2019 Spring

"Advanced Physical Metallurgy"

- Non-equilibrium Solidification -

10.29.2019

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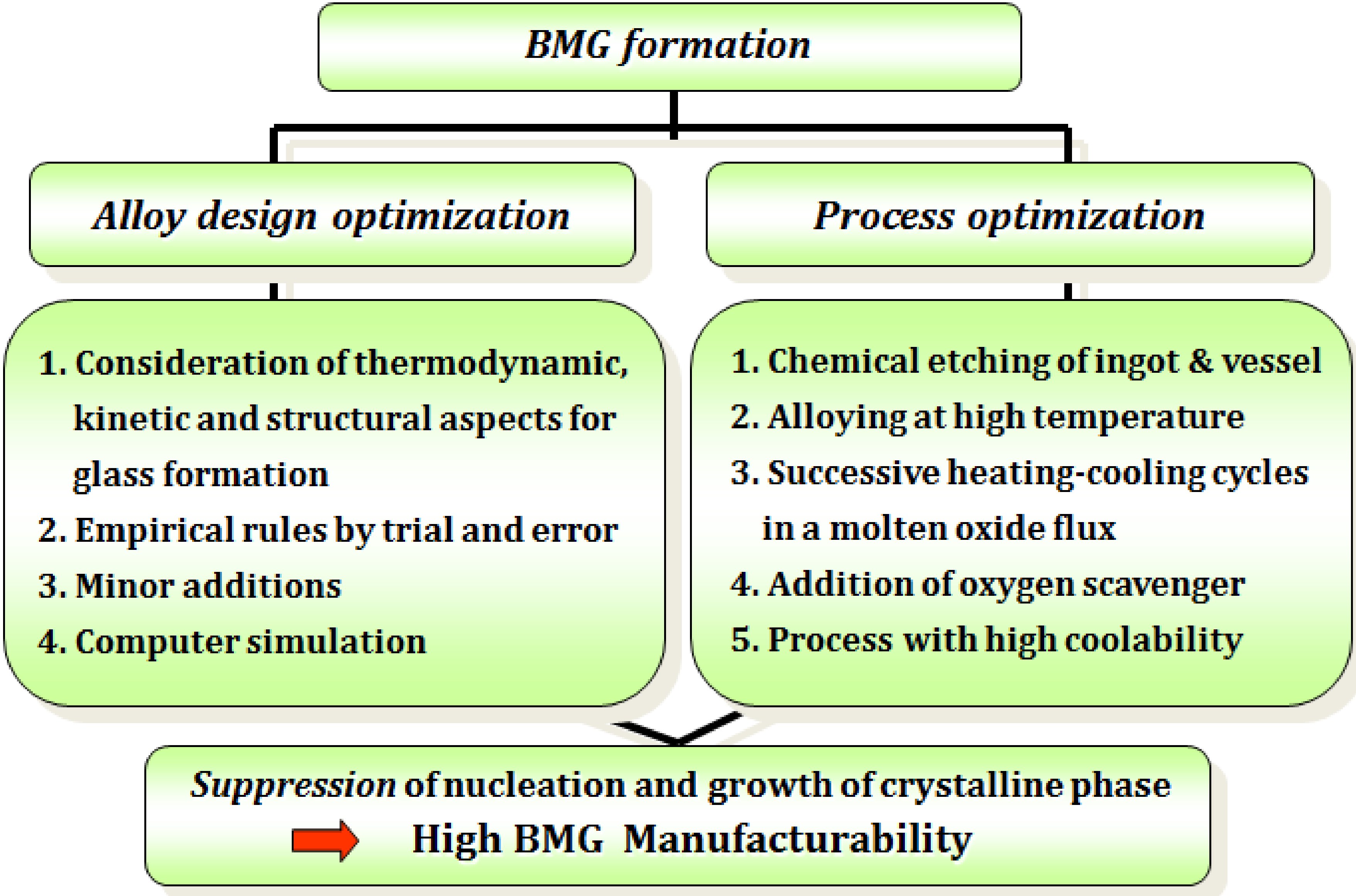
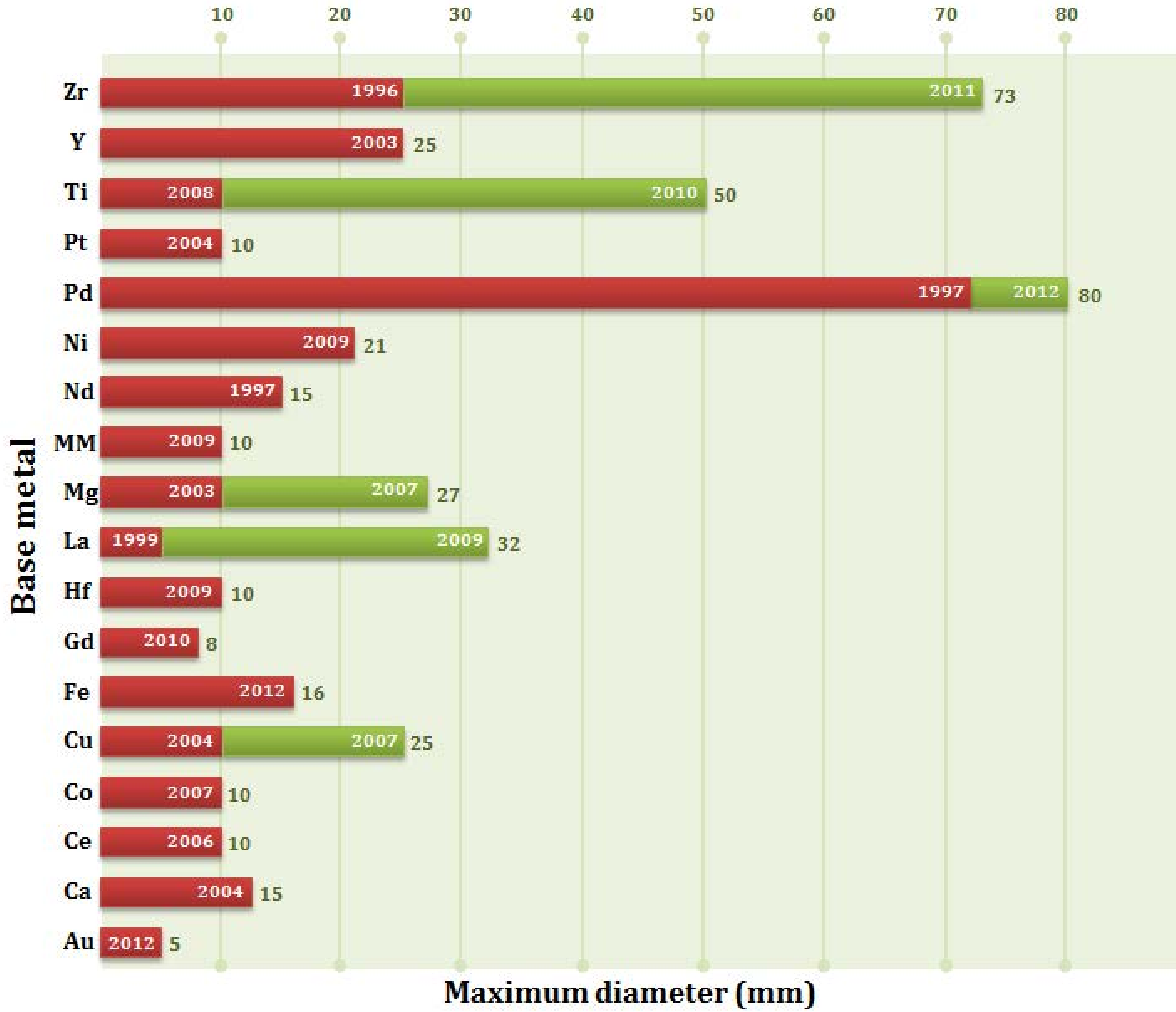
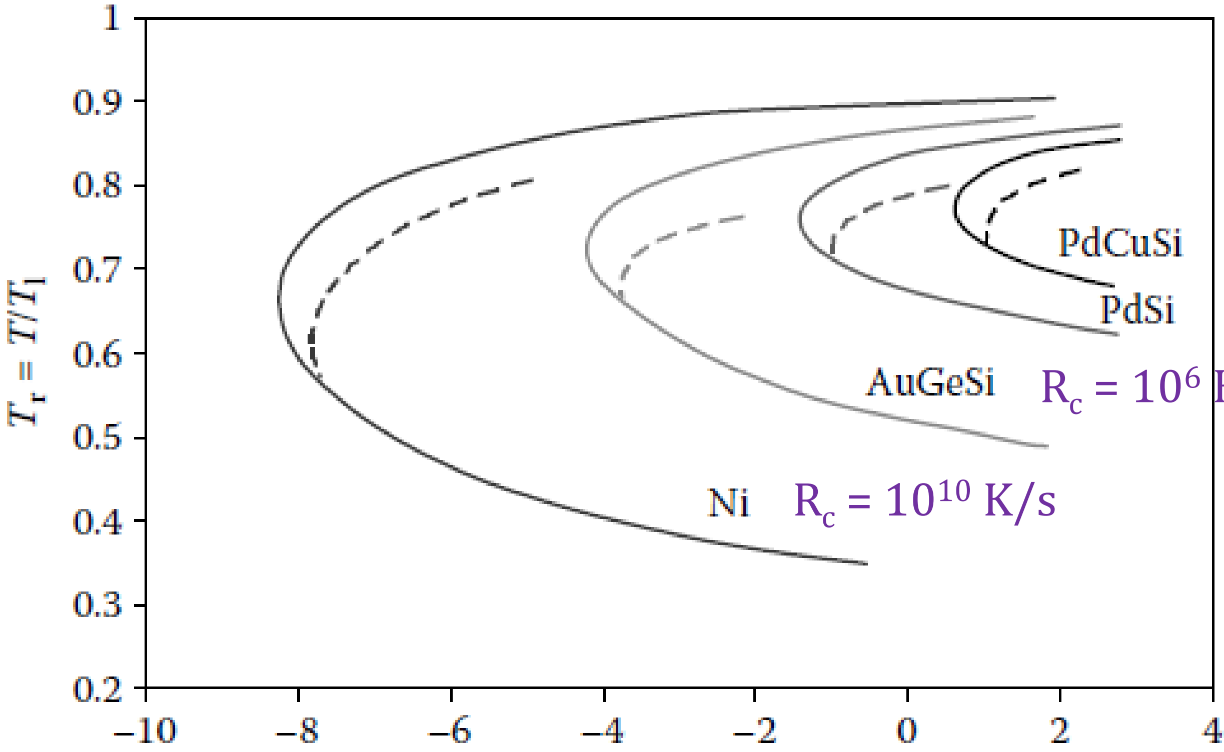

BMG formation
Alloy design optimization
Process optimization
1. Consideration of thermodynamic, kinetic and structural aspects for glass formation
2. Empirical rules by trial and error
3. Minor additions
4. Computer simulation
1. Chemical etching of ingot & vessel
2. Alloying at high temperature
3. Successive heating-cooling cycles in a molten oxide flux
4. Addition of oxygen scavenger
5. Process with high coolability
Suppression of nucleation and growth of crystalline phase
High BMG Manufacturability

Recent BMGs with critical size ≥ 10 mm



3. Glass-Forming Ability of Alloys: R_c

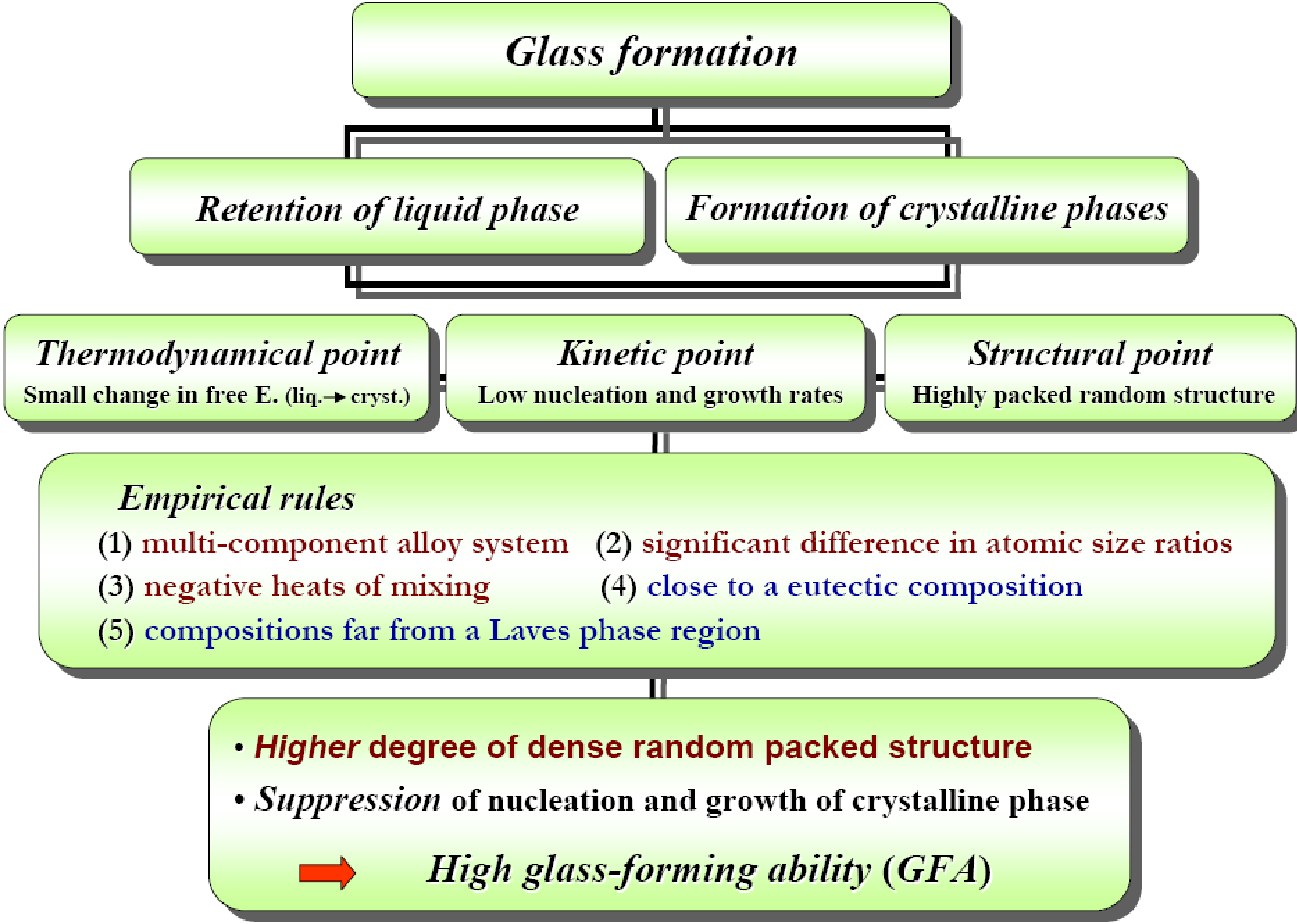
$> 10^{10-12}$ K/s	10^{4-6} K/s	10^2 K/s	1.3×10^{-2} or 0.067 K/s	10^{-5} to 10^{-4} K/s
pure metals	binary metallic liquids	typically multicomponent	$Pd_{37.5}Cu_{32.5}Ni_{10}P_{20}$ $Pd_{30}Pt_{17.5}Cu_{32.5}P_{20}$	Oxide glasses



$$R_c = \frac{\Delta T}{t_n}$$

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 $Au_{78}Ge_{14}Si_8$, $Pd_{82}Si_{18}$, and $Pd_{78}Cu_6Si_{16}$ alloys.

T_{rg}	Ni	$Au_{78}Ge_{14}Si_8$	$Pd_{82}Si_{18}$	$Pd_{78}Cu_6Si_{16}$
		1/4	1/2	2/3


Glass formation
Retention of liquid phase
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Thermodynamical point
Small change in free E. (liq.→ cryst.)
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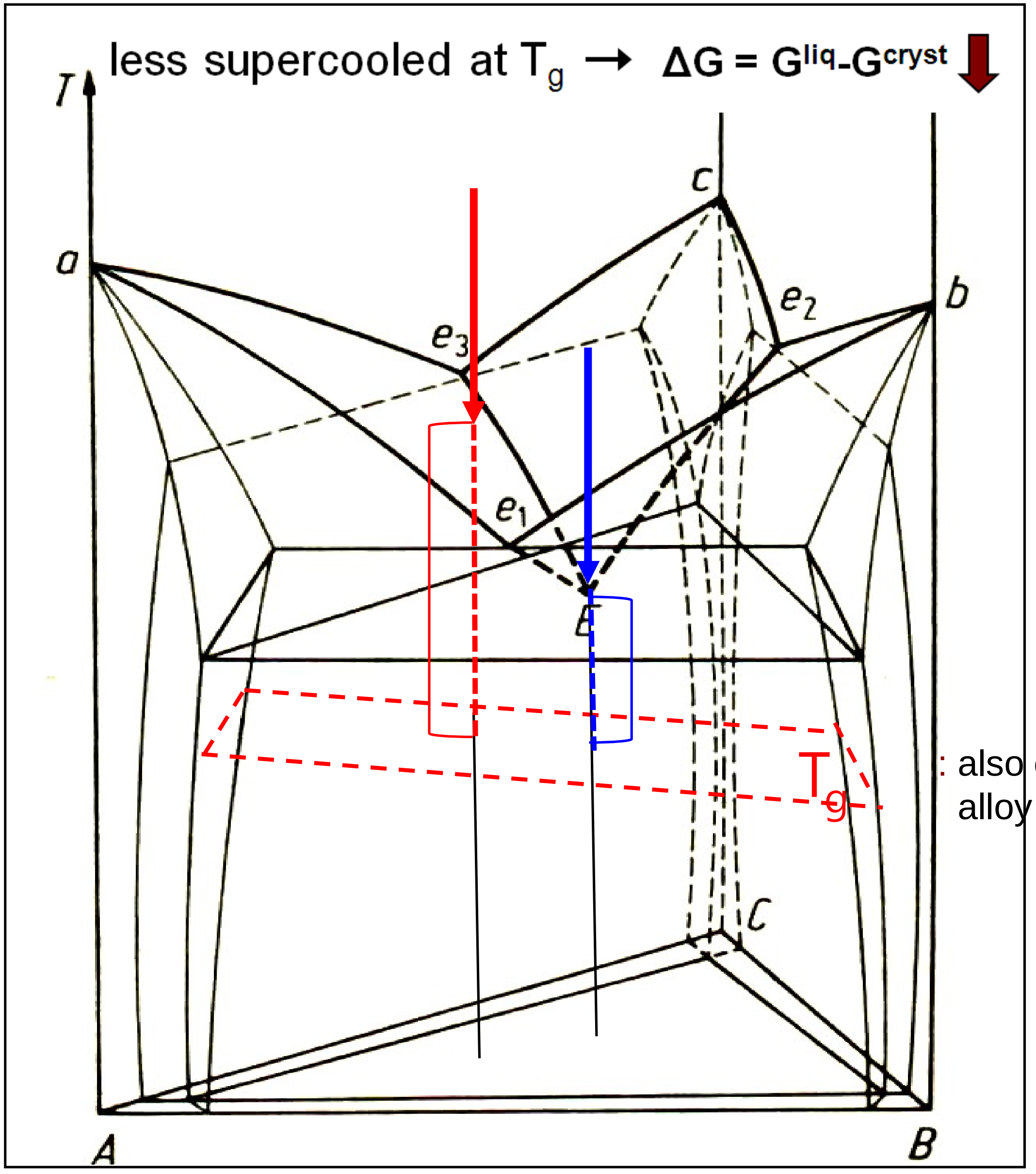
Low nucleation and growth rates
Structural point
Highly packed random structure
Empirical rules
(1) multi-component alloy system
(2) significant difference in atomic size ratios
(3) negative heats of mixing
(4) close to a eutectic composition
(5) compositions far from a Laves phase region
• Higher degree of dense random packed structure
• Suppression of nucleation and growth of crystalline phase
High glass-forming ability (GFA)

Multi-component eutectic alloys with strong negative heat of mixing



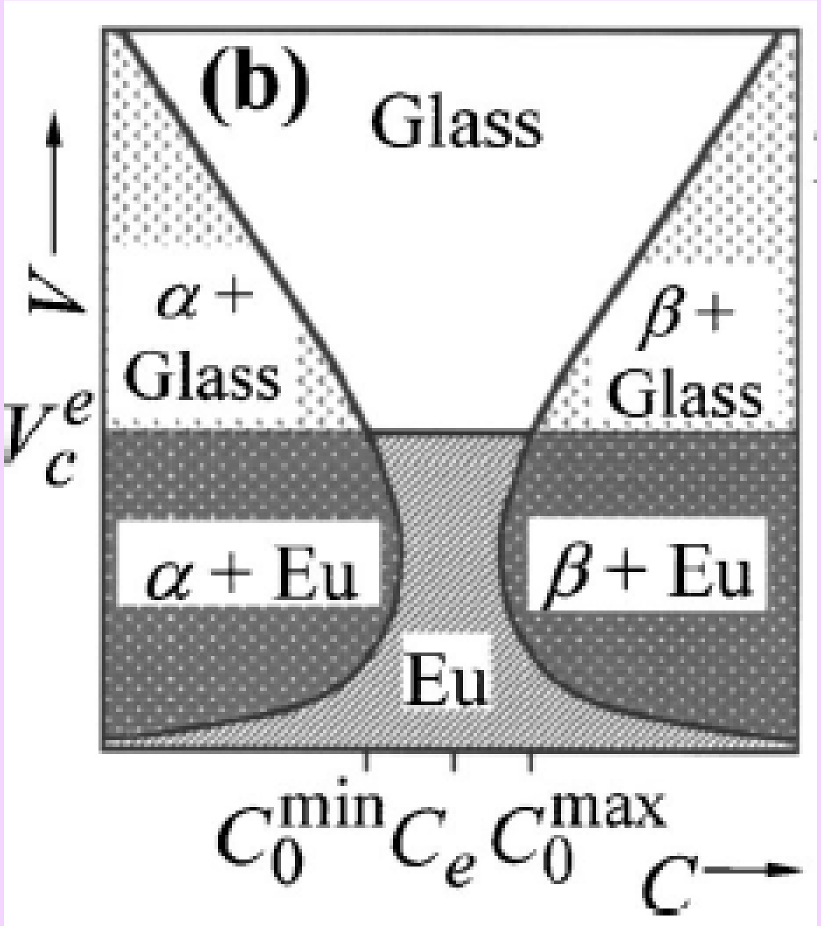
: also changes depending on alloy composition

P. Haasen, Physical Metallurgy 3rd ed

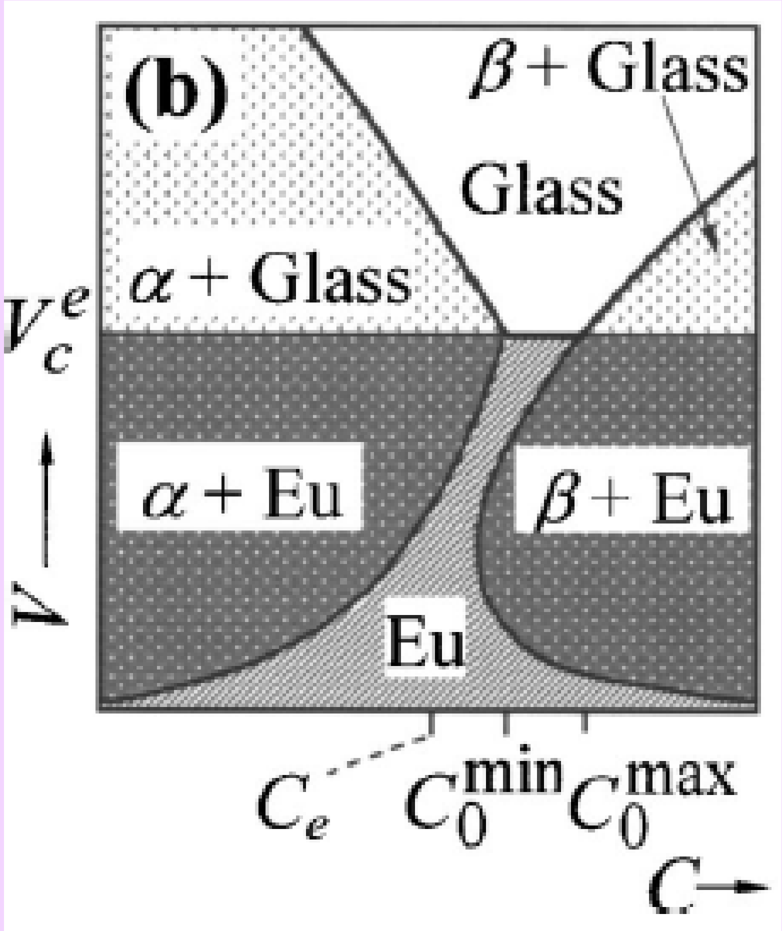
Appl. Phys. Lett., Vol. 84, No. 20, 17 May 2004
Appl. Phys. Lett. 86, 191906 (2005)

Strategy for pinpointing the best glass-forming alloys

< Symmetric Eutectic>



< Non-symmetric Eutectic>



- Glass region is located between composites with different 2nd phases.

⇨ Useful to find the composition with maximum GFA

3.5 Topological Model (Structural aspect for glass formation)

Metallic glasses produced by RSP methods in the form of thin ribbons have been traditionally classified into two groups, viz., metal–metalloid and metal–metal types. Structural models of the metal-metalloid-type metallic glasses have identified that the best composition to form a glass is one that contains about 80 at.% of the metal component and 20 at.% of the metalloid component. The actual glass composition ranges observed are 75–85 at.% of the metal and 15–25 at.% of the metalloid. As stated in Chapter 2, the 80 at.% of the metal can be either a single transition metal or a combination of transition metals or one or a combination of noble metals. Similarly, the 20 at.% of the metalloid content could be made up of just one component or a mixture of a number of components. In the case of metal-metal types, however, there is no such restriction on compositions. Metal-metal-type metallic glasses have been observed to form over a wide range of compositions, starting from as low as 9 at.% of solute. Some typical compositions in which metal-metal type glasses have been obtained are $Cu_{25-72.5}Zr_{27.5-75}$, $Fe_{89-91}Zr_{9-11}$, $Mg_{68-75}Zn_{25-32}$, $Nb_{55}Ir_{45}$, and $Ni_{58-67}Zr_{33-42}$ [65].

* Metallic glass : Randomly dense packed structure

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

→ M is located at interior of the tetrahedron of four metal atoms (TM_4M)

→ 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

Irrespective of the actual size of the voids and whether the above model is valid or not, it is of interest to note that the metal-metalloid-type binary phase diagrams exhibit deep eutectics at around a composition of 15–25 at.% metalloid. Some typical examples are Fe–B (17 at.% B), Au–Si (18.6 at.% Si), and Pd–Si (17.2 at.% Si). Therefore, the concepts of deep eutectics and structural models also seem to converge in obtaining glasses in the (transition or noble) metal-metalloid types.

3.5.2. Egami and Waseda Criterion

One of the possible ways by which a crystalline metallic material can become glassy is by the introduction of lattice strain. The lattice strain introduced disturbs the crystal lattice and once a critical strain is exceeded, the crystal becomes destabilized and becomes glassy. In fact, Egami takes pains to state that "In general, alloying makes glass formation easier, not because alloying stabilizes a glass, but because it destabilizes a crystal" [72, p. 576]. Using the atomic scale elasticity theory, Egami and Waseda [73] calculated the atomic level stresses in the solid solution (the solute atoms are assumed to occupy the substitutional lattice sites in the solid solution) and the glassy phase. They observed that in a glass, neither the local stress fluctuations nor the total strain energy vary much with solute concentration, when normalized with respect to the elastic moduli. But, in a solid solution, the strain energy was observed to increase continuously and linearly with solute content. Thus, beyond a critical solute concentration, the glassy alloy becomes energetically more favorable than the corresponding crystalline lattice. From the vast literature available on the formation of binary metallic glasses obtained by RSP methods, the authors noted that a minimum solute concentration was necessary in a binary alloy system to obtain the stable glassy phase by RSP methods.

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

By Egami & Waseda: in A-B binary system

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

v: atomic volume
A: matrix, B: solute

minimum concentration of B for glass formation

→ Inversely proportional to atomic volume mismatch

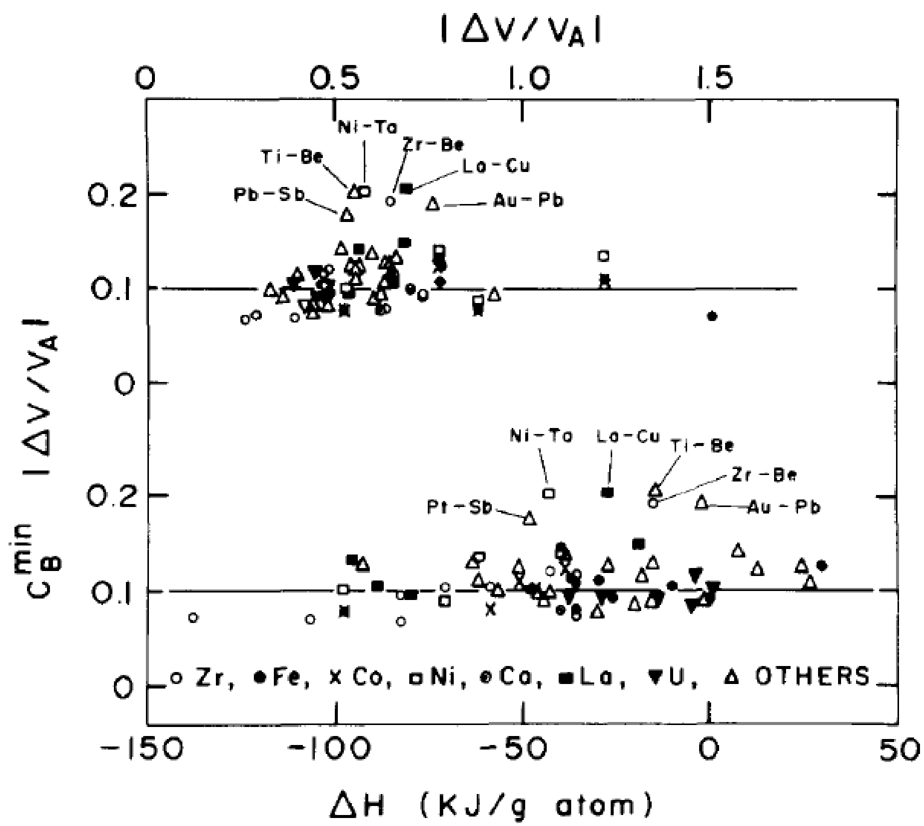


Fig. 1. Relation between $|\lambda_0| = C_B^{\min}\,|\Delta v/v_A|$, and $|\Delta v/v_A|$ and ΔH, for 66 binary systems which can be vitrified by liquid quenching.

3.5.3. Nagel and Tauc Criterion

Nagel and Tauc [74,75] proposed that a glass is most likely to form if its electronic energy lies in a local metastable minimum with respect to composition change. They showed that if the structure factor corresponding to the first strong peak of the diffuse scattering curve, K_p, satisfies the relationship $K_p = 2\,k_F$, where k_F is the wave vector at the Fermi energy, then the electronic energy does indeed occupy a local minimum.

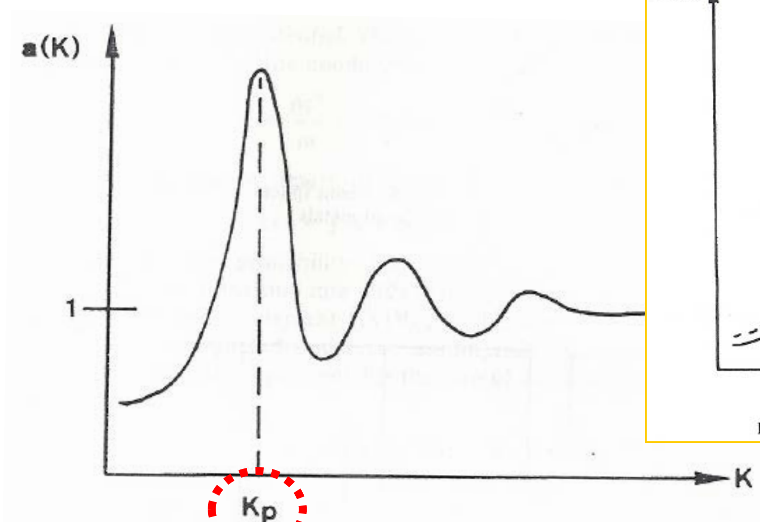


Fig. 7. Schematic structure factor a(K)

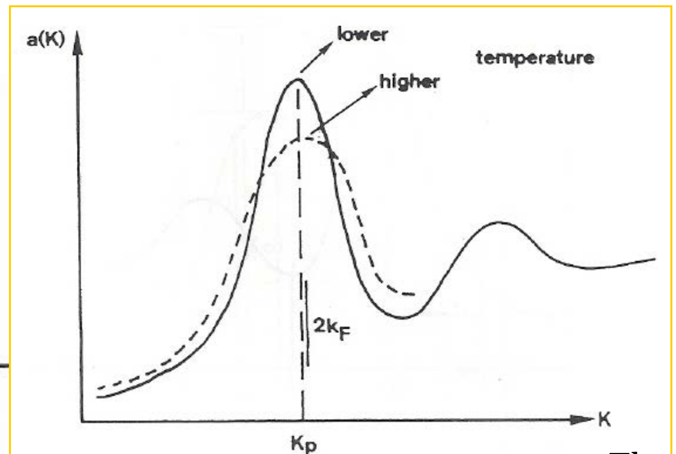
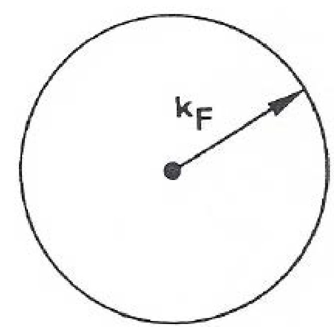


Fig. 11. a(K) versus K for lower and higher temperatures



$Kp = 2\ k_F$

The conduction electrons are suppose to form a degenerate free-electron gas with a spherical Fermi surface.

$$2K_F = 2(3\pi^2 n)^{1/3} = 2\left(\frac{3\pi^2}{eR_H}\right)^{1/3}$$

a(K) Fourier transform of the pair correlation function g(r)

Kp Nearest neighbor distance of the liquid metal in K-space : Diameter of Fermi surface

3.6 Bulk Metallic Glasses

Since 1989, intense research has been carried out in synthesizing and characterizing BMGs with a section thickness or diameter of a few millimeters to a few centimeters.

First, phase diagrams are not available for the multicomponent alloy systems.

Therefore, we do not know where the eutectic compositions lie, and much less about deep eutectics.

Additionally, because the number of components is really large, determining the minimum solute content will be a formidable problem since the contribution of each component to the volumetric strain is going to be different depending on their atomic sizes.

Therefore, newer criteria have been proposed to explain glass formation in BMGs in view of the large number of components present.

3.7 Inoue Criteria – Empirical Rules

1. The alloy must contain at least three components. The formation of glass becomes easier with increasing number of components in the alloy system.

a) Thermodynamic point of view

Since the value of ΔS_f can be significantly increased by increasing the number of components in the alloy, it has been relatively easy to produce BMGs in multicomponent alloys. Since an increase in ΔS_f also leads to an increase in the degree of the dense random packing of atoms, this results in a decrease in ΔH_f and also an increase in the solid–liquid interfacial energy, σ. Both these factors contribute to a decrease in the free energy of the system.

b) Kinetic point of view

Since the equation for homogeneous nucleation rate for the formation of crystalline nuclei from a supercooled melt (Equation 2.4) contains η, α, and β, control of these parameters can lead to a reduction in the nucleation rate. For example, a reduction in ΔH_f, and an increase in σ and/or ΔS_f can be achieved by an increase in α and β values. This, in turn, will decrease the nucleation rate and consequently promote glass formation. An increase in the viscosity of the melt will also lead to a reduction in both nucleation and growth rates.

3.7 Inoue Criteria – Empirical Rules

2. A significant atomic size difference should exist among the constituent elements in the alloy. It is suggested that the atomic size differences should be above about 12% among the main constituent elements.

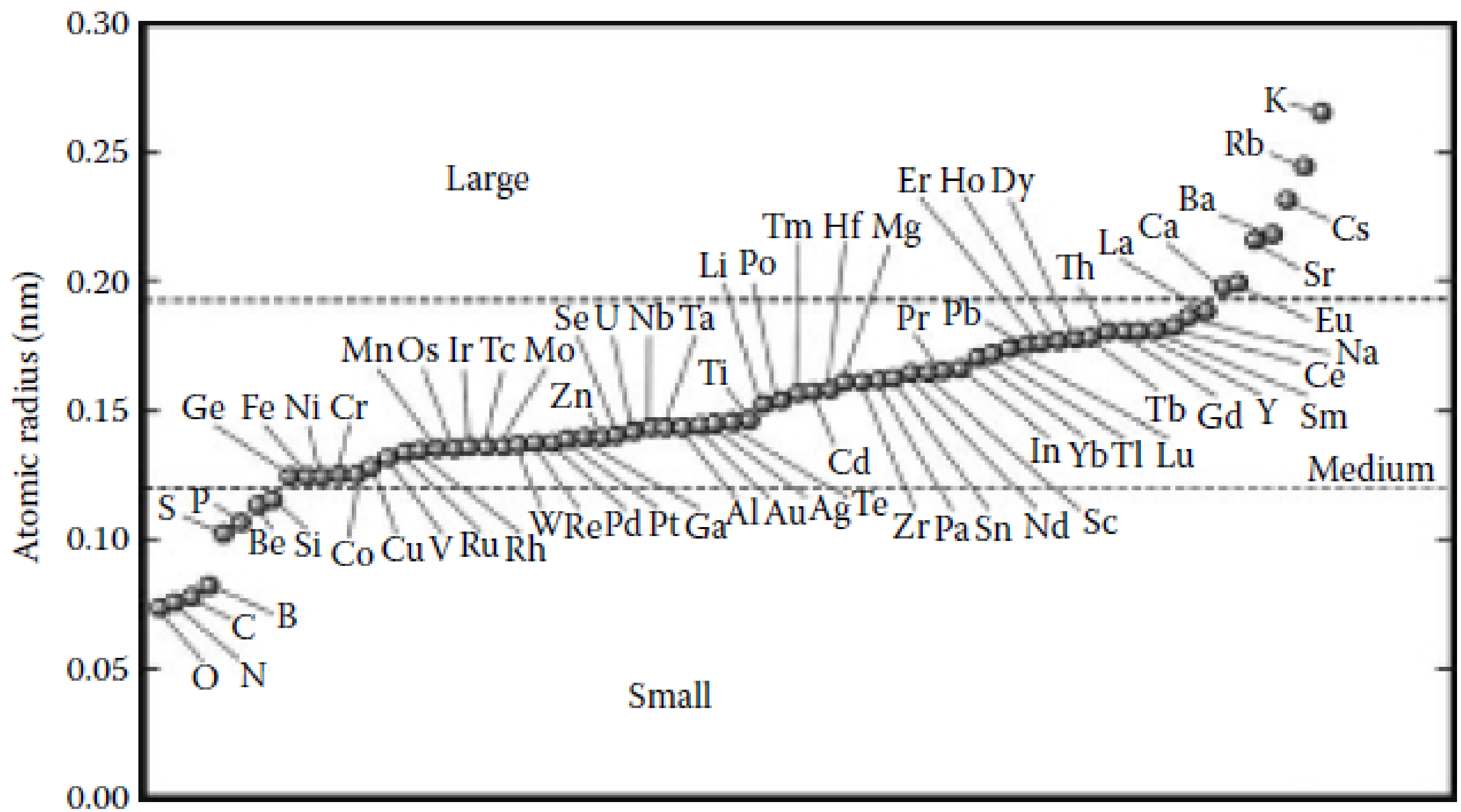
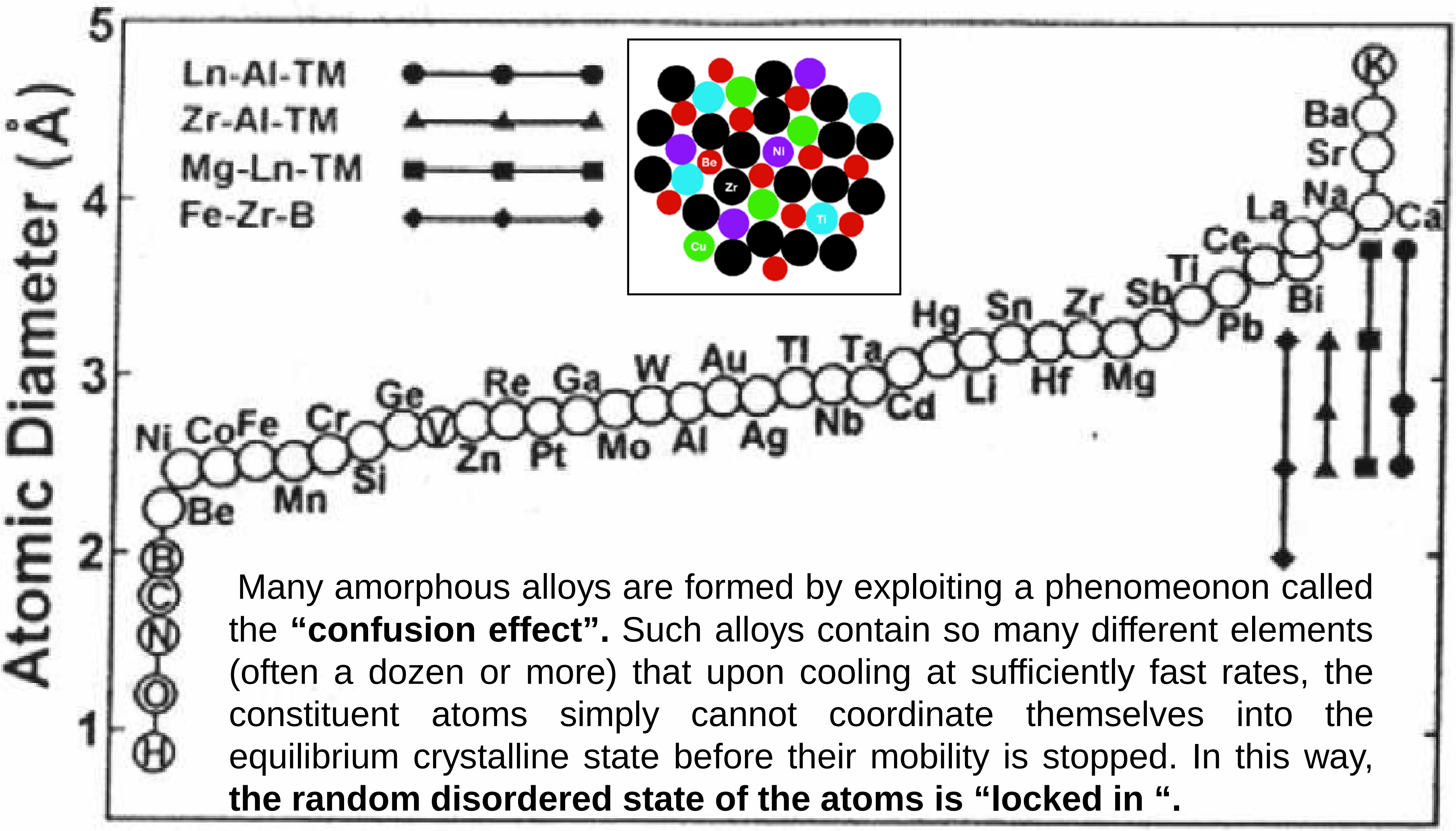


FIGURE 3.4
Atomic diameters of the elements that constitute bulk metallic glasses. These can be classified into three major groups of large, medium, and small sizes.

< significant difference in atomic size ratios >



Many amorphous alloys are formed by exploiting a phenomeonon called the **“confusion effect”.** Such alloys contain so many different elements (often a dozen or more) that upon cooling at sufficiently fast rates, the constituent atoms simply cannot coordinate themselves into the equilibrium crystalline state before their mobility is stopped. In this way, **the random disordered state of the atoms is “locked in “.**

3.7 Inoue Criteria – Empirical Rules

3. There should be negative heat of mixing among the (major) constituent elements in the alloy system.

The combination of the significant differences in atomic sizes between the constituent elements and the negative heat of mixing is expected to result in efficient packing of clusters (see Section 3.12.2) and consequently increase the density of random packing of atoms in the supercooled liquid state. This, in turn, leads to increased liquid–solid interfacial energy, σ and decreased atomic diffusivity, both contributing to enhanced glass formation.

Table 3.3

Nearest Neighbor Distances (r) and Coordination Numbers (N) of the Different Atomic Pairs in a Glassy $Zr_{60}Al_{15}Ni_{25}$ Alloy Both in the As-Quenched and Crystallized States

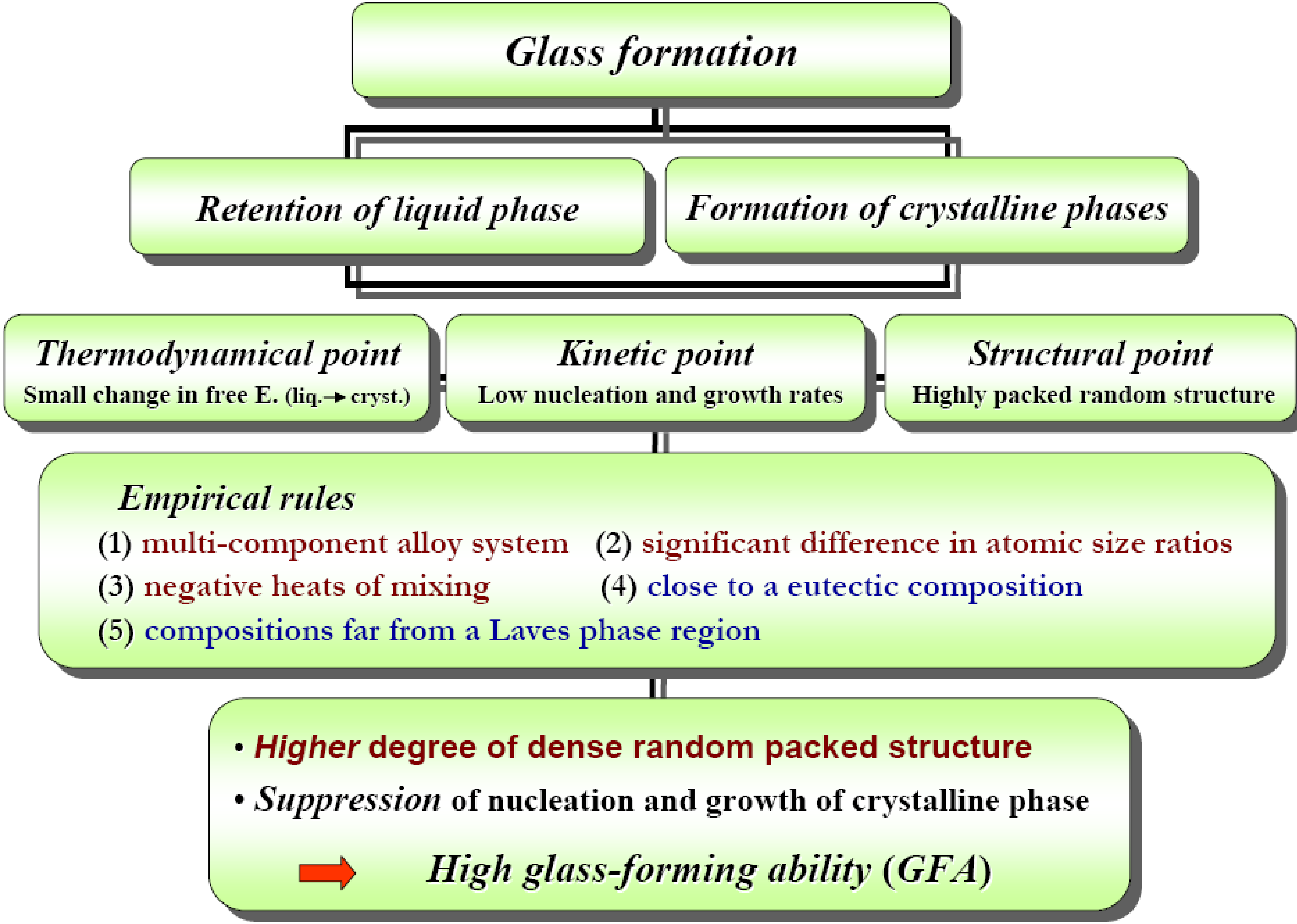
Condition		r_1 (nm)	N_{Zr-Ni}	r_2 (nm)	N_{Zr-Zr}	N_{Zr-Al}
As-quenched	(a)	0.267 ± 0.002	2.3 ± 0.2	0.317 ± 0.002	10.3 ± 0.7	−0.1 ± 0.9
	(b)	0.267 ± 0.002	2.1 ± 0.2	—	—	—
	(c)	0.269 ± 0.002	2.3 ± 0.2	—	—	—
Crystallized	(a)	0.268 ± 0.002	3.0 ± 0.2	0.322 ± 0.002	8.2 ± 0.7	0.8 ± 0.9
	(b)	0.267 ± 0.002	3.0 ± 0.2	—	—	—
	(c)	0.273 ± 0.002	2.3 ± 0.2	—	—	—

Source: Matsubara, E. et al., *Mater. Trans. JIM*, 33, 873, 1992. With permission.
Notes: Data from (a) ordinary radial distribution function (RDF), (b) conventional RDFs for Zr, and (c) conventional RDFs for Ni. "—" means that no values were given in the original publication.

Significant change in the coordination # of Zr-Al atomic pairs on crystallization

→ This suggests that there is necessity for long-range diffusion of Al atoms around Zr atoms during crystallization, which is difficult to achieve due to the presence of dense randomly packed clusters.

The presence of dense randomly packed atomic configurations in the glassy state of BMGs can also be inferred from the small changes in the relative densities of the fully glassy and the corresponding fully crystalline alloys (see Table 6.1). It is noted that the densities of the glassy alloys are lower than those in the crystallized state. The difference between the fully glassy and fully crystalline alloys is typically about 0.5%, but is occasionally as high as 1% (see, for example, Ref. [81]). Further, the density difference between the structurally relaxed and fully glassy states is about 0.11%–0.15%. Thus, the small density differences between the glassy and crystallized conditions suggest that the glassy alloys contain dense randomly packed clusters in them.


Glass formation
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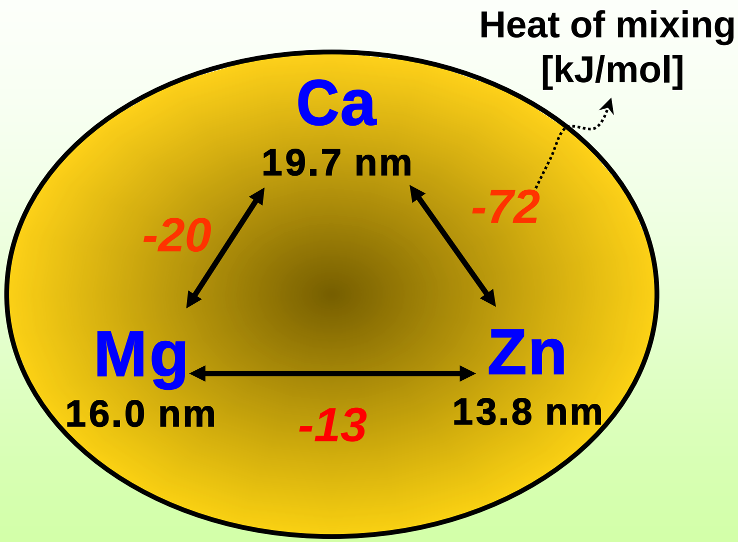
High glass-forming ability (GFA)

Alloy design and new BMG development

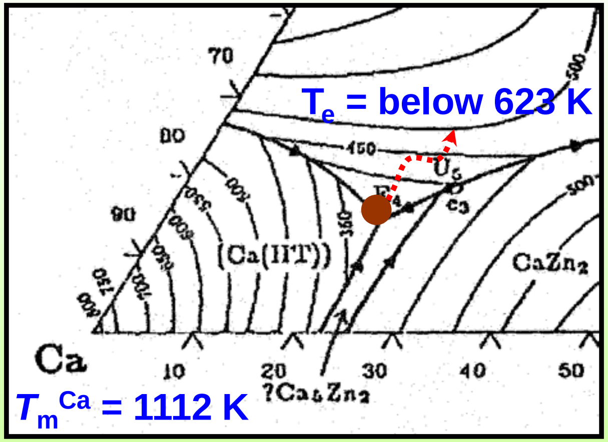
Ca-Mg-Zn alloy system

- Dense packed structure



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

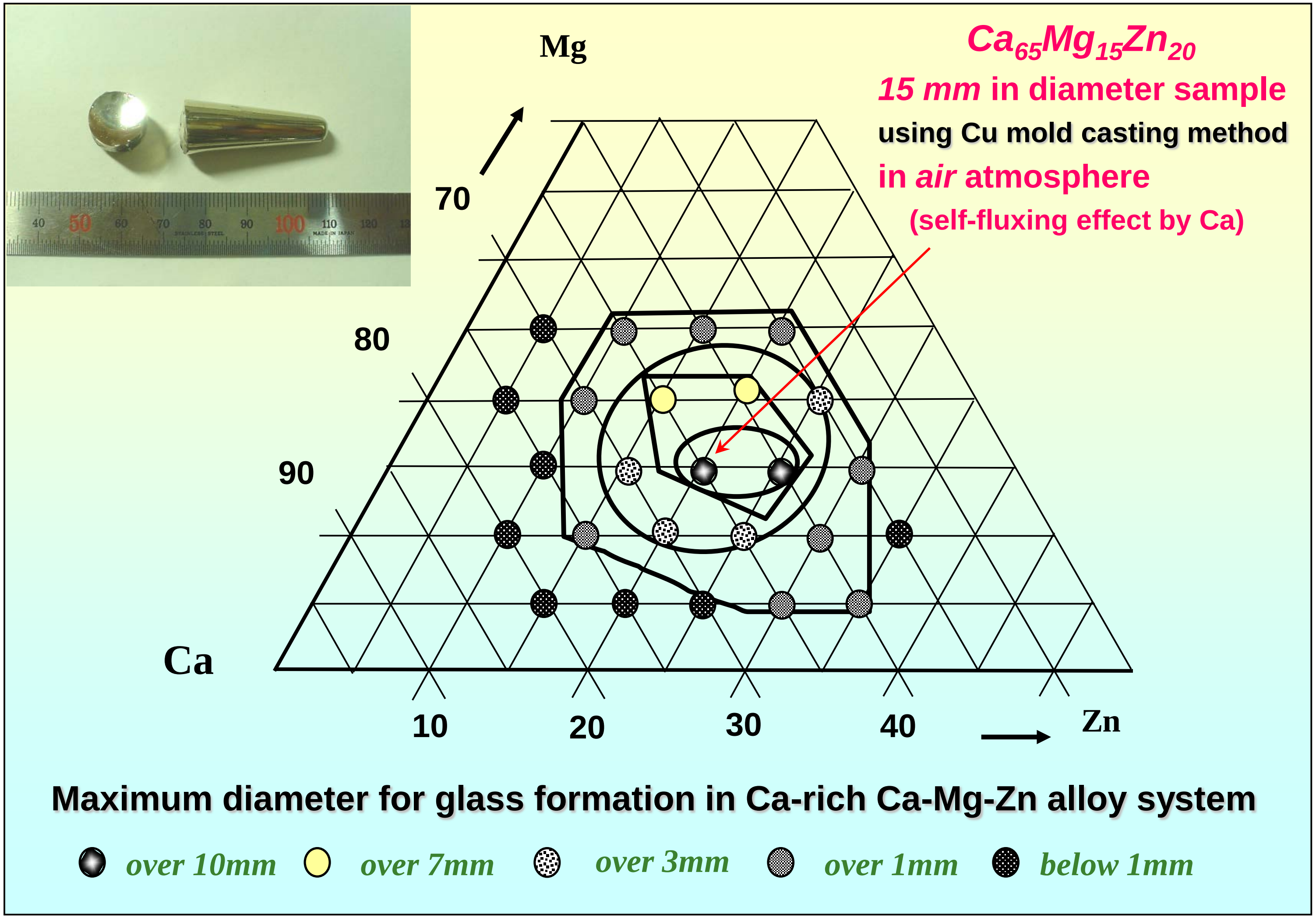
- Decrease of melting temp.



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)

3.8 Exceptions to the Above Criteria

3.8.1 Less Than Three Components in an Alloy System – Binary BMGs

One of the apparent exceptions to this empirical rule appears to be that BMGs have been produced in binary alloy systems such as Ca–Al [59], Cu–Hf [49], Cu–Zr [51], Ni–Nb [37], and Pd–Si [42].

Two important points:

1) The maximum diameter of the glassy rods obtained in these binary alloys is relatively small, i.e. a maximum of only about 2 mm.
2) The "glassy" rods of the binary BMG alloys often seem to contain some nanocrystalline phases. (?)

Even though glassy (BMG) alloys of 1 or 2 mm diameter are produced in binary alloy compositions., their GFA improves dramatically with the addition of a third component. This observation again proves that a minimum of three components is required to produce a BMG alloy with a reasonably large diameter.

Hattori et al. [90] had conducted very careful high-pressure experiments on elemental Zr and Ti using a newly developed in situ angle-dispersive XRD using a two-dimensional detector and x-ray transparent anvils. These authors noted that despite the disappearance of all the Bragg peaks in the one-dimensional energy-dispersive data, two-dimensional angle-dispersive data showed several intense Bragg spots even at the conditions where amorphization was reported in these two metals. This investigation clearly confirms that pure metals cannot be amorphized

3.8.2 Negative Heat of Mixing

Phase separation is generally expected to occur in alloy systems containing elements that exhibit a positive heat of mixing. This is indicated by the presence of a miscibility gap in the corresponding phase diagram. Therefore, if phase separation has occurred, one immediately concludes that the constituent elements have a positive heat of mixing

It has been suggested that it is theoretically possible to observe phase separation in alloy systems containing three or more elements, even though the heat of mixing is negative between any two elements in the alloy system. According to Meijering [94,95], a ternary alloy phase, consisting of components A, B, and C, can decompose into two phases with different compositions even when the enthalpy of mixing between any two components is negative. This is possible when the enthalpy of mixing, ΔH for one of the three possible binary alloy systems is significantly more negative than the others. For example, it is possible that in a ternary alloy system A–B–C, ΔH_{A-B} is much more negative than $\Delta H_{B-C} \approx \Delta H_{A-C}$. This argument suggests that a miscibility gap could be present in a ternary (or higher-order) BMG alloy system even when all the constituent elements have a negative enthalpy of mixing. In other words, phase separation is possible even in an alloy with a reasonably good GFA.

3.9 New Criteria: to develop better and more precise criteria to predict the GFA of alloy systems

All the new criteria that have been proposed in recent years to explain the high GFA of BMGs can be broadly grouped into the following categories:

1. *Transformation temperatures of glasses*. In this group, the GFA is explained on the basis of the characteristic transformation temperatures of the glasses such as T_g, T_x, and T_l, and the different combinations of these three parameters.

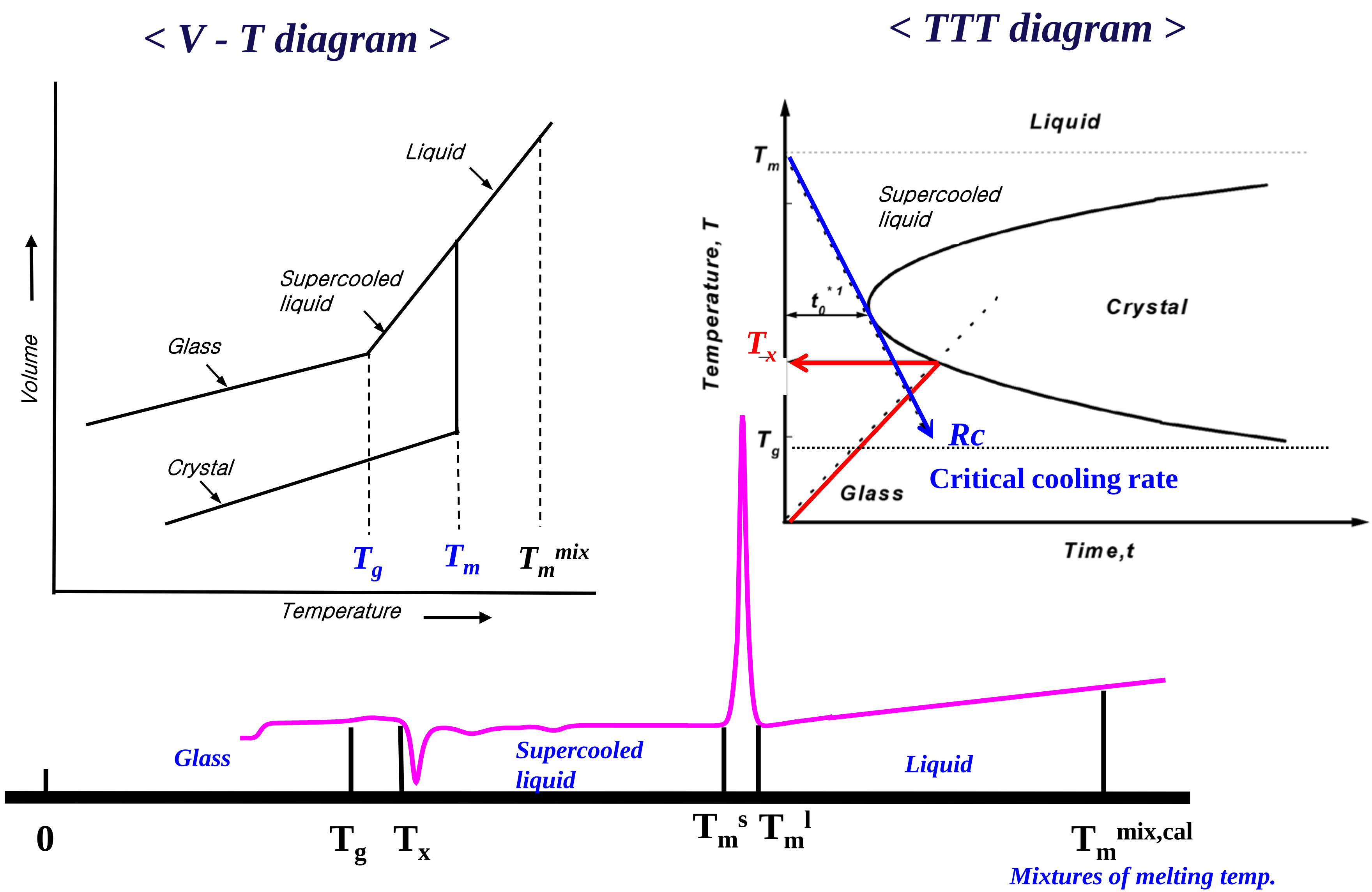
2. *Thermodynamic modeling*. Thermodynamic parameters such as heat of mixing are used in this group to predict the glass formation and evaluate GFA in a given alloy system.

3. *Structural and topological parameters*. In this group, consideration is given to the atomic sizes of the constituent elements, their electronegativity, electron-to-atom ratio, heat of mixing, etc. Majority of the work in this area has been due to Egami [107] and Miracle [108,109].

4. *Physical properties of alloys*. This group considers the physical properties of materials such as the viscosity of the melt, heat capacity, activation energies for glass formation and crystallization, bulk modulus, etc.

5. *Computational approaches*. These methods help in predicting the GFA of alloys from basic thermodynamic data [110,111], and without the necessity of actually conducting any experiments to synthesize the glass and determine the GFA.

3.10 Transformation Temperatures of Glasses



Representative GFA Parameters

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)

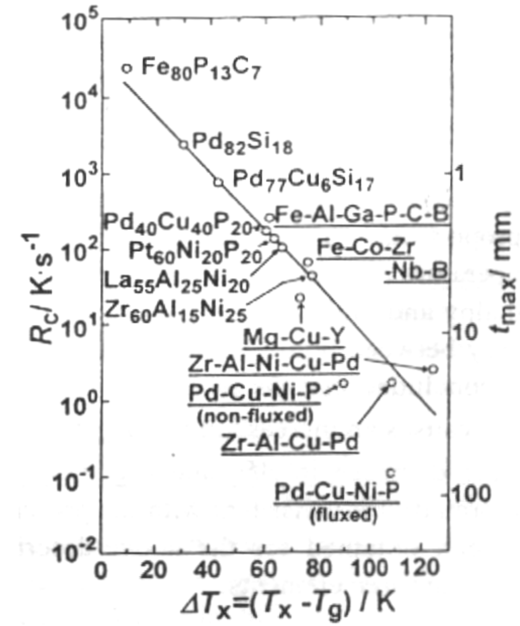
Based on thermodynamic and atomic configuration aspects

$\sigma = \Delta T^* \times P'$ — 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

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

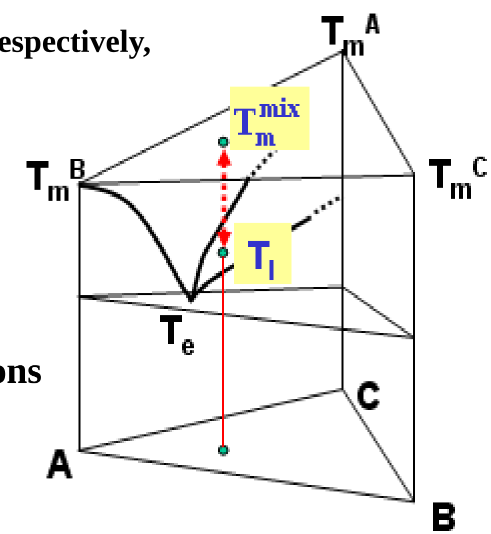
2) K parameter = $(T_x-T_g)/(T_l-T_x) = \Delta T_x/(T_l-T_x)$

- 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.)

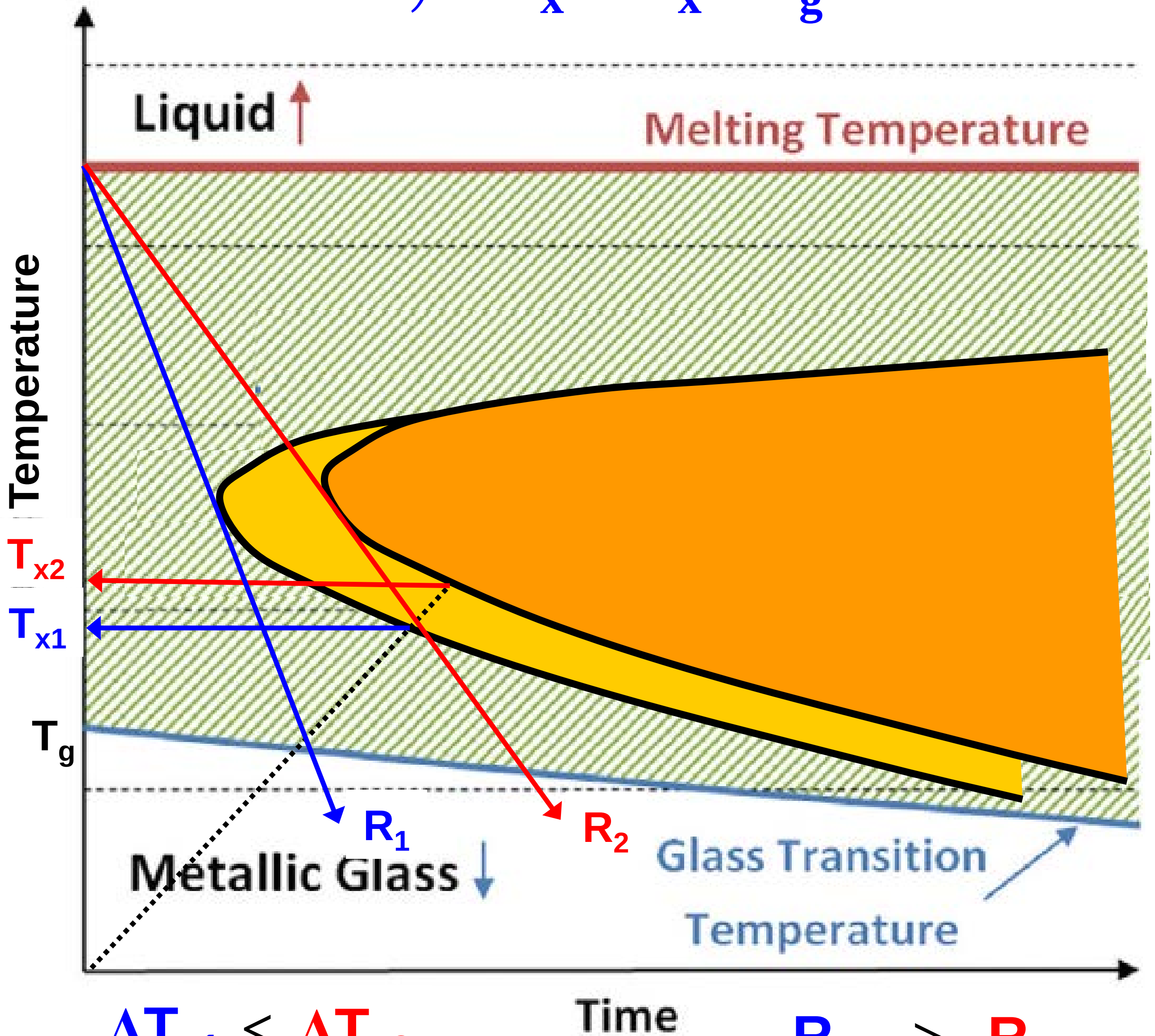


- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA

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

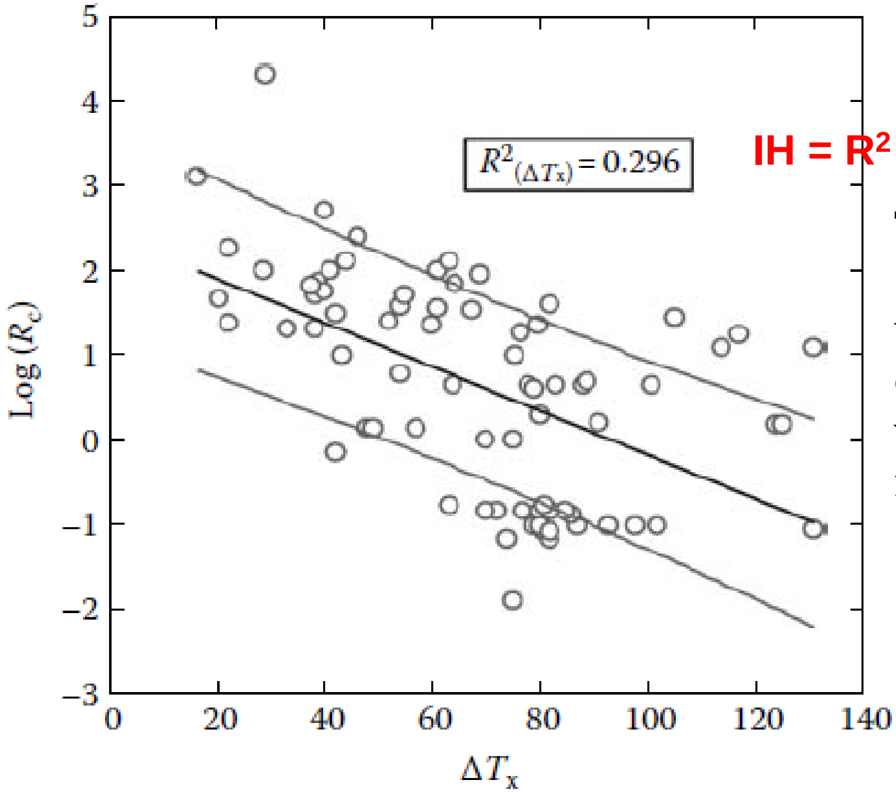
Time Temperature Transformation diagram:

1) $\Delta T_x = T_x - T_g$



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

From the above discussion, it is clear that the description of the GFA of alloys using the ΔT_x parameter as a criterion has not been found universally applicable in all situations and for all alloy systems. Some exceptions have been certainly noted. But, it should, however, be emphasized in this context that this was one of the most successful parameters in the early years of research on BMGs.

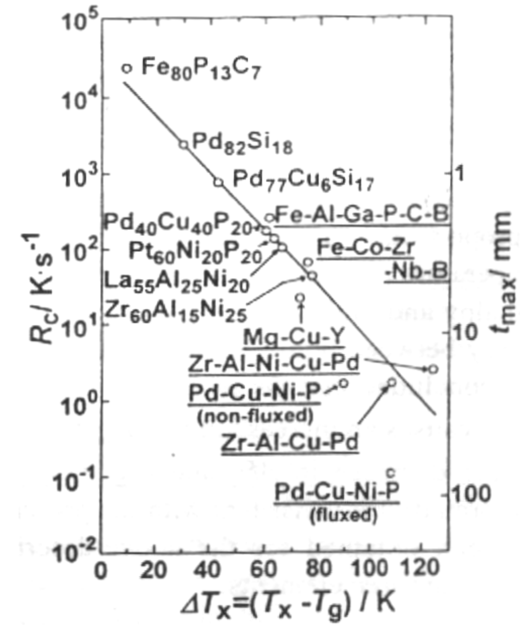


IH = R^2 : regression coefficient

The R^2 vale can range from 0 to 1 and is an indicator of the reliability of the correlation. The higher R^2 value, the more reliable the regression is.

FIGURE 3.5
Variation of the critical cooling rate, R_c with the width of the supercooled liquid region, ΔT_x for a number of multicomponent bulk metallic glasses. Data for some of the binary and ternary metallic glasses reported earlier are also included for comparison.

GFA Parameters on the basis of thermodynamic or kinetic aspects :



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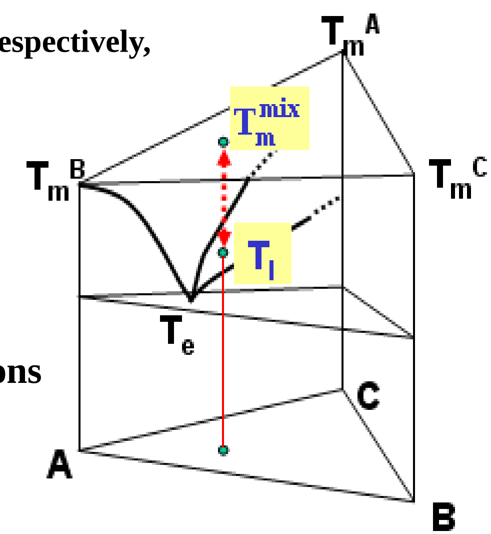
- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

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.)

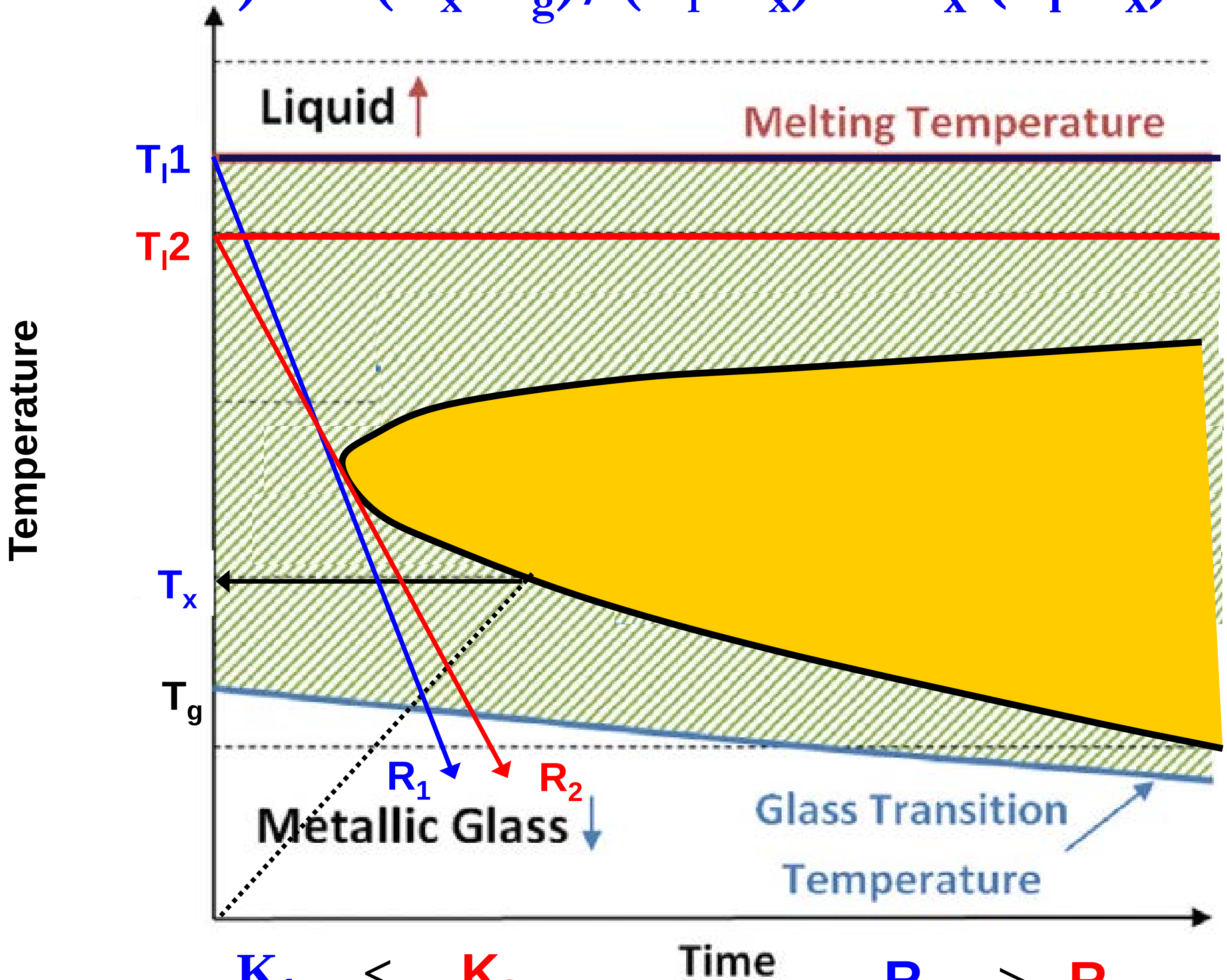


- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA

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

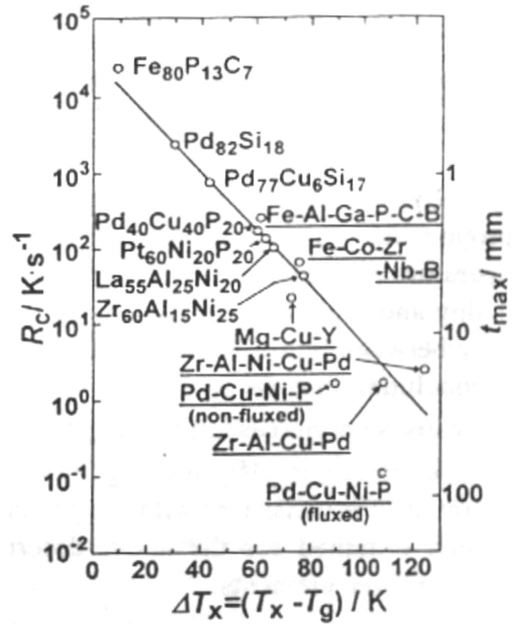
Time Temperature Transformation diagram:

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



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

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 = $(T_x-T_g)/(T_l-T_x) = \Delta T_x/(T_l-T_x)$

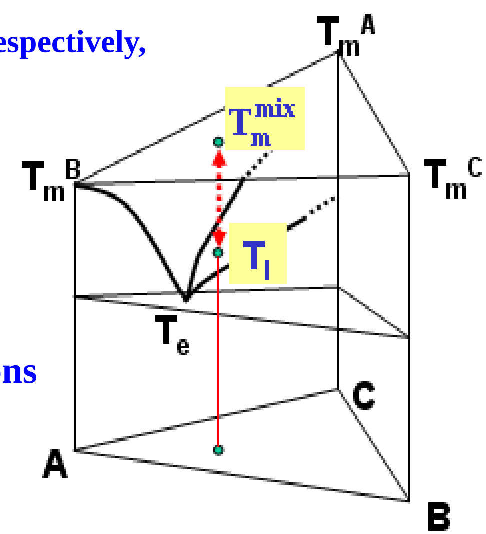
- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

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

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}

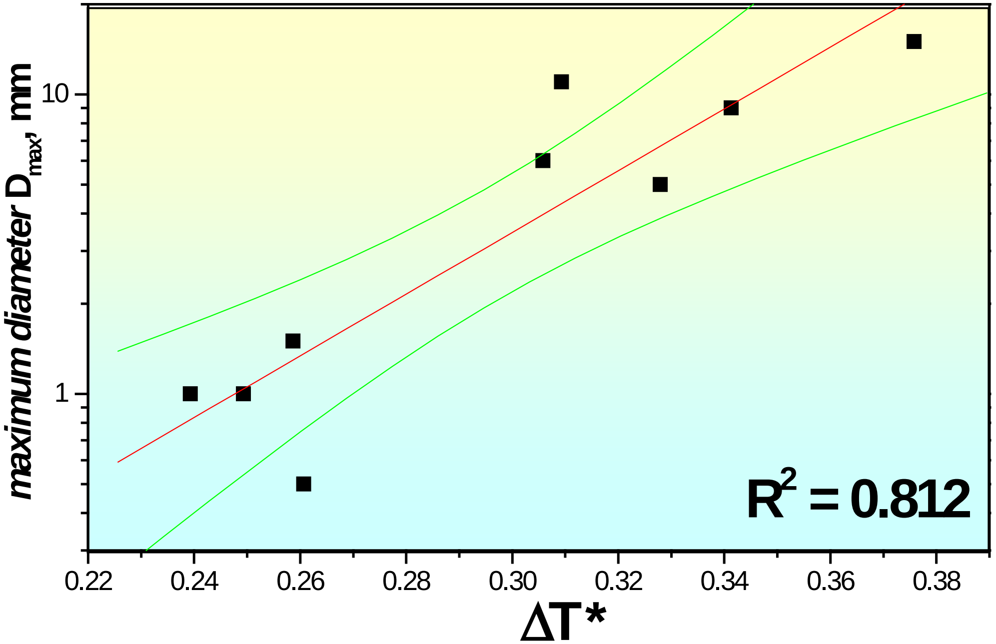
$$\Delta T^* = \frac{T_m^{mix} - T_l}{T_m^{mix}}$$

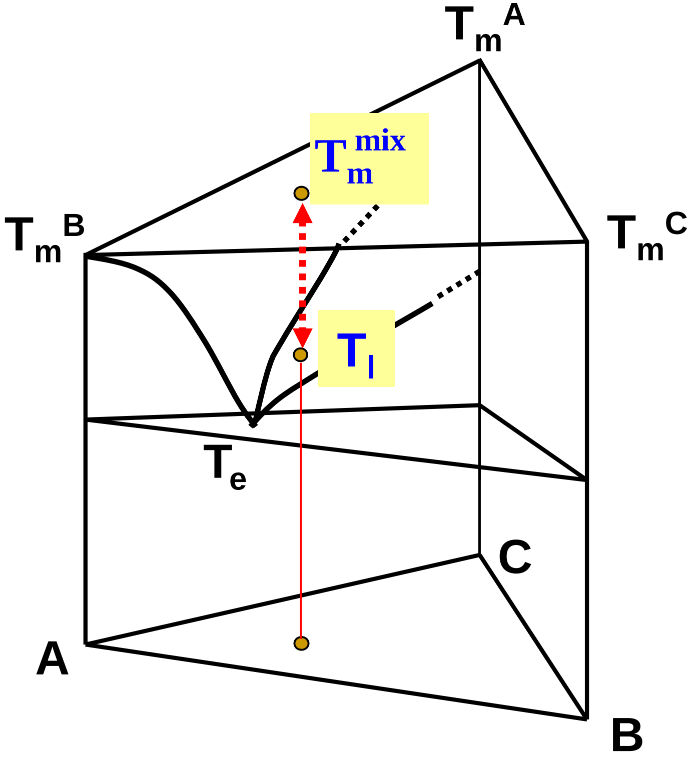
(where, $T_m^{mix} = \sum x_i T_m^i$, x_i = molefraction, T_m^i = melting point)

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

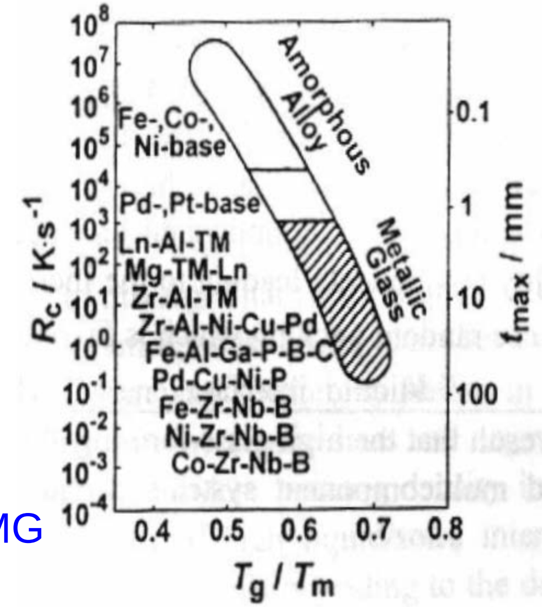




GFA Parameters on the basis of thermodynamic or kinetic aspects :

4) T_{rg} parameter = T_g/T_l

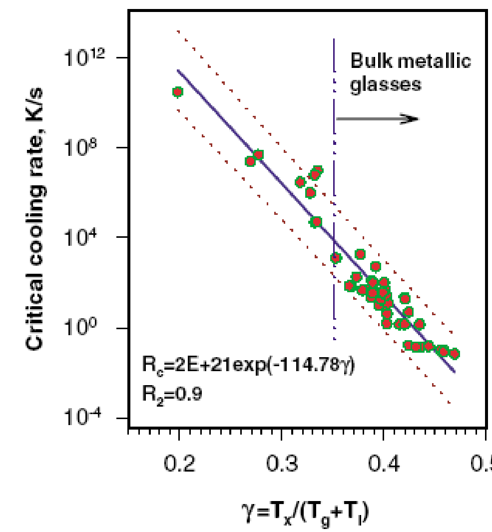
- kinetic approach to avoid crystallization before glass formation
- Viscosity at T_g being constant, the higher the ratio T_g/T_l, the higher will be the viscosity at the nose of the CCT curves, and hence the smaller R_c
- T_l ↓and T_g ↑ ► lower nucleation and growth rate ► GFA ↑



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

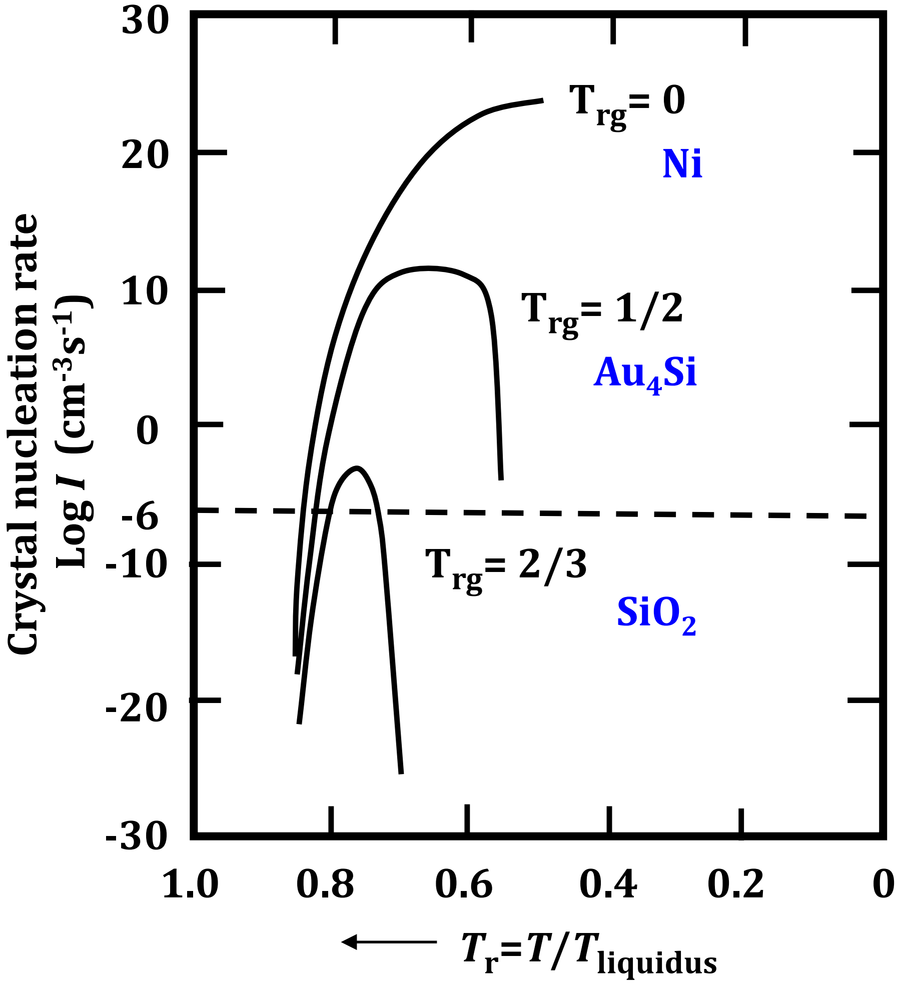
5) γ parameter = T_x / (T_l + T_g)

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



T_{rg} **parameter** $= T_g/T_l \sim \eta$ **: the higher T_{rg}, the higher η, the lower R_c**

: ability to avoid crystallization during cooling



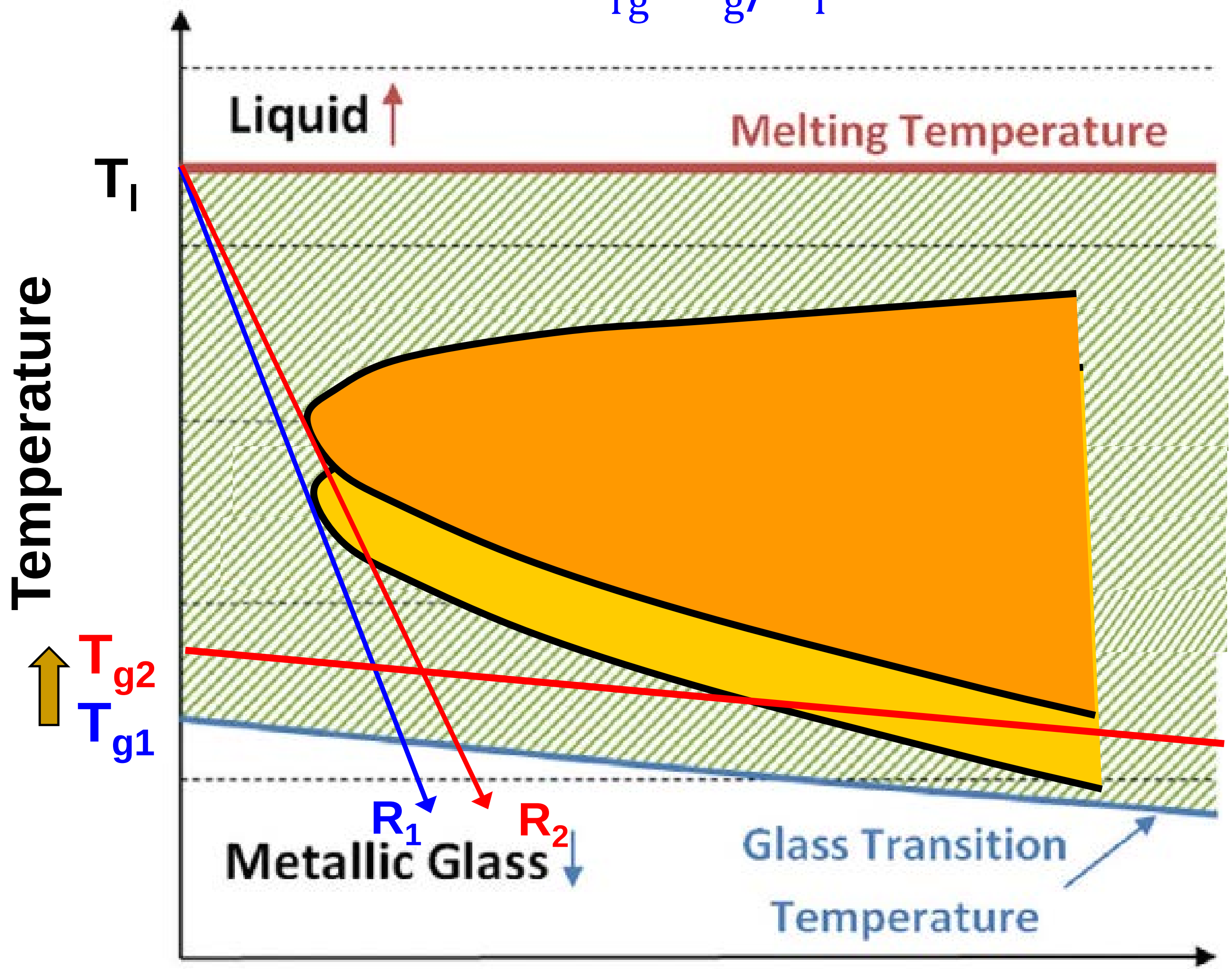
$$T_{rgNi} < T_{rgAu4Si} < T_{rgSiO2}$$

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

Turnbull, 1959 ff.

Time Temperature Transformation diagram:

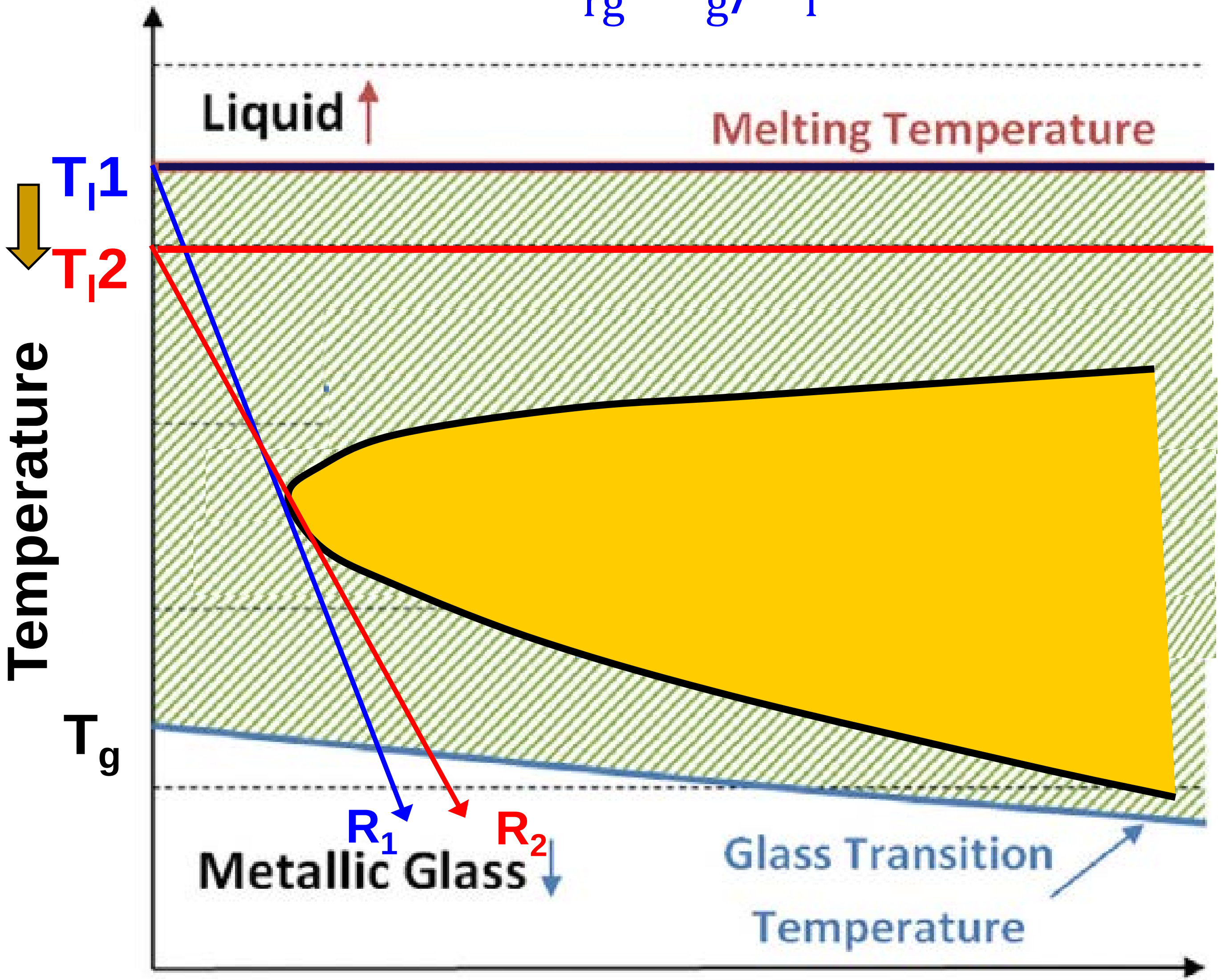
$T_{rg} = T_g / T_l$



$T_{rg1} < T_{rg2}$ $R_1 > R_2$

Time Temperature Transformation diagram:

$$T_{rg} = T_g / T_l$$



T_{rg1} < T_{rg2} R_1 > R_2

GFA Parameters on the basis of thermodynamic or kinetic aspects :

4) T_{rg} parameter = T_g/T_l

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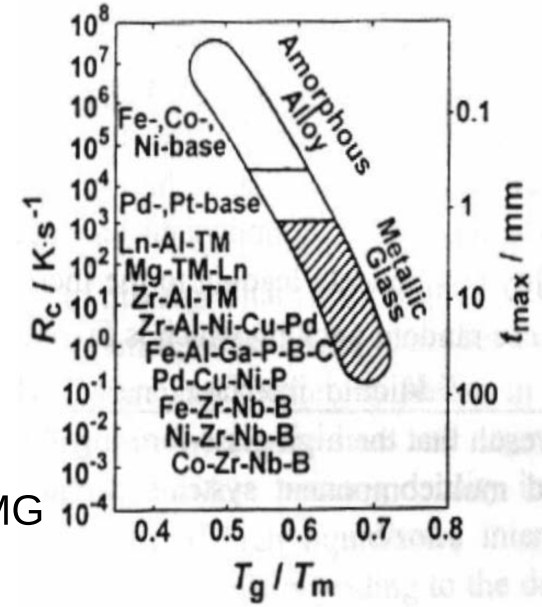
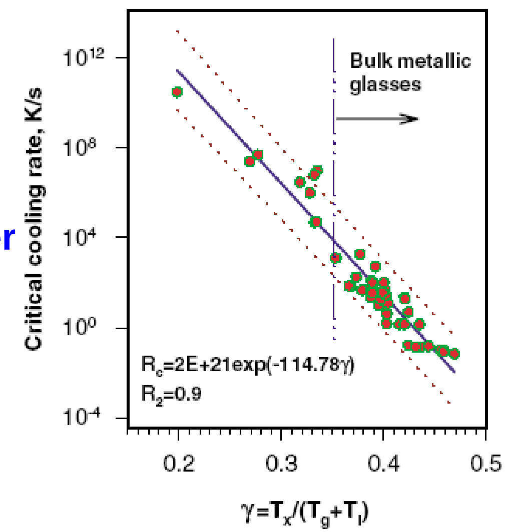
- T_l ↓and T_g ↑ ► lower nucleation and growth rate ► GFA ↑



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

5) γ 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



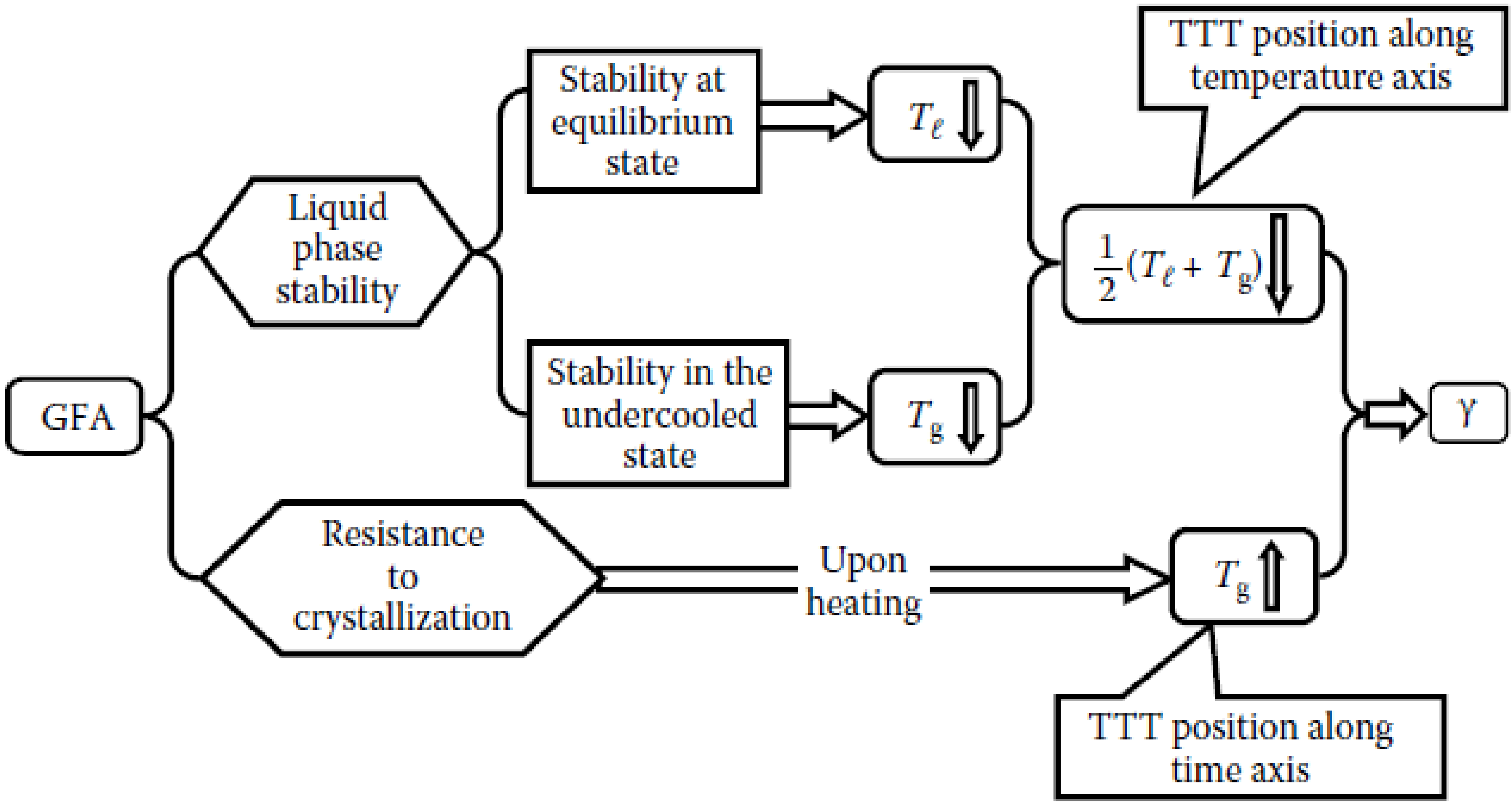
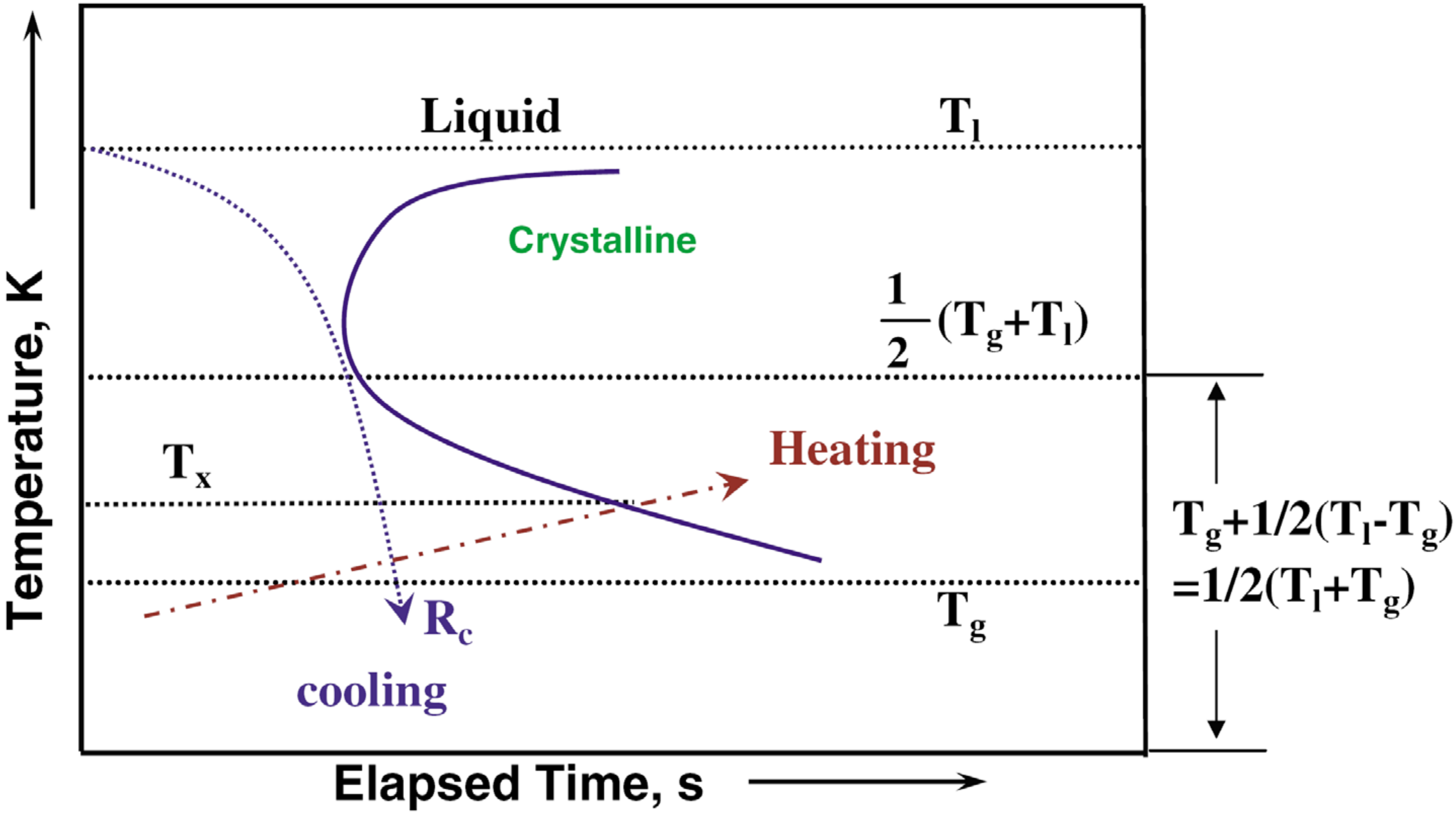


FIGURE 3.8
Schematic to illustrate the different factors involved in deriving the γ parameter to explain the GFA of alloys. (Reprinted from Lu, Z.P. and Liu, C.T., *Intermetallics*, 12, 1035, 2004. With permission.)

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



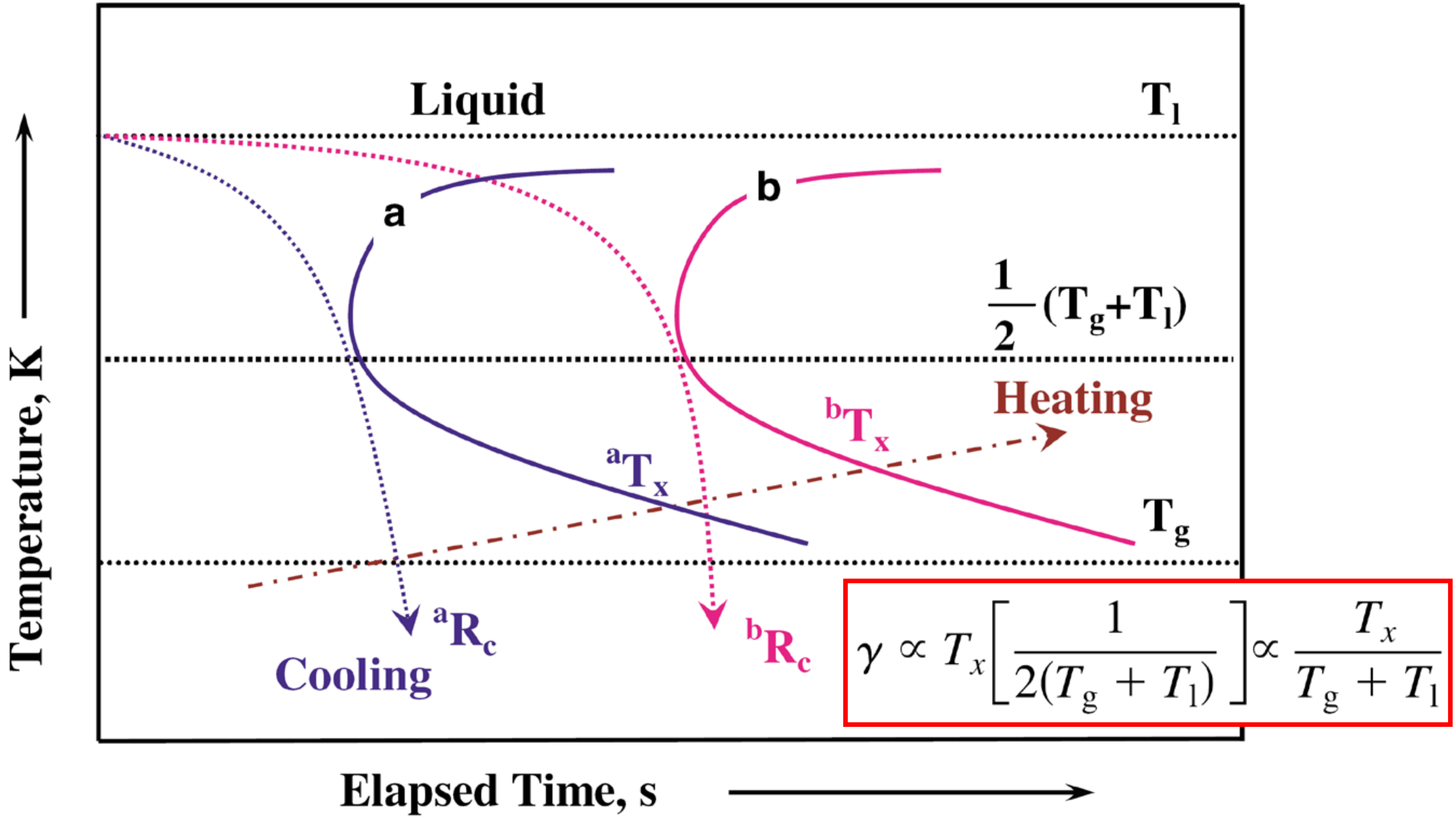
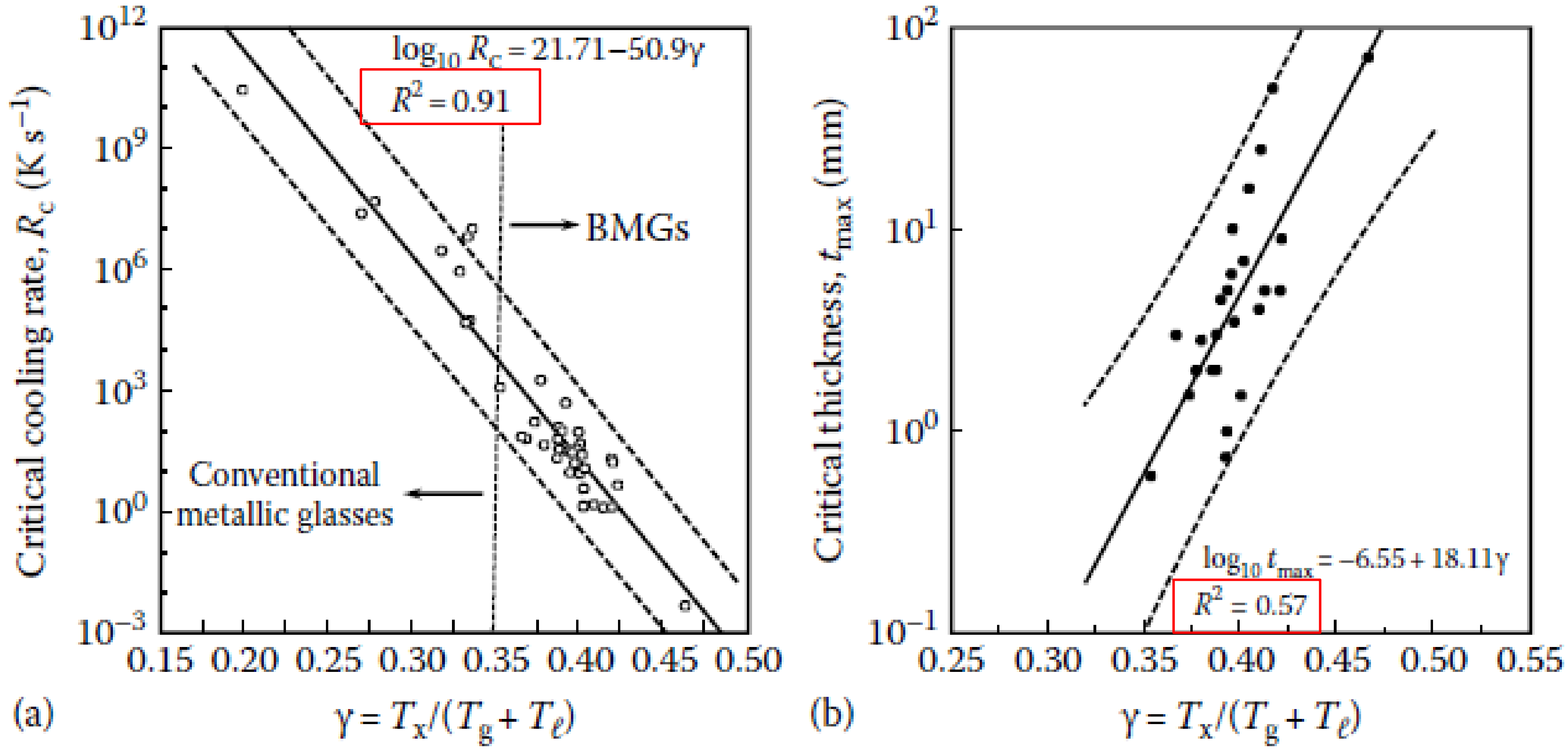


FIG. 2 (color online). Schematic TTT curves showing the effect of T_x measured upon continuous heating for different liquids with similar T_l and T_g; liquid b with higher onset crystallization temperature ${}^bT_x$ (${}^aT_x < {}^bT_x$) shows a lower critical cooling rate ${}^bR_c$ (${}^bR_c < {}^aR_c$).

$$\log_{10} R_c = (21.71 \pm 1.97) - (50.90 \pm 0.71)\gamma \qquad \log_{10} t_{max} = (-6.55 \pm 1.07) + (18.11 \pm 0.70)\gamma$$

$$R_c = R_0 \exp\left[\left(-\frac{\ln R_0}{\gamma_0}\right)\gamma\right] \qquad t_{max} = t_0 \exp\left[\left(-\frac{\ln t_0}{\gamma_1}\right)\gamma\right]$$

$$R_c = 5.1 \times 10^{21} \exp(-117.2\gamma) \qquad t_{max} = 2.80 \times 10^{-7} \exp(41.7\gamma)$$



Wide scatter for the t_{max} correlation

FIGURE 3.9

(a) Correlation between the critical cooling rate (R_c) and the γ parameter for BMGs. (b) Correlation between the maximum section thickness (t_{max}) and the γ parameter for BMGs. (Reprinted from Lu, Z.P. and Liu, C.T., *Acta Mater.*, 50, 3501, 2002. With permission.)

GFA Parameters *on the basis of thermodynamic or kinetic aspects*

GFA parameters	Expression	Year established	
T_{rg}	T_g / T_l	1969	D.Turnbull,Contemp.Phys.10(1969) 473
K	$(T_x-T_g) / (T_l-T_x)$	1972	A.Hruby, Czech. J.Phys. B 22 (1972) 1187
ΔT^*	$(T_m^{mix}–T_l) / T_m^{mix}$	1978	I.W.Donald, J.Non-Cryst.Solids 30 (1978) 77
ΔT_x	$T_x – T_g$	1993	A.Inoue, J.Non-Cryst.Solids 156-158(1993)473
γ	$T_x / (T_l+T_g)$	2002	Z.P.Lu, C.T.Liu, Acta Mater. 50 (2002) 3501
δ	$T_x / (T_l-T_g)$	2005	Q.J.Chen,Chiness Phys.Lett.22 (2005) 1736
α	T_x / T_l	2005	K.Mondal, J.Non-Cryst.Solids 351(2005) 1366
β	$T_x / T_g + T_g / T_l$	2005	K.Mondal, J.Non-Cryst.Solids 351(2005) 1366
φ	$(T_g / T_l)(T_x-T_g / T_g)^a$	2007	G.J.Fan,J.Non-Cryst. Solids 353 (2007) 102
γ_m	$(2T_x – T_g) / T_l$	2007	X.H.Du,J.Appl.phys.101 (2007) 086108
β	$(T_g / T_l- T_g)(T_g / T_l- T_g)$	2008	Z.Z.Yuan, J. Alloys Compd.459 (2008)
ξ	$\Delta T_x / T_x + T_g / T_l$	2008	X.H.Du,Chinese Phys.B 17(2008) 249