2018 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

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5.7. Annealing of Bulk Metallic Glasses: SR → SCLR (& PS) → Crystallization

5.7.1 Structural Relaxation

RELAXATION BEHAVIOR

Structural relaxation = stabilization

On annealing, the as-synthesized glass slowly transforms toward an "ideal" glass of lower energy through structural relaxation. = annihilation of "defects" or free volume, or recombination of the defects of opposing character, or by changes in both topological and compositional SRO

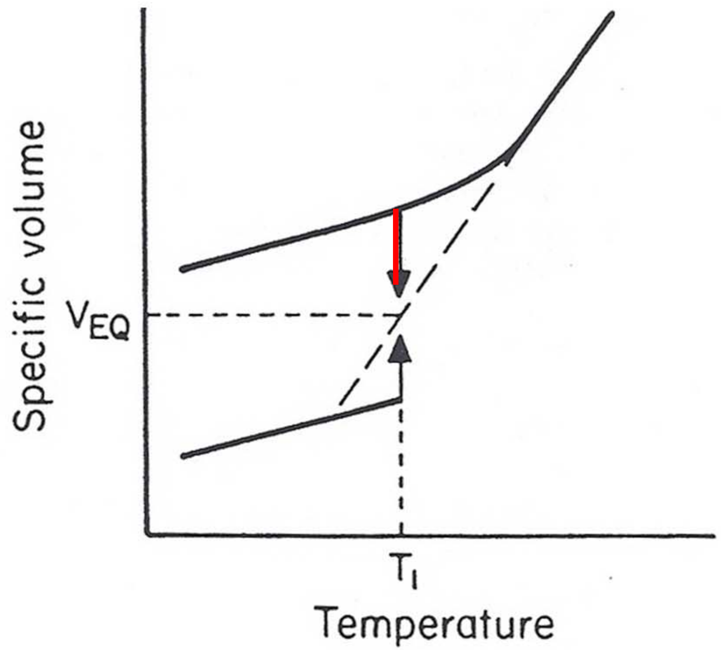

Fig. 9a. Relaxation from initial volumes above and below the equilibrium volume (schematic)

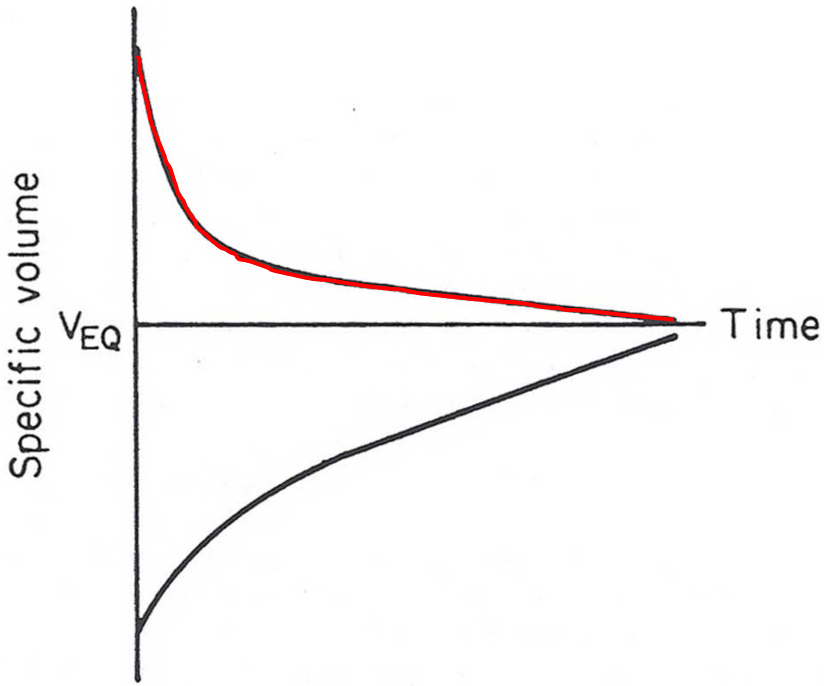

Fig. 9b. Variation of volume with time for initial volumes above and below the equilibrium volume (schematic)

5.7.1 Structural Relaxation

CSRO: Chemical short-range order ⟺ TSRO: Topological short-range order

* Relaxation process

(a) Low temp. regimes (sub-sub-Tg, i.e., Tg-200K <Ta<Tg-100K)

(b) High temp. regimes (sub-Tg, i.e., Ta ≥ Tg-100K)

Exception: Pd-Si, Fe-B and Zr-Cu : undergo structural relaxation just above RT

* Structural relaxation in metallic glasses by a low temperature annealing process

→ does not cause crystallization but significant changes in physical properties

* Relaxed glass : decreased specific heat, reduced diffusivity, reduced magnetic anisotropy, increased elastic constants (by about 7%), significantly increased viscosity (by more than 5 orders of magnitude) and loss of (bend) ductility in some glasses, in addition to changes in elastic resistivity (by about 2 %), Curie temperature (by as much as 40 K), enthalpy (by about 200-300 cal/mol), superconductivity, and several other structure-sensitive properties.

& Density changes: a small increase in density (about 0.5% for melt-spun ribbons and a smaller value of about 0.1%-0.15% for BMG alloys)

5.7.1 Structural Relaxation

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TABLE 5.3

Changes in the Bulk Densities, ρ (g cm^{-3}) of Metallic Glassy Alloys in the As-Solidified and Structurally Relaxed Conditions

Alloy Composition	Synthesis Method	Rod Diameter (mm)/Ribbon Thickness	$\rho_{as\text{-}solidified}$	$\rho_{relaxed}$	$\Delta\rho_{relaxed}$ (%)	Reference
$Pd_{77.5}Cu_6Si_{16.5}$	Melt spinning	30 μm thick ribbon	10.46	10.51	0.48	[68]
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	Melt spinning	40 μm thick ribbon	9.318	9.337	0.2	[69]
$Pd_{77.5}Cu_6Si_{16.5}$	Water quenching	2 mm dia rod	10.48	10.51	0.29	[68]
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	Cu-mold casting	5 mm dia rod	9.27	9.28	0.11	[70]
$Zr_{55}Cu_{30}Al_{10}Ni_5$	Cu-mold casting	5 mm dia rod	6.82	6.83	0.15	[70]

Note: $\Delta\rho_{relaxed} = \dfrac{\rho_{relaxed} - \rho_{as\text{-}solidified}}{\rho_{as\text{-}solidified}}$.

* Measurement of structural relaxation in metallic glasses:

- Electrical resistivity measurements (CSRO < TSRO) and DSC (most popular technique)
- Mossbauer spectroscopy (determine the atomic environments)
- Hardness measurement (increased)
- Diffraction techniques (X-ray, neutron, and electron scattering methods)

(sharpening of the PDF peaks, without shifting their position)

→ The first stage of relaxation was suggested to be related to the elimination of short and long inter-atomic distances and the second stage to the local chemical reordering in the glassy phase (phase separation and nano-crystallization after annealing at higher temp.

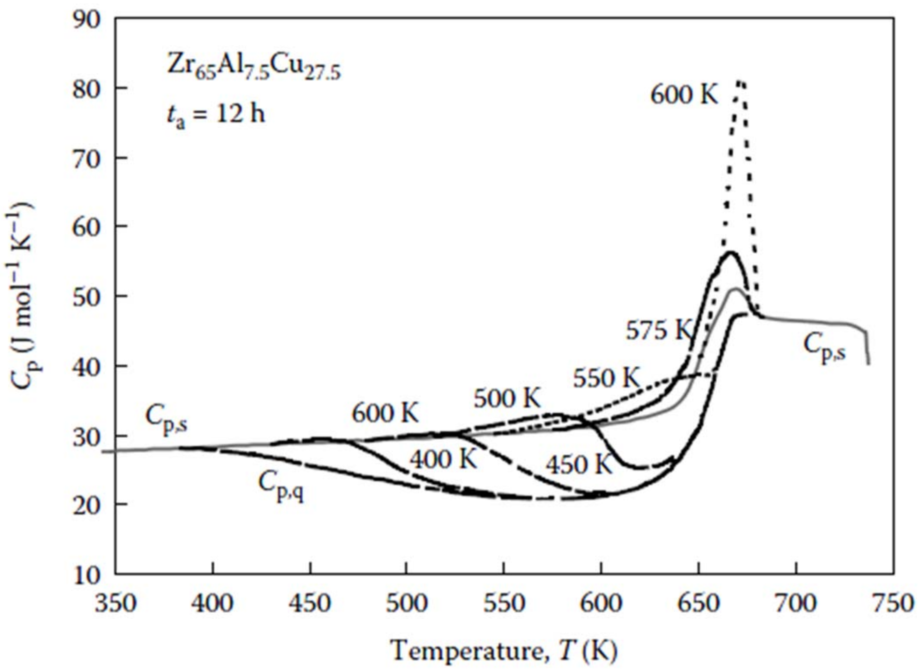
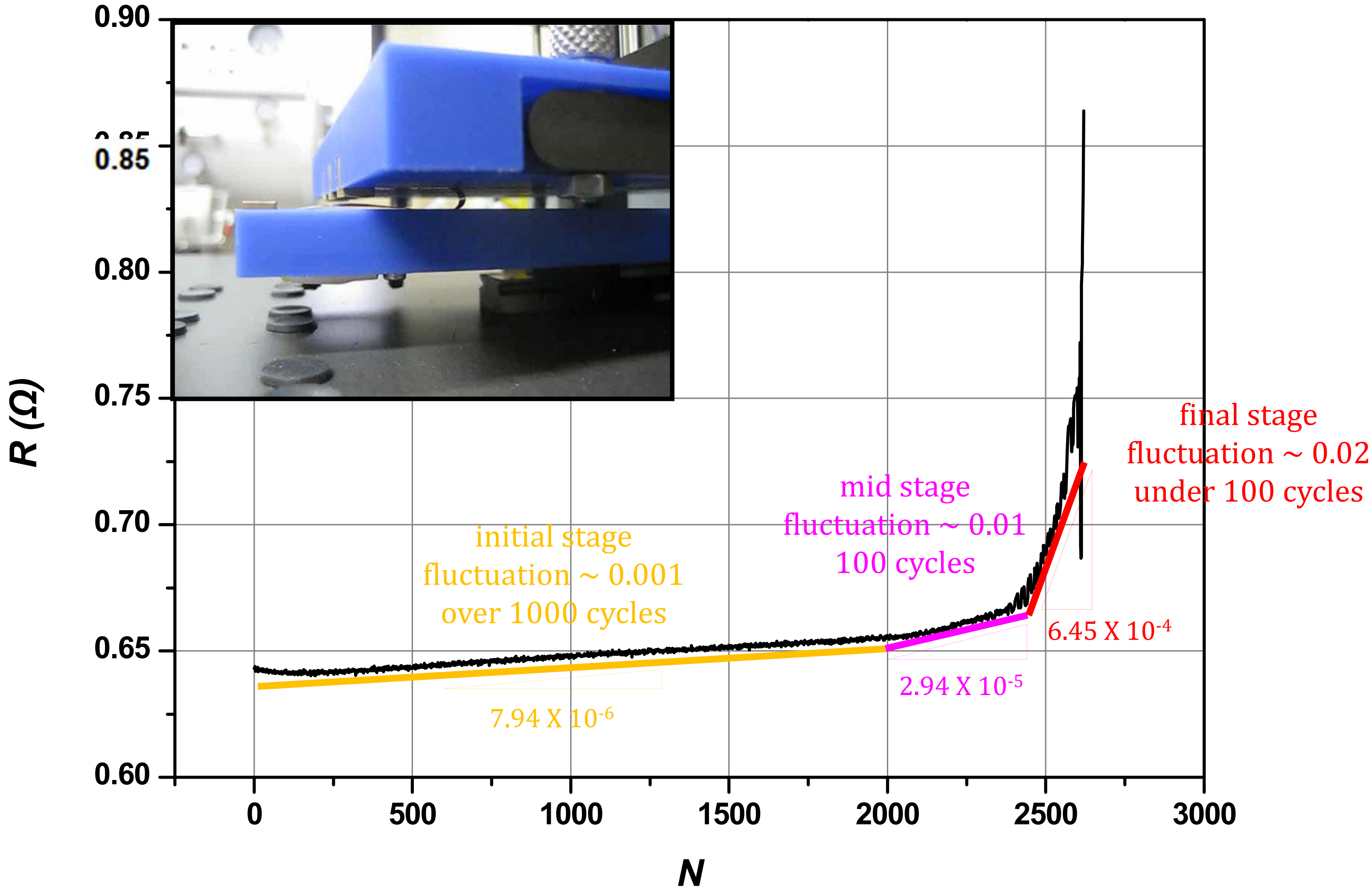


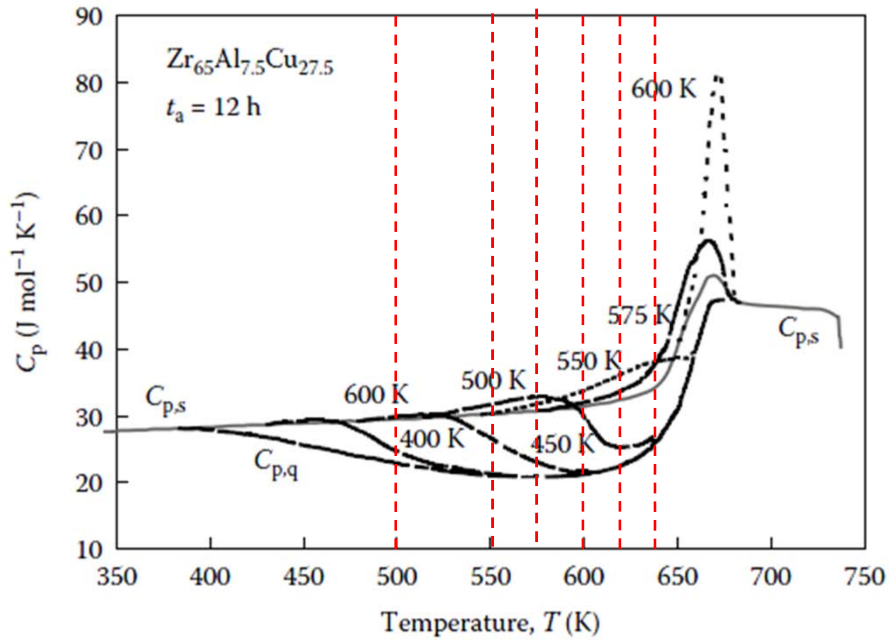
FIGURE 5.12
The variation of specific heat, C_p with annealing temperature, T_a for a glassy $Zr_{65}Al_{7.5}Cu_{27.5}$BMG alloy annealed for 12 h at different temperatures from 400 to 620 K. The solid line represents the variation of C_p for the reference sample annealed for 12 h at 690 K. (Reprinted from Inoue, A. et al., *J. Non-Cryst. Solids*, 150, 396, 1992. With permission.)

→ dependent on thermal history, excess endothermic peak (recoverable), exothermic broad peak (irrecoverable)

* Electrical resistivity measurement during bending fatigue test



With increasing T_a, the maximum in $\Delta C_{p,endo}$ for the two alloys initially increases gradually, followed by a rapid increase at temperatures just below T_g, and then a rapid decrease above T_g.



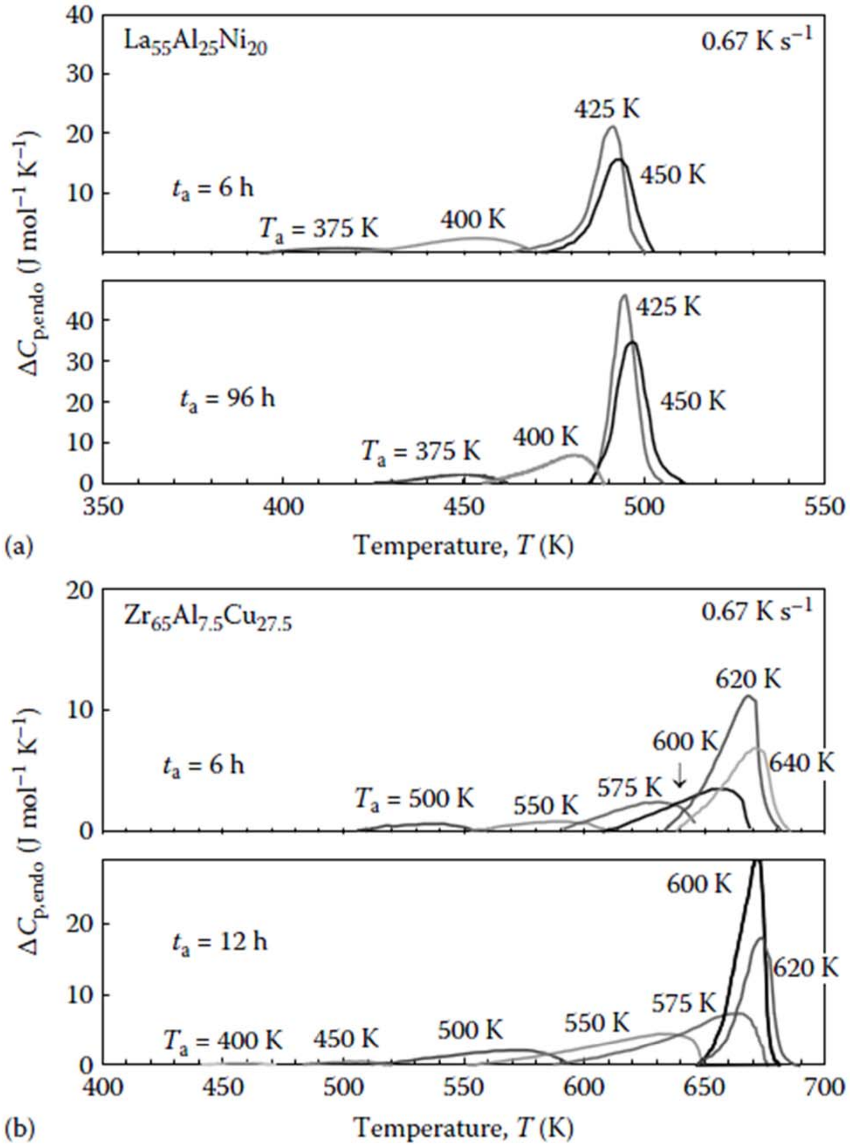


FIGURE 5.13
The differential specific heat, $\Delta C_p(T)$, between the reference and annealed samples for the glassy (a) $La_{55}Al_{25}Ni_{20}$ and (b) $Zr_{65}Al_{7.5}Cu_{27.5}$ alloys annealed for 6 and 96 h for the $La_{55}Al_{25}Ni_{20}$ alloy and for 1 and 12 h in the case of $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy at different temperatures. The samples have been heated in a DSC at 0.67 K s^{-1} (40 K min^{-1}). (Reprinted from Inoue, A. et al., *J. Non-Cryst. Solids*, 150, 396, 1992. With permission.)

* Assuming that the change in enthalpy is entirely due to structural changes in the glassy state and that the average free volume per atom (=V_f/V_m, where V_f is the free volume and V_m is the atomic volume) is proportional to the change in enthalpy:

$$\frac{V_f}{V_m} = C\Delta H \qquad (5.5)$$

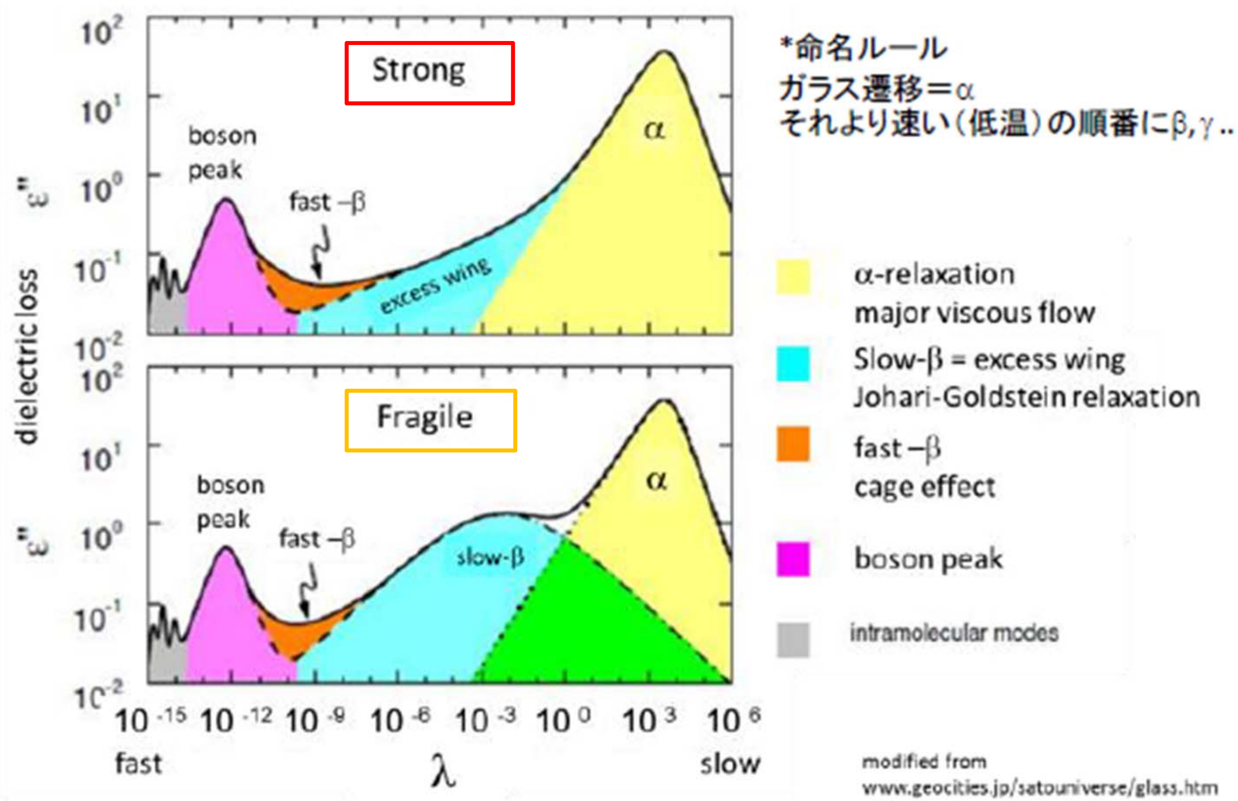
where C is a constant. The proportionality constant C is determined by first calculating V_f using the Grest and Cohen model [83]:

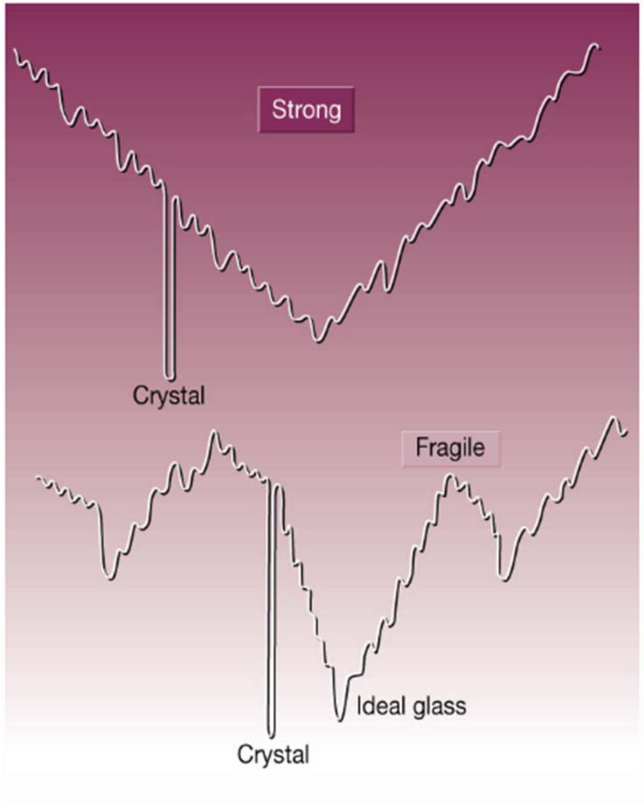
$$V_f = \frac{k}{2s_0}\left(T - T_0 + \sqrt{(T - T_0)^2 + \frac{4V_a s_0}{k}T}\right) \qquad (5.6)$$

where k is the Boltzmann constant. The appropriate fit parameters for the above $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ glassy alloy were reported to be: $bV_m s_0/k = 4933\,K$ with $b = 0.105$, $4V_a s_0/k = 162\,K$, $T_0 = 672\,K$. V_m for this alloy has been reported to be 1.67×10^{-29} m^3 near the liquidus temperature. Thus, by calculating V_f from Equation 5.6, V_f/V_m can be calculated.

→ The mechanical properties of metallic glasses (including the BMGs) are affected by the magnitude of free volume present in them. Hence, it becomes important to be able to quantitatively determine the free volume present in the glass to relate the magnitude of free volume to the changes in mechanical properties.

Dynamic mechanical relaxations in typical glasses



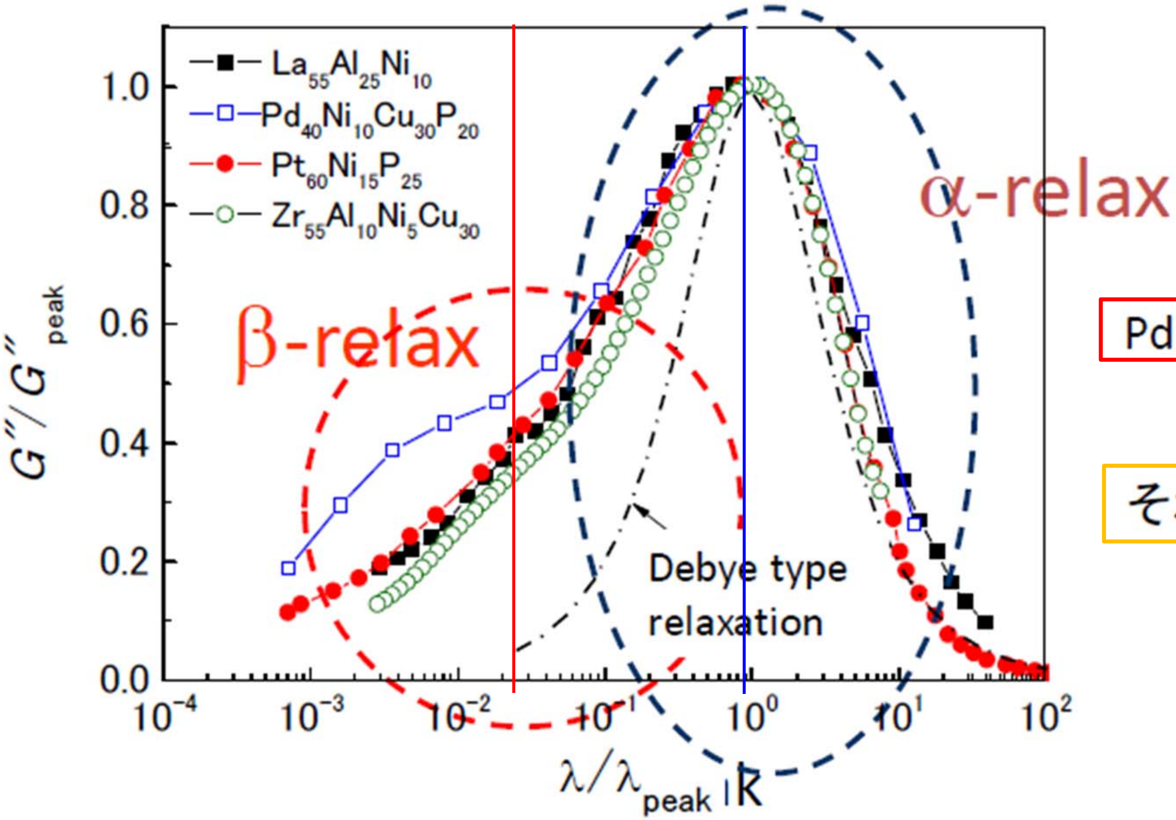


Strong: small deviation of activation E
between α relaxation and β relaxation

Fragile: large deviation of activation E
between α relaxation and β relaxation

Schematic representation of the energy landscapes of strong and fragile substances.

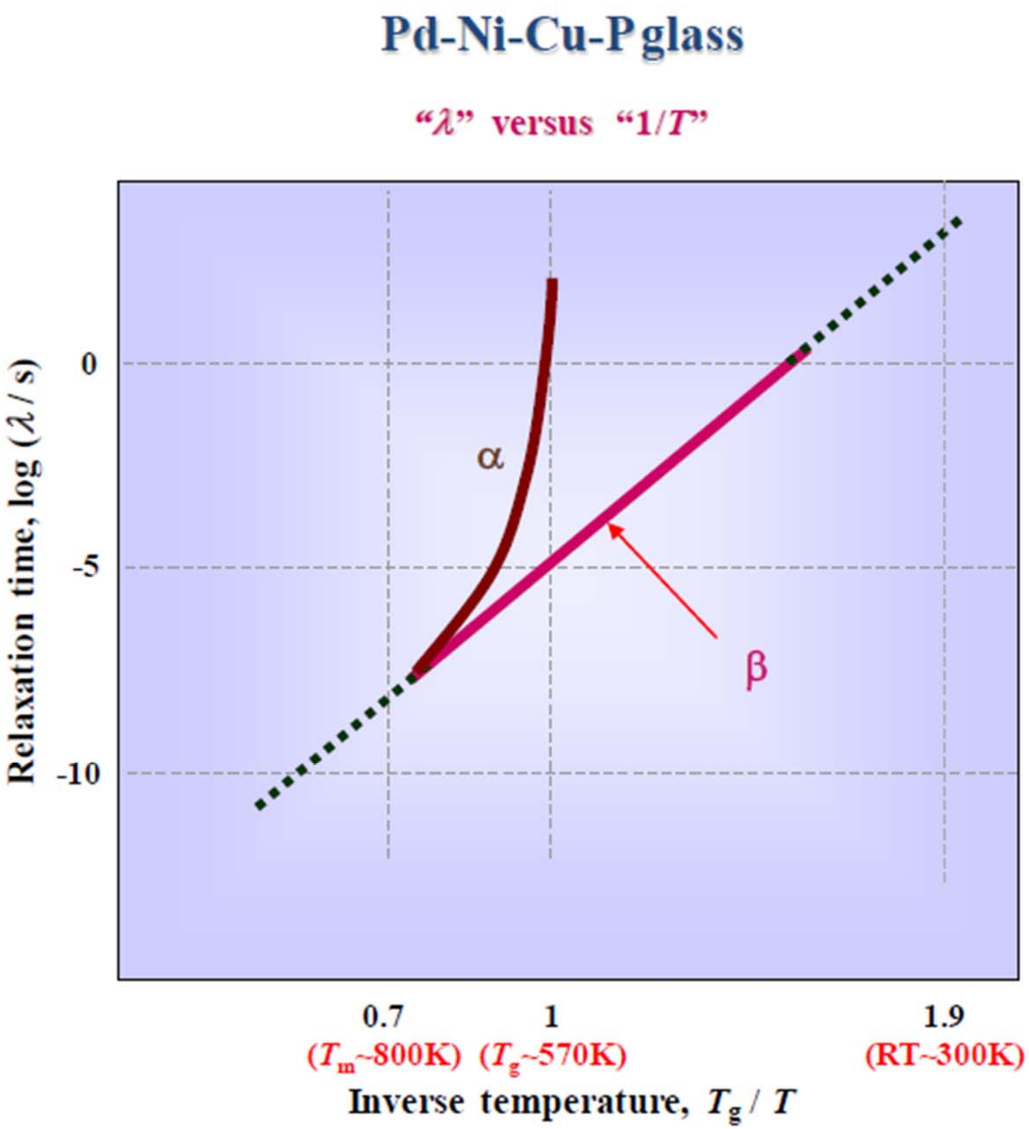
α & β-relaxations observed on the loss modulus in other metallic glasses (La, Pd & Pt based alloys) at ~ their T_g

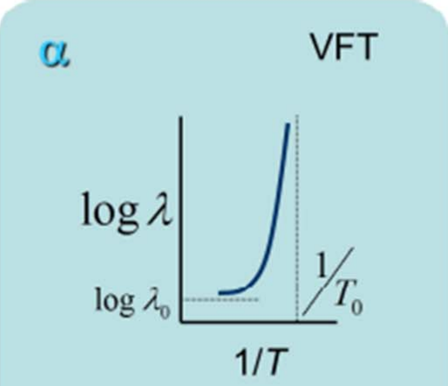


PdNiCuP: α緩和とβ緩和の活性化エネルギー差が大

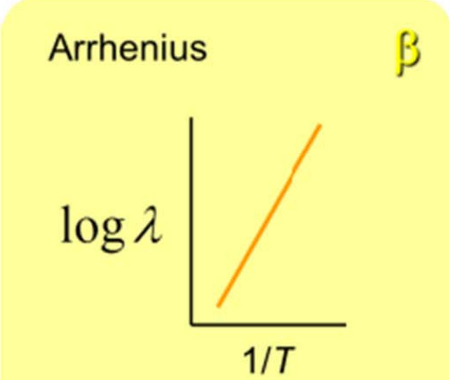
それ以外: α緩和とβ緩和の活性化エネルギー差が小

Temperature dependence of relaxation time
: α relaxation (VFT) & β relaxation (Arrhenius)



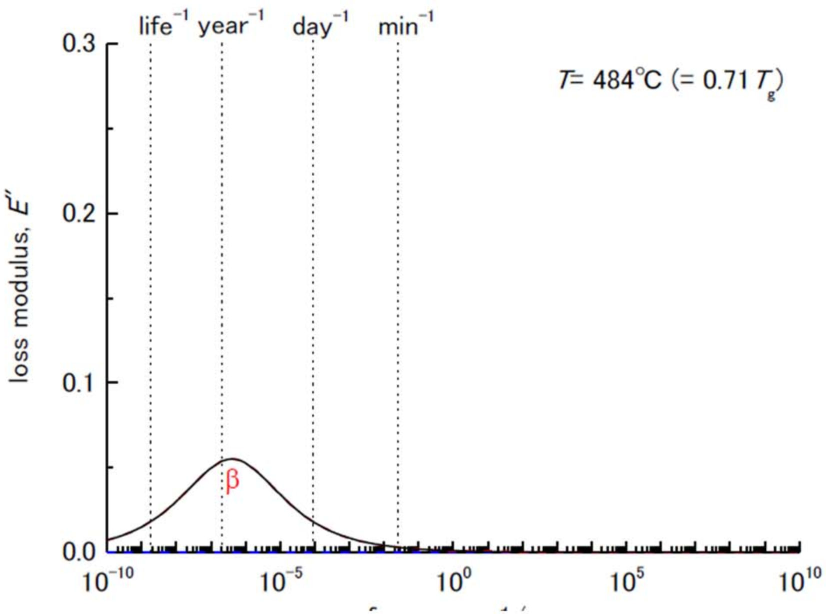


$$\lambda_\alpha = \lambda_{\alpha 0} \exp\left(\frac{Q_\alpha}{T - T_0}\right)$$



$$\lambda_\beta = \lambda_{\beta,0} \exp\left(\frac{Q_\beta}{kT}\right)$$

緩和が観測されるタイムスケールの温度依存性



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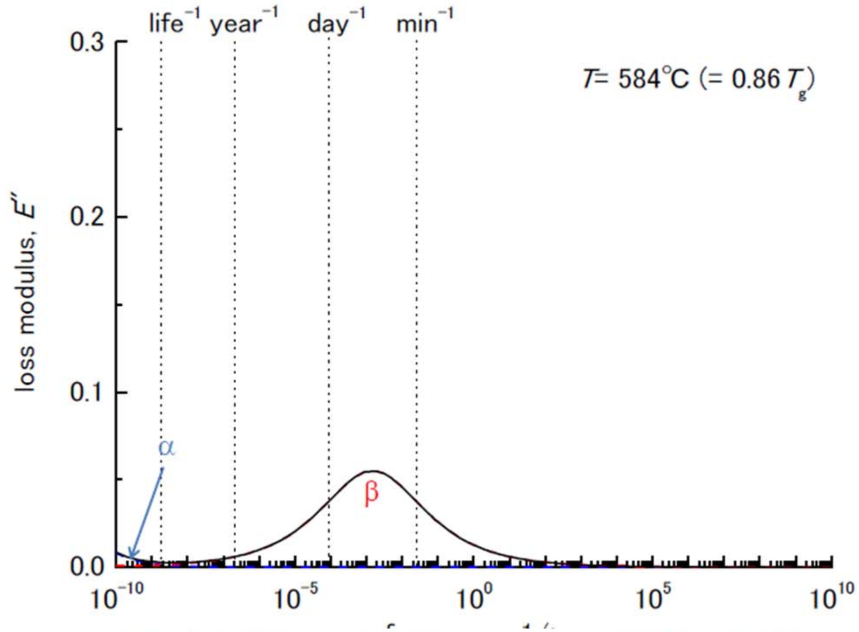

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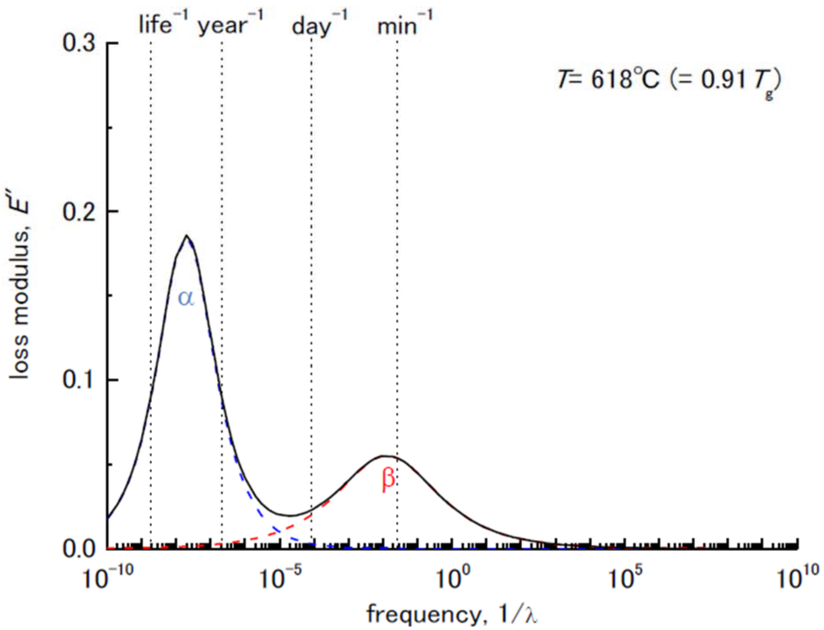

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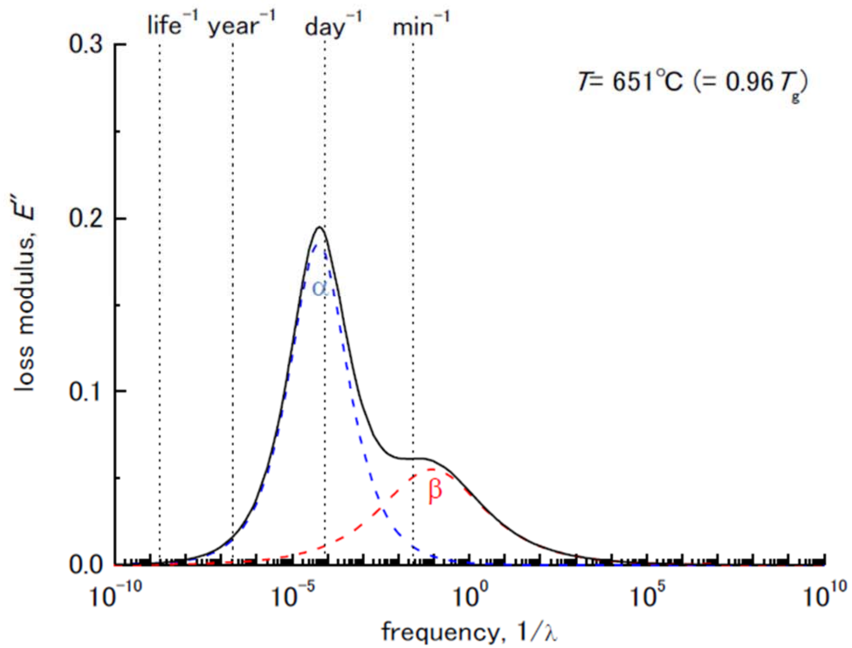

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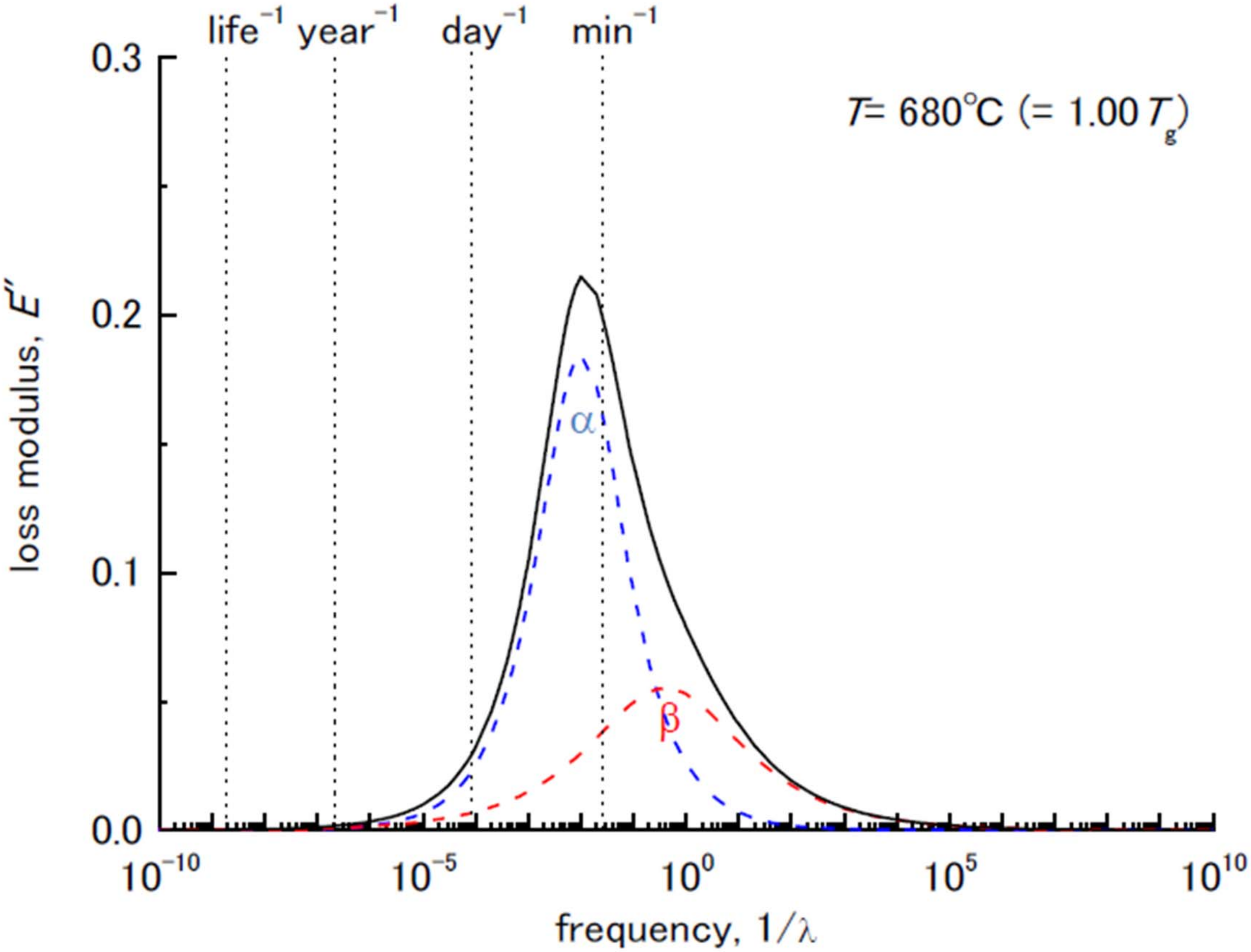


what is the slow-β relaxation, and where it comes from?

Under argument for 40 years

◆ Homogeneous process

<u>Williams & Watts</u>, Trans. Faraday Soc. **67**, 1971 (1971).
Fast, small-angle reorientations of all molecules.
This motion is restricted to smaller amplitudes than the primary process.

◆ Inhomogeneous process "Islands of mobility"

<u>Johari & Goldstein</u>, J. Phys. Chem. **53**, 2372 (1970).
In regions of lower density "islands of mobility" molecules can partially reorient, giving rise to the process.

➢ **Johari-Goldstein relaxation**

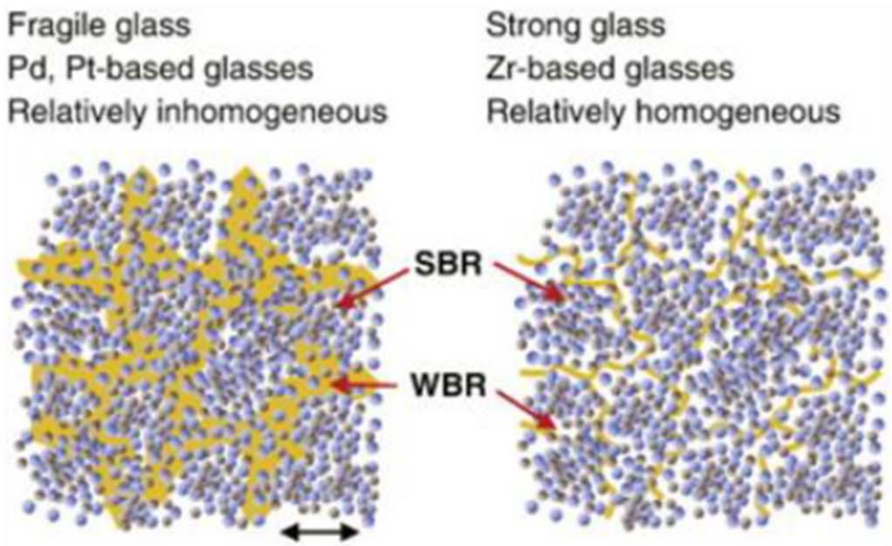
Which is true for metallic glass?

structural inhomogeneity correlating to slow-β

- Weakly & strongly bonded regions

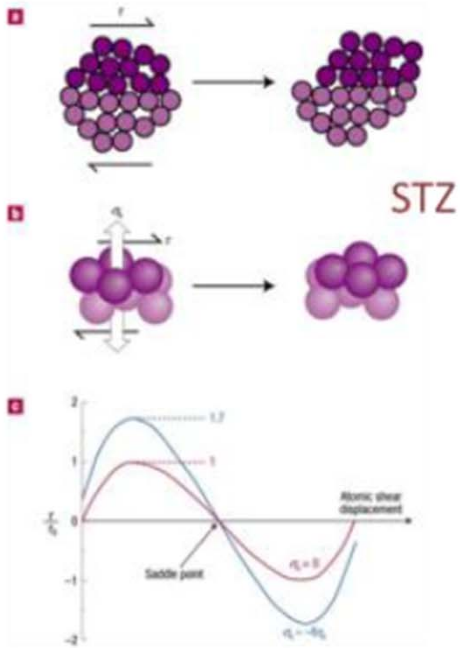
  Ichitsubo et al, PRL95, 245501 (2005)
  & JNCS357, 494 (2011)

  The size ξ of SBR
  ~ 4 nm in Pd-Ni-Cu-P
  ~1.5 nm in Zr-Al-Ni-Cu

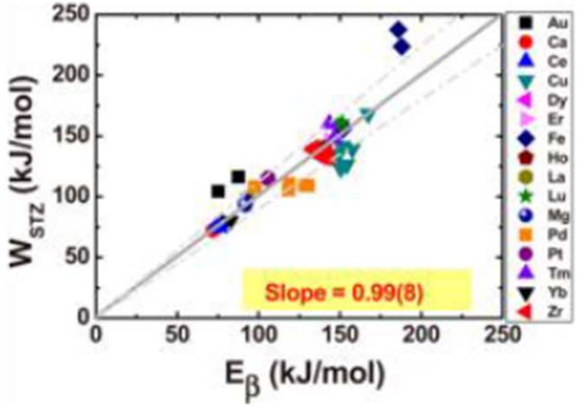


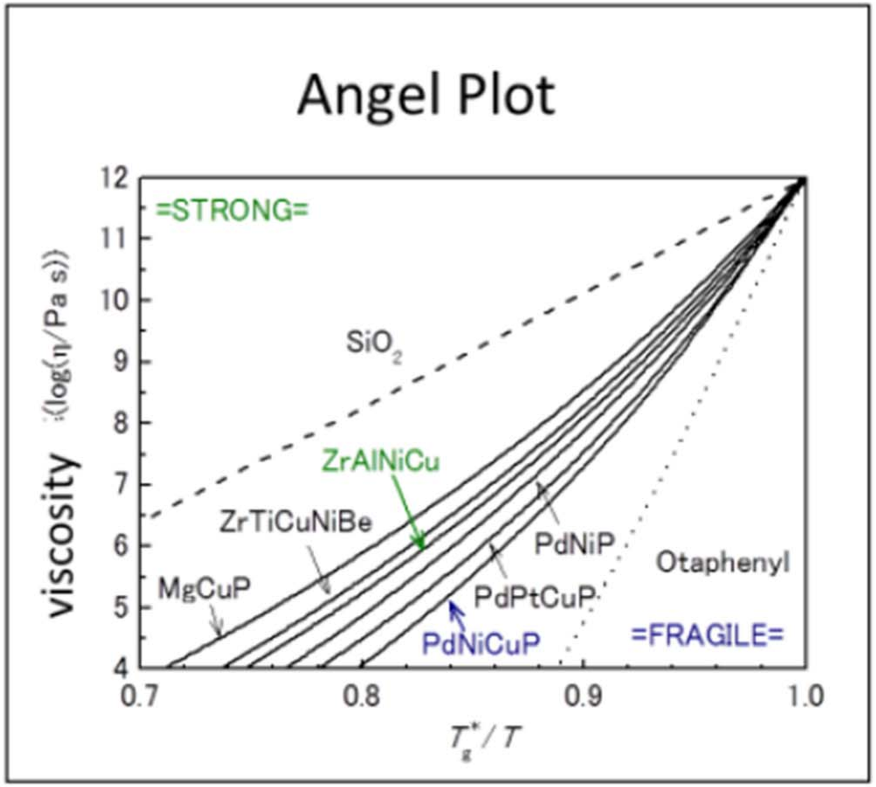
WBR, JG-relaxation & STZ

Wang et al, PRB75, 174201 (2007)
Local motion in the loser region below Tg
Q_β~ 28.4RTg (alloy dependence)

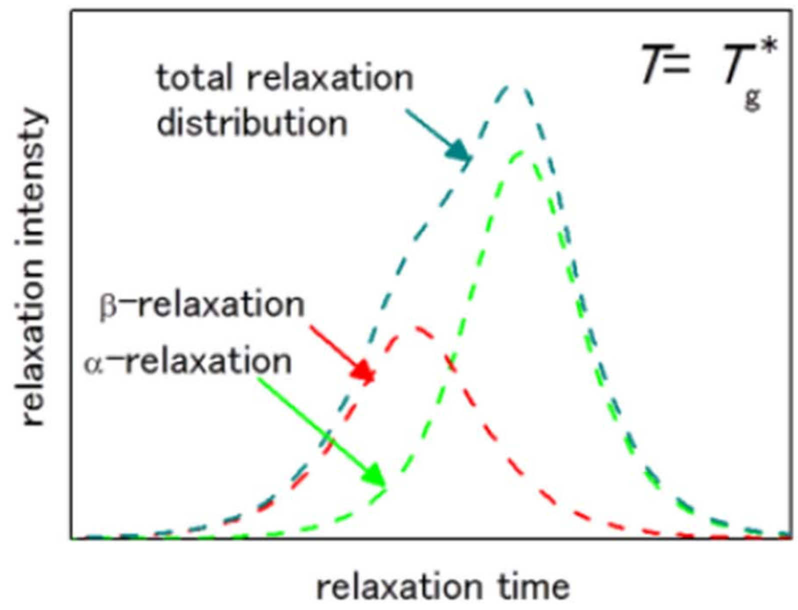


Wang et al, PRB81, 220201(R) (2010)
Slow β site ~ Shear Transformation Zone
by showing direct correlation between W_{STZ}~E_β.





Schematic illustration of relaxation time distribution



viscosity and its temperature dependence is determined by the correlation between α- & β-relaxations.

dominating as the same with plasticity, toughness at RT

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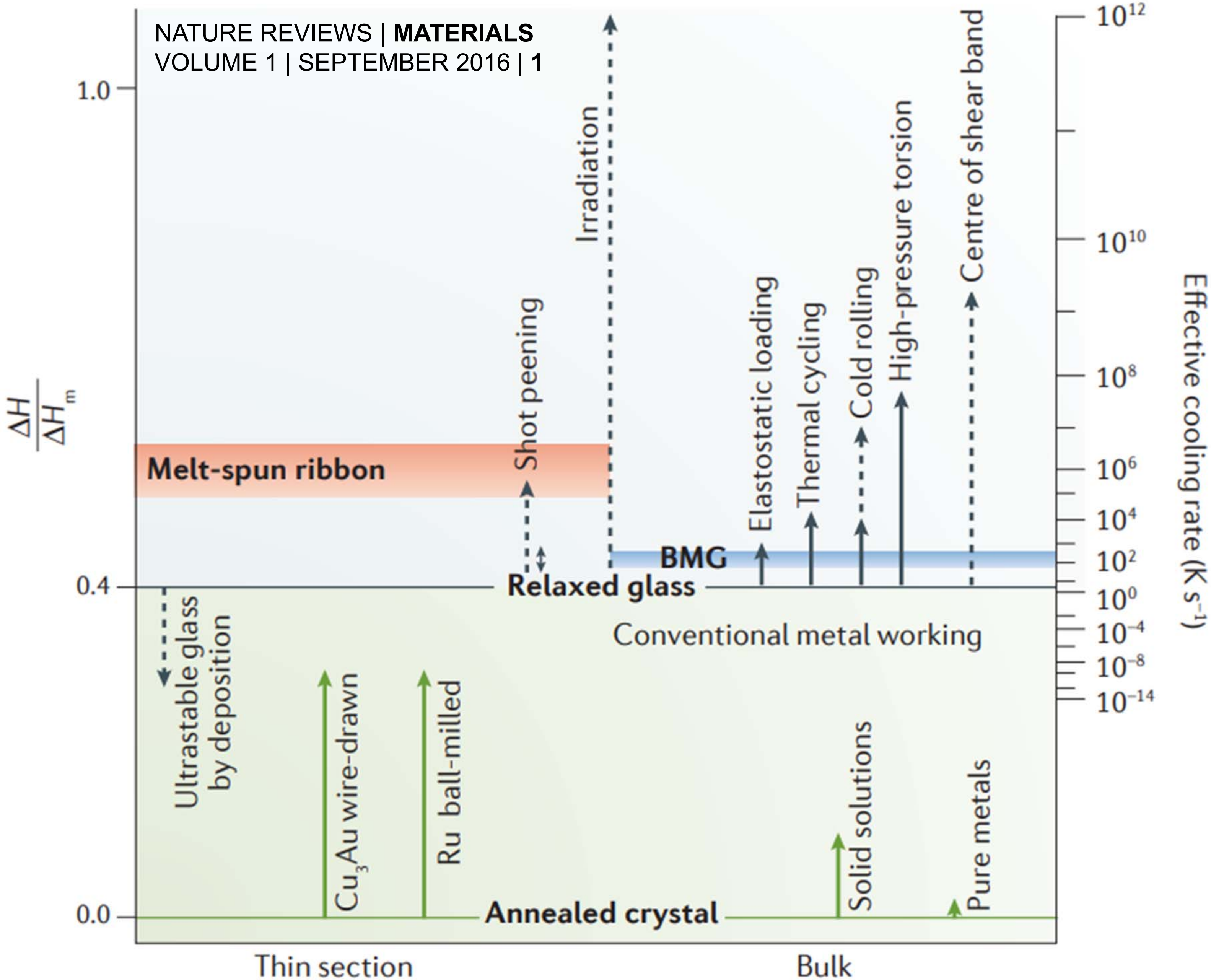

Figure 3 | **Relative enthalpies of deformed metallic states at room temperature.**