2016 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

05.18.2016

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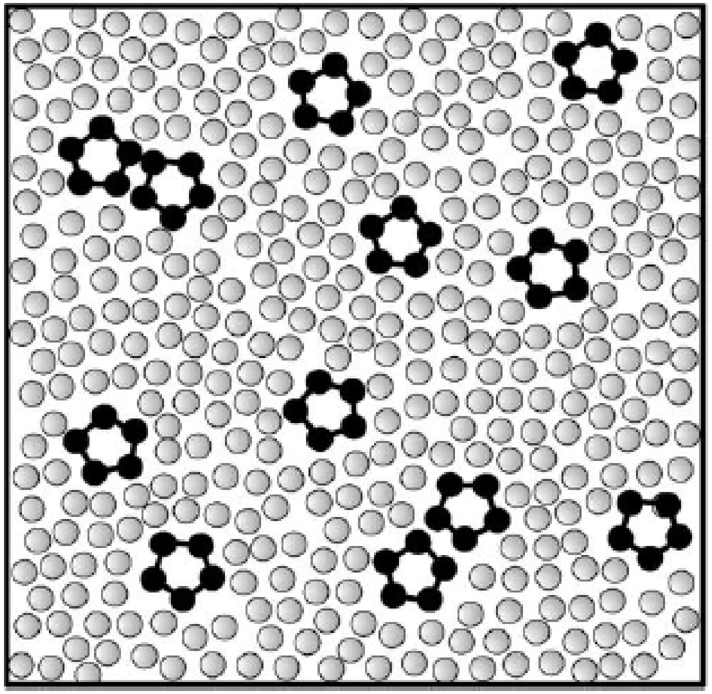
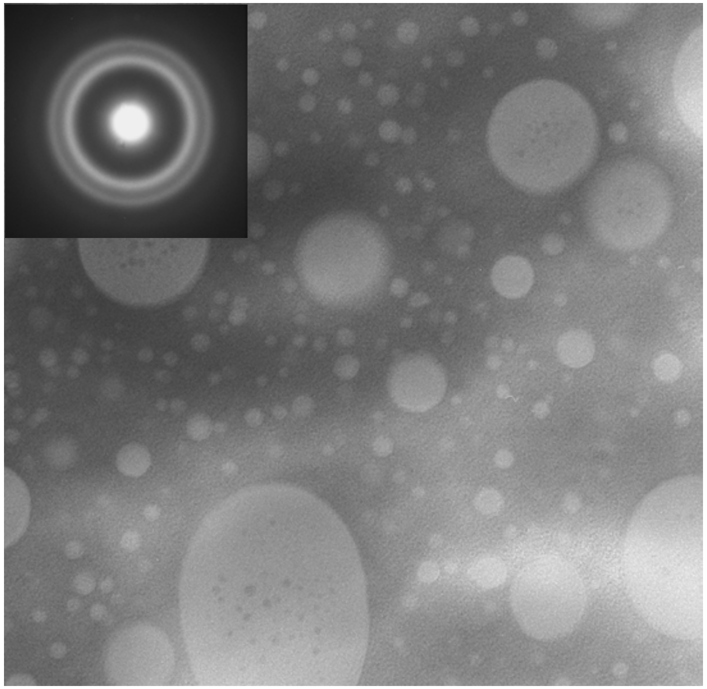
Effect of element with positive enthalpy of mixing among constituent elements

atomic scale heterogeneity



Enhancement of plasticity in BMGs

Phase separating metallic glasses



Unique properties

Homework8:

Summary (page 265 – page 360)

Chapter 6_Physical Properties & Chapter 7_Corrosion Behavior

density, thermal expansion,

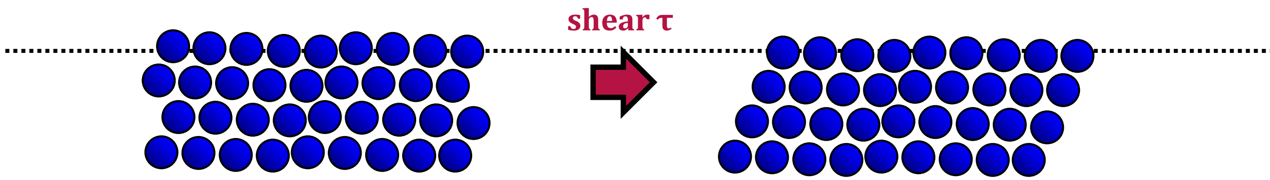
diffusion, electrical resistivity

specific heat, viscosity

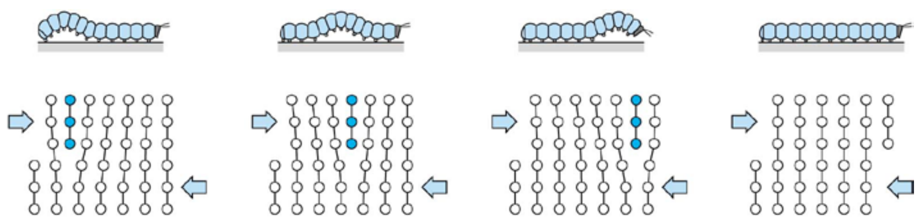
You should submit your summary until 13 June. ☺

Deformation behavior: crystalline VS. amorphous

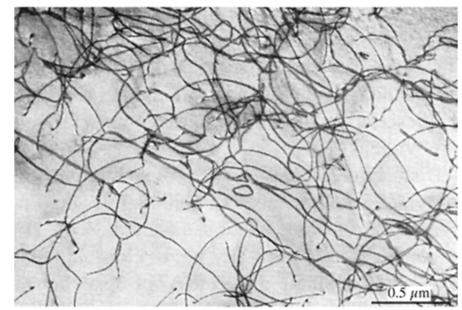
Crystalline



ordered structure | **constant volume**



Dislocation motion in crystalline metal



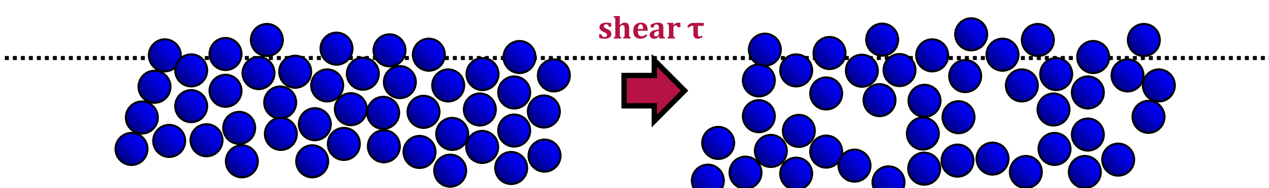
Dislocations

- **"Incrementally breaking bonds"**
- **Has relatively low strength, performs work hardening**
- **Slip plane + Slip direction = Slip system**
  (preferred crystallographic planes and directions)

Amorphous metal do not have slip system.

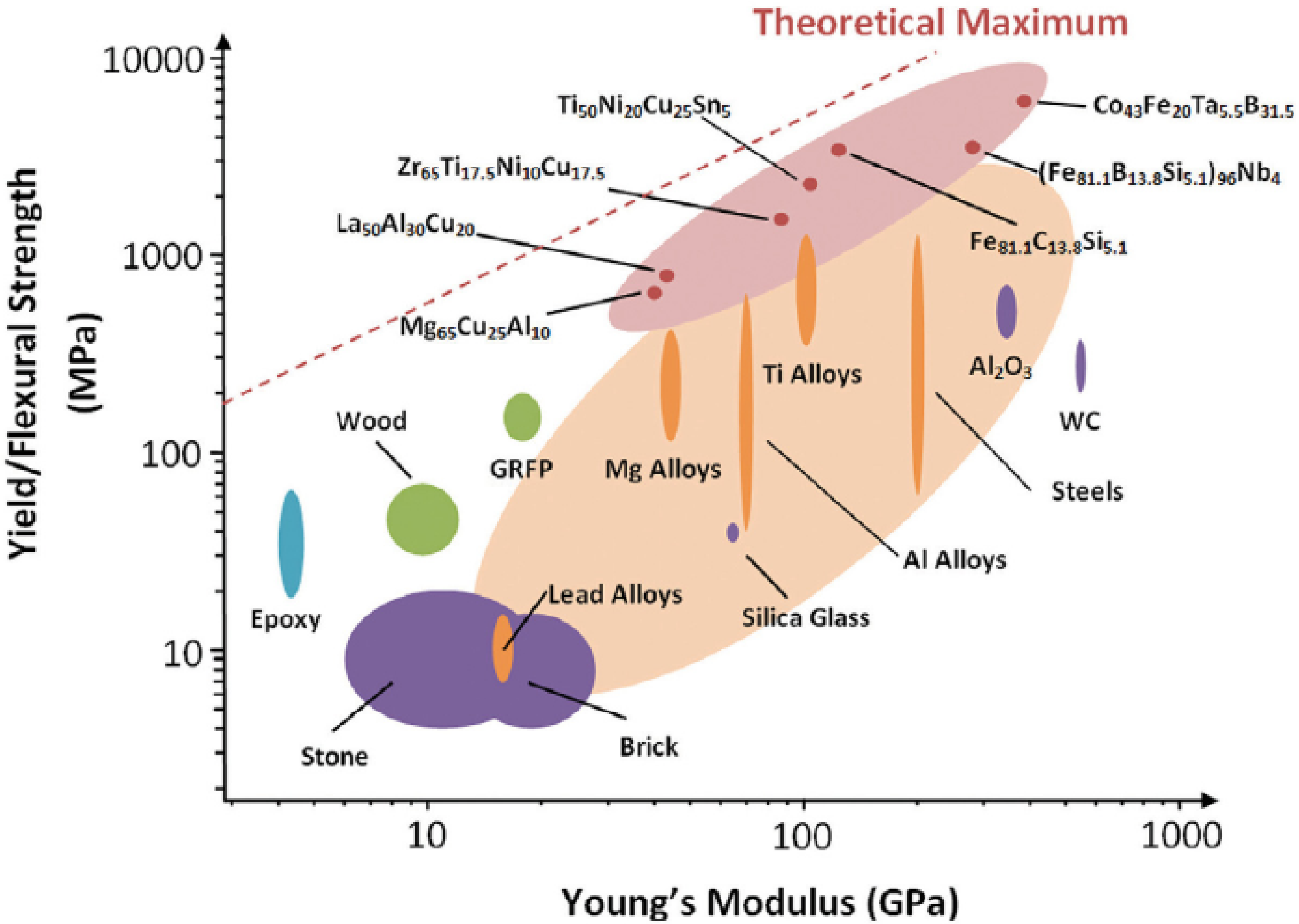
How to deform ?

Amorphous



random structure | **increase free volume (dilatation)**

a) High strength of Bulk Metallic Glasses



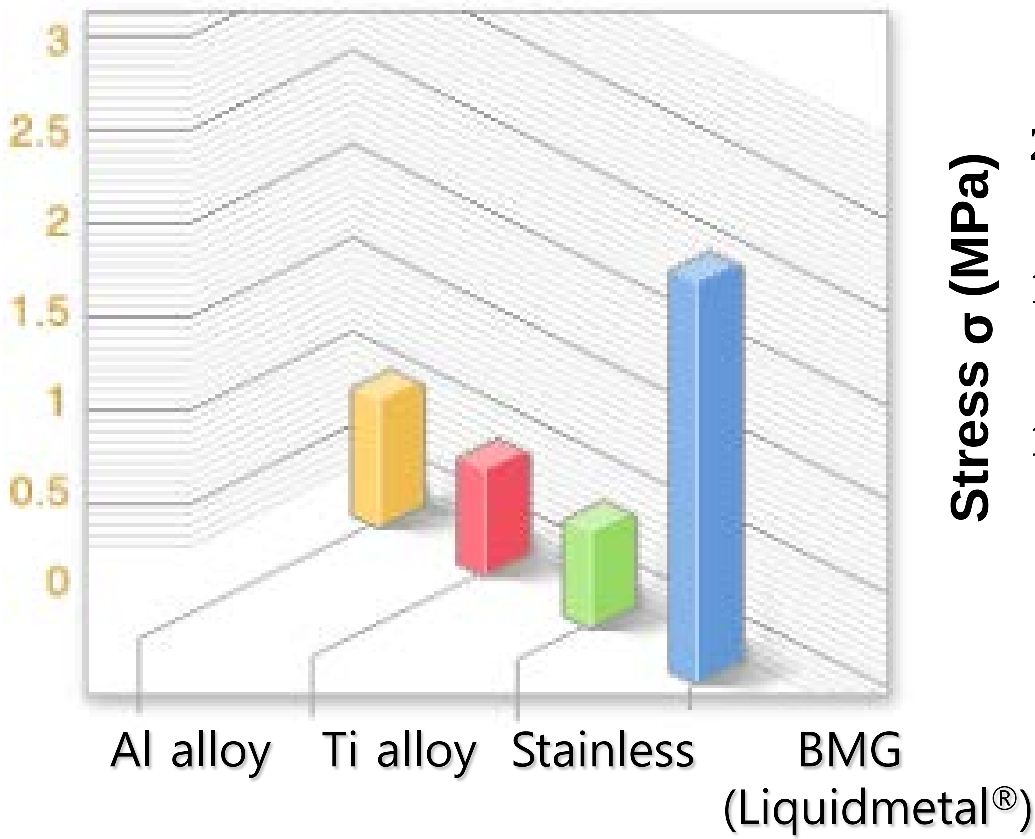
High fracture strength over 5 GPa in Fe-based BMGs

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

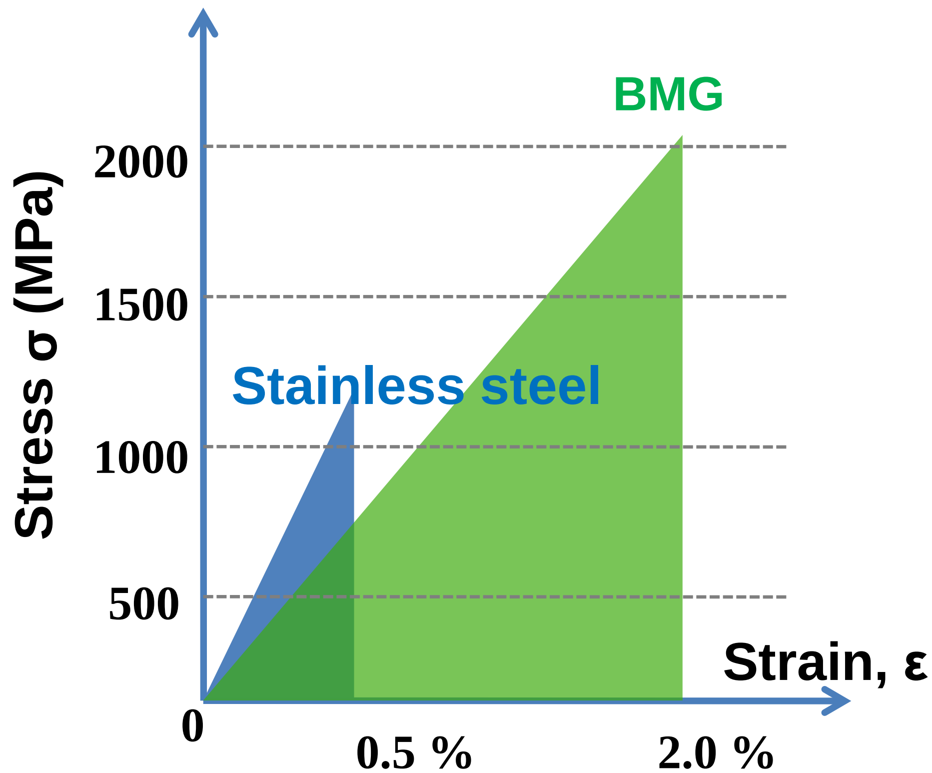
2) Large elastic strain limit of BMGs

Elastic Strain Limit

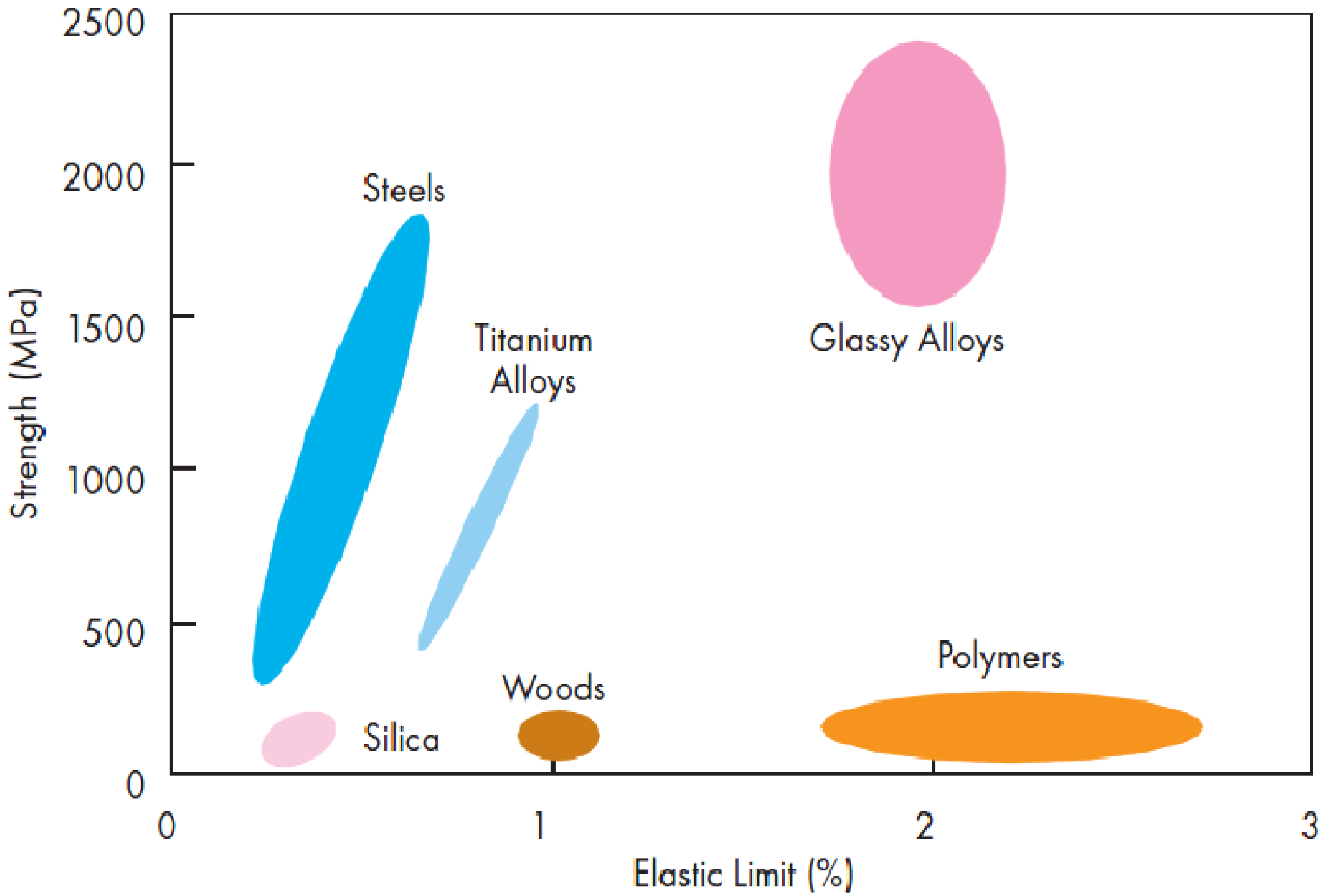
[as % of Original Shape]



Stress-Strain Curve

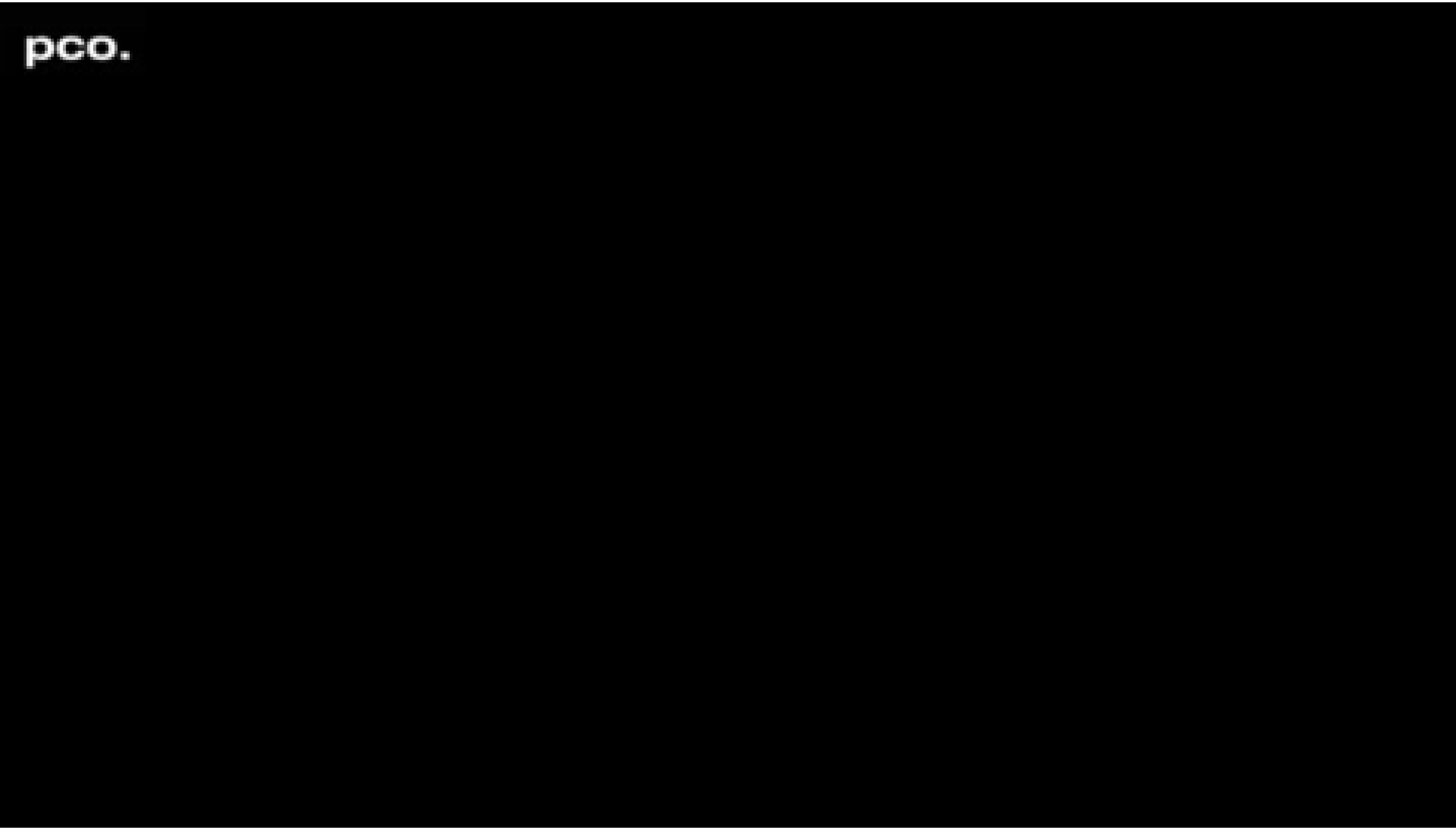


* BMGs with high strength & high elastic limit



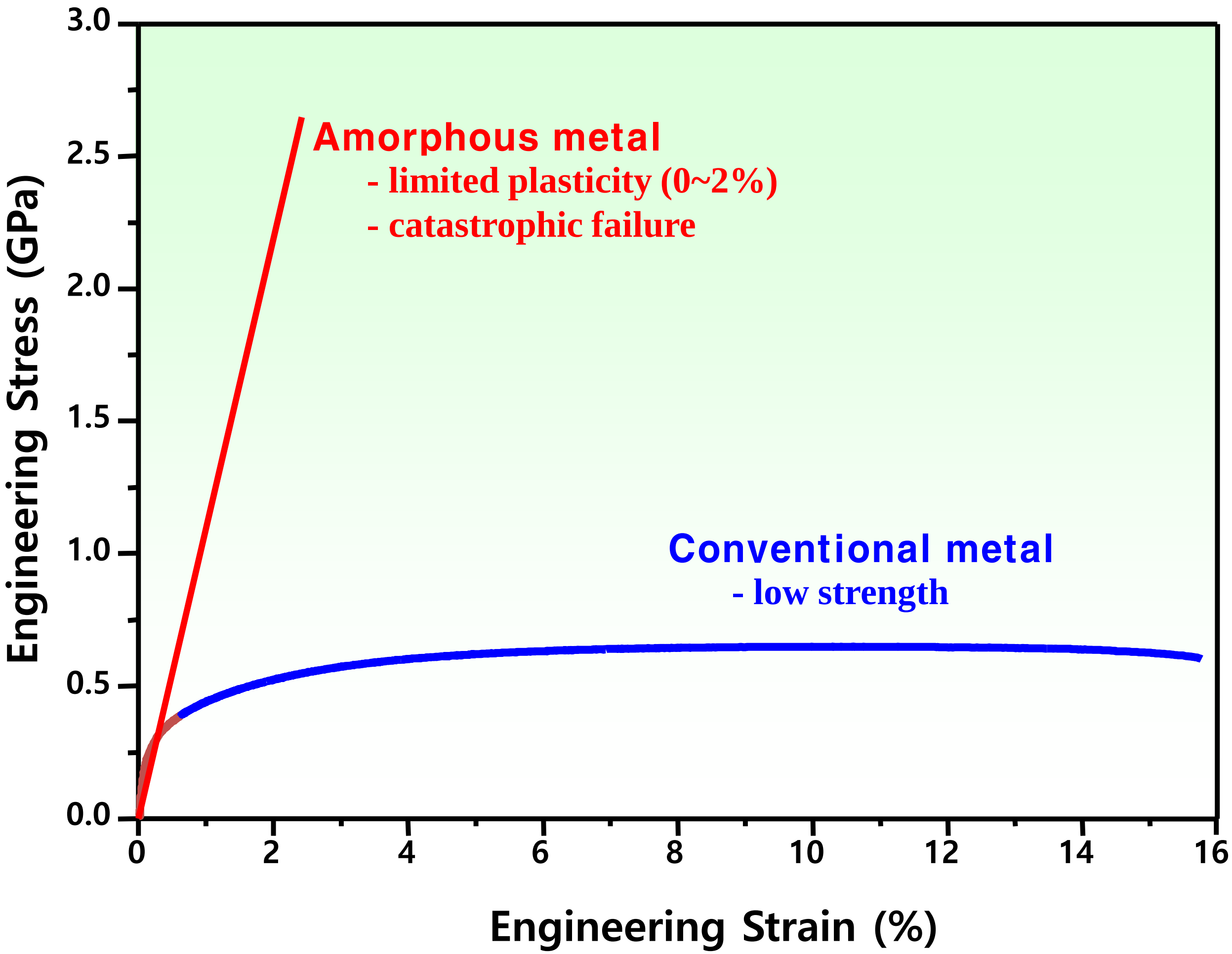
: Metallic Glasses Offer a Unique Combination of High Strength and High Elastic Limit

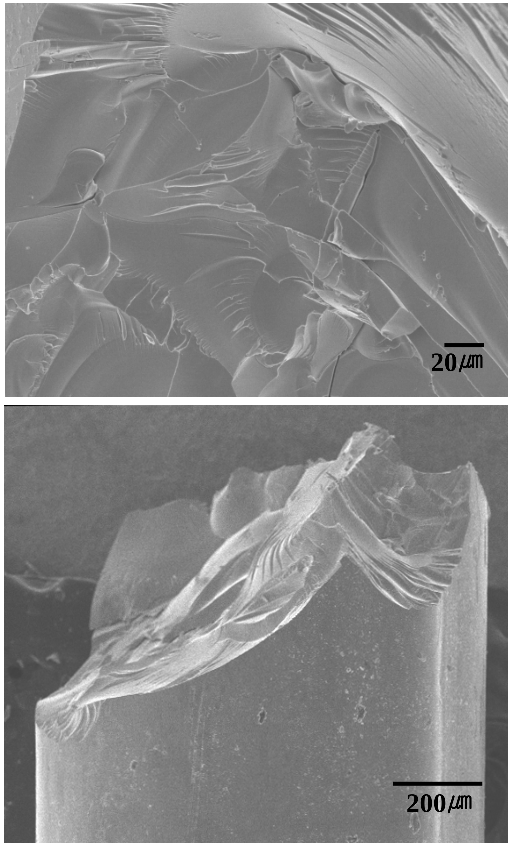
Drawback of BMGs as a Structural Materials



Limited plasticity by shear softening and shear band

- Microscopically brittle fracture
  - ➡ Death of a material for structural applications





8.2 Deformation Behavior

Deformation behavior of Metallic glass

8.2.2 Homogeneous Deformation

- high temp. (>0.7T_g) and in the SCLR/ high strain rate
- Viscous flow → significant plasticity

  : achieve net-shape forming capability
- Newtonian (high temp. & low stress) vs non-Newtonian (high temp. & applied stress) : associated with the precipitation of nanocrystals

⇩

Homogeneous deformation

8.2.1 Inhomogeneous Deformation

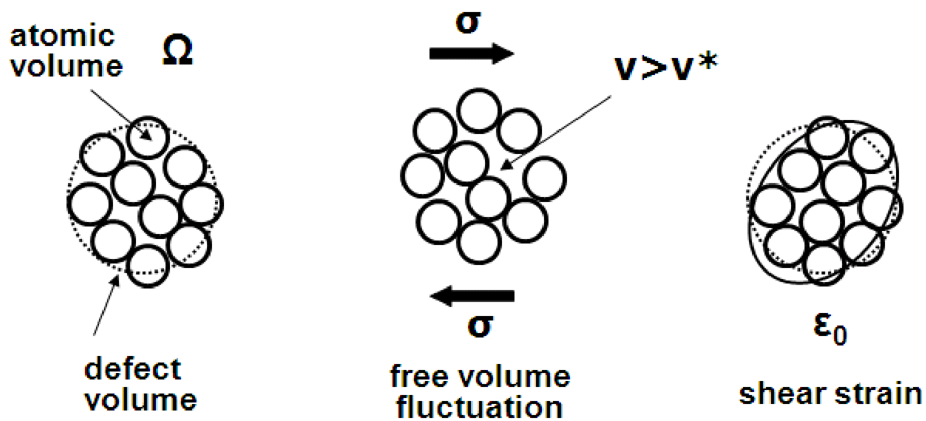
- Low temp. (<0.5T_g)/ high stress
- Localized shear band/ 45° to the loading axis
- Strain softening: deformed at lower stress and higher rate

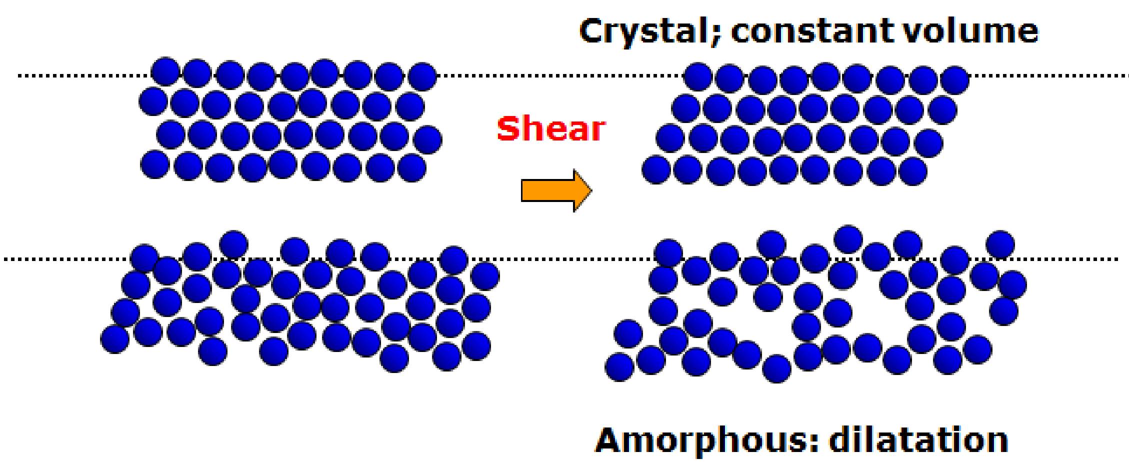
⇩

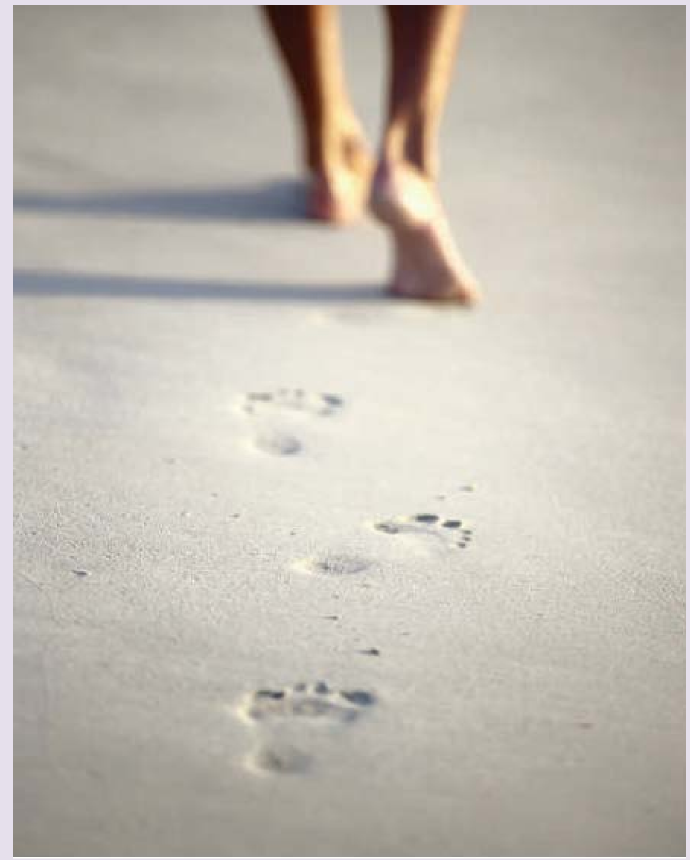
Catastrophically Failure

8.2.1 Inhomogeneous Deformation

Elementary flow events in metallic glasses







Footprints in sand.
Water quickly disappears underneath

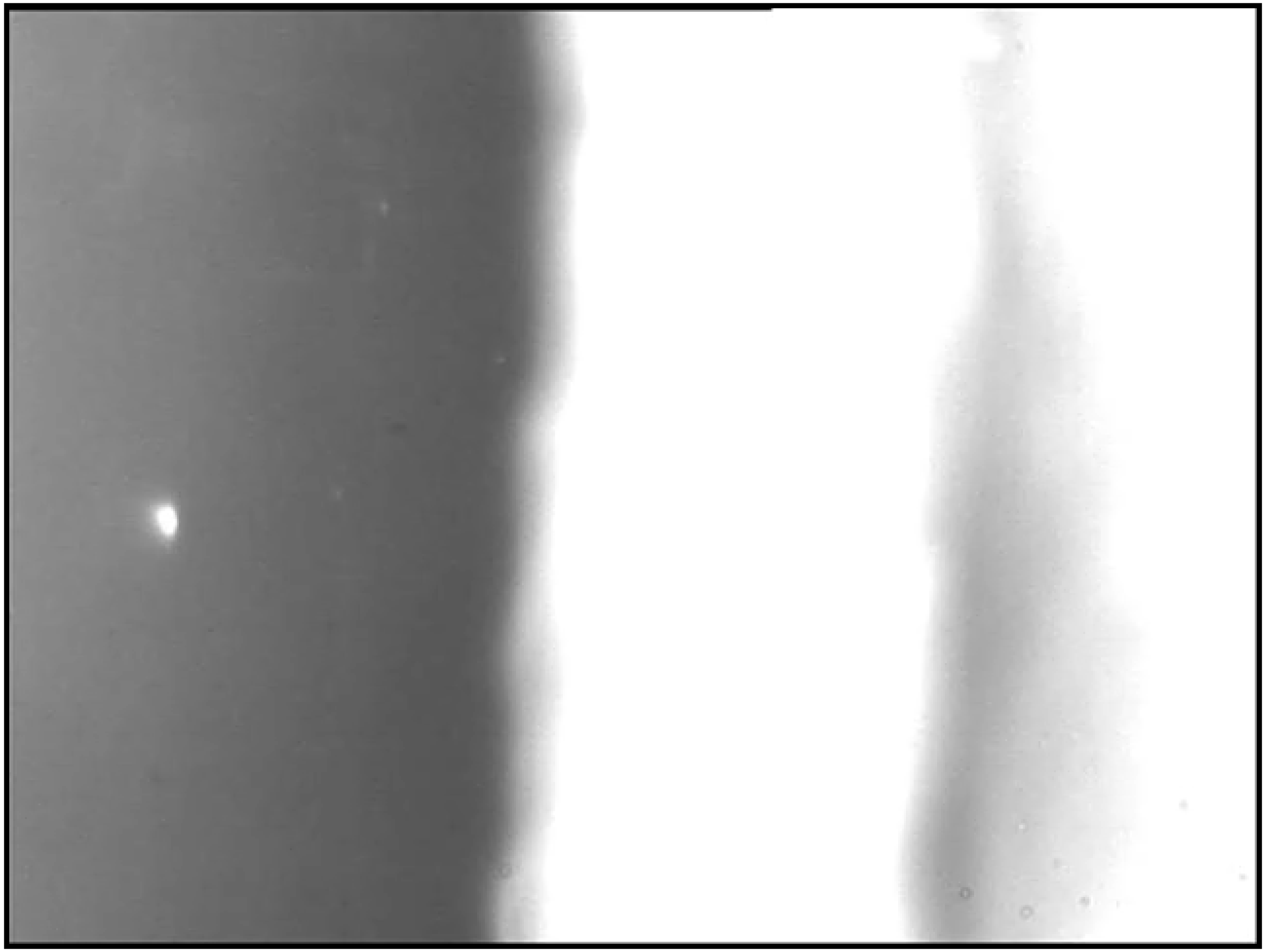
➡ Shear bands form by accumulation of defects during deformation.

nature materials | VOL 5 | JANUARY 2006 | www.nature.com/naturematerials

Effect of local favored structure on SB nucleation

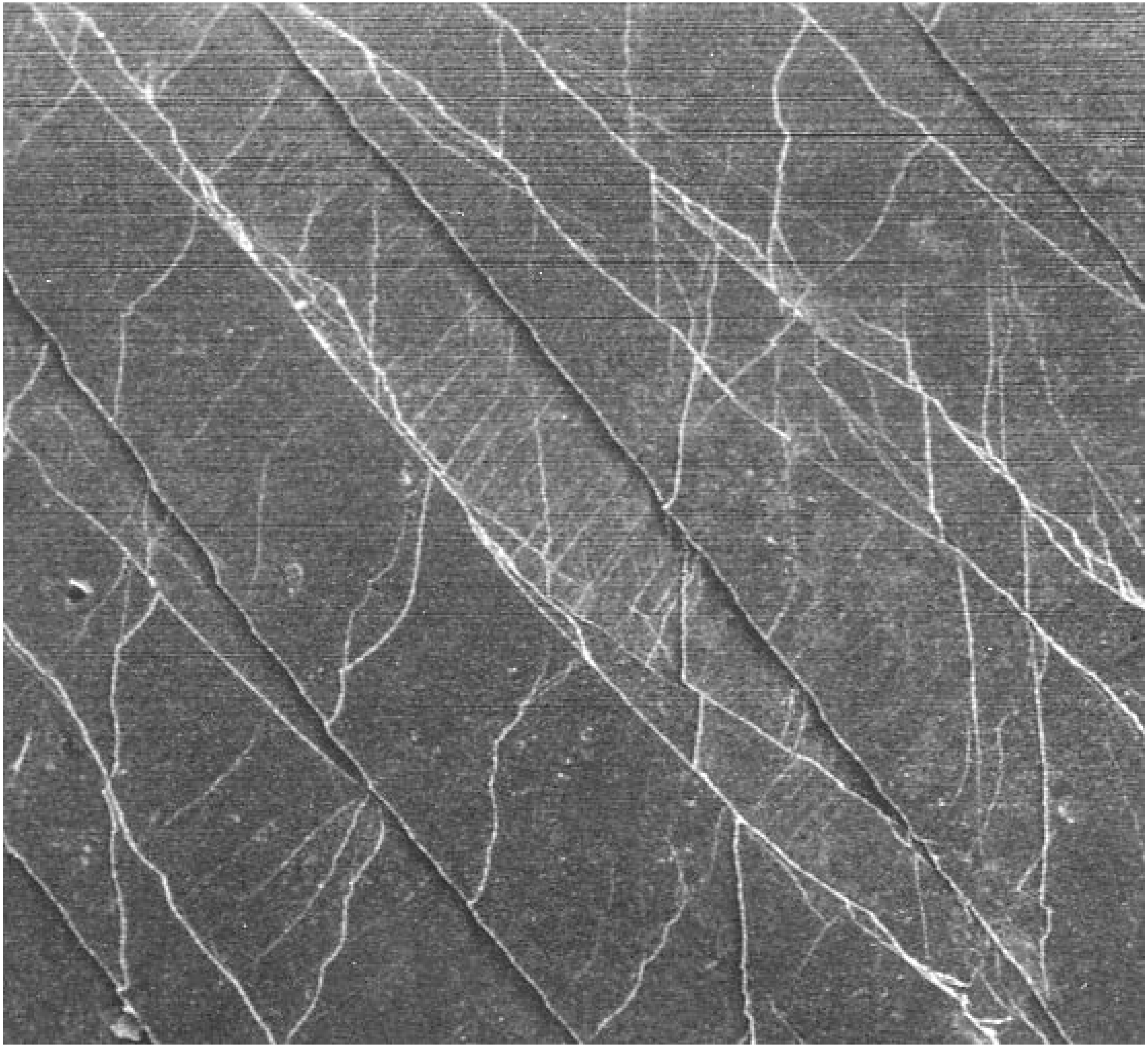
- $Ni_{60}Nb_{40}$: fully amorphous phase

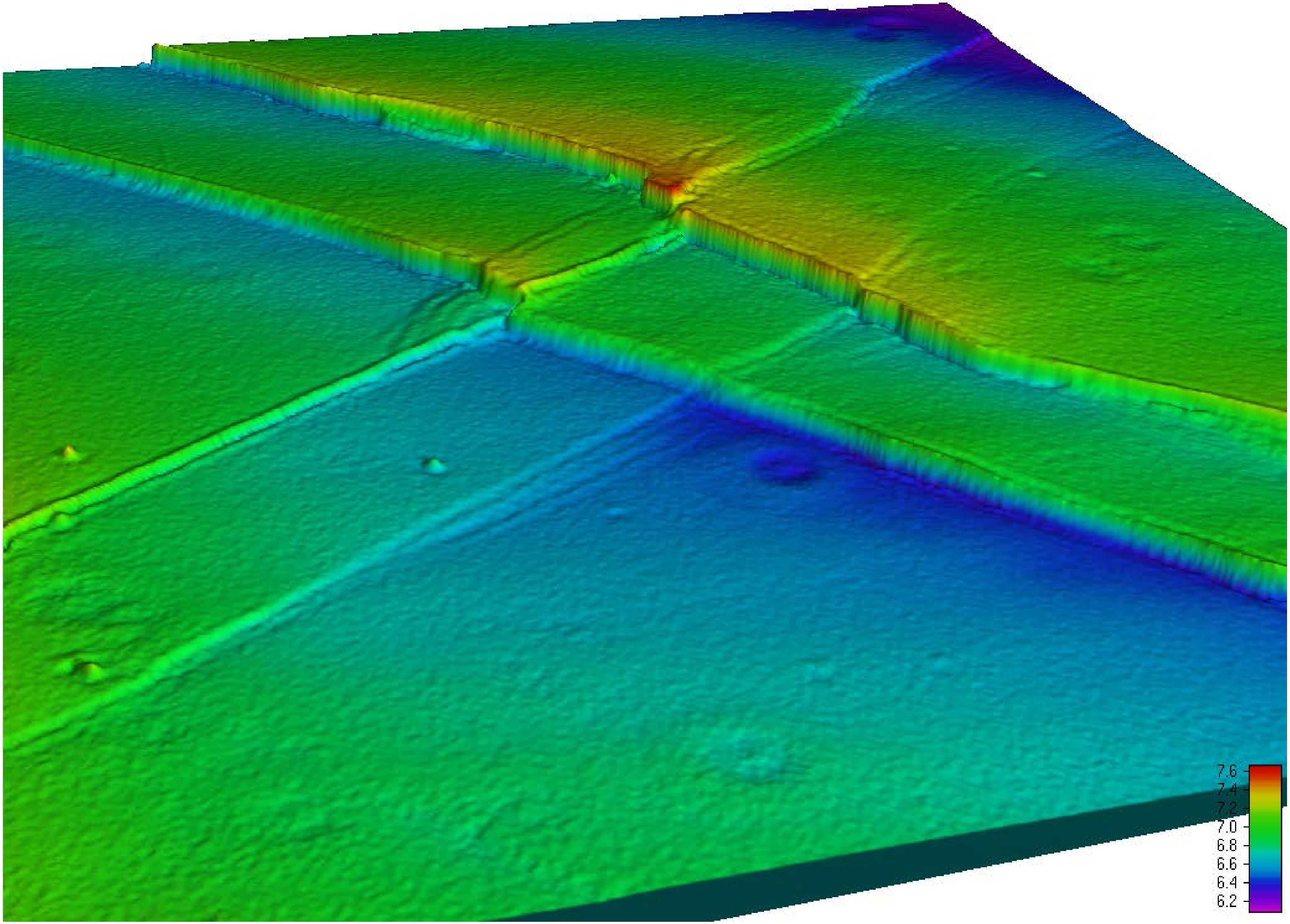
S=0.016 mm/sec



100 μm

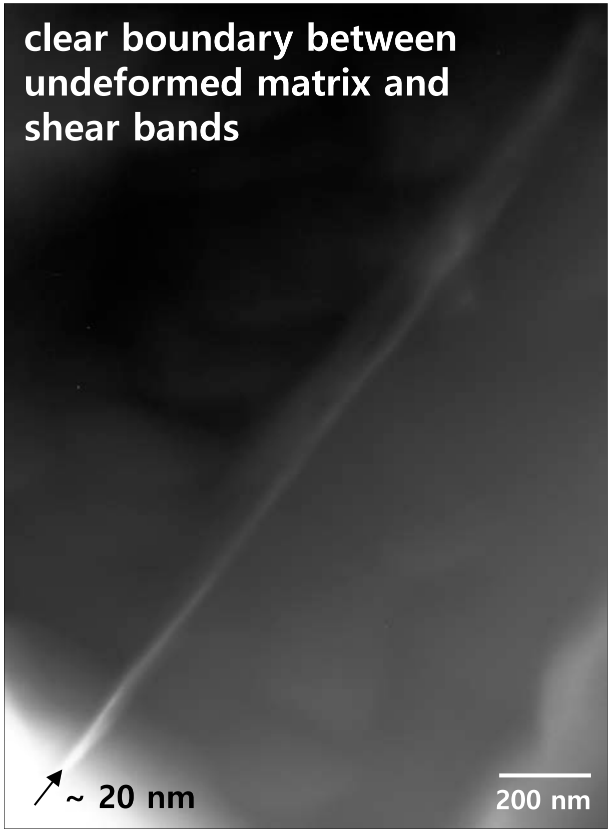
Formation of multiple shear bands during deformation

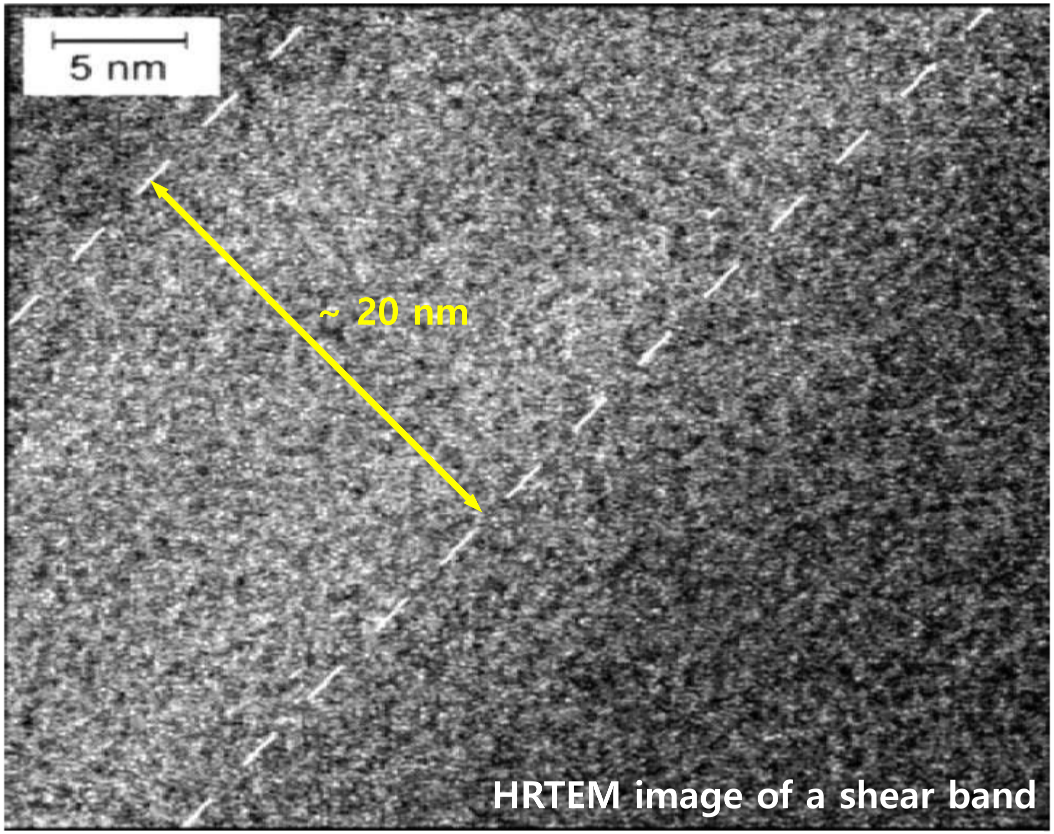



7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2

Formation of shear bands : variation of free volume

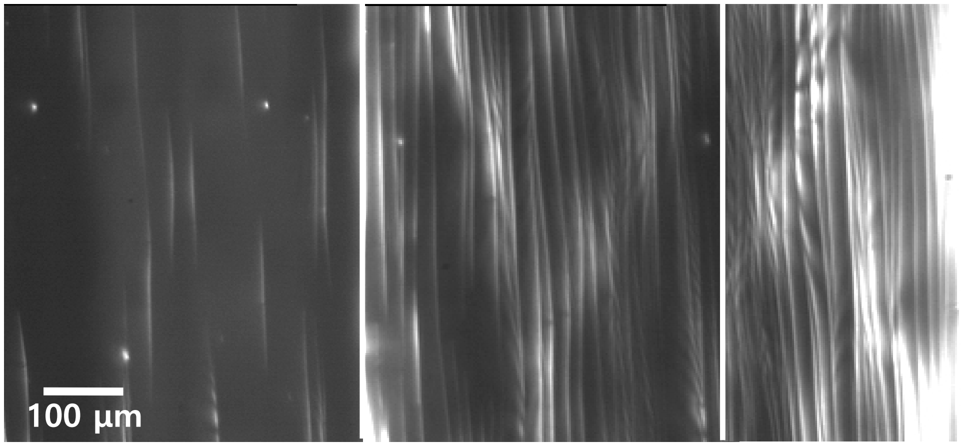
Shear bands form by accumulation of defects during deformation.



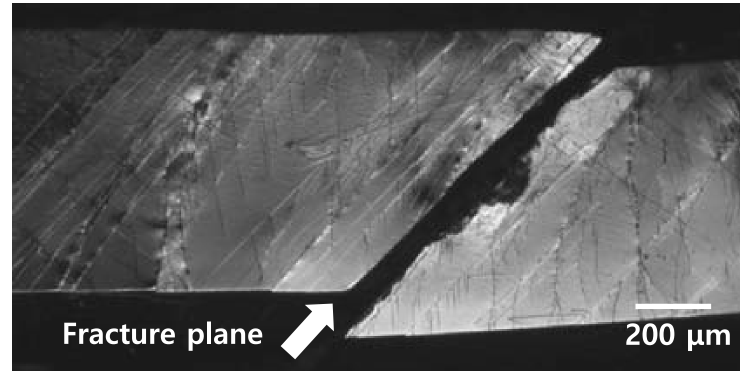


Shear deformed areas with the same composition & different density of free volume

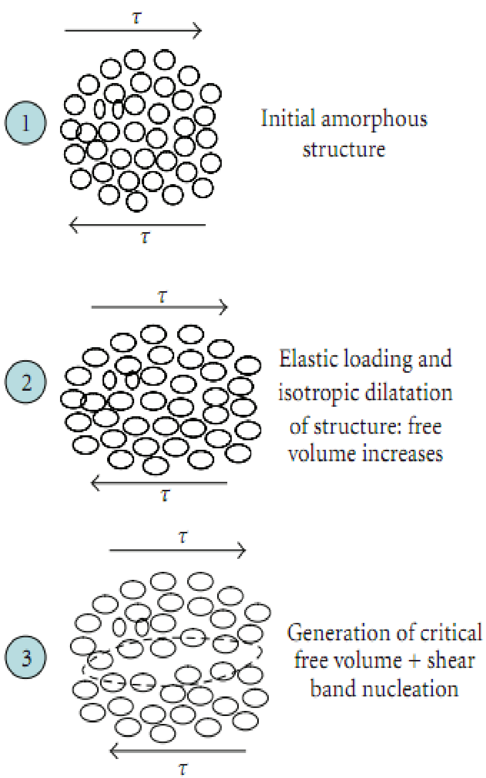
Shear band nucleation and propagation: strain softening



Shear band formation and propagation in the ribbon bending test



Formation of multiple shear bands in an $Ni_{50}Pd_{30}P_{20}$ BMG specimen subjected to compression testing.
K. Wang et al. / *Acta Mater.* ***56*** *(2008)* 2834.



Plastic deformation of metallic glass

controlled by shear band behavior **Nucleation & Propagation**

Excess volume → **Connect to form a shear band**

Plastic strain localized into these shear bands → **Catastrophic failure**

Elastic energy rises local temperature

Decrease in the viscosity → **Shear softening**

Enhancement of ductility ····· **Increase of the shear band density**

SB nucleation and propagation : Multiple serrations, observed only at slow strain rates → temperature rise

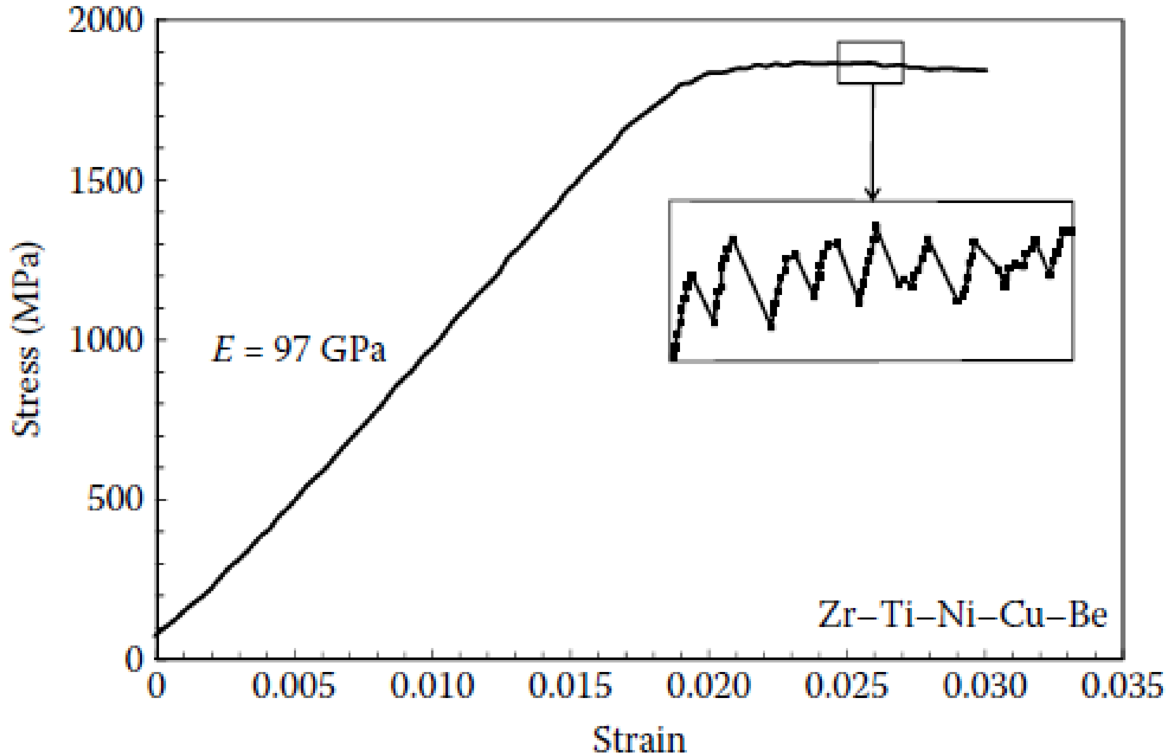


FIGURE 8.1
Compressive stress–strain curve for $Zr_{40}Ti_{14}Ni_{10}Cu_{12}Be_{24}$ BMG alloy tested at a strain rate of $1 \times 10^{-4} s^{-1}$. (Reprinted from Wright, W.J. et al., *Mater. Trans.*, 42, 642, 2001. With permission.)

SB nucleation and propagation : Multiple serrations
→ temperature rise

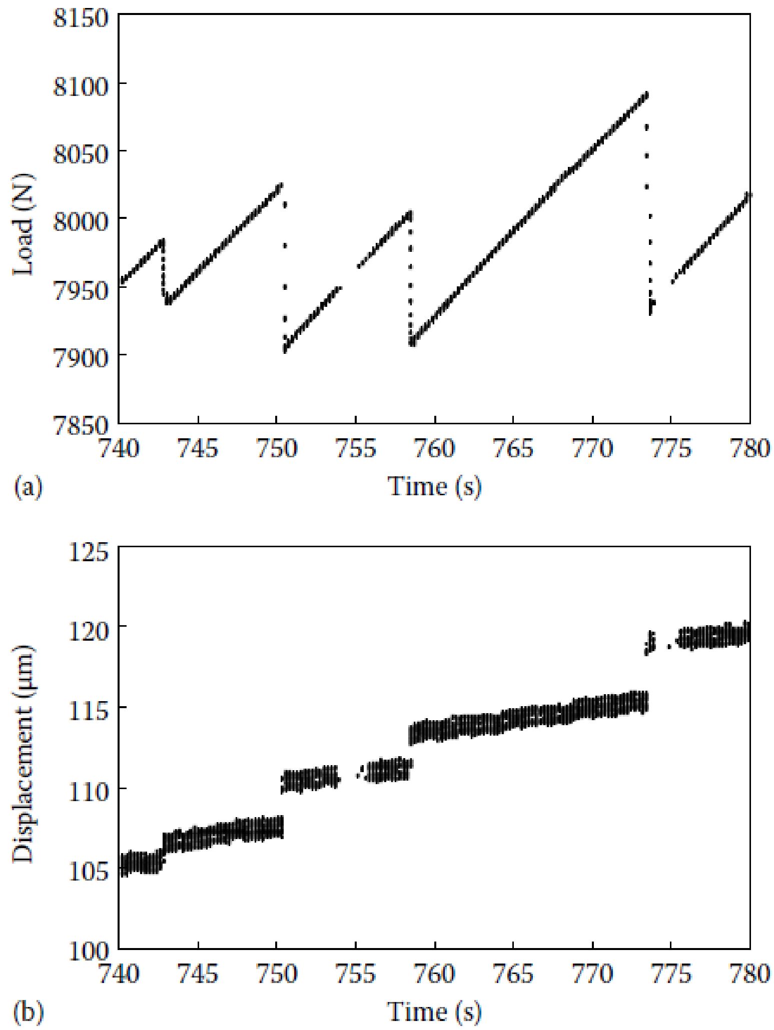


FIGURE 8.2
(a) Load as a function of time and (b) total displacement as a function of time in the serrated flow region of the $Zr_{40}Ti_{14}Ni_{10}Cu_{12}Be_{24}$ BMG alloy tested in uniaxial compression. (Reprinted from Wright, W.J. et al., *Mater. Trans.*, 42, 642, 2001. With permission.)

Serrated flow is also observed during nano-indentation,

but only at "slow loading rates". Activation of each individual shear band is associated with the occurrence of a discrete "pop-in" event (sudden rise in load).

High loading rate → multiple shear bands → smooth load-displacement curve

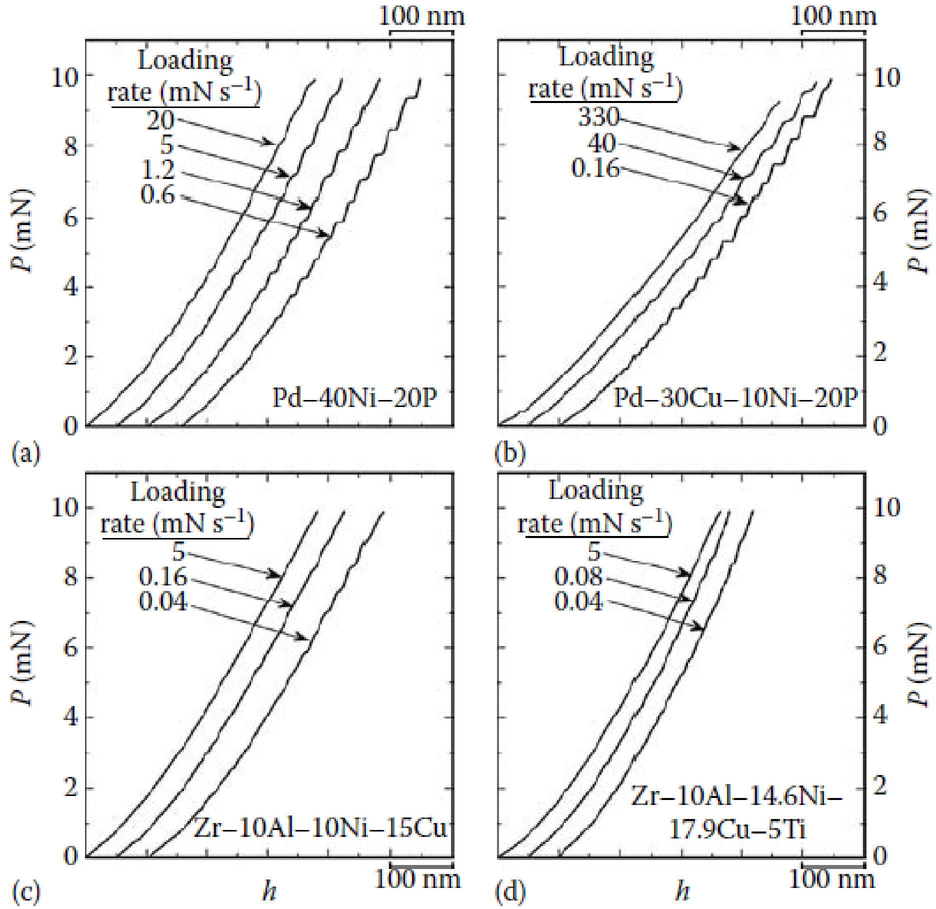


FIGURE 8.3

Typical load–displacement (P–h) curves measured on the loading portion of nanoindentation experiments, for four different BMGs investigated. (a) $Pd_{40}Ni_{40}P_{20}$, (b) $Pd_{40}Cu_{30}Ni_{10}P_{20}$, (c) $Zr_{65}Al_{10}Ni_{10}Cu_{15}$, and (d) $Zr_{52.5}Al_{10}Ni_{14.6}Cu_{17.9}Ti_5$. Curves are offset from the origin for clear viewing, and the rate of indentation loading is specified in each graph. (Reprinted from Schuh, C.A. and Nieh, T.G., *Acta Mater.*, 51, 87, 2003. With permission.)

8.4 Temperature rise at shear bands

Most of the plastic strain is localized in narrow shear bands, which form approximately on the planes of maximum resolved shear stress. The inhomogeneous flow in metallic glasses appears to be related to a local decrease in the viscosity in shear bands. One of the reasons suggested for this was the local adiabatic heating that could lead to a substantial increase in the temperature.

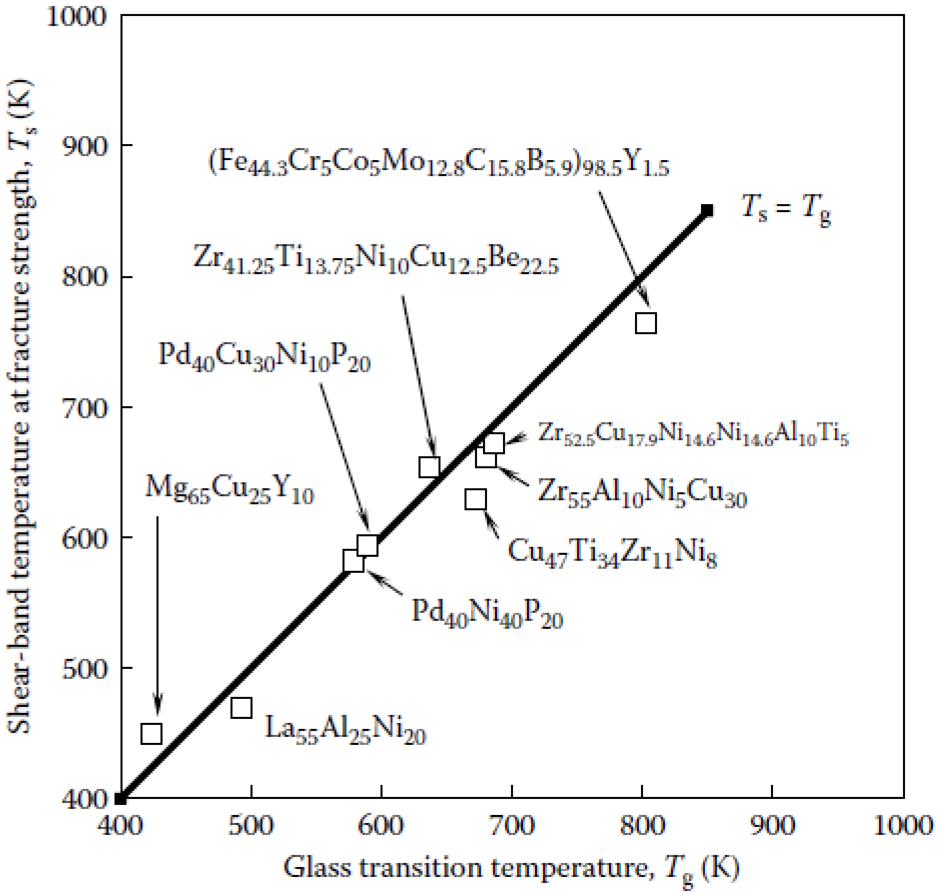


FIGURE 8.8
Temperature rise, ΔT in the shear bands at the time of fracture for different BMG alloys plotted against the glass transition temperature, T_g. (Reprinted from Yang, B. et al., *J. Mater. Res.*, 21, 915, 2006. With permission.)

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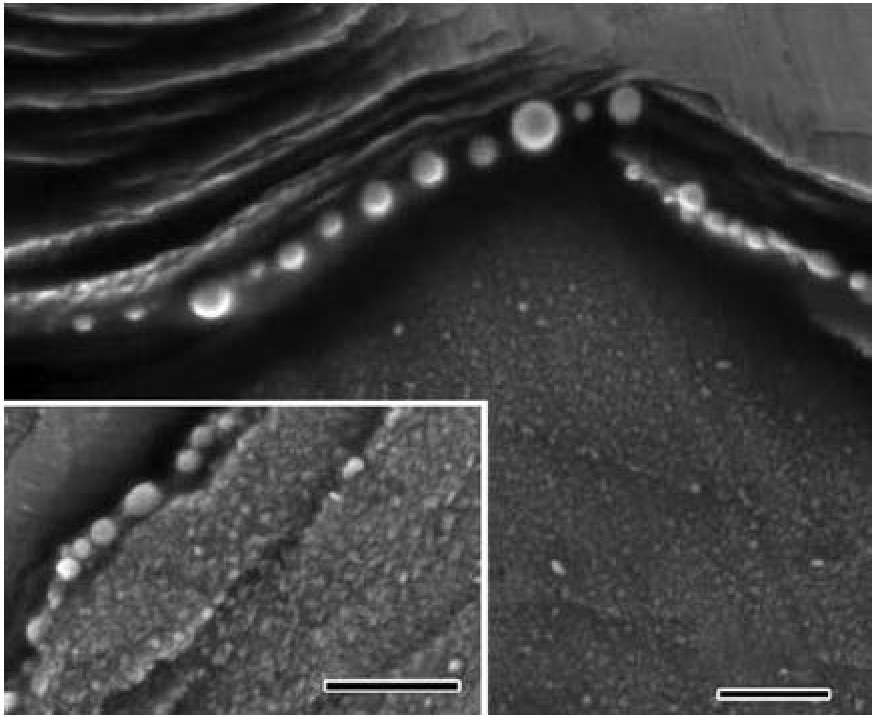
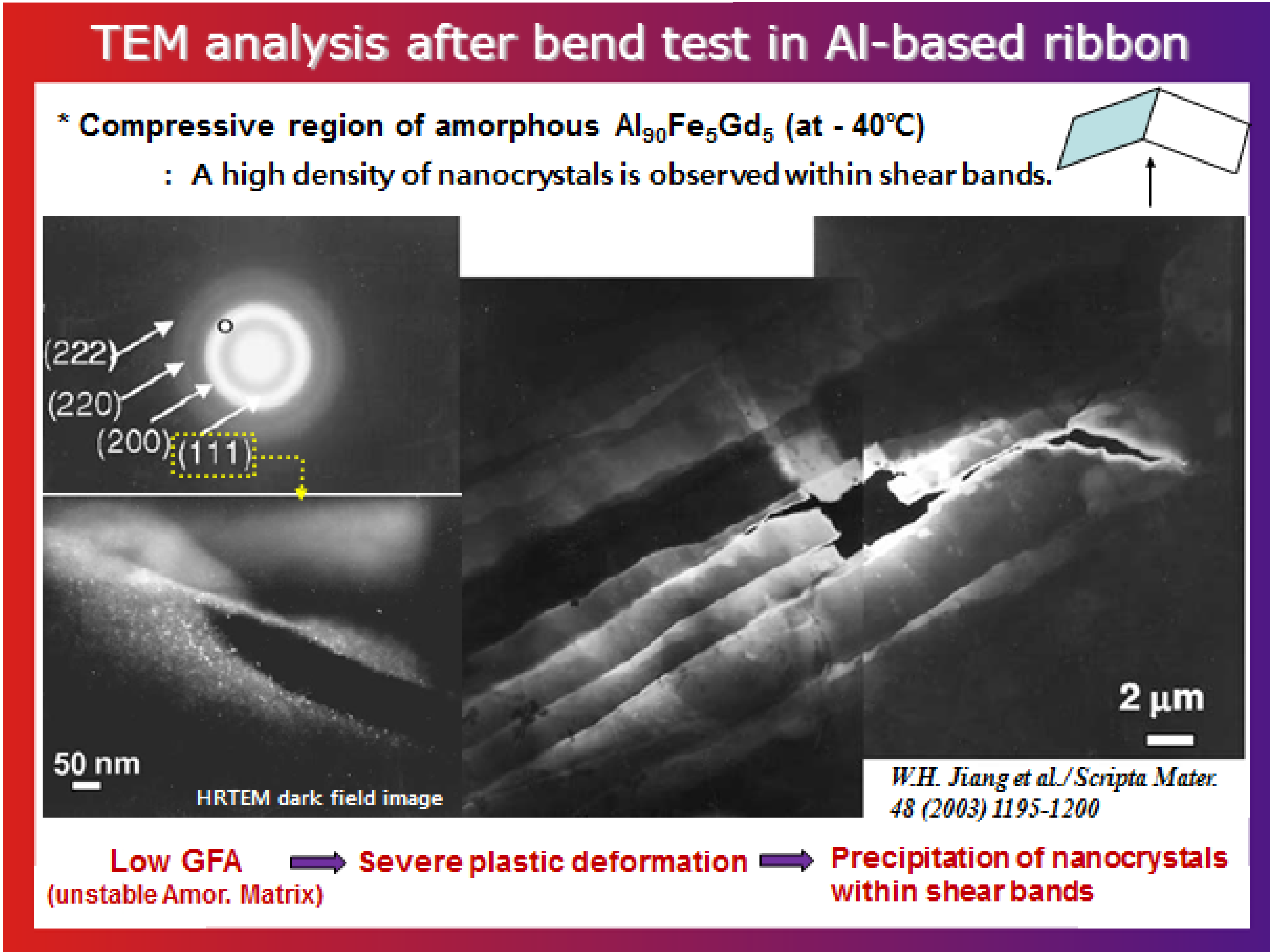


FIGURE 8.9
Scanning electron micrograph of the surface of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG, which was originally coated with a tin coating. During deformation, the "fusible coating" had melted near the shear bands. The round shape of the tin beads clearly suggests that the coating had melted due to the temperature rise as a result of deformation and had resolidified. The bar in the micrographs corresponds to 1 µm. (Reprinted from Lewandowski, J.J. and Greer, A.L., *Nat. Mater.*, 5, 15, 2006. With permission.)

8.4.1 Nanocrystallization near Shear Bands

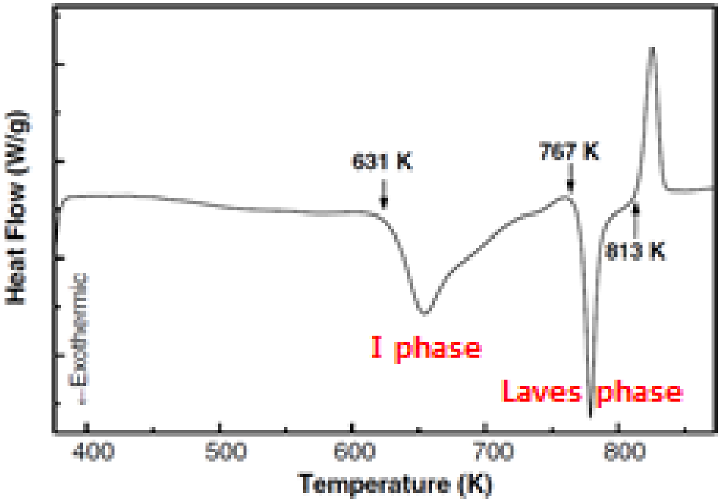


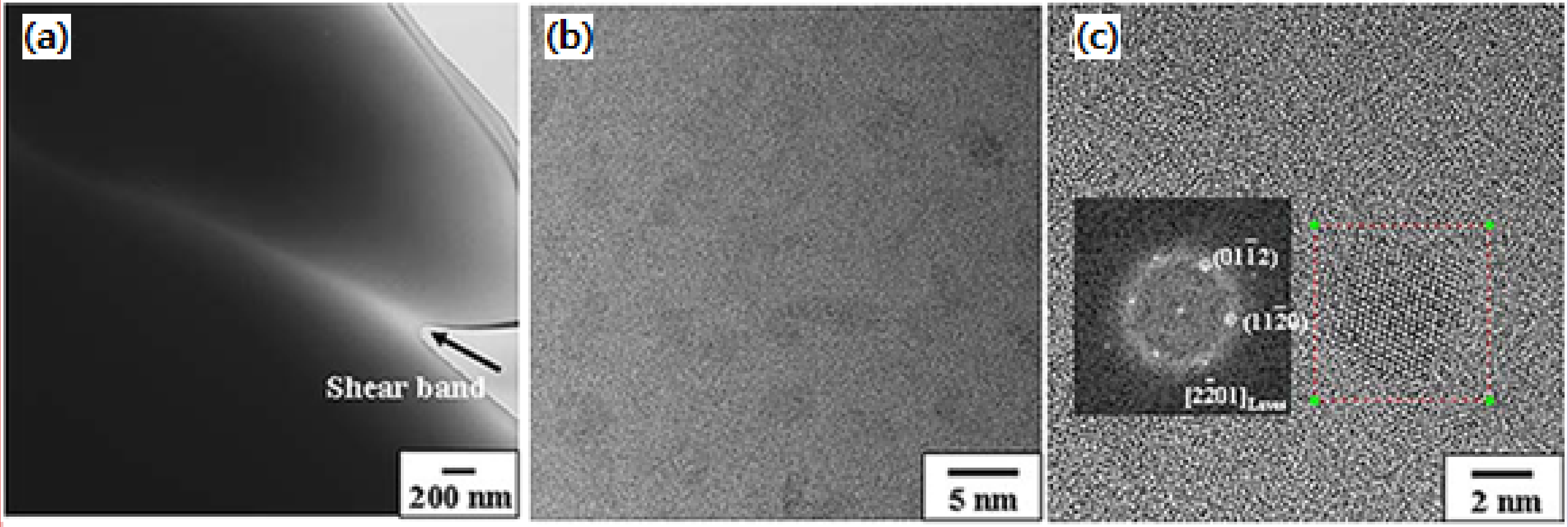
TEM analysis after severe compressive loading

* Quasi-forming $Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ BMG exhibits large plastic strain.

: nanocrystals is observed within shear bands.

H.J. Chang et al./ Scripta Mater. 55 (2006) 509-512

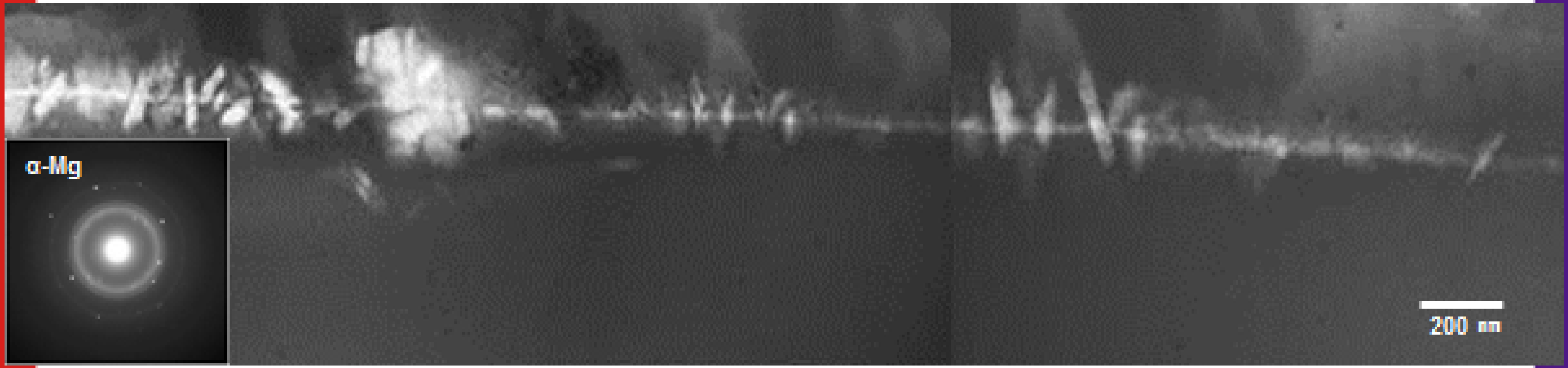


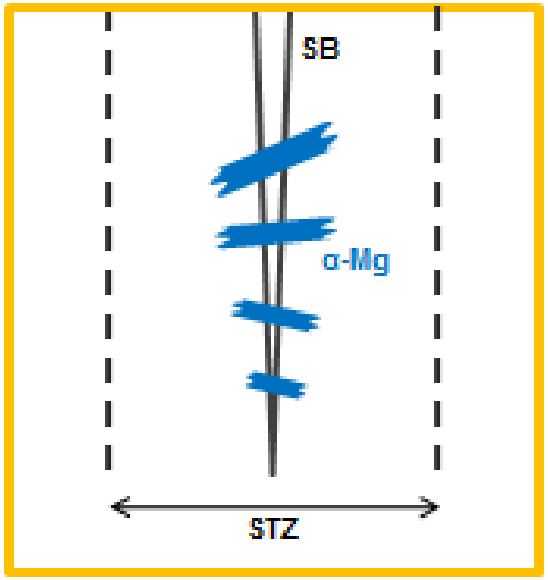


Unstable Amor. Matrix ➡ Severe plastic deformation ➡ Precipitation of nanocrystals within shear bands

TEM analysis after severe compressive loading

* Mg-rich $Mg_{80}Cu_{15}Gd_5$ BMGC ~ large plastic strain





Precipitation of several hundreds nm scale α-Mg in SB & STZ region occurs during the severe compressive deformation, which is related to relatively low T_g (or T_x) value as well as unstable amorphous matrix in Mg-rich BMGC.

J.I. Lee will present the detail at July 8 (11: 45, room E7)

Unstable Amor. Matrix & relatively low T_g (or T_x) ➡ Severe plastic deformation ➡ Precipitation of nanocrystals in SB and STZ region

Atomistic models for plastic deformation in metallic glasses

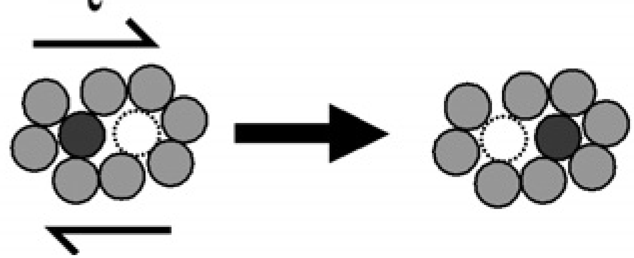
Free volume theory ⟷ STZ model

F. Spaepen

Free volume theory

Homogeneous flow @ <u>steady state</u>

Inhomogeneous flow @ <u>steady state</u>



Single-atom/ Diffusion-like model/ Internal volume creation

Steady state inhomogeneous flow : dynamic equilibrium between shear-induced disordering (creation of free volume) & diffusional annihilation of structural disorder

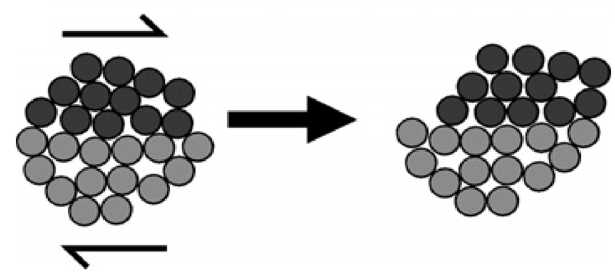
Forward – backward process
Thermally activated, similar energy scales
Dilatational mechanism

A. S. Argon

Shear transformation zone (STZ)

Homogeneous plastic flow | Steady / Non-steady

Inhomogeneous plastic flow



Spontaneous & cooperative reorganization of a small cluster of randomly close-packed atoms

**STZ motion = local shear transformation
STZ pushes apart the atoms around free volume site along activation path**

Plastic flow in metallic glass in which strain is produced by local shear transformations nucleated under the applied stress & the assistance of thermal fluctuations in regions around free volume sites (adiabatic heating)

Atomic bond topology

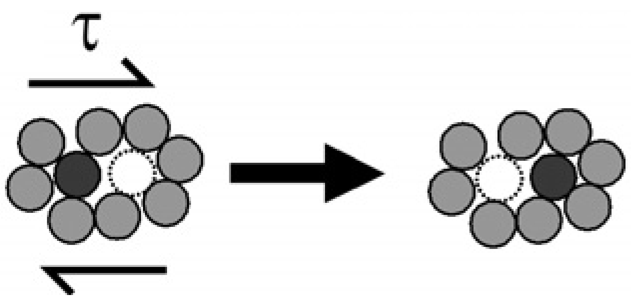
Free volume theory ⟺ STZ model

F. Spaepen

Free volume theory

Homogeneous flow @ <u>steady state</u>

Inhomogeneous flow @ <u>steady state</u>



T. Egami

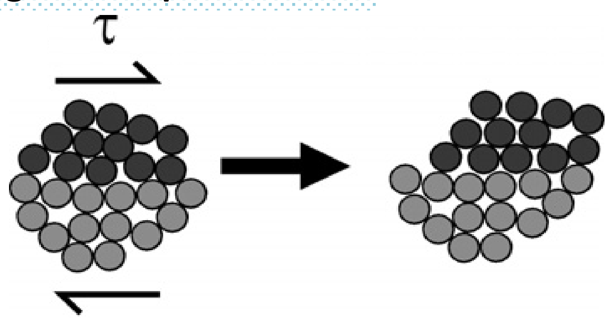
Atomic bond topology

A. S. Argon

Shear transformation zone (STZ)

Homogeneous plastic flow — Steady / Non-steady

Inhomogeneous plastic flow

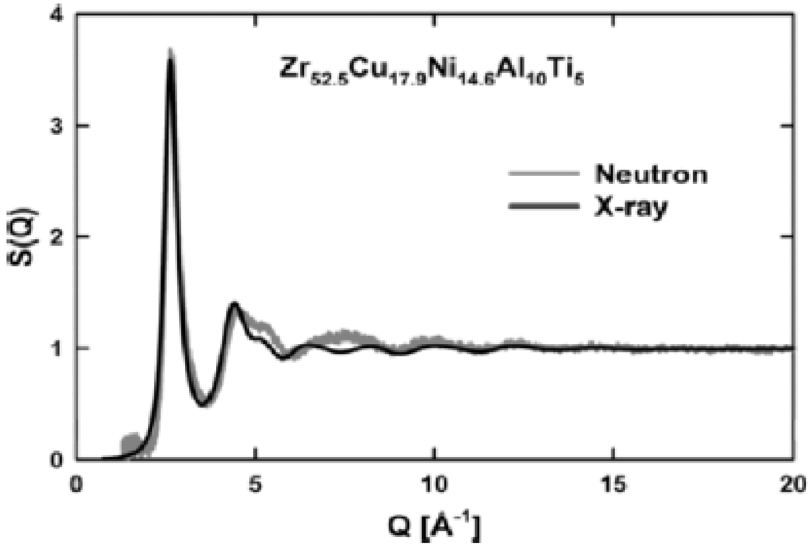


STZ: basic shear unit
(a few to perhaps up to 100 atoms)

- **Free volume approach**
  (1) dense random packing of hard spheres
  (2) free volume cannot be described by the volume alone, and we have to consider the shape
- **Network of atomic connectivity / topology of the atomic structure**

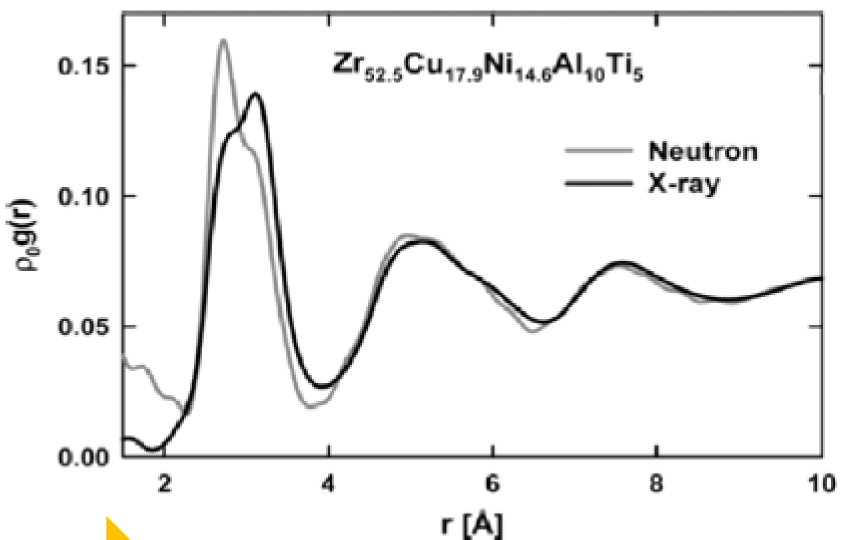
Atomistic theory of metallic liquids and glasses – T. Egami

- Structure of liquids and glasses is usually described in terms of the atomic pair-density correlation function (PDF; $\rho_0 g(r)$) or the radial distribution function (RDF; $4\pi r^2 \rho_0 g(r)$)
- PDF : distribution of the distances between pairs of atoms, averaged over the volume and angle.



Structure function S(Q) of BMG $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$

fourier transformation



PDF of BMG $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$

- The idea most frequently used in discussing atomic transport and deformation is free volume.
- Free volume is a space between atoms, and it is intuitively reasonable to assume that atoms need some space for moving around.

Bond-exchange mechanism of shear deformation

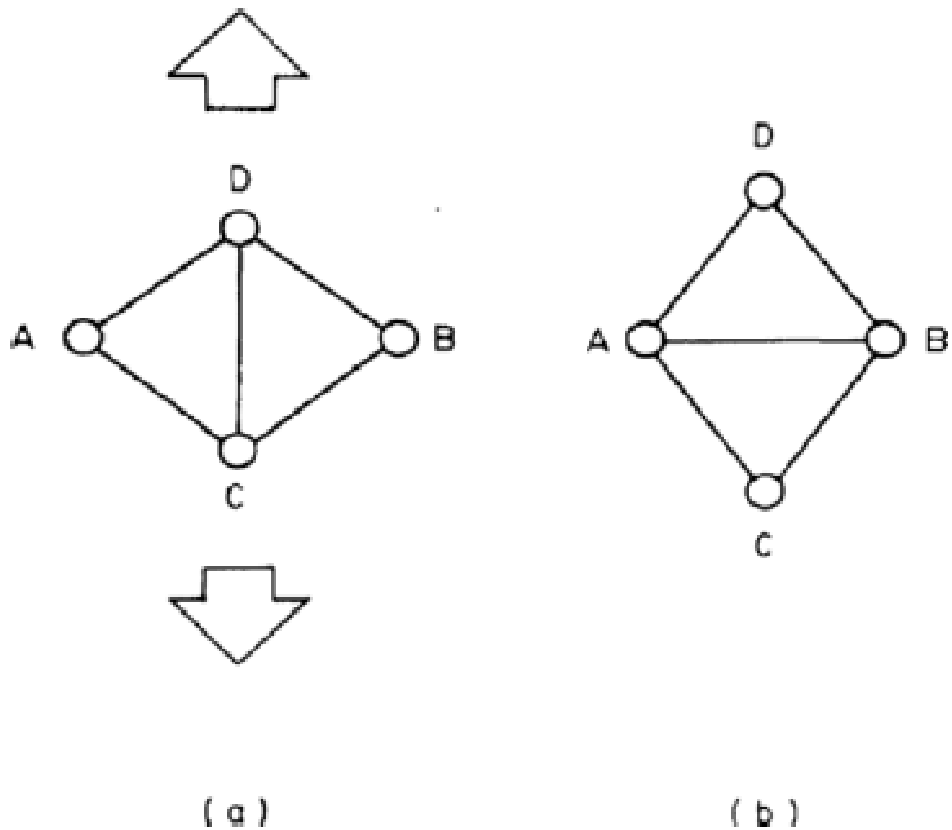
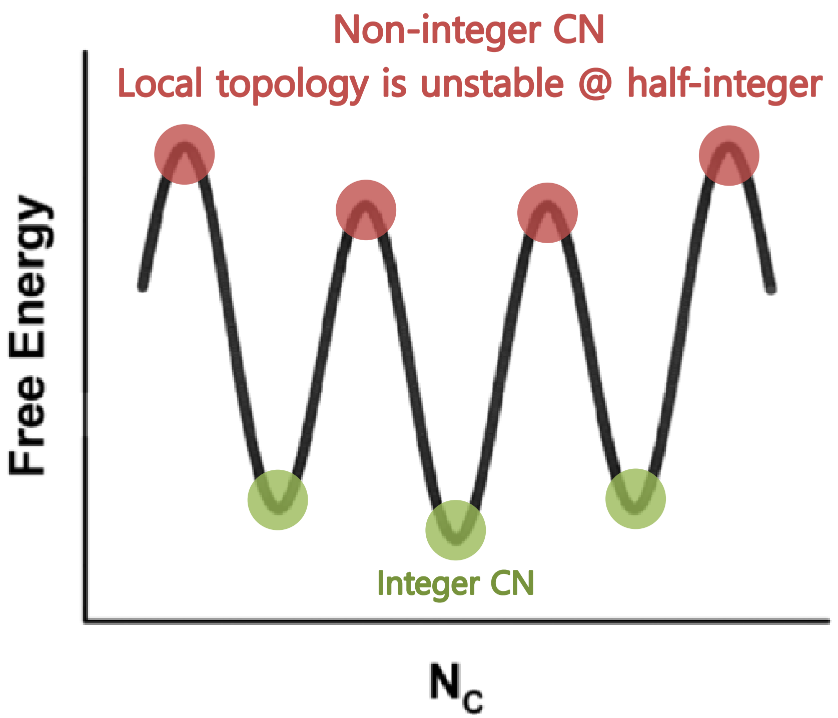


Fig. 2.17. The bond-exchange mechanism of shear deformation.[44] When a vertical tensile stress is applied the bond C–D is cut, and the new bond A–B is formed. The total number of bonds remains unchanged, but the distribution of orientation becomes anisotropic. Bond orientational anisotropy (BOA) is formed as a result of such a bond-exchange process (reprinted from reference [44] with permission from the American Physical Society)

T. Egami: Local topological instability



The energy landscape of an atom as a function of $x=r_A/r_B$

$$\Delta x = \frac{1/2}{\partial N_C(x)/\partial x},$$

$$\frac{\partial N_C(x)}{\partial x} = 8\pi\left(1-\frac{\sqrt{3}}{2}\right)\left[1+x+\sqrt{x(x+2)}+\frac{1}{2\sqrt{x(x+2)}}\right]$$

Δx caused by : local volume strain / uniform expansion

Homogeneous volume strain $\quad \langle \varepsilon_v \rangle = (3/2)\Delta x / x,$

x=1, $\quad \varepsilon_v^{crit}(H) = \frac{3}{2}\Delta x\Big|_{x=1} = \frac{6\sqrt{3}-9}{8\pi} = 0.0554.$

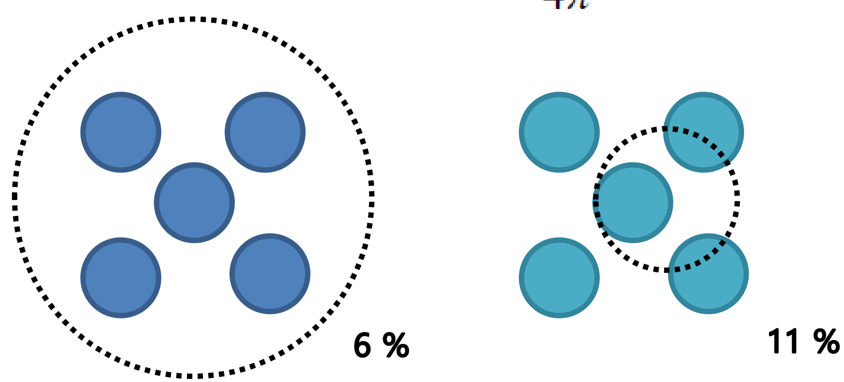
Local volume strain $\quad \varepsilon_v = 3\Delta x / x,$

x=1, $\quad \varepsilon_v^{crit}(L) = 3\,\Delta x\Big|_{x=1} = \frac{6\sqrt{3}-9}{4\pi} = 0.111.$

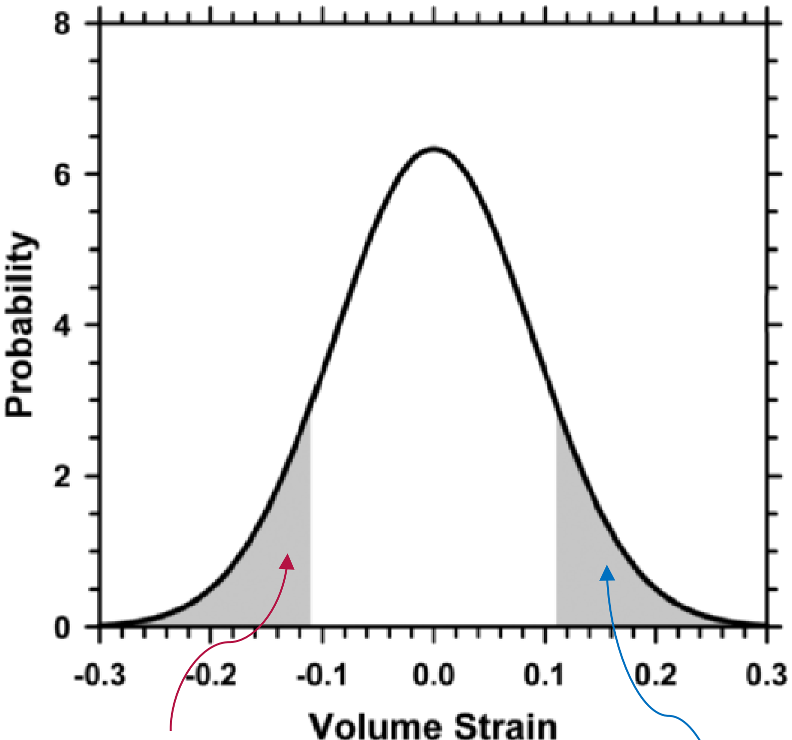
Total volume expands more than 6 %: unstable structure

Local volume strain is larger than 11 %: the site is topologically unstable; local CN may change

This leads to the definition of the free-volume in terms of the critical local volume strain.

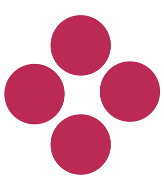


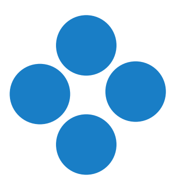
T. Egami: Local topological fluctuation



Free volume site (n-type defect)
Negative (dilatational) volume strain > 11 %
$\varepsilon_V < -\varepsilon_V^{crit}(L)$

Antifree volume site / p-type defect
Positive (compressive) volume strain > 11 %
$\varepsilon_V^{crit}(L) < \varepsilon_V$





- **Defect sites are *liquid-like* / topologically unstable**
  ***Solid-like* / topologically stable sites (ε_V < 11 %)**

여기에서 제안된 critical local volume strain은 free-volume theory에서 정의된 v*와 같은 order of magnitude를 가진다. 즉, free-volume은 원자 크기만큼의 부피가 아니라, 11 % 정도의 local dilatation이 원자 topology를 불안정하게 하여 CN을 1 정도 바꿈

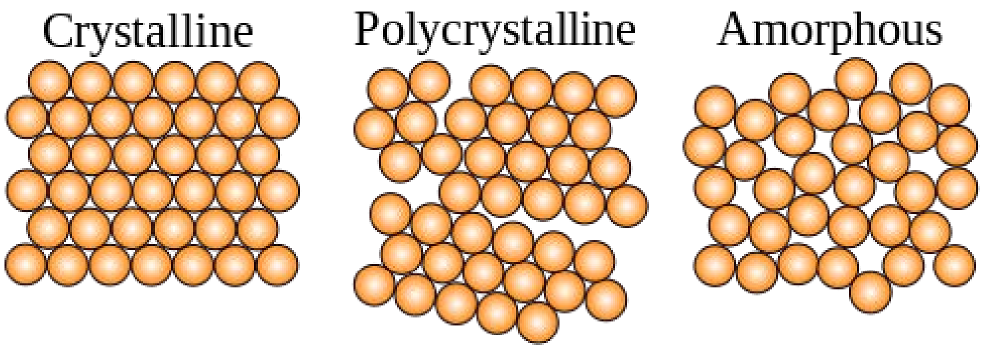
- **Deformation of metallic glasses**

본 조건에서 정의된 defect는 negative와 positive 양 방향의 strain이 가능하기 때문에, 기존의 hard sphere model에서처럼 소성변형에 반드시 free volume이 필요한 것은 아니다. Free volume은 주로 소성변형의 결과로 생겨나는 것이지 꼭 pre-existing할 필요는 없다.

Microscopic bases for the mode-coupling theory

$$m = \left.\frac{\partial \log \eta(T)}{\partial (T_g / T)}\right|_{T=T_g} = \frac{13}{1-(T_g / T_s)} = 13K_\alpha = \frac{39(1-\nu)}{2(1-2\nu)}.$$

Atomic processes and deformation mechanisms



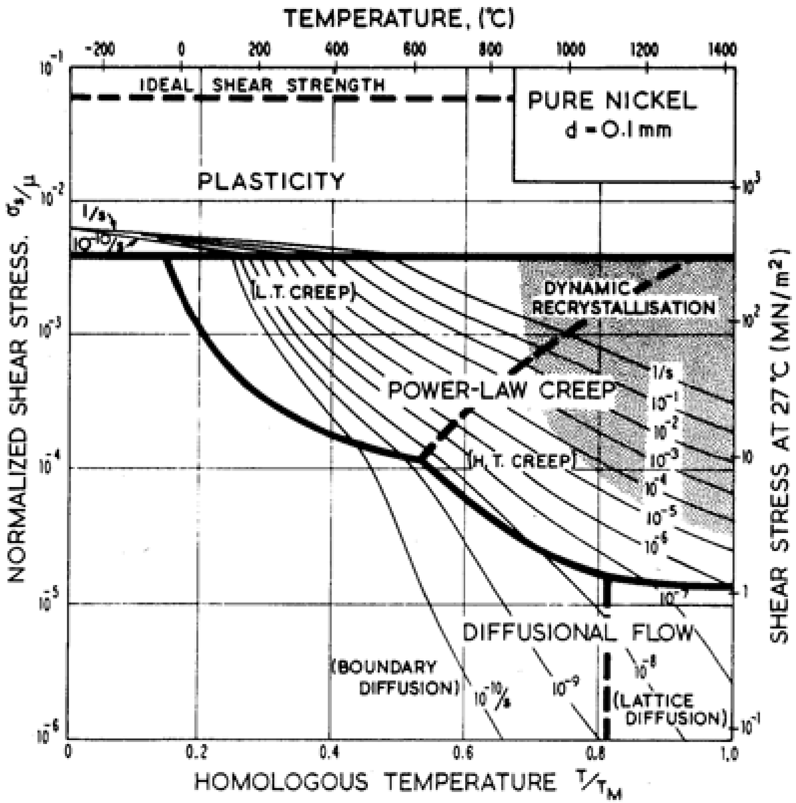
- Plastic flow is **a *kinetic process.***
- At absolute zero, **polycrystalline solid** as having a well defined **yield strength**, below which it does not flow and above which flow is rapid.
- Variables that solid strength depends on : **strain, strain-rate, and temperature**. (atomistic processes : glide-motion of dislocation lines, their coupled glide and climb, the diffusive flow of individual atoms, the relative displacement of grains by grain boundary sliding, mechanical twinning etc.)
- **Deformation mechanisms** were considered to describe polycrystal plasticity (or flow); they divided into five groups.

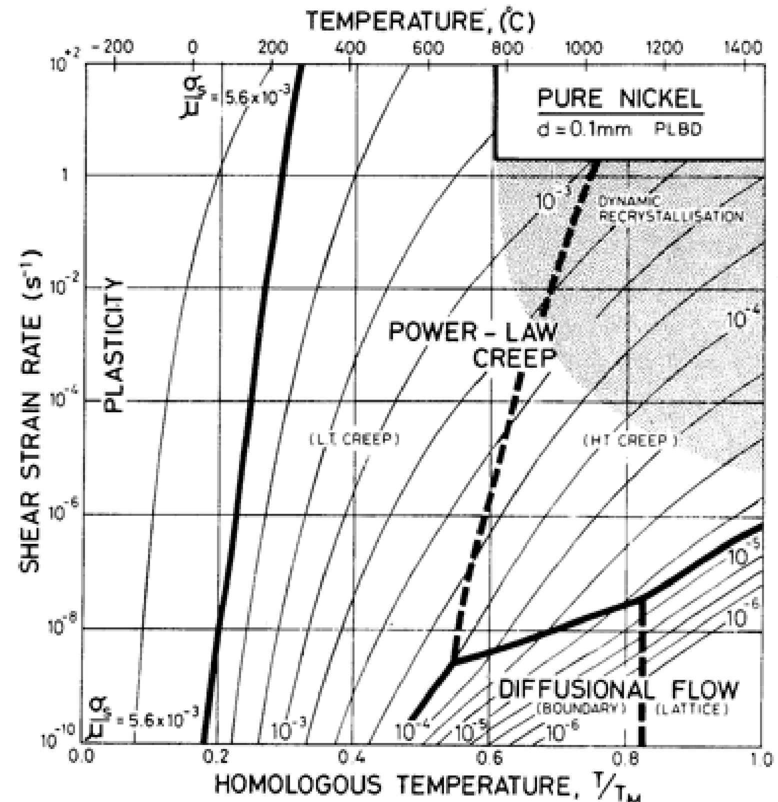
  1. Collapse at the ideal strength
  2. Low-temperature plasticity by dislocation glide
  3. Low-temperature plasticity by twinning
  4. Power-law creep by dislocation glide, or glide-plus-climb
  5. Diffusional flow

- It's possible to superimpose upper mechanisms. (superplastic flow etc.)

Ashby deformation maps for crystalline materials

Delineating the different modes and mechanism of plastic deformation of a material as a function of stress, temperature, and structure





- Rate equations $\dot{\gamma} = \left(\frac{2}{3}\left((\dot{\varepsilon}_1 - \dot{\varepsilon}_2)^2 + (\dot{\varepsilon}_2 - \dot{\varepsilon}_3)^2 + (\dot{\varepsilon}_3 - \dot{\varepsilon}_1)^2\right)\right)^{\frac{1}{2}}$ ➡ $\dot{\gamma} = f(\tau, T, \text{structure})$

  steady-state constitutive flow law

- **Deformation-mechanism map shows how to combine each plastic deformation mechanisms.**
- normalized stress σ_s/μ
  homologous temperature, T/T_M (where μ is the shear modulus and T_M the melting temperature)
  shear strain γ'

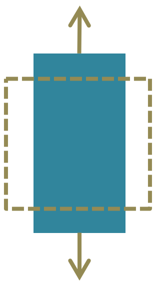
Empirical deformation mechanism maps for metallic glasses

Developed by Spaepen using the results for melt-spun metallic glasses,
Explained by using the concept of free volume model

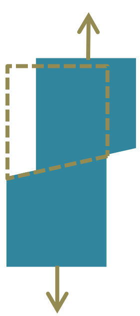
Flow Mechanisms

❖ Basic Modes of Deformation

- **Homogeneous Flow**
  - Each volume element undergoes the same strain.



- **Inhomogeneous Flow**
  - Strain is concentrated in a few thin shear bands.



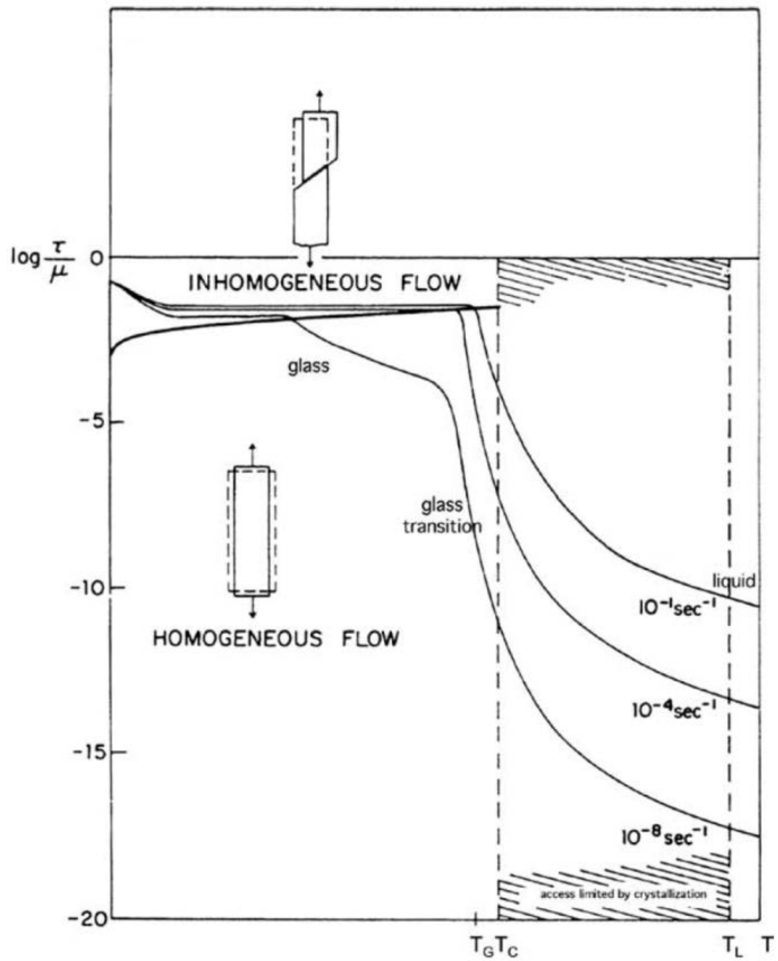
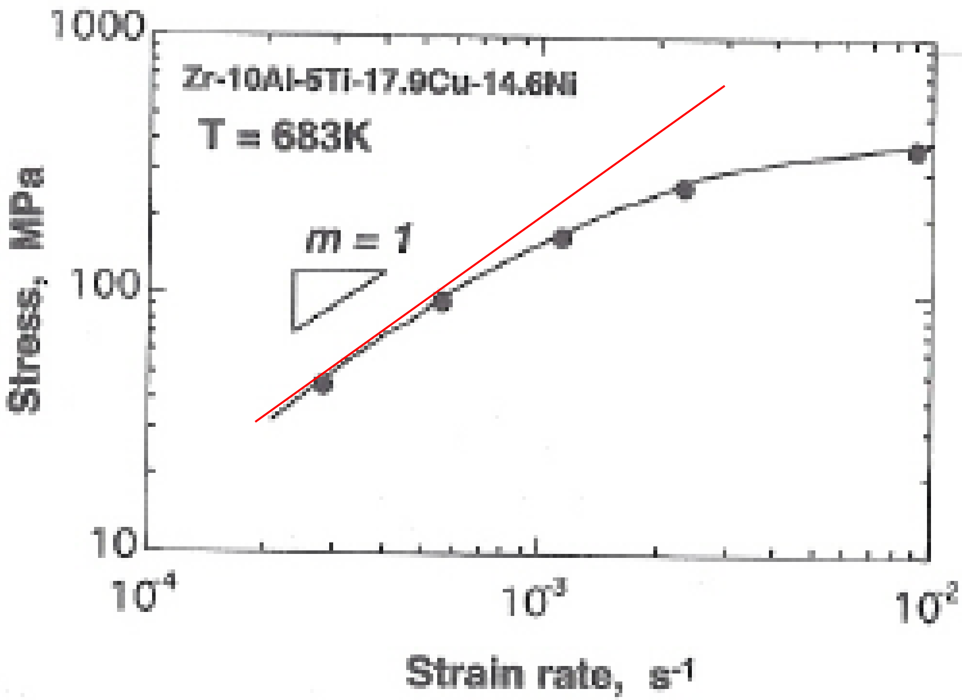


Fig. 1. Deformation mechanism map for a metallic glass.

Homogeneous Deformation



- Under low strain rate
  → Homogeneous deformation
  (= Newtonian fluid)

- Under high strain rate
  → Inhomogneous deformation
  (= non-Newtonian fluid)

- Newtonian to non-Newtonian transition is dependent on the test temperature.

Liquid Flow

❖ Liquid Region (above and near T_g)

- Homogeneous Flow
- Low stress in liquid region
- Strain rate is proportional to the stress
- Viscosity is not dependent on stress, but temperature.

$$\sinh\left[\frac{\varepsilon_0 v_0 \sigma}{2kT}\right] \approx \frac{\varepsilon_0 v_0 \sigma}{2kT}$$ @ low stress

- Newtonian Viscous Flow

$$\tau = \eta \cdot \dot{\gamma}$$

Shear stress | **Viscosity** | Strain rate

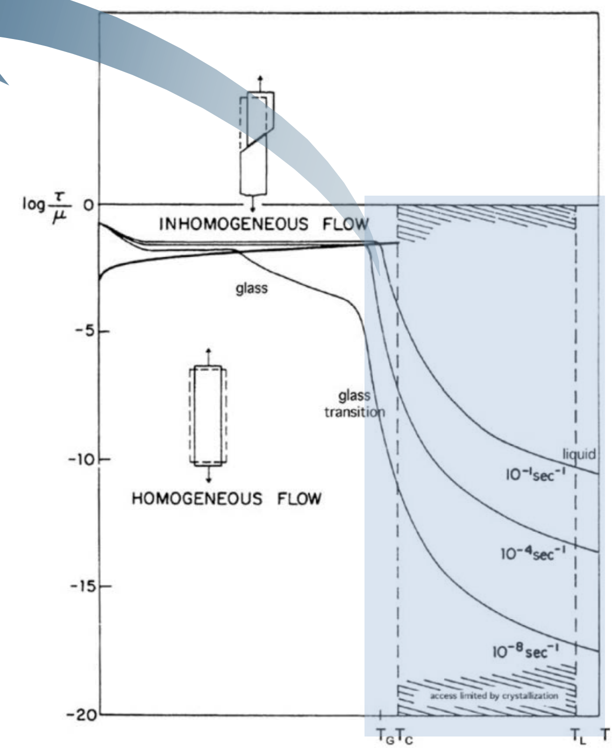


Fig. 1. Deformation mechanism map for a metallic glass.

Deformation-induced Softening

- Softening : Lowering of viscosity in the shear bands
- Structural Change : Creation of free volume due to high stress level

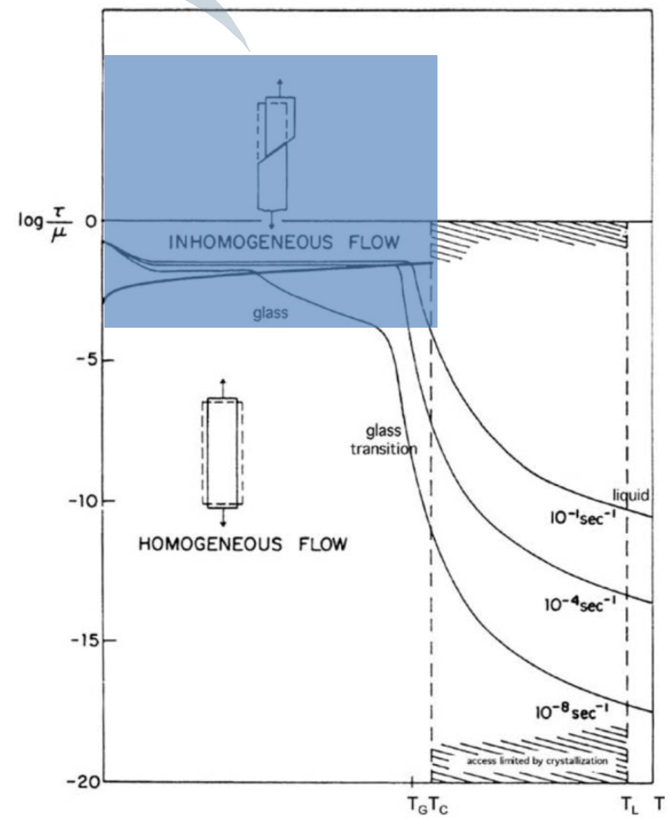
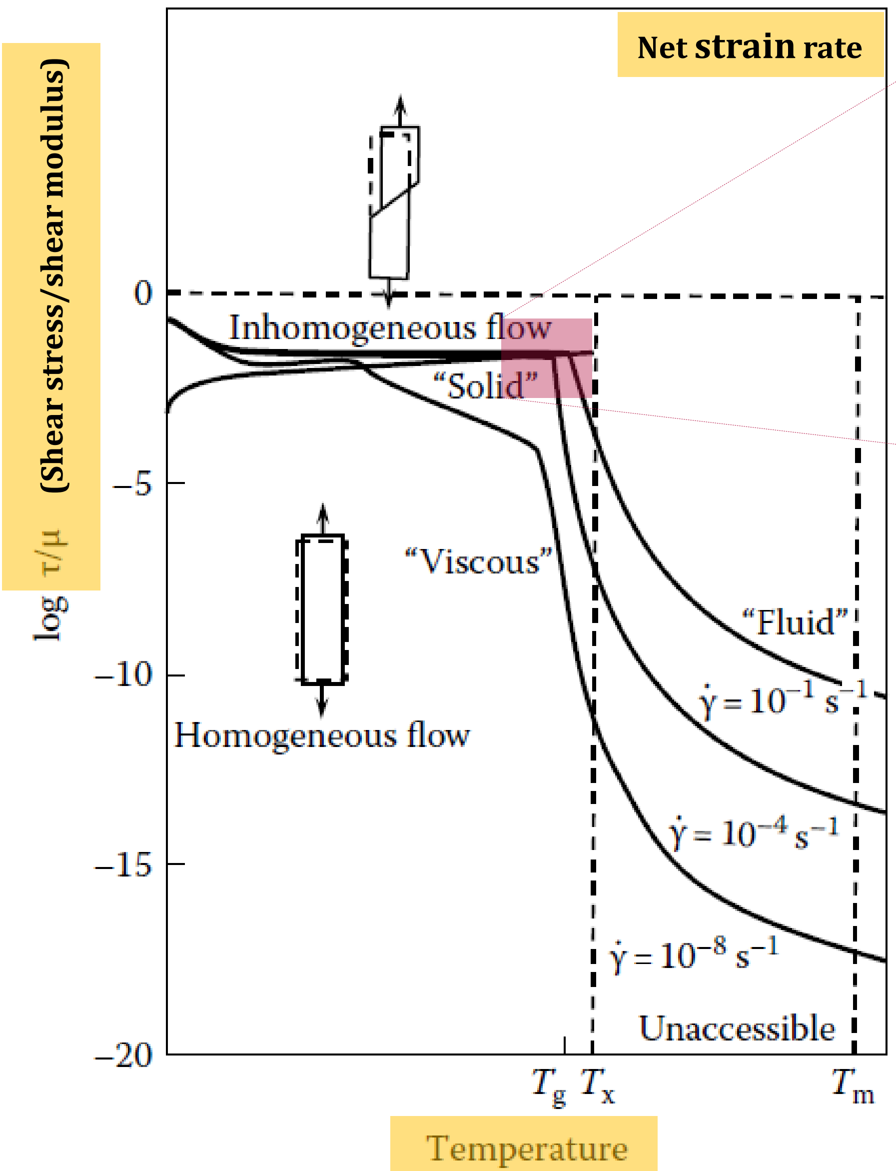
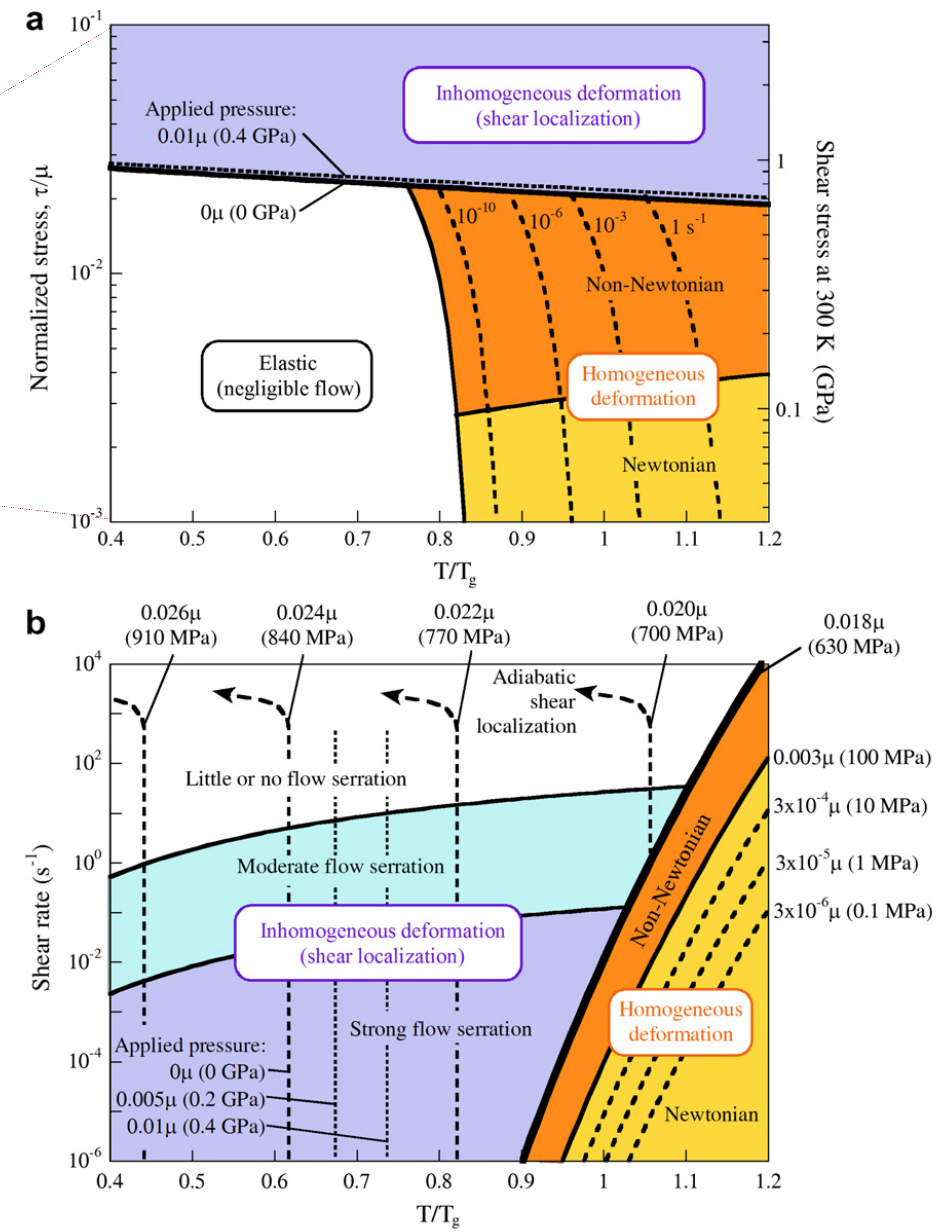


Fig. 1. Deformation mechanism map for a metallic glass.

Empirical deformation mechanism maps for metallic glasses

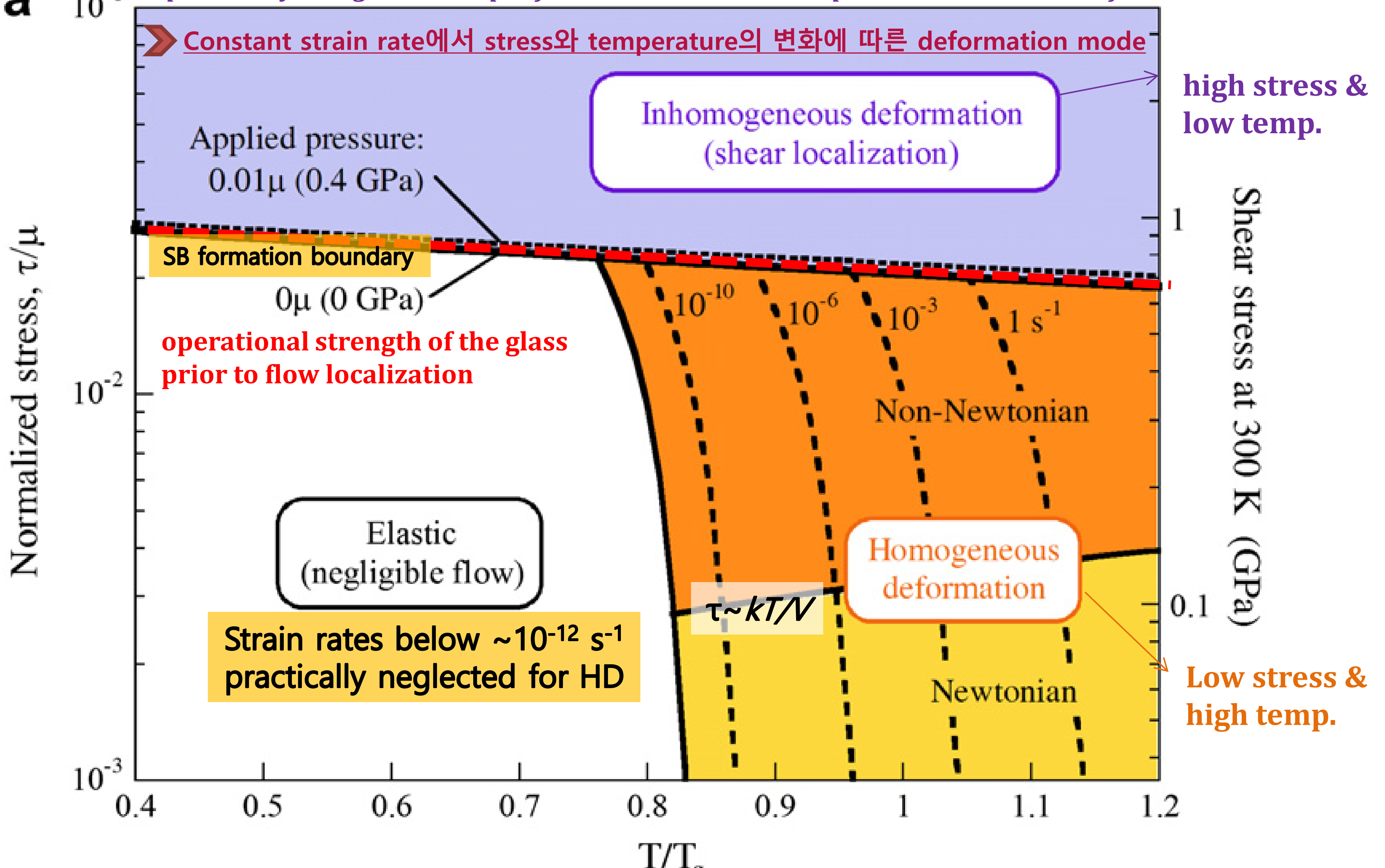
Developed by Spaepen using the results for melt-spun metallic glasses,
Explained by using the concept of free volume model





Deformation map drawn by C.A. Schuh

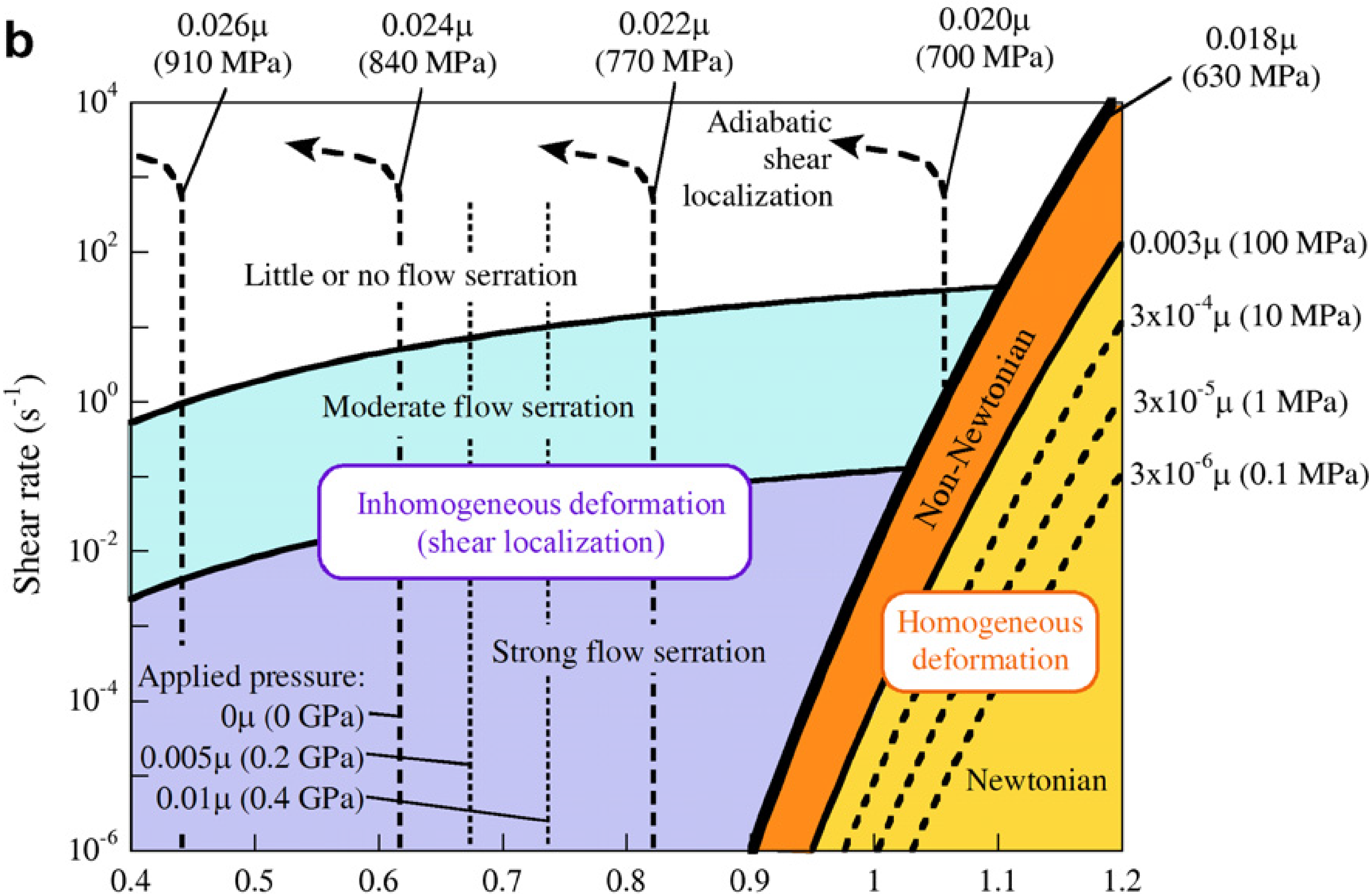
Explained by using the concept of STZ, strain rates are represented as a series of contours.



The Newtonian-non-Newtonian transition is delineated at ~ $10^{-5}S^{-1}$. However, it is important to note that at high enough shear rates, non-Newtonian flow as well as shear localization can occur at high temperature – even in the supercooled liquid region.

Deformation map drawn by C.A. Schuh

Explained by using the concept of STZ, stress is represented as a series of contours.



➤ Constant stress

Roughly parallel to a family of iso-stress contours that can be drawn in the homogeneous regime.

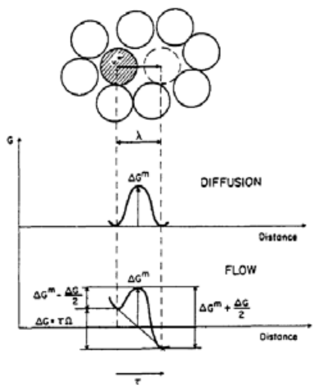
Deformation modes

Plastic deformation

(γ', τ, T)

F. Spaepen : Free volume theory

Homogeneous flow @ steady state

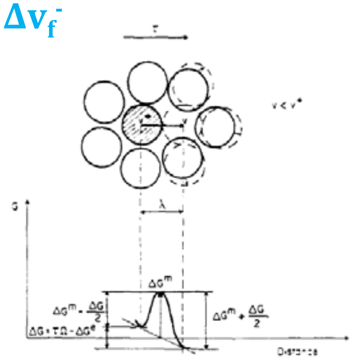


Inhomogeneous flow @ steady state

Competition of shear-induced disordering and a diffusion controlled reordering;

creation of FV vs. relaxation

$\Delta v_f^+ = \Delta v_f^-$



A. S. Argon / C. A. Schuh: STZ model

Homogeneous plastic flow

Viscous flow of a SCL

Steady-state flow

Structural disordering과 ordering,
즉 free volume creation과 annihilation 사이의 균형.
$\Delta v_f^+ = \Delta v_f^-$
Local diffusive jump 또는 STZ operation이 stress를 분산시키고, dilatation을 통해 free volume을 만들지만 동시에 relaxation이 진행되어 free volume을 없앤다.
Structural maintanance

Non-steady-state flow

Structural transience가 일어남.
균형이 이루어지지 않아 net gain / loss of free volume이 일어날 수 있다.
"overshoot" "undershoot"

Inhomogeneous plastic flow

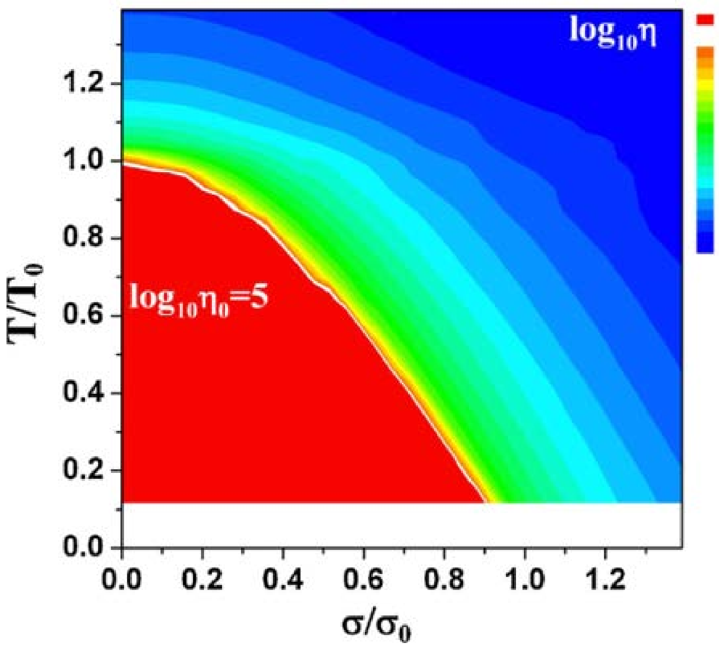
Localization → Shear band formation
local production of FV (dilatation)
local evolution of structural order due to STZ operation
redistribution of internal stresses

Summary

- **Plastic deformation in metallic glasses controlled by shear band nucleation and propagation.**

- **Atomistic views of deformation of metallic glasses**

  F. Spaepen: Free volume theory
  A.S. Argon: Shear transformation zone theory
  T. Egami: Atomic bond topology



- Free volume theory: liquid 상에서의 free volume 개념이 모호, MD simulation 결과와는 맞지 않음

- Free volume theory는 현상을 설명하기에 매우 적합하지만 그 자체로 microscopic theory가 될 수는 없다. (free volume이 없어도 변형 가능)

- Local topological fluctuation은 원자 수준의 stress를 온도에 따라 재배열함에 따라 thermal property를 설명할 수 있다.

- **Deformation map predicts the deformation modes of metallic glasses**

  normalized stress σ_s/μ, homologous temperature T/T_M, shear strain γ'

Mechanical behavior of nanoscale metallic glasses

Bulk metallic glass

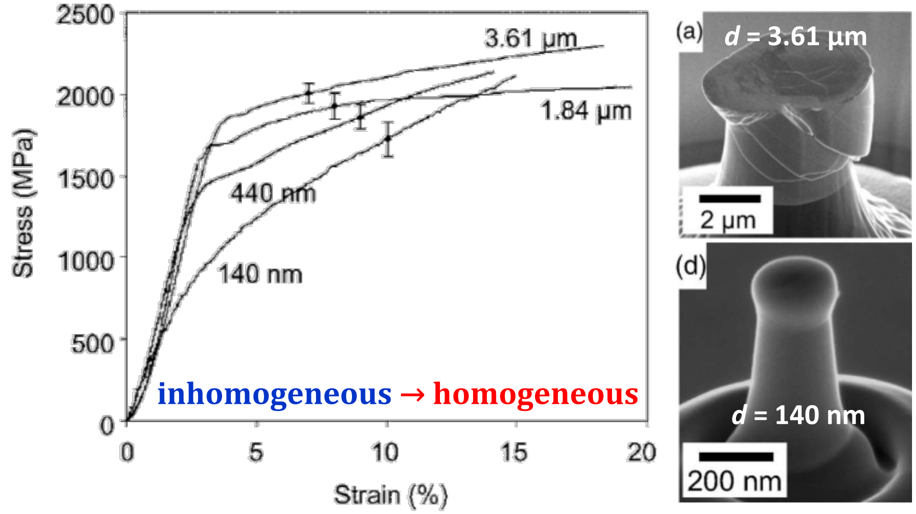
(Brittleness, Strength ~*0.02E*)

Nanosized metallic glass

- Deformation mode transition?
- Distinct behavior in nucleation & propagation of shear bands?
- Size effect on strength & elastic strain limit?

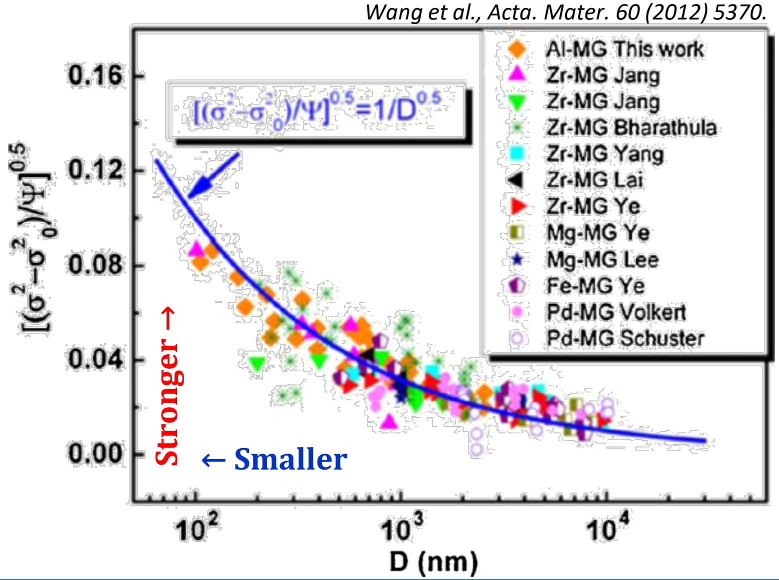
▸ **Deformation mode transition in nanosized MG**

Volkert et al., J. Appl. Phys. 103 (2008) 083539.

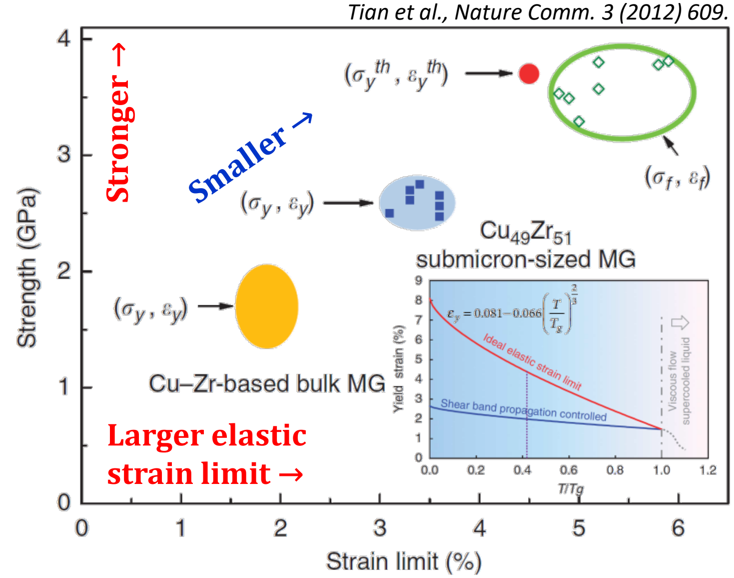


▸ **Sample size effect on the strength and elastic limit of metallic glasses**

Wang et al., Acta. Mater. 60 (2012) 5370.



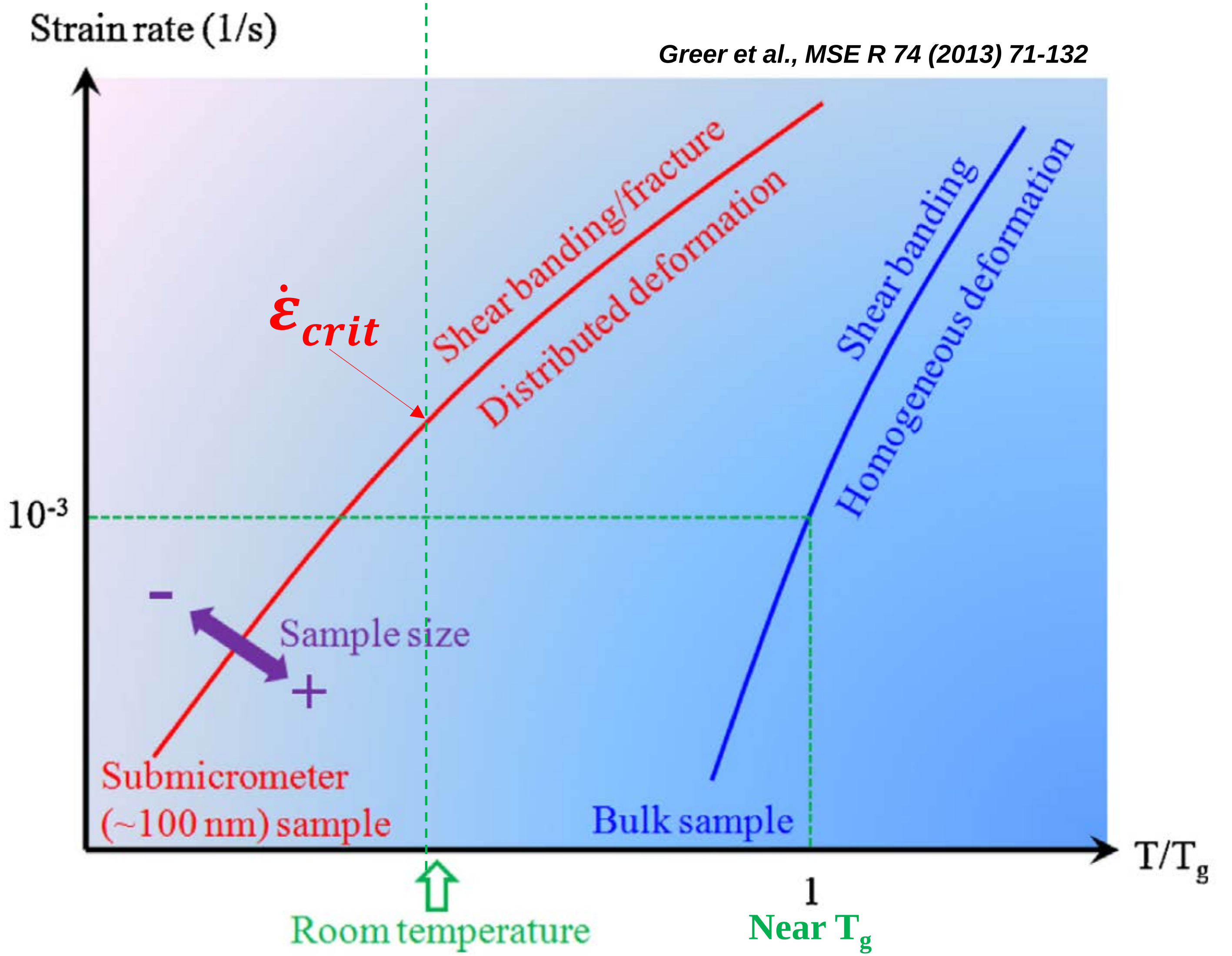
Tian et al., Nature Comm. 3 (2012) 609.



Deformation map of metallic glasses: size effect of the critical strain rate, $\dot{\varepsilon}_{crit}$

$\dot{\varepsilon}_{crit}$: critical strain rate for deformation mode transition

→ shifted by sample size (diameter of spherical particles)



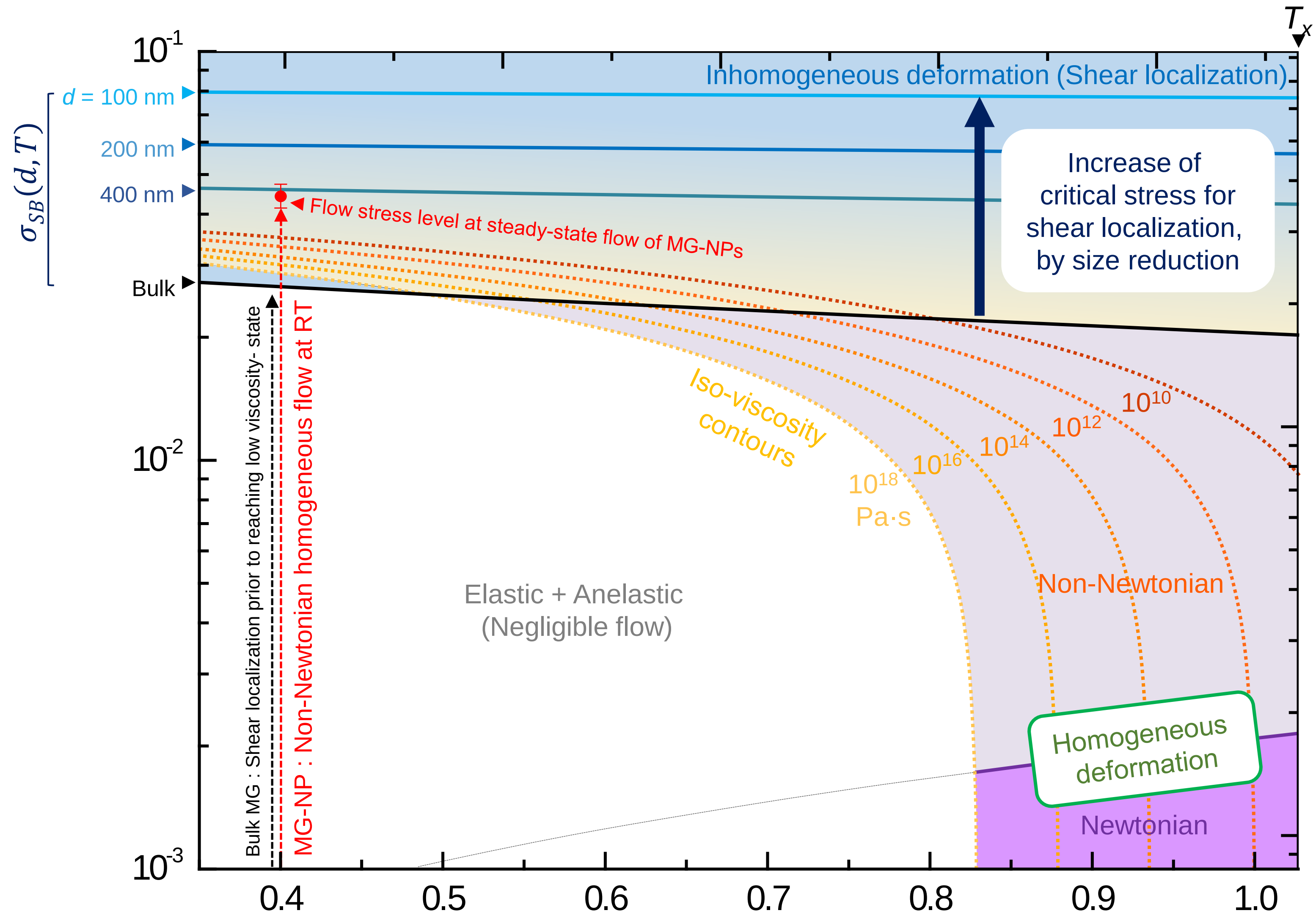


Figure 5 | Deformation map of metallic glass including iso-viscosity contours and the effect of sample size reduction.