2014 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

04.17.2014

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

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.

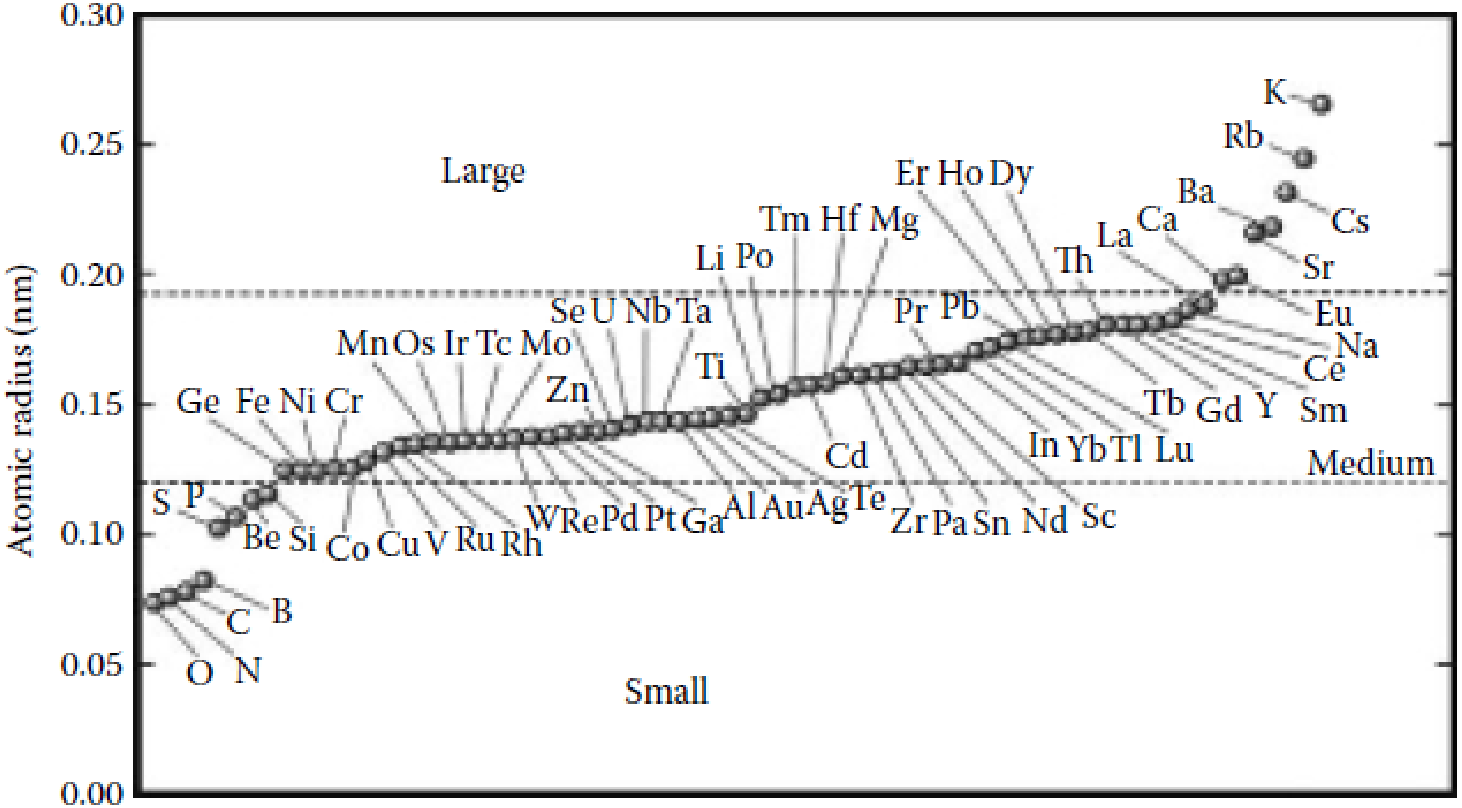
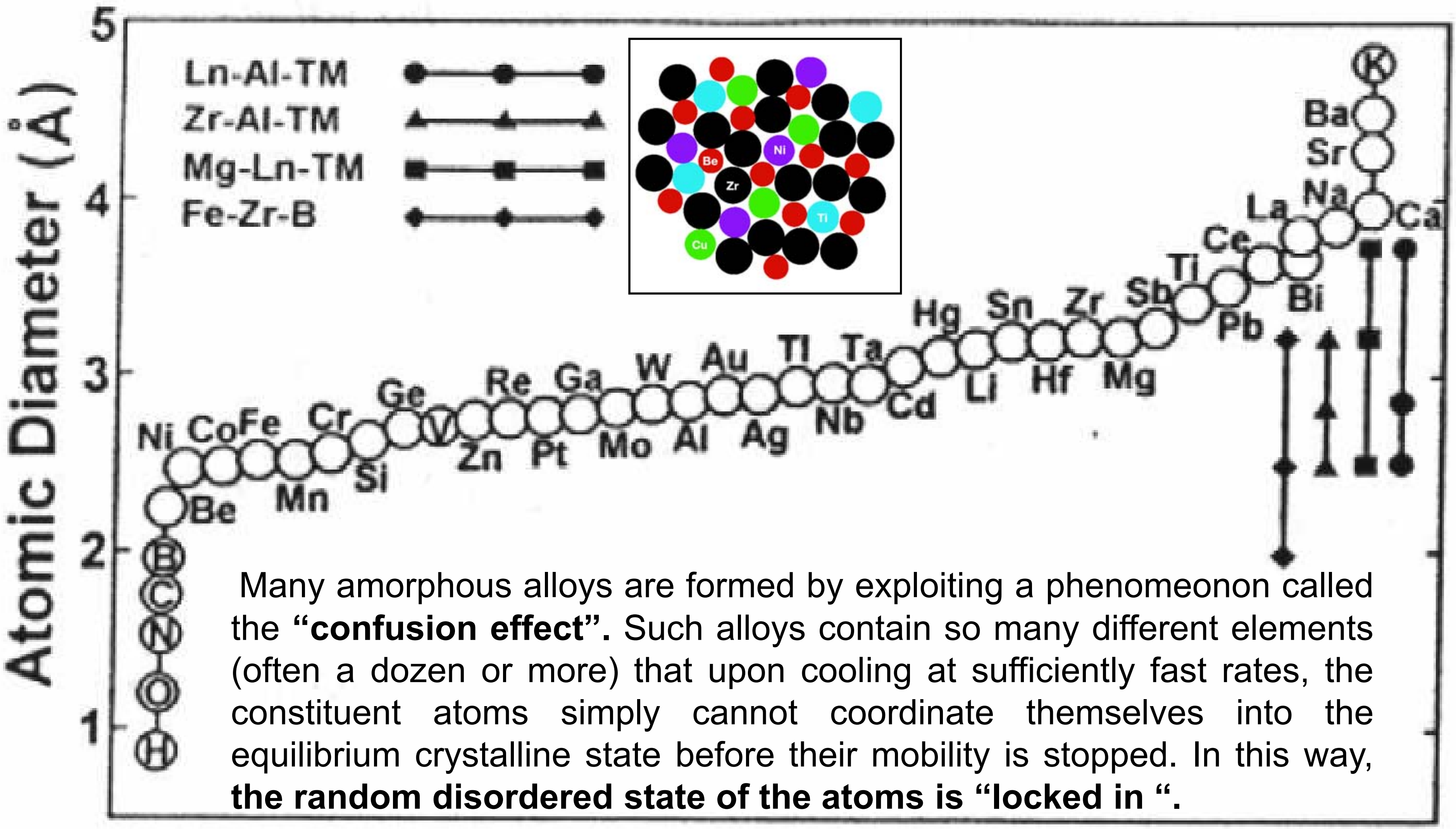


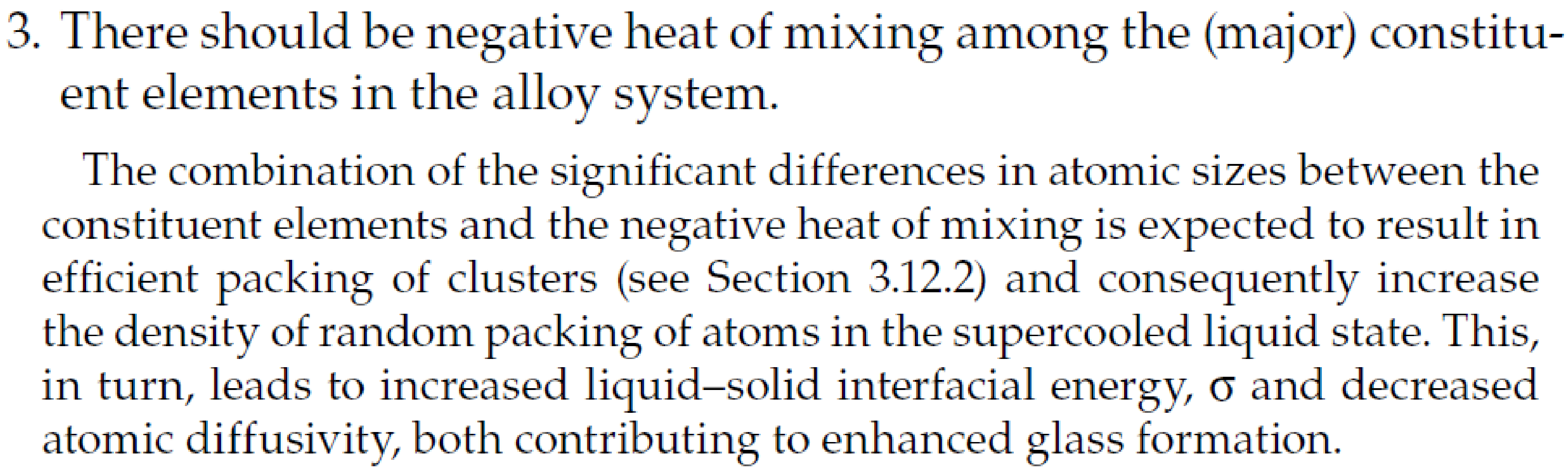
FIGURE 3.4
Atomic diameters of the elements that constitute bulk metallic glasses. These can be classified into three major groups of large, medium, and small sizes.

< 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.

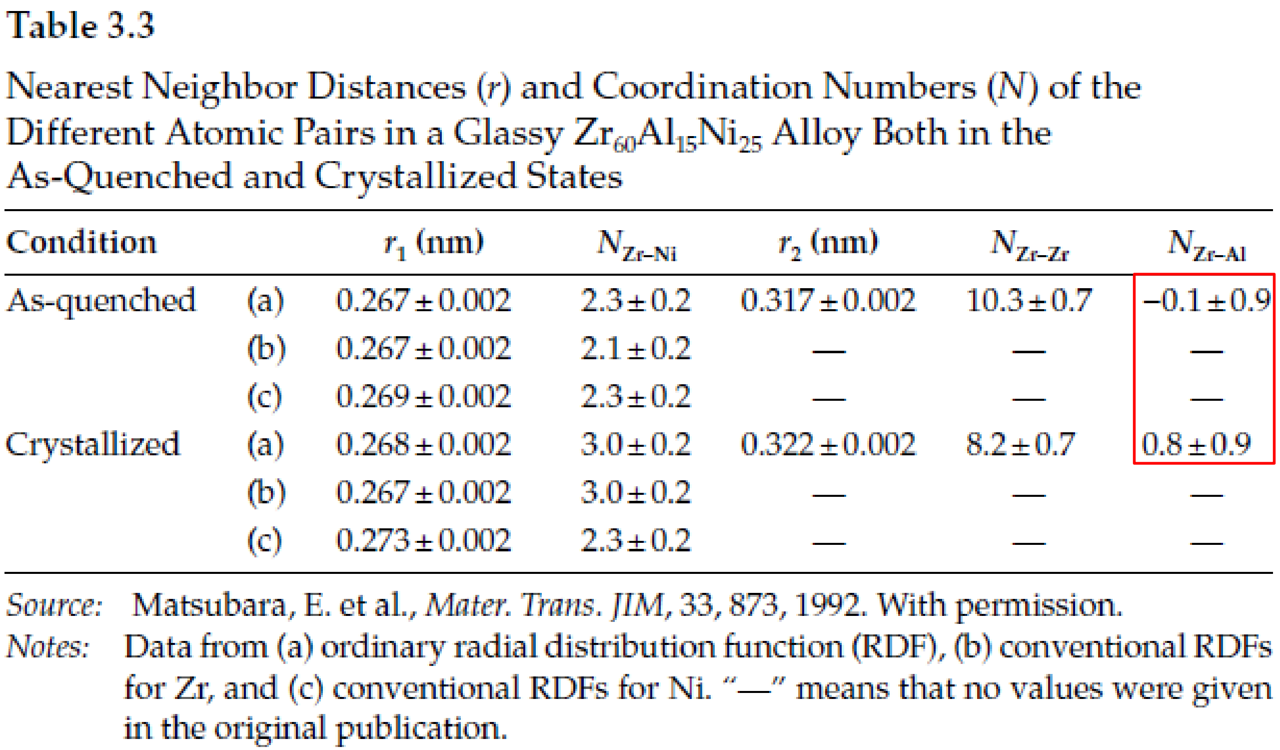


Table 3.3

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	—	—	—

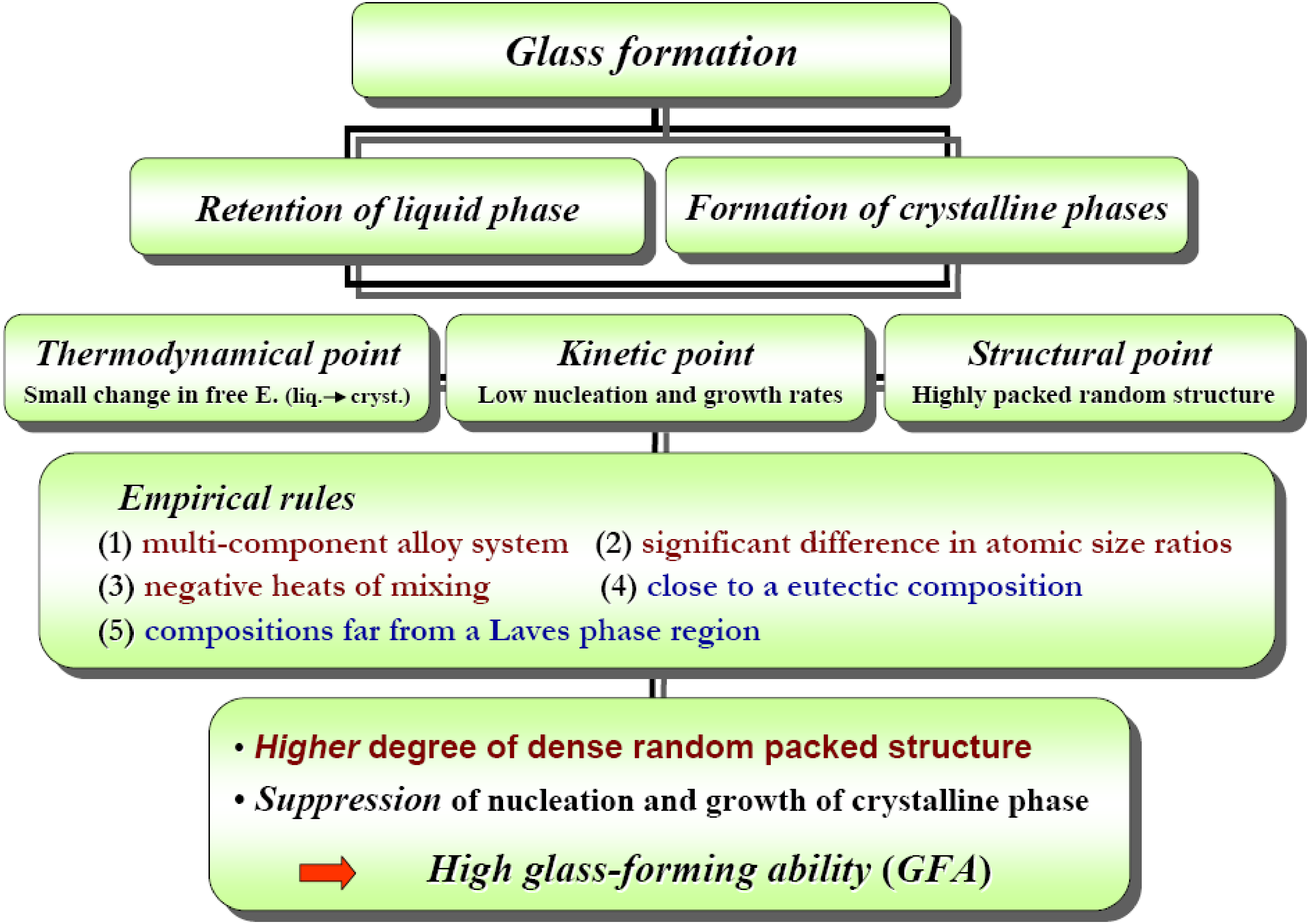
Source: Matsubara, E. et al., *Mater. Trans. JIM*, 33, 873, 1992. With permission.

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

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

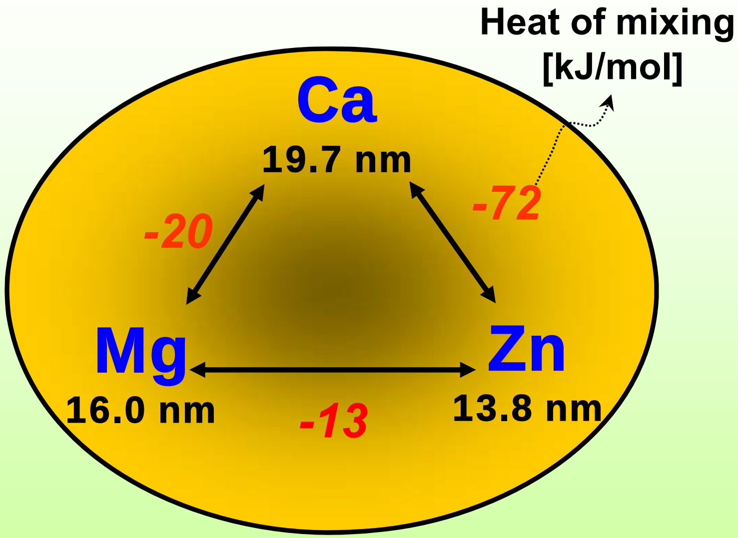
- ***Higher*** **degree of dense random packed structure**
- *Suppression* **of nucleation and growth of crystalline phase**

➡ *High glass-forming ability (GFA)*

Alloy design and new BMG development

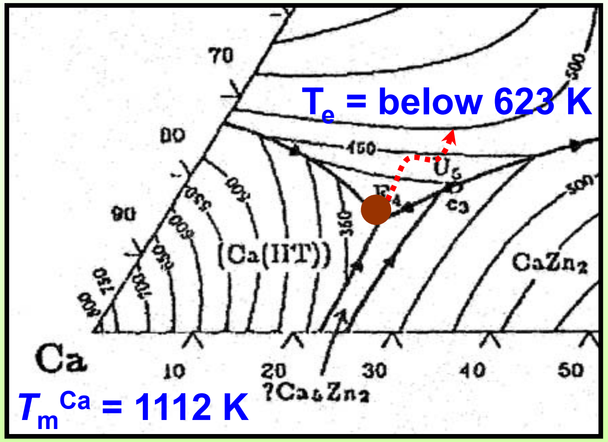
Ca-Mg-Zn alloy system

- **Dense packed structure**



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

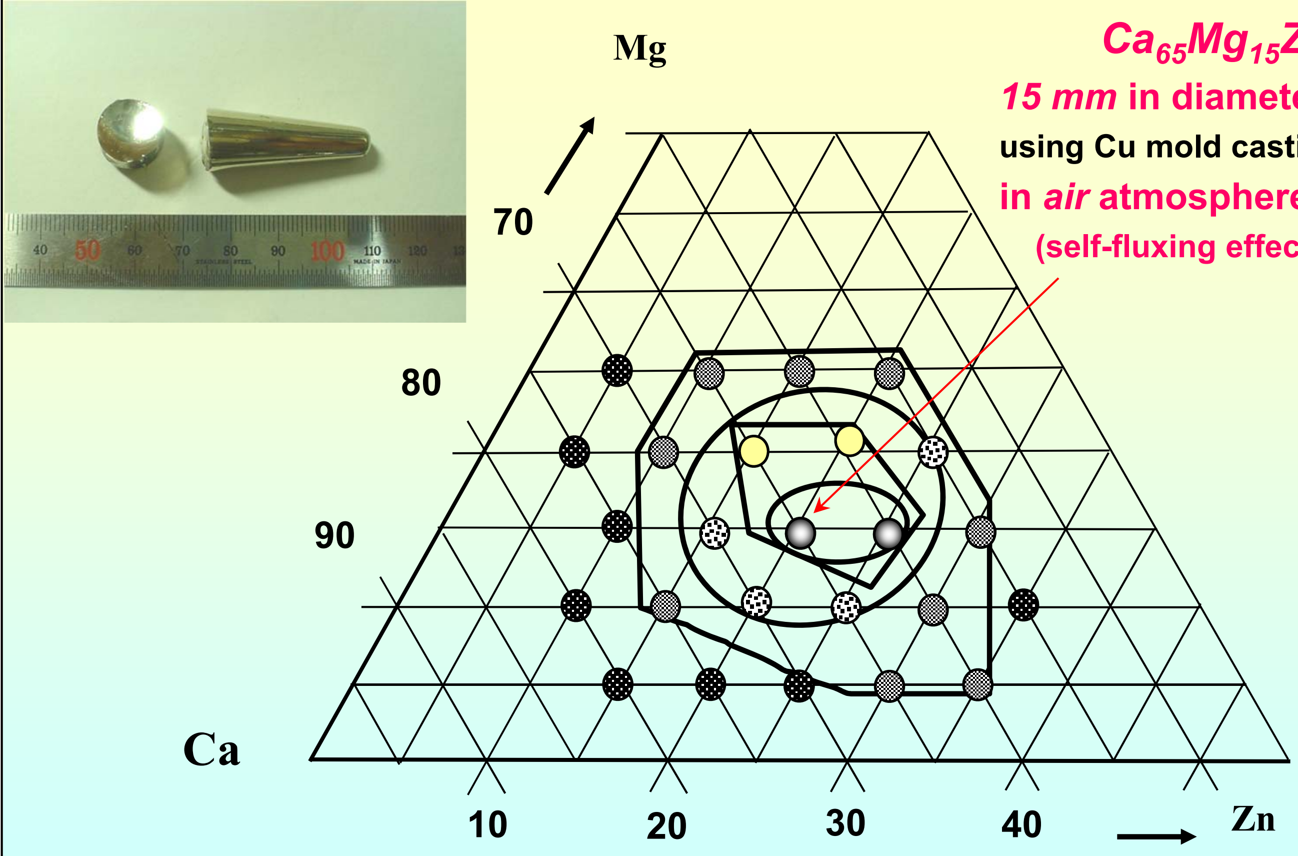
- **Decrease of melting temp.**



Deep eutectic condition

$T_e / T_m^{Ca} = 0.560$

Ca-Mg-Zn alloy system



$Ca_{65}Mg_{15}Zn_{20}$

***15 mm* in diameter sample**

using Cu mold casting method

in *air* atmosphere

(self-fluxing effect by Ca)

Maximum diameter for glass formation in Ca-rich Ca-Mg-Zn alloy system

● *over 10mm* ○ *over 7mm* ▨ *over 3mm* ▨ *over 1mm* ● *below 1mm*

* 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:

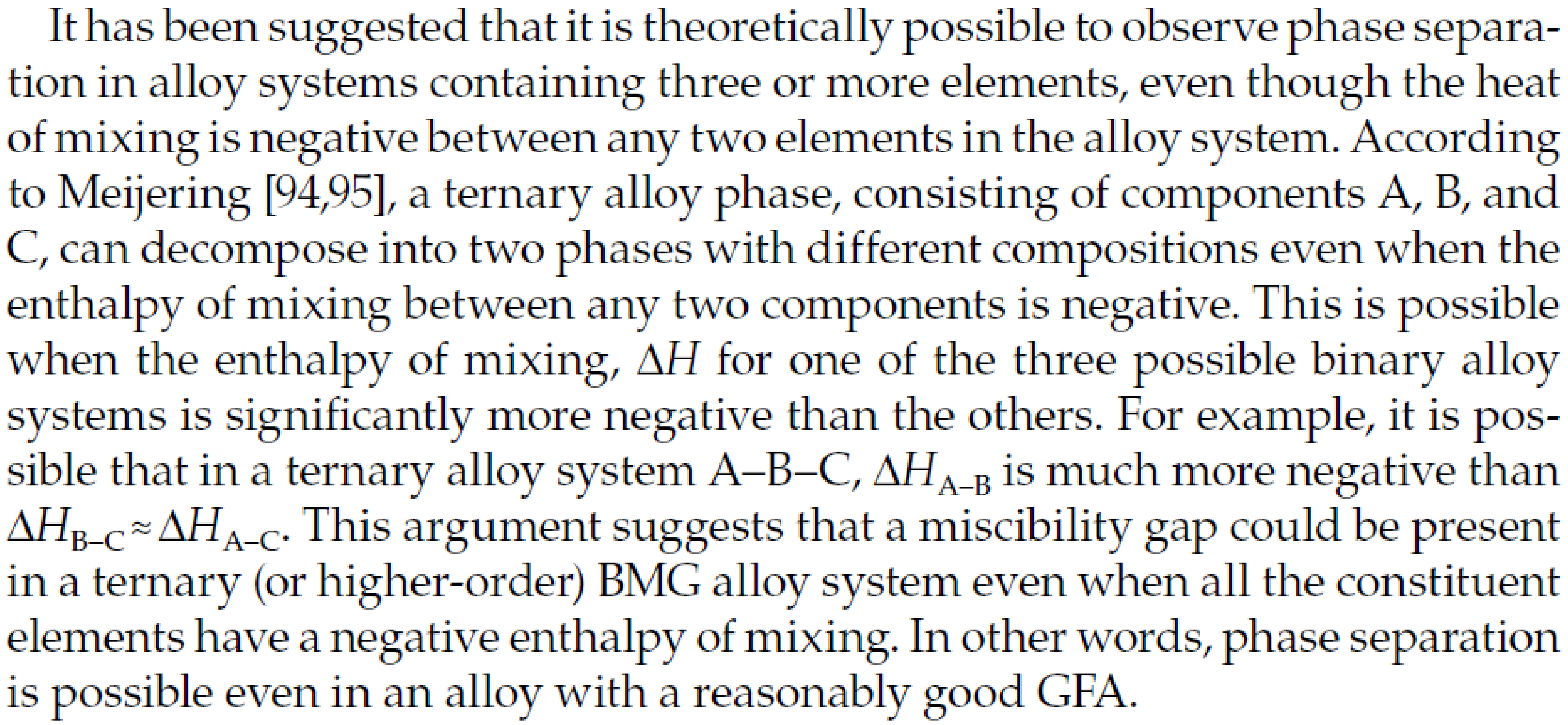
1) The maximum diameter of the glassy rods obtained in these binary alloys is relatively small, i.e. a maximum of only about 2 mm.
2) The "glassy" rods of the binary BMG alloys often seem to contain some nanocrystalline phases. (?)

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



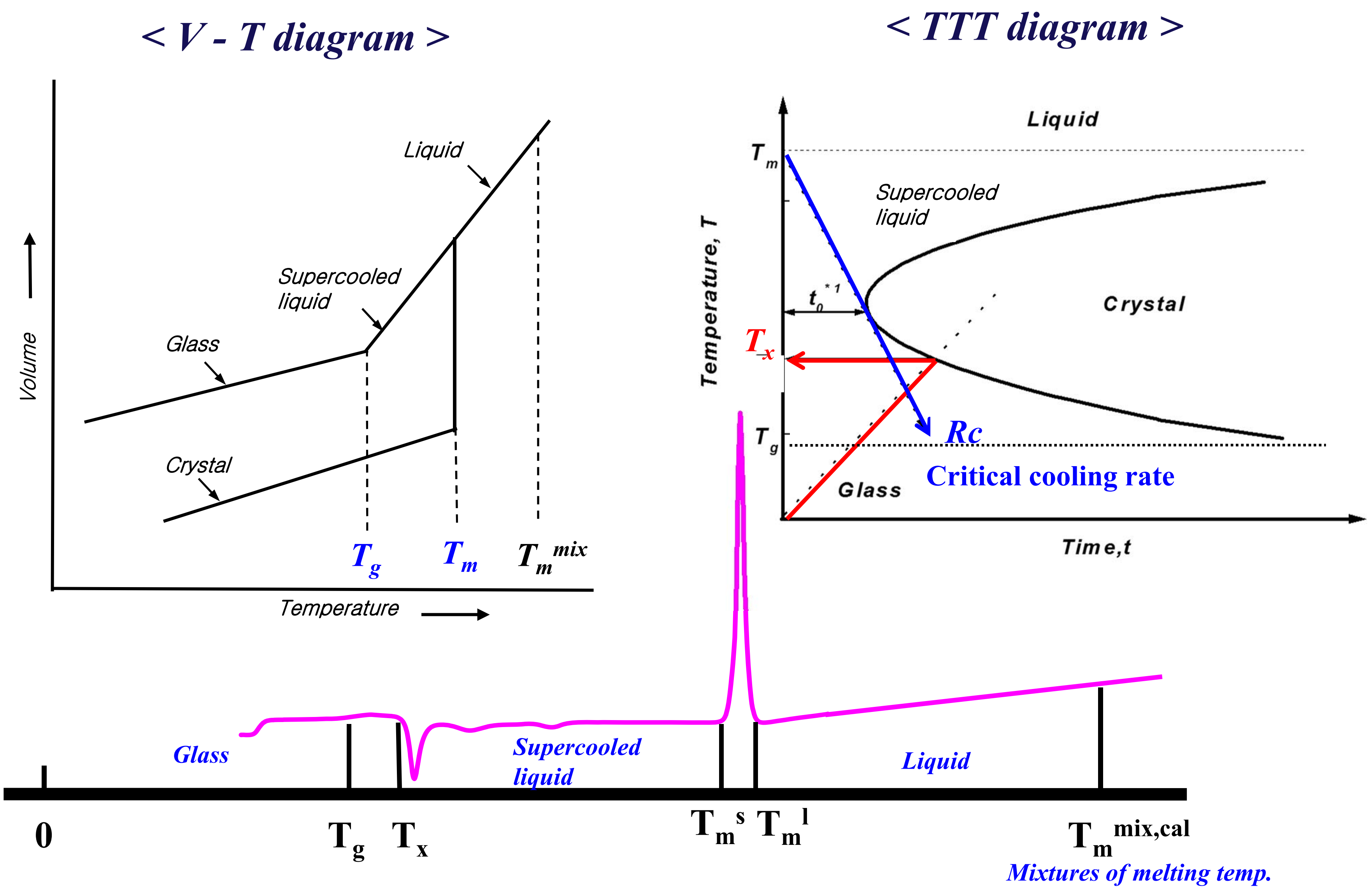
It has been suggested that it is theoretically possible to observe phase separation in alloy systems containing three or more elements, even though the heat of mixing is negative between any two elements in the alloy system. According to Meijering [94,95], a ternary alloy phase, consisting of components 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



< V - T diagram >

< TTT diagram >

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)

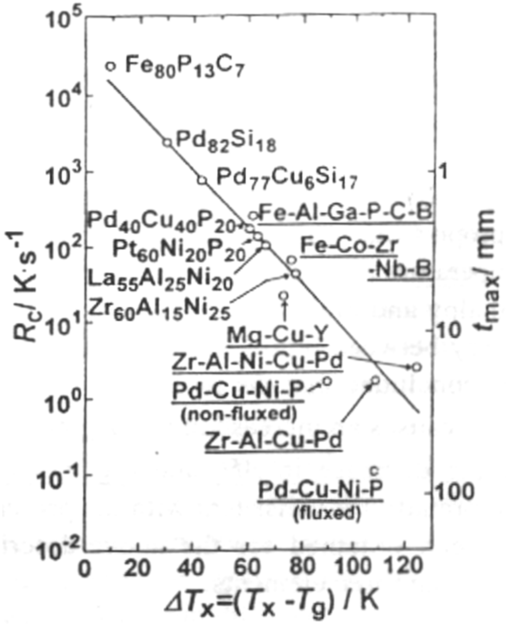
Based on thermodynamic and atomic configuration aspects

$\sigma = \Delta T^* \times P'$	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 = $T_x - T_g$

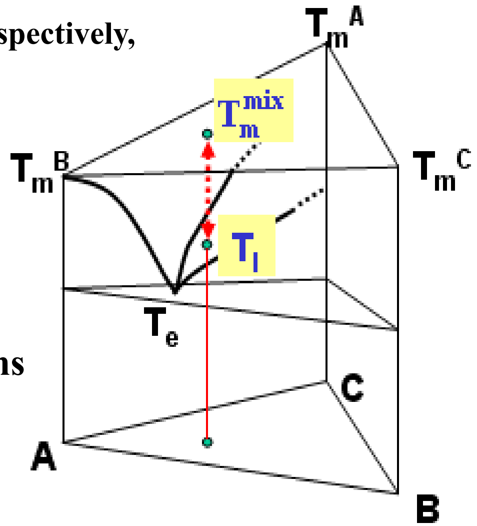
- quantitative measure of glass stability toward crystallization upon reheating the glass above T_g: stability of glass state
- cannot be considered as a direct measure for GFA

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.)

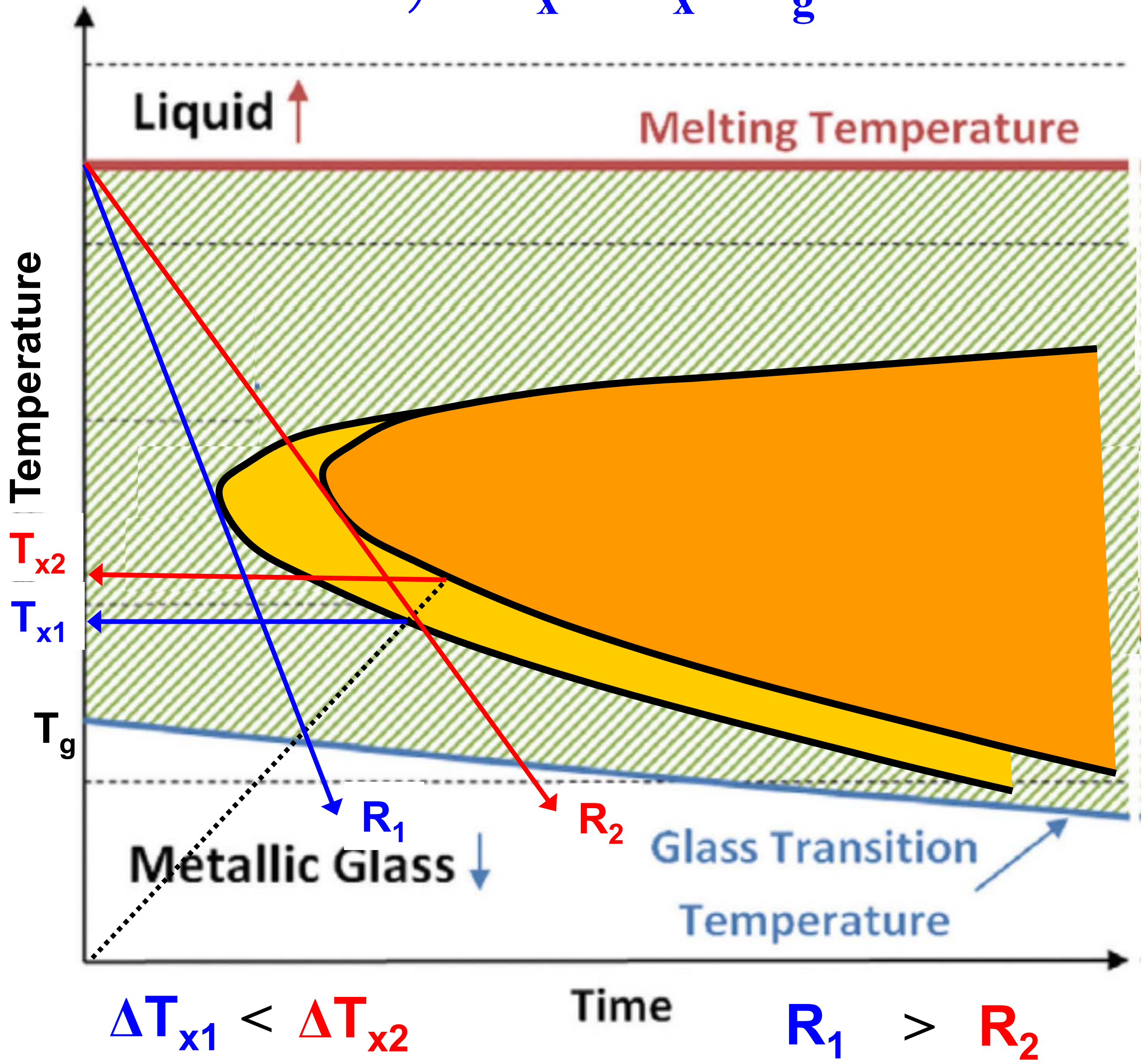


- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA

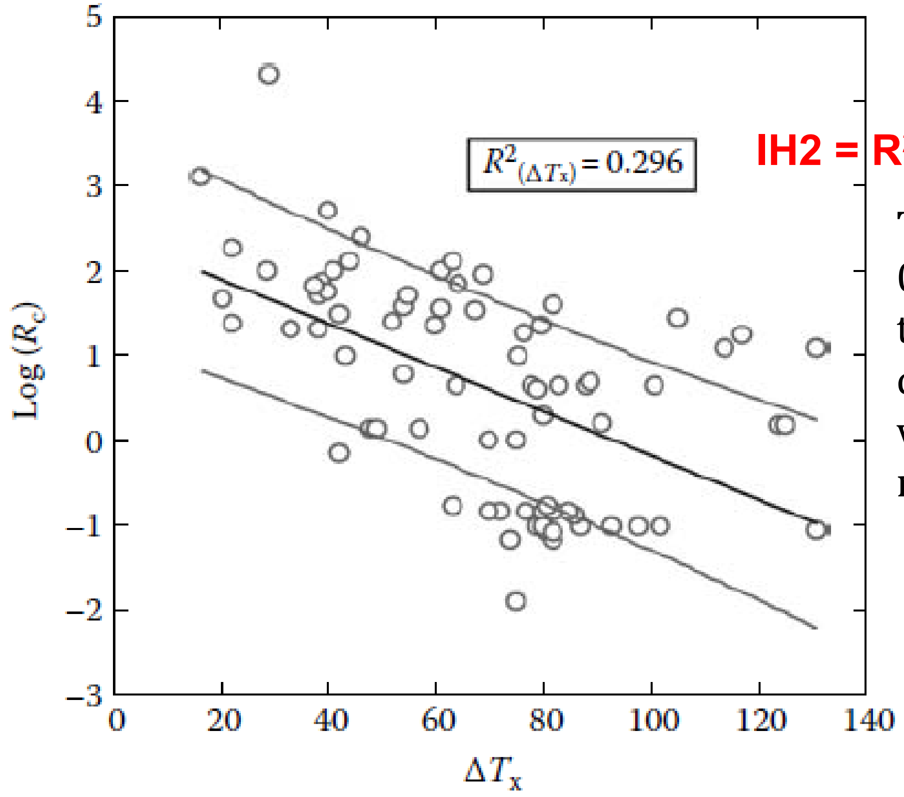
T_m^{mix} represents the fractional departure of T_m with variation of compositions and systems from the simple rule of mixtures melting temperature

Time Temperature Transformation diagram:

1) $\Delta T_x = T_x - T_g$



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.

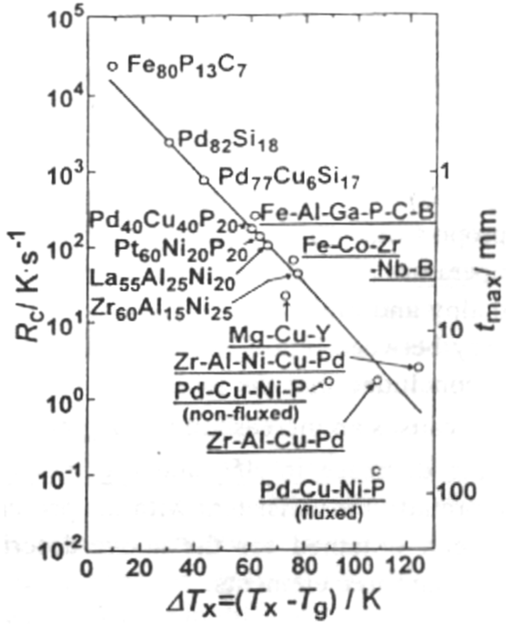


IH2 = R^2 : regression coefficient

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 :



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

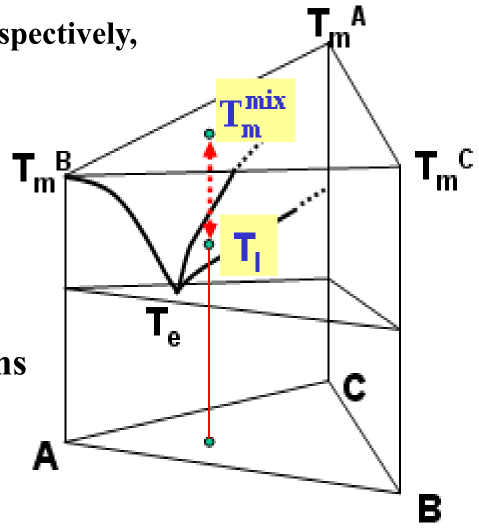
2) K parameter = $(T_x - T_g)/(T_l - T_x) = \Delta T_x/(T_l - T_x)$

- 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.)

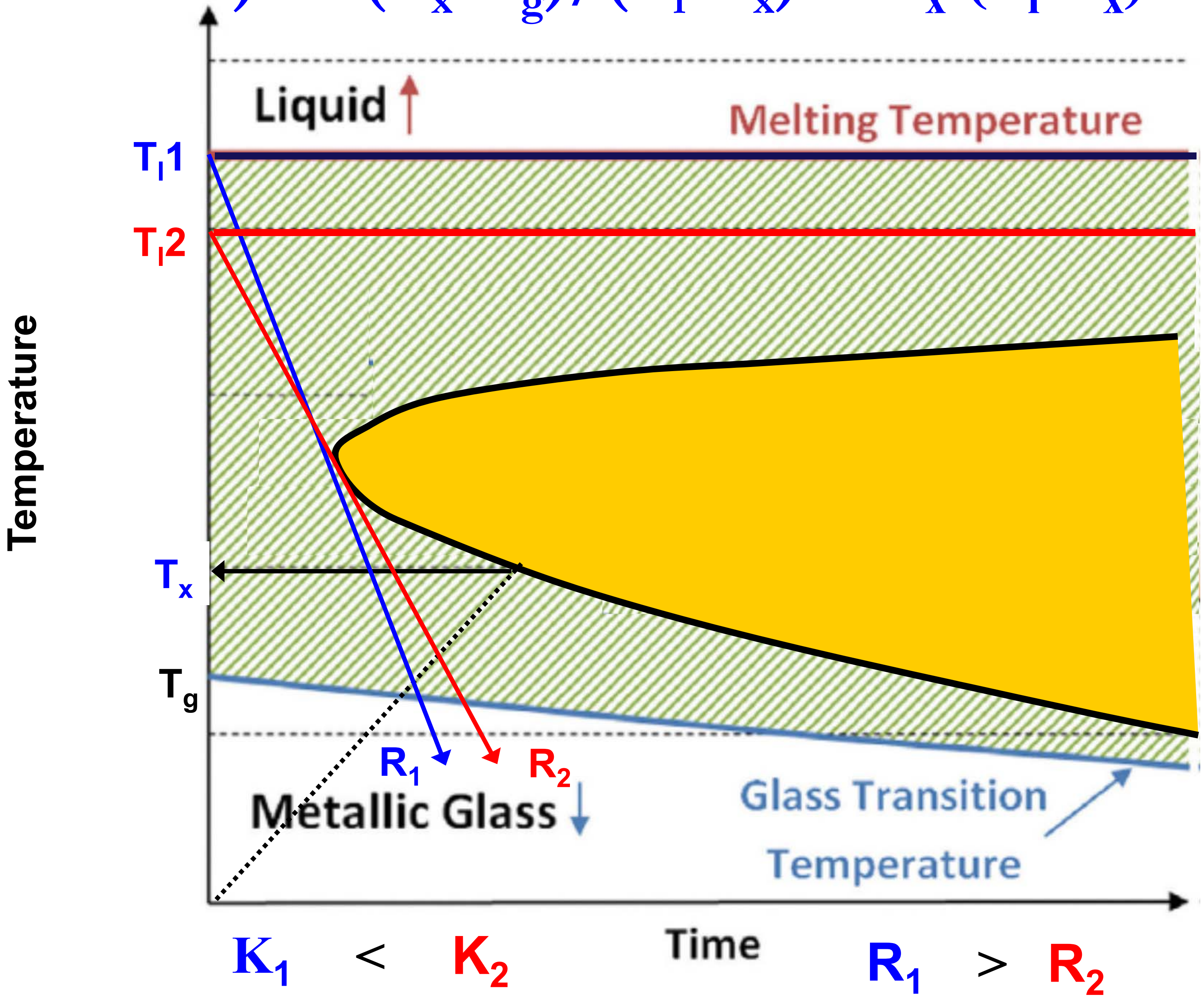


- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA

➡ 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:

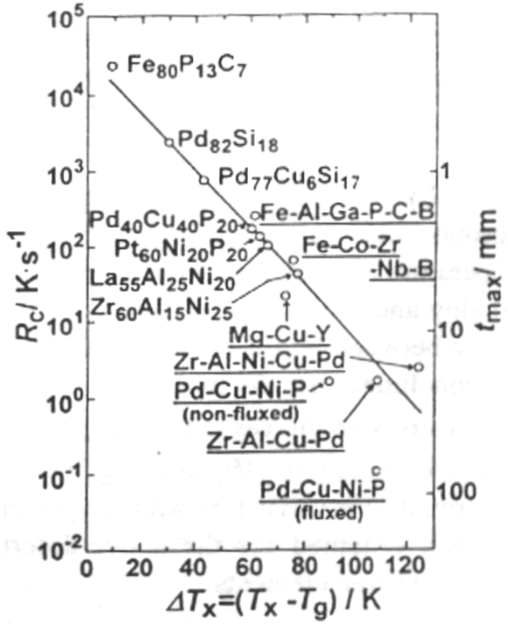
2) $K=(T_x-T_g)/(T_l-T_x)=\Delta T_x/(T_l-T_x)$



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

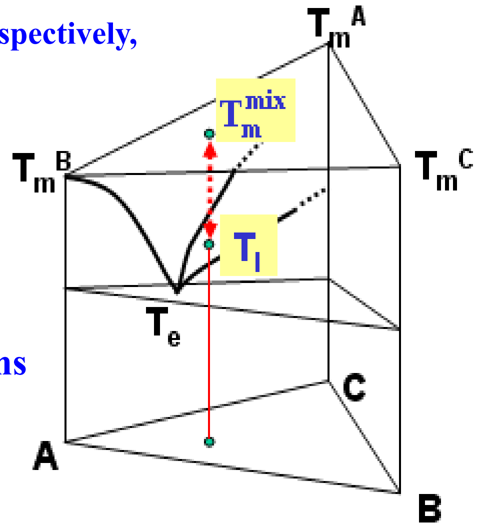
- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

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}**

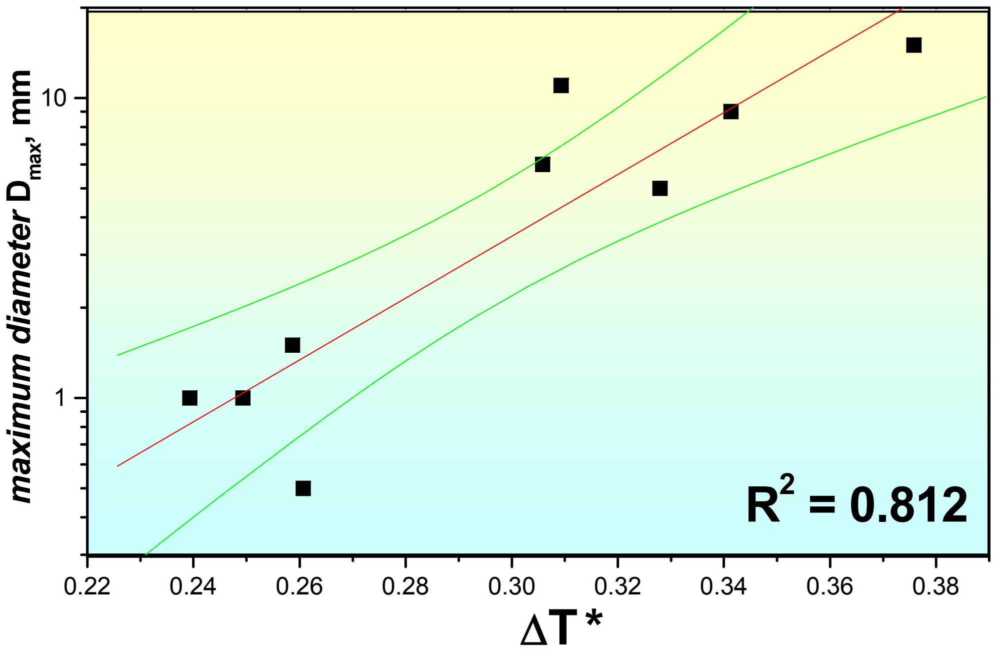
$$\boxed{\Delta T^* = \frac{T_m^{mix} - T_l}{T_m^{mix}}}$$

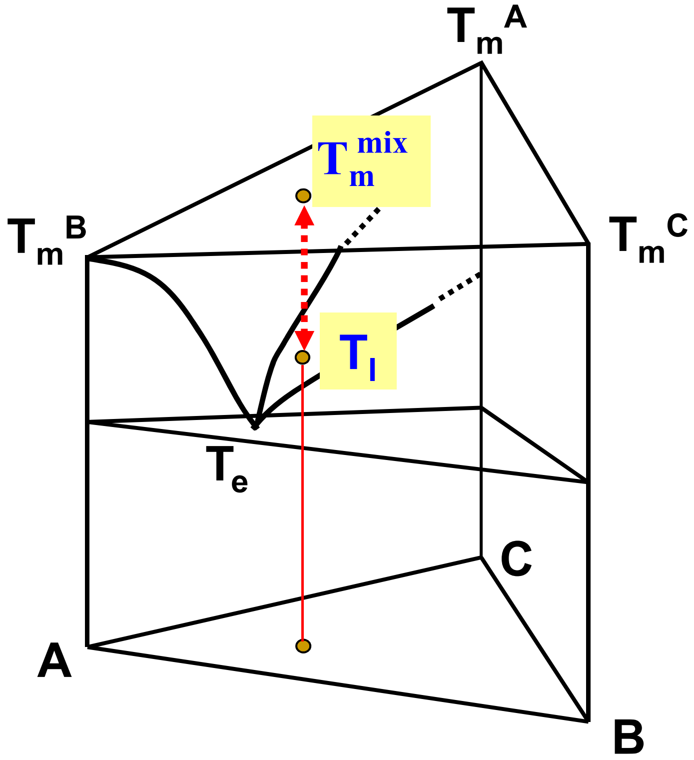
(where, $T_m^{mix} = \sum x_i T_m^i$, $x_i =$ molefraction, $T_m^i =$ melting point)

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

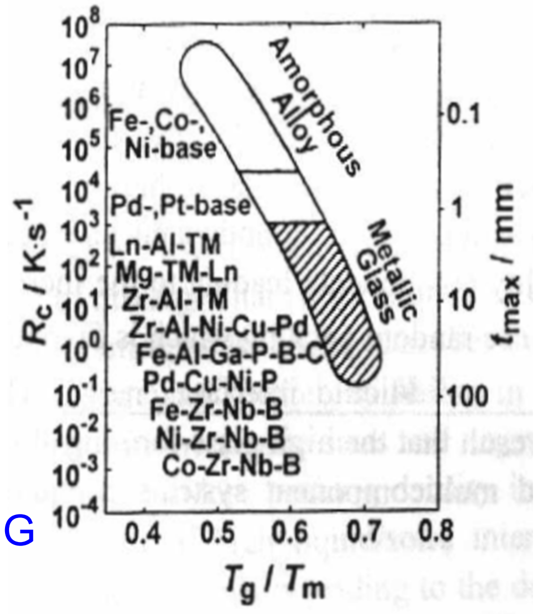




GFA Parameters on the basis of thermodynamic or kinetic aspects :

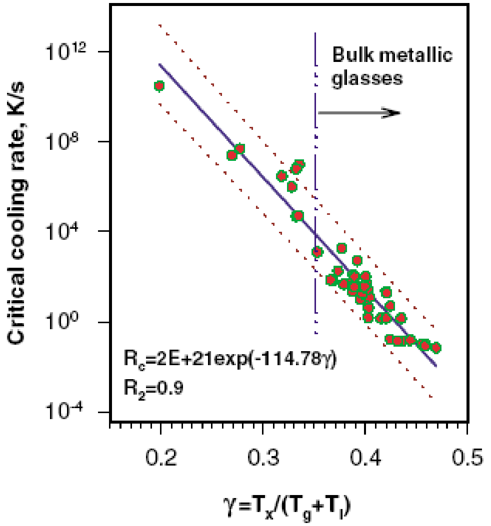
4) T_{rg} parameter = T_g/T_l

- 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



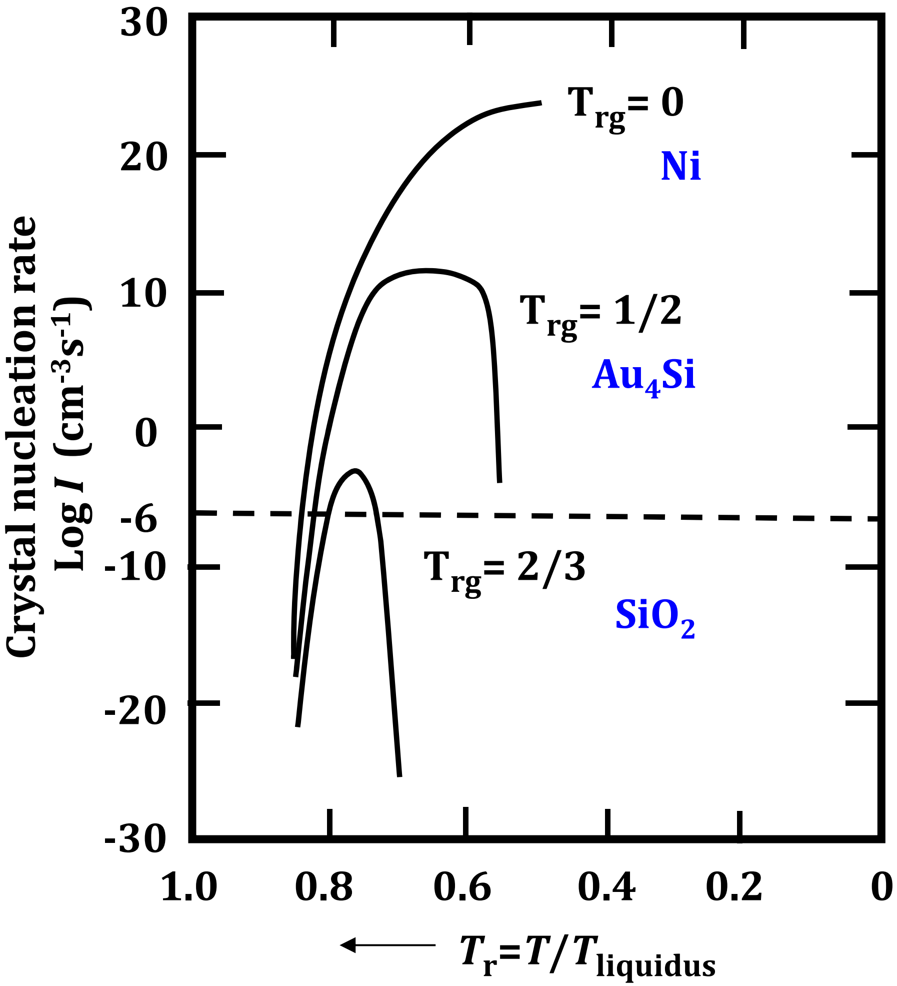
5) γ parameter = T_x / (T_l + T_g)

- 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



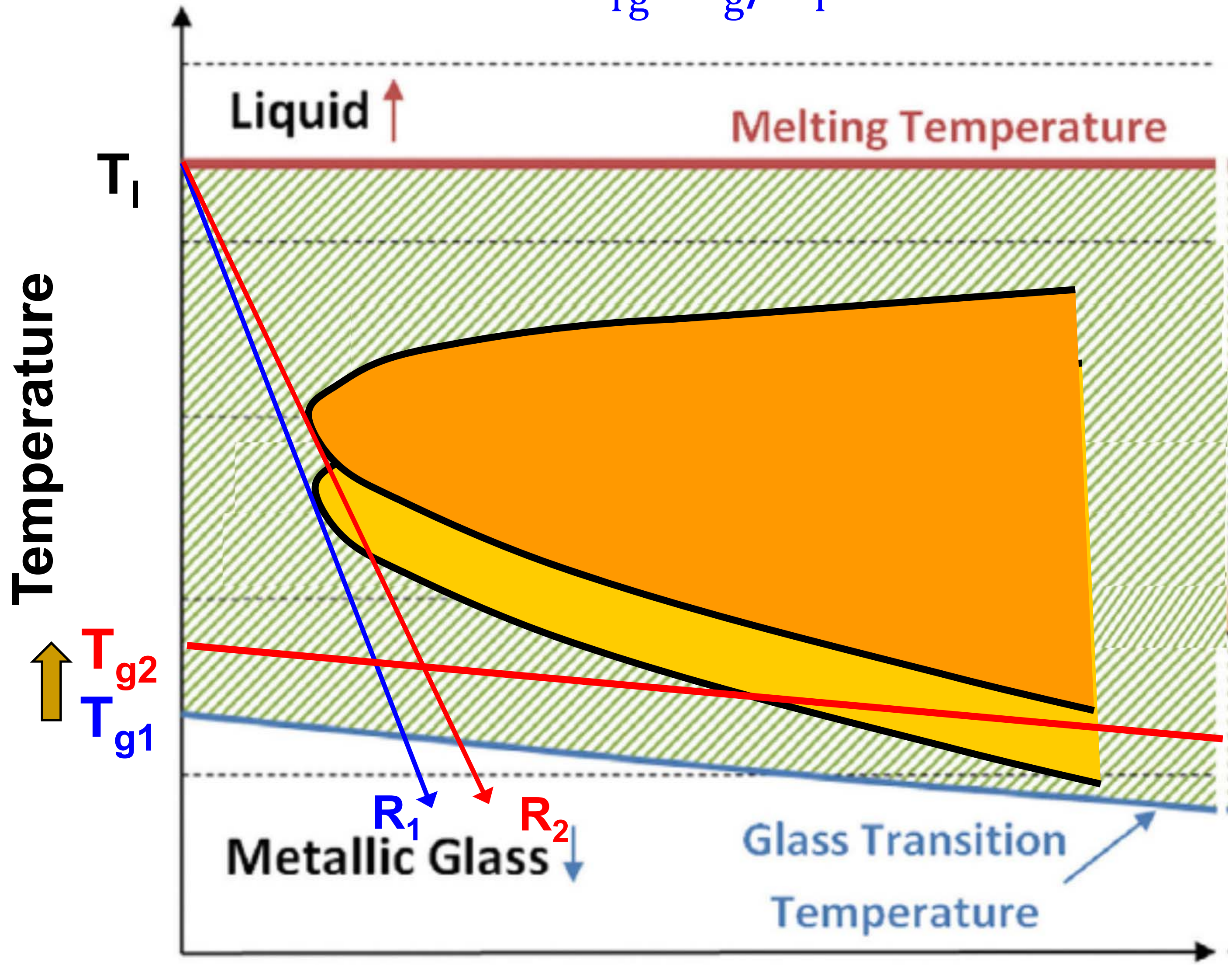
$T_{rgNi} < T_{rgAu4Si} < T_{rgSiO2}$

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

Turnbull, 1959 ff.

Time Temperature Transformation diagram:

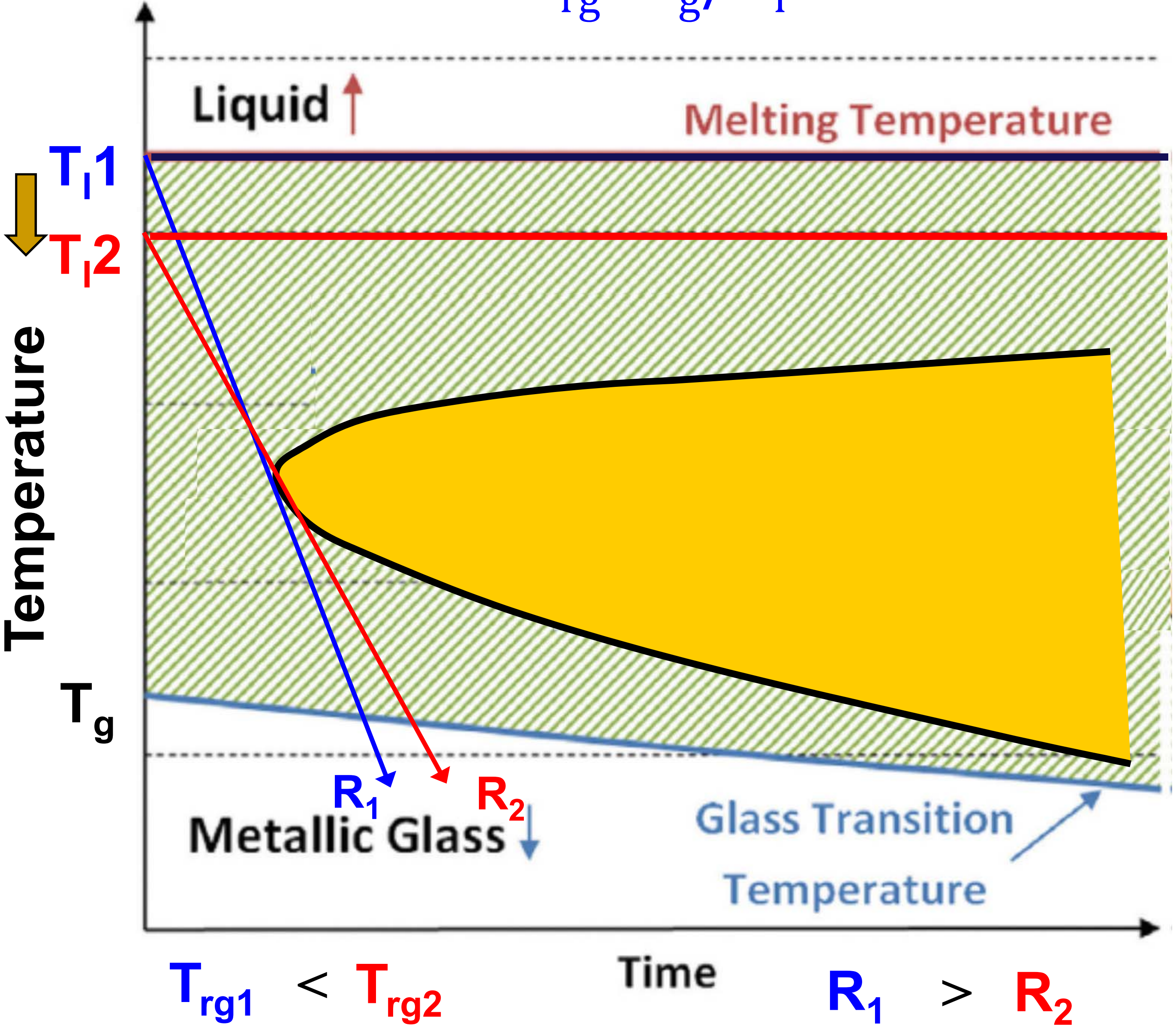
$T_{rg}=T_g/T_l$



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

Time Temperature Transformation diagram:

$T_{rg} = T_g / T_l$



GFA Parameters on the basis of thermodynamic or kinetic aspects :

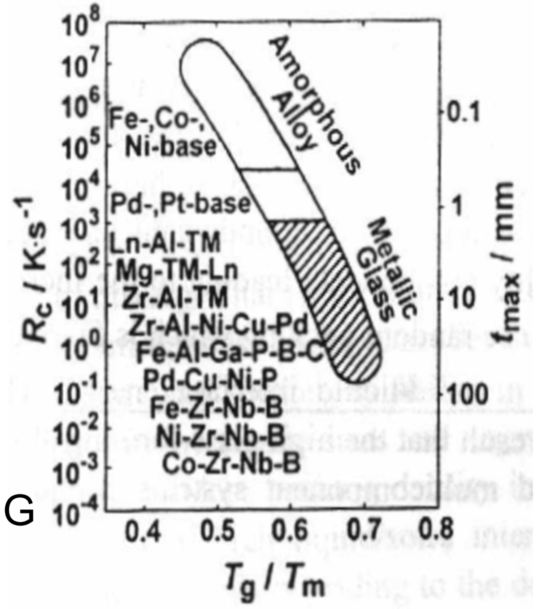
4) T_{rg} parameter = T_g/T_l

- 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

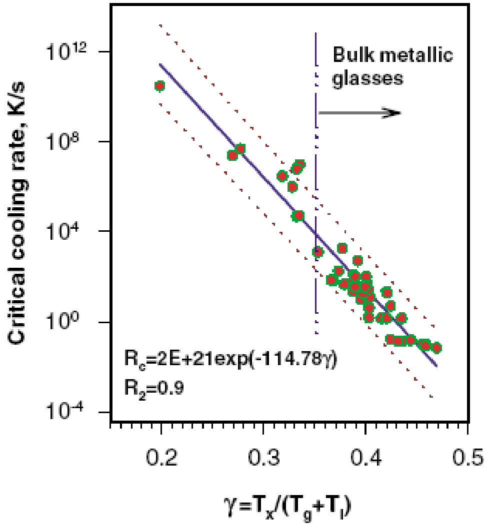
▪ insufficient information on temperature-viscosity relationship

► 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



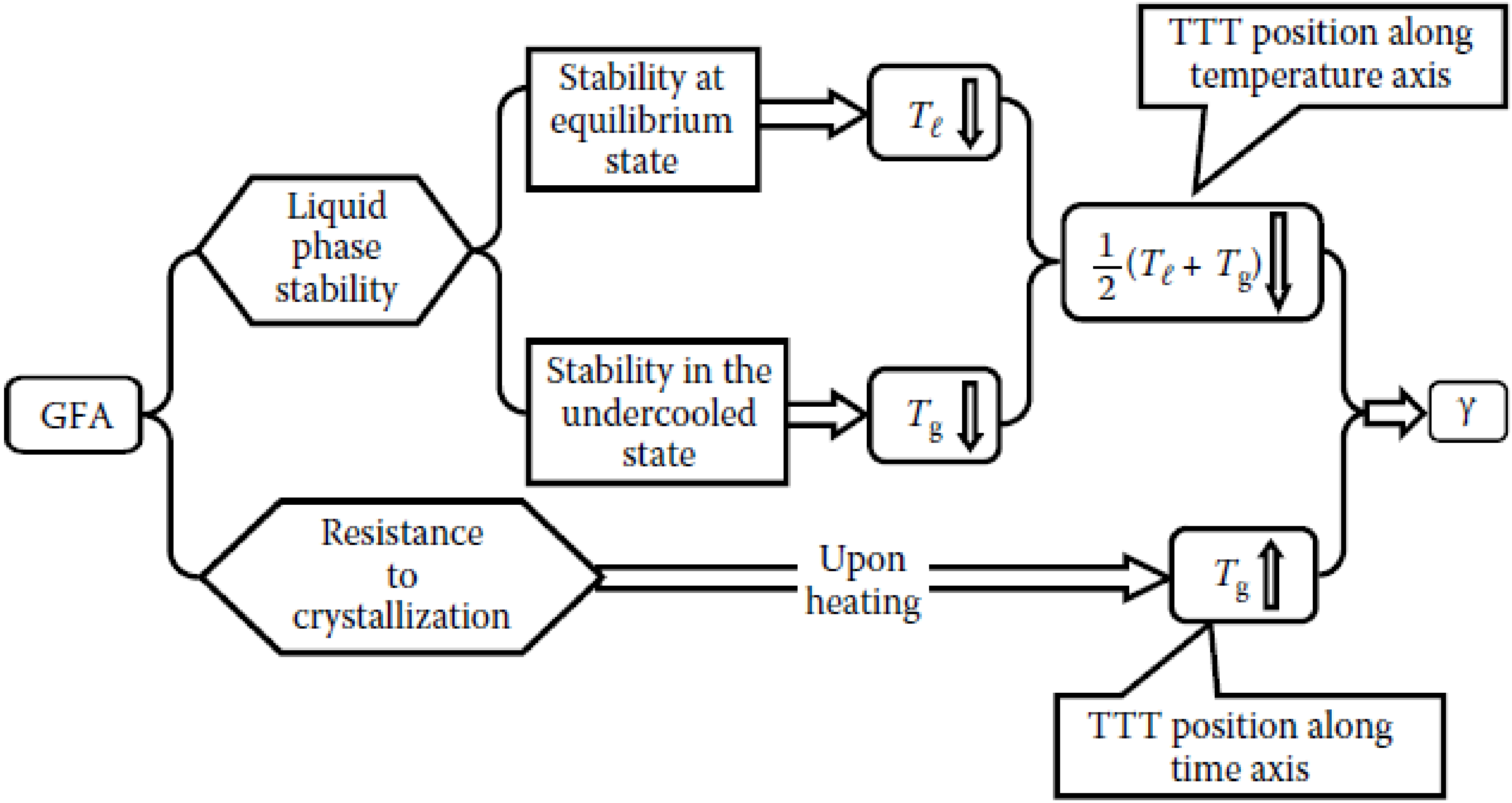
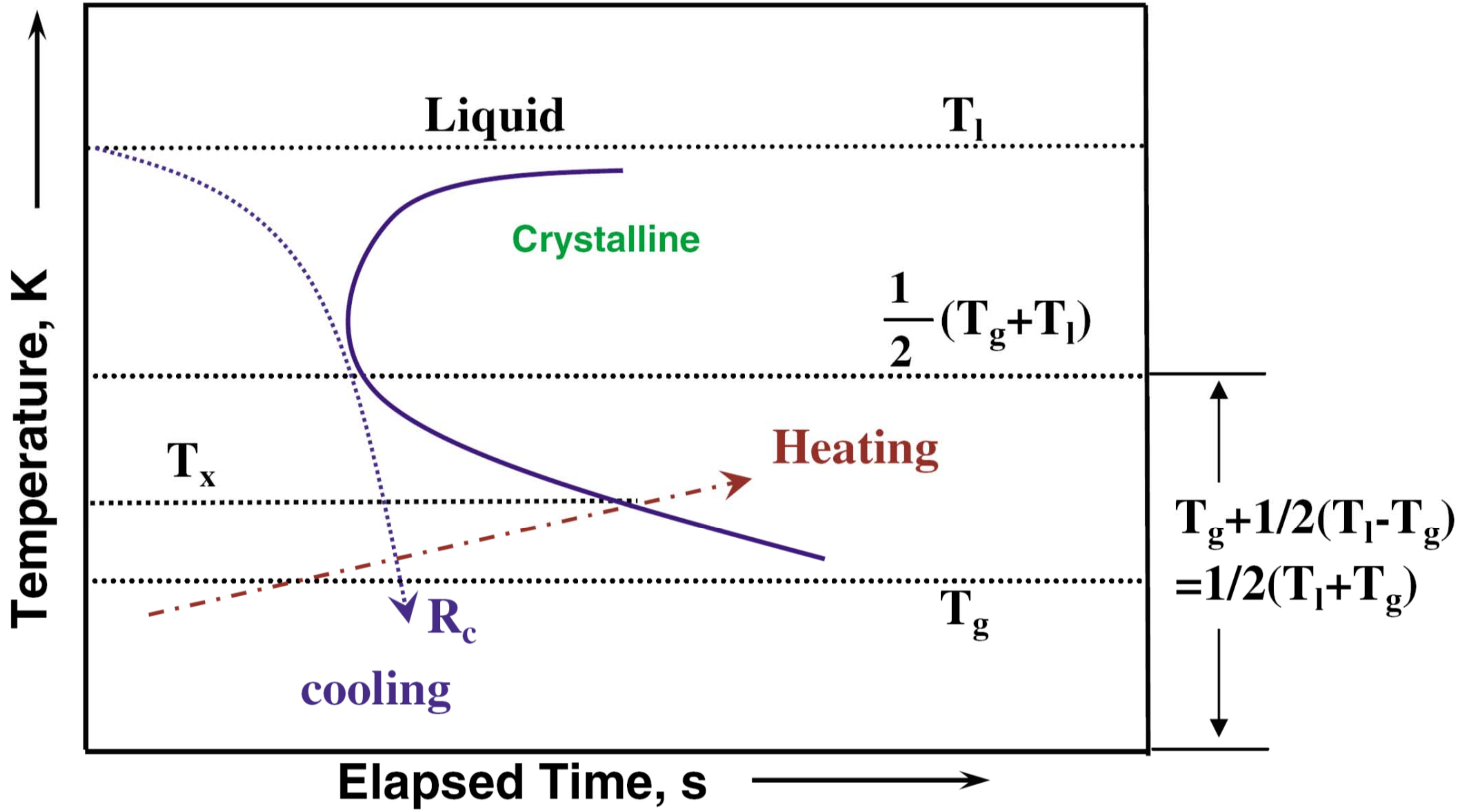
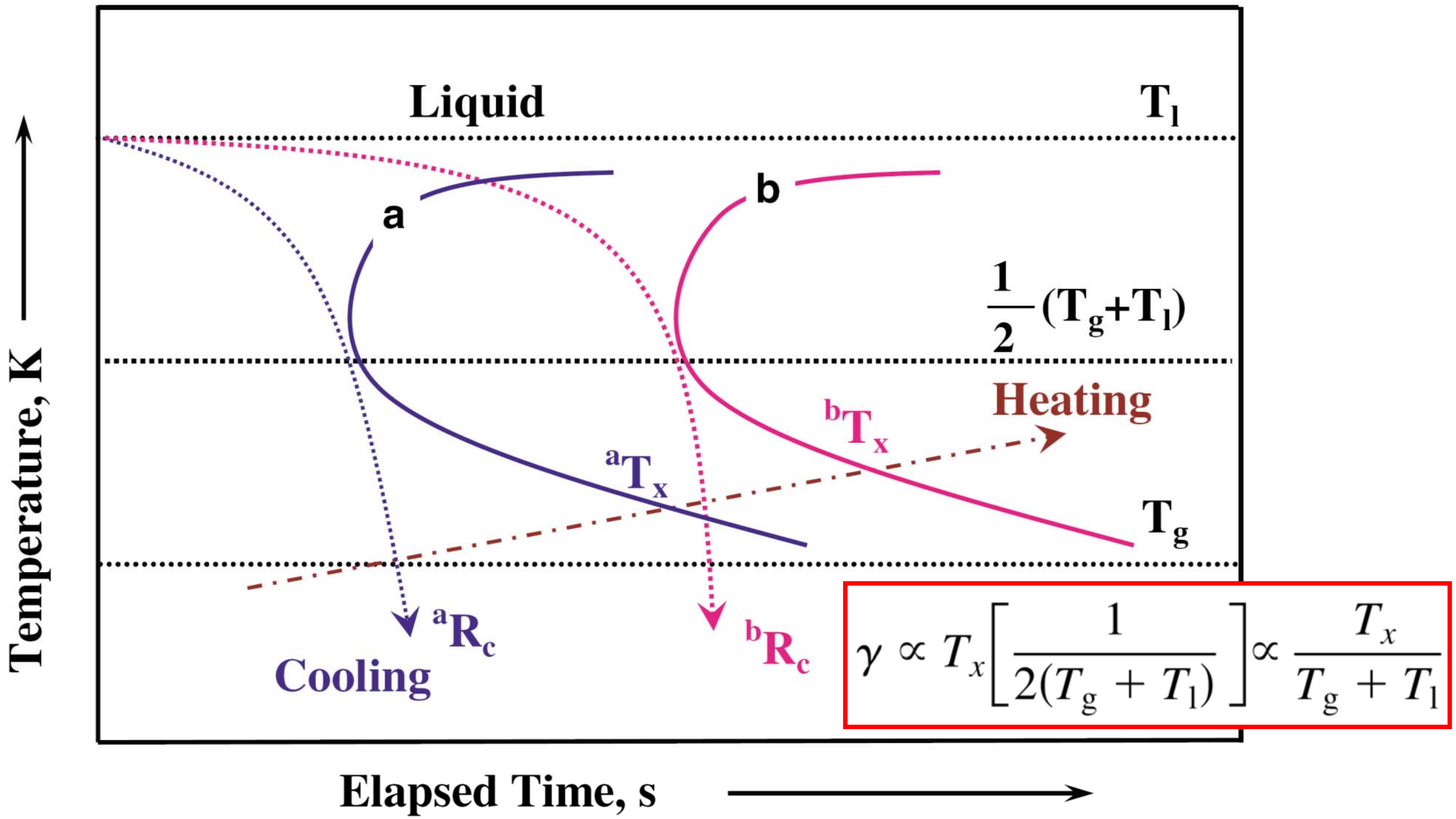


FIGURE 3.8
Schematic to illustrate the different factors involved in deriving the γ parameter to explain the GFA of alloys. (Reprinted from Lu, Z.P. and Liu, C.T., *Intermetallics*, 12, 1035, 2004. With permission.)

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





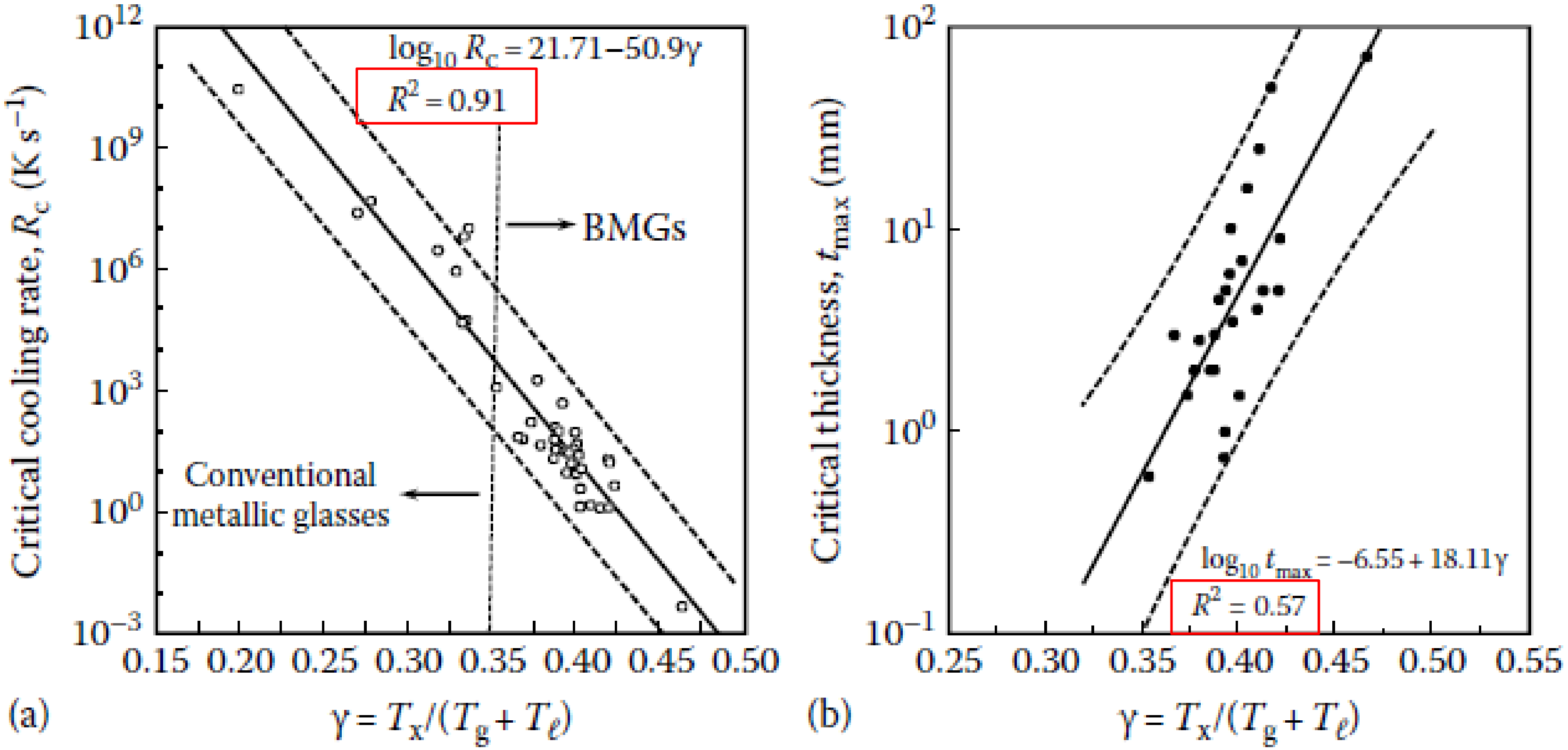
$$\gamma \propto T_x\left[\frac{1}{2(T_g+T_l)}\right]\propto \frac{T_x}{T_g+T_l}$$

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

No universal model **to predict and evaluate what families of alloy compositions are likely to form BMGs**

Combination of categories

that are viewed as decisive in the formation of amorphous alloys

New criterion

for predicting and evaluating Glass Forming Ability

- **useful guideline for BMG alloy system design**

- save time and experimental cost

→ new alloy system with enhanced GFA

Approach 1. combine thermodynamic and structural points

$$\sigma = \Delta T^* \times \ P'$$

ΔT^* : **Relative decrease of melting temp.** **P'** : **Effective atomic mismatch per solute atom**

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

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

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

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

Approach 2. combine thermodynamic and kinetic points

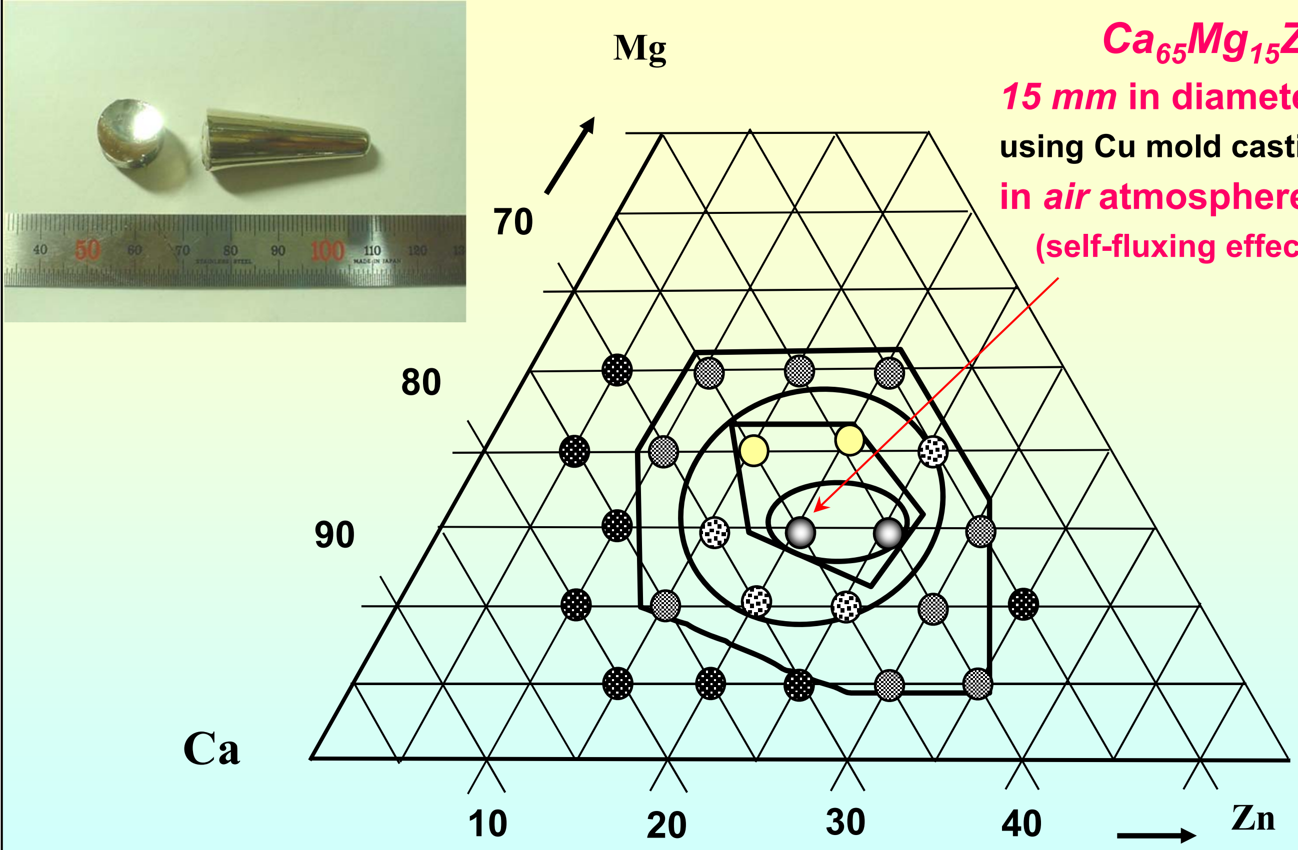
$$\varepsilon \ = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$$

$\Delta Tm + \Delta Tx$: ***Liquid phase stability*** + ***Tx*** : ***Resistance to cristallization***

(where, ΔTm = Tmmix – Tl , ΔTx = Tx – Tg)

(where, Tx = crystallization onset temperature)

Ca-Mg-Zn alloy system



$Ca_{65}Mg_{15}Zn_{20}$

***15 mm* in diameter sample**

using Cu mold casting method

in *air* atmosphere

(self-fluxing effect by Ca)

Maximum diameter for glass formation in Ca-rich Ca-Mg-Zn alloy system

◉ *over 10mm* ○ *over 7mm* ▒ *over 3mm* ▨ *over 1mm* ● *below 1mm*

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

Thermodynamic aspect for glass formation

- ***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}

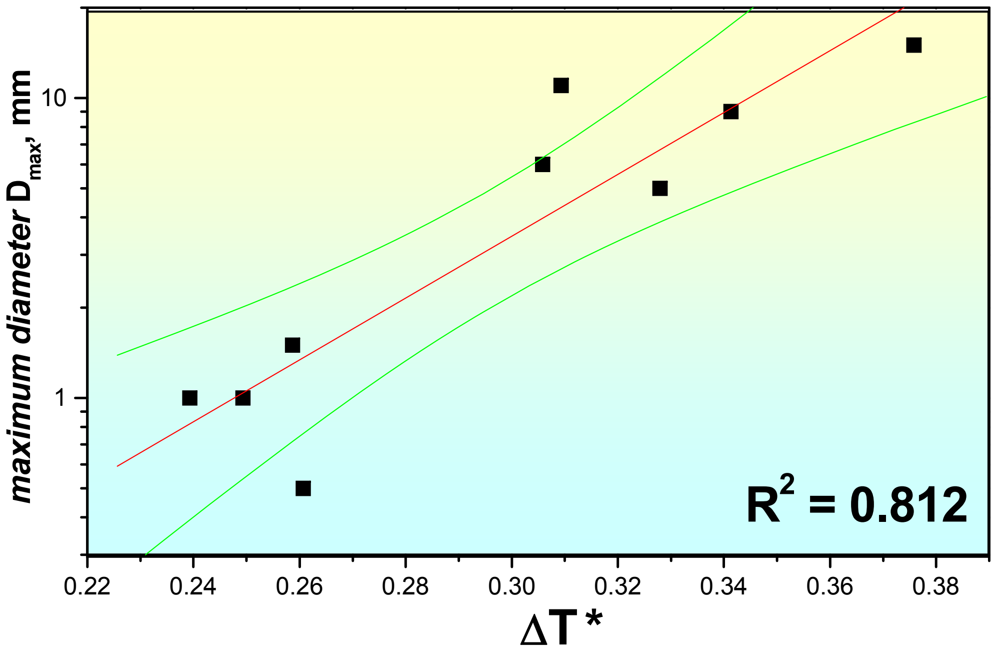
$$\Delta T^* = \frac{T_m^{mix} - T_l}{T_m^{mix}}$$

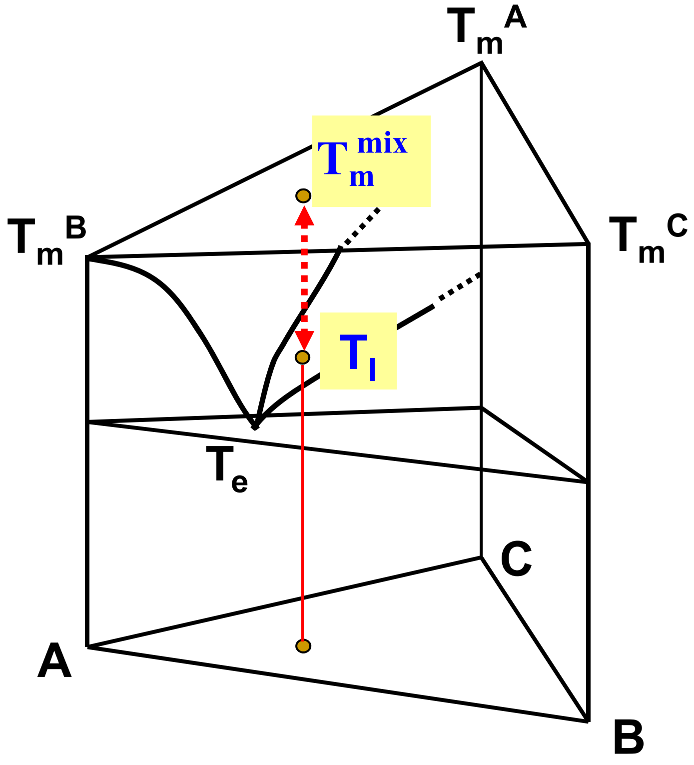
(where, $T_m^{mix} = \sum x_i T_m^i$, $x_i =$ molefraction, $T_m^i =$ melting point)

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





Structural aspect for glass formation

- **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

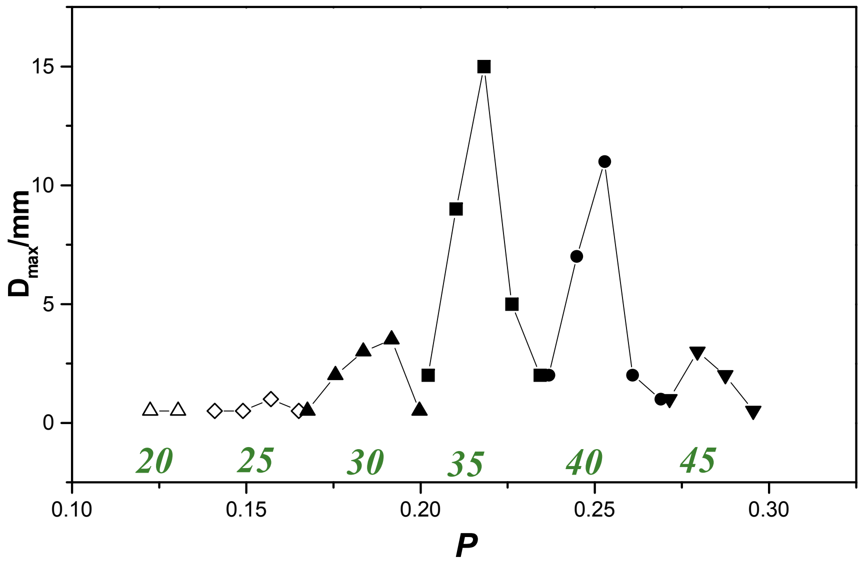
$$P' = \frac{C_B}{C_B + C_C}\left|\frac{v_B - v_A}{v_A}\right| + \frac{C_C}{C_B + C_C}\left|\frac{v_C - v_A}{v_A}\right|$$

; effective atomic mismatch of solute atom

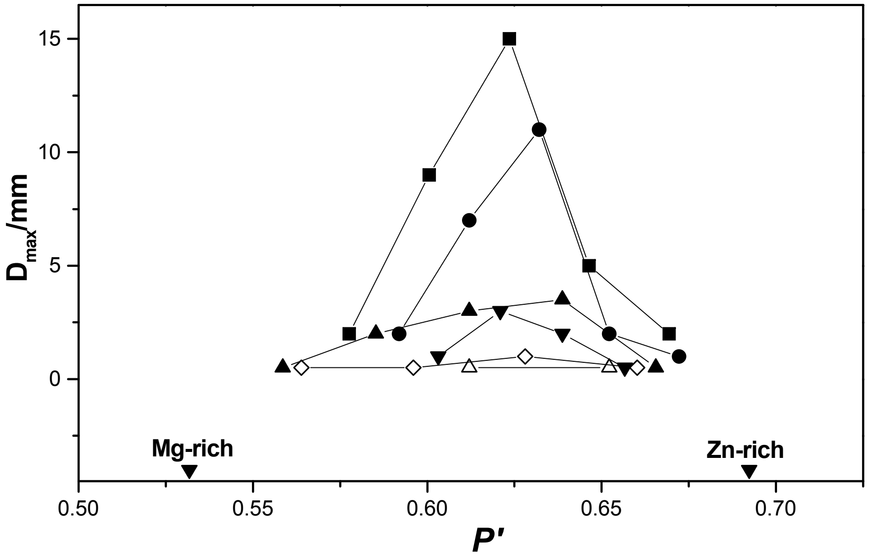
by dividing by the total amount of solute contents

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

Ca-Mg-Zn alloy system



Similar trend of D_{max} with P



Maximum dia.(D_{max}) at P'=0.625

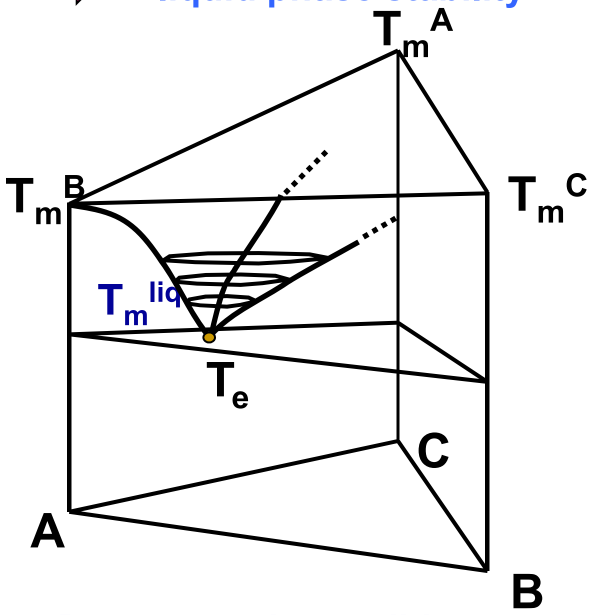
σ parameter (thermodynamic and atomic configuration aspects)

ΔT^* : Relative decrease of melting temp.

→ liquid phase stability

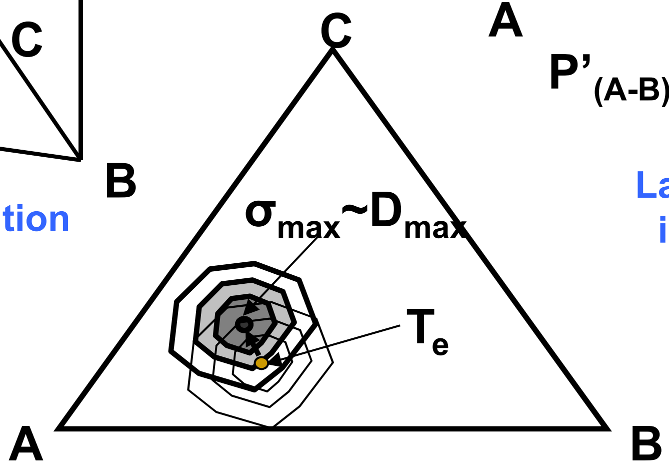
P' : Effective atomic mismatch per solute atom

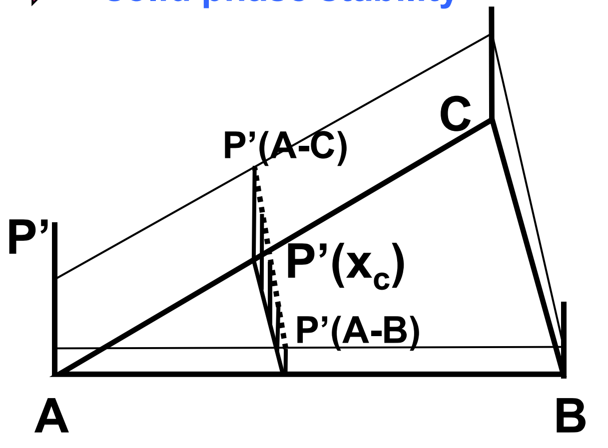
→ solid phase stability



Deep eutectic condition

×





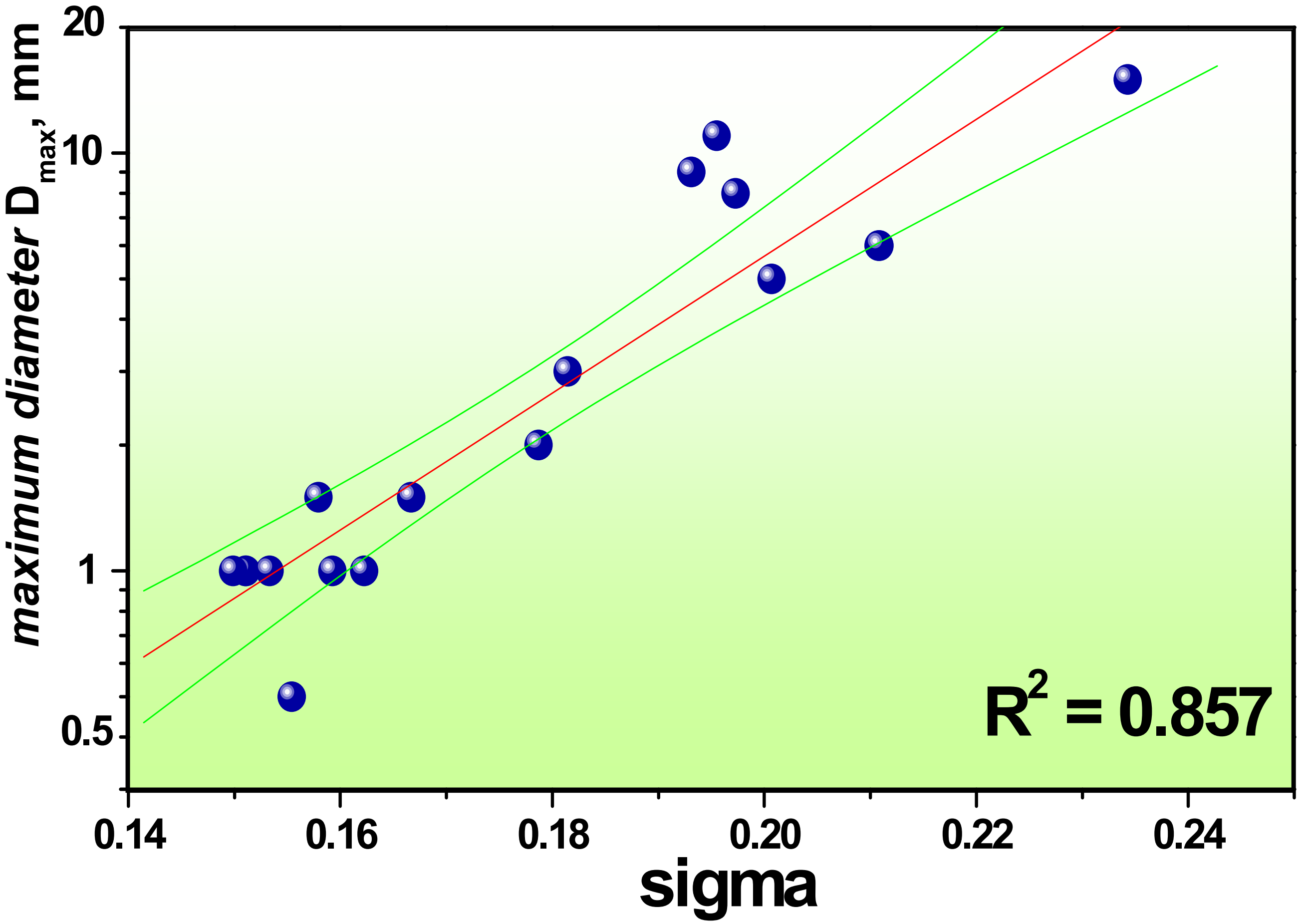
$P'_{(A\text{-}B)} \leq P'(Xc) \leq P'_{(A\text{-}C)}$

Large difference in atomic size

New criterion for GFA, σ parameter $\sigma = \Delta T^* \times P'$

* Appl. Phys. Lett., 86, 061907 (2005)

1) Calculation of GFA parameters in Ca-Mg-Zn alloy system



*** Sigma, σ parameter has a stronger correlation with GFA** than other parameters suggested so far (ΔT_x: R^2=0.358, T_{rg}: R^2=0.787, K : R^2=0.607) in Ca-Mg-Zn alloy system.

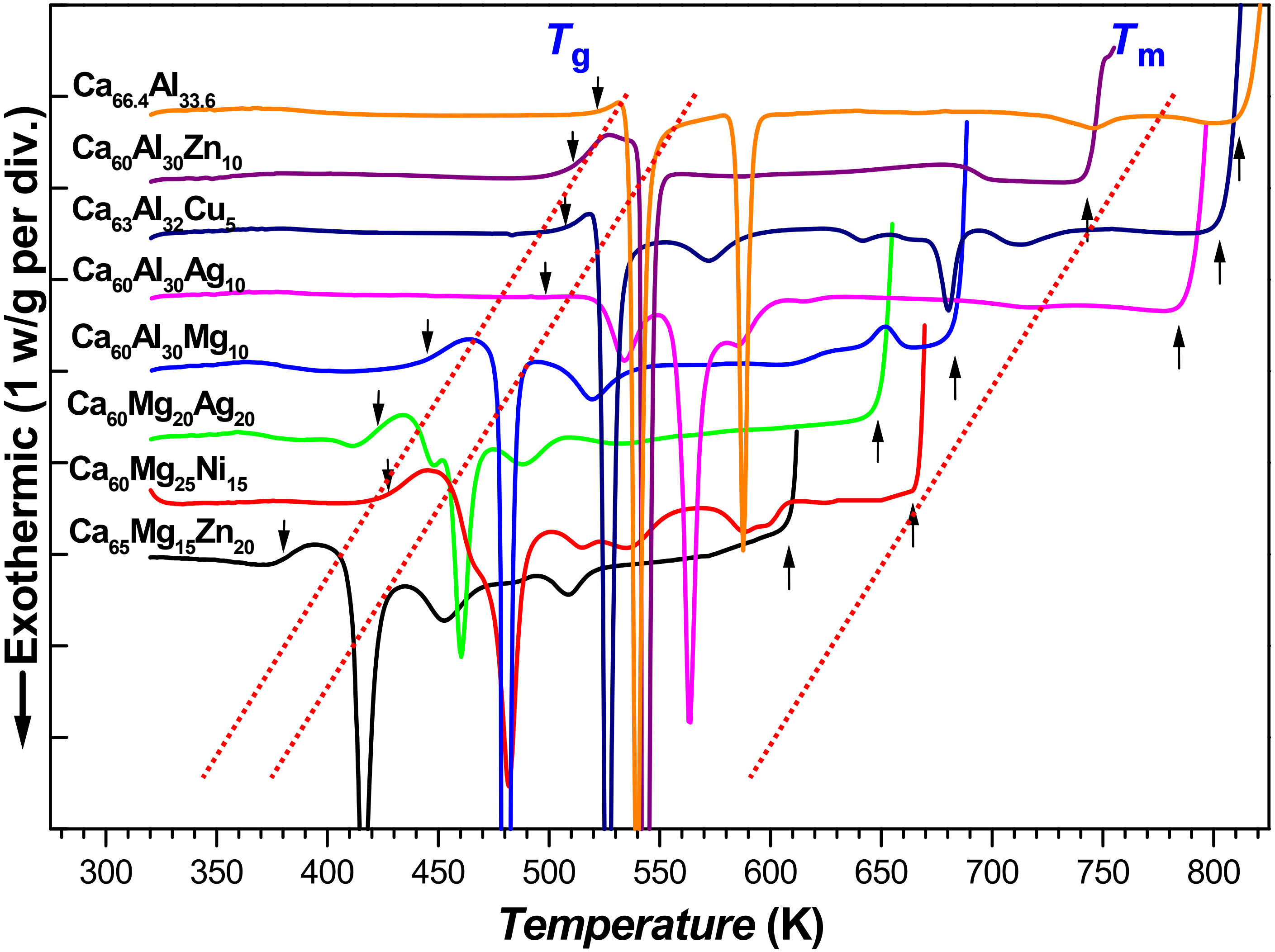
* J. Metastable and Nanocrystalline Materials, 24-25, 697 (2005)

2) Application of σ parameter for BMG-forming Ca-based ternary systems

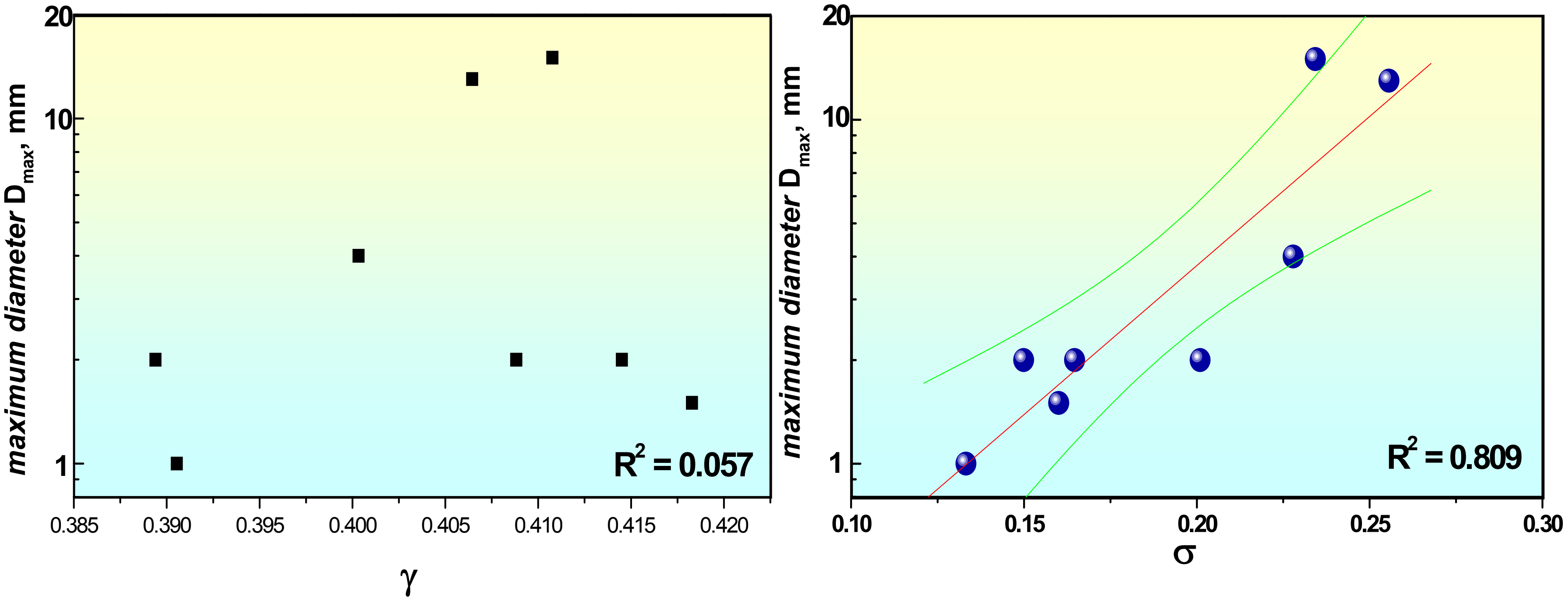
Thermal analysis, GFA parameters and maximum diameter (D_{max})
for glass formation in the Ca-based ternary BMG systems

	T_g	T_x	T_l	T_l-T_g	ΔT_x	T_{rg}	K	γ	ΔT*	σ	D_{max}
$Ca_{65}Mg_{15}Zn_{20}$	379	412	624	245	33	0.607	0.156	0.411	0.376	0.234	15
$Ca_{60}Mg_{25}Ni_{15}$	431	453	683	252	22	0.631	0.095	0.406	0.409	0.256	13
$Ca_{65}Mg_{20}Ag_{20}$	422	440	677	255	18	0.624	0.075	0.400	0.384	0.228	4
$Ca_{60}Al_{30}Mg_{10}$	449	474	709	260	24	0.634	0.103	0.409	0.318	0.201	2
$Ca_{60}Al_{30}Ag_{10}$	483	534	805	322	51	0.600	0.187	0.415	0.248	0.165	2
$Ca_{63}Al_{32}Cu_5$	512	523	831	320	11	0.615	0.037	0.389	0.221	0.150	2
$Ca_{60}Al_{30}Zn_{10}$	517	540	775	258	24	0.667	0.100	0.418	0.238	0.160	1.5
$Ca_{66.4}Al_{33.6}$	527	534	841	315	8	0.626	0.025	0.391	0.200	0.133	1

DSC traces for BMG-forming Ca-based ternary systems



2) Calculation of GFA parameters in Ca-based BMG alloy systems



Sigma, σ parameter has a stronger correlation with GFA than other parameters suggested so far (ΔT_x: $R^2=0.056$, T_{rg}: $R^2=0.080$, K : $R^2=0.148$) in Ca-based BMG alloy systems.

* Appl. Phys. Lett. 86, 201912 (2005)

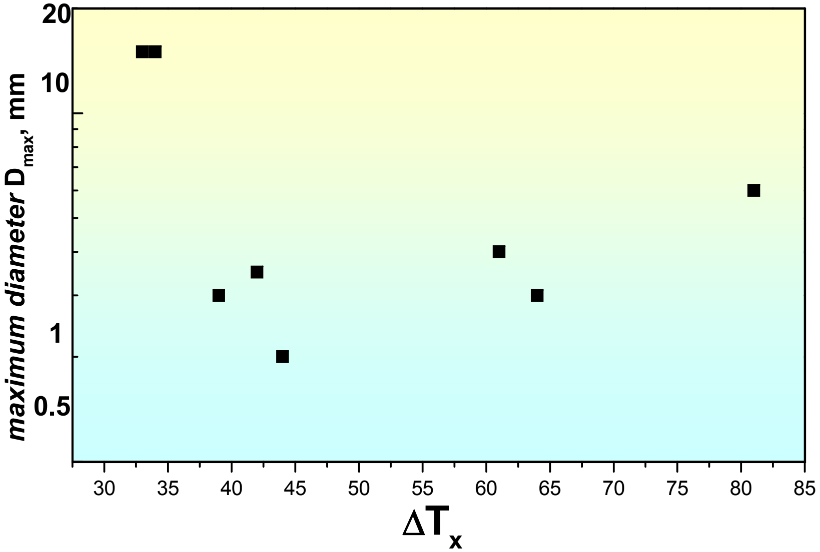
3) Application of σ parameter for BMG-forming ternary systems

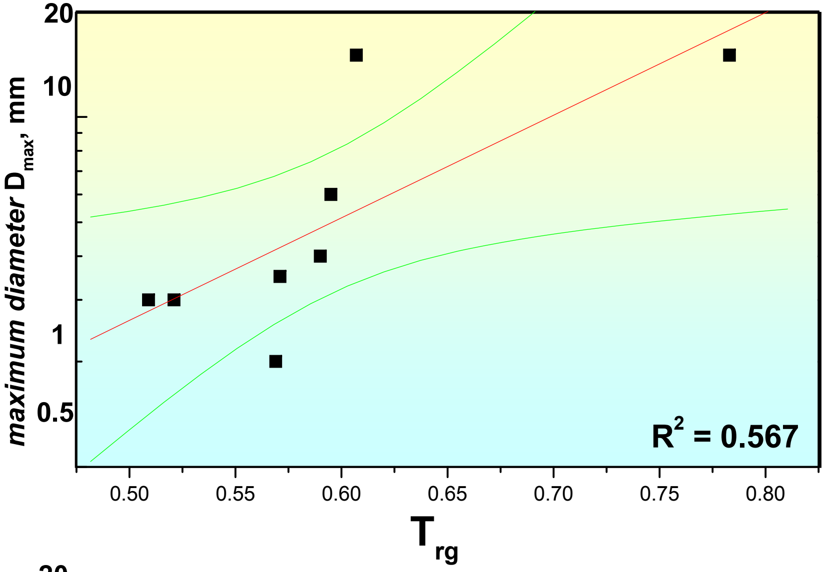
Thermal analysis, GFA parameters and maximum diameter (D_{max})
for glass formation in the ternary BMG systems

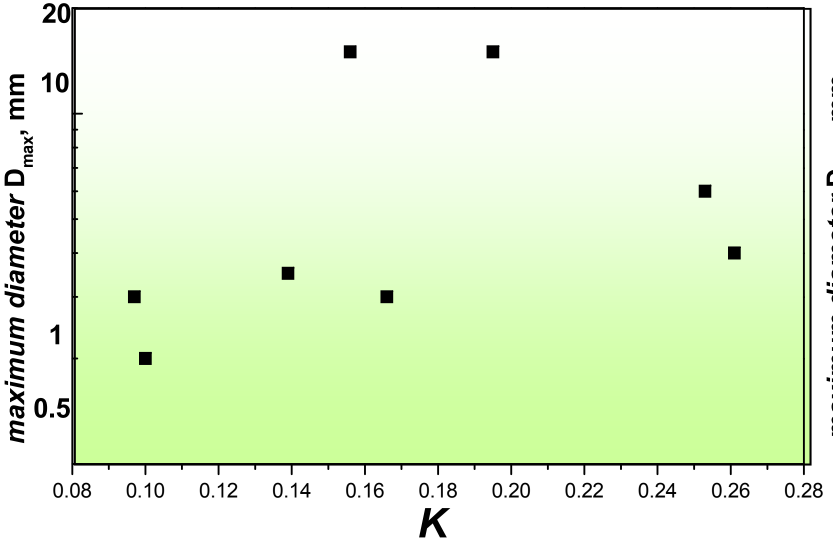
	T_g	T_x	T_l	T_m^{mix}	ΔT_x	T_{rg}	K	γ	ΔT*	P'	σ	D_{max}
$Ca_{65}Mg_{15}Zn_{20}$	379	412	624	1032	33	0.607	0.156	0.411	0.395	0.624	0.234	15
$Nd_{60}Fe_{30}Al_{10}$	750	784	958	1385	34	0.783	0.195	0.459	0.308	0.620	0.199	15
$Pd_{40}Ni_{40}P_{20}$	590	671	991	1519	81	0.595	0.253	0.424	0.348	0.476	0.158	6
$Mg_{65}Cu_{25}Y_{10}$	425	486	720	1062	61	0.590	0.261	0.424	0.322	0.470	0.167	4
$Mg_{65}Ni_{20}Nd_{15}$	459	501	805	1076	42	0.571	0.139	0.397	0.252	0.504	0.148	3.5
$La_{55}Al_{25}Ni_{20}$	491	555	941	1226	64	0.521	0.166	0.388	0.232	0.623	0.148	3
$La_{55}Al_{25}Cu_{20}$	456	495	896	1166	39	0.509	0.097	0.366	0.231	0.613	0.139	3
$Pd_{73.5}Cu_{10}Si_{16.5}$	642	686	1128	1785	44	0.569	0.100	0.388	0.368	0.300	0.107	2

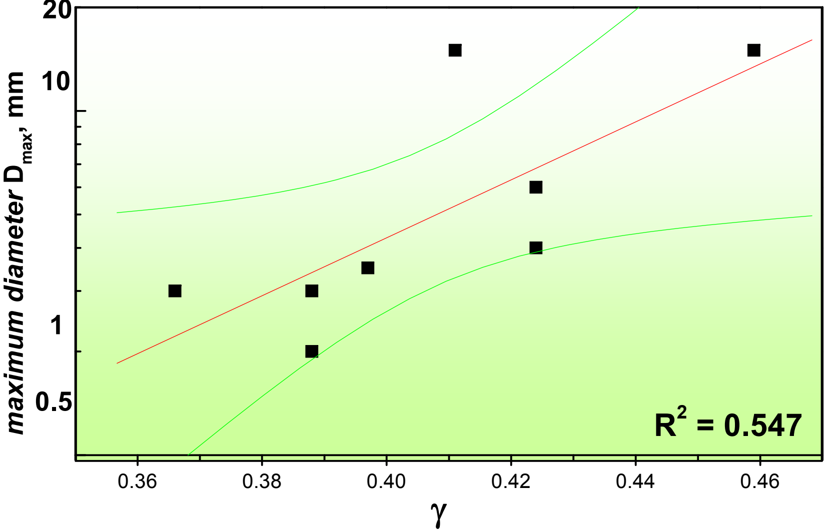
Calculation of G.F.A parameters

Ternary BMG system

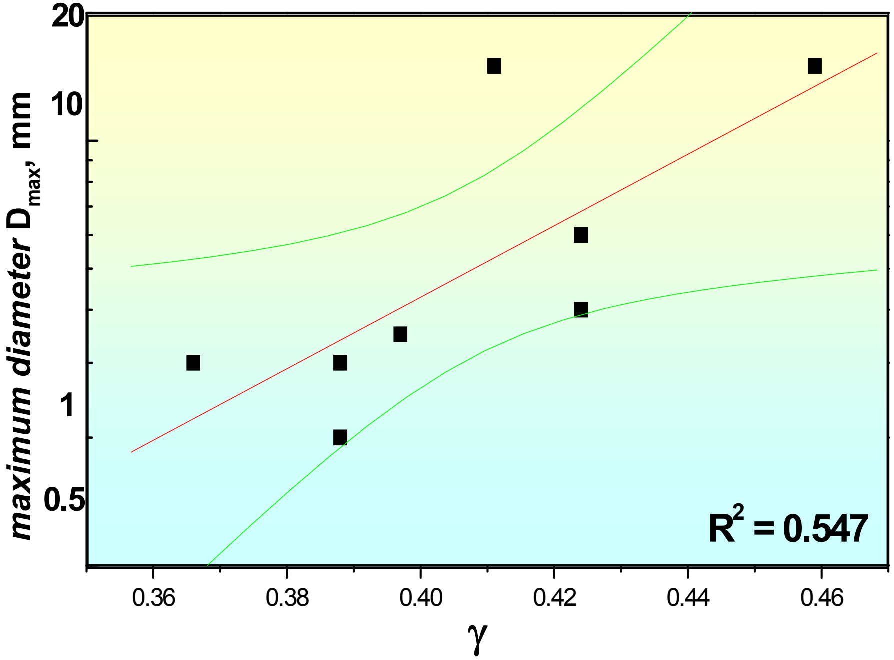


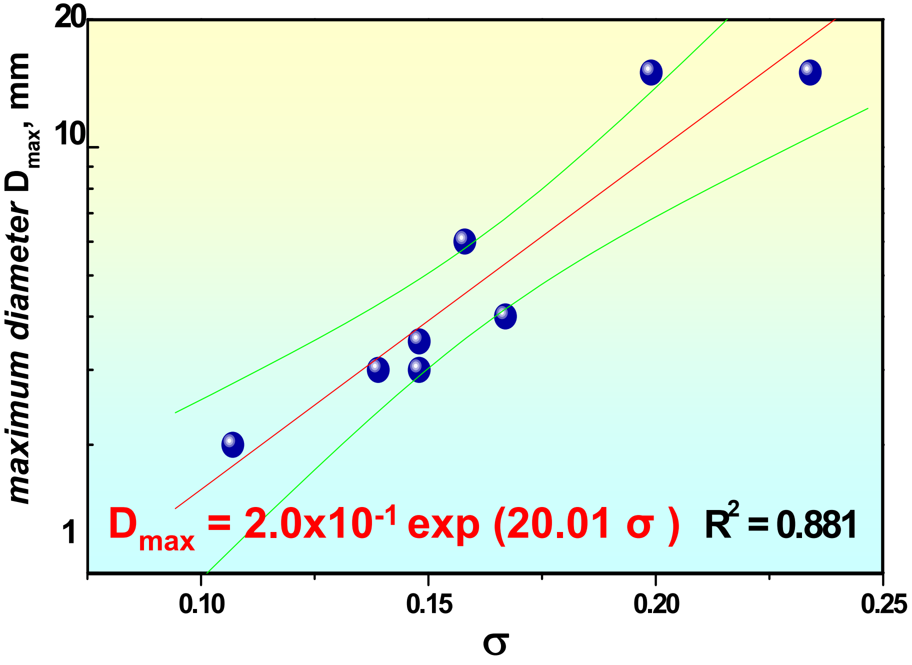






3) Calculation of GFA parameters in ternary BMG alloy systems

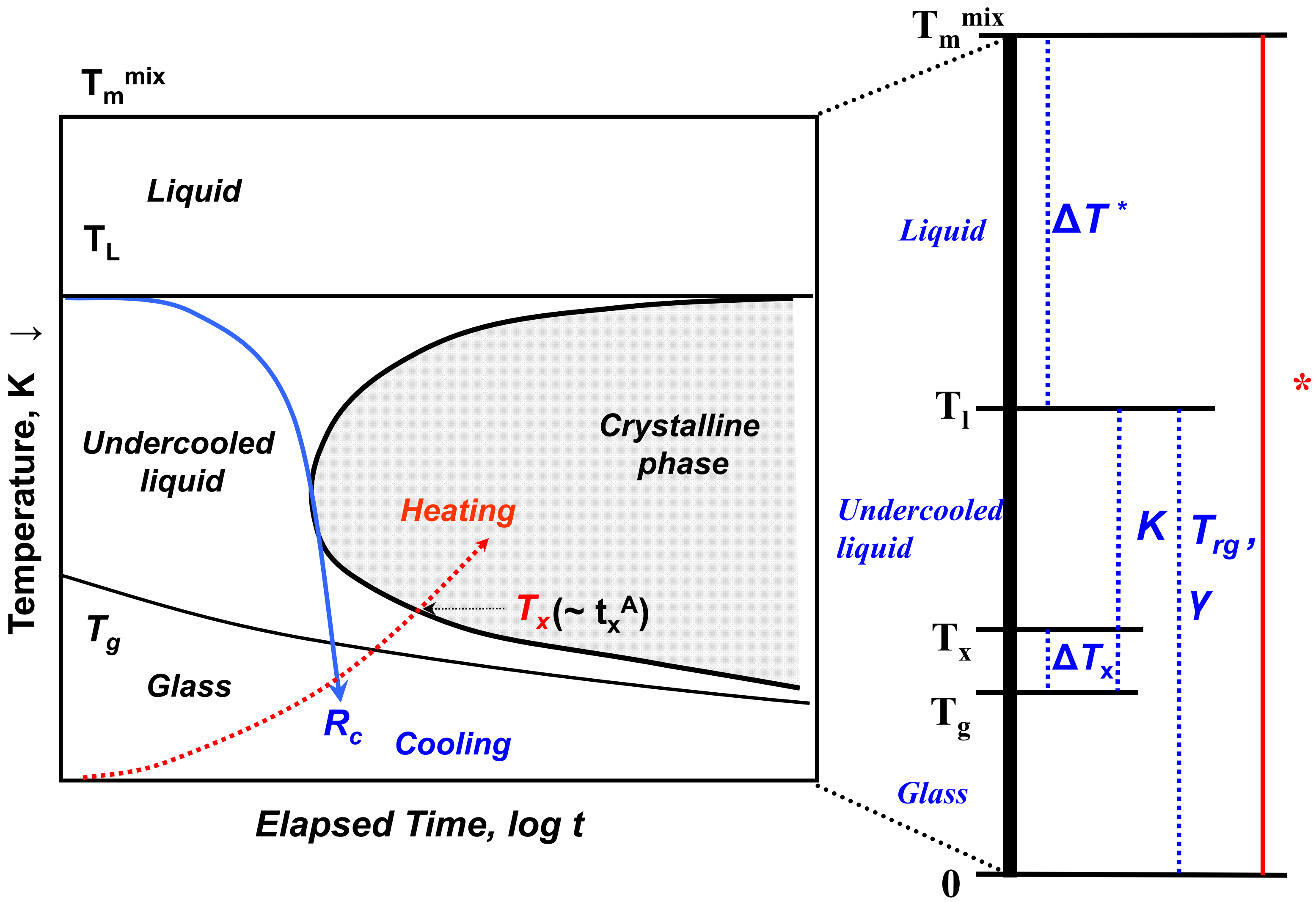




*** Sigma, σ parameter has a stronger correlation with GFA** than other parameters suggested so far (ΔT_x: R^2=0.085, T_{rg}: R^2=0.567, K : R^2=0.136) in ternary BMG alloy systems.

* Appl. Phys. Lett., 86, 061907 (2005)

Motivation for new criterion **(1) : temperature range related with GFA parameters**



Motivation for new criterion (2) : Role of characteristic temp. for GFA

Positive Temperature Factor		Negative Temperature Factor
T_x	$\xleftrightarrow{\Delta T_x}$	T_g
T_g	$\xleftrightarrow{T_{rg}}$	T_l
$T_m^{mix} - T_l$	$\xleftrightarrow{\Delta T^*}$	T_m^{mix}
ΔT_x	$\xleftrightarrow{K}$	$T_l - T_x$
T_x	$\xleftrightarrow{\gamma}$	$T_l + T_g$

With T_x ↑and T_l ↓, GFA parameter ↑. But, the role of T_g is not consistent.

Role of T_g with respect to GFA : Two different viewpoints

- from thermodynamic consideration

γ : stability of metastable liquid for glass formation

T_g ↓ ➡ GFA ↑

- Stability of the liquid during undercooling (i.e. metastable state, T_g)
: Liquid with lower Tg has the potential to be undercooled to lower temp., inducing its higher stability.

- from kinetic consideration

- constant cooling to temp. below Tg

$$X(T) = \frac{4\pi}{3R^4}\int_{T_1}^{T_g} I(T')\left[\int_{T'}^{T_g} U(T'')\mathrm{d}T''\right]^3 \mathrm{d}T'$$

X(T) : time dependent volume fraction of crystalline phase

If glass formation : $X<10^{-6}$

$$R_c^4 = \frac{4\pi}{3\times10^{-6}}\int_{T_1}^{{}_g} I(T')\left[\int_{T'}^{{}_g} U(T'')\mathrm{d}T''\right]^3 \mathrm{d}T'$$

I & U = the steady-state nucleation frequency
and the crystal growth rate

$$I = \frac{10^{35}}{\boxed{\eta}}\exp\left[\frac{-16\pi}{3}\cdot\frac{\boxed{\Delta S_f}\alpha_m^3 T^2}{N_A k(\boxed{T_l}-T)^2}\right]$$

and

$$U = \frac{kT}{3\pi a_0^2\boxed{\eta}}\left[1-\exp\left(-\frac{(\boxed{T_l}-T)\boxed{\Delta S_f}}{R_g T}\right)\right]$$

$1/R_c \propto$ increasing glass transition temp. Tg
viscosity of the supercooled liq.,
activation E for viscous flow, fusion entropy
decreasing liquidus temp. Tl

- T_{rg} : crystallization kinetics on GFA

T_g ↓ ➡ nucleation and growth rate ↑ -> GFA ↓

Points of issue for new GFA parameter

1. Combination of categories for glass formation

- γ parameter: thermodynamic/ kinetic aspects

➡ New parameter combining thermodynamic/ kinetic aspects

2. Temperature scale for GFA parameter

ΔT_x parameter : T_x - T_g

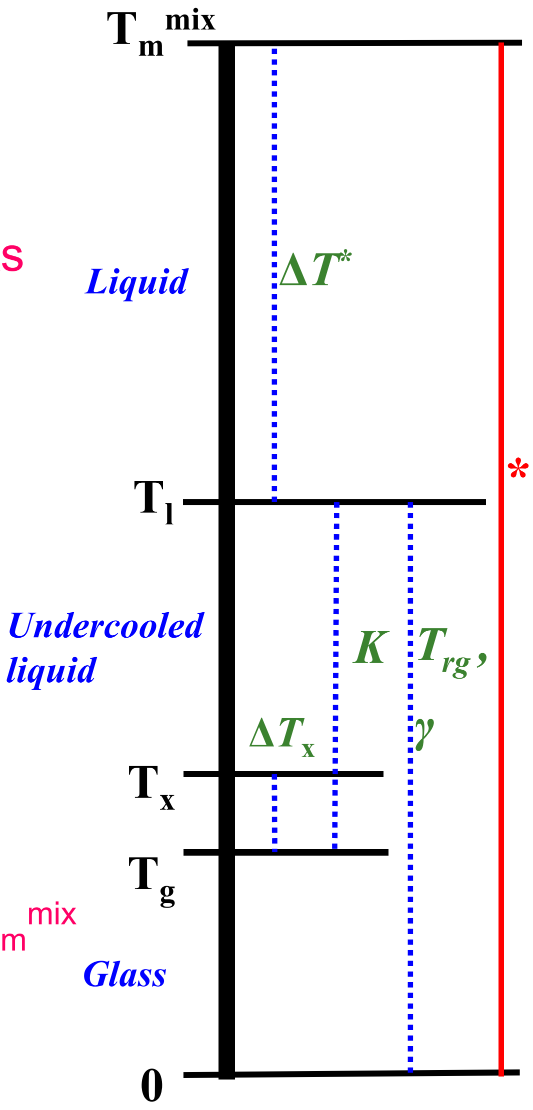
K parameter : T_g - T_x - T_l

T_{rg} parameter : T_g - T_l

γ parameter : T_g - T_x - T_l

ΔT* parameter : T_l - T_m^{mix}

➡ New parameter covering temperature range T_g - T_x - T_l - T_m^{mix} with considering about two different role of T_g



A new criterion for GFA : ε parameter

a. Liquid phase stability :

- Relative stability of stable liquid : distance from the T_m^{mix} to liquidus melting temp.,

$$\Delta T_m = T_m^{mix} - T_l \qquad (\gamma \text{ parameter: } T_l)$$

- Stability of metastable liquid : range of supercooled liquid,

$$\Delta T_x = T_x - T_g \qquad (\gamma \text{ parameter: } T_g)$$

b. Resistance to crystallization : T_x (γ parameter: T_x)

- relative difficulties for the formation (nucleation and crystal growth) of the competing crystalline phases in various BMG forming alloy system

- Retarding incubation time for crystallization : relative position of the CCT curves along the time axis

c. nomalizing : T_m^{mix}

- Exclusion of systematic and compositional effects in various BMG alloy systems

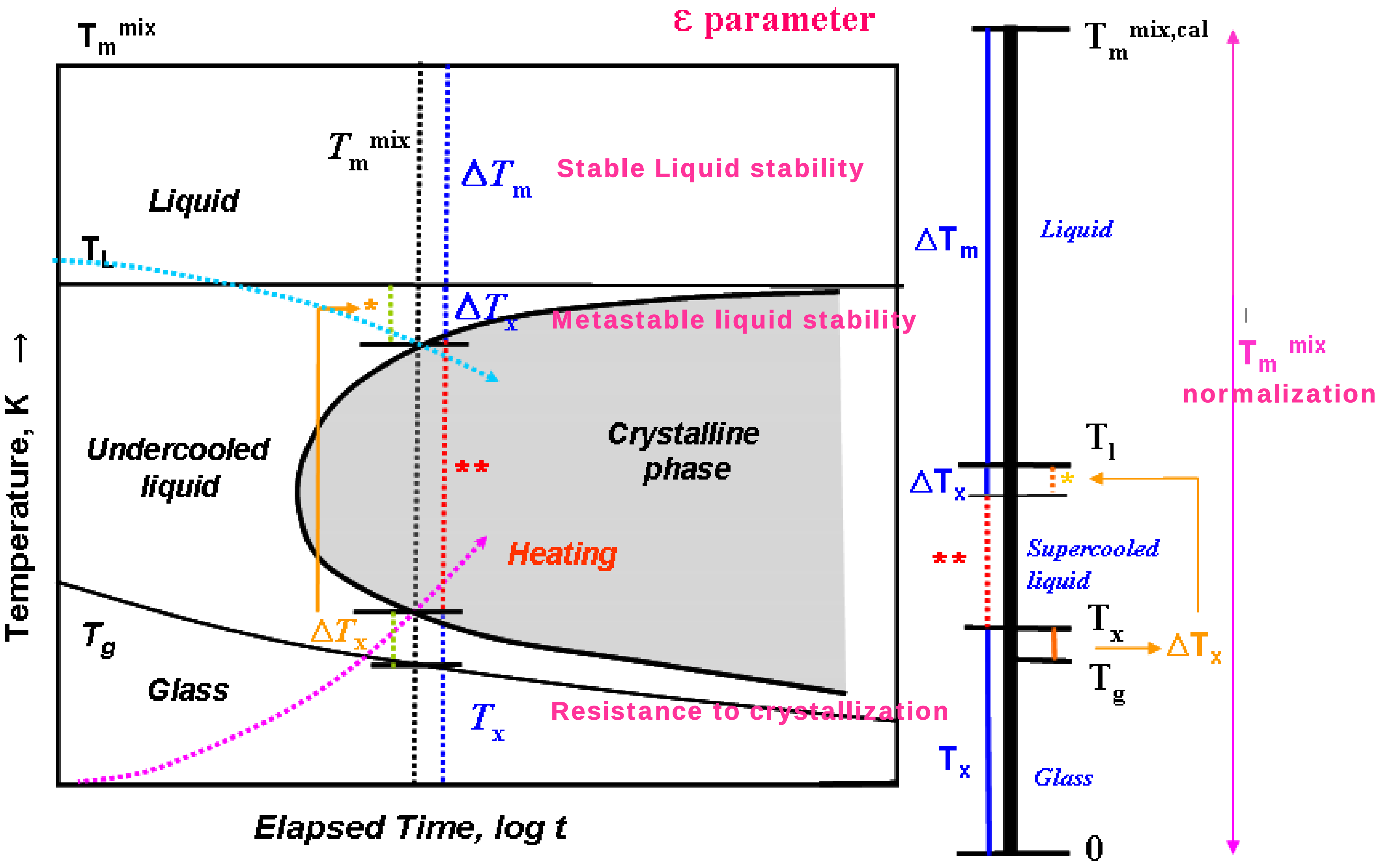
A New criterion for GFA of BMGs

$$\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$$

E. S. Park et al., *submitted to Acta Mater.* (2005)

ε parameter (thermodynamic and kinetic aspects)

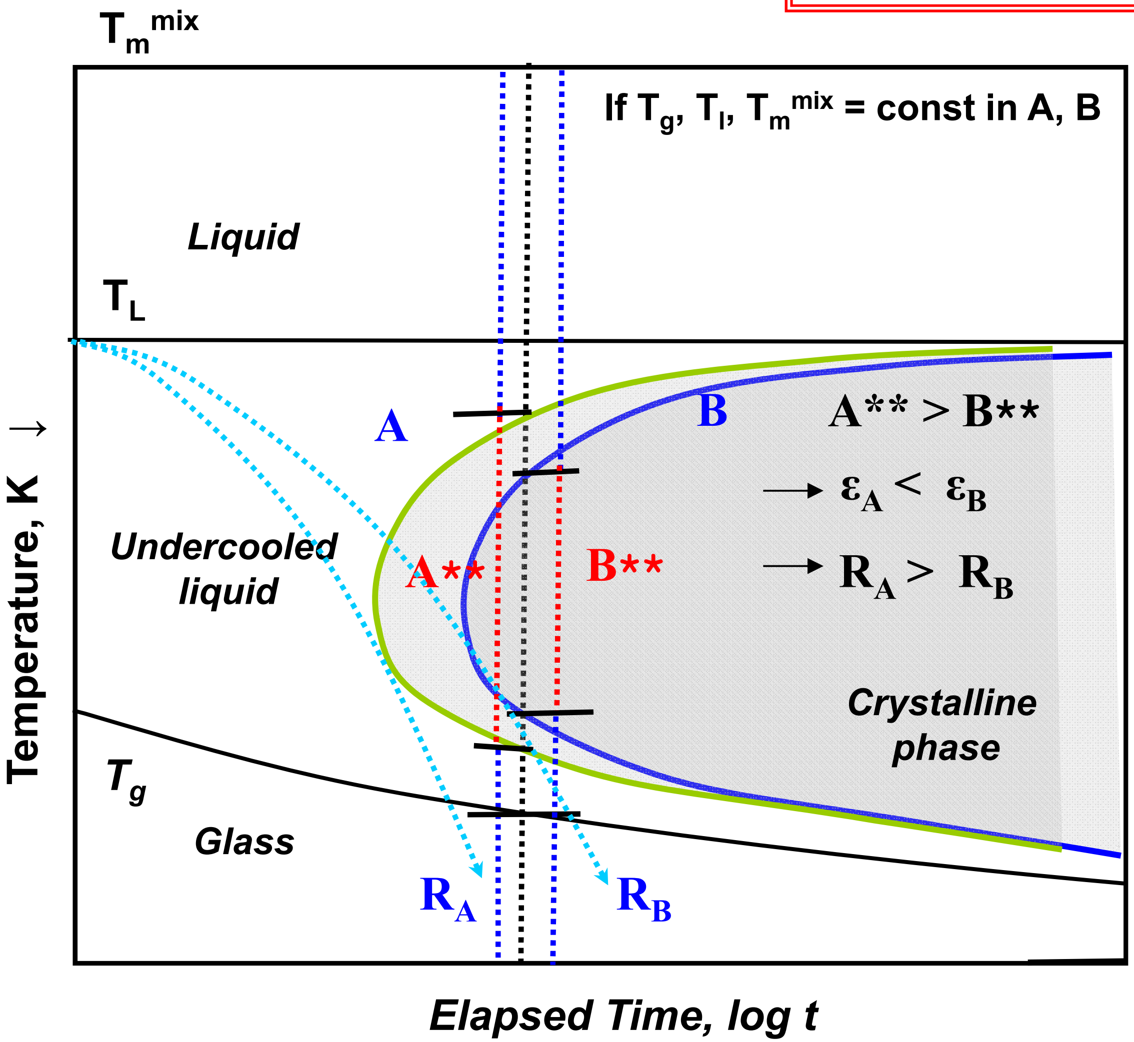
** CCT curve showing temperature range for ε parameter*



ε parameter (thermodynamic and kinetic aspects)

A New criterion for GFA of BMGs

$$\boxed{\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}}$$



Cu-based

Cu-Zr
Cu-Zr-Al
Cu-Zr-Al-Al
Cu-Zr-Al-Y
Cu-Zr-Ti
Cu-Zr-Ti-Be
Cu-Zr-Ti-Ni-(Si,Sn)

Fe-based

Fe-B
Fe-Ni-B
Fe-Si-B
Fe-P-C
Fe-Nb-Y-B
Fe-Cr-Mo-C-B-(Y)

Mg-based

Mg-Ni-Nd
Mg-Cu-Y-(Ag)
Mg-Cu-Gd-(Ag)
Mg-Cu-Ag-Pd-Gd
Mg-Cu-Ni-Zn-Ag-Y-(Gd)

Ni-based

Ni-Nb
Ni-Nb-Ta
Ni-Nb-Ti-Hf
Ni-Si-B
Ni-Zr-Ti-(Sn-Si)
Ni-Zr-Ti-Si-Sn-Nb

Zr-based

Zr-Al-Ni
Zr-Al-Cu-Ni
Zr-Al-Cu-Ni-Ti
Zr-Be-Cu-Ni-Ti

Ca-based

Ca-Al
Ca-Al-Cu
Ca-Mg-Ni
Ca-Mg-Zn

Co-based

Co-Si-B
Co-Fe-Ta-B
Co-Fe-Nb-Zr-B

Nd-based

Nd-Al-Fe
Nd-Al-Ni-Cu-Co
Nd-Al-Ni-Cu-Fe

La-based

La-Al-Ni
La-Al-Cu
La-Al-Ni-Cu
La-Al-Ni-Co-Cu

Y-based

Y-Al-Co
Y-Al-Co-Sc
Y-Al-Co-Ni-Sc

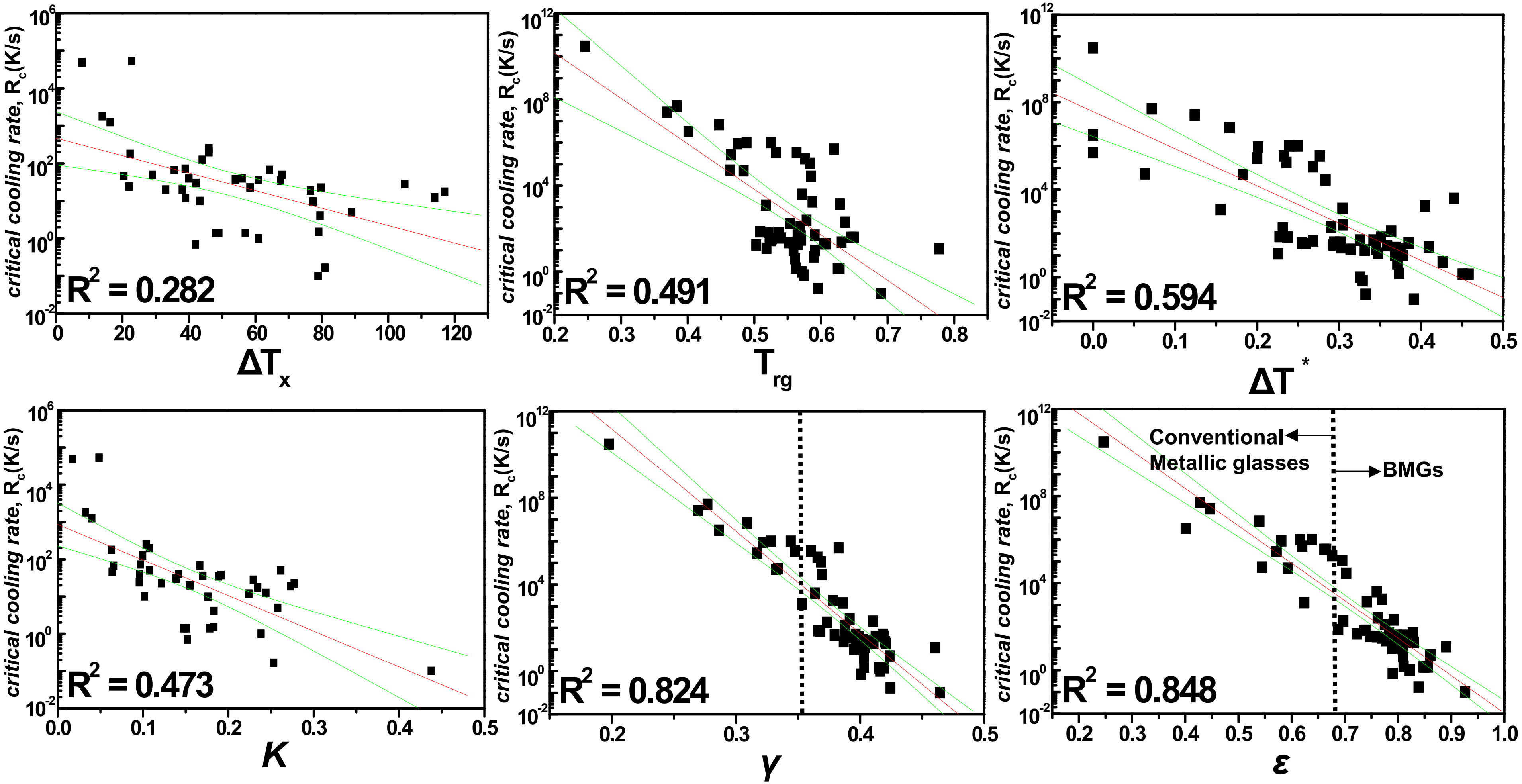
Pt-based

Pt-Ni-P
Pt-Cu-Ni-P
Pt-Cu-Co-P

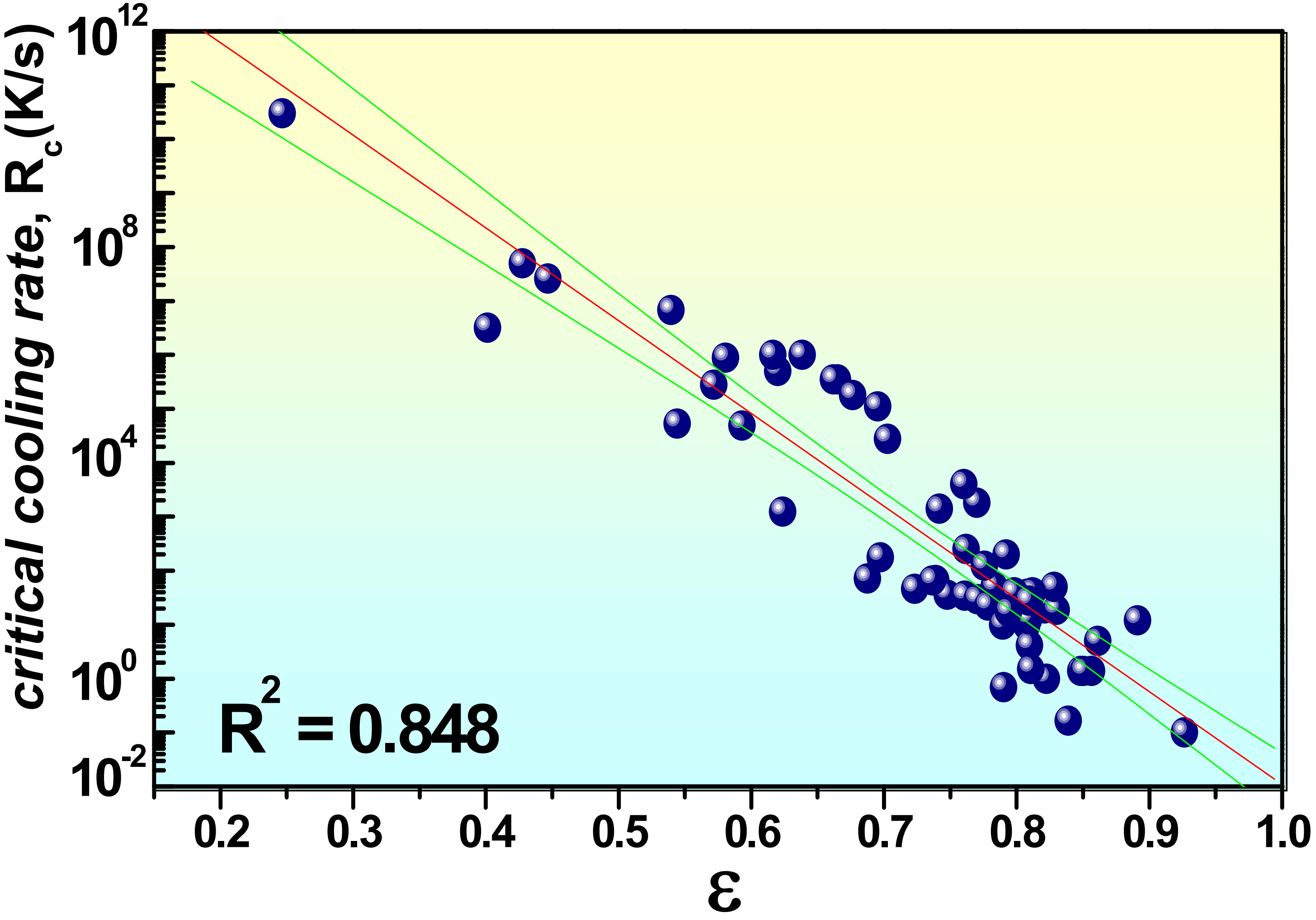
Pd-based

Pd-Si
Pd-Cu-Si
Pd-Ni-P
Pd-Cu-Ni-P

Critical cooling rate (R_c) vs. *GFA parameters*

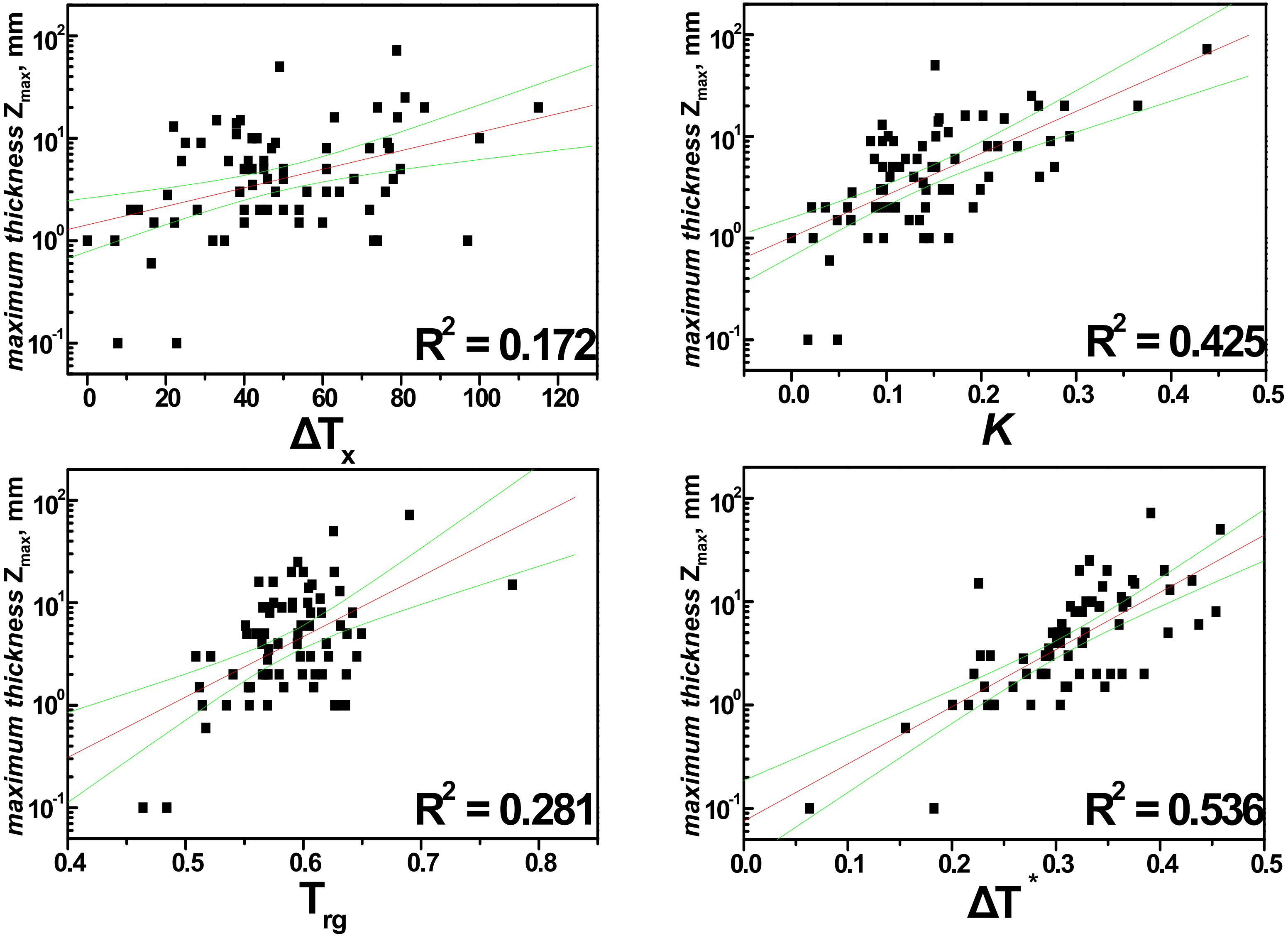


Correlation between R_c and ε parameter

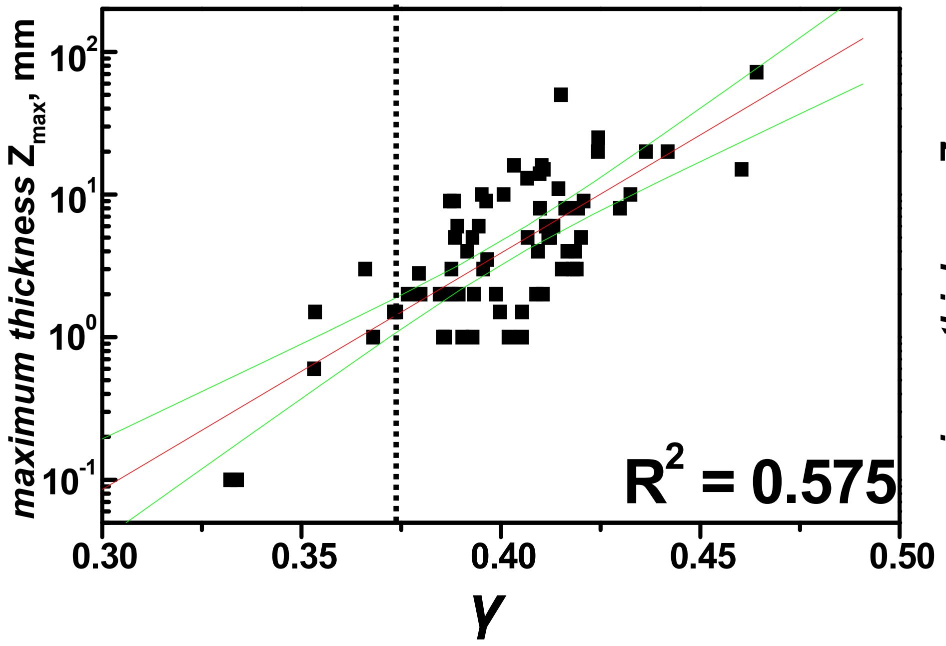


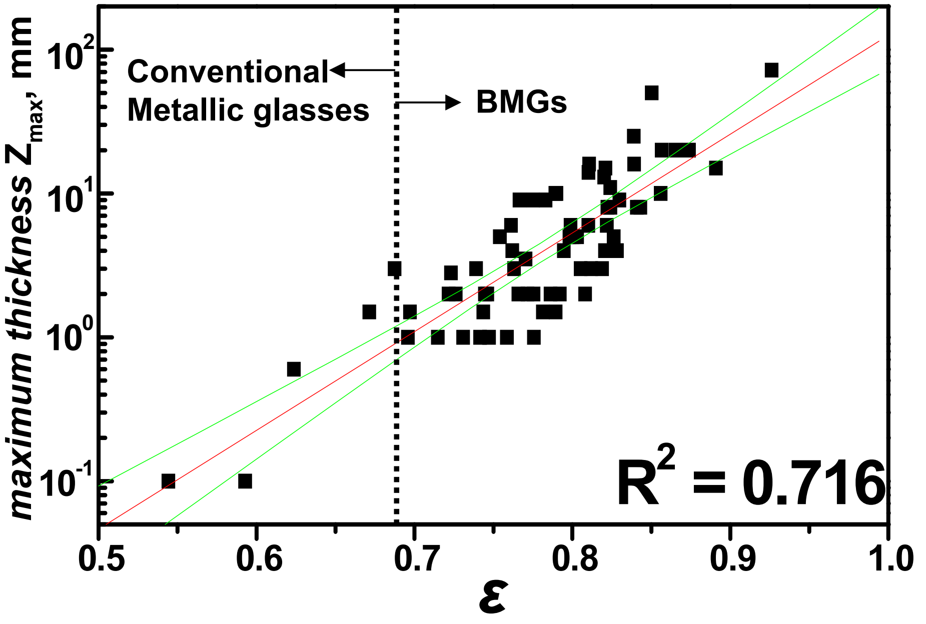
* Epsilon has a stronger correlation with R_c than other parameters suggested so far (ΔT_x: R^2=0.282, T_{rg}: R^2=0.491, ΔT^*: R^2=0.594, γ : R^2=0.824) in various BMG alloy systems.

Maximum section thickness of BMGs (Z_{max}) vs. GFA parameters

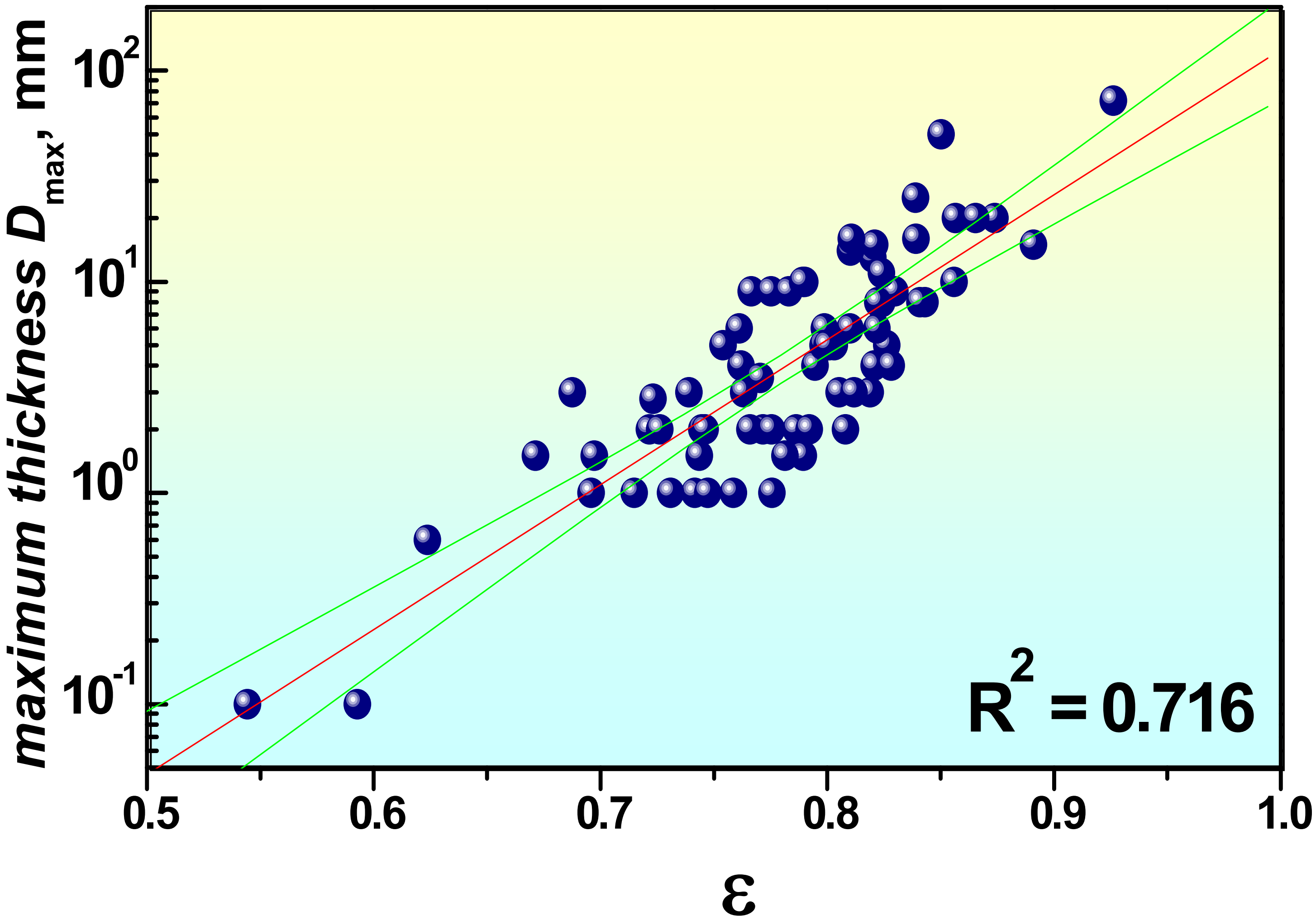


Maximum section thickness of BMGs (Z_{max}) vs. *GFA parameters*





Correlation between D_{max} and ε parameter



- **Epsilon parameter has a stronger correlation with D_{max}** than other parameters suggested so far (ΔT_x: R^2=0.172, T_{rg}: R^2=0.281, ΔT^*: R^2=0.536, γ: R^2=0.536) in various BMG alloys.

Application of ε parameter

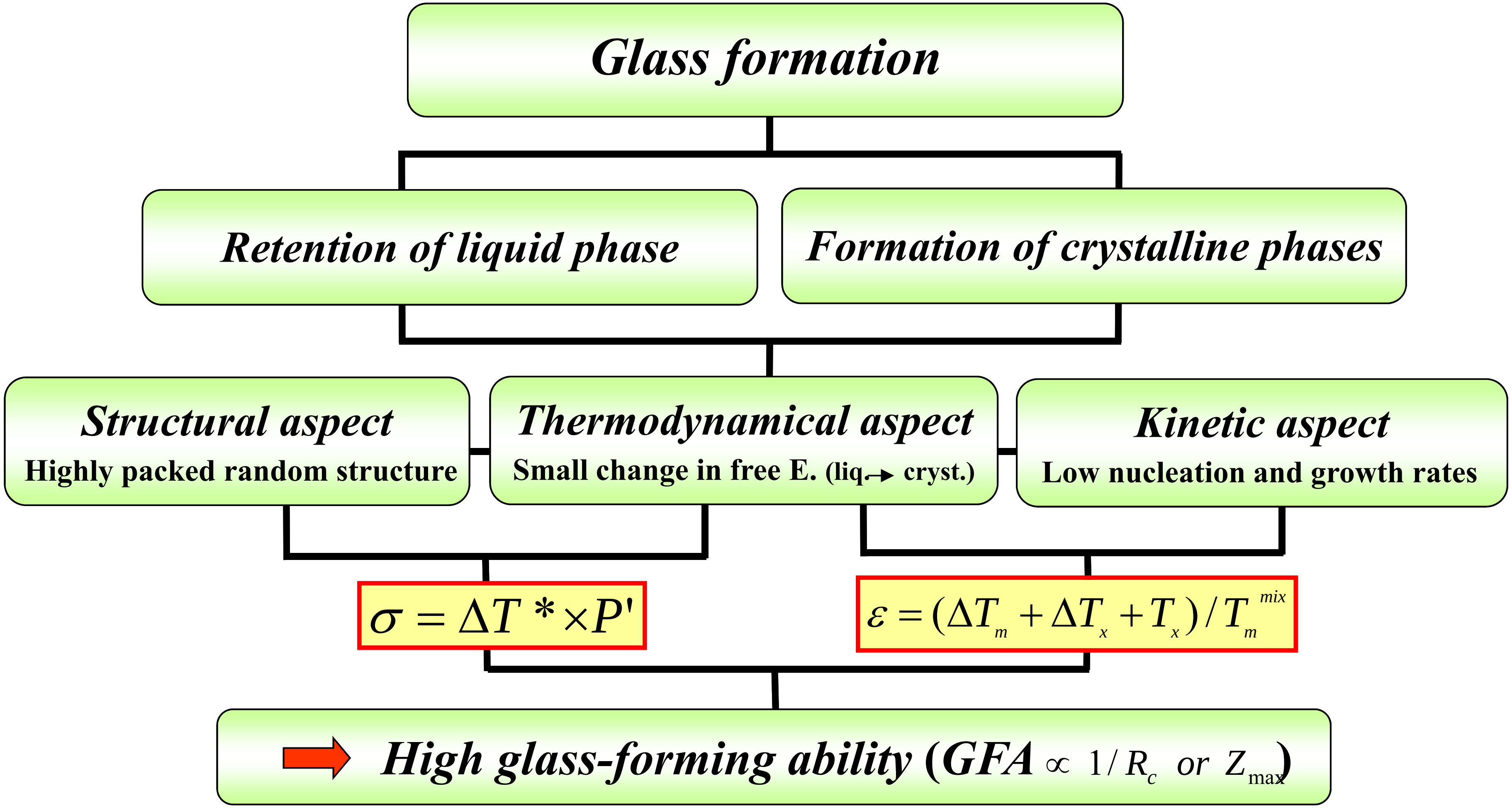
Estimation of the attainable maximum thickness for newly developed BMGs

*** Relationship between ε and maximum section thickness D_{max} :**

$$D_{max}(\text{mm}) = 1.71 \times 10^{-5} \exp(15.81\varepsilon)$$

	ΔT_x	T_{rg}	ΔT^*	K	γ	ε	$Z_{max, exp}$ (mm)	$Z_{max, cal}$ (mm)
$Ca_{66.4}Al_{33.6}$	7	0.627	0.201	0.023	0.390	0.715	1	1.4
$Ni_{60}Nb_{30}Ta_{10}$	13	0.599	0.287	0.021	0.380	0.726	2	1.7
$Fe_{74}Nb_6Y_3B_{17}$	48	0.597	0.290	0.094	0.396	0.763	3	2.9
$Ni_{59}Zr_{16}Nb_7Ti_{13}Si_3Sn_2$	40	0.650	0.302	0.096	0.412	0.798	5	5.1
$Ti_{45}Zr_5Ni_{15}Cu_{25}Be_7Sn_3$	61	0.595	0.328	0.152	0.407	0.800	5	5.3
$Cu_{54}Zr_{27}Ti_9Be_{10}$	42	0.637	0.310	0.114	0.412	0.801	5	5.3
$Mg_{65}Cu_{25}Gd_{10}$	61	0.572	0.325	0.238	0.416	0.822	8	7.5
$Cu_{46}Zr_{42}Al_7Y_5$	100	0.604	0.335	0.293	0.432	0.856	10	12.8
$Y_{36}Al_{24}Co_{20}Sc_{20}$	115	0.600	0.322	0.365	0.442	0.874	20	17.0

Improvement of GFA



Glass formation

Retention of liquid phase

Formation of crystalline phases

Structural aspect
Highly packed random structure

Thermodynamical aspect
Small change in free E. (liq.→ cryst.)

Kinetic aspect
Low nucleation and growth rates

$\sigma = \Delta T^* \times P'$

$\varepsilon = (\Delta T_m + \Delta T_x + T_x) / T_m^{mix}$

➡ ***High glass-forming ability*** **(*GFA*** $\propto 1/R_c$ or $Z_{\max}$**)**

In estimating the GFA, the combinational effects of thermodynamic, kinetic and structural aspects for glass formation should be considered.

IH1: What is the glass with lowest T_g which is close to T_K? &

Please make a table for T_g and T_K of BMGs.

IH2: Explain the detail how to get R^2 (regression coefficient) during fitting.

IH3: Please make a summary of other GFA parameters based on termo-dynamic modeling, structural and topological parameters, physical properties of alloys, computational approches, etc. You can read and summarize our text from 93 page to 135 page or find other references.

Midterm: 29th April (Tuesday) 7 PM – 9 PM

Scope: text ~ 144 pages/ teaching note ~ #14/ and references