2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

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Definition of metallic glass

• Non-crystalline metallic solid lacking long-range periodicity of atomic arrangement and showing glass transition.

Bulk metallic glass (BMG)

• Metallic glass having a minimum dimension of 1mm which is equivalent to a critical cooling rate of about 10^3 to 10^4 K/s.

Glass Formation

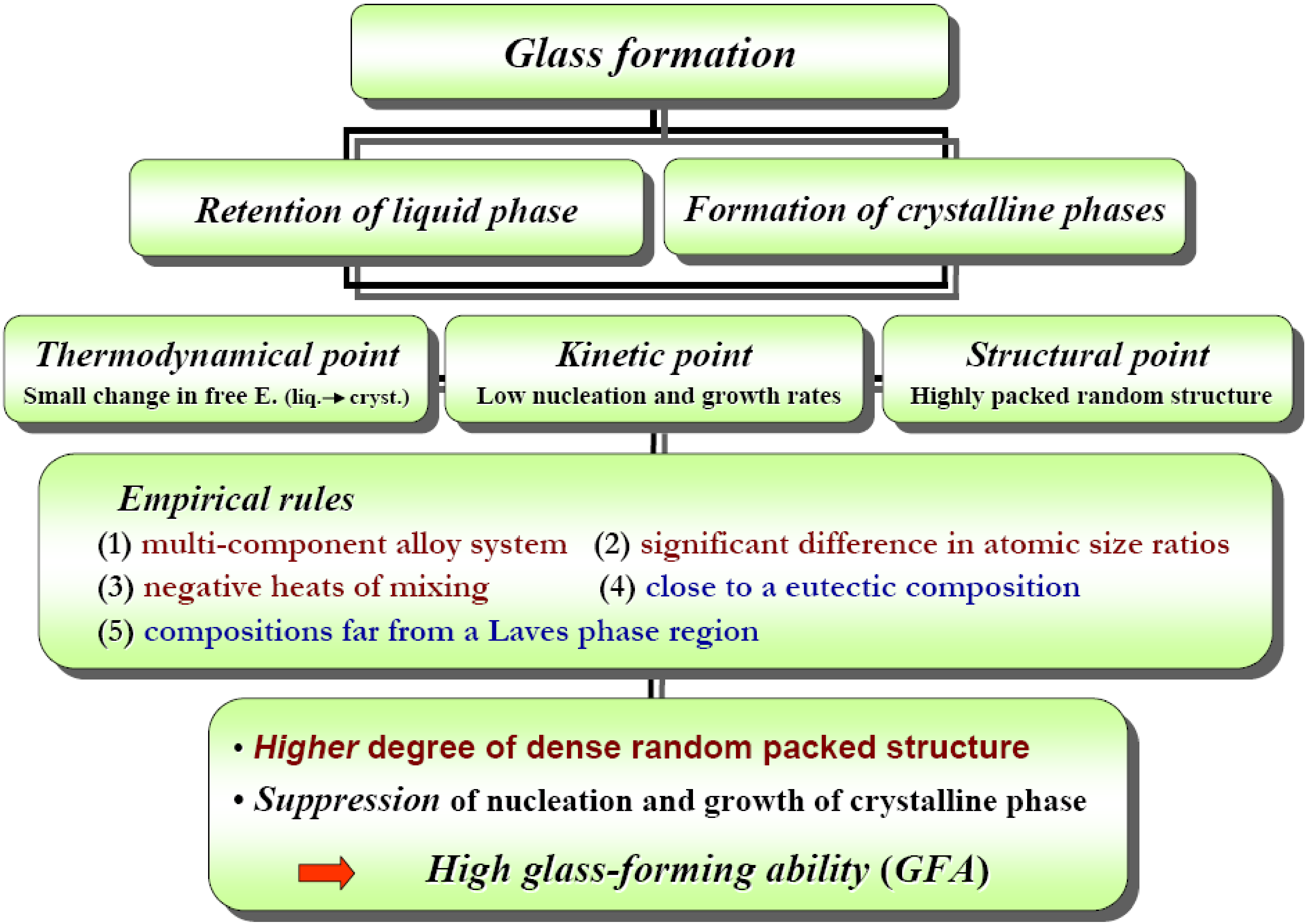
• Competing process between retention of liquid phase and formation of crystalline phases

a. Liquid phase stability

- Stability of the liquid in the equilibrium state (i.e. stable state, T_l)
- Stability of the liquid during undercooling (i.e. metastable state, T_g)

b. Resistance to crystallization

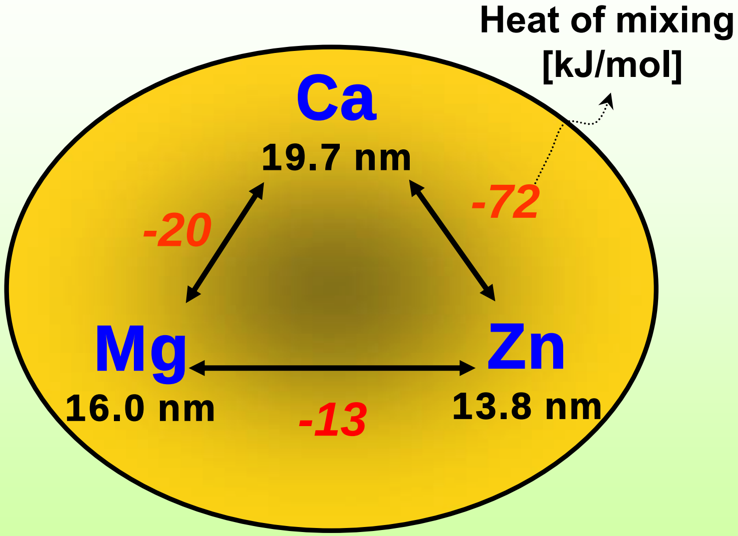
- Nucleation and growth of the competing crystalline phases


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)

Alloy design and new BMG development

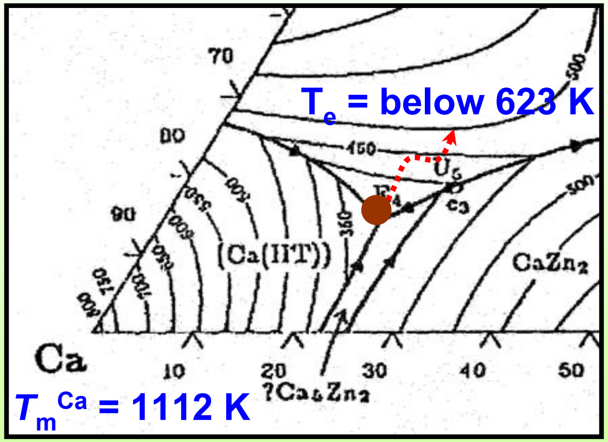
Ca-Mg-Zn alloy system

- **Dense packed structure**



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

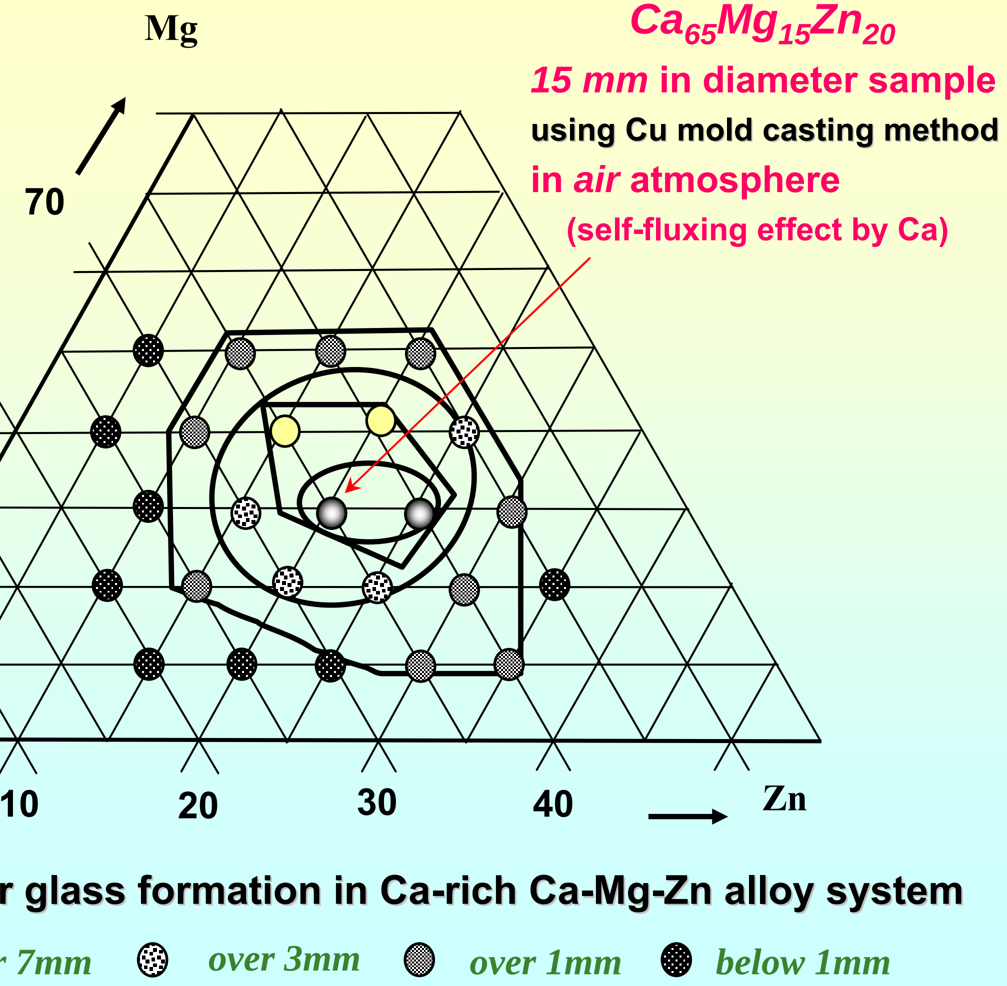
- **Decrease of melting temp.**



Deep eutectic condition

$T_e / T_m^{Ca} = 0.560$

Ca-Mg-Zn alloy system

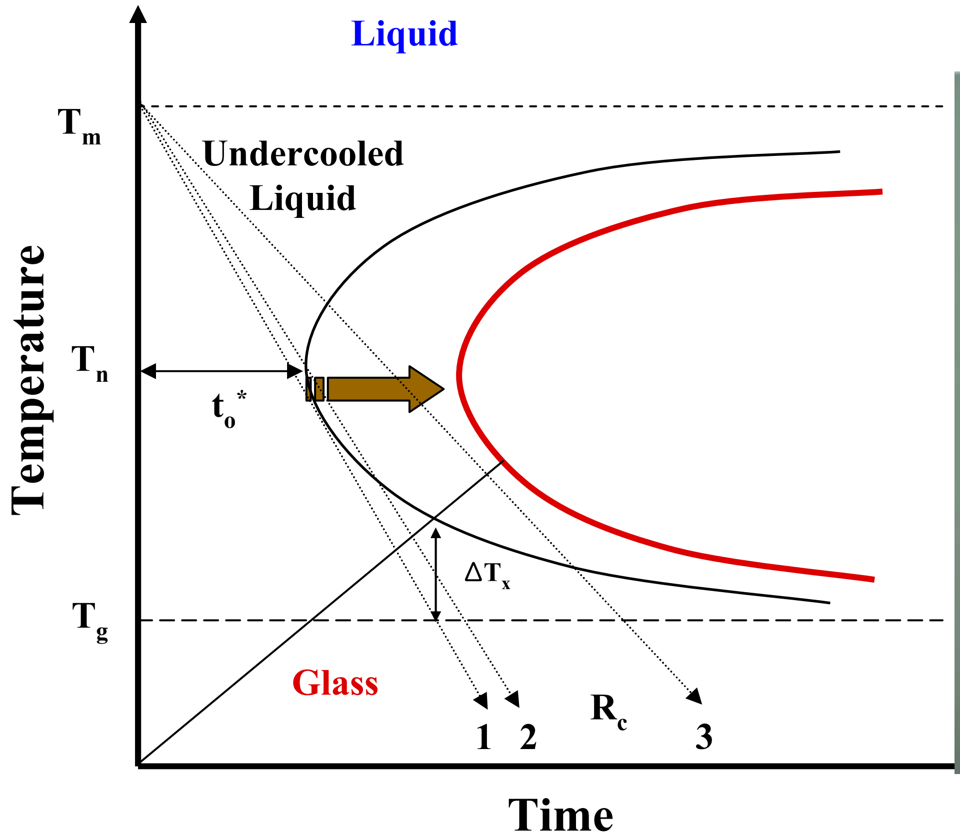


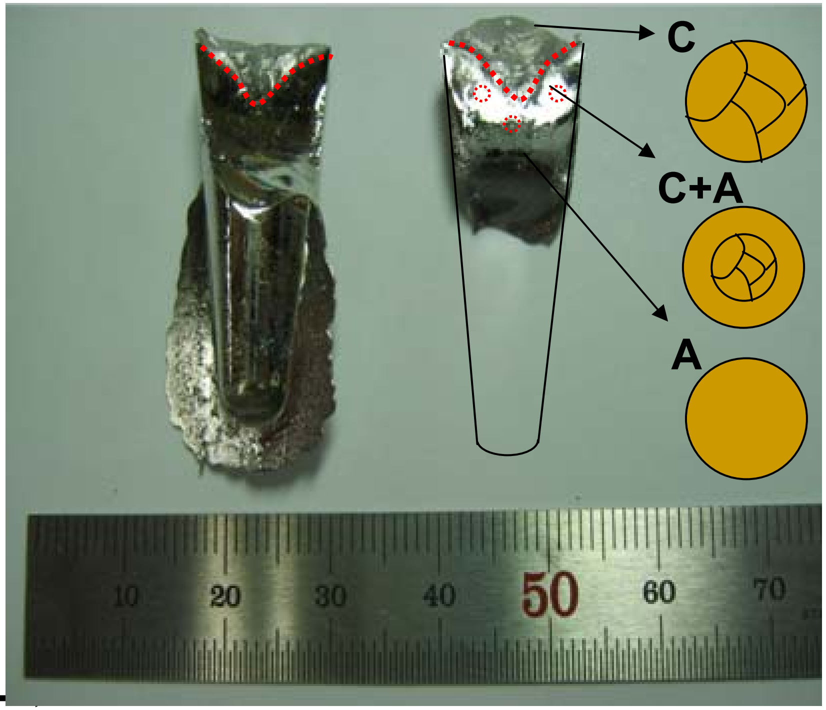
* J. Mater. Res. 19, 685 (2004)
* Mater. Sci. Forum 475-479, 3415 (2005)

Evaluation of Glass-forming ability

Critical cooling rate

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

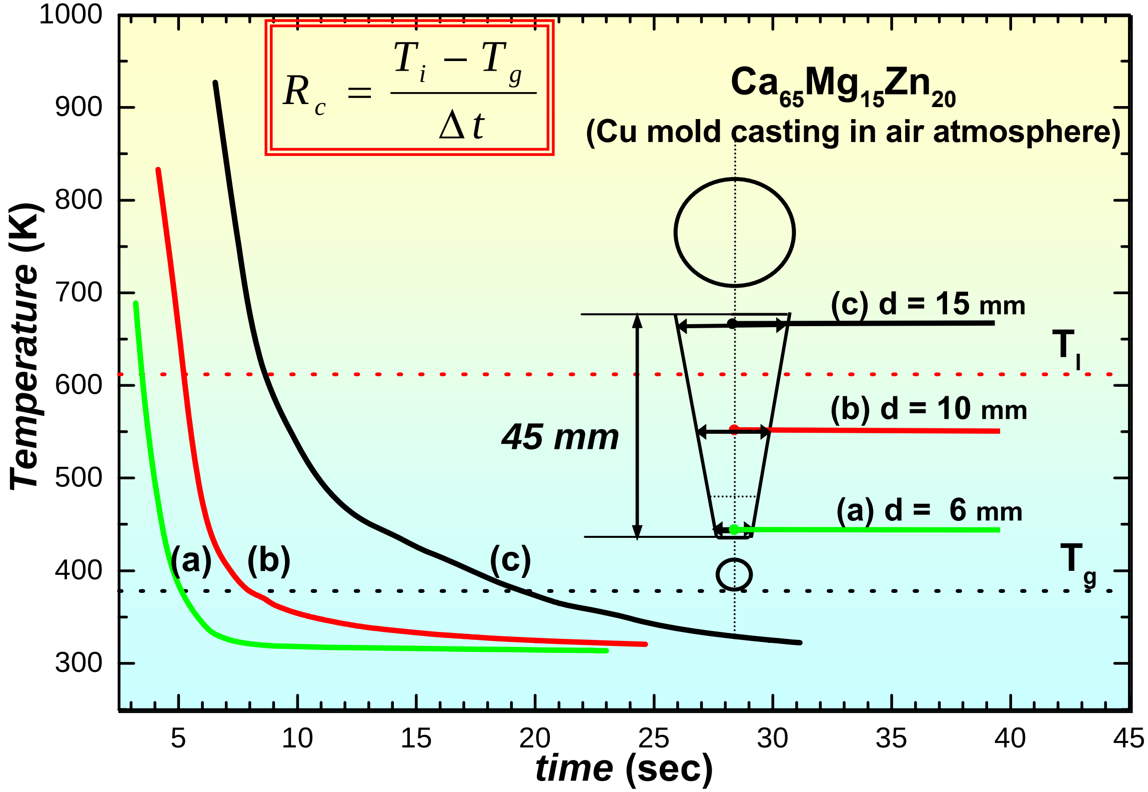




Critical cooling rate is inversely proportional to the diameter of ingot.

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

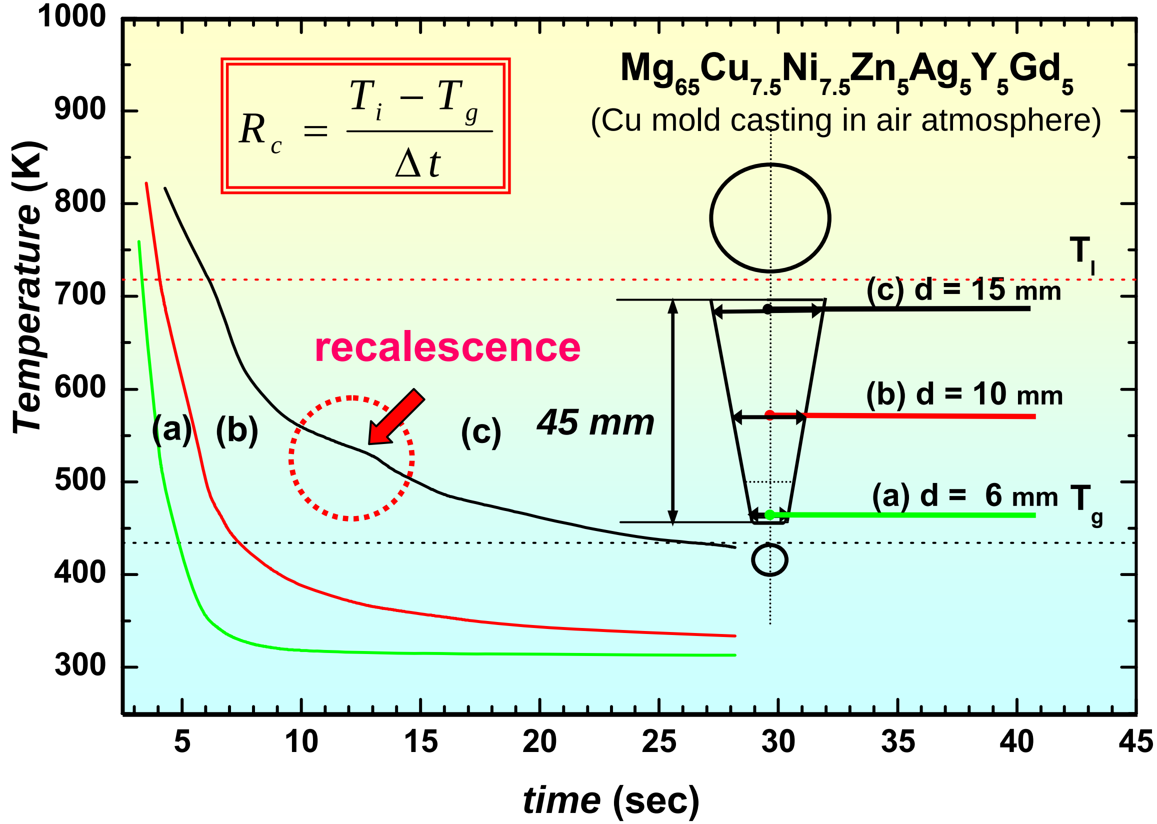


(a) bottom position : 149 K/s (b) middle position : 93 K/s (c) top position : 20 K/s

⇒ 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)

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**

Parameters for GFA suggested so far :

Based on thermal analysis (T_g, T_x and T_l): thermodynamic and kinetic aspects

$T_{rg} = T_g/T_l$ — D. Turnbull et al., *Contemp. Phys.*, 10, 473 (1969)

$K = (T_x - T_g) / (T_l - T_x)$ — A. Hruby et al., *Czech.J.Phys.*, B22, 1187 (1972)

$\Delta T^* = (T_m^{mix} - T_l) / T_m^{mix}$ — I. W. Donald et al., *J. Non-Cryst. Solids*, 30, 77 (1978)

$\Delta T_x = T_x - T_g$ — A. Inoue et al., *J. Non-Cryst. Solids*, 156-158, 473 (1993)

$\gamma = T_x / (T_l + T_g)$ — Z.P. Lu and C. T. Liu, *Acta Materialia*, 50, 3501 (2002)

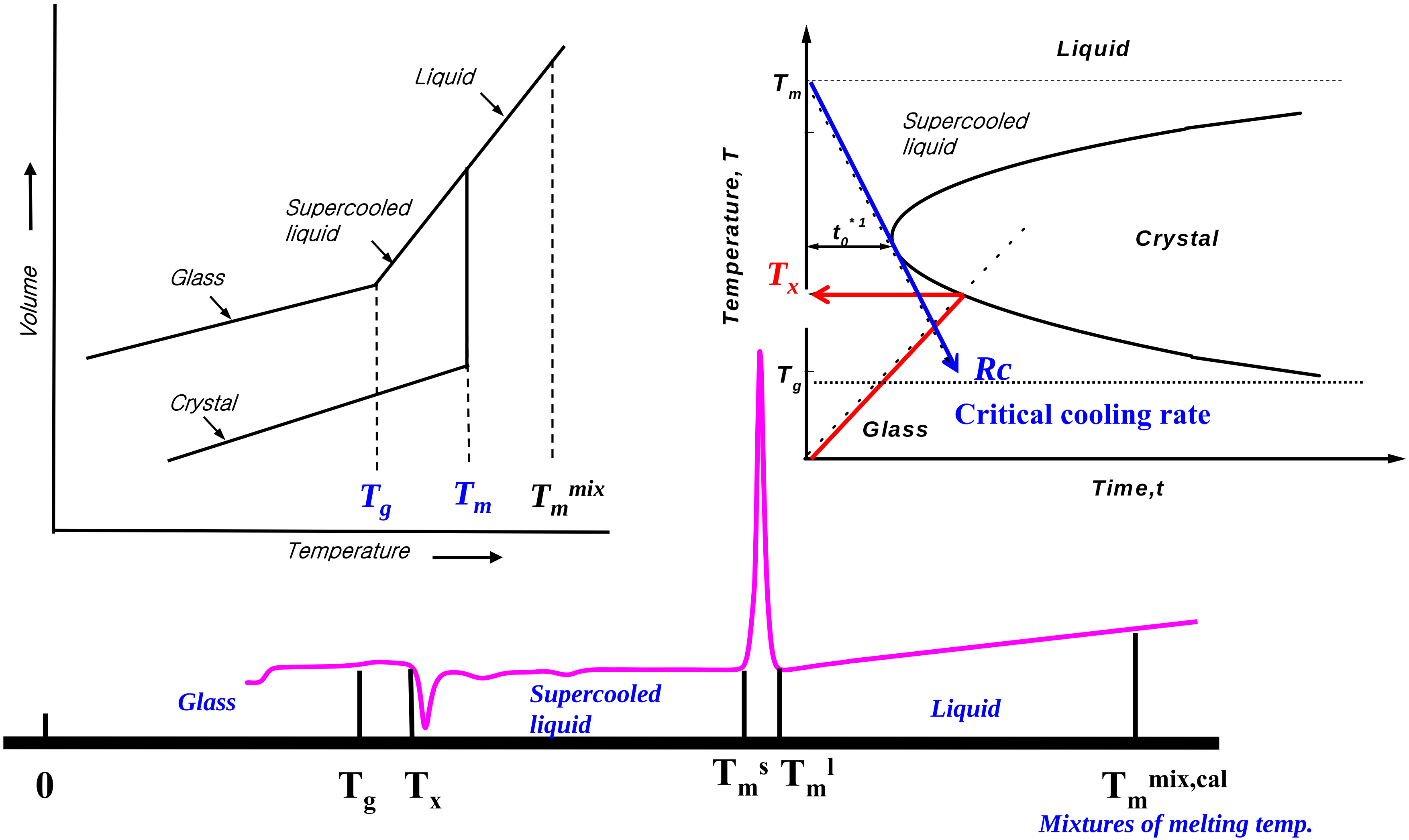
Based on thermodynamic and atomic configuration aspects

$\sigma = \Delta T^* \times P'$ — E. S. Park et al., *Appl. Phys. Lett.*, 86, 061907 (2005)

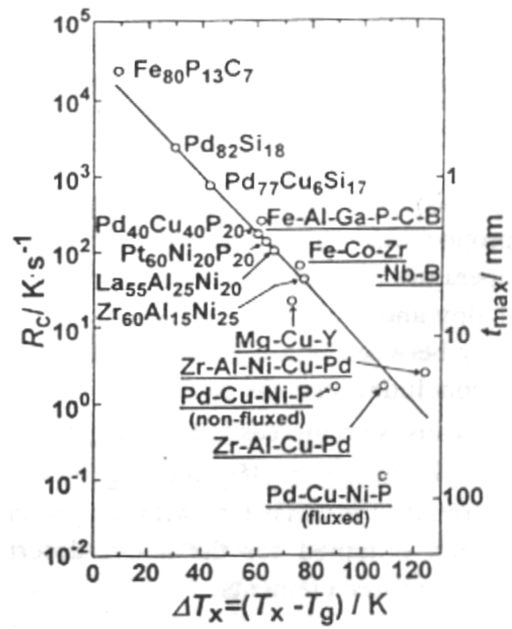
ΔT* : **Relative decrease of melting temperature + *P'* : atomic size mismatch**

: can be calculated simply using data on melting temp. and atomic size

< V - T diagram >   < TTT diagram >



GFA Parameters on the basis of thermodynamic or kinetic aspects :



1) ΔT_x parameter = $T_x - T_g$

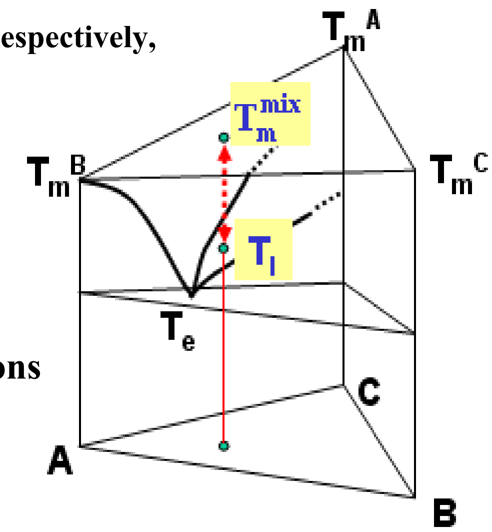
- quantitative measure of glass stability toward crystallization upon reheating the glass above T_g: stability of glass state
- cannot be considered as a direct measure for GFA

2) K parameter = $(T_x-T_g)/(T_l-T_x) = \Delta T_x/(T_l-T_x)$

- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

3) ΔT^* parameter = $(T_m^{mix} - T_l)/ T_m^{mix}$

- $$T_m^{mix} = \sum_i^n n_i \cdot T_m^i$$ (where n_i and T_m^i are the mole fraction and melting point, respectively, of the *i* th component of an *n*-component alloy.)

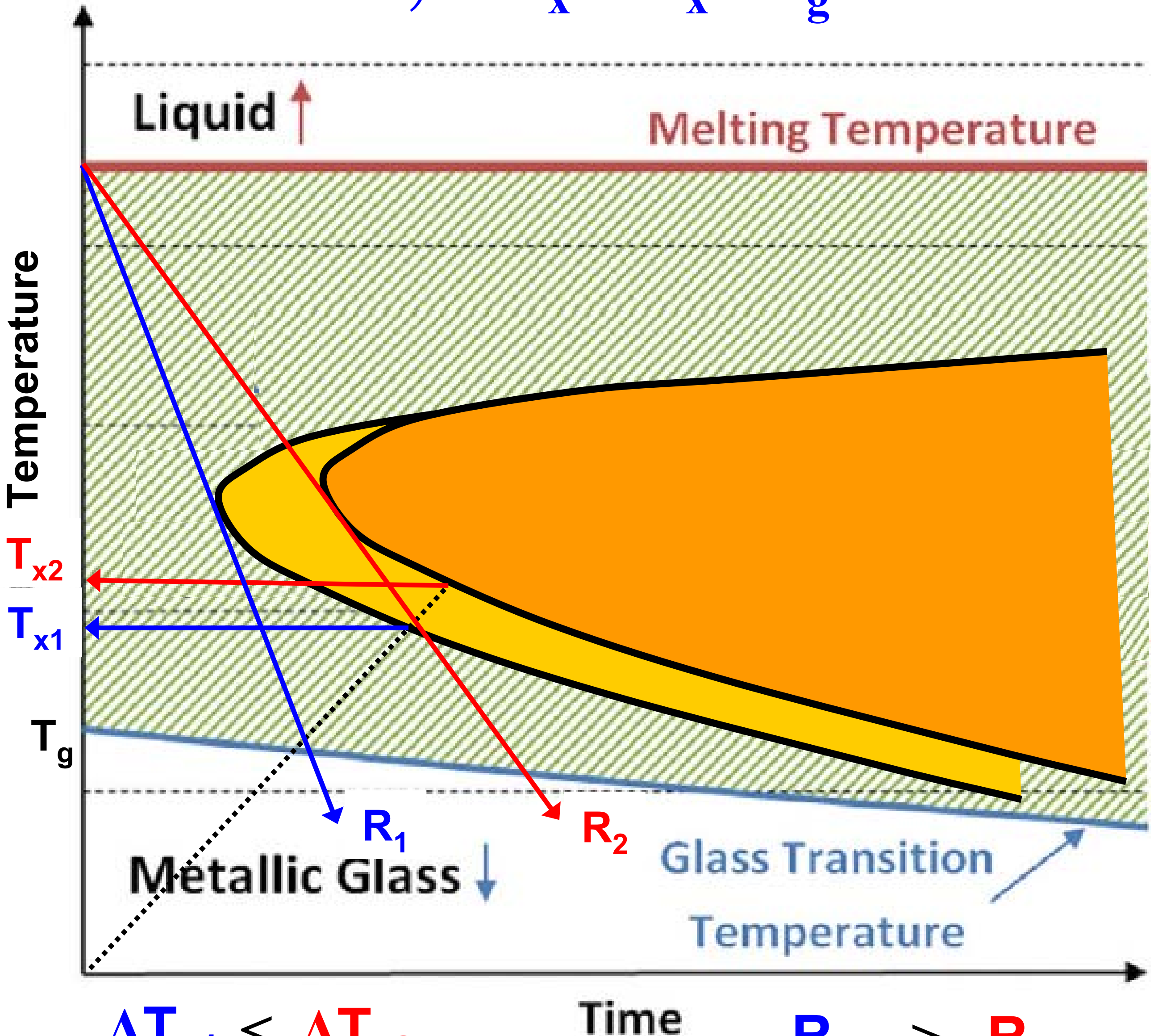


- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA

➡ T_m^{mix} represents the fractional departure of T_m with variation of compositions and systems from the simple rule of mixtures melting temperature

Time Temperature Transformation diagram:

1) $\Delta T_x = T_x - T_g$



$\Delta T_{x1} < \Delta T_{x2}$ $R_1 > R_2$

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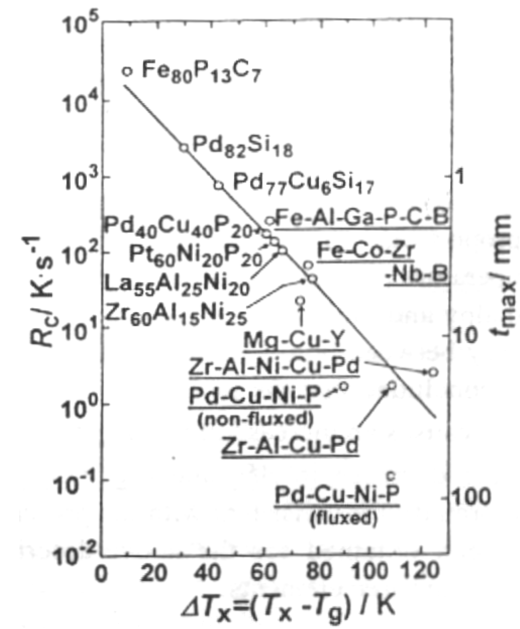

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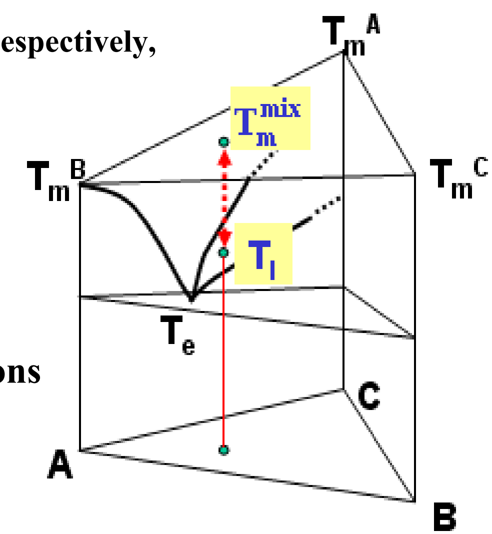

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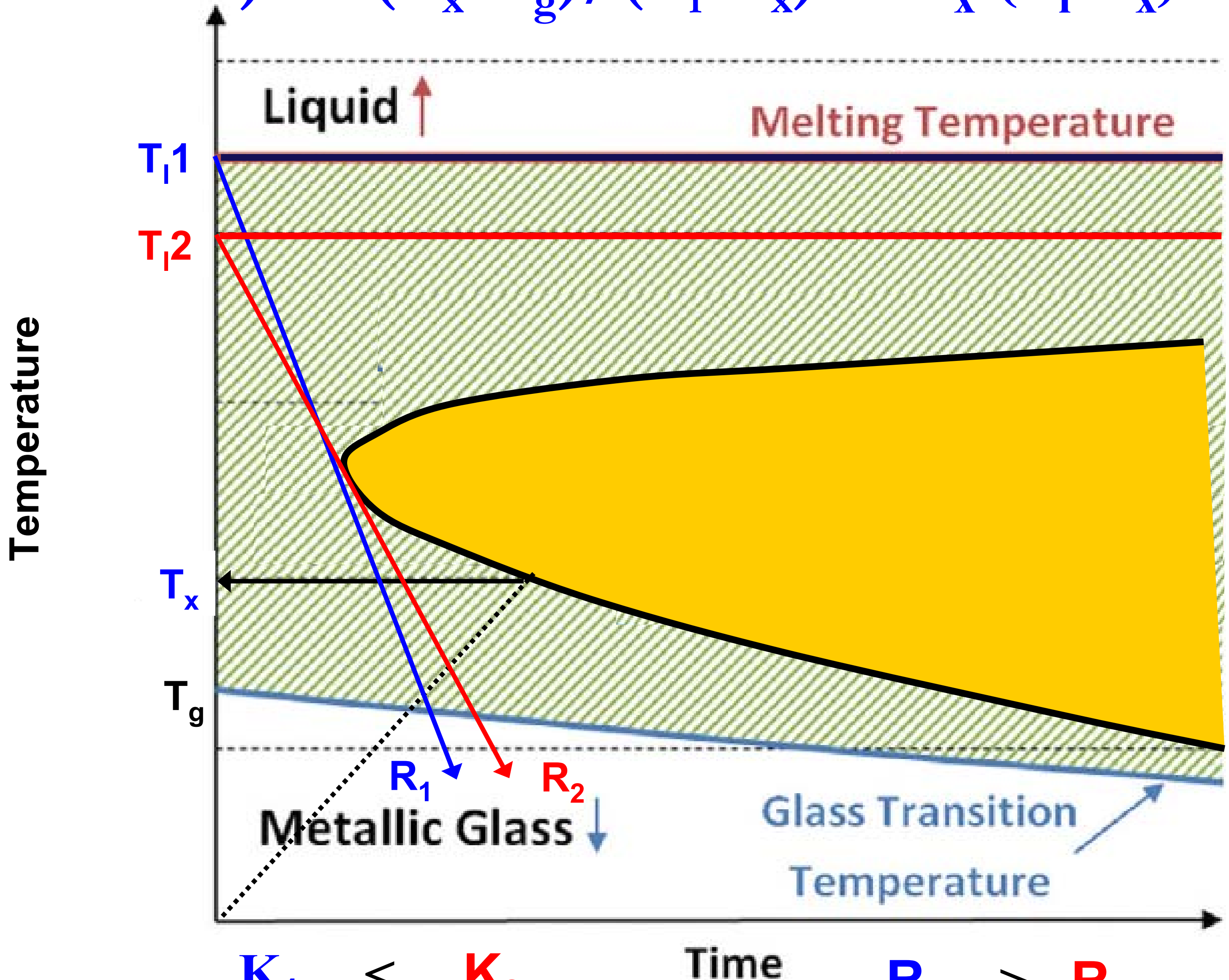

$K_1 < K_2$ $\quad R_1 > R_2$

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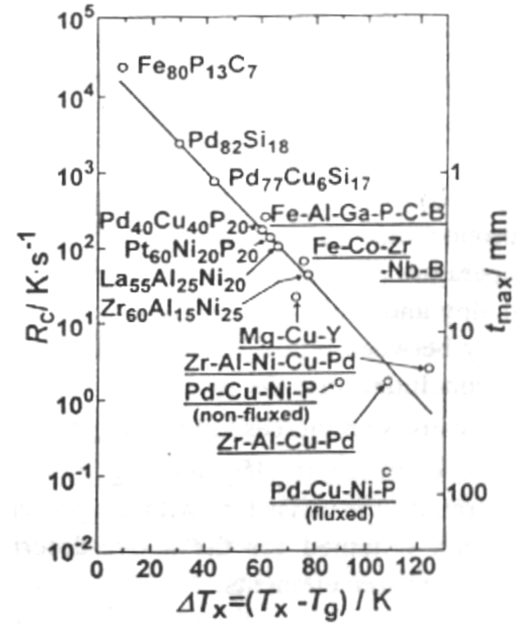

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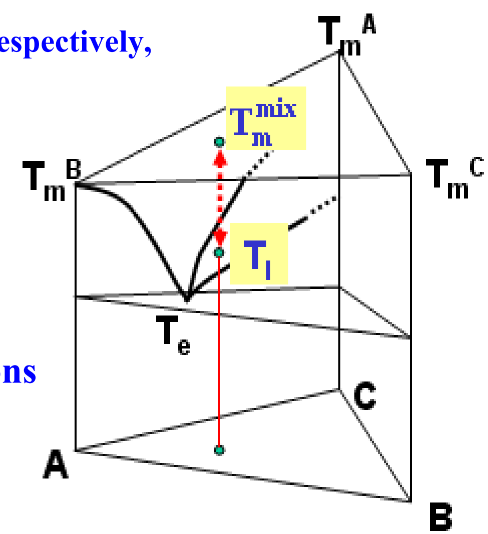

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Relative decrease of melting temperature

: **ratio of Temperature difference between liquidus temp. T_l and imaginary melting temp. T_m^{mix} to T_m^{mix}**

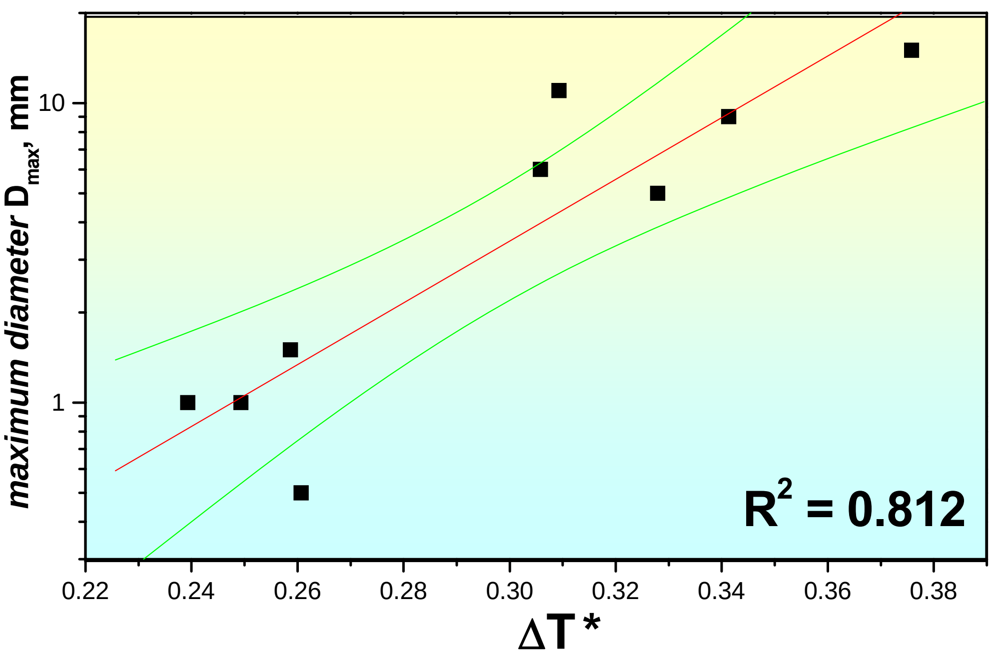
$$\Delta T^* = \frac{T_m^{mix} - T_l}{T_m^{mix}}$$

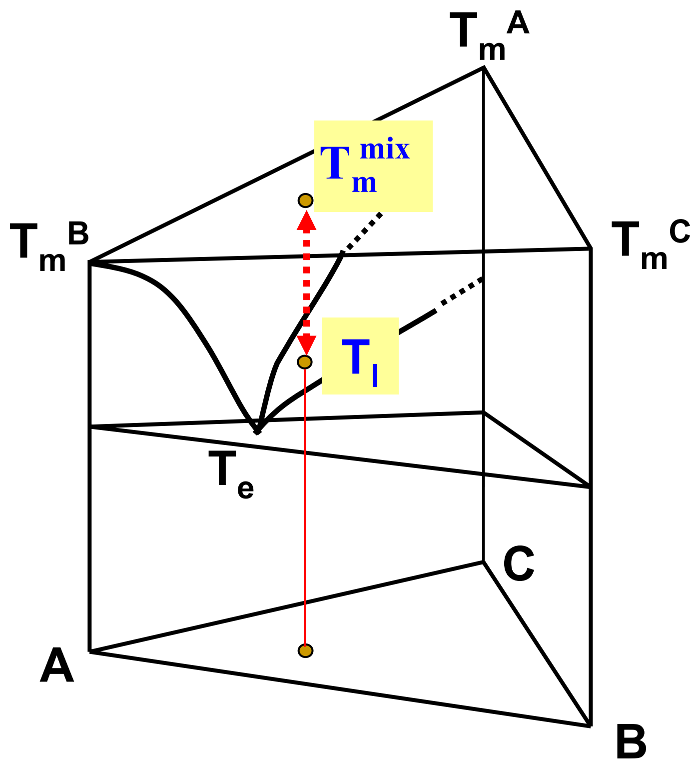
(where, $T_m^{mix} = \sum x_i T_m^i$, x_i = molefraction, T_m^i = melting point)

by I.W. Donald et al. (*J. Non-Cryst. Solids*, 30, 77 (1978))

$\Delta T^* \geq 0.2$ **in most of glass forming alloys**

Ca-Mg-Zn alloy system

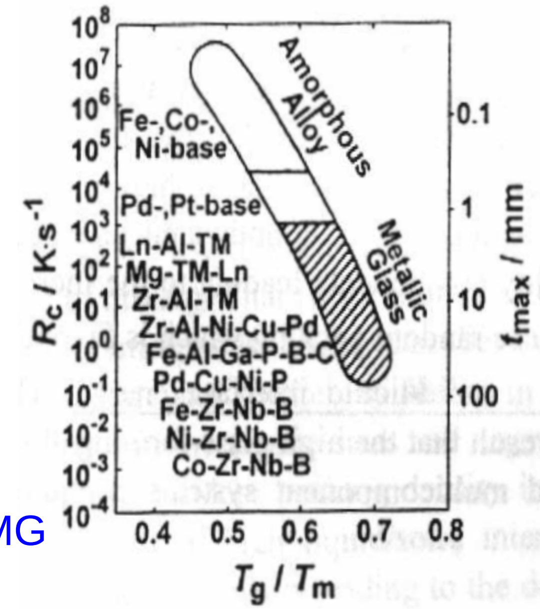




GFA Parameters on the basis of thermodynamic or kinetic aspects :

4) T_{rg} parameter = T_g/T_l

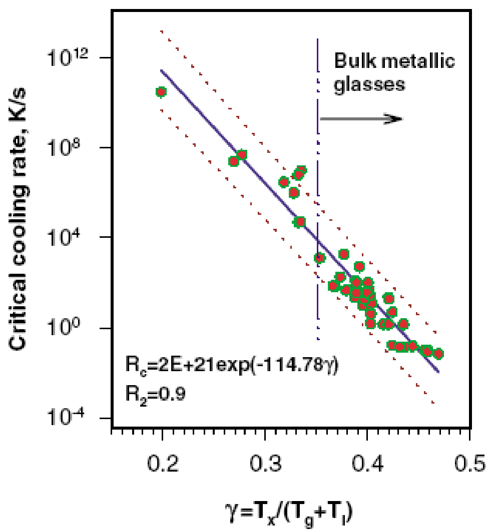
- kinetic approach to avoid crystallization before glass formation
- Viscosity at T_g being constant, the higher the ratio T_g/T_l, the higher will be the viscosity at the nose of the CCT curves, and hence the smaller R_c
- T_l ↓ and T_g ↑ ► lower nucleation and growth rate ► GFA ↑



- ▪ significant difference between T_l and T_g in multi-component BMG
- ▪ insufficient information on temperature-viscosity relationship
- ► insufficient correlation with GFA

5) ɣ parameter = T_x / (T_l + T_g)

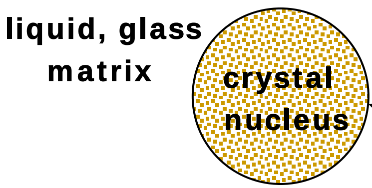
- thermodynamic and kinetic view points - relatively reliable parameter
- stability of equilibrium and metastable liquids: T_l and T_g
- resistance to crystallization: T_x



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)

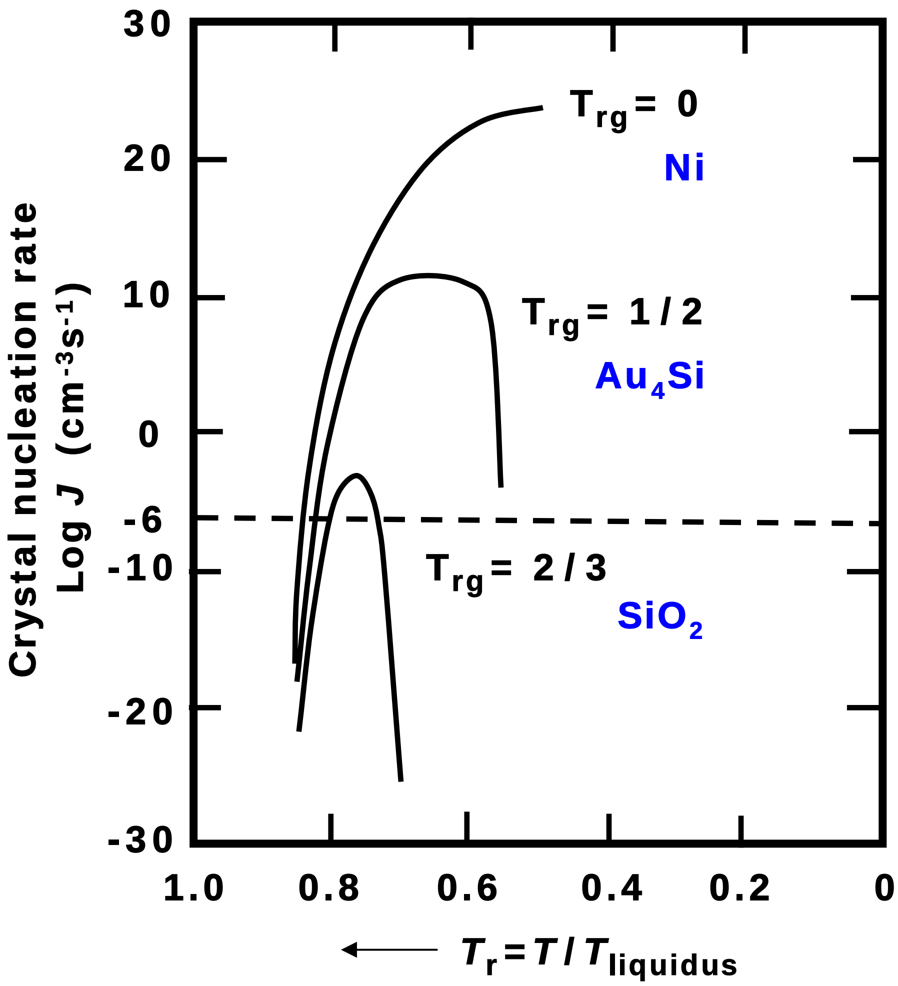
(b) simplified Vogel-Fulcher-Tamman (VFT) equation $\eta = 10^{-3.3} \exp\left(\frac{3.34}{T_r - T_{rg}}\right)$

(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



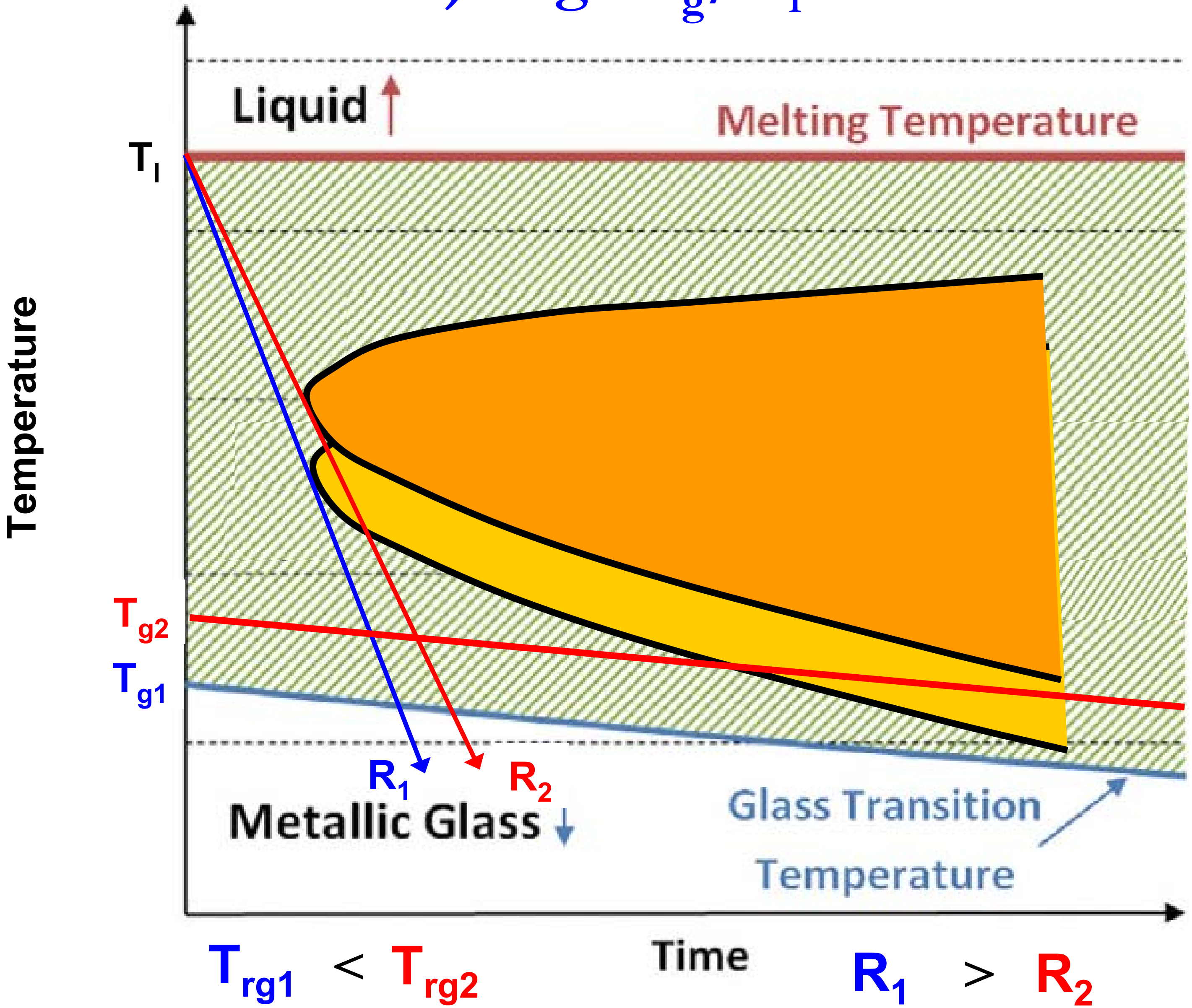
$T_{rgNi} < T_{rgAu4Si} < T_{rgSiO2}$

$R_{Ni} > R_{Au4Si} > R_{SiO2}$

Turnbull, 1959 ff.

Time Temperature Transformation diagram:

4) Trg= T_g / T_l



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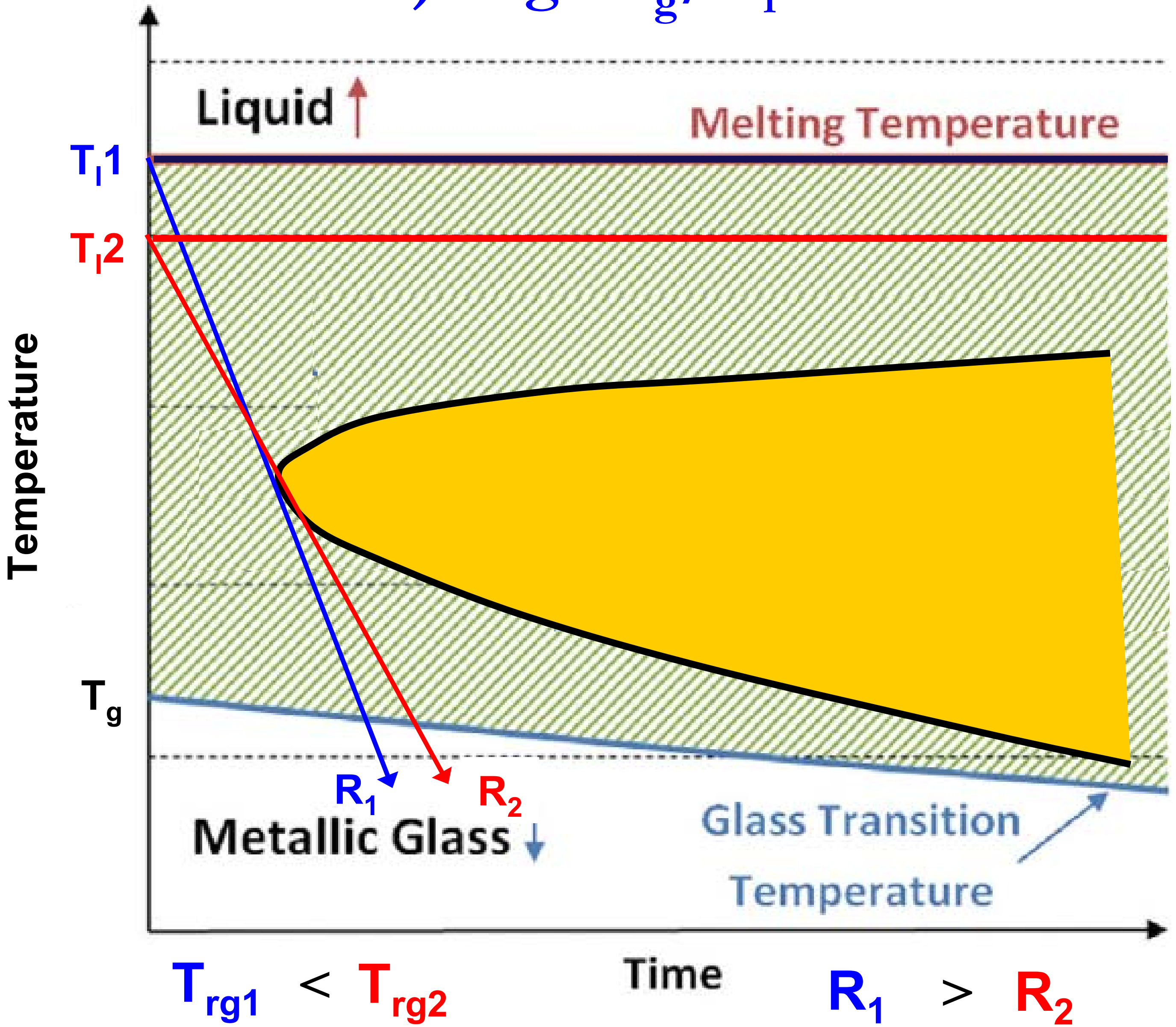

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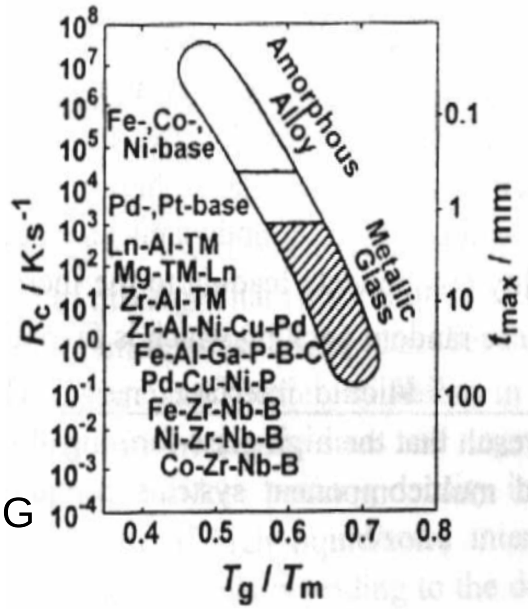

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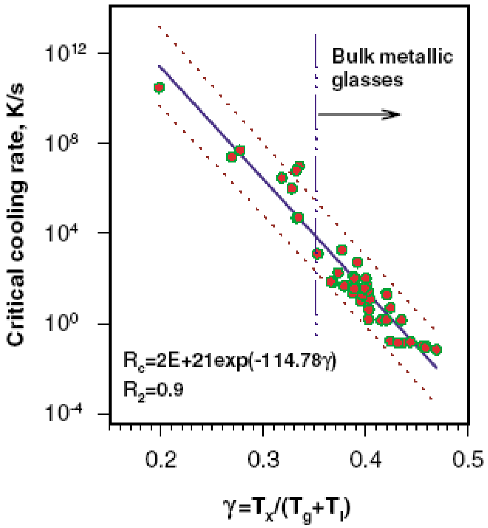
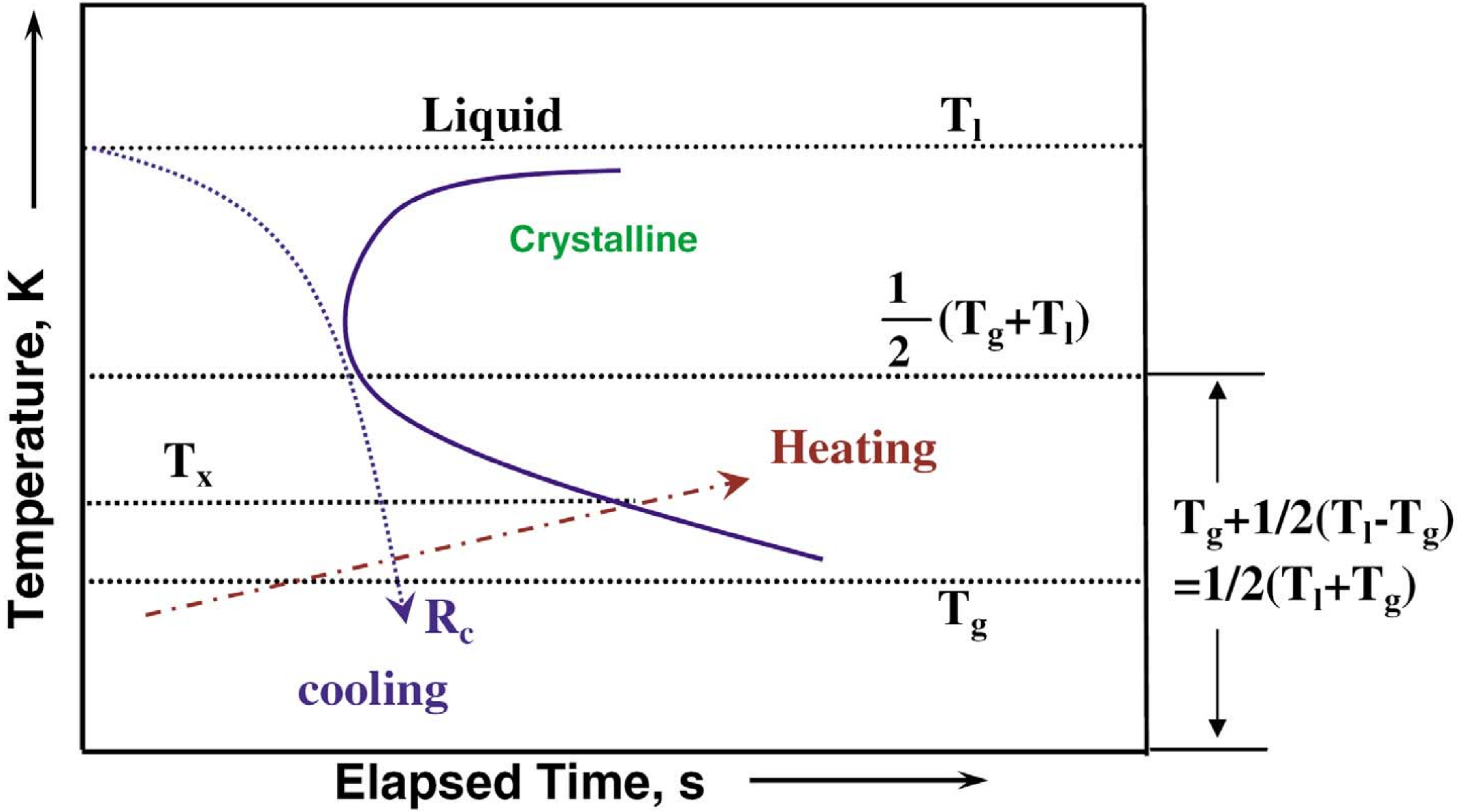


$$\gamma \propto T_x \left[\frac{1}{2(T_g + T_l)} \right] \propto \frac{T_x}{T_g + T_l}$$



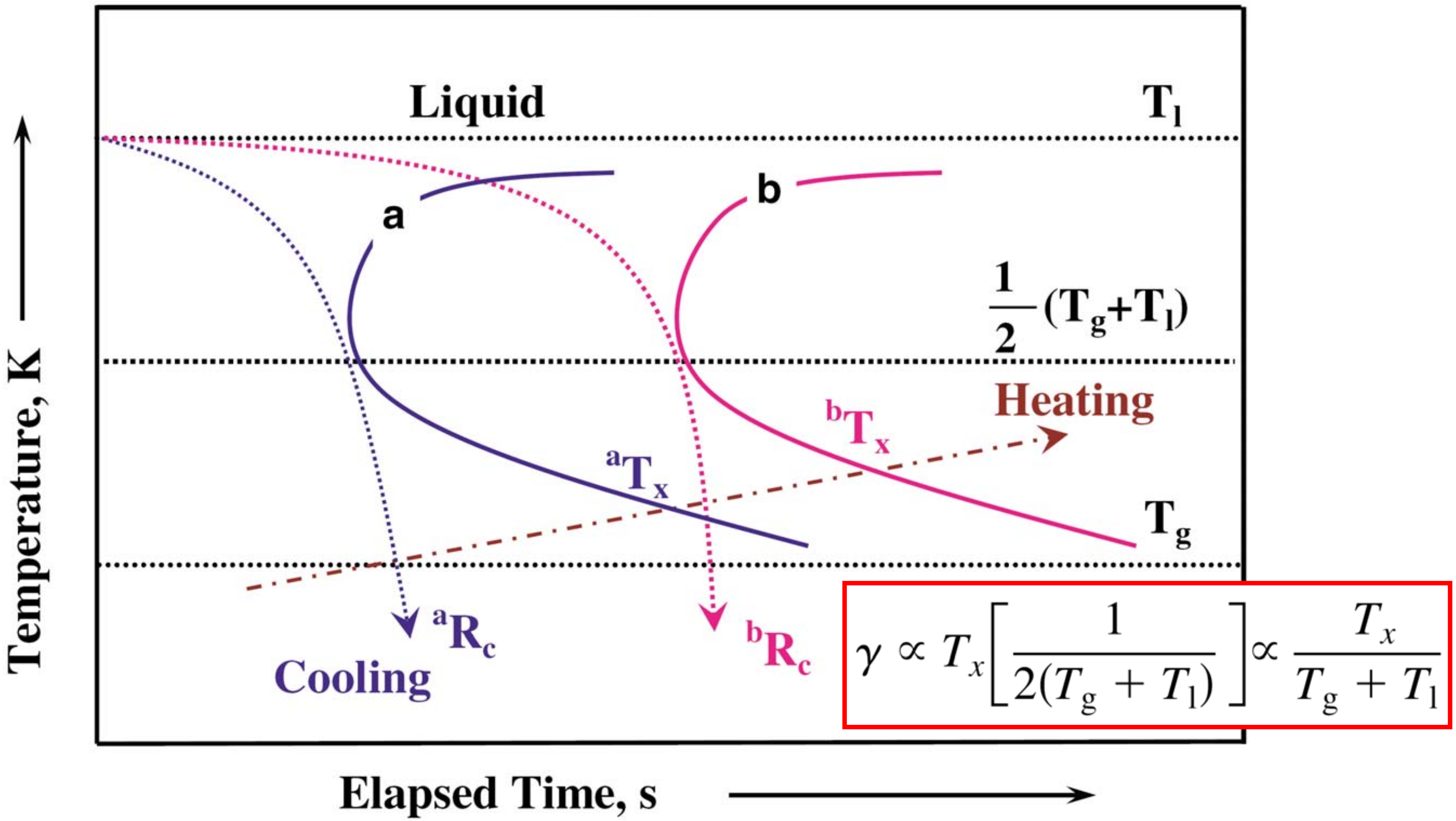
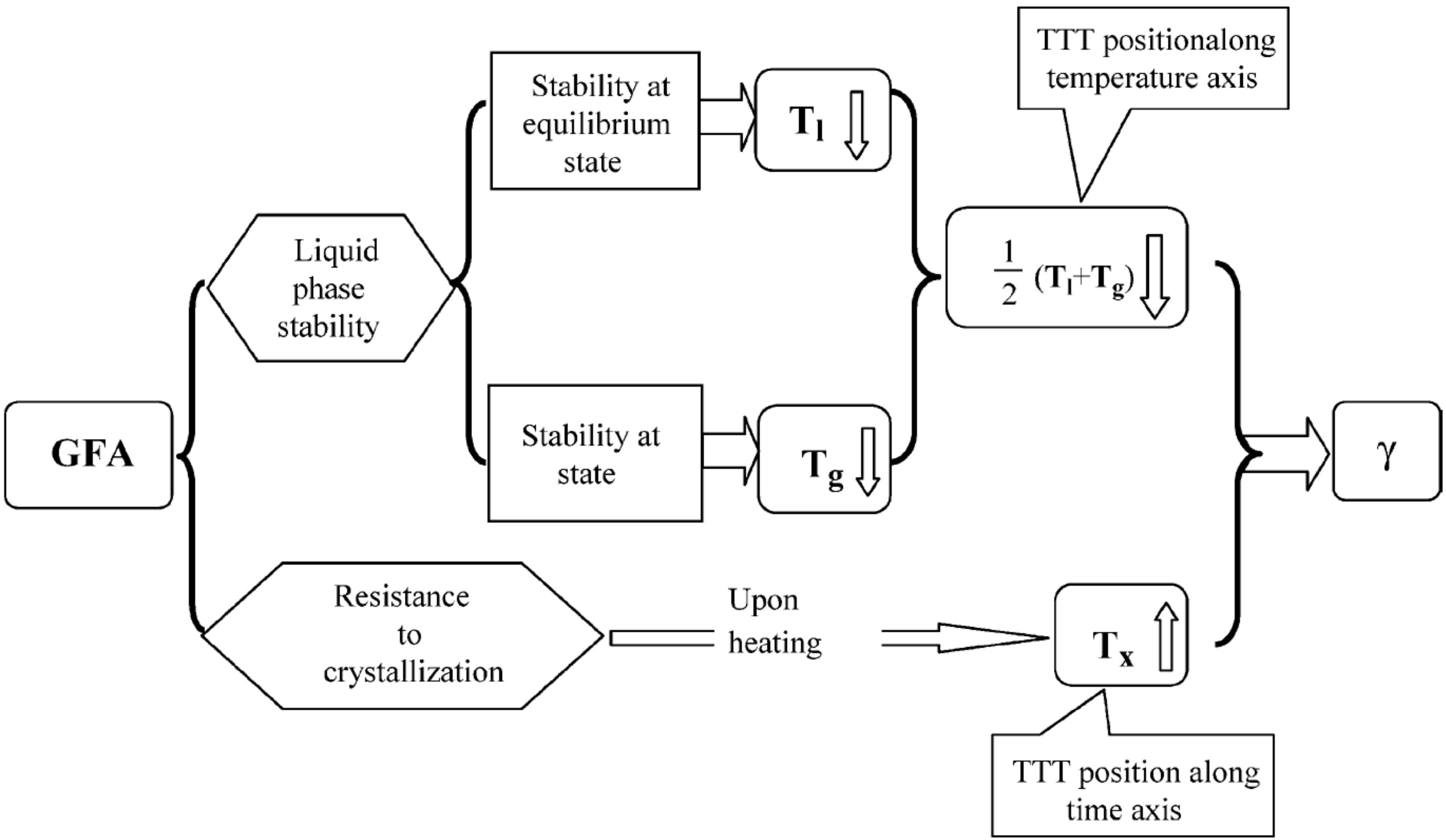


FIG. 2 (color online). Schematic TTT curves showing the effect of T_x measured upon continuous heating for different liquids with similar T_l and T_g; liquid b with higher onset crystallization temperature ${}^bT_x$ (${}^aT_x < {}^bT_x$) shows a lower critical cooling rate ${}^bR_c$ (${}^bR_c < {}^aR_c$).



TTT positionalong temperature axis
Stability at equilibrium state
T_l
GFA
Liquid phase stability
$\frac{1}{2}(T_l+T_g)$
Stability at state
T_g
γ
Resistance to crystallization
Upon heating
T_x
TTT position along time axis