2010 Spring

“Amorphous Materials”

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Contents for previous class

Glass formation

Retention of liquid phase

Formation of crystalline phases

Alloy Design Optimization

Process Optimization

Consideration of Thermodynamic, Kinetic and Structural aspects for glass formation

Empirical Rules

Minor additions

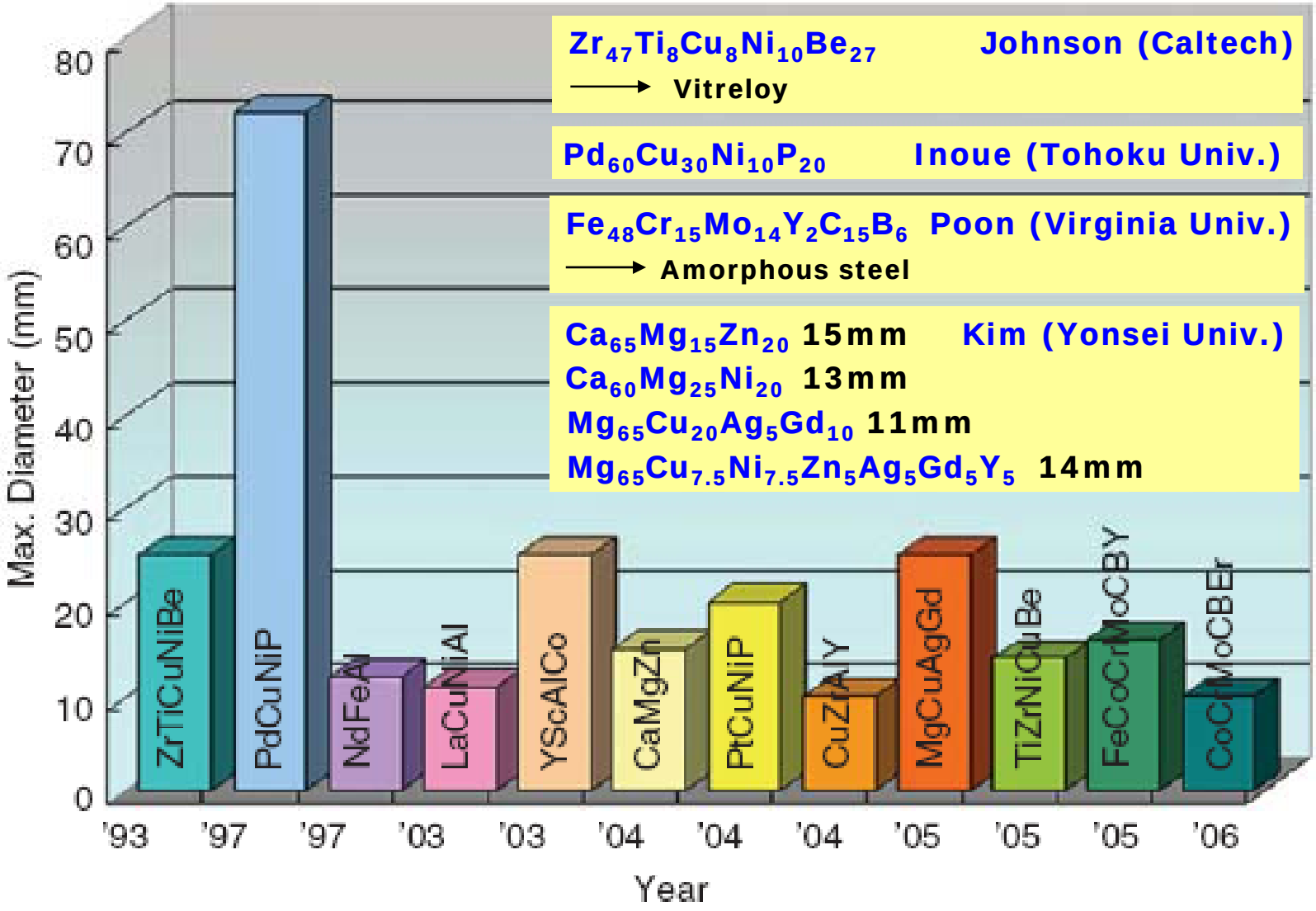
Trial and Errors

1. Chemical etching of ingot
2. Vessel cleaning
3. Successive heating-cooling cycles in a molten oxide flux
4. Alloying at high temperature
5. Process with high cooling rate

Suppression of nucleation and growth of crystalline phase

→ *High glass-forming ability(GFA)*

Recent BMGs with critical size ≥ 10 mm

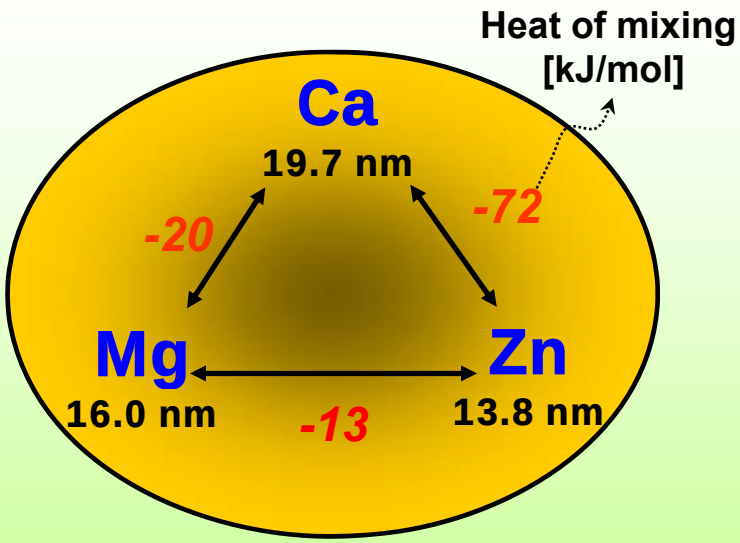


A.L. Greer, E. Ma, MRS Bulletin, 2007; 32: 612.

Alloy design and new BMG development

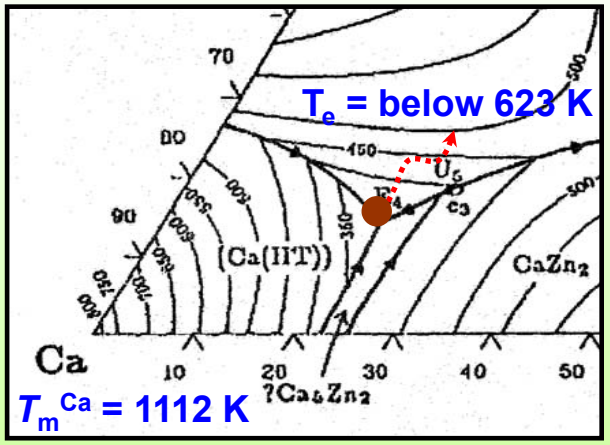
Ca-Mg-Zn alloy system

- **Dense packed structure**



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

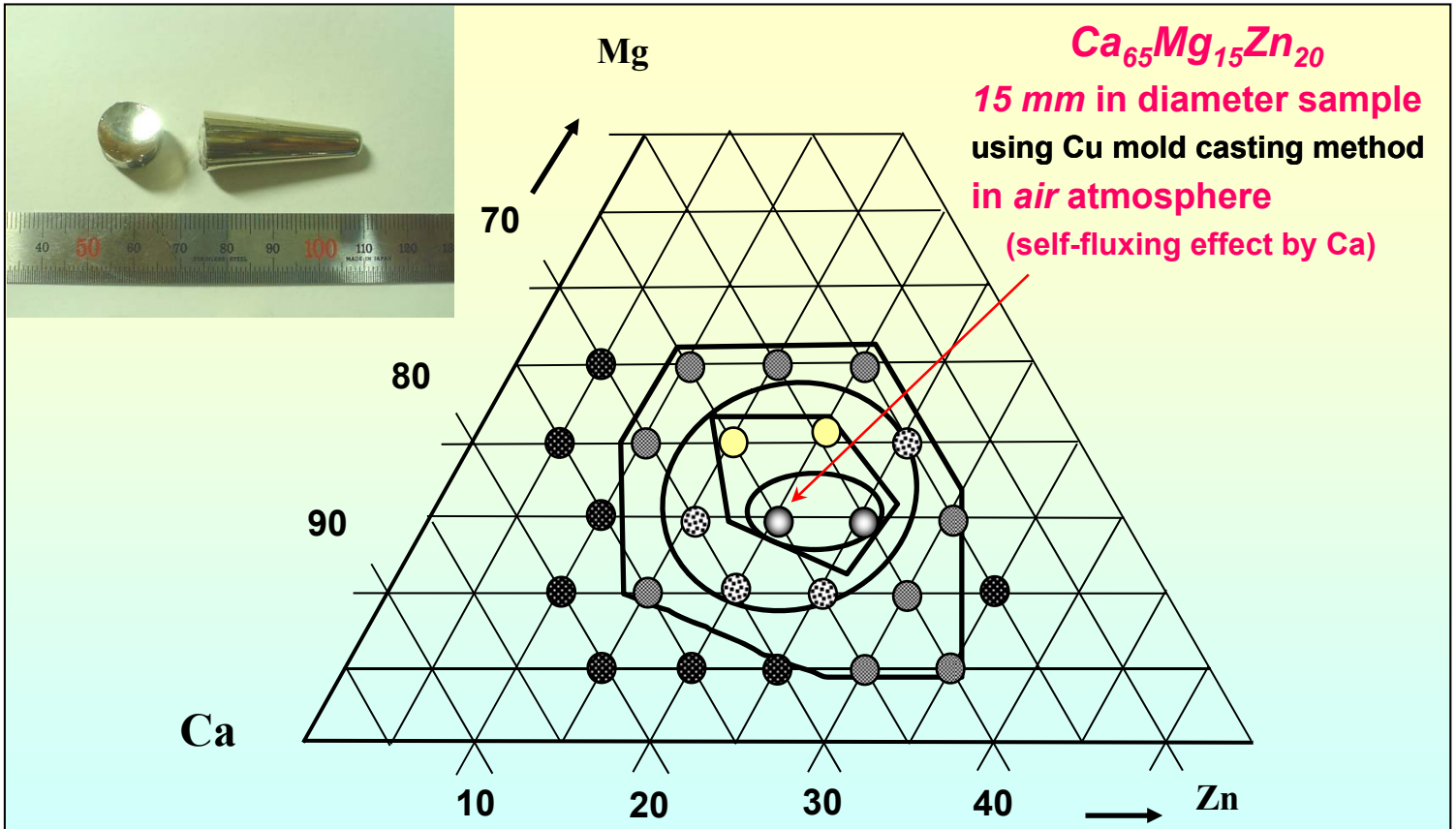
- **Decrease of melting temp.**



Deep eutectic condition

$T_e / T_m^{Ca} = 0.560$

Ca-Mg-Zn alloy system



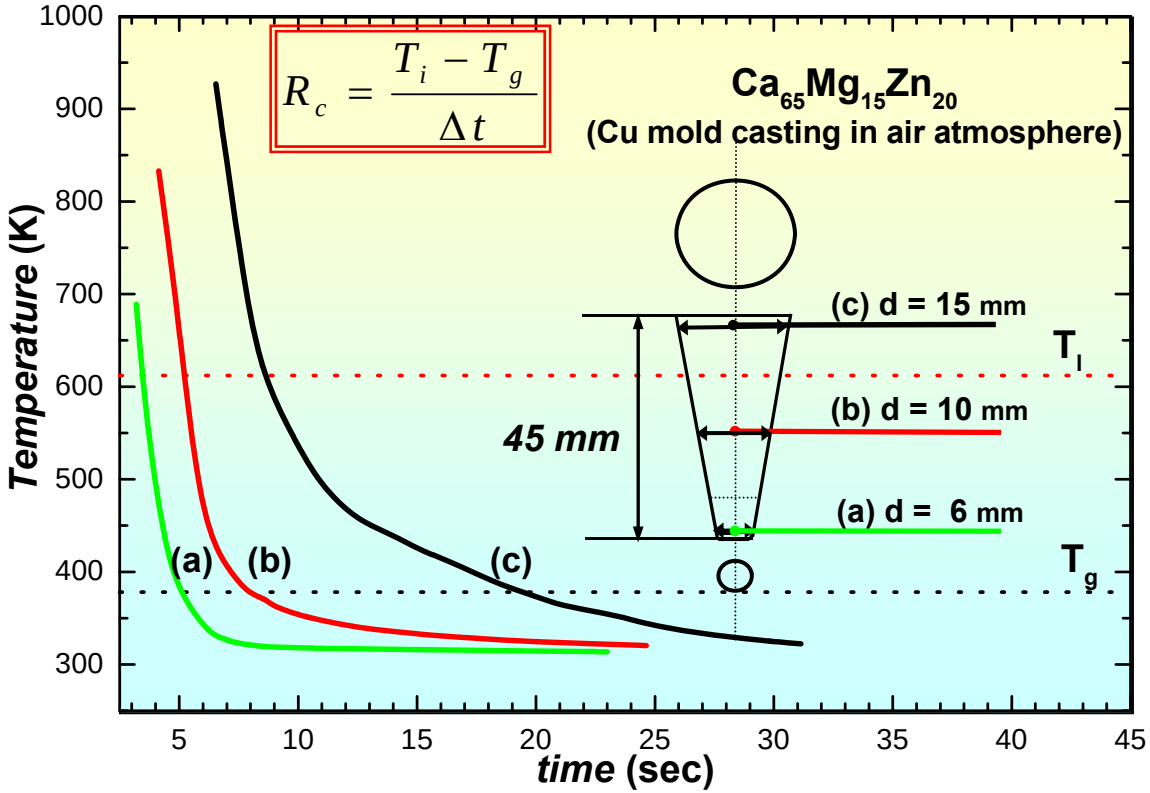
Maximum diameter for glass formation in Ca-rich Ca-Mg-Zn alloy system

over 10mm *over 7mm* *over 3mm* *over 1mm* *below 1mm*

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

Measurement and calculation of R_c in $Ca_{65}Mg_{15}Zn_{20}$ alloy system

*** Cooling curves measured at the center of the three transverse cross sections**

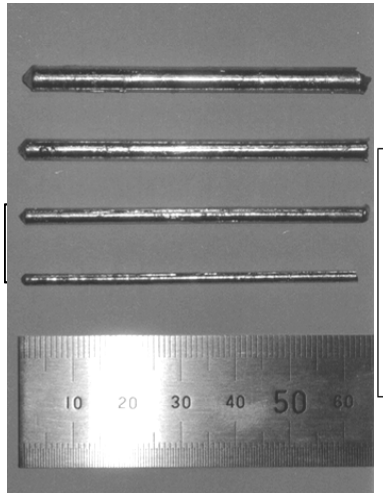


(a) bottom position : 149 K/s (b) middle position : 93 K/s (c) top position : 20 K/s

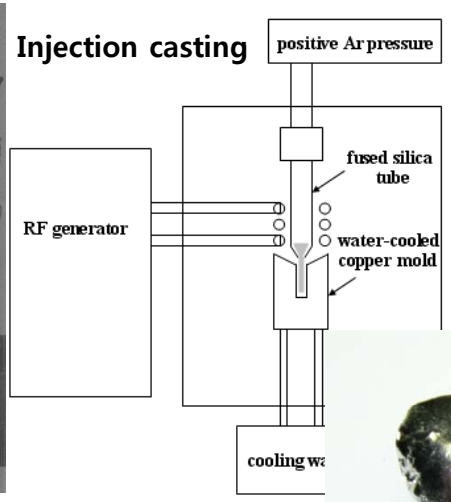
⇒ **Critical cooling rate for glass formation calculated from CCT and CHT curves is in good agreement with measured value.**

* Trans. Indian Inst. Met. 58, 739 (2005)
* Met. Mater. –Int. 11, 1 (2005)

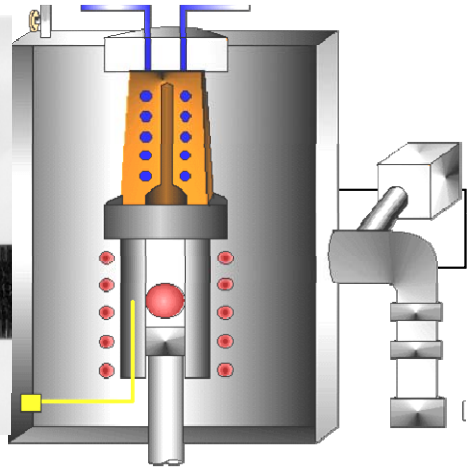
Development of Mg-based BMGs



Injection casting



Squeeze casting



Conventional copper mold casting

Mg-Cu-Y
(ID_{max}= 4)

Mg-Cu-Gd
(D_{max}= 8)

Mg-Cu-X-Y
(x = Ag,Ni,Zn, Al)
(ID_{max}= 6, SD_{max} = 10, 2000)

Mg-Cu-X-Gd
(x = Ag, Ni)
(D_{max}= 11, 2005)

Mg-Cu-Ag-Ni-Zn-Y
(ID_{max}= 9, 2003)

Mg-Cu-Ag-Ni-Zn-Y-Gd
(D_{max}= 14) (strong oxygen resistance)

Mg-Cu-Ag-Ni-Zn-Gd
(D_{max}= 11)

Mg-Cu-Ag-Pd-Y
(WQD_{max}= 12, 2001, ID_{max}=7)

Mg-Cu-Ag-Pd-Gd
(D_{max}= 10, 2003)

Discovering inch-diameter metallic glasses in three-dimensional composition space

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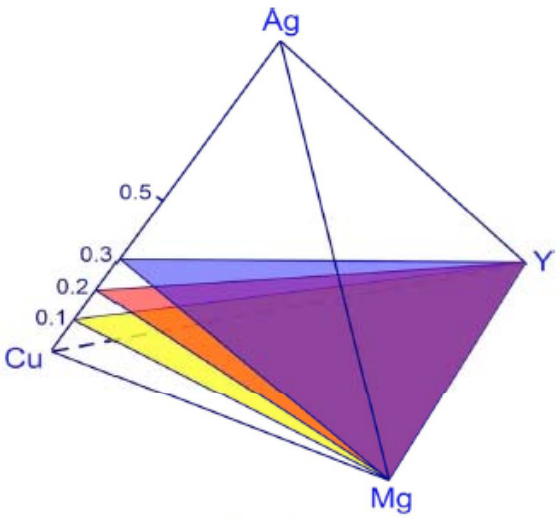
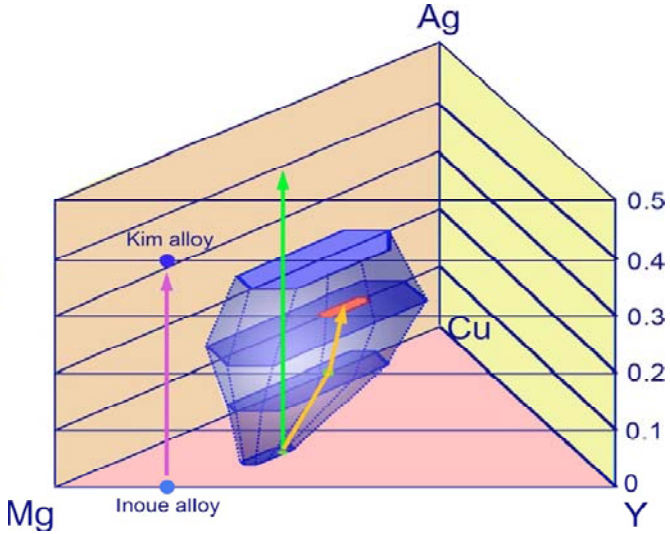
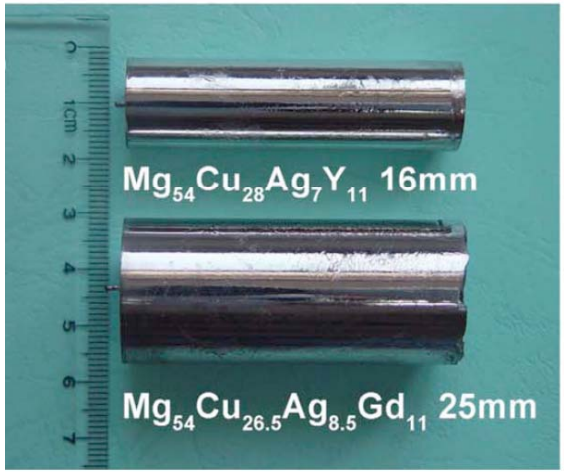
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, 110016, China

Y. Li[b)]
Department of Materials Science, National University of Singapore, Lower Kent Ridge Road, Singapore

E. Ma[c)]
Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

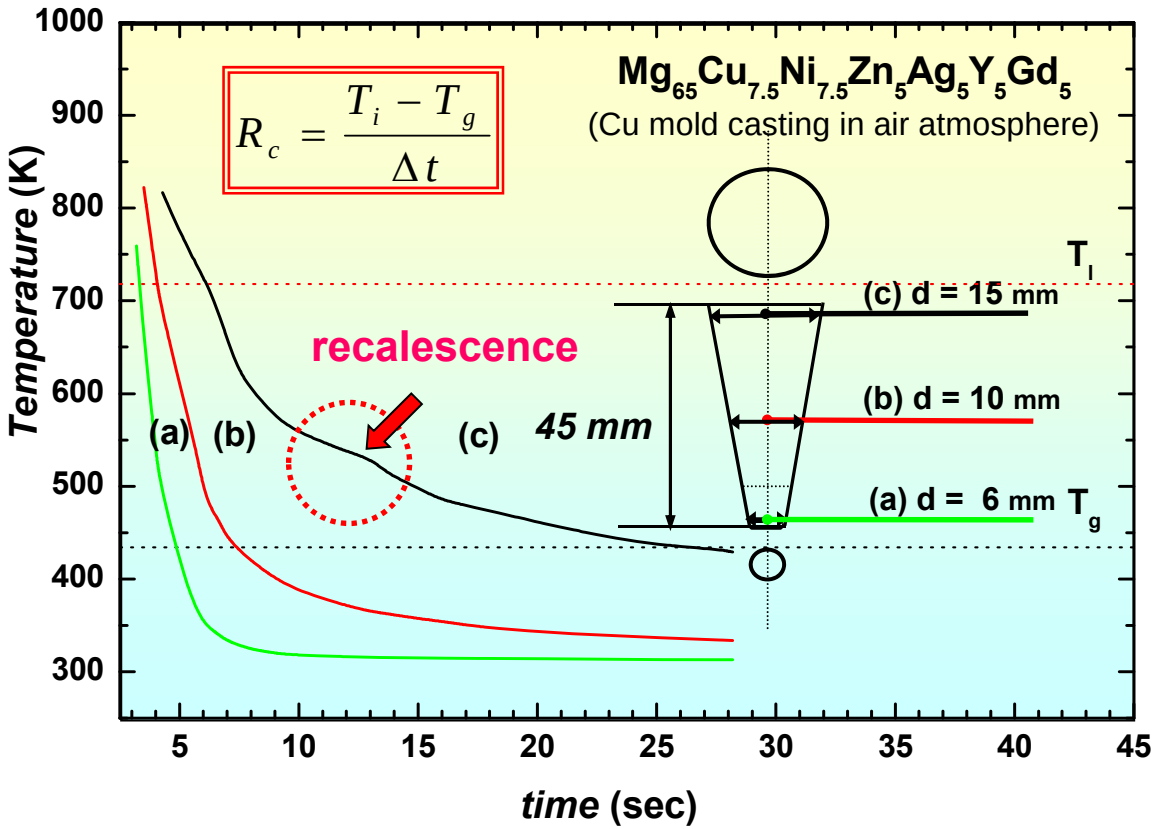






APPLIED PHYSICS LETTERS **87**, 181915 (2005)

Measurement of R_c in Mg BMG (D_{max}=14 mm)



top position : recalescence

middle position : 64K/s

bottom position : 137 K/s

*** Cooling curves measured at the center of the three transverse cross sections**

Parameters for GFA suggested so far :

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

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

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

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

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

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

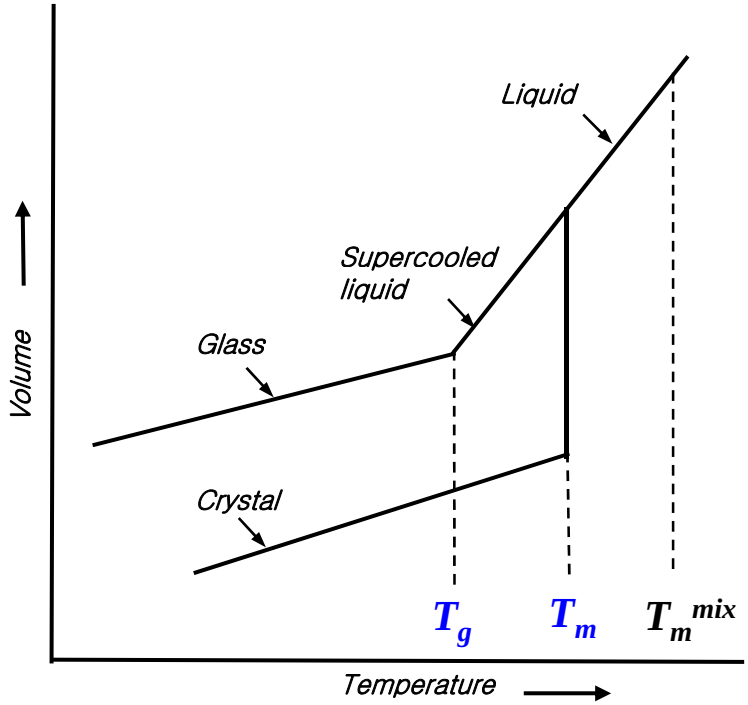
Based on thermodynamic and atomic configuration aspects

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

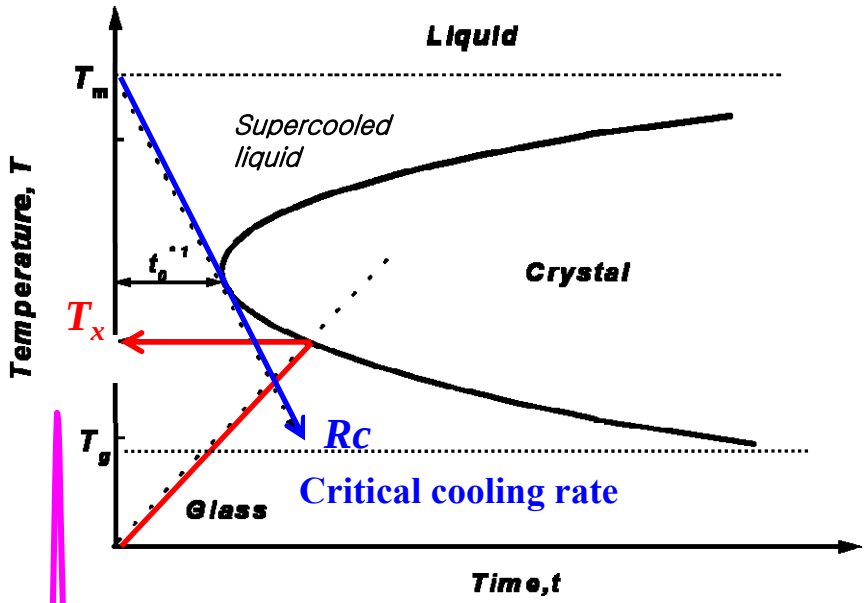
*ΔT** : Relative decrease of melting temperature + *P'* : atomic size mismatch

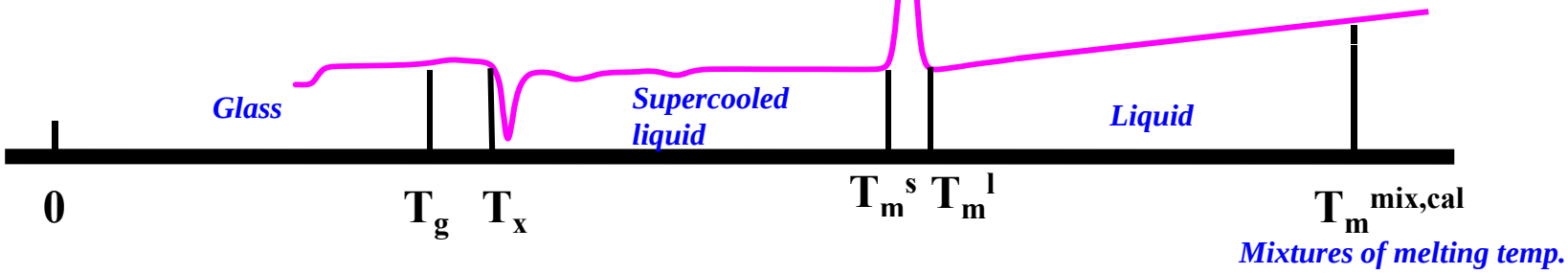
: can be calculated simply using data on melting temp. and atomic size

< V - T diagram >



< TTT diagram >

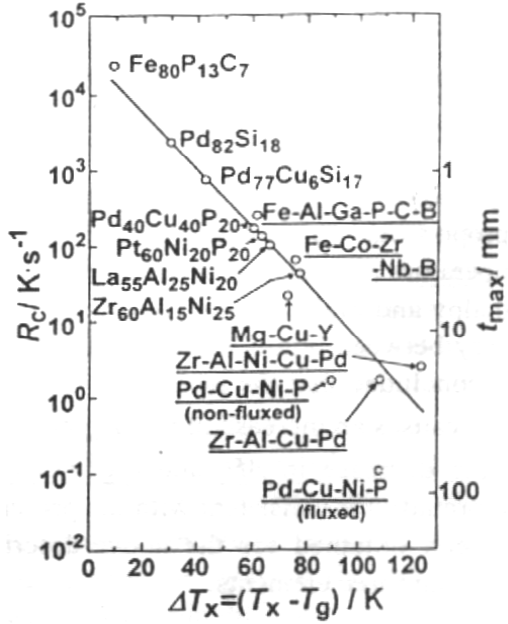




GFA Parameters on the basis of thermodynamic or kinetic aspects :

1) ΔT_x parameter = T_x - T_g

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



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

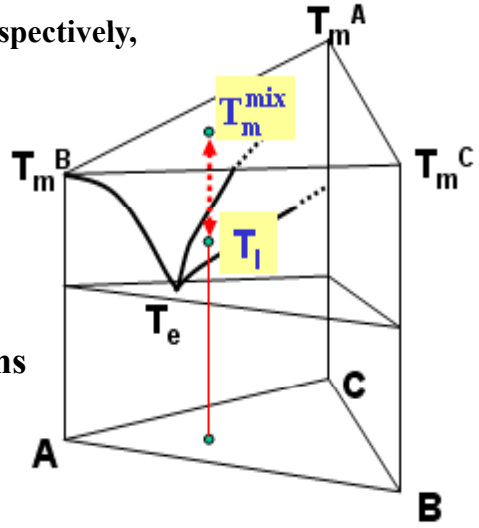
- based on thermal stability of glass on subsequent reheating
- includes the effect of T_l , but similar tendency to ΔT_x

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

- $$T_m^{mix} = \sum_i^n n_i \cdot T_m^i$$

(where n_i and T_m^i are the mole fraction and melting point, respectively, of the i th component of an n-component alloy.)

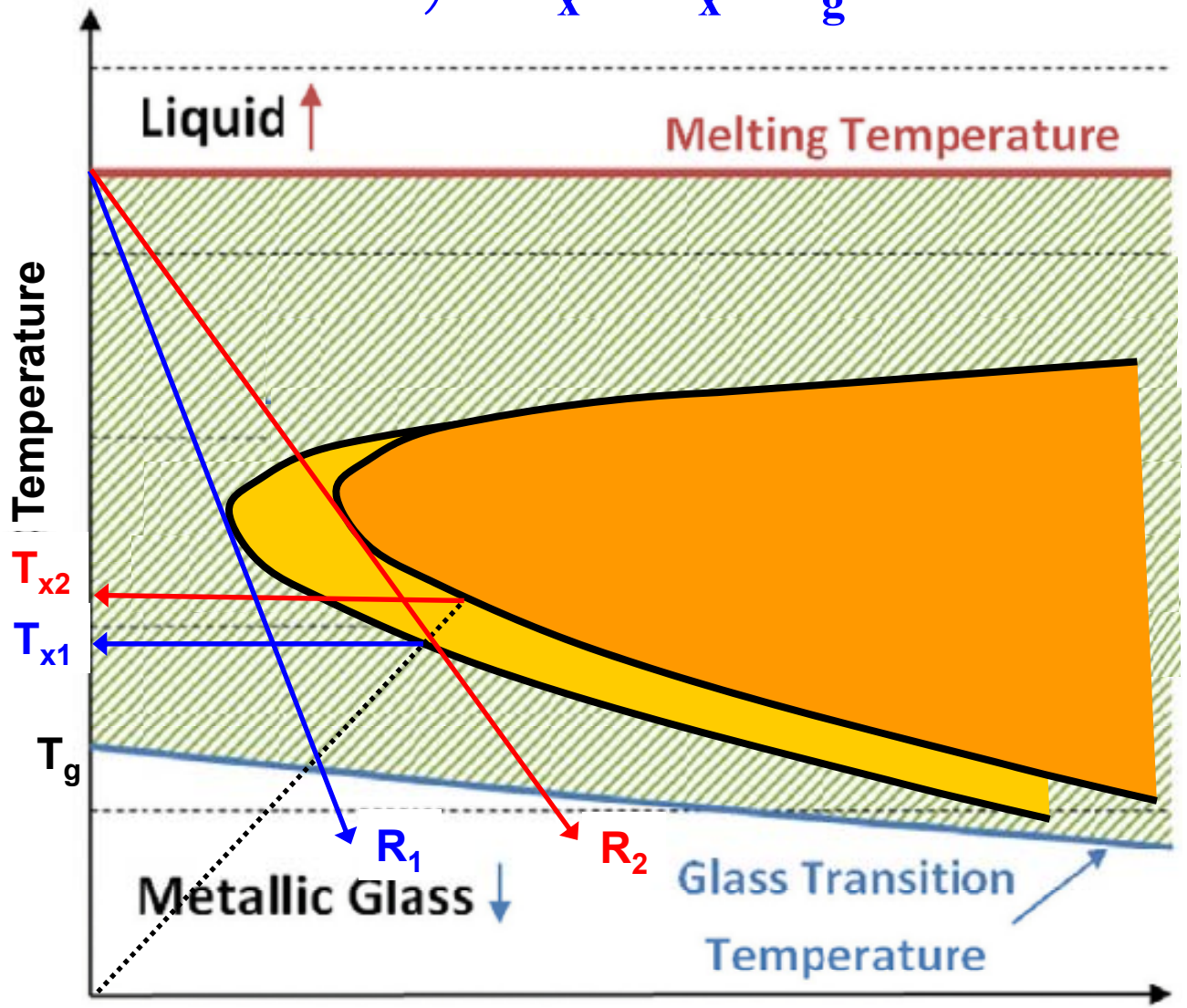
- evaluation of the stability of the liquid at equilibrium state
- alloy system with deep eutectic condition ~ good GFA
- for multi-component BMG systems: insufficient correlation with GFA



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

Time Temperature Transformation diagram:

1) $\Delta T_x = T_x - T_g$



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

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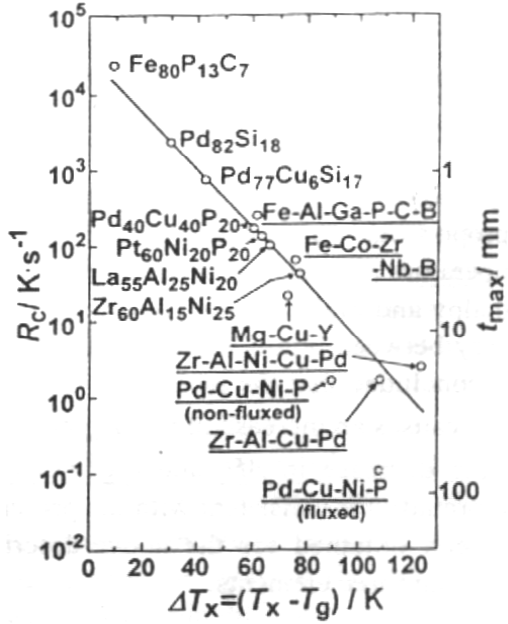

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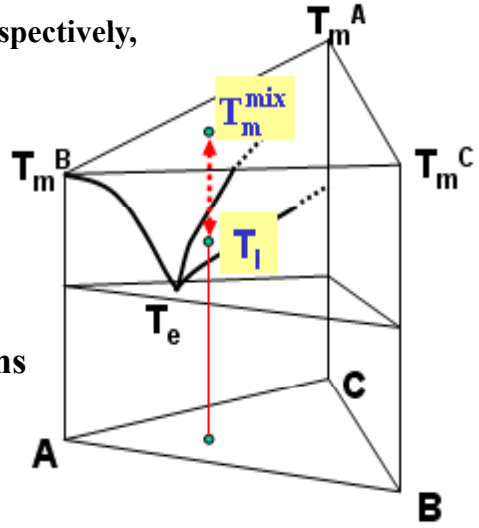

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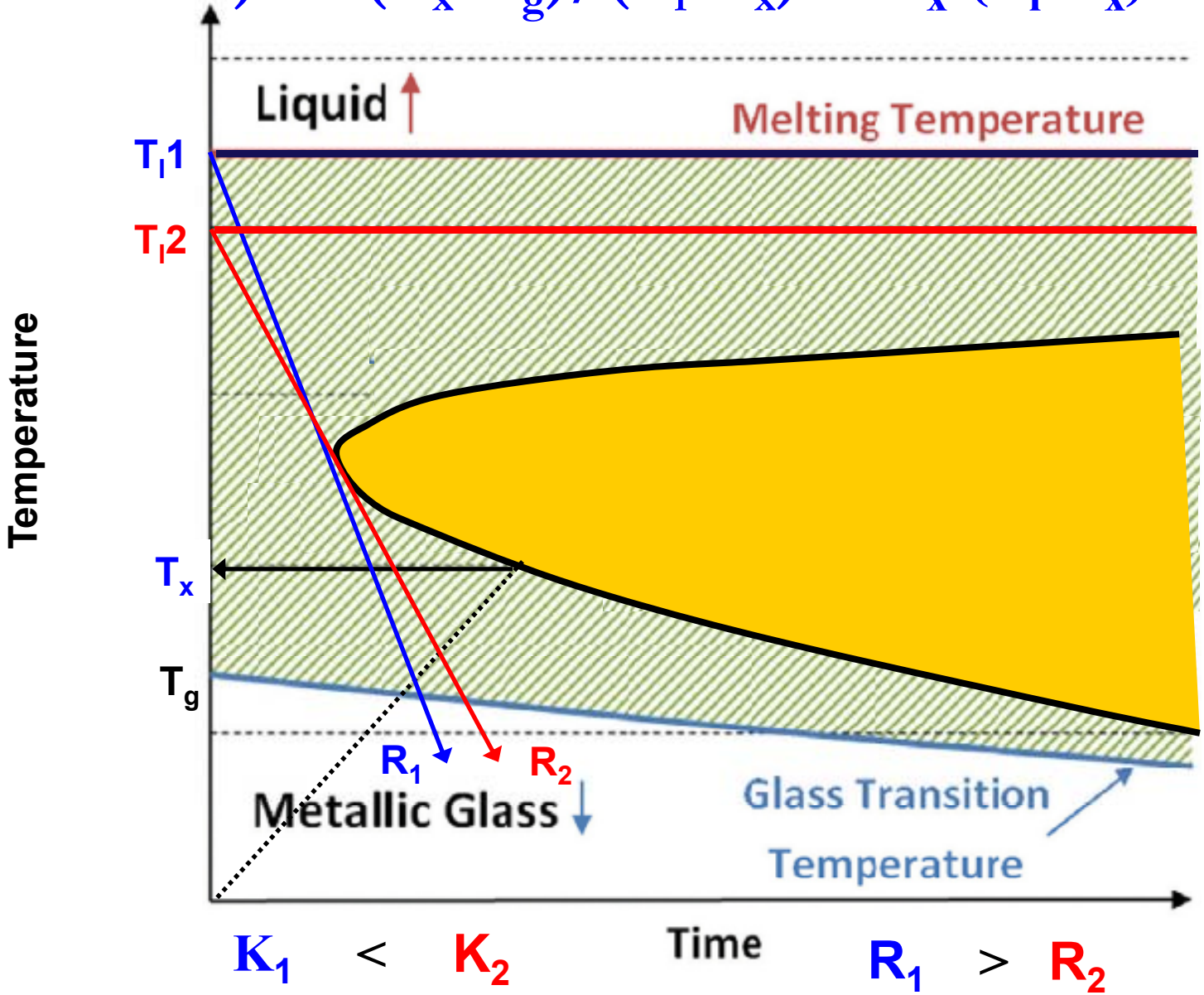

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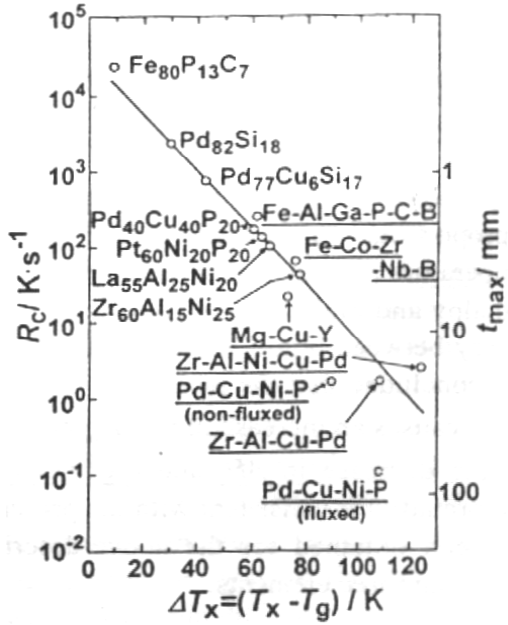

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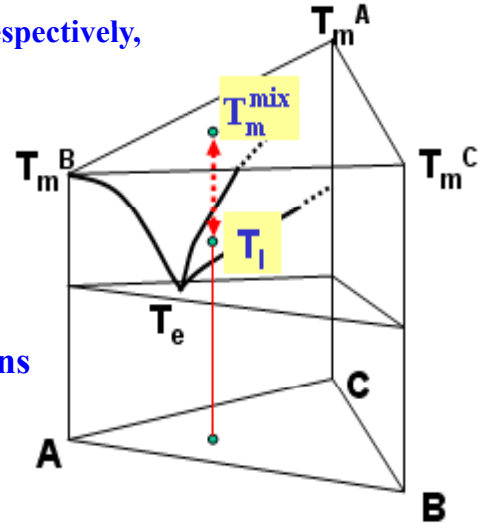


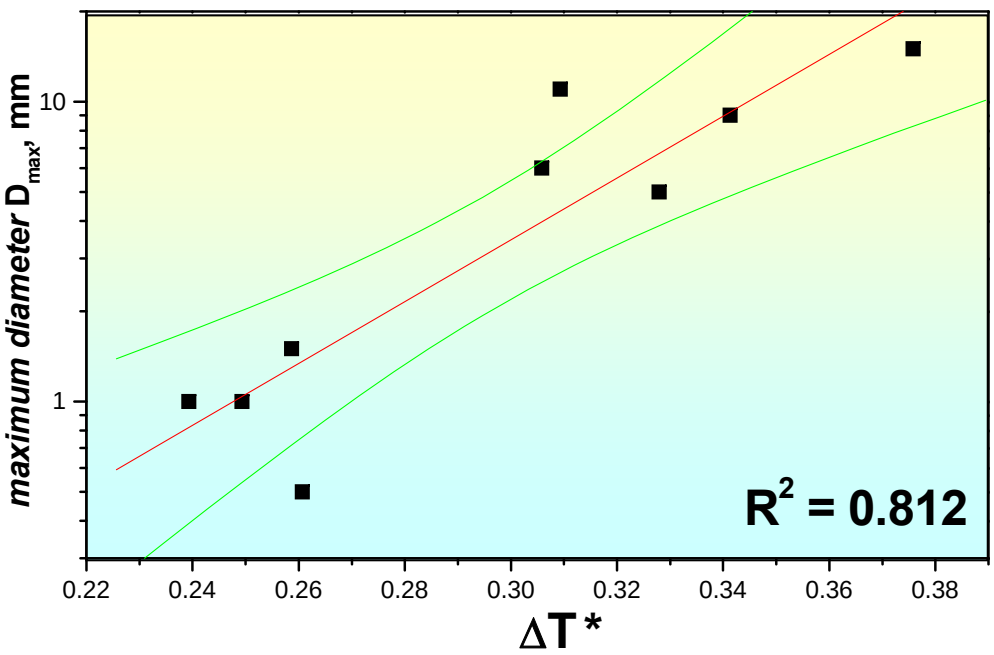
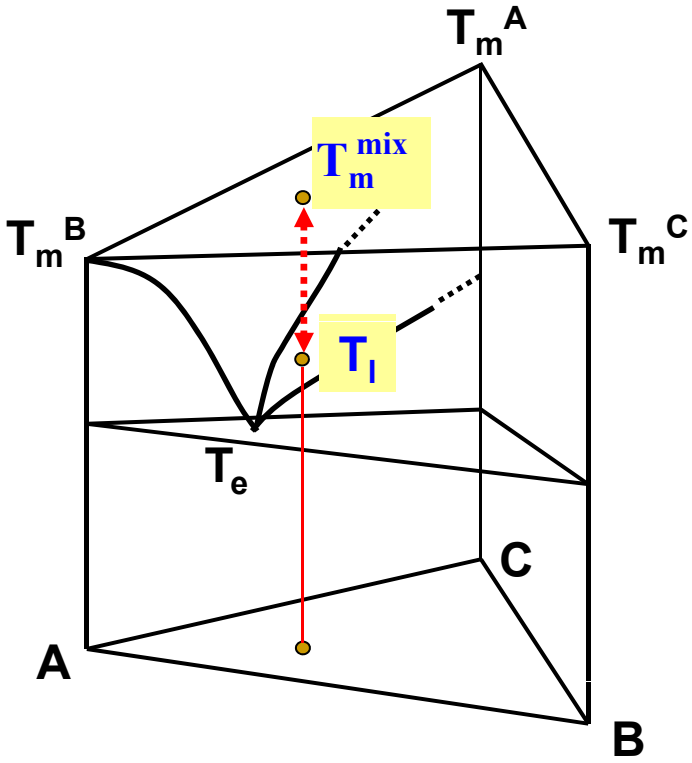
Relative decrease of melting temperature

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

: **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**

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