# Onset of plasticity and mechanical softening of Ti-based bulk metallic glass

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# Outline

- **Introduction**
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  - Structural, thermal and elastic properties
  - Mechanical properties
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# Introduction

- **Interesting correlations in metallic glasses:**
  - Relationship between $\sigma_y$ and $T_g$ (Yang et al., Appl. Phys. Lett. 88 (2006) 221911):

$$\sigma_y = 50\frac{\Delta T_g}{V}$$

  Here $\Delta T_g$ is the temperature difference between $T_g$ and room temperature and $V$ is the molar volume of the MG.

  - Larger plasticity for alloys with larger Poisson's ratio (Lewandowski et al., Phil. Mag. Lett. 85 (2005) 77). "Tough" behaviour for $\nu > 0.34$

# Introduction

- Fracture angle and yielding in metallic glasses

- Polycrystalline materials typically fracture forming an angle of 45º with respect to the loading axis (Tresca or von Mises yield criterion).
- Metallic glasses fracture forming an angle:
  - Smaller than 45º under compression.
  - Larger than 45º under tension
- This occurs because MGs following pressure-depending Mohr-Coulomb criterion:

$$\tau_C = \tau_0 - \beta_{M-C}\sigma_n$$

$\tau_C$ shear stress at yielding

$\tau_0$ cohesion

$\sigma_n$ normal stress at yielding

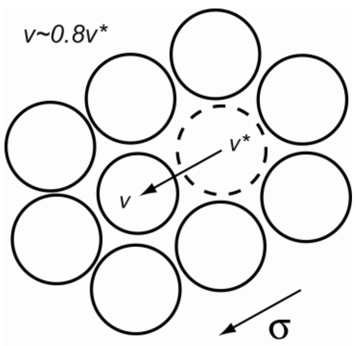
$\theta_{C,F}$ fracture angle

$\beta_{M-C}$ friction coefficient

$$\beta_{M-C} = \frac{\cos 2\theta_{C,F}}{\sin 2\theta_{C,F}}$$

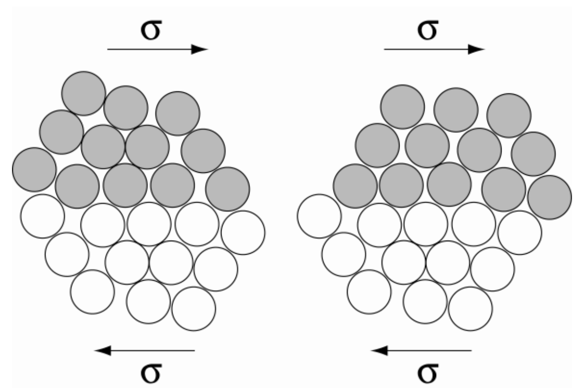
# Introduction

- Plastic flow in metallic glasses (MGs) is accompanied by dilatation (i.e., creation of excess free volume).




**Single atomic jumps**

*Spaepen, Acta Metall. 1977;25:407.*




**Shear transformation zones**

*Argon, Acta Metall. 1979;27:47*

*Falk and Langer . Phys. Rev. E 1998;57:7192.*

<u>Plastic flow equation:</u>

$$\dot{\gamma} = 2\Delta f c_f k_f \left( \frac{\varepsilon_0 v_0}{\Omega} \right) \sinh\left( \frac{\tau \varepsilon_0 v_0}{2 k_B T} \right)$$

$\dot{\gamma}$: is the shear strain rate  $\tau$: is the shear stress

$c_f = \exp(-\gamma v^*/\langle v_f \rangle)$ flow defect concentration

$k_B$ Boltzmann constant

$k_f$ temperature-dependent rate constant

$\Delta f$ volume fraction of potential flow units

$\varepsilon_0 v_0$: activation volume for a flow event and $\Omega$: atomic volume.

# Introduction

- Production term of free volume during deformation

$$\left.\frac{dc_f}{dt}\right)_{def} = P = a_x \dot{\varepsilon}\, c_f \ln^2 c_f$$

[De Hey et al. Acta Mater. 1998;46:5873]

with: $$a_x = \frac{k_B T \Omega}{v_f S \varepsilon_0 \nu_0}$$

*S*: stiffness [M. Heggen, et al. J. Appl. Phys. 2005;97:033506]

- Strain rate during nanoindentation

$$\dot{\varepsilon} = \frac{1}{h}\frac{dh}{dt}$$

[Schuh et al., Acta Mater. 2004; 52, 5879]

→ $c_f(h, c_{f,ini}, a_x)$

# Introduction

- **Why Ti-based metallic glasses ?**

  - Considerable plasticity, high yield stress, large Young's modulus.

  - Good glass forming ability and high glass transition temperature.

  - Relatively low-cost and rather low density.

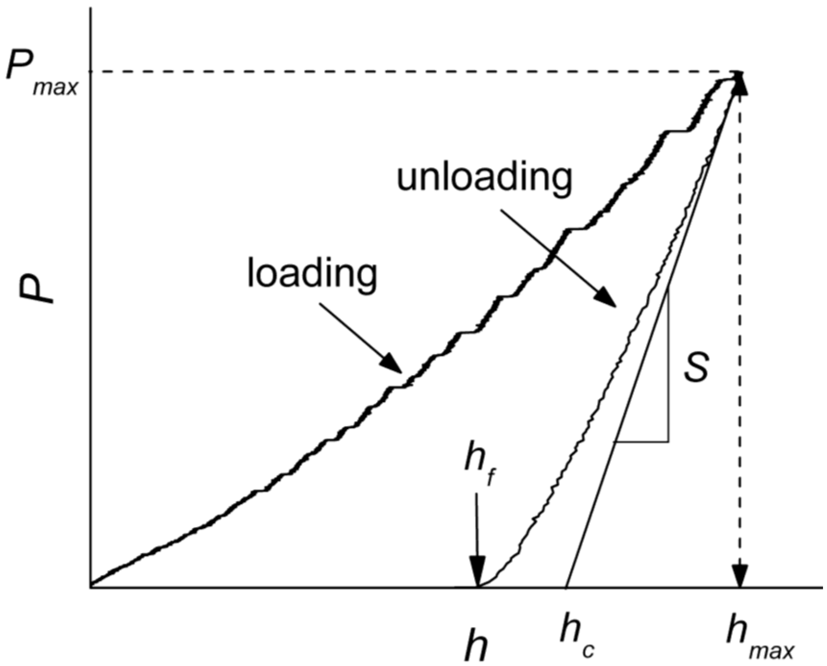
# Experimental details

- **Metallic glass rods** ($\Phi$ = 3 mm) prepared by Cu-mold casting

**Composition:** $Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18}$

- **Characterization**
  - Structural and thermal properties investigated by **X-ray diffraction** and **differential scanning calorimetry**.
  - Elastic properties measured by **acoustic measurements** (pulse-echo technique)
  - **Compression tests** on cylindrical specimens with 2:1 aspect ratio and loading rate of 1.8 x $10^{-4}$ $s^{-1}$.
  - **Nanoindentation tests**: UMIS (Fischer-Cripps Lab.) and Nanoindenter XP (MTS)
    - Diamond pyramidal-shaped (Berkovich-type) tip.
    - Load control mode: - Range of forces: 4 - 500 mN.
    - Dynamic measurements using the continuous stiffness method (45 Hz).
    - Hardness evaluated using the method of Oliver and Pharr at the beginning of unloading segment.

# Experimental: Determination of hardness and Young's modulus from nanoindentation




Stiffness: $S = \frac{dP}{dh}$

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

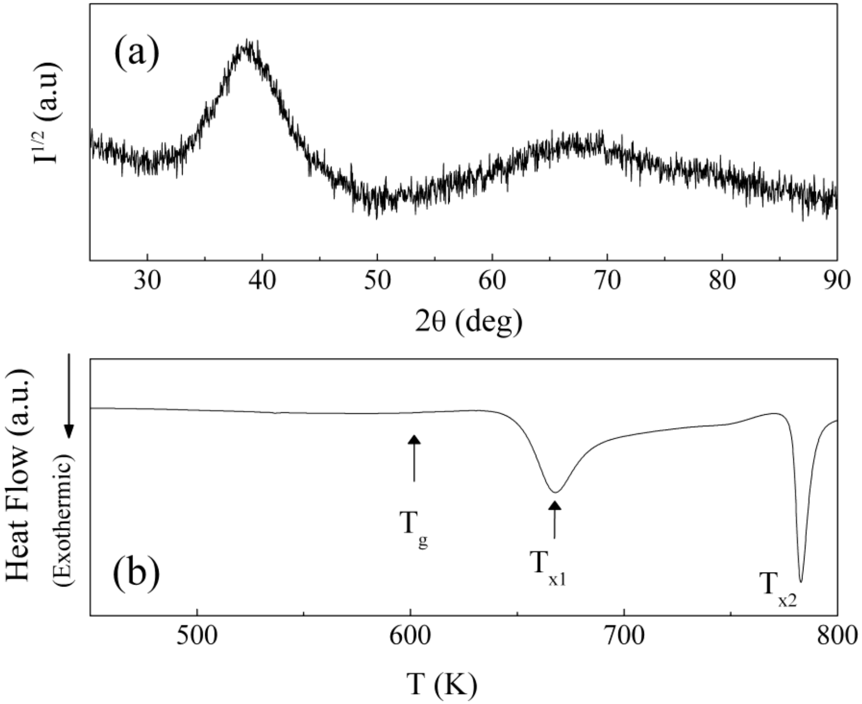
*A* is the contact area
$\beta$ = 1.034 (King's factor)
$E_r$ is the Reduced Young's Modulus

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

For diamond $E_i$ = 1140 GPa and $\nu_i$ = 0.07.

*H* is the hardness: $H = \frac{P_{max}}{A}$

# Results
## Structural and thermal properties




- Broad halos, absence of crystalline peaks

| Composition | $T_g$ (K) | $\Delta T$ ($T_x$-$T_g$) | $\frac{RT}{T_g}$ |
|---|---|---|---|
| $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ | 610 | 58 | 0.49 |

# Results: Elastic properties

$\rho$ = 5.6 g/cm$^3$ (20% lower than for Zr-based MG, 55 % lower than for Pd-based MG; 60% lower than for Pt-based)

| $\nu$ | $K_\alpha$ | *G* (GPa) | | | *B* (GPa) | | | *E* (GPa) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Acoustic | Calculated using Eq. 1 | Calculated using Eq. 2 | Acoustic | Calculated using Eq. 1 | Calculated using Eq. 2 | Acoustic | Calculated (using Eq. 1) | Calculated using Eq. 2 |
| 0.357 | 3.4 | 34.10 | 44.71 | 31.91 | 108.88 | 115.13 | 101.50 | 92.62 | 113.05 | 86.60 |

**Equation 1: Rule of mixtures**

$$M^{-1} = \sum f_i M_i^{-1}$$

*M* is an elastic constant ; $f_i$ are the atomic percentages

**Equation 2: Correlation elastic-thermal properties**

$$\frac{k_B T_g}{2B\Omega_0} = \frac{(\varepsilon_{v,crit})^2}{K_\alpha} \qquad K_\alpha = \frac{3(1-\nu)}{2(1-2\nu)}$$

$(\varepsilon_{v,crit})^2 = 0.092$ is the critical volume strain before the system relaxes

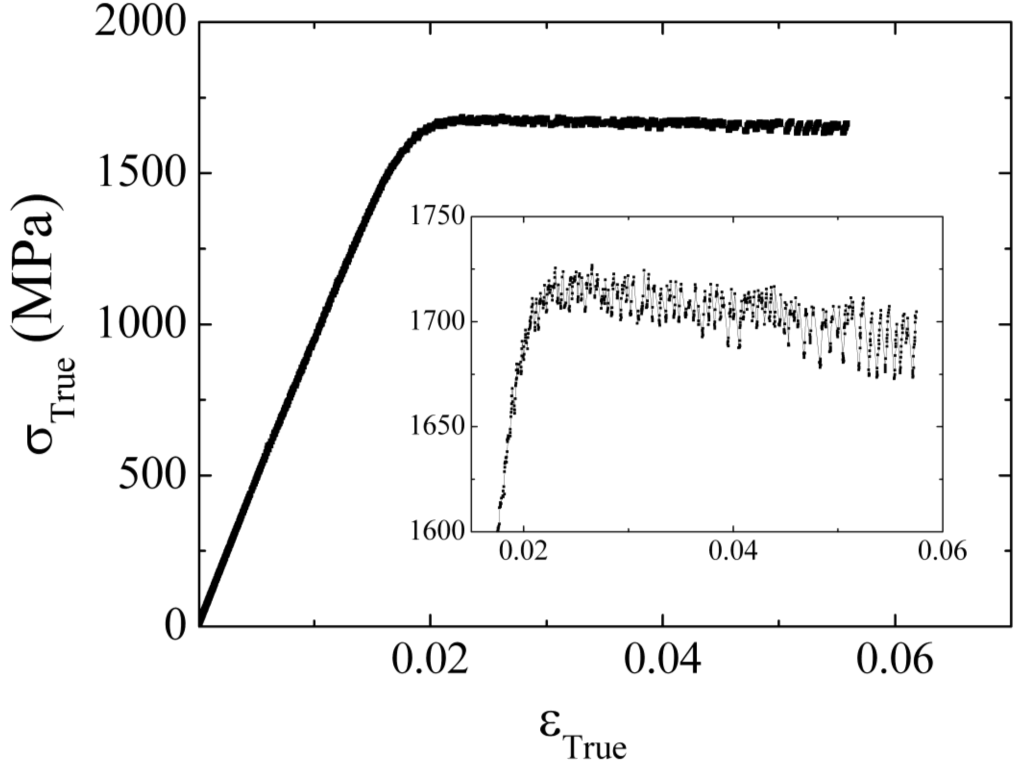
$\Omega_0$ is the average atomic volume

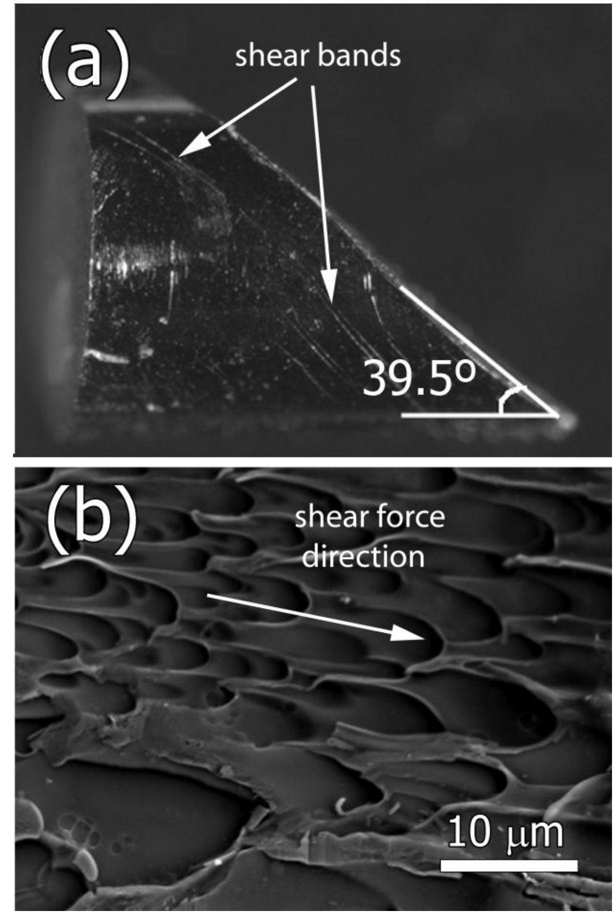
T. Egami et al. *Phys. Rev. B* **2007**, *76*, 024203.

- Equation 1 overestimates the elastic properties, i.e., BMGs exhibit <u>elastic softening</u>

# Results

## Compression Tests



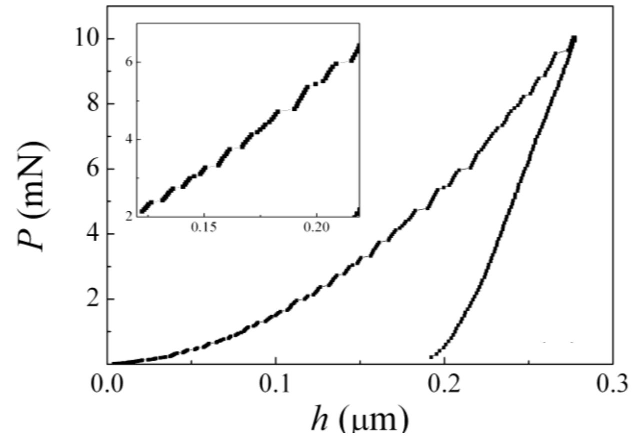




$$\sigma_y = 50\frac{\Delta T_g}{V} = 1680MPa$$

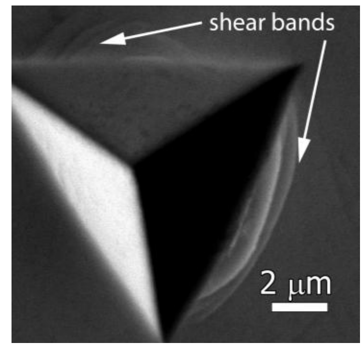
$$\beta_{M-C} = \frac{\cos 2\theta_{C,F}}{\sin 2\theta_{C,F}}$$

| Composition | $\varepsilon_{total}$ | $\sigma_{C,F}$ (MPa) | $\theta_{C,F}$ | $\beta_{M\text{-}C}$ | $E$ (GPa) | |
|---|---|---|---|---|---|---|
| | | | | | Compression test | Acoustic |
| $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ | 0.056 | 1720 | 39.5° | 0.194 | 98 | 92.62 |

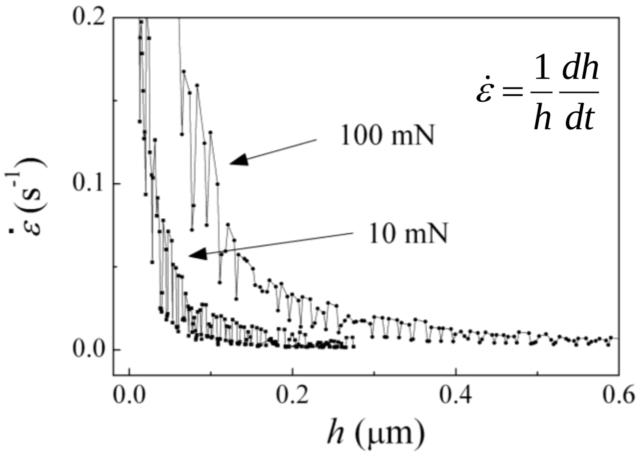
# Results: Quasi-static nanoindentation




- Pop-in events observed during loading.




$P_{Max}$ = 100 mN



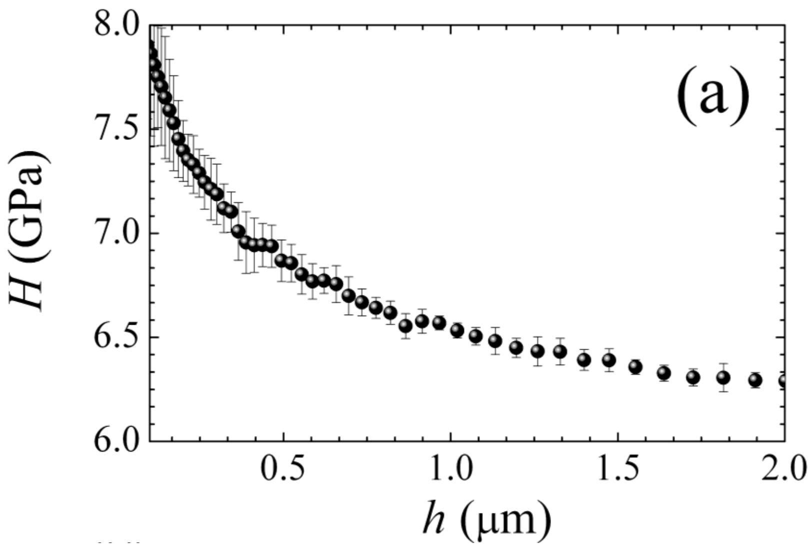

- Inhomogeneous plastic flow expected since:

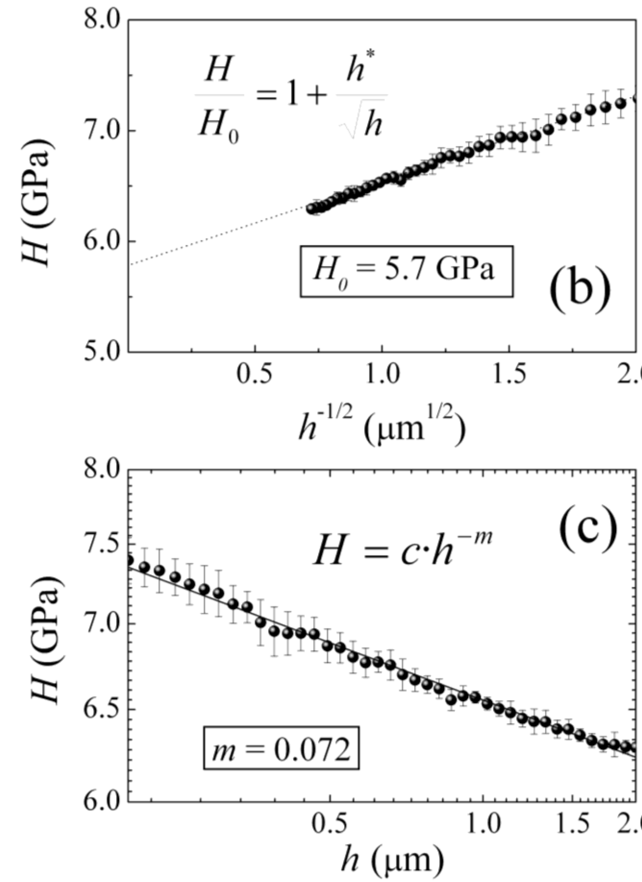
$$\frac{RT}{T_g} = 0.49$$

Deformation map from:
Schuh et al. Acta Mater. 55, (2007) 4067

| H (GPa) | E (GPa) | |
|---|---|---|
| Nanoindentation | Compression test | Nanoindentation |
| 6.9 (10 mN)<br>6.3 (100 mN) | 98 | 105 |

# Results: Dynamic nanoindentation (CSM method)




- **Indentation size effect** (ISE) observed:

H decreases from 7.8 GPa (at 1 mN) to 6.3 GPa at 450 mN. The assyptotic hardness value is 5.7 GPa.

*m* (ISE) lower than for crystalline metals

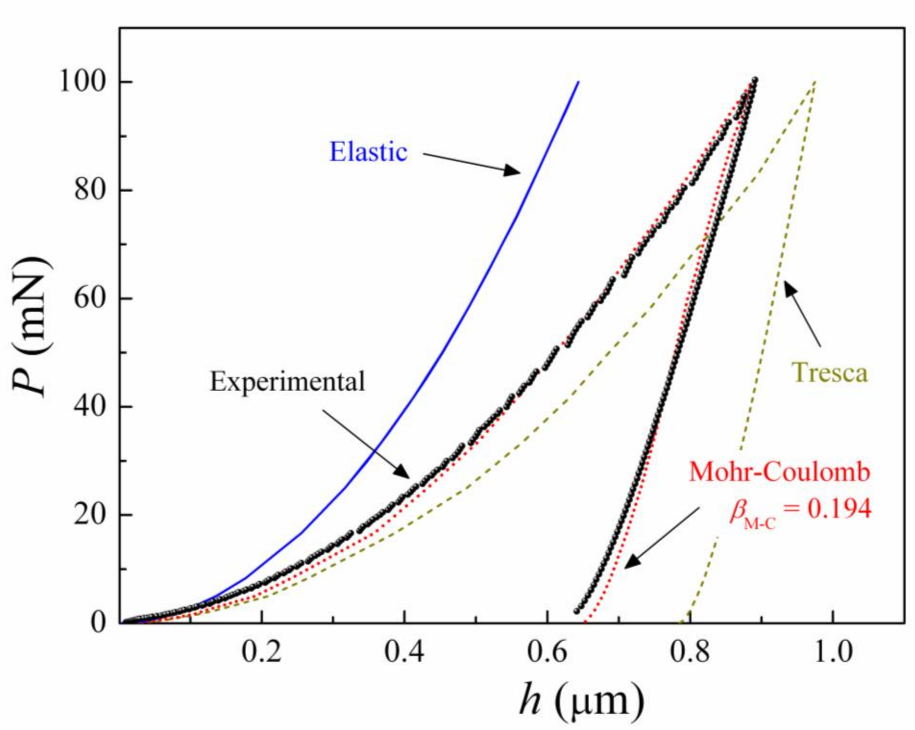
($m_{cryst}$ = 0.1 - 0.3, Manika et al. Acta Mater. 54 (2004) 2049)

# Results: Finite element simulations

Strand7 software, developed by G+D Computing Pty Ltd.

Application of the Mohr-Coulomb yield criterion:

$$\tau_y = \tau_0 - \beta_{M-C}\sigma_n \qquad \beta_{M-C} = \frac{\cos 2\theta_C}{\sin 2\theta_C} = 0.194$$

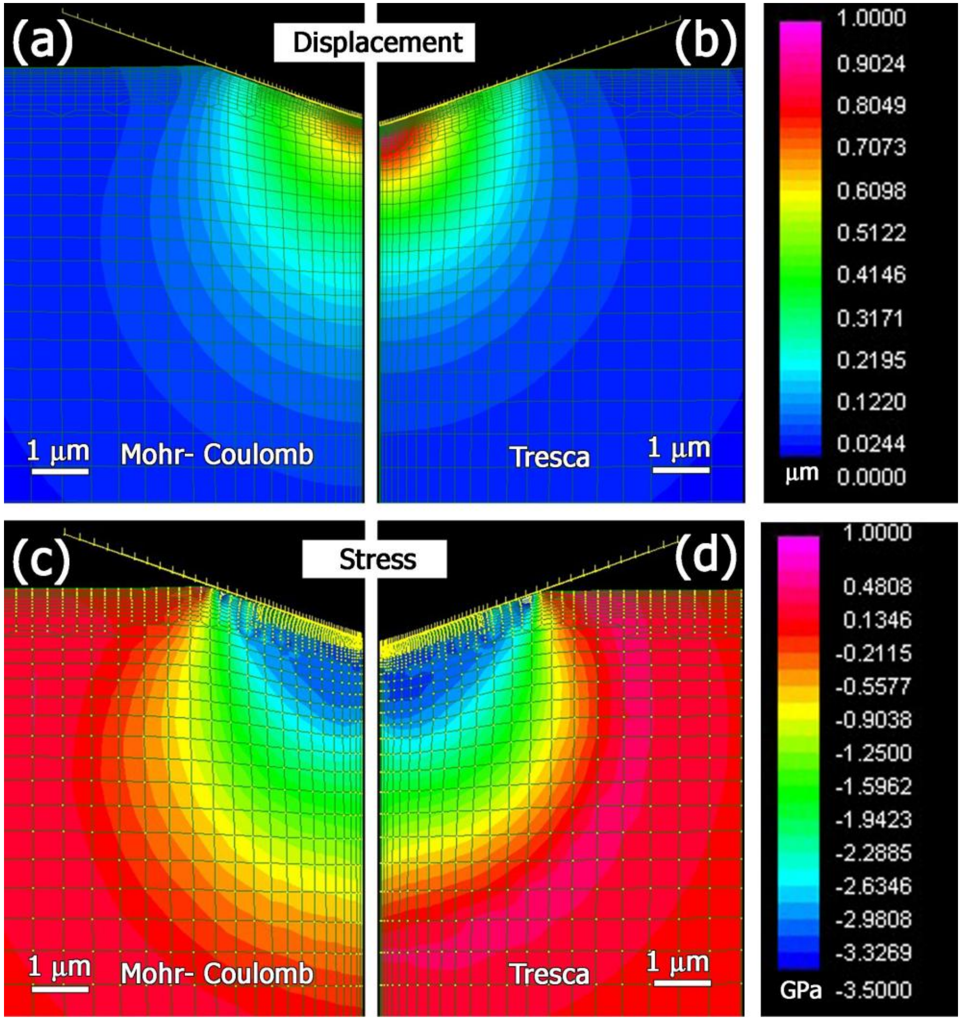



**The simulations confirm pressure-sensitive yielding**

- The elastic (Herzian) solution is far from the experimental data
- The Tresca criterion overestimates the maximum penetration depth
- The Mohr-Coulomb criterion allows for proper adjustment of the experimental nanoindentation data

# Results: Finite element simulations

**Displacement and Circumferential stress ($\sigma_{\theta\theta}$) contour mappings**




- Application of the Mohr-Coulomb yield criterion results in an extended plastic zone beneath the indenter

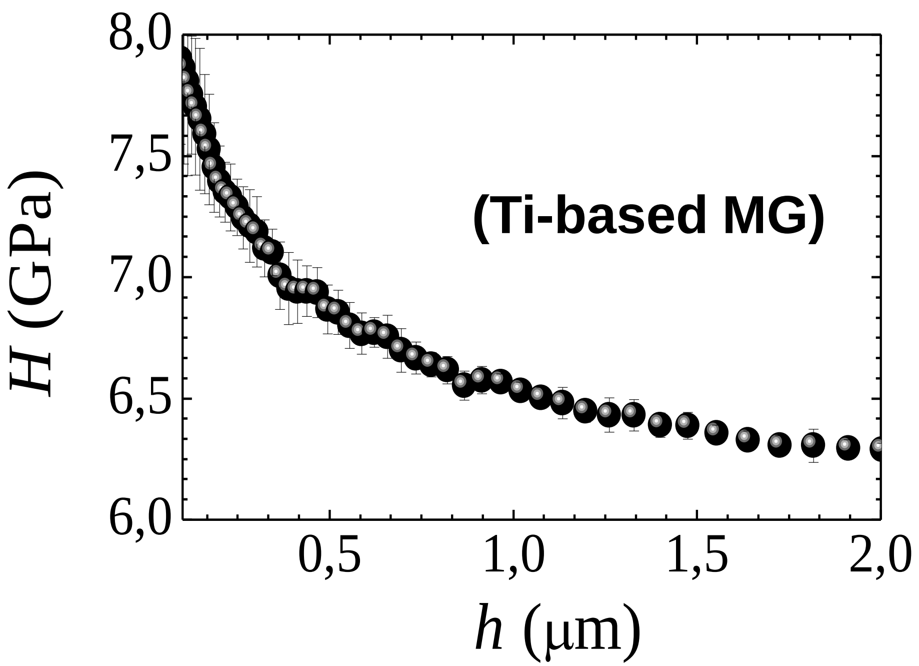
  In agreement with:

  Narashiman Mech. Mater. 36 (2004) 633.

- Similar conclusions about yielding of metallic glasses (obtained from simulations) by:

  Vaidyanathan et al., Acta Mater. 49 (2001) 3781.
  Anand and Su, J. Mech. Phys. Solids, 53 (2005) 1362.
  Schuh et al. Acta Mater. 55 (2007) 4067.

# Results: "Simplified" modeling the ISE using the free volume concept




$$\dot{\gamma} \approx 0.16\ \dot{\varepsilon}_i = 0.16\ \frac{1}{h}\frac{dh}{dt}$$

[Schuh et al., Acta Mater. 2004; 52, 5879]

Application of the Mohr-Coulomb yield criterion:

$$\tau_y = \frac{H}{C}\sin\theta_C\cos\theta_C - \beta_{M-C}\frac{H}{C}\sin^2\theta_C$$

$C = H/\sigma_{y,c}$ = 3.3 is the constraint factor.

$\theta_C$ is the fracture angle (39.5º in this alloy)

$\beta_{M-C}$ is the internal friction coefficient:

$$\beta_{M-C} = \frac{\cos 2\theta_C}{\sin 2\theta_C} = 0.194$$

$$\Rightarrow \quad H \approx 8\tau_y$$

# Results: "Simplified" modeling the ISE using the free volume concept

Flow Equation

$$\dot{\gamma} = 2\Delta f c_f k_{f,0}\left(\frac{\varepsilon_0 v_0}{\Omega}\right)\sinh\left(\frac{\tau\varepsilon_0 v_0}{2k_B T}\right)\exp\left(\frac{-\Delta F_0}{k_B T}\right)$$

$$H \approx 8\tau_y$$

$$H = \frac{16k_B T}{\varepsilon_0 v_0}\sinh^{-1}\left(\frac{\dot{\gamma}\Omega}{2\varepsilon_0 v_0 c_f \Delta f k_{f,0}}\exp(\frac{\Delta F_0}{k_B T})\right)$$

$$\sinh^{-1}(y) = \ln(y+\sqrt{y^2+1}) \approx \ln(2y)$$

for $y >> 1$

$$\frac{dc_f}{dt} \approx a_x \dot{\varepsilon} c_f \ln^2 c_f$$

$$\dot{\varepsilon} = \frac{1}{h}\frac{dh}{dt}$$

$$H = \frac{16k_B T}{\varepsilon_0 v_0}\left(\frac{\Delta F_0}{k_B T} + \ln(\frac{\dot{\gamma}\Omega}{\varepsilon_0 v_0 \Delta f k_{f,0}}) - \ln(c_f)\right)$$

$$\ln(c_f) = \left[\frac{1}{\ln(c_{f,ini})} - a_x \ln(\frac{h}{h_{ini}})\right]^{-1}$$

Relationship between H and h

# Results: Deformation-induced creation of free volume

Flow equation: $\dot{\gamma} = 2\Delta f c_f k_f \left(\frac{\varepsilon_0 v_0}{\Omega}\right) \sinh\left(\frac{\tau \varepsilon_0 v_0}{2k_B T}\right)$

$$\dot{\gamma} \approx 0.16\ \dot{\varepsilon}_i = 0.16\ \frac{1}{h}\frac{dh}{dt}$$

[Schuh et al., Acta Mater. 2004; 52, 5879]

- Assuming $k_f$ and $\Delta f$ remain constant

$$k_f = k_{f,0} \exp\left(\frac{-\Delta F_0}{k_B T}\right)$$

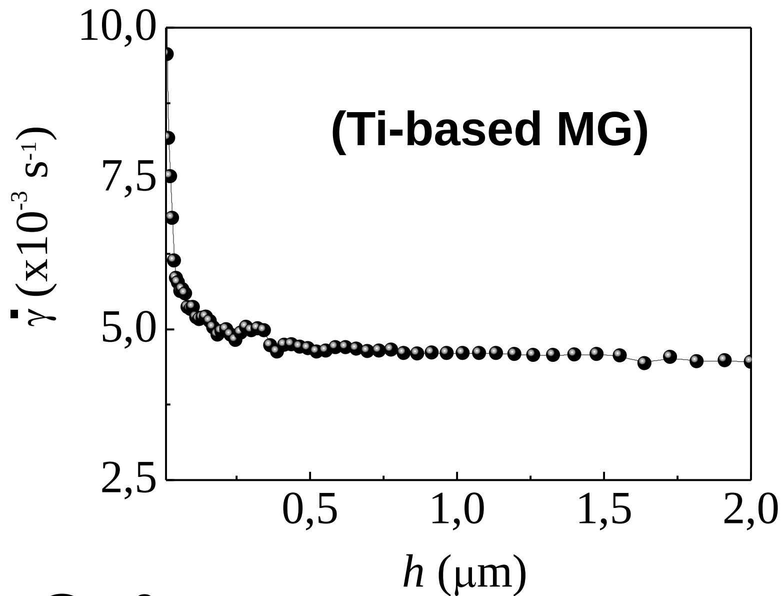
**$c_{f,(h = 2 \mu m)} \approx 9 \cdot c_{f,(h = 0.1\ \mu m)}$**

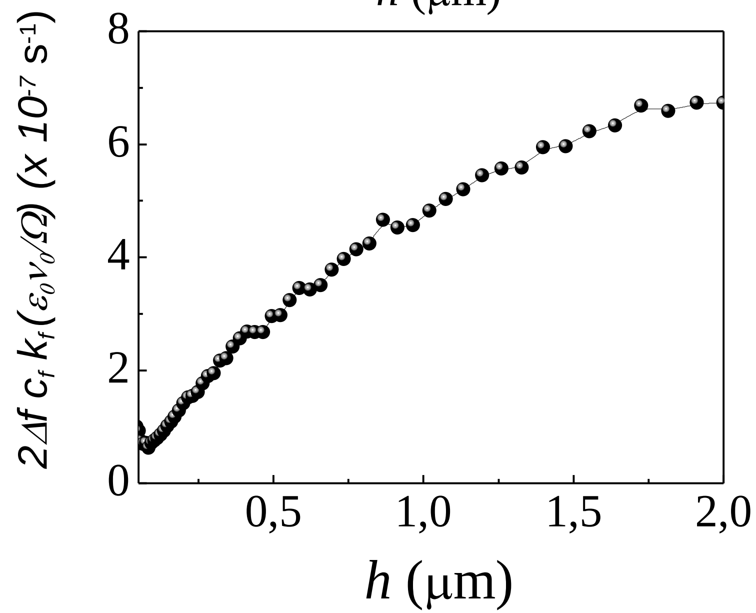
$\Delta F_0$ free energy of a shear flow. Probably decreases during deformation.

**$c_f = \exp(-\gamma v^*/\langle v_f \rangle)$**

- **Increase of reduced free volume, $\langle v_f \rangle/\gamma v^*$, of 10 % (or less).**

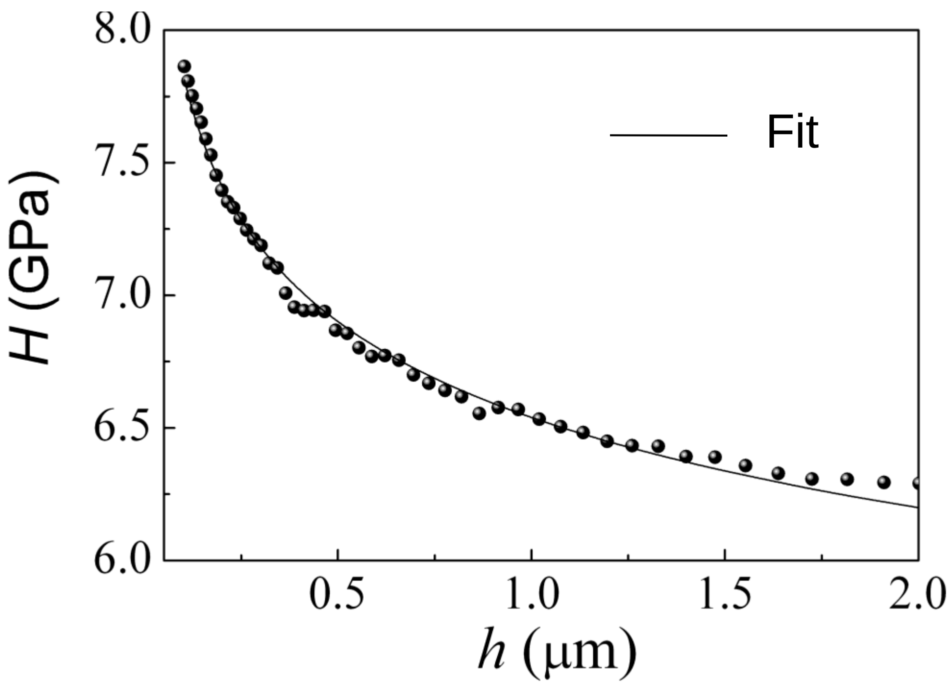
- Of the same order as reported for cold-rolled Zr-based MG (increase of 4.4 %) [Kanugo et al. Intermetallics 2004, 12, 1073].



# Results: “Simplified” modeling the ISE using the free volume concept

| Parameter | Value | Reference |
| --- | --- | --- |
| $\dot{\varepsilon}(h)$ | $\frac{1}{h}\frac{dh}{dt}$ $s^{-1}$ | Calculated |
| $\Omega$ | $1.5 \cdot 10^{-29}$ $m^3$ | Calculated |
| $\varepsilon_0 \nu_0$ | $2 \cdot 10^{-28}$ $m^3$ | van Aken et al., Mater. Sci. Eng. A 278 (2000) 247 |
| $\Delta f$ | 0.8 | Argon, Acta Metall. 27 (1979) 47 |
| $\Delta F_0$ | 1.5 eV | Schuh et al. Acta Mater. 55, (2007) 4067 |
| $k_{f,0}$ | $10^{24}$ $s^{-1}$ | Daniel et al., Mech. Time-Depend. Mat. 6 (2002) 193 |
| $\tau(h)$ | $H(h)$ / 8 | Calculated |
| $h_{ini}$ | 8 nm | Fitted |
| $-(\ln(c_{f,ini}))^{-1}$ | 0.055 | Fitted |
| $a_x$ | 0.006 | Fitted |



# Conclusions

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- $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ exhibits relatively high compressive yield stres and reasonable plasticity, which correlates well with the thermal and elastic properties of the alloy.

- Yielding is influenced by normal stress components acting on the shear plane. This results in a compressive fracture angle lower than 45º.

- Finite element simulations of nanoindentation curves also reveal that the Mohr-Coulomb yield criterion is more appropriate to describe yielding of this material than the pressure-independent Tresca one.

- A mechanical softening behavior is observed by nanoindentation (indentation size effect). This can be modeled, to some extent, using the free volume concept.

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- To Dr. Fischer-Cripps for helpful discussions in the field of nanoindentation.


# References


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- J. Sort et al., J. Mater. Res. 24 (2009) 918.