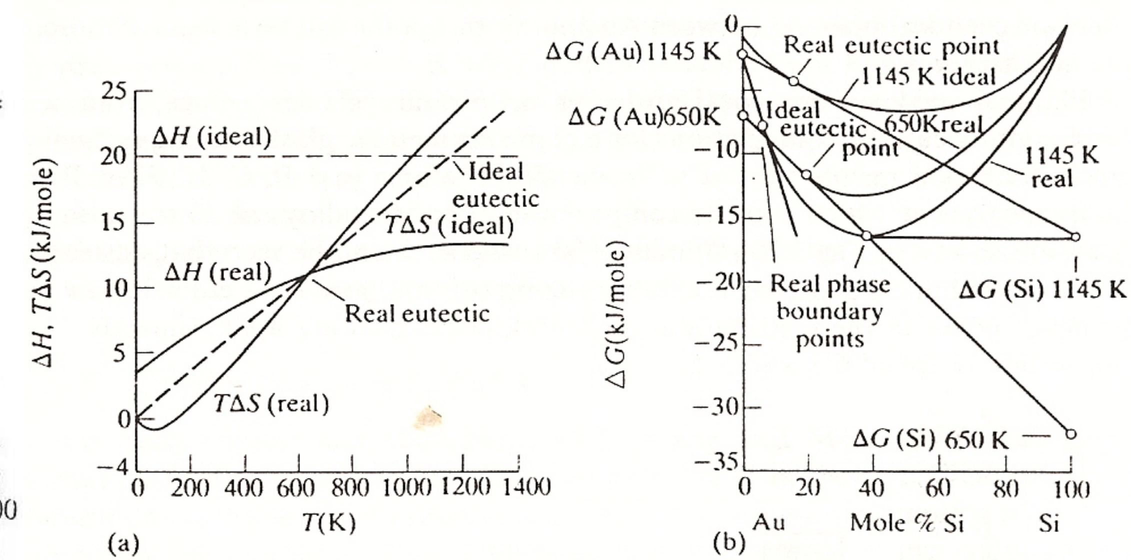
2. Thermodynamic aspect

- ***In Au-Si alloy system,***

  - ***The real eutectic temp. is lowered considerably from the value of expected for an ideal solution.***

  - ***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.***





2. Thermodynamic aspect

→ **Enthalpy of deep eutectic (A-B)**

$$G = G_0 + G_{AB}^E$$

Excess free energy of mixing

$$G_{AB}^E(x,T) = H^E(x,T) - TS^E(x,T)$$

x: composition, T: temperature

$$ex) = \{a_0 + a_1 x + a_2 x^2 + T[b_0 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4] + cT\ln T + dT^2\}x(1-x)$$

$$decision \quad of \quad (a_i, b_i, c, d) \Rightarrow \boxed{G_{AB}^E}$$

can be calculated.

2. Thermodynamic aspect

→ **Free energy of liquid**

$$G^L = (1-x)G_A^L + xG_B^L + G_{AB}^L$$

Pure A　　Pure B　　mixing

$$G_{AB}^L = G_{AB}^I + G_{AB}^E$$

Ideal　　Excess

$$(G_{AB}^E = H_{AB}^E - TS_{AB}^E)$$

$$G_{AB}^I = -TS^I \qquad (H^{ideal} = 0)$$

$$= RT(x\ln x + (1-x)\ln(1-x))$$

If x, T is const., ⇨ fixed.

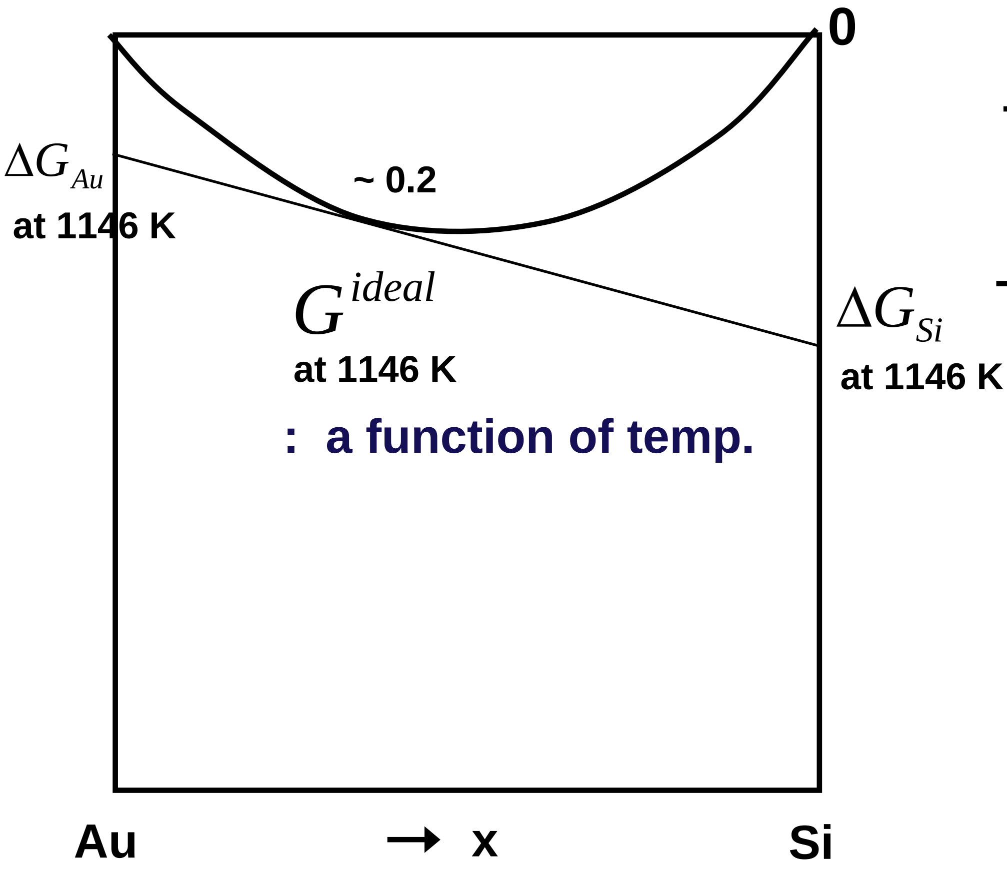
Ideal state → $G_{AB}^{ideal} (G_{AB}^E = 0)$

real state → $G_{AB}^{real} (G_{AB}^E \neq 0)$ ↑ ⇨ deep eutectic

2. Thermodynamic aspect

- **Au-Si system**

→ **Eutectic composition and temperature: common tangent method**



Left & Right axes

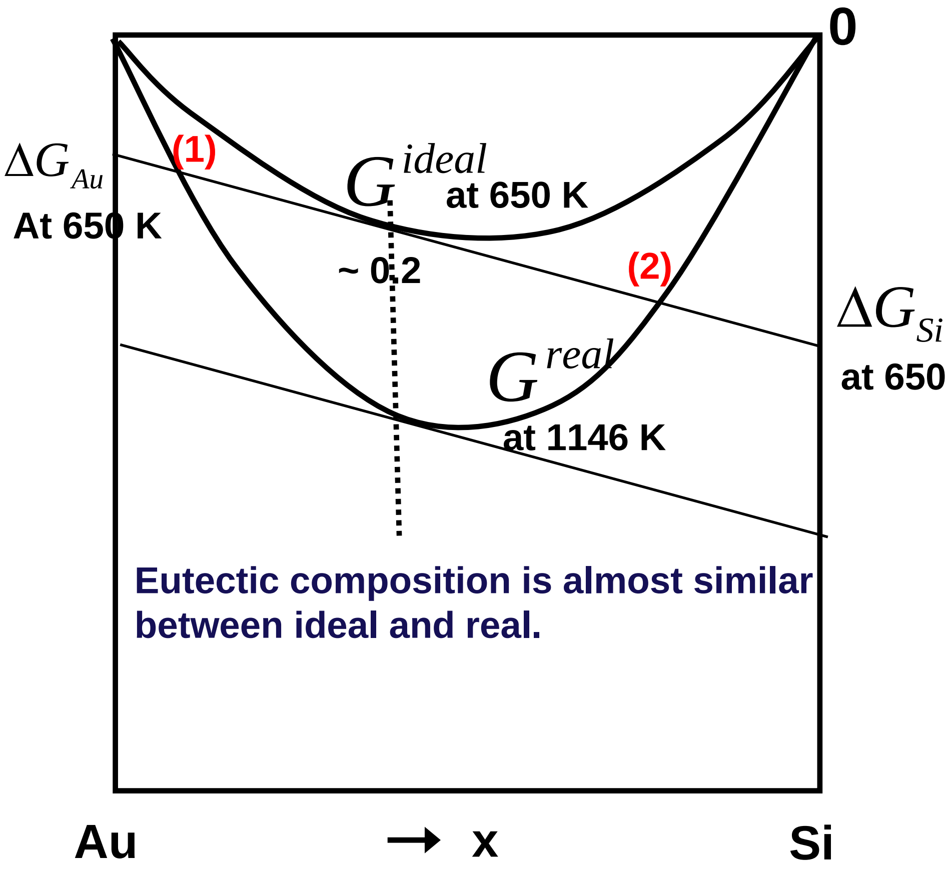
→ **Free energy difference between Solid and liquid in Au and Si**

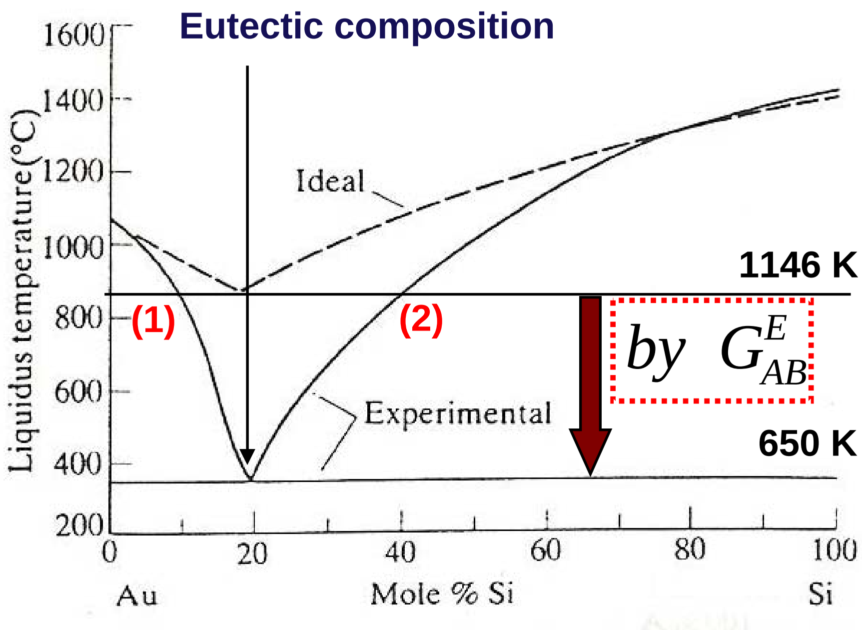
→ $G_A^S - G_A^L$ **: a function of temp.**

$$ex)\Delta G_{Au} = -12550(1 - T/1336)$$

2. Thermodynamic aspect

- **Au-Si system : decision of composition using G values**





1) G_{AB}^{E} ↑ → **deep eutectic**

2) $eutectic \quad compositio\ n :$

- **Almost similar between ideal and real**
- **Approximately calculated by pure component A and B of** ΔG^{S-L}

- **Contribution of enthalpy in excess free energy**

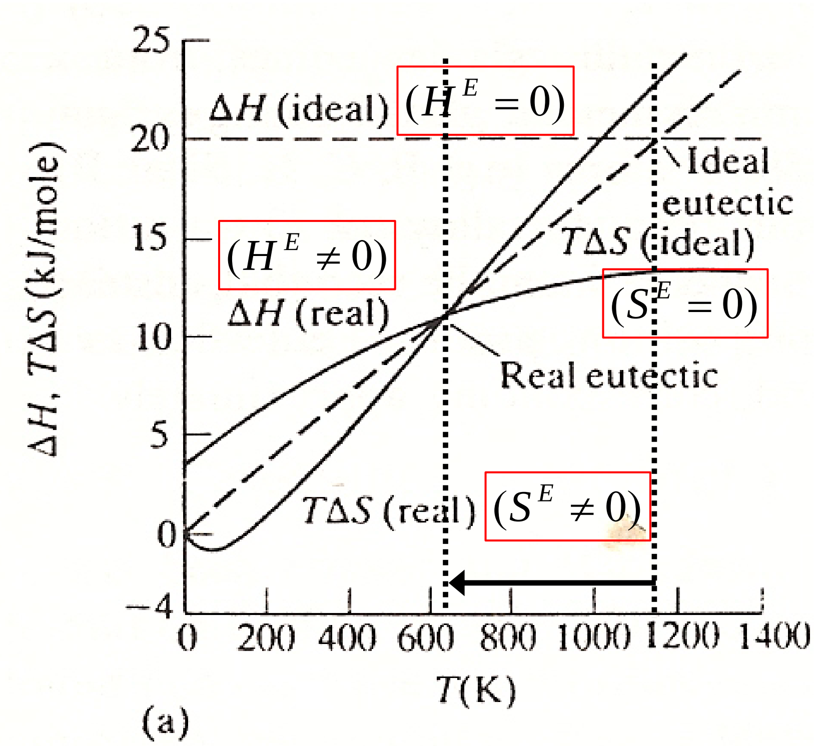
$$G = H - TS$$

At eutectic point, $G^L = G^S \rightarrow \boxed{\Delta H = T\Delta S}$

$$\Delta H = H^L - H^S = H^E + (1-x)[H_A^L - H_A^S] + x[H_B^L - H_B^S]$$

$$(H^I = 0)$$

$$\Delta S = S^L - S^S = S^I + S^E + (1-x)[S_A^L - S_A^S] + x[S_B^L - S_B^S]$$



*** Temperature dependence of the S and H contributions to the free energy balance**
at the eutectic points of real and ideal liquids

$T\Delta S^{ideal}$ vs $T\Delta S^{real}$: **Similar**

ΔH^{ideal} vs ΔH^{real} : **Big different**

$\therefore$ **decrease of T_E by excess enthalpy of mixing**

$\rightarrow$ **deep eutectic** $\rightarrow$ **GFA** ⬆

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

- Excess entropy: relatively less dominant to decrease eutectic temperature

Ex) Au-Si system

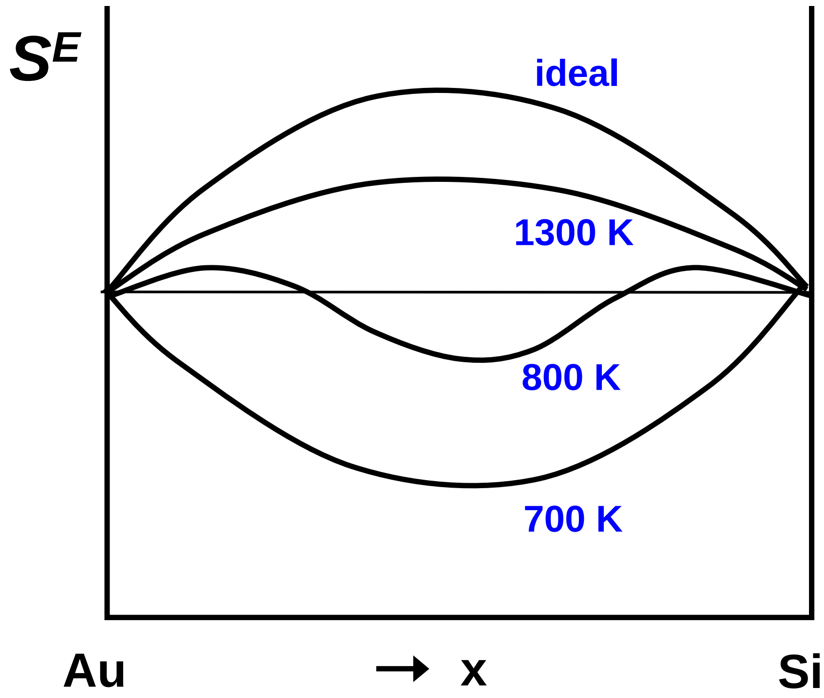
→ Positive excess entropy

→ But, at eutectic temperature

$$S^E < 0$$ by SRO

disturb to decrease of eut. temp.

→ canceled out by effect of enthalpy

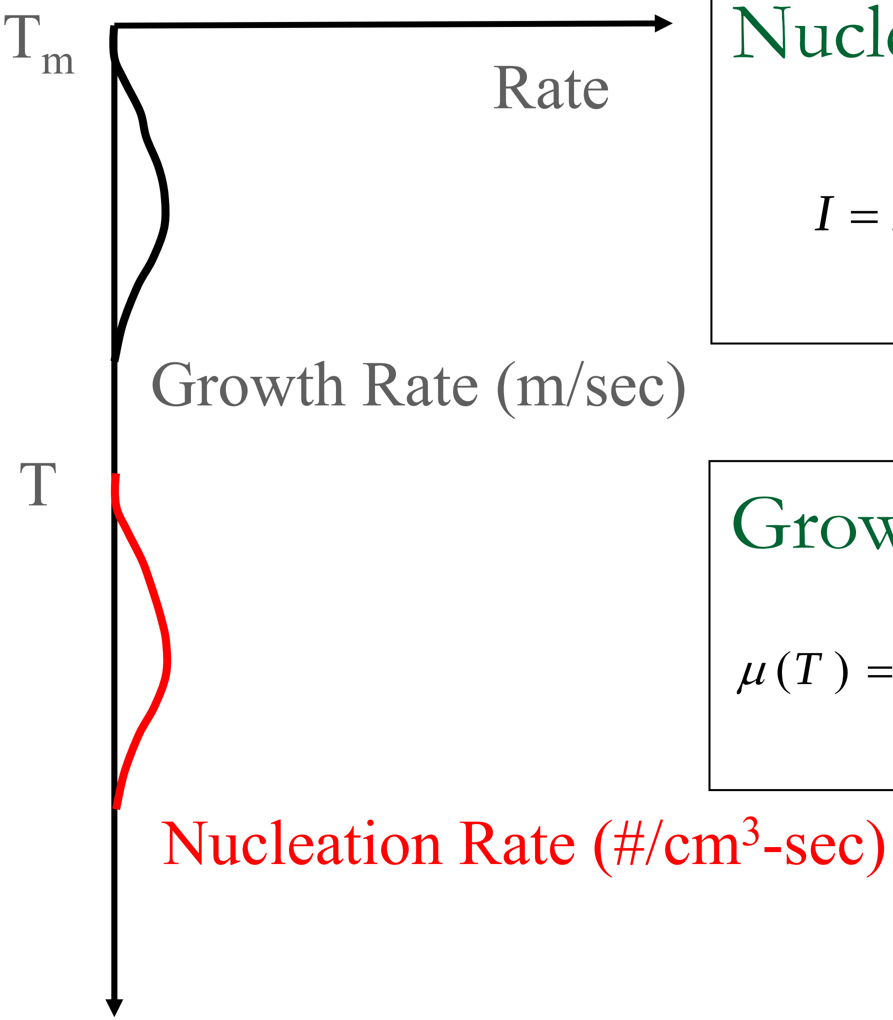


∴ Occurrence of SRO at eutectic composition (especially deep eutectic)

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

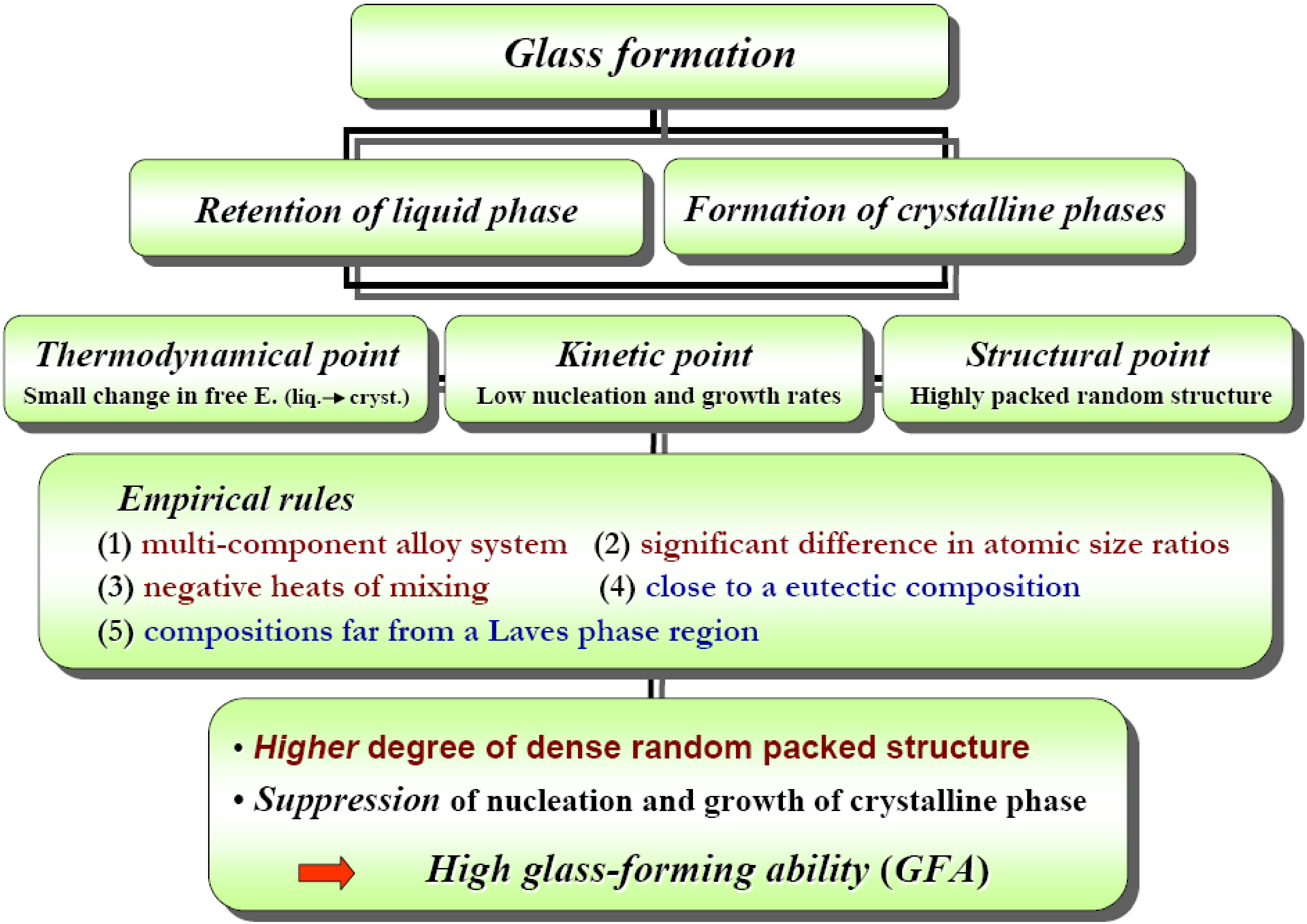


Nucleation Rate I(T)

$$I = n\nu \exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

Growth Rates μ(T)

$$\mu(T) = \left(\frac{fRT}{3N\pi a^2\eta(T)}\right)\left(1 - \exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)$$


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)

REFERENCE

- Phase Transformation in Metals and Alloys
  < Chapter 1 >
  D.A. Porter and K.E. Easterling