2018 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

04.16.2018

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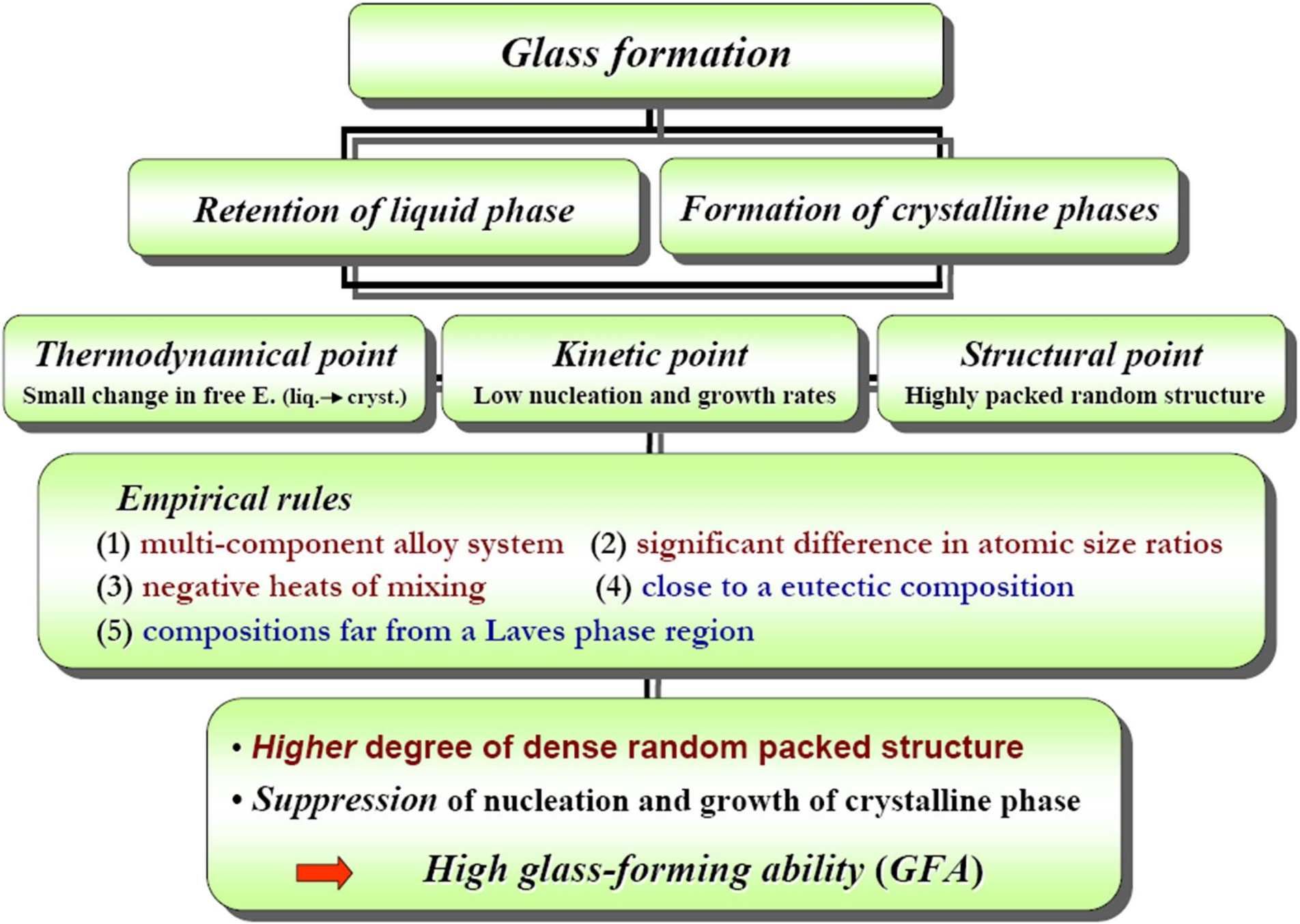

Glass formation
Retention of liquid phase
Formation of crystalline phases
Thermodynamical point
Small change in free E. (liq.→cryst.)
Kinetic point
Low nucleation and growth rates
Structural point
Highly packed random structure
Empirical rules
(1) multi-component alloy system
(2) significant difference 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)

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.

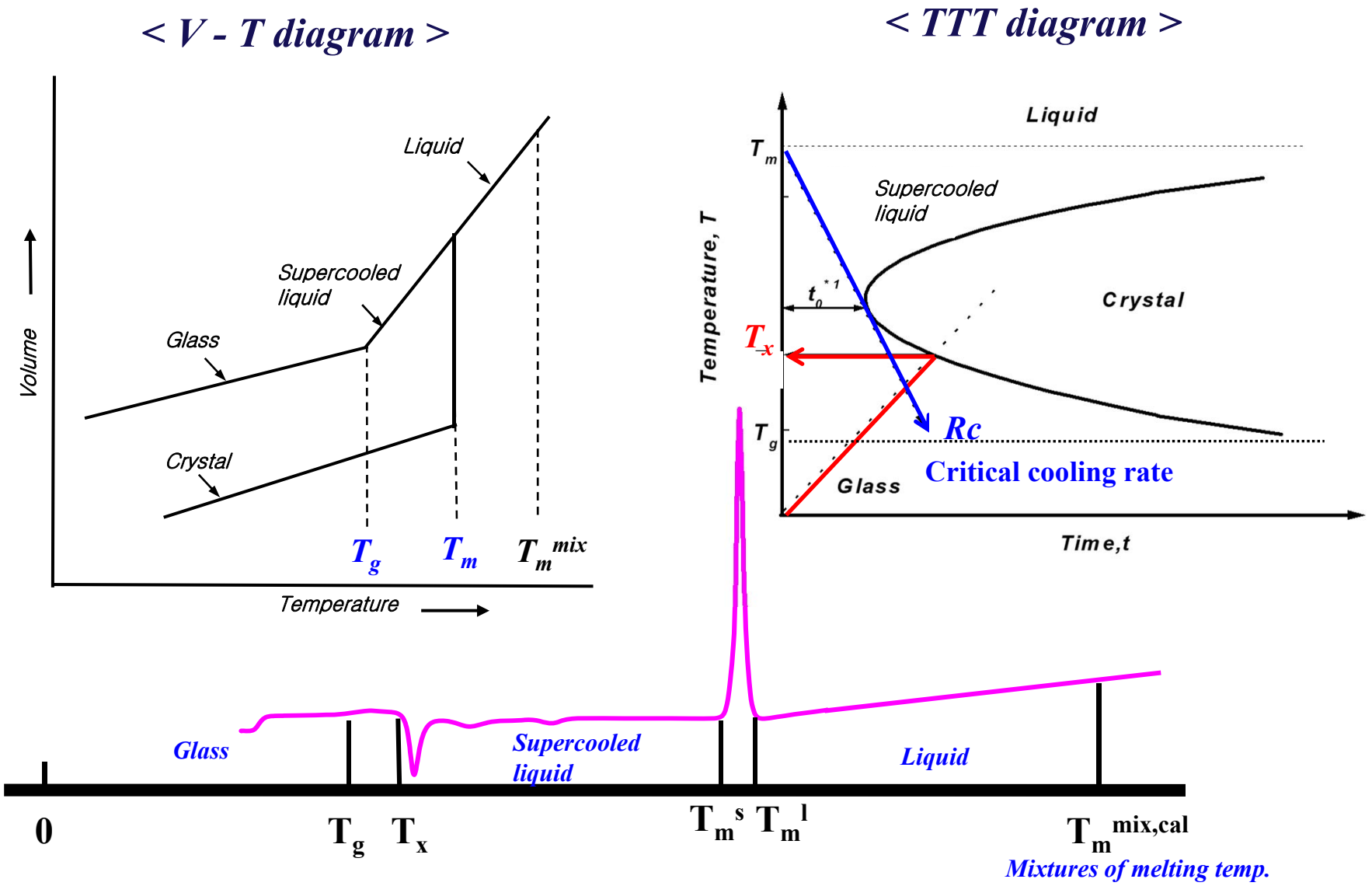
2. *Thermodynamic modeling*. Thermodynamic parameters such as heat of mixing are used in this group to predict the glass formation and evaluate GFA in a given alloy system.

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)

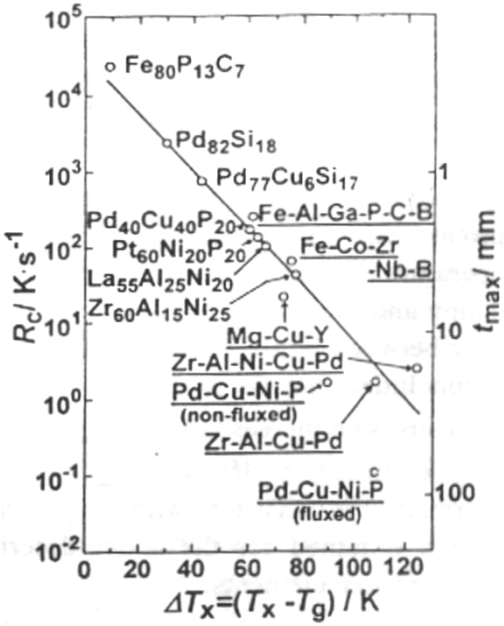
ΔT :* Relative decrease of melting temperature + *P'* : atomic size mismatch

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

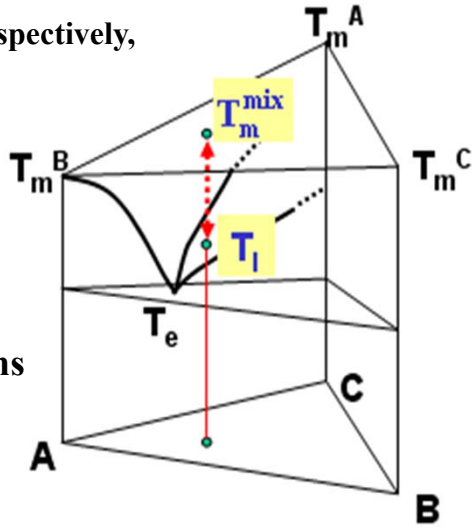
- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

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.)

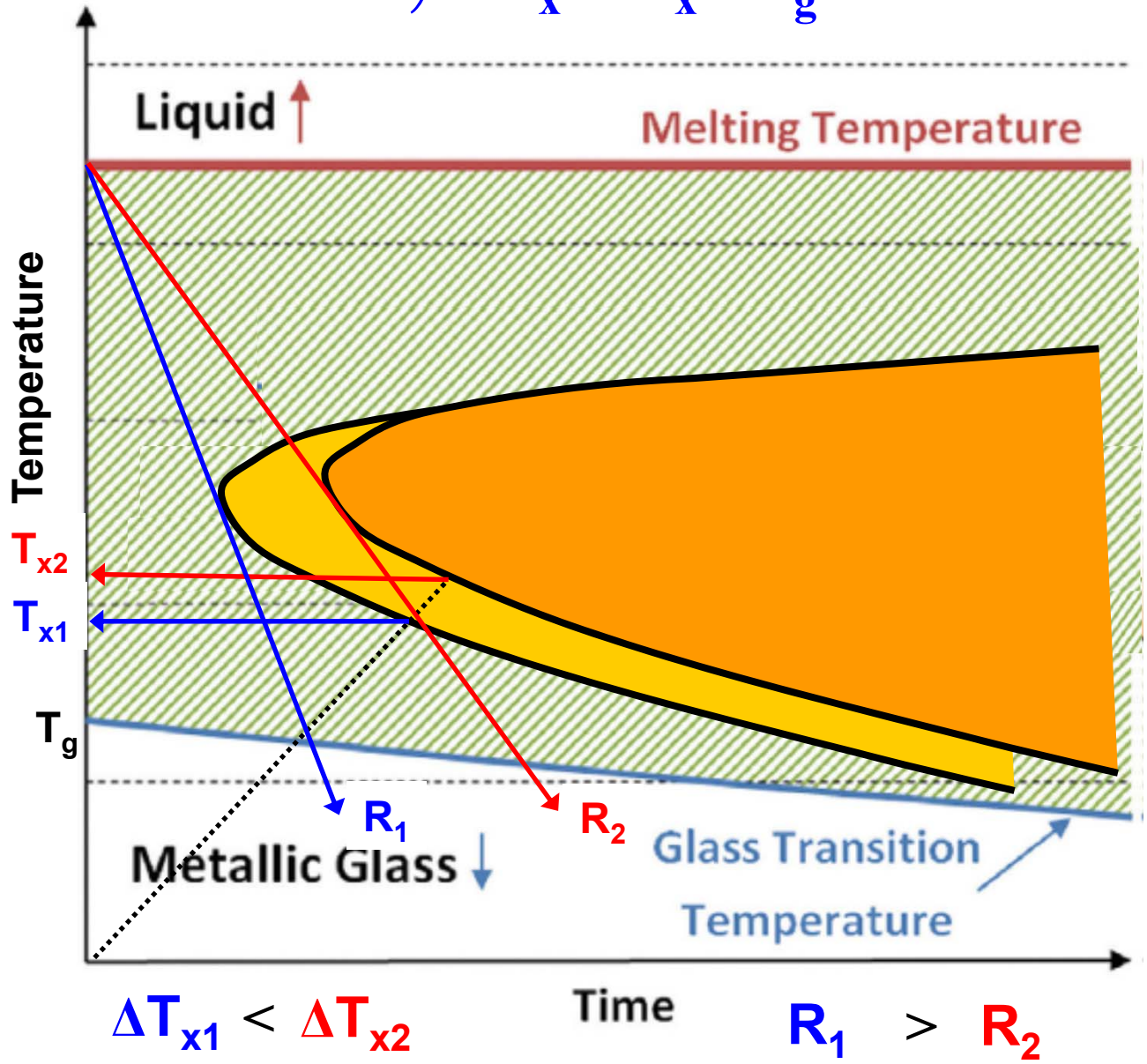
- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA



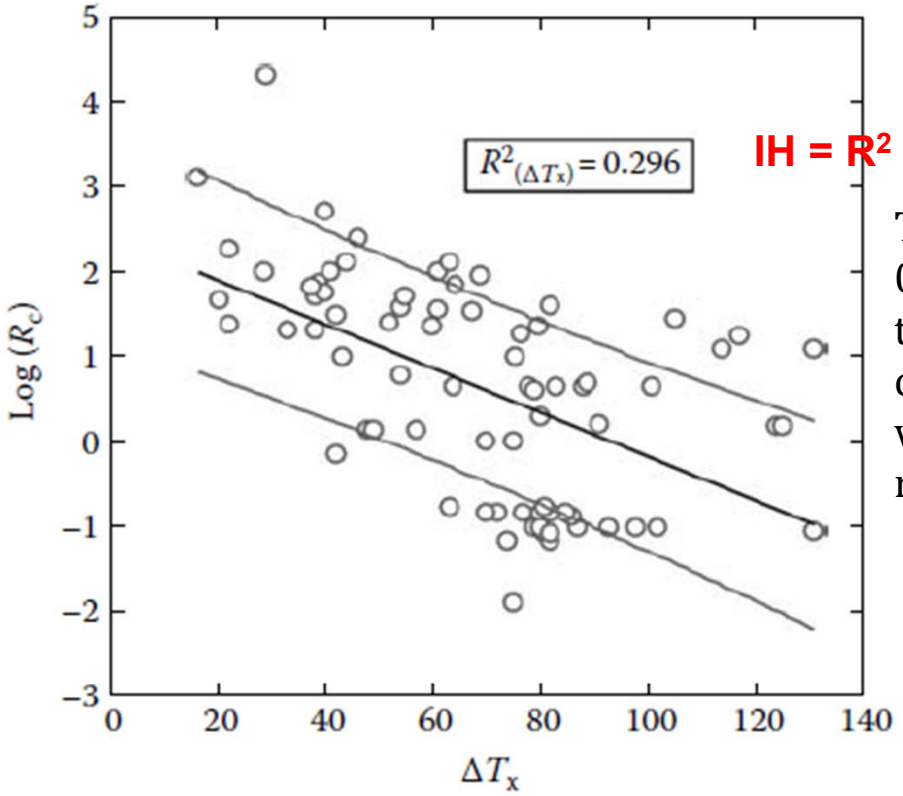
→ $T_m{}^{mix}$ represents the fractional departure of T_m with variation of compositions and systems from the simple rule of mixtures melting temperature

Time Temperature Transformation diagram:

1) $\Delta T_x = T_x - T_g$



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.

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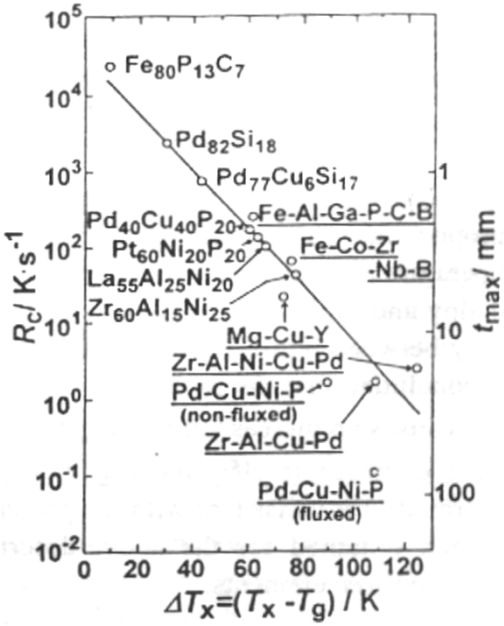

2) K parameter = $(T_x-T_g)/(T_l-T_x) = \Delta T_x/(T_l-T_x)$

- 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.)

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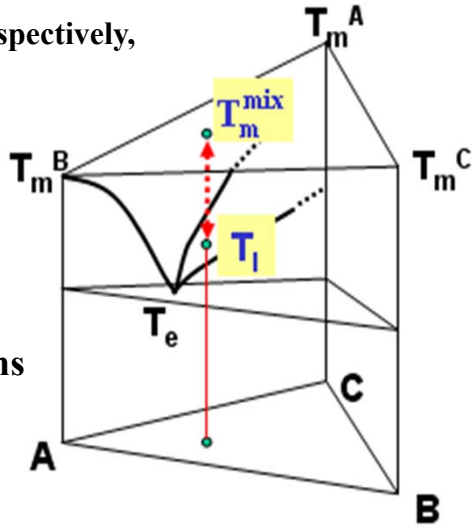
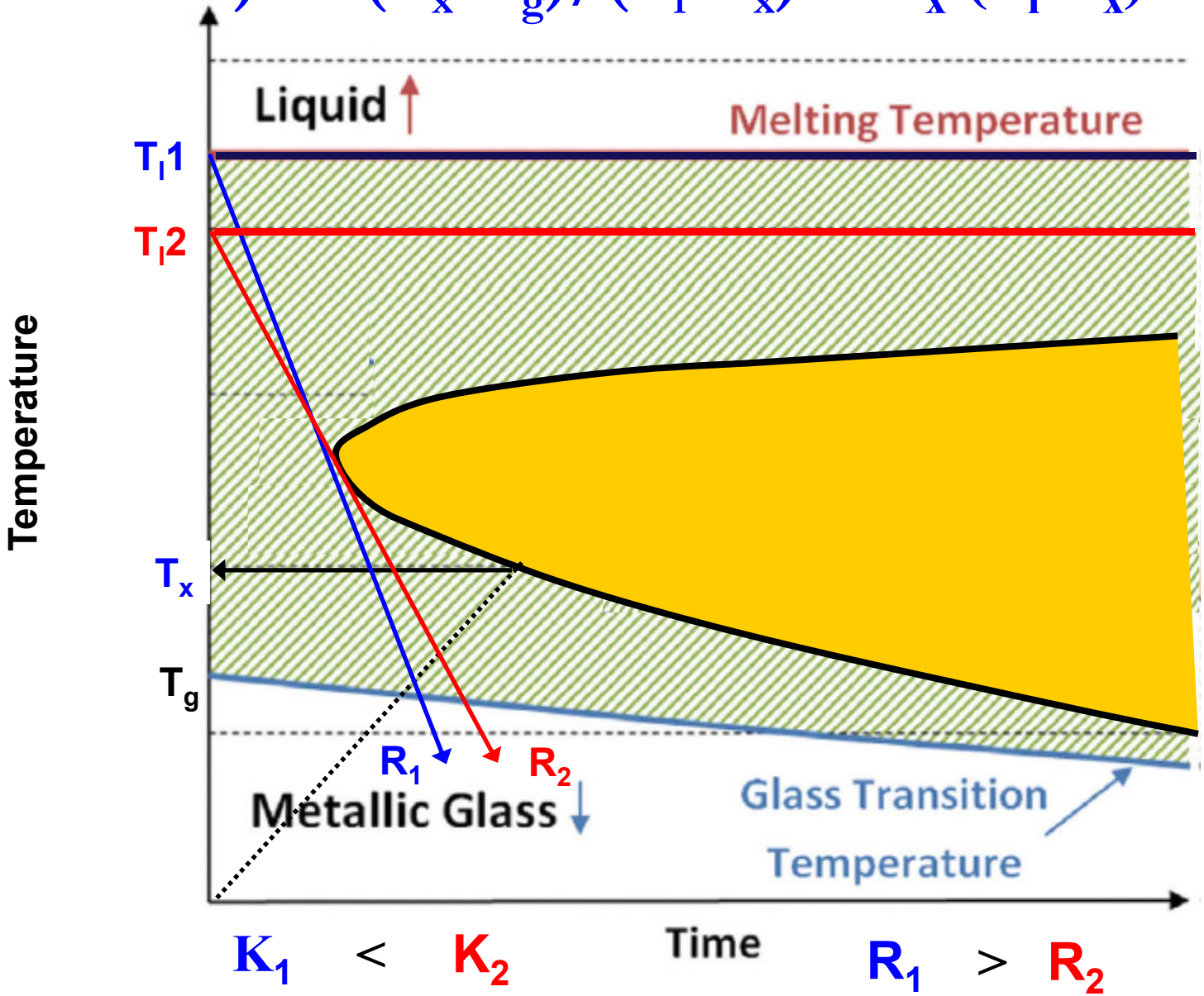


➡ T_m^{mix} represents the fractional departure of T_m with variation of compositions and systems from the simple rule of mixtures melting temperature

Time Temperature Transformation diagram:

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



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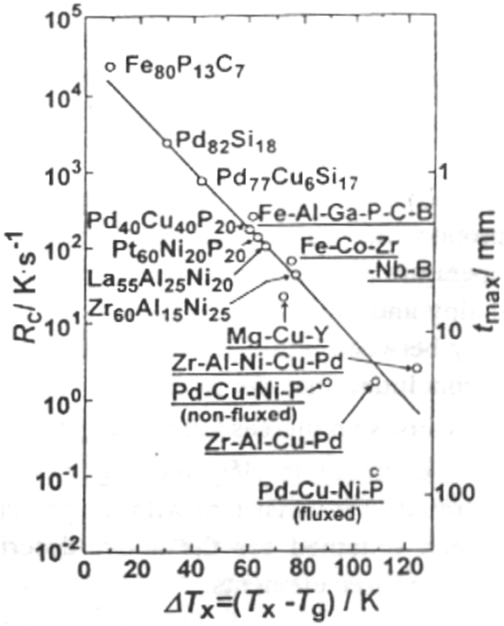

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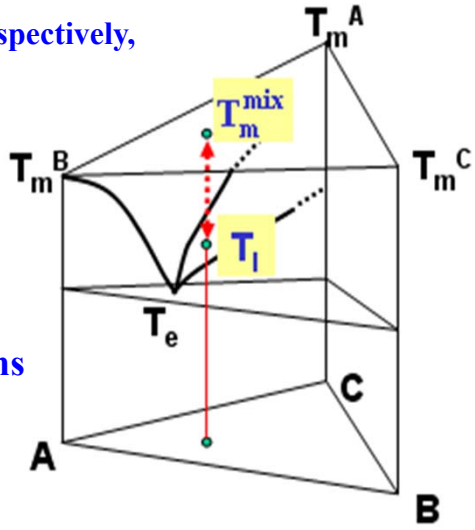

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Relative decrease of melting temperature

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

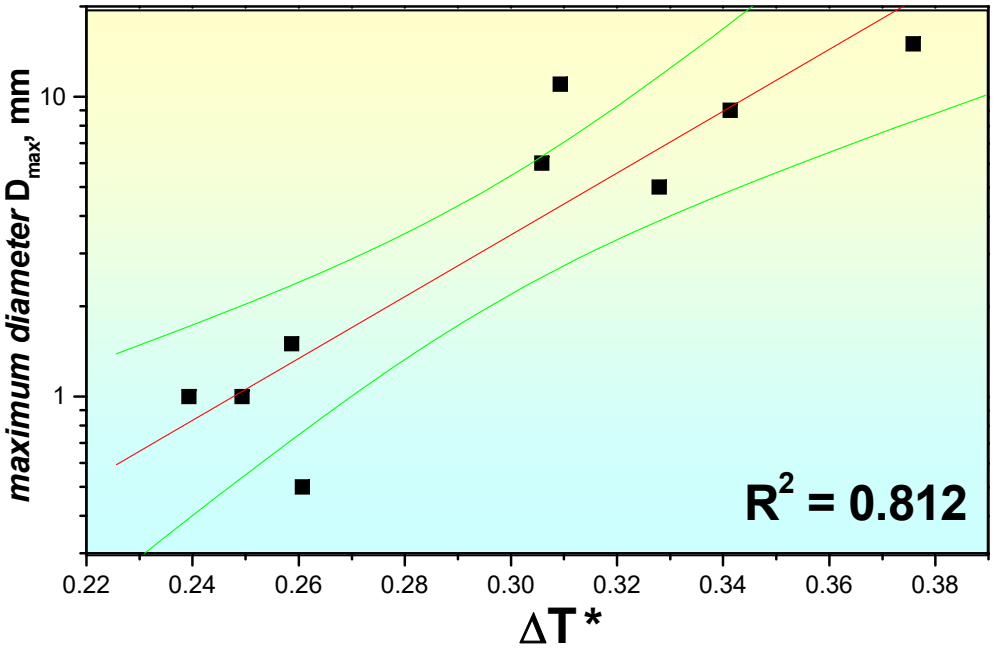
: ratio of Temperature difference between liquidus temp. T_l and imaginary melting temp. T_m^{mix} to T_m^{mix}

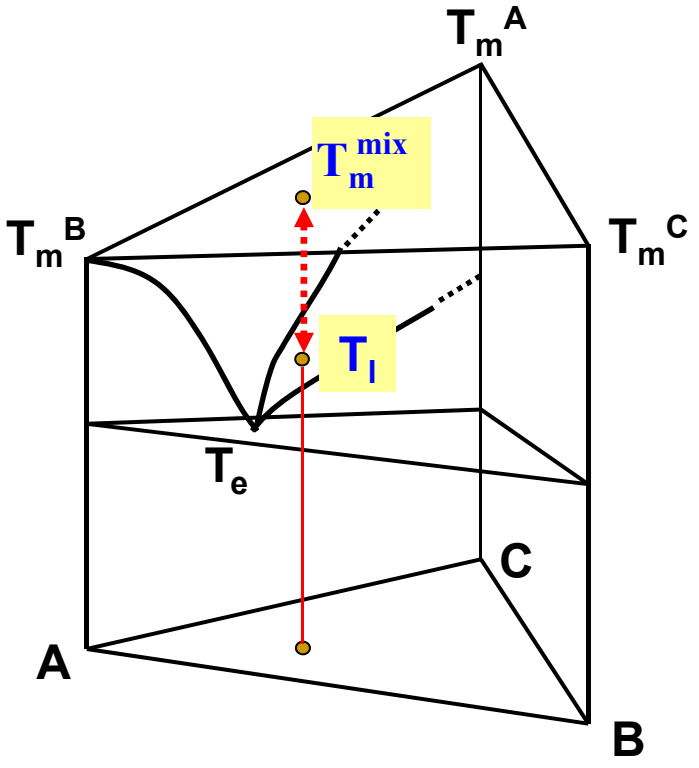
(where, $T_m^{mix} = \sum x_i T_m^i$, x_i = molefraction, T_m^i = melting point)

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

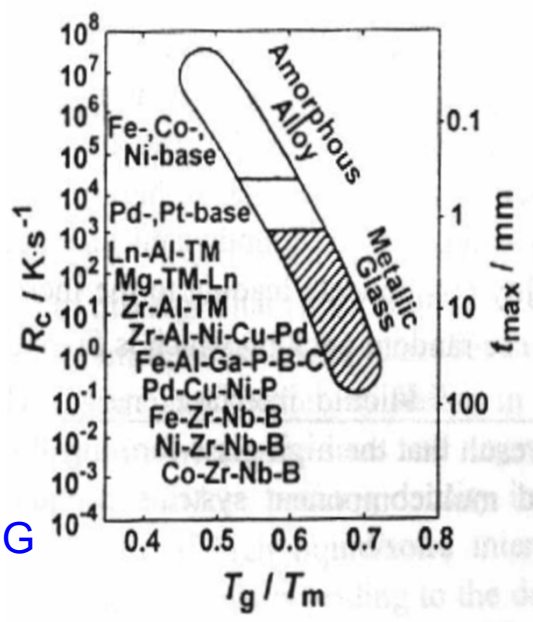




GFA Parameters on the basis of thermodynamic or kinetic aspects :

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 ↑

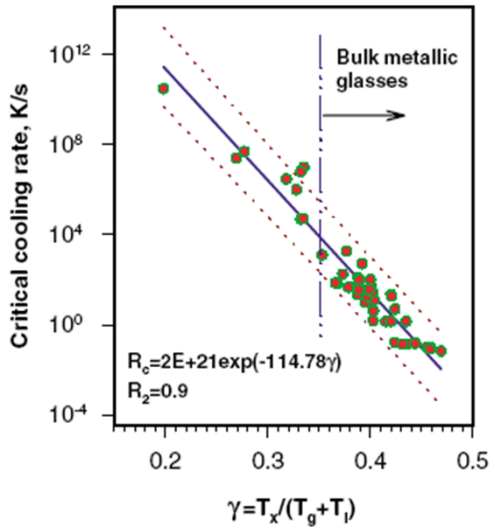


- significant difference between T_l and T_g in multi-component BMG
- insufficient information on temperature-viscosity relationship

► insufficient correlation with GFA

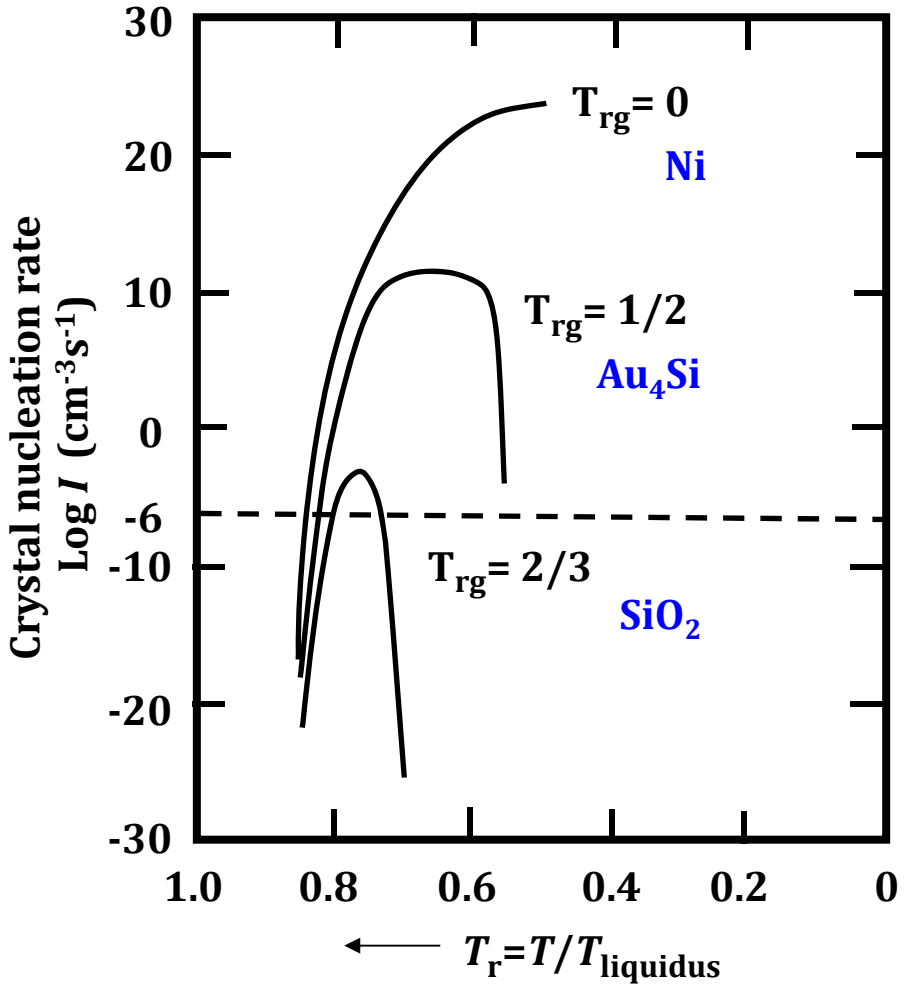
5) γ parameter = T_x / (T_l + T_g)

- 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 ~ η : the higher T_{rg}, the higher η, the lower R_c

: ability to avoid crystallization during cooling



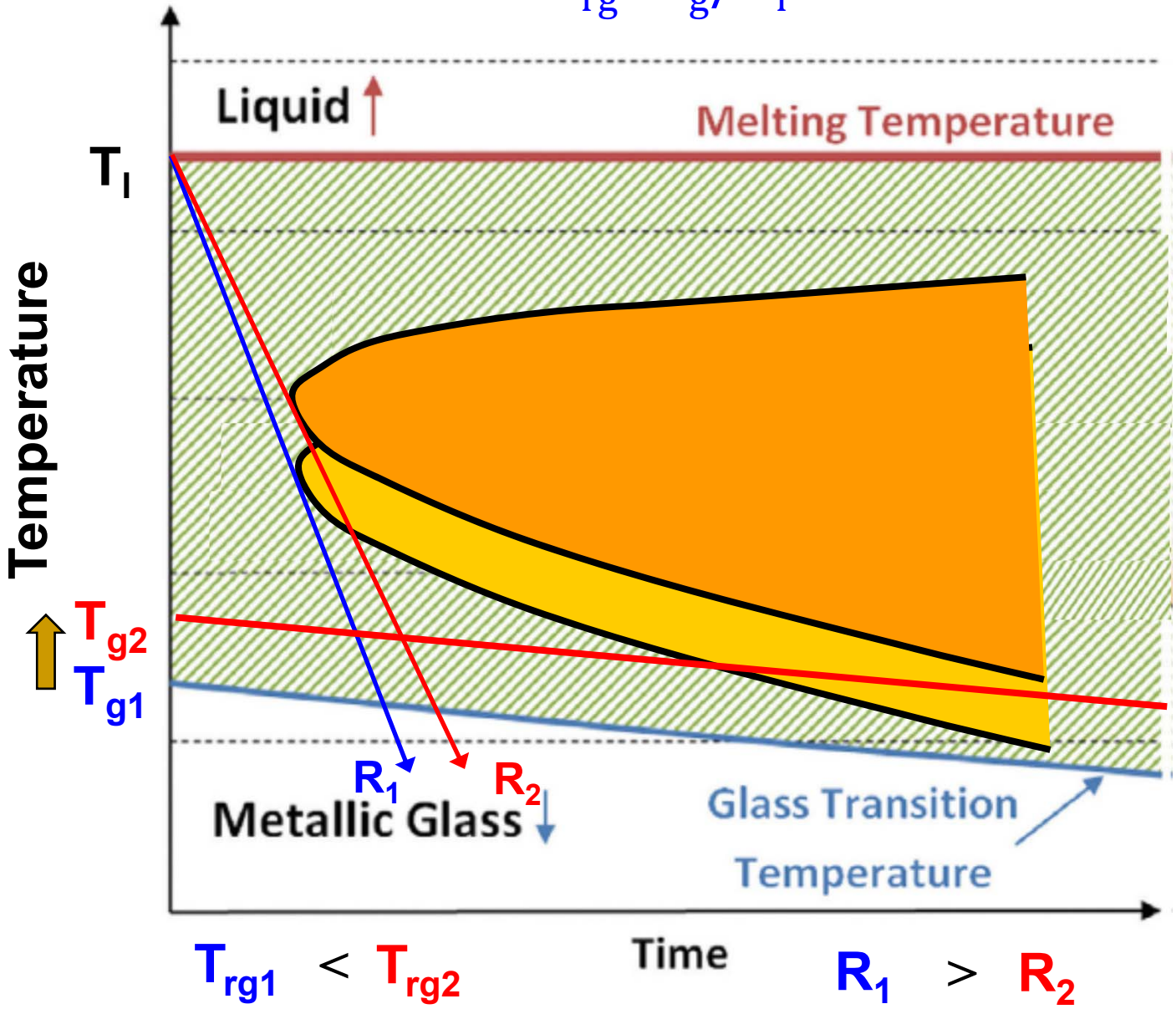
$T_{rgNi} < T_{rgAu4Si} < T_{rgSiO2}$

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

Turnbull, 1959 ff.

Time Temperature Transformation diagram:

$T_{rg}=T_g/T_l$



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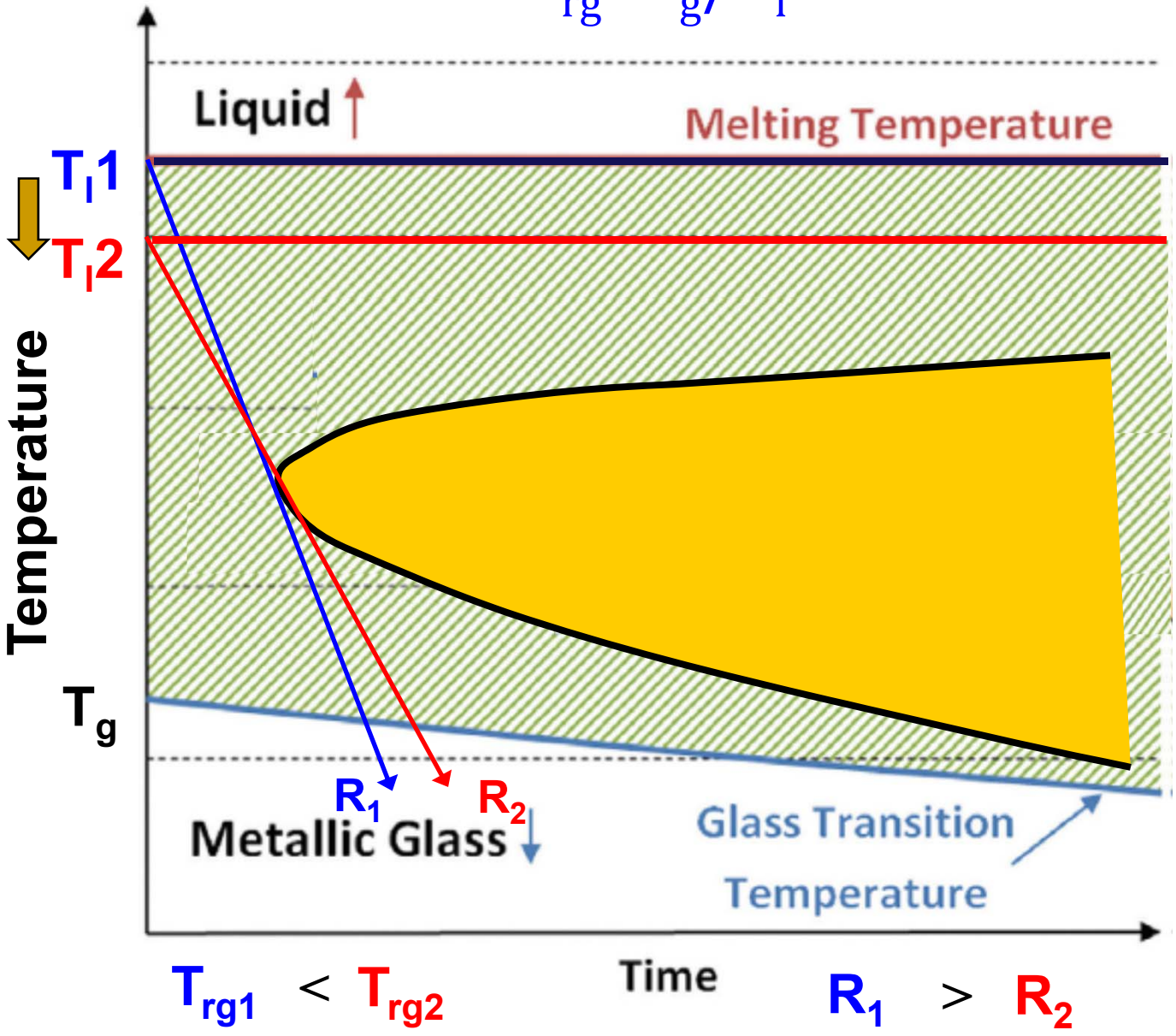

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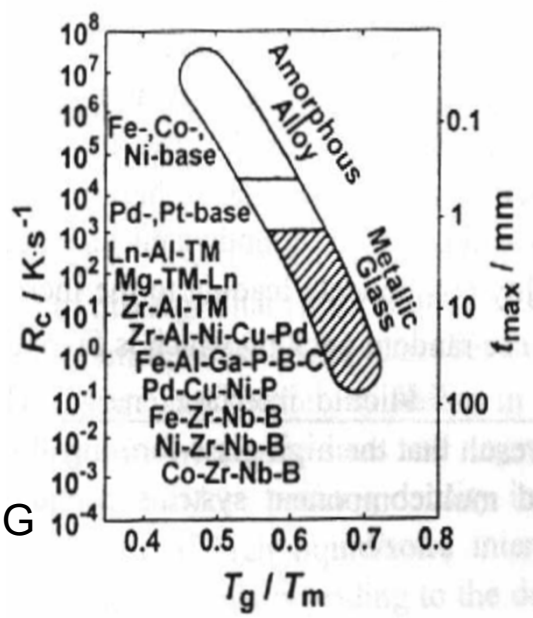

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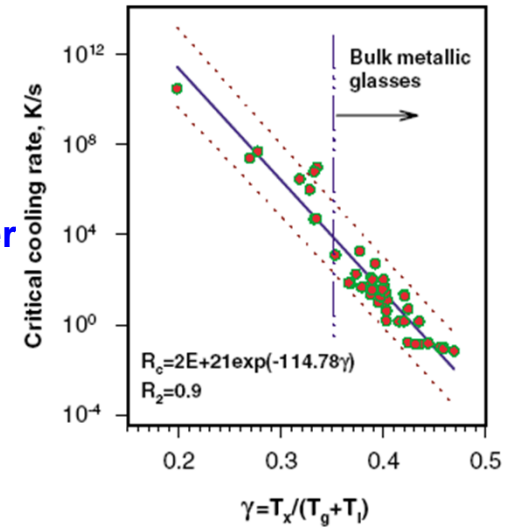


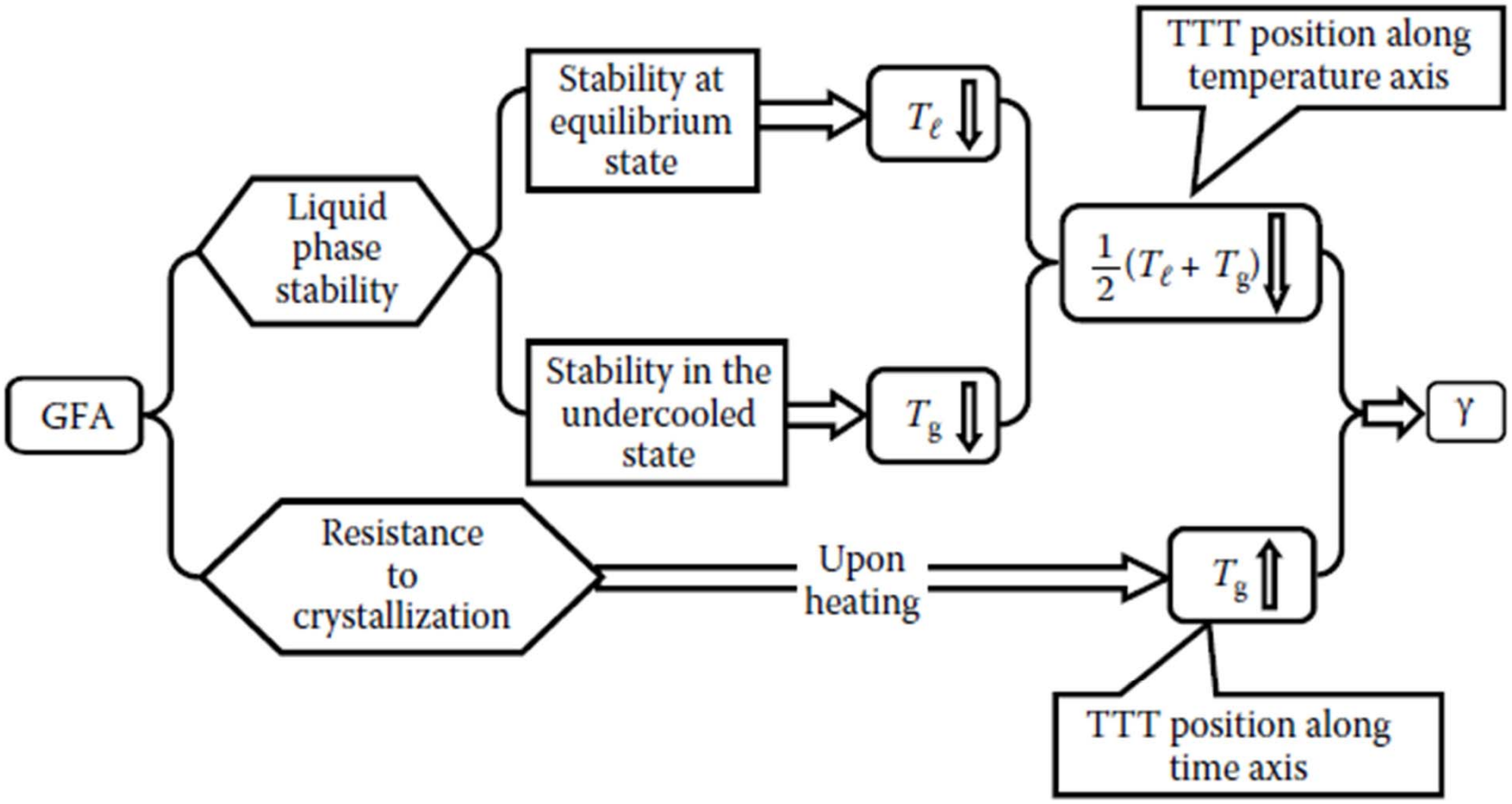
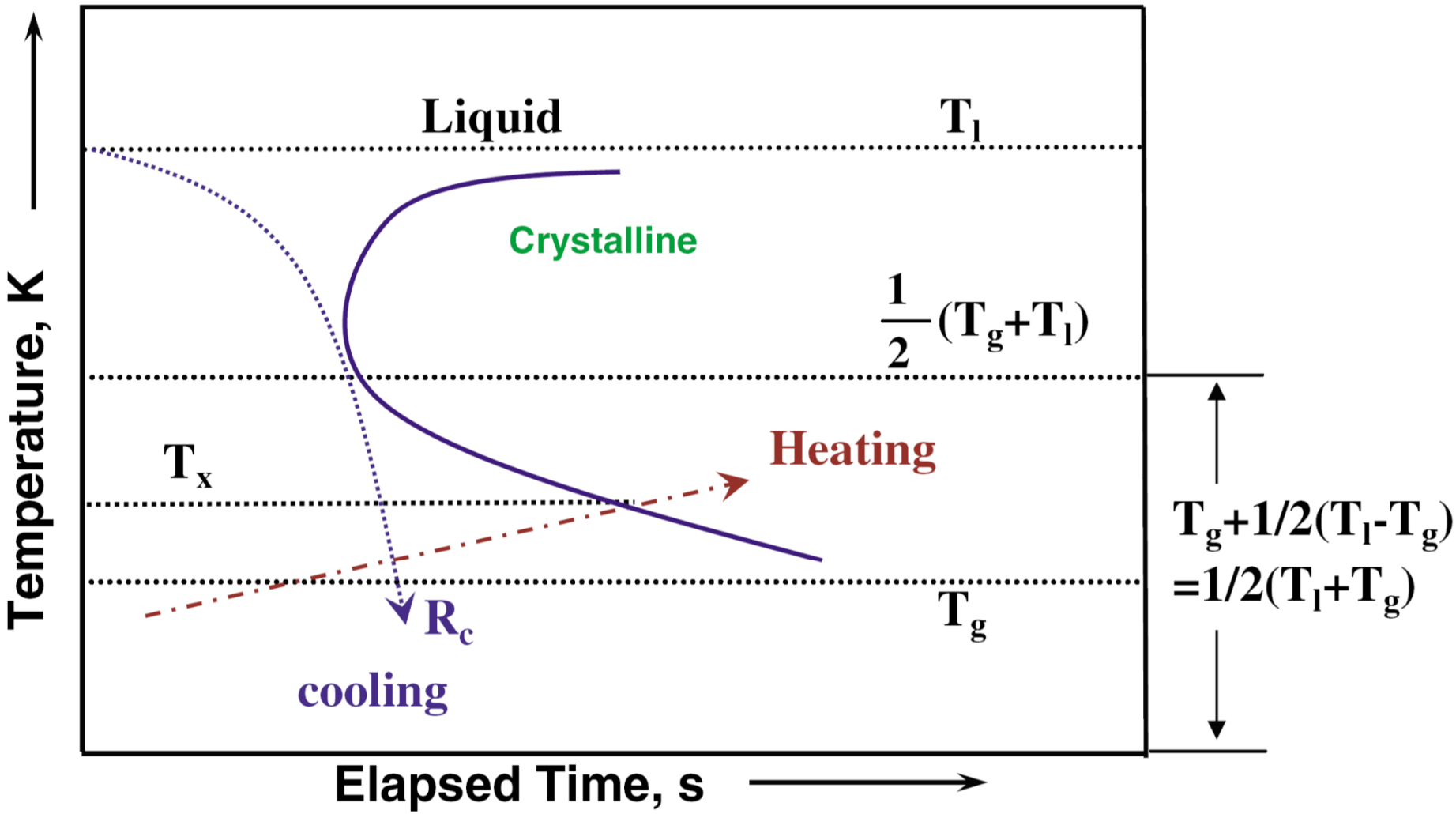


FIGURE 3.8
Schematic to illustrate the different factors involved in deriving the γ parameter to explain the GFA of alloys. (Reprinted from Lu, Z.P. and Liu, C.T., *Intermetallics*, 12, 1035, 2004. With permission.)

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



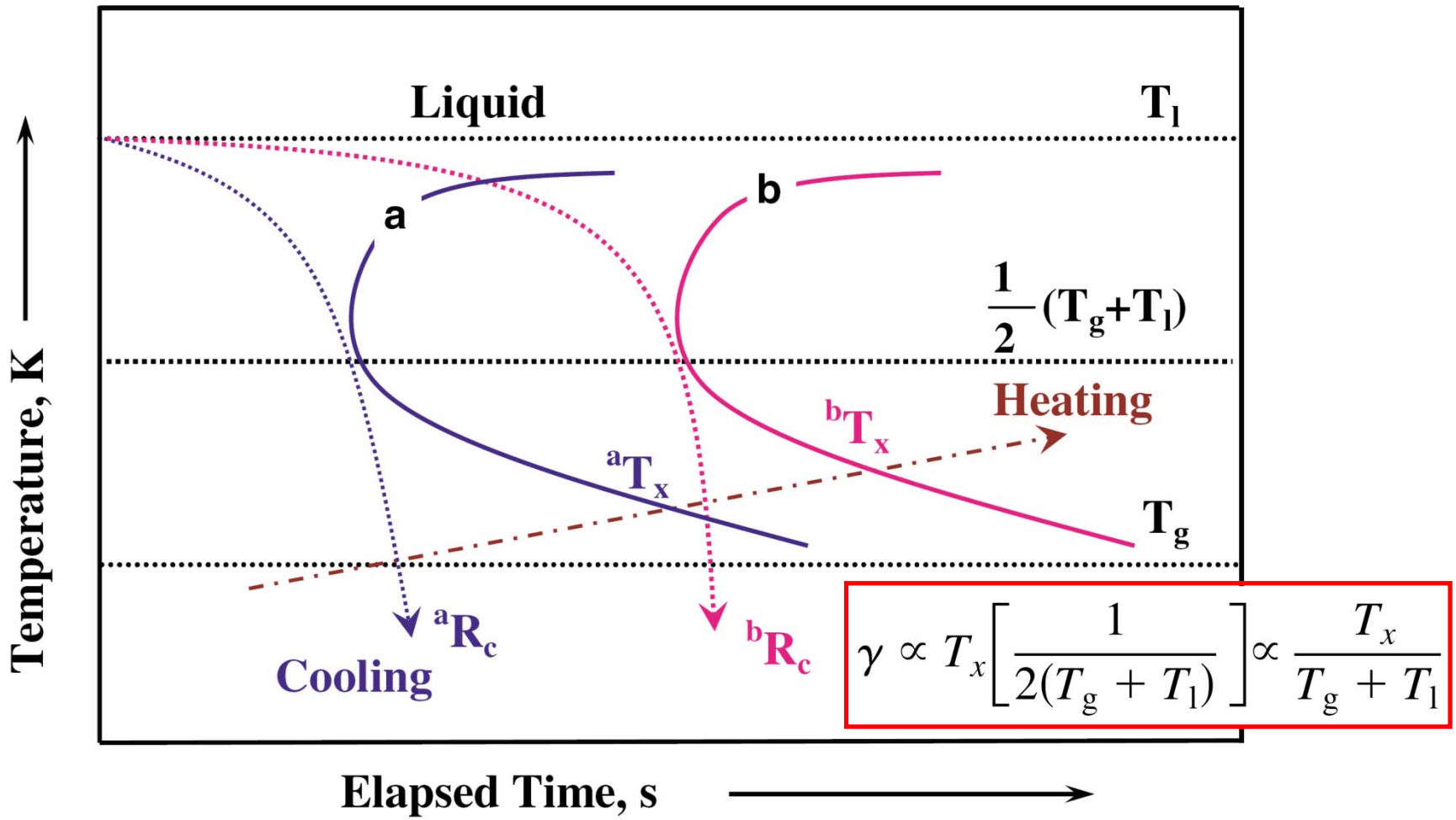
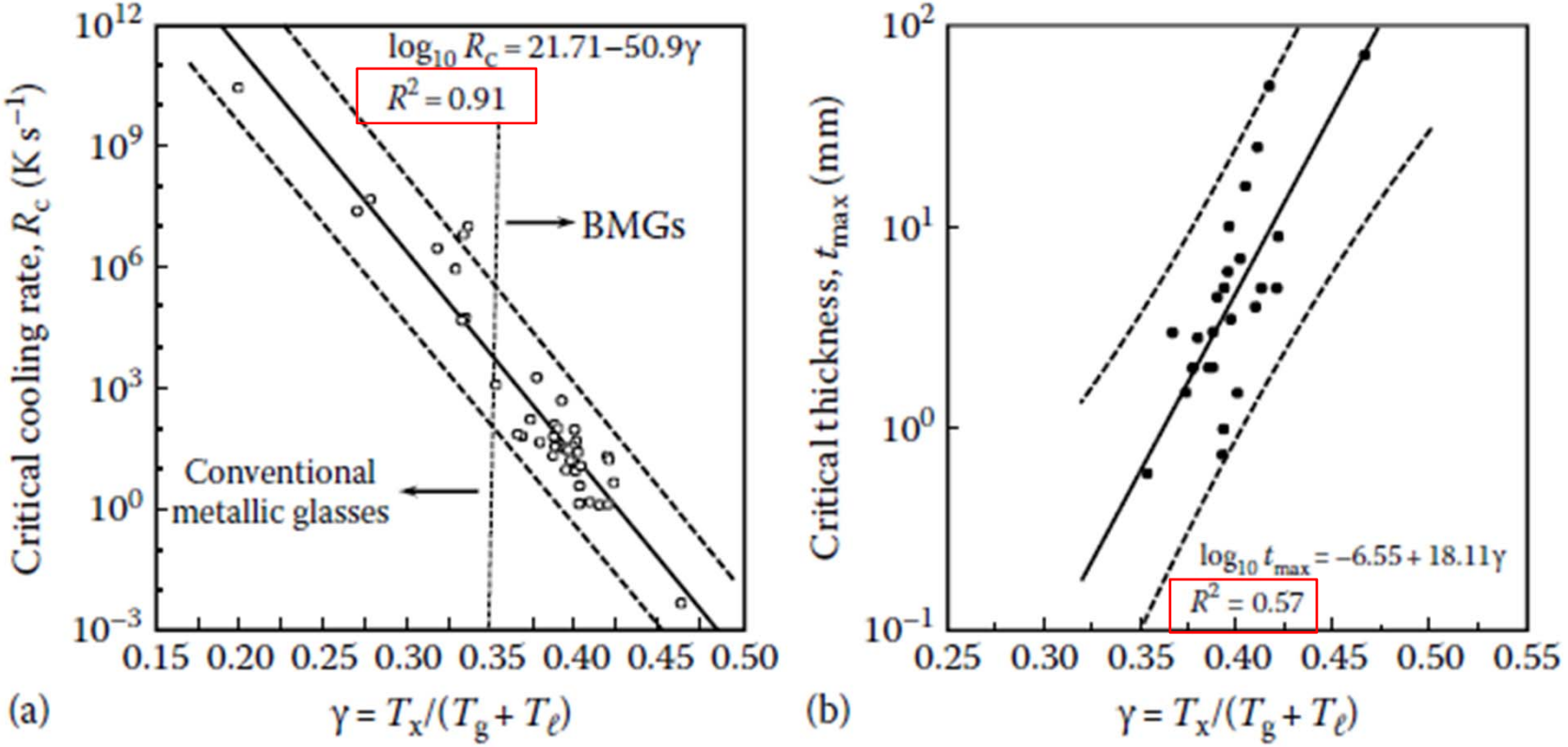


FIG. 2 (color online). Schematic TTT curves showing the effect of T_x measured upon continuous heating for different liquids with similar T_l and T_g; liquid b with higher onset crystallization temperature ^bT_x ($^aT_x < {}^bT_x$) shows a lower critical cooling rate ^bR_c ($^bR_c < {}^aR_c$).

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

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

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



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

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

$$\sigma = \Delta T^{*} \times \quad P'$$

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

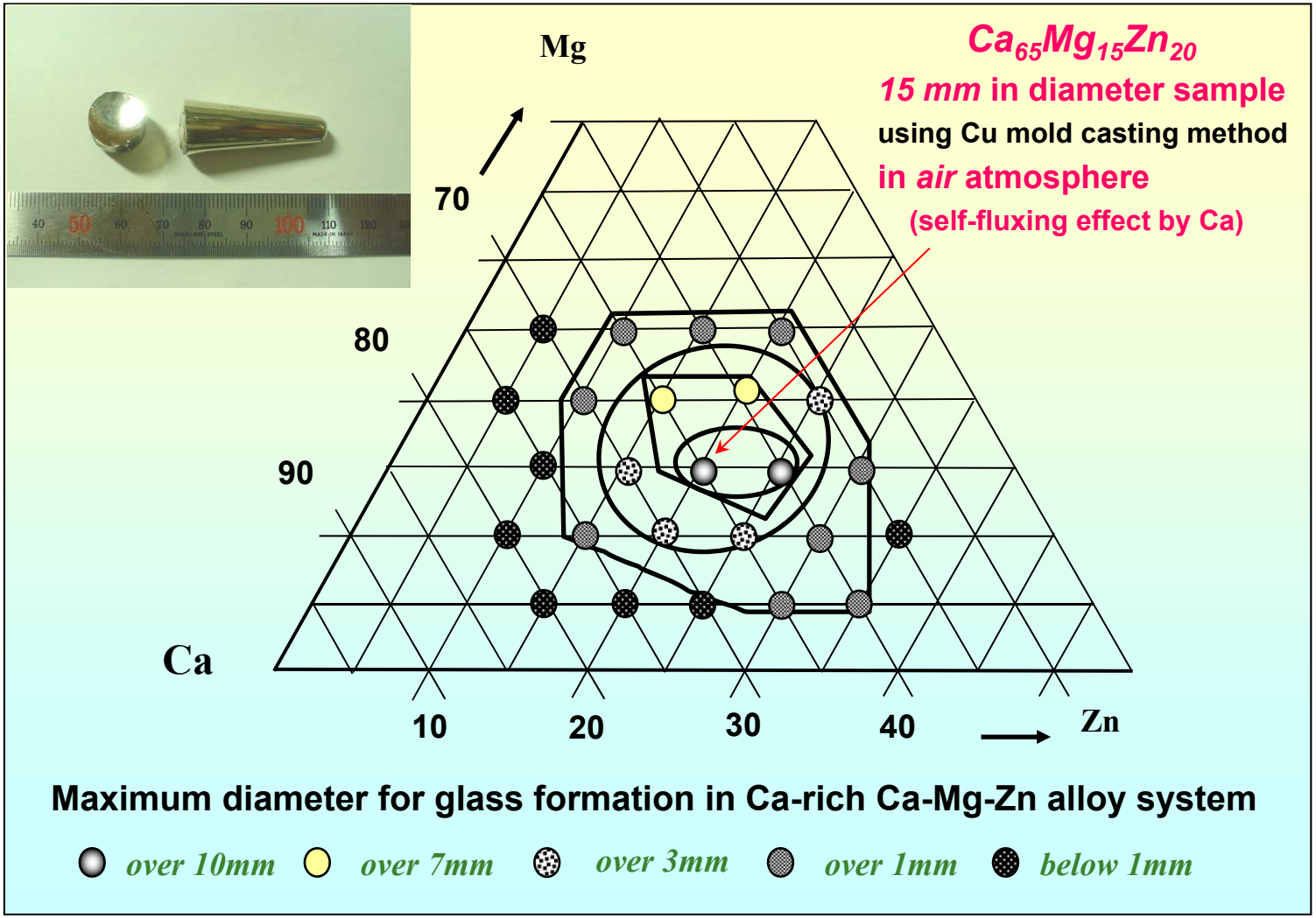
$$\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$$

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

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

(where, Tx = crystallization onset temperature)

Ca-Mg-Zn alloy system



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

Thermodynamic aspect for glass formation

Relative decrease of melting temperature

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

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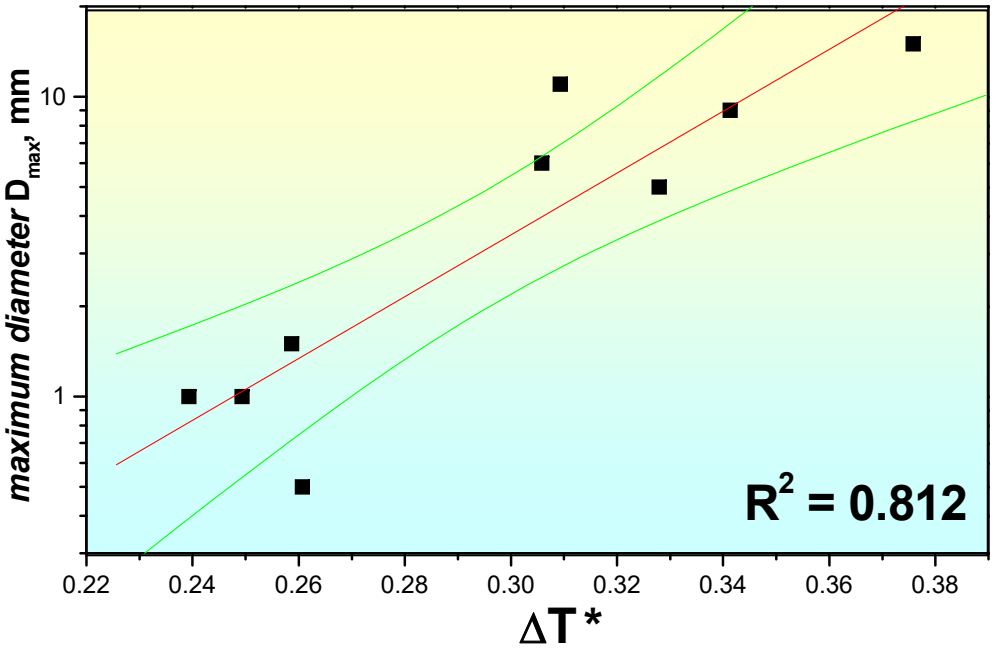
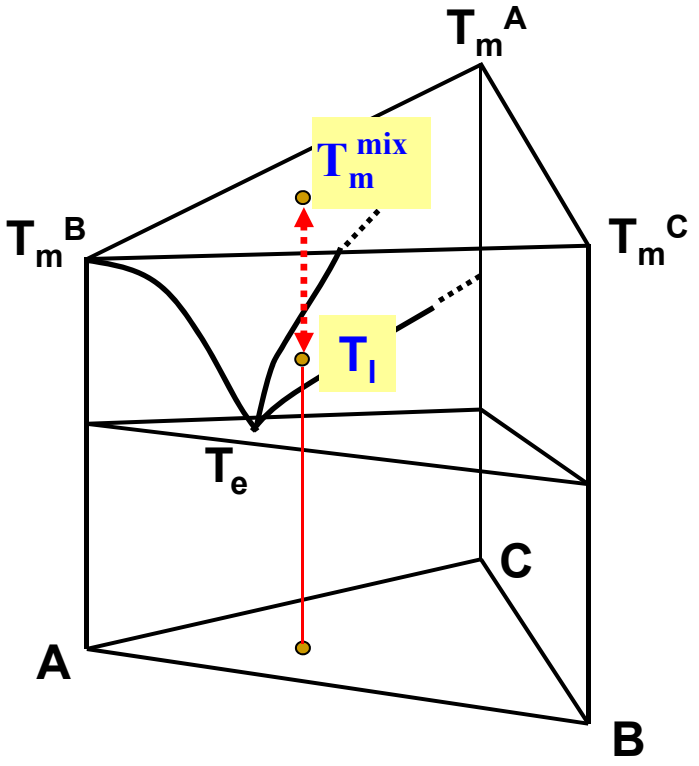




Structural aspect for glass formation

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

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

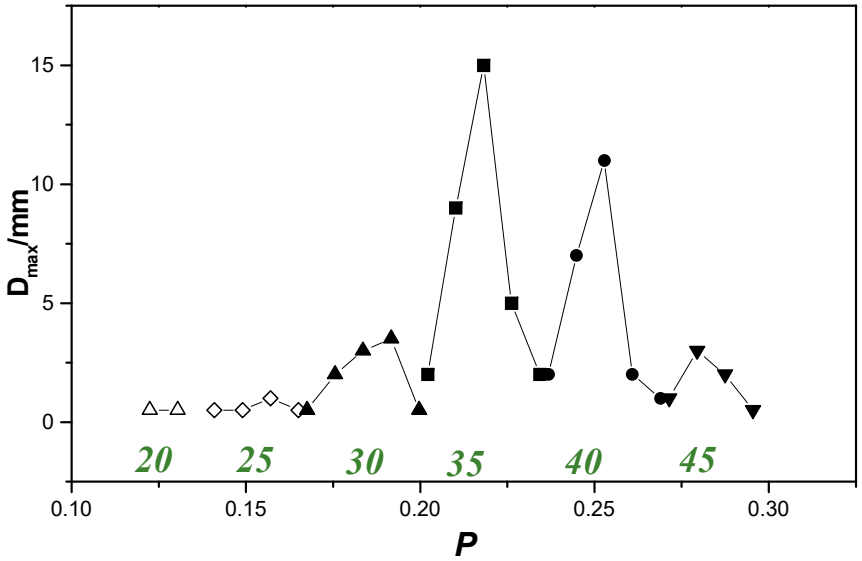
$$P' = \frac{C_B}{C_B + C_C} \left| \frac{v_B - v_A}{v_A} \right| + \frac{C_C}{C_B + C_C} \left| \frac{v_C - v_A}{v_A} \right|$$

Where, C_i(i=A,B,C) = solute, v_i = content atomic volume ; effective atomic mismatch of solute atom

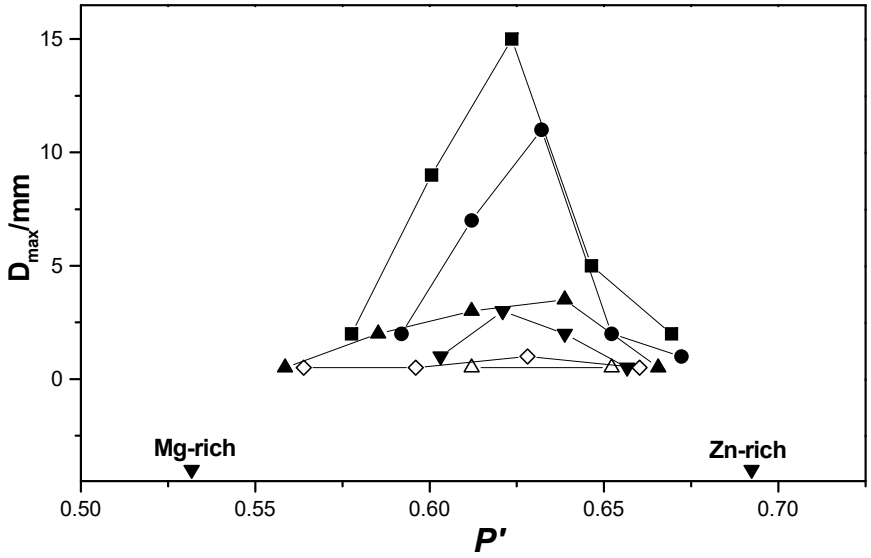
by dividing by the total amount of solute contents

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

Ca-Mg-Zn alloy system



Similar trend of D_{max} with P

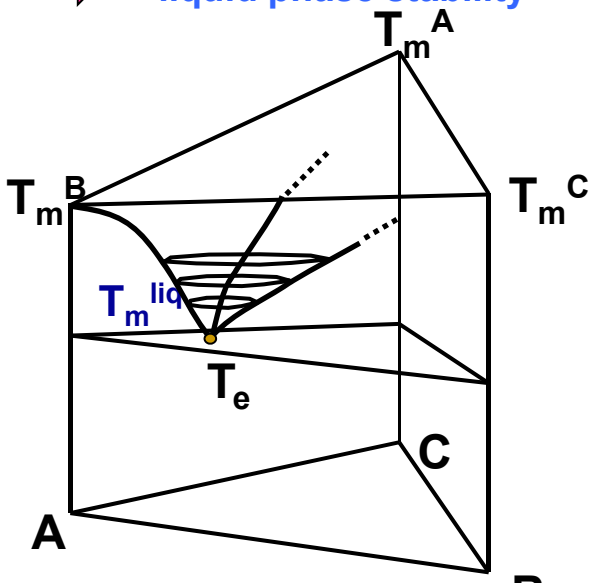


Maximum dia.(D_{max}) at P'=0.625

σ parameter (thermodynamic and atomic configuration aspects)

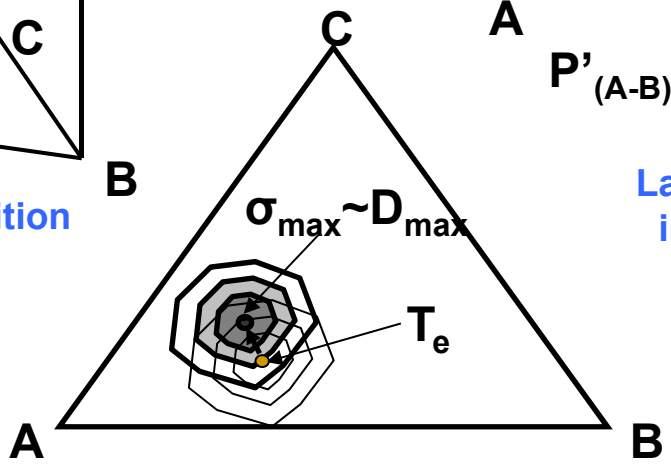
ΔT^* : Relative decrease of melting temp.

➡ liquid phase stability



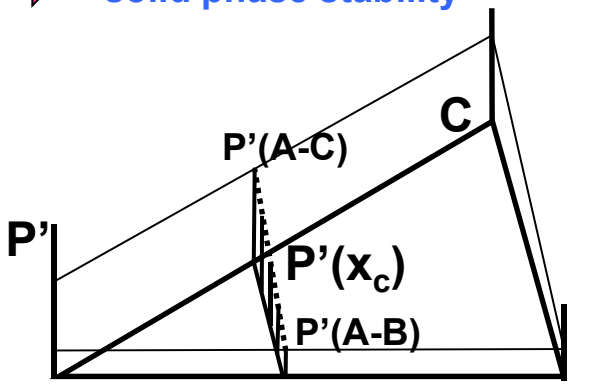
Deep eutectic condition

×



P' : Effective atomic mismatch per solute atom

➡ solid phase stability



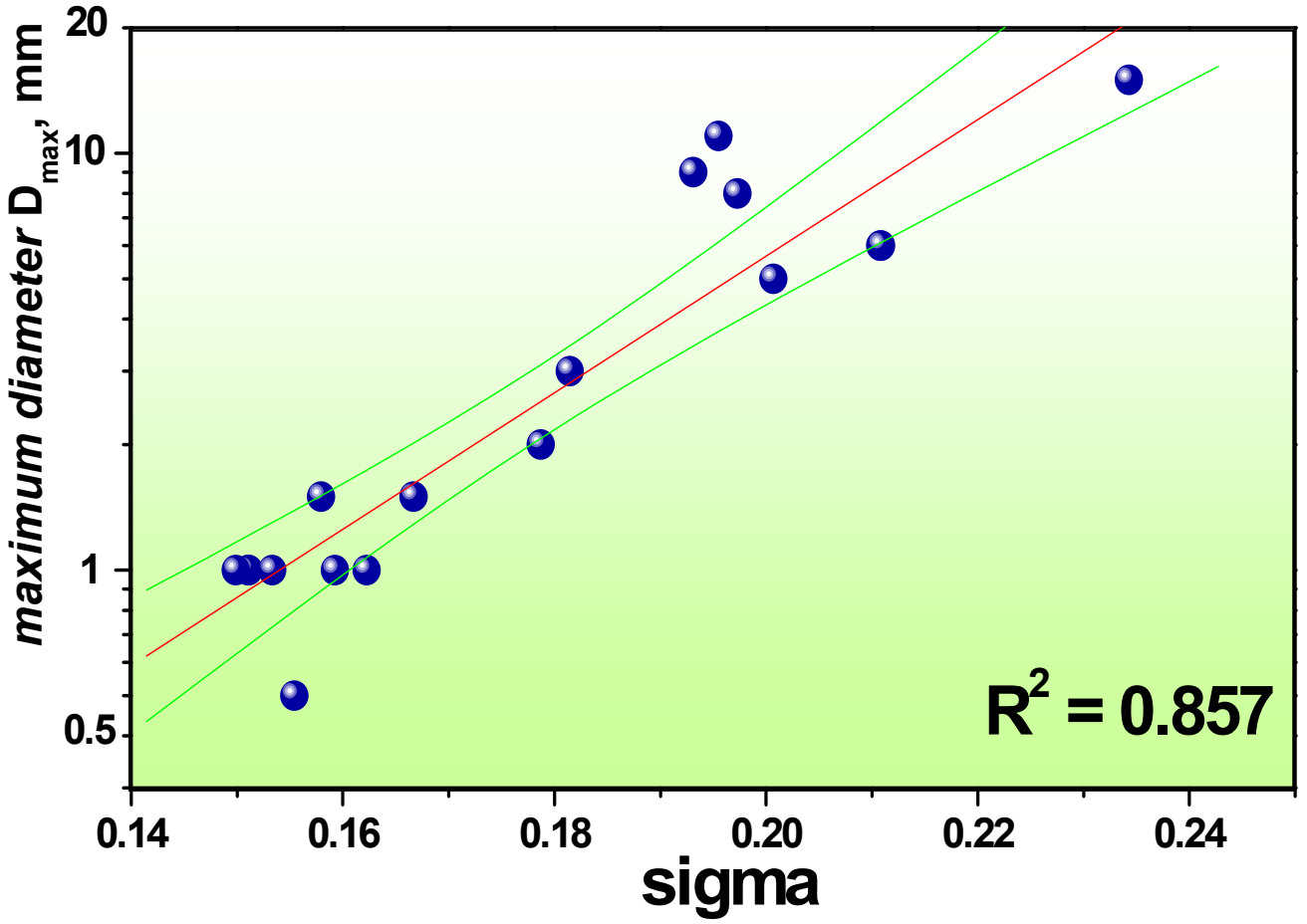
$P'_{(A-B)} \leq P'(Xc) \leq P'_{(A-C)}$

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.**

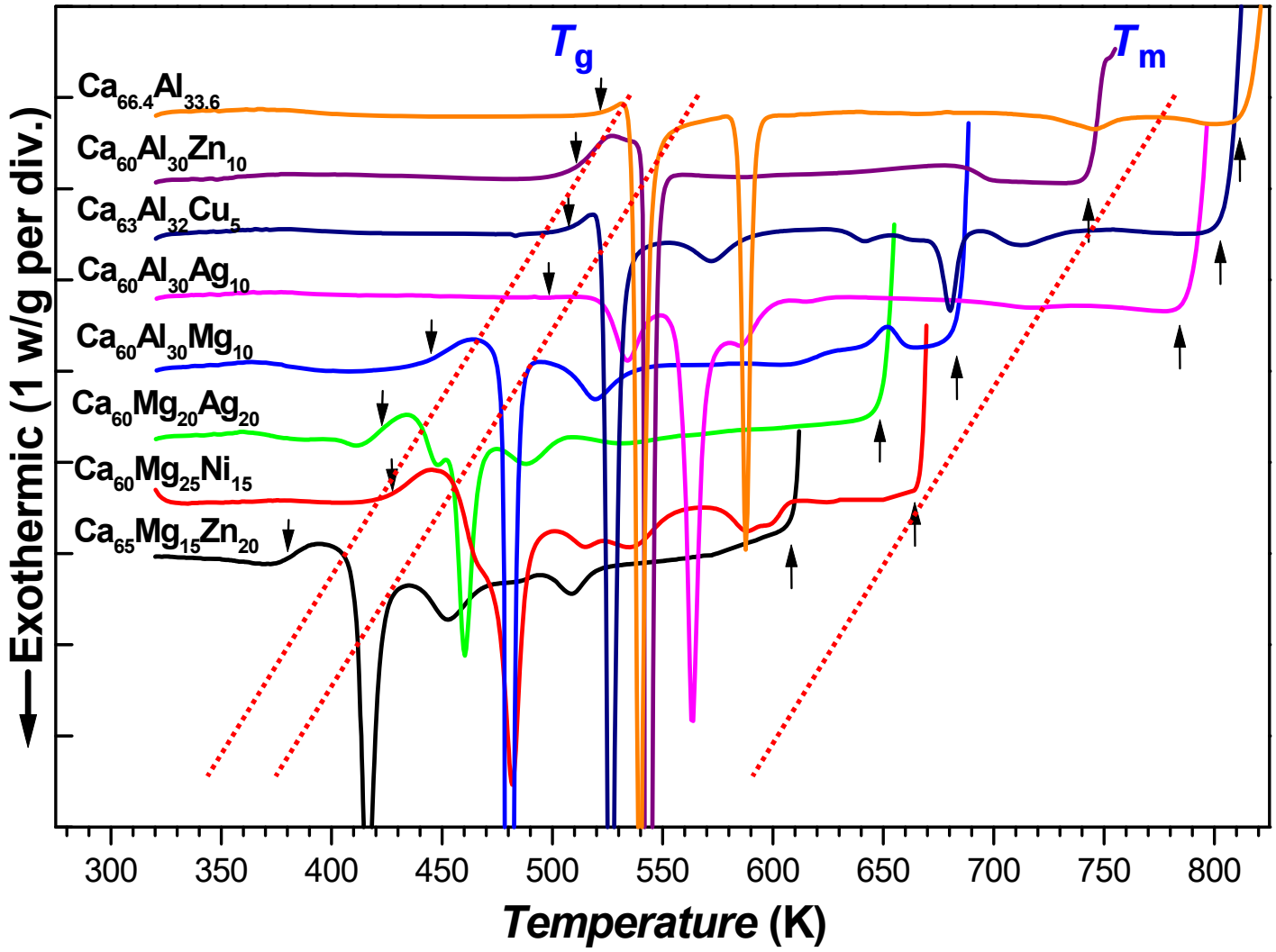
* J. Metastable and Nanocrystalline Materials, 24-25, 697 (2005)

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

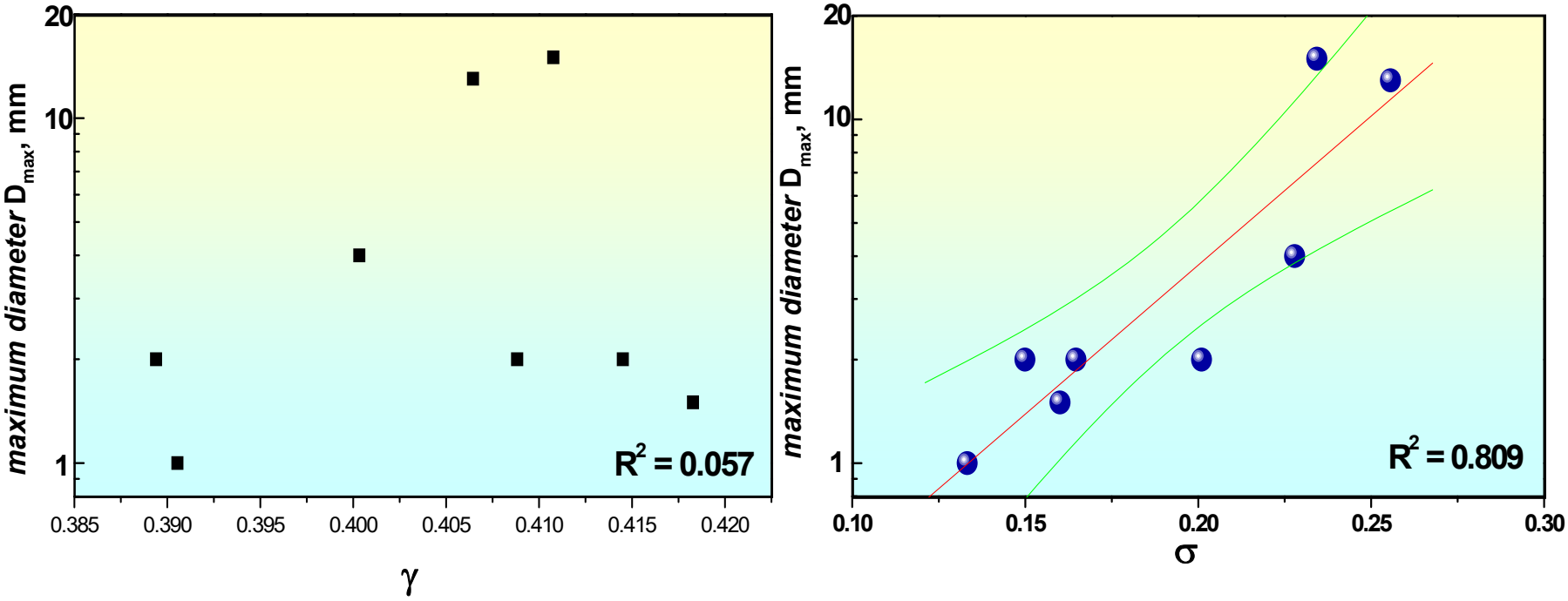
Thermal analysis, GFA parameters and maximum diameter (D_{max}) for glass formation in the Ca-based ternary BMG systems

	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)

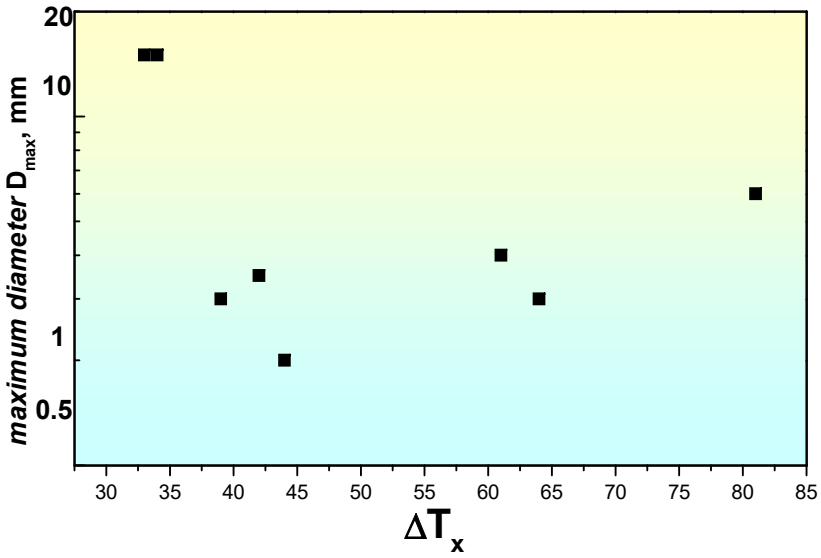
3) Application of σ parameter for BMG-forming ternary systems

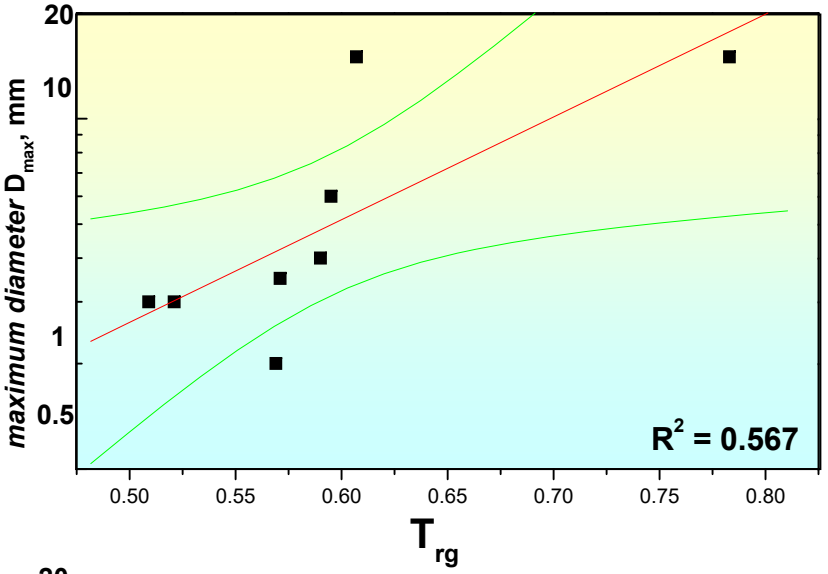
Thermal analysis, GFA parameters and maximum diameter (D_{max}) for glass formation in the ternary BMG systems

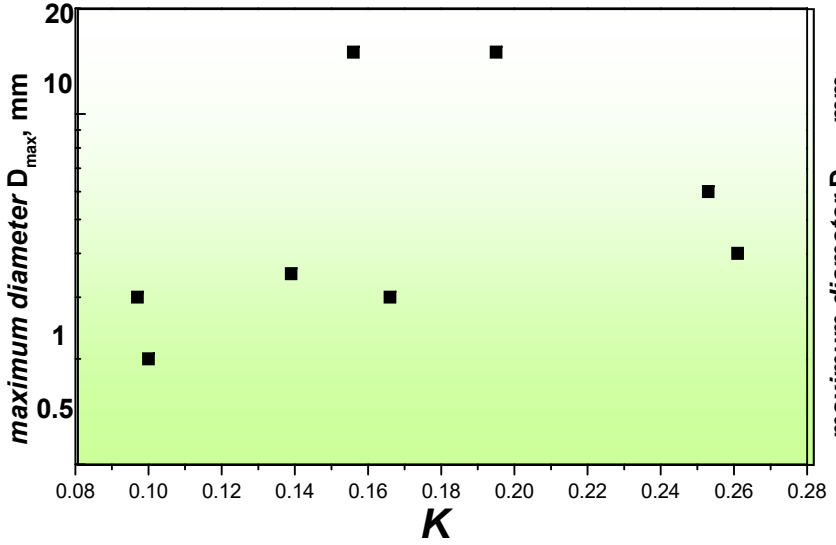
	T_g	T_x	T_l	T_m^{mix}	ΔT_x	T_{rg}	K	γ	ΔT*	P'	σ	D_{max}
$Ca_{65}Mg_{15}Zn_{20}$	379	412	624	1032	33	0.607	0.156	0.411	0.395	0.624	0.234	15
$Nd_{60}Fe_{30}Al_{10}$	750	784	958	1385	34	0.783	0.195	0.459	0.308	0.620	0.199	15
$Pd_{40}Ni_{40}P_{20}$	590	671	991	1519	81	0.595	0.253	0.424	0.348	0.476	0.158	6
$Mg_{65}Cu_{25}Y_{10}$	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

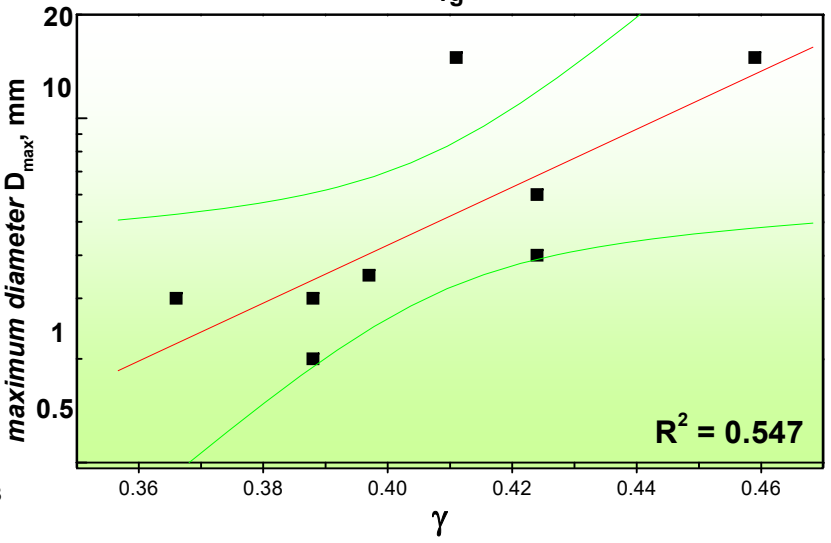
Calculation of G.F.A parameters

Ternary BMG system

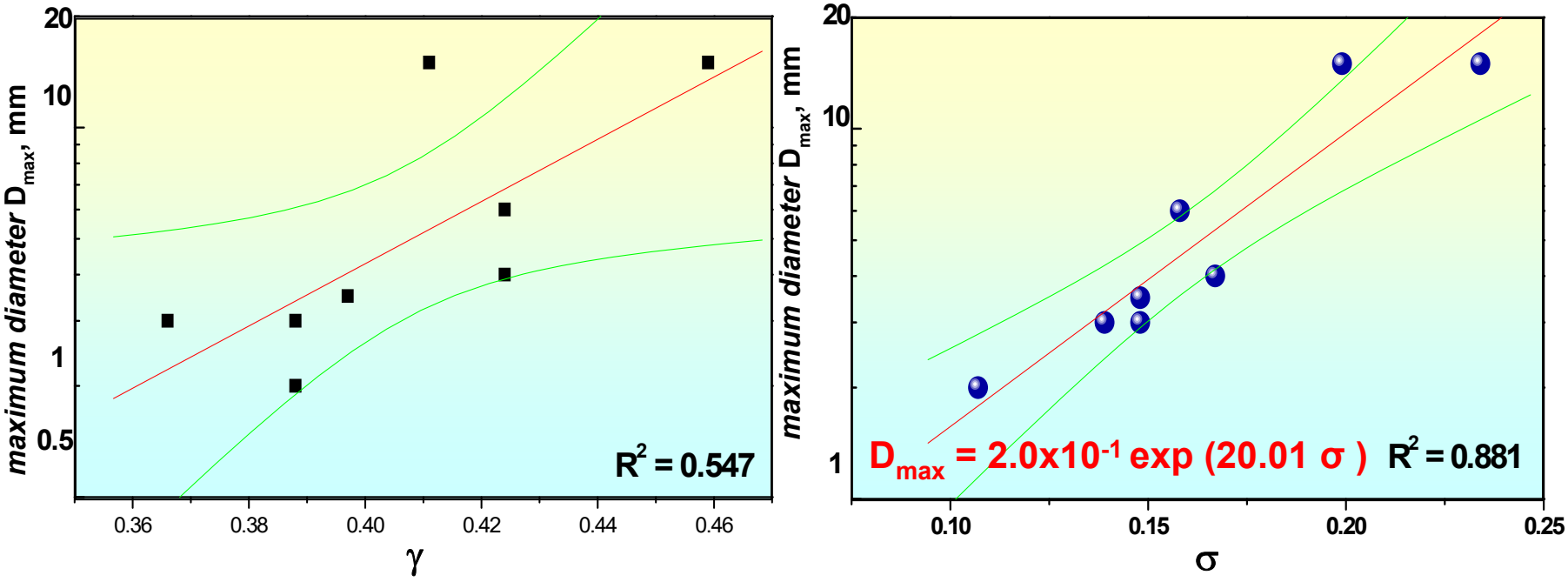








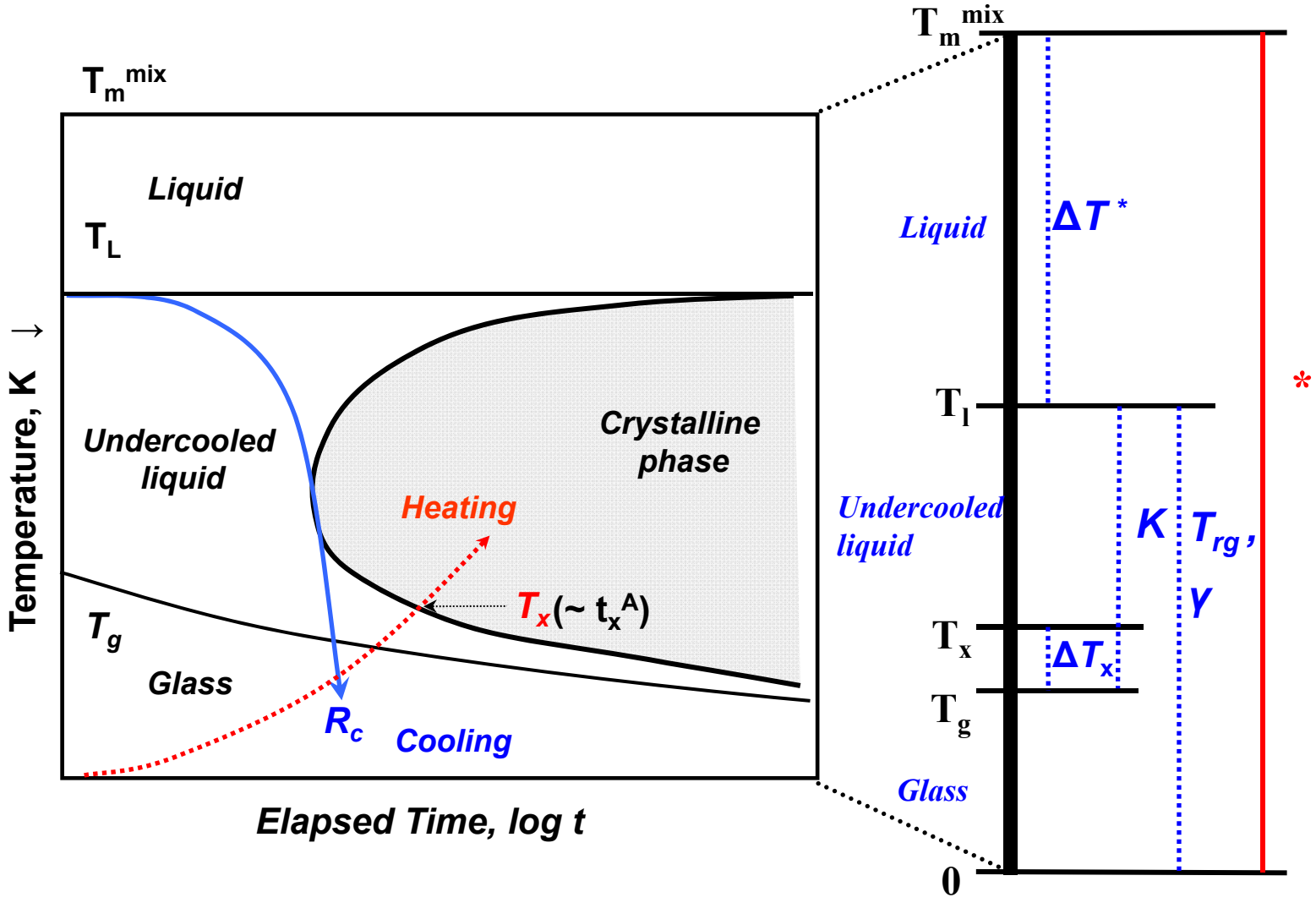
3) Calculation of GFA parameters in ternary BMG alloy systems



* 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	ΔT_x	T_g
T_g	T_{rg}	T_l
$T_m^{mix} - T_l$	ΔT^*	T_m^{mix}
ΔT_x	K	$T_l - T_x$
T_x	γ	$T_l + T_g$

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

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

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

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

$$R_c^4 = \frac{4\pi}{3\times 10^{-6}}\int_{T_l}^{T_g} I(T')\left[\int_{T'}^{T_g} U(T'')\mathrm{d}T''\right]^3 \mathrm{d}T'$$

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

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

and

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

$1/R_c \propto$ 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 : $T_x - T_g$

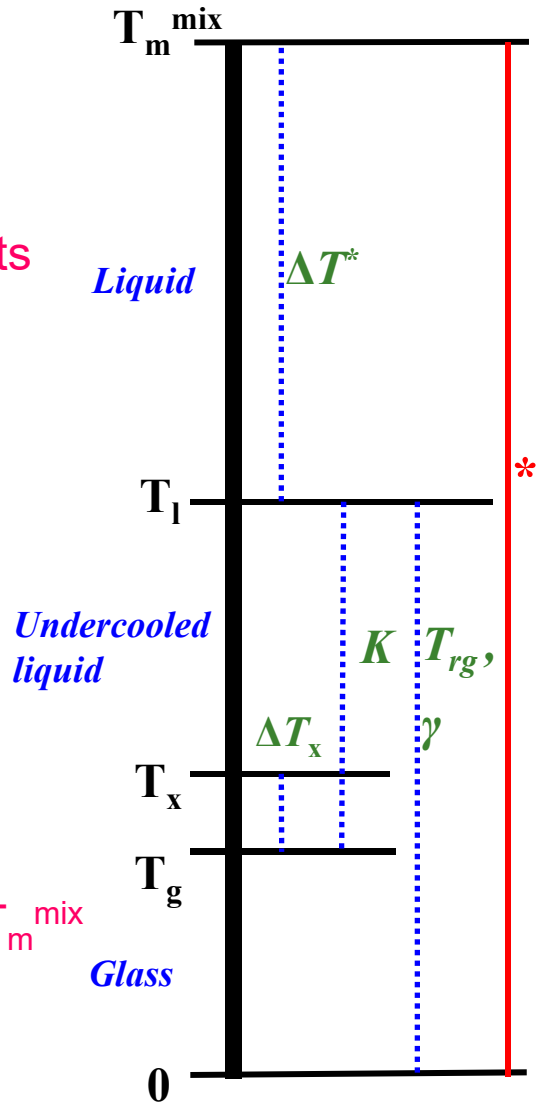
K parameter : $T_g - T_x - T_l$

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



$$\mathrm{GFA} \propto (\Delta T_m, \Delta T_x, T_x).$$

As discussed above, in evaluating the GFA, the thermodynamic stability of the liquid phase should be considered. The stability of the liquid phase can be considered in two states, i.e., equilibrium state (above T_l) and the metastable state (T_l–T_g). The effect of the stability of liquid at equilibrium state on GFA can be reflected by considering the relative depression of T_l. To reflect the degree of relative depression of T_l, T_m^{mix} can be utilized as a departure of the alloy liquidus temperature from the rule of mixtures liquidus temperature.[8] Although T_m^{mix} is an imaginary temperature, it can be calculated from melting points and composition of the constituent elements, thereby being able to effectively reflect the compositional effects on the depression of T_l as used in the ΔT^* parameter. Therefore, the temperature range between T_m^{mix} and T_l ($=\Delta T_m$) can be used as a temperature factor reflecting the stability of stable liquid.

$$\mathrm{GFA} \propto (\Delta T_m, \Delta T_x, T_x).$$

The effect of the stability of liquid at metastable state on GFA can be reflected by considering the relative depression of T_g. From the thermodynamic point of view, T_g as a temperature factor is expected to play an important role in evaluating the GFA. However, if T_g is directly included as the temperature factor in the GFA parameter, it creates a conflict in the fractional expression of GFA parameter because the stability of the liquid in metastable state increases with a decrease in T_g but the nucleation and growth rate also increase with a decrease in T_g. Thus, the stability of the liquid at metastable state (i.e., glass phase) is reflected by ΔT_x instead of T_g. Although ΔT_x alone is not sufficient to represent the GFA, ΔT_x can resolve the contradiction of T_g as one of the temperature factors in the GFA parameter, reflecting the stability of undercooled liquid.

$$\mathrm{GFA} \propto (\Delta T_m,\ \Delta T_x,\ T_x).$$

In principle, the kinetic aspect for glass formation would better be approached by considering how liquid can easily avoid the nucleation and growth of the crystalline phase during cooling as considered in T_{rg}. However, as mentioned above, directly, including T_g can cause some vagueness in evaluating the GFA. Thus, we consider kinetic resistance to crystallization of the glass state by the quantity of T_x,[38] because it is possible to determine the lower part of crystallization curve (C curve) in CCT diagram from rate dependent thermal analysis upon reheating of the glass samples. The glass with higher T_x can be regarded to exhibit longer time for onset of crystallization, i.e., higher resistance to crystallization. Therefore, T_x can be used as one of the temperature factors, reflecting resistance to crystallization of the glass phase.

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

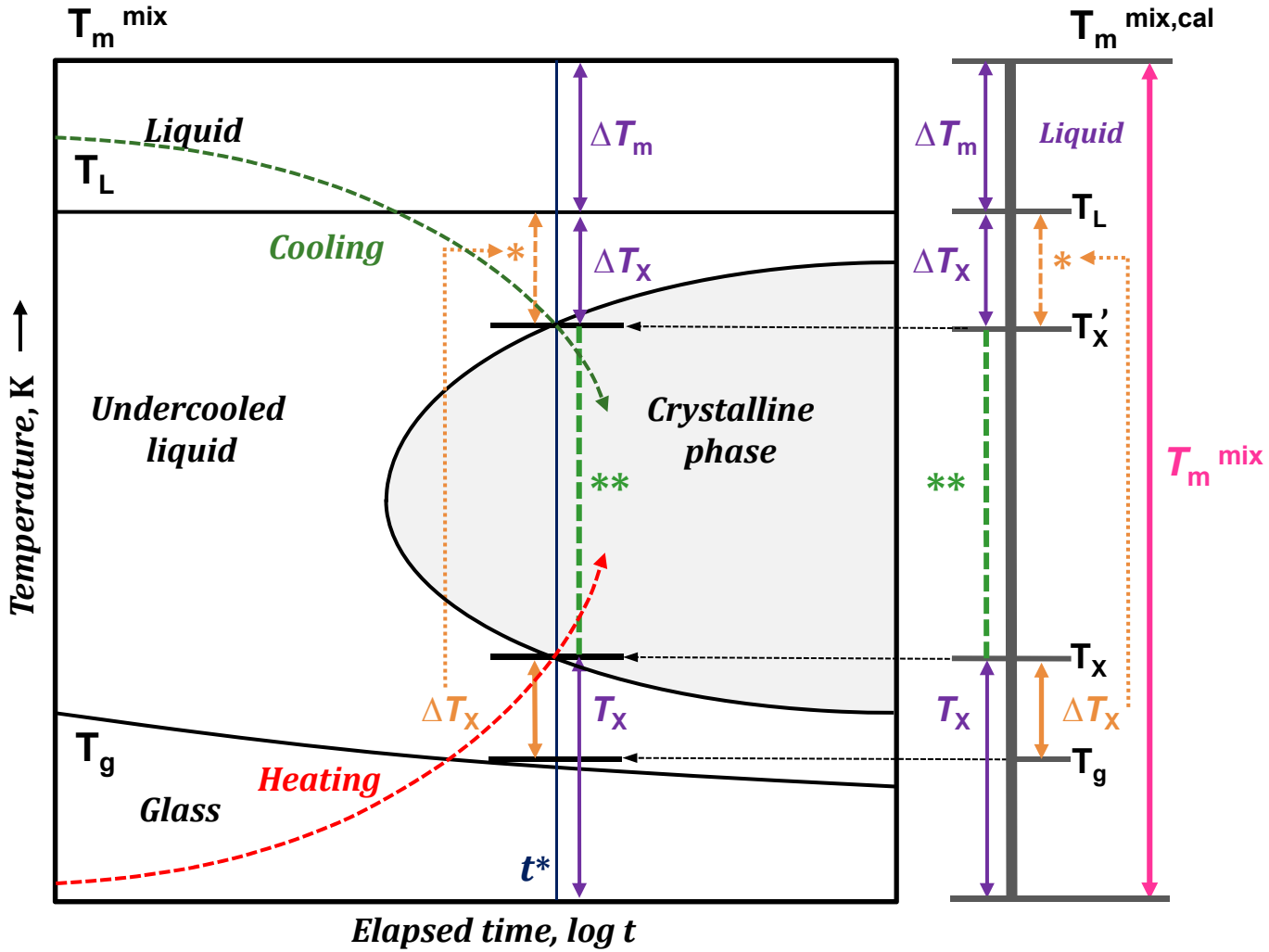
$$\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$$

E. S. Park et al., *JAP (2015)*

ε parameter (thermodynamic and kinetic aspects)

A New criterion for GFA of BMGs

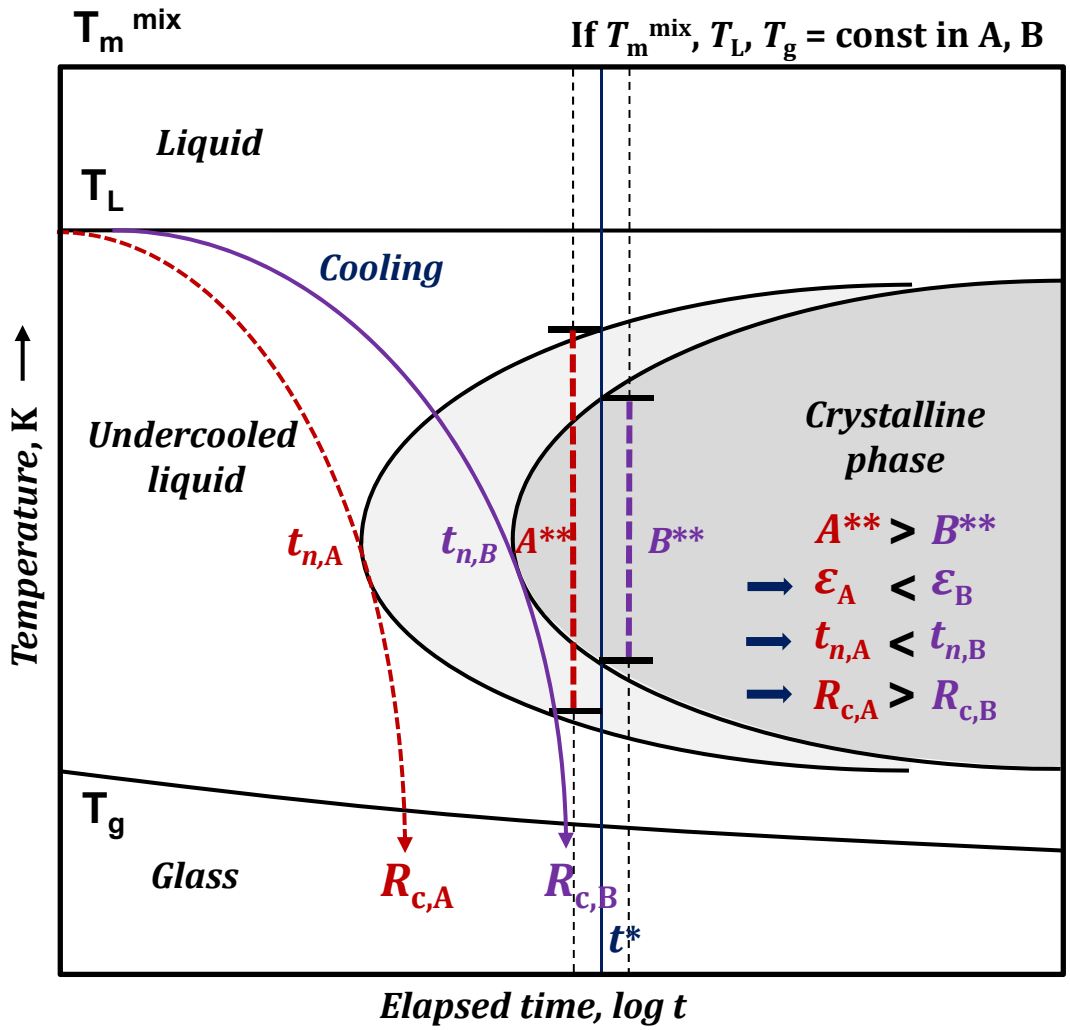
$$\varepsilon = \frac{\Delta T_m + \Delta T_x + T_x}{T_m^{mix}}$$



ε parameter (thermodynamic and kinetic aspects)

A New criterion for GFA of BMGs

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



ε parameter (thermodynamic and kinetic aspects)

A New criterion for GFA of BMGs

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

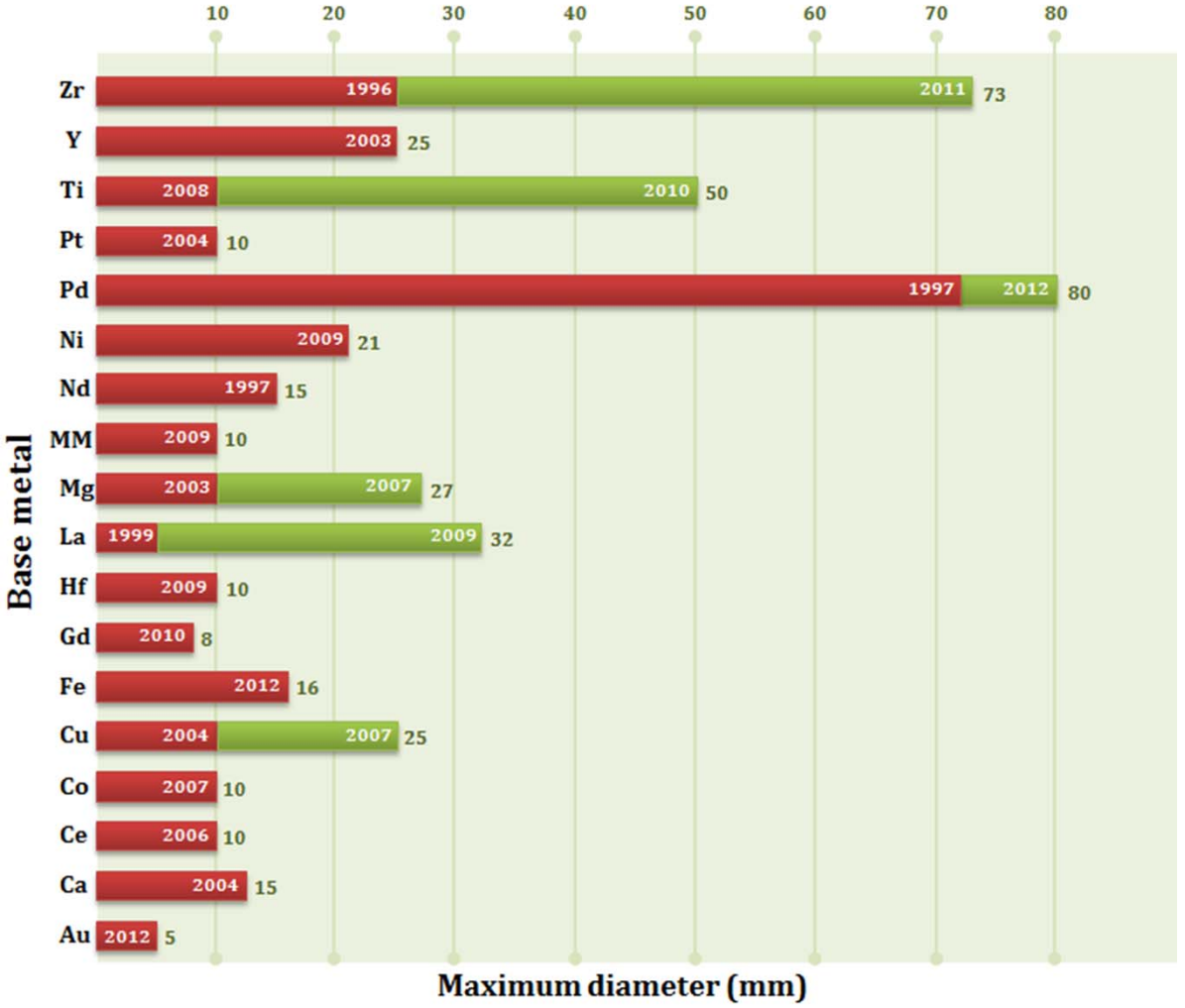


TABLE III. Results of thermal analysis, Z_{max}, and R_c for the various BMG-forming alloy systems, including the data for some conventional metallic glasses previously reported.

Alloy	T_g (K)	T_x (K)	T_l (K)	T_m^{mix} (K)	Z_{max} (mm)	R_c (K/s)	References
Ge	750	750	1210	1210	…	5.0×10^5	Ref. 39
Ni	425	425	1725	1725	…	3.0×10^{10}	Ref. 39
Te	290	290	723	723	…	3.2×10^6	Ref. 39
$Au_{55}Cu_{25}Si_{20}$	348	383	654	1412	0.5	…	Ref. 40
$Au_{46}Ag_5Cu_{29}Si_{20}$	395	420	664	1408	1	…	Ref. 40
$Au_{52}Pd_{2.3}Cu_{29.2}Si_{16.5}$	393	427	651	1412	2	…	Ref. 40
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$	401	459	644	1405	5	…	Ref. 40
$Ca_{66.4}Al_{33.6}$	527	534	841	1052	1	…	Ref. 41
$Ca_{63}Al_{32}Cu_5$	512	523	831	1067	2		Ref. 41
$Ca_{60}Mg_{25}Ni_{15}$	431	453	683	1157	13	24	Ref. 34
$Ca_{65}Mg_5Zn_{30}$	382	414	743	977	1	…	Ref. 42
$Ca_{65}Mg_{10}Zn_{25}$	378	414	686	988	6	…	Ref. 42
$Ca_{65}Mg_{15}Zn_{20}$	379	412	624	1000	15	20	Refs. 42 and 43
$Ce_{70}Al_{10}Cu_{20}$	341	408	722	1112	2	…	Ref. 44
$Ce_{68}Al_{10}Cu_{20}Fe_2$	352	423	708	1127	5	…	Ref. 44
$Ce_{68}Al_{10}Cu_{20}Nb_2$	345	421	721	1146	8	…	Ref. 44
$Ce_{68}Al_{10}Cu_{20}Co_2$	352	419	716	1126	10	…	Ref. 44
$Co_{75}Si_{15}B_{10}$	785	785	1393	1815		3.5×10^5	Ref. 39
$Co_{40}Fe_{22}Nb_6Zr_2B_{30}$	903	1000	1585	2022	1	…	Ref. 47
$Co_{43}Fe_{20}Ta_{5.5}B_{31.5}$	910	982	1492	2048	2	…	Refs. 45 and 46
$Co_{48}Cr_{15}Mo_{14}C_{15}B_6\ Er_2$	848	933	1394	2345	10	…	Ref. 48

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

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Pd-based

Pd-Si

Pd-Cu-Si

Pd-Ni-P

Pd-Cu-Ni-P

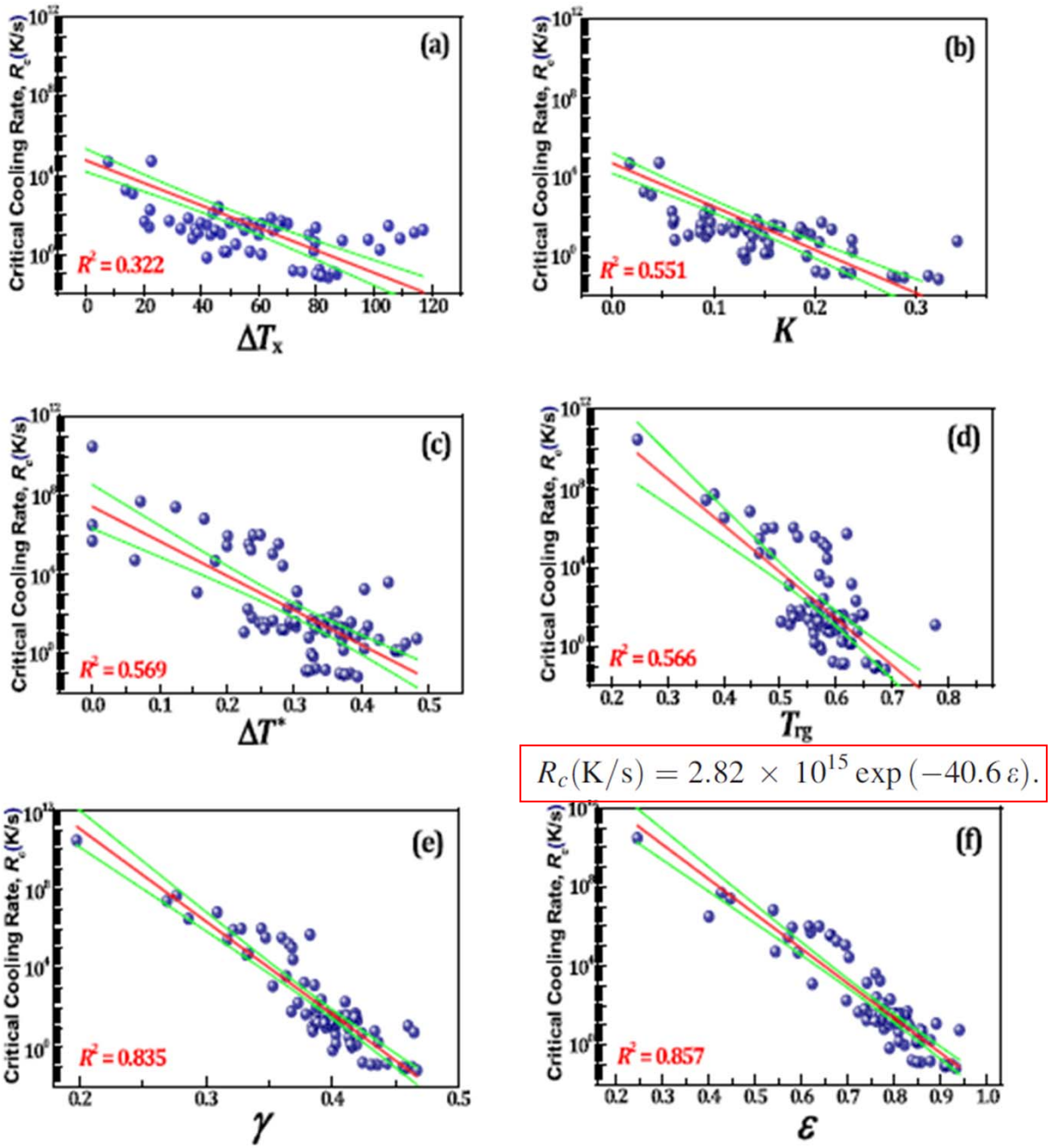


FIG. 4. A correlation between the parameters for GFA (ΔT_x, K, T_{rg}, ΔT^*, γ, and ε parameters) and R_c for the various glass-forming alloy systems reported previously.

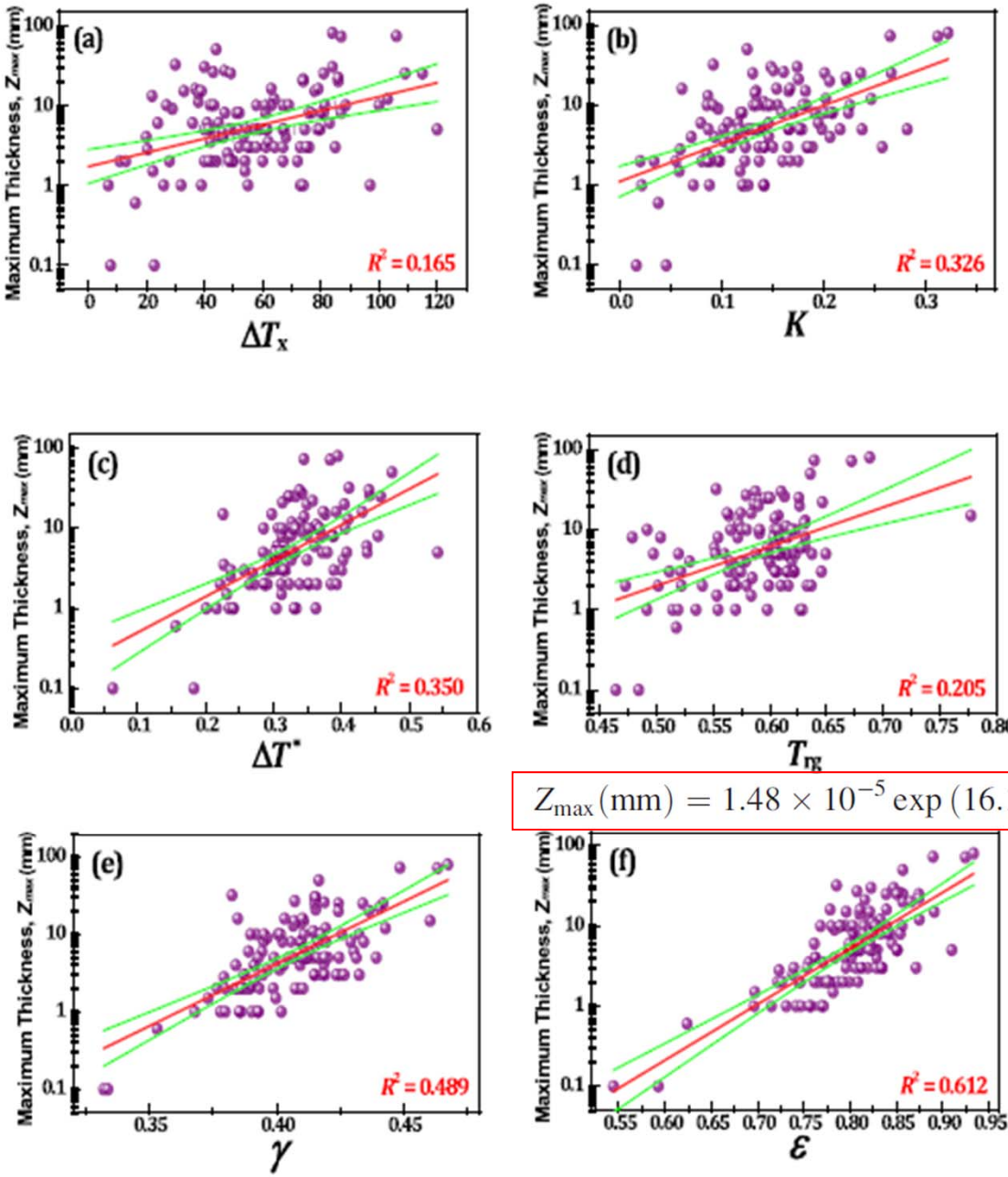
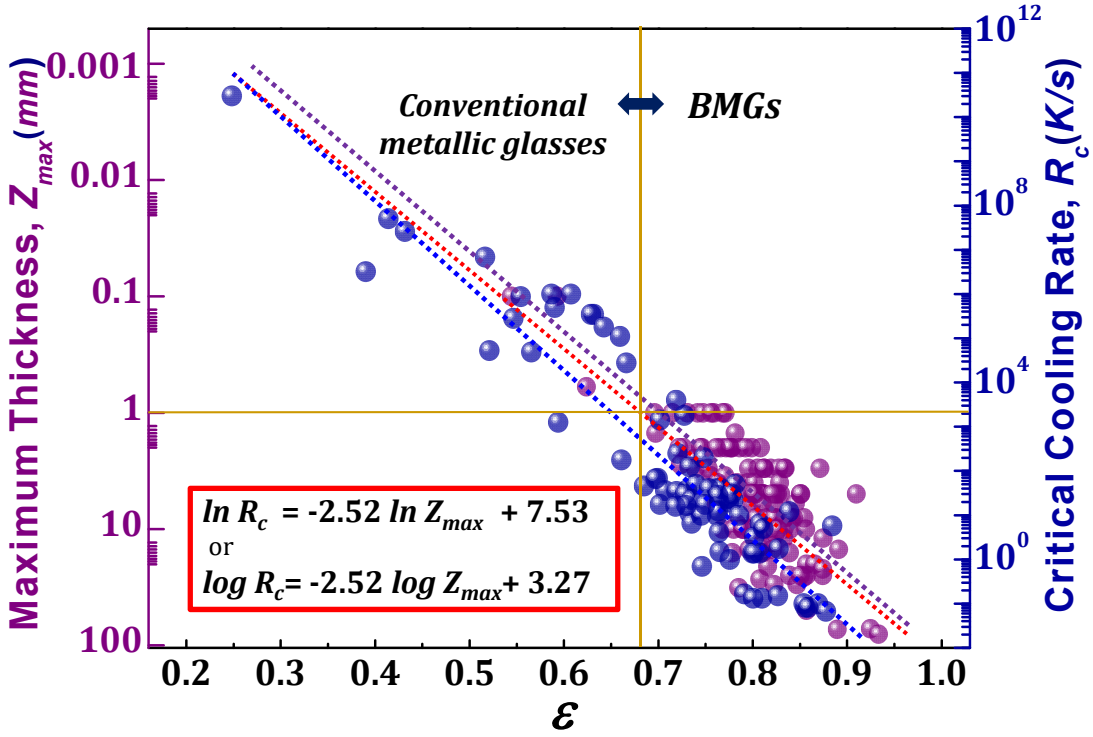


FIG. 5. A correlation between the parameters for GFA (ΔT_x, K, T_{rg}, ΔT^*, γ, and ε parameters) and Z_{max} for the various BMG-forming alloy systems reported previously.

$$R_c(\mathrm{K/s}) = 2.82 \times 10^{15} \exp(-40.6\,\varepsilon).$$

$$Z_{\max}(\mathrm{mm}) = 1.48 \times 10^{-5} \exp(16.1\,\varepsilon).$$

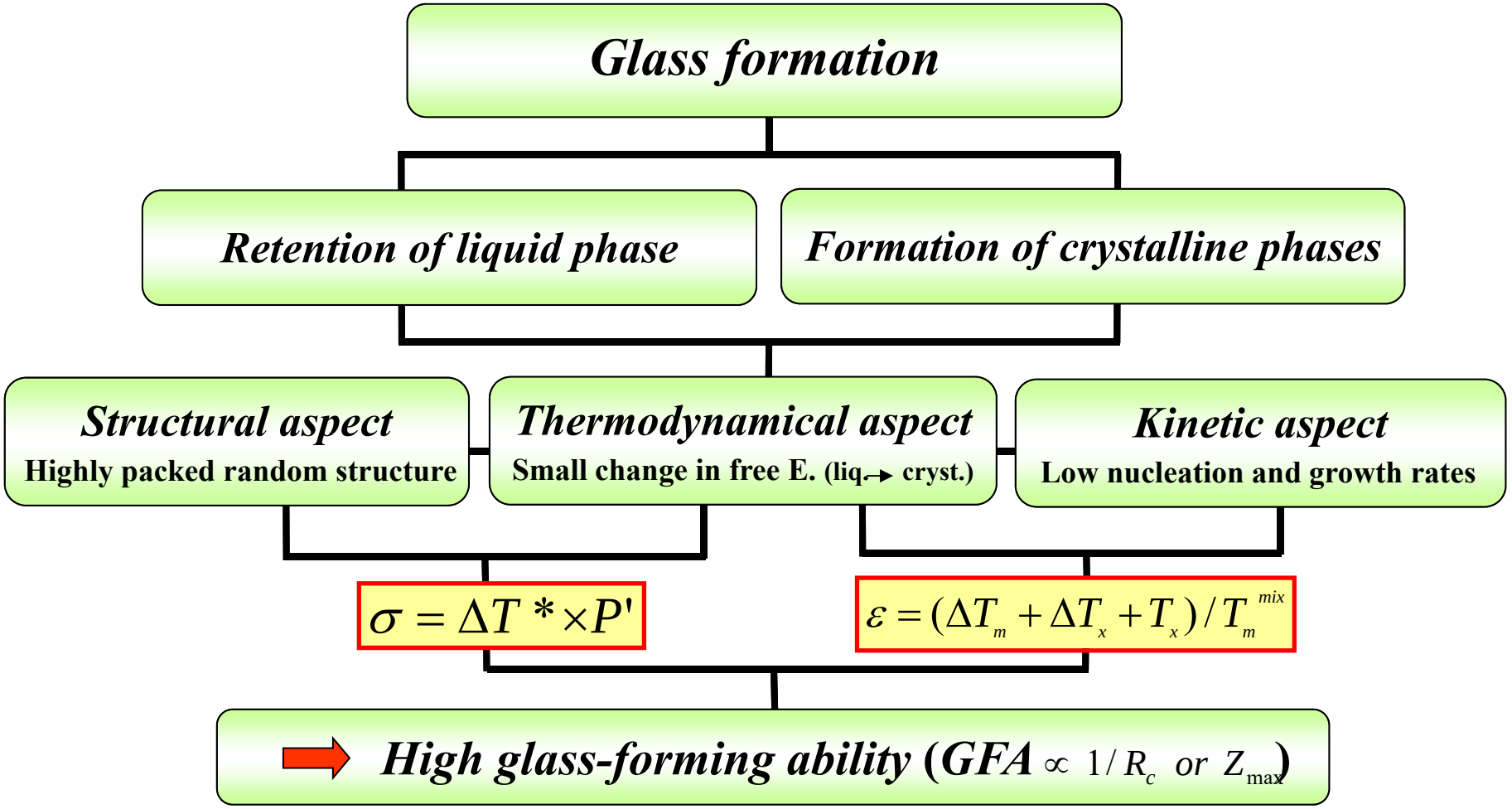


$$R_c = 2.82 \times 10^{15} \exp(-40.6\,\varepsilon)$$

or

$$Z_{\max} = 1.48 \times 10^{-5} \exp(16.1\,\varepsilon).$$

Improvement of GFA



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

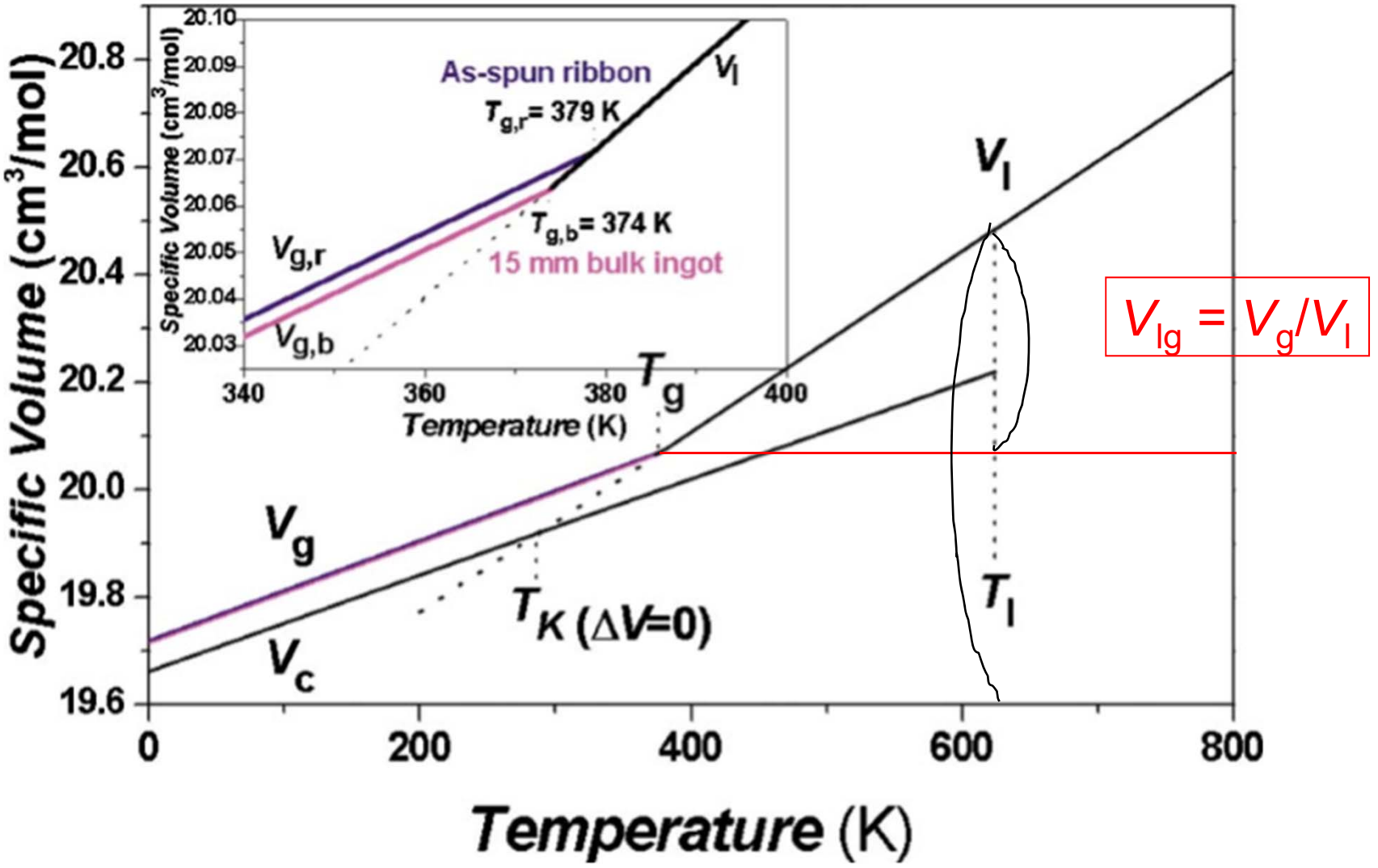
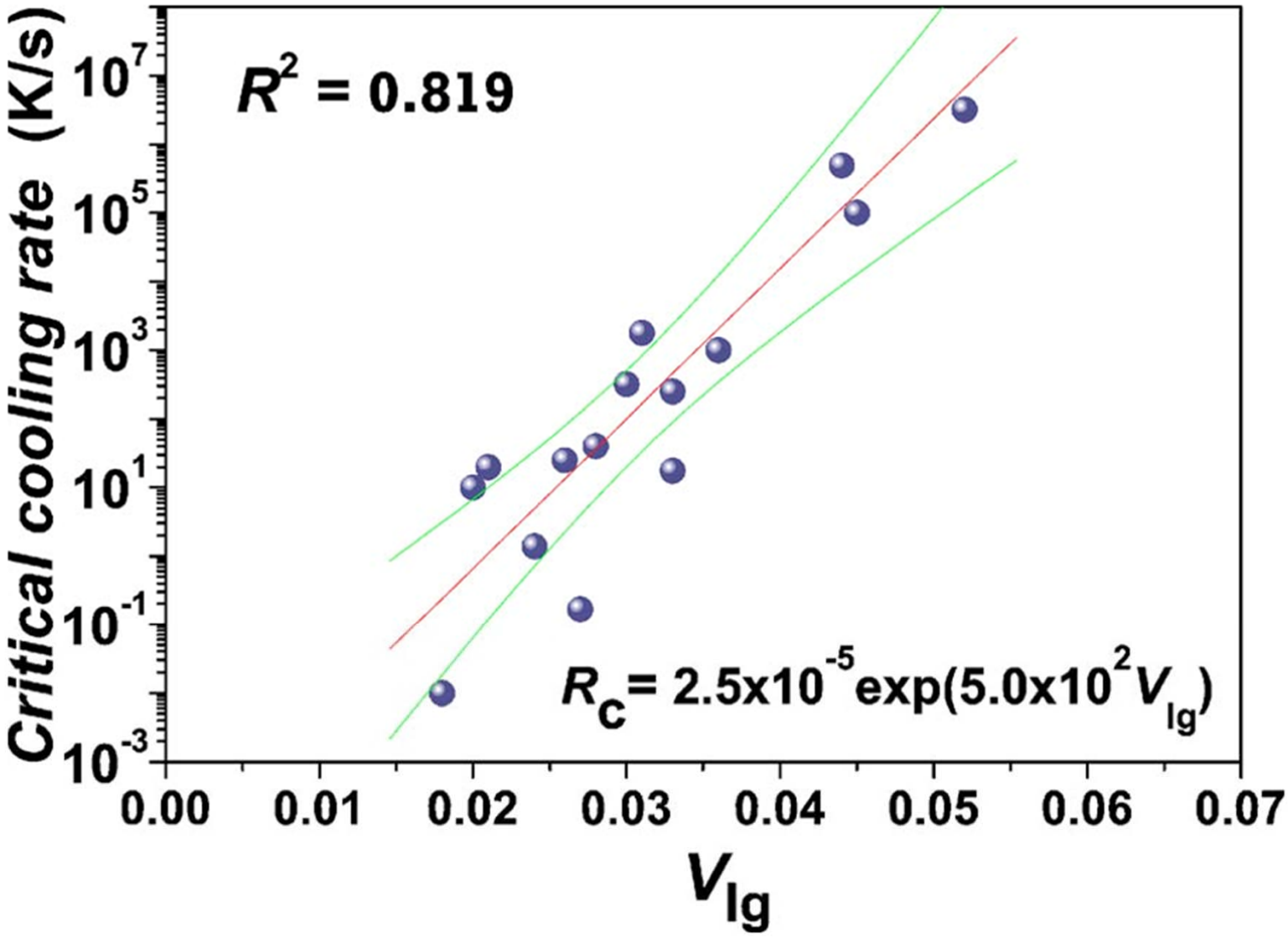


FIG. 1. (Color online) Specific volume as a function of temperature in the liquid V_l, glass V_g, and crystalline V_c of $Ca_{65}Mg_{15}Zn_{20}$ alloy.

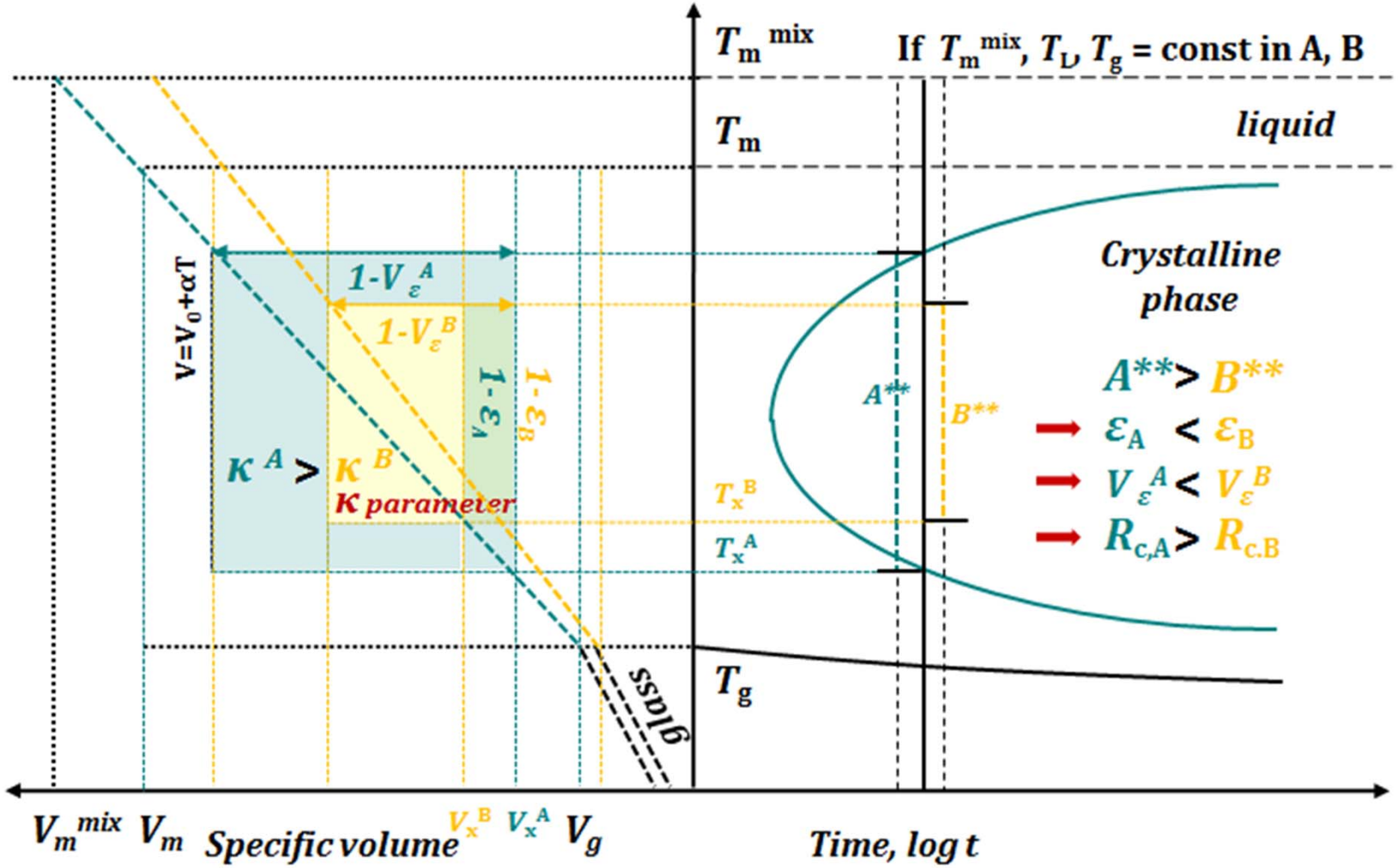
TABLE I. Summaries of thermal analysis (T_g and T_l), V_g, V_l, β_l/T_l, T_{rg}, V_{lg}, and R_c for various MGAs.

Composition	T_g (K)	T_l (K)	V_g (cm^3/g)	V_l (cm^3/g)	β_l/T_l ($\times 10^{-8}$)	T_{rg}	V_{lg}	R_c (K/s)
$Pd_{43}Cu_{27}Ni_{10}P_{20}$	576	845	0.108	0.110	7.999	0.682	0.018	0.01
$Pd_{40}Ni_{40}P_{20}$	583	974	0.108	0.111	7.097	0.599	0.027	0.167
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	623	996	0.163	0.167	6.447	0.626	0.024	1.40
$Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$	682	1115	0.147	0.150	4.143	0.612	0.020	10
$Zr_{55}Al_{22.5}Co_{22.5}$	753	1323	0.162	0.167	4.376	0.569	0.033	17.5
$Ca_{65}Mg_{15}Zn_{20}$	379	624	0.469	0.479	13.66	0.607	0.021	20
$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$	675	1090	0.152	0.156	5.668	0.619	0.026	25
$Cu_{46}Zr_{42}Al_7Y_5$	675	1123	0.147	0.151	5.663	0.601	0.028	40
$Ni_{59.5}Nb_{40.5}$	920	1448	0.116	0.120	4.360	0.635	0.033	250
$Pd_{77.7}Cu_6Si_{16.5}$	653	1015	0.096	0.099	8.247	0.643	0.030	320
$Cu_{50}Zr_{50}$	670	1219	0.134	0.139	5.363	0.550	0.036	1000
$Pd_{82}Si_{18}$	629	1071	0.095	0.098	6.467	0.587	0.031	1800
$Ni_{80}P_{20}$	618	1192	0.128	0.134	6.544	0.518	0.045	1.0×10^5
Ge	750	1210	0.174	0.182	7.897	0.620	0.044	5.0×10^5
Te	290	723	0.163	0.172	16.71	0.401	0.052	3.2×10^6

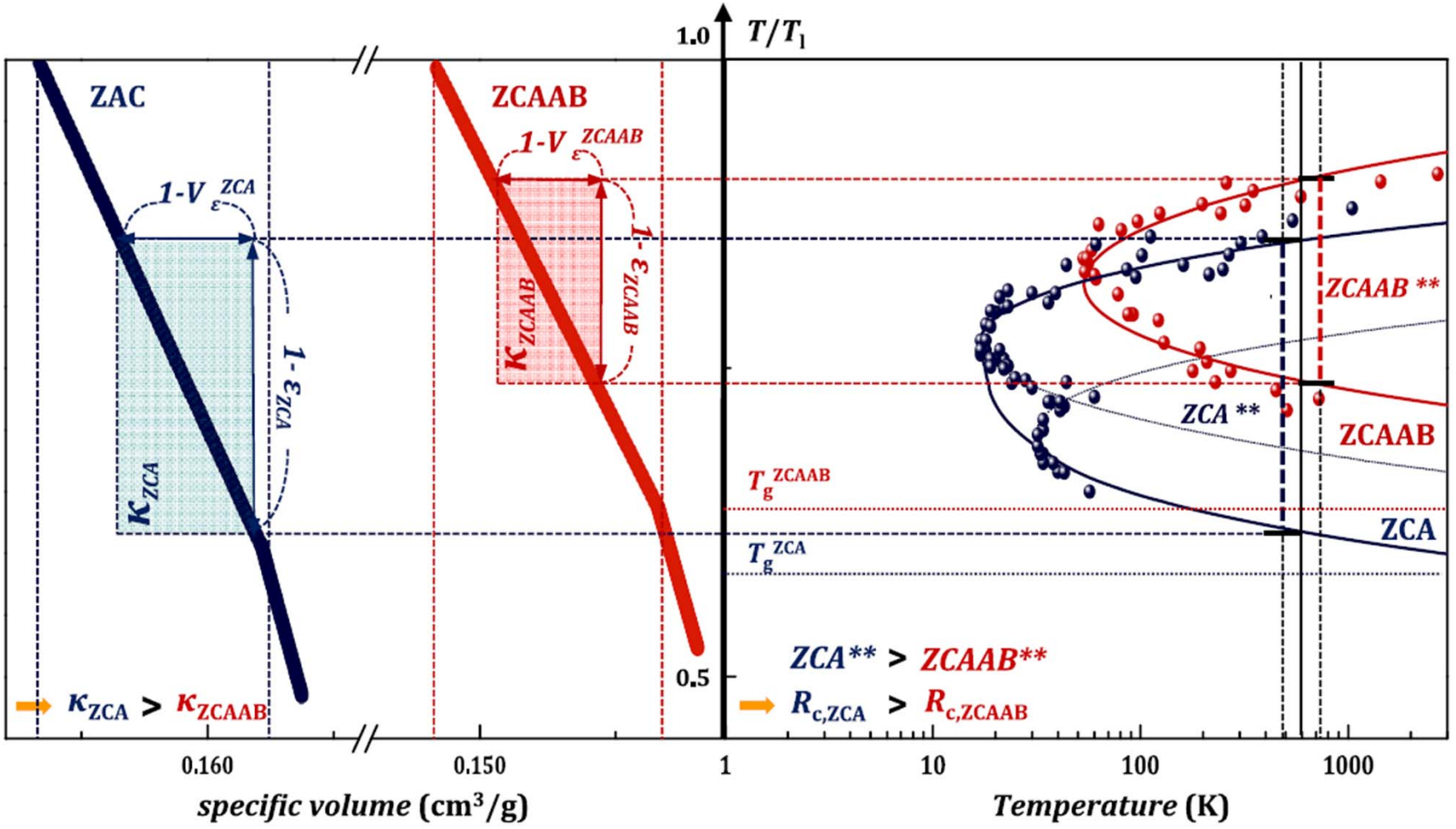

Critical cooling rate (K/s)
10^{7}
10^{5}
10^{3}
10^{1}
10^{-1}
10^{-3}
R^2 = 0.819
R_c= 2.5x10^{-5}exp(5.0x10^{2}V_{lg})
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
V_{lg}

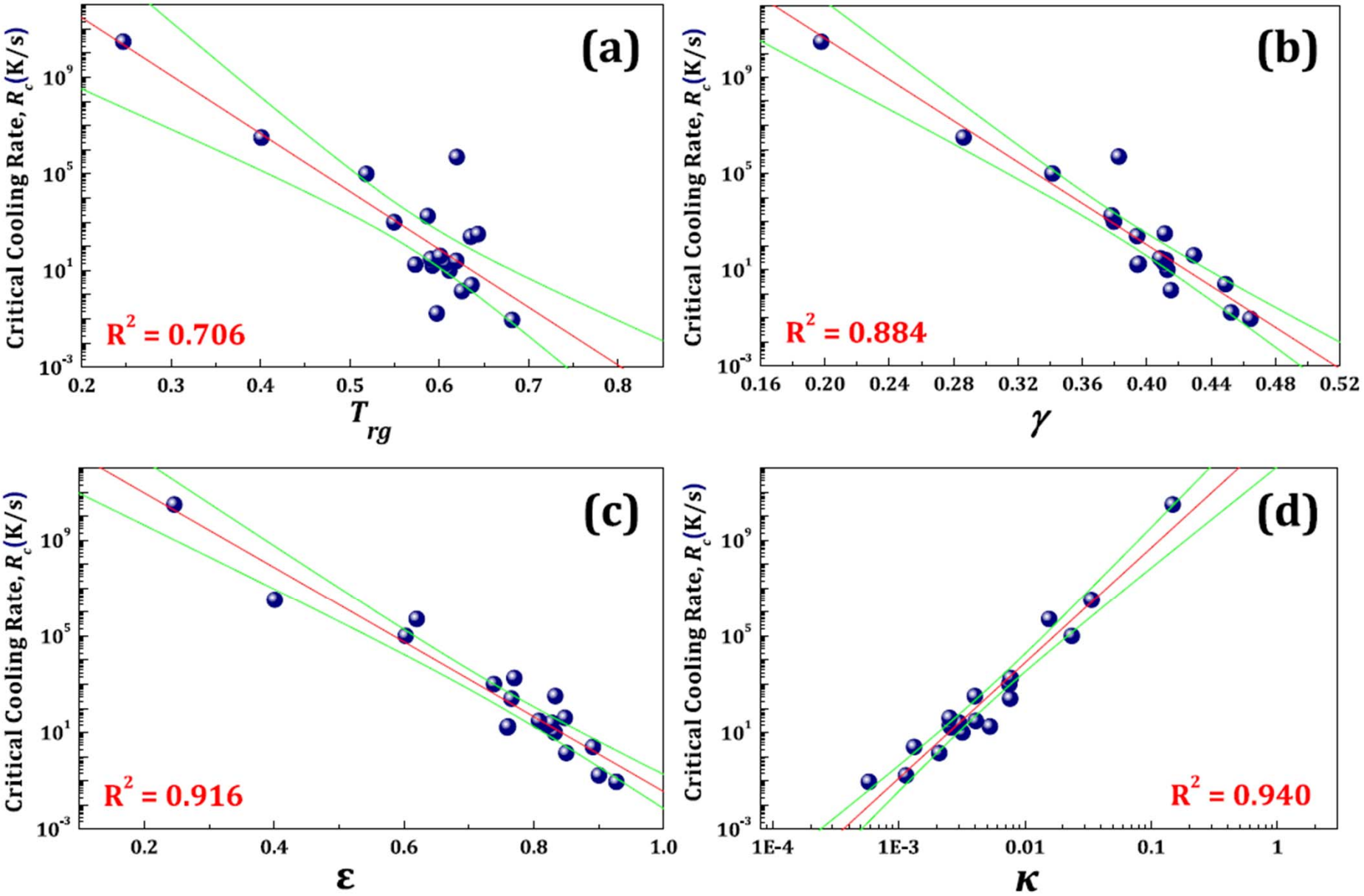
$$\mathrm{GFA} \propto (\varepsilon,\ V_{epsilon} = \frac{V(T_m^{mix} - T_l) + V(T_x - T_g) + V(T_x)}{V(T_m^{mix})})$$

$$\kappa = (1-\varepsilon)\times(1-V_\varepsilon)$$



Indeed, the area indicating $(1-\varepsilon)\times(1-V_\varepsilon)$ characterizes how effectively the volume relaxation of undercooled melts slows down as they are cooled toward the glass transition.




(a)
Critical Cooling Rate, R_c (K/s)
10^9
10^5
10^1
10^{-3}
R^2 = 0.706
0.2
0.3
0.4
0.5
0.6
0.7
0.8
T_{rg}
(b)
Critical Cooling Rate, R_c (K/s)
10^9
10^5
10^1
10^{-3}
R^2 = 0.884
0.16
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.48
0.52
γ
(c)
Critical Cooling Rate, R_c (K/s)
10^9
10^5
10^1
10^{-3}
R^2 = 0.916
0.2
0.4
0.6
0.8
1.0
ε
(d)
Critical Cooling Rate, R_c (K/s)
10^9
10^5
10^1
10^{-3}
R^2 = 0.940
1E-4
1E-3
0.01
0.1
1
κ

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

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

Midterm: 30th April (Monday) 7 PM – 9 PM

Scope: text ~ 144 pages/ teaching note ~ #10/ and references