Microstructural
Kinetics
Group

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CAMBRIDGE

Mechanical Properties of Metallic Glasses

A. L. Greer
Dept. of Materials Science & Metallurgy
University of Cambridge

Emerging Concepts in Glass Physics
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A.R. Yavari
W.H. Wang
Y. Zhang

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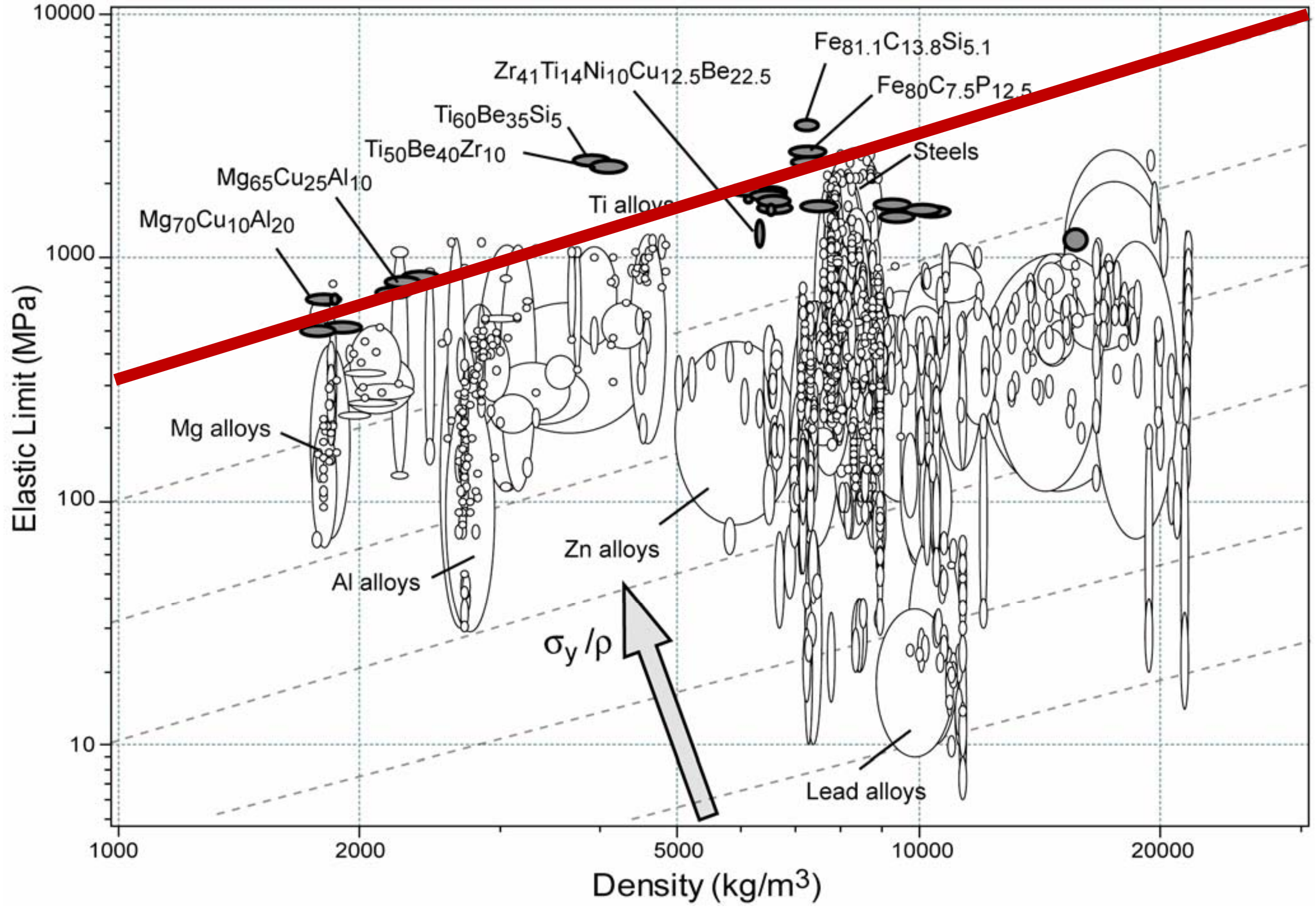
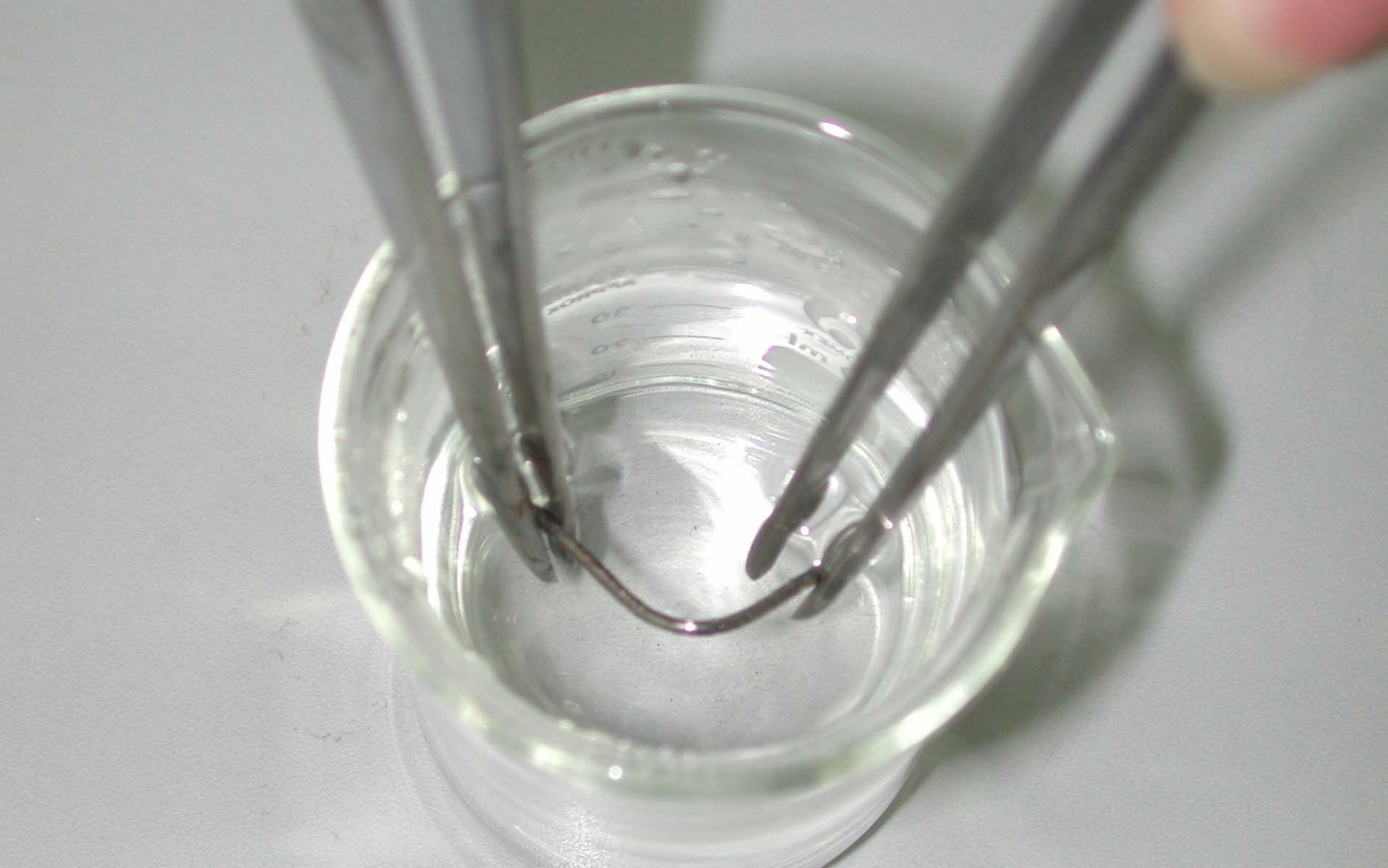
WPI-AIMR, Tohoku Univ., Sendai, Japan

Metallic glasses for structural applications



Elastic limit σ_y plotted against **density** ρ for 1507 metals, alloys, metal-matrix composites and metallic glasses. The contours show the **specific strength** σ_y/ρ.

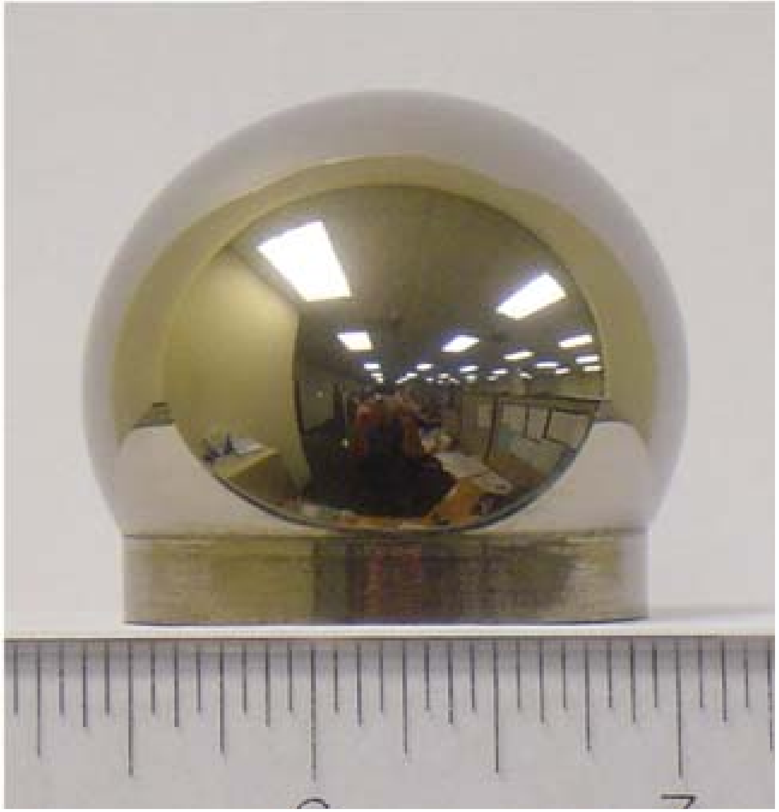
M.F. Ashby & A.L. Greer: *Scripta Materialia* **54** (2006) 321.
(in Viewpoint Set on *Mechanical Behavior of Metallic Glasses*, edited by T.C. Hufnagel)



$Ce_{70}Al_{10}Cu_{20}$ — T_g = 338 K, T_x = 390 K

B. Zhang, D.Q. Zhao, M.X. Pan, W.H. Wang & A.L. Greer:
“Amorphous metallic plastic”, *Phys. Rev. Lett.* **94** (2005) 205502.

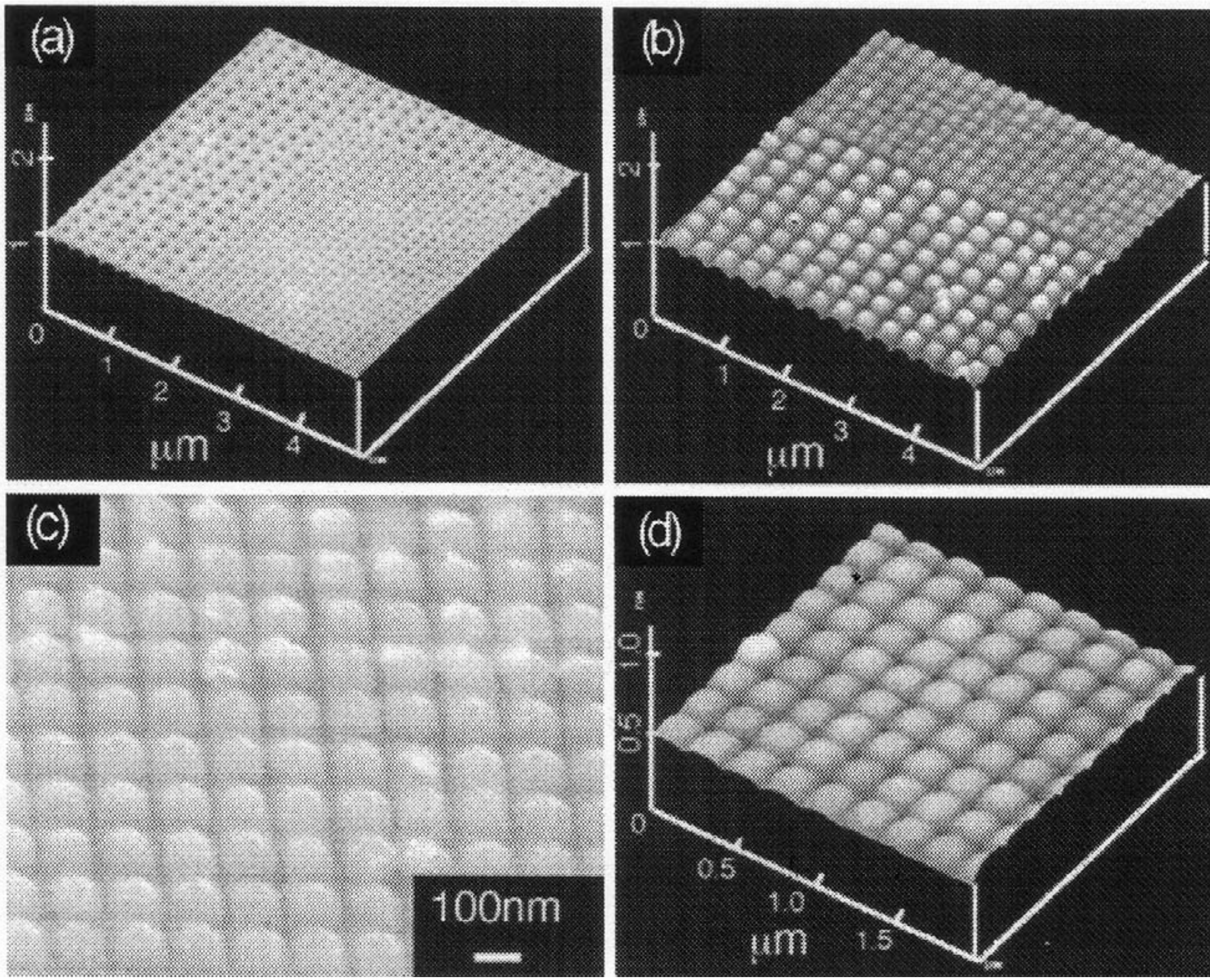

No. 2 POT
ARCH



J Schroers *et al*., *Scripta Mater*. (2007) **57**, 341

Microformability of BMGs

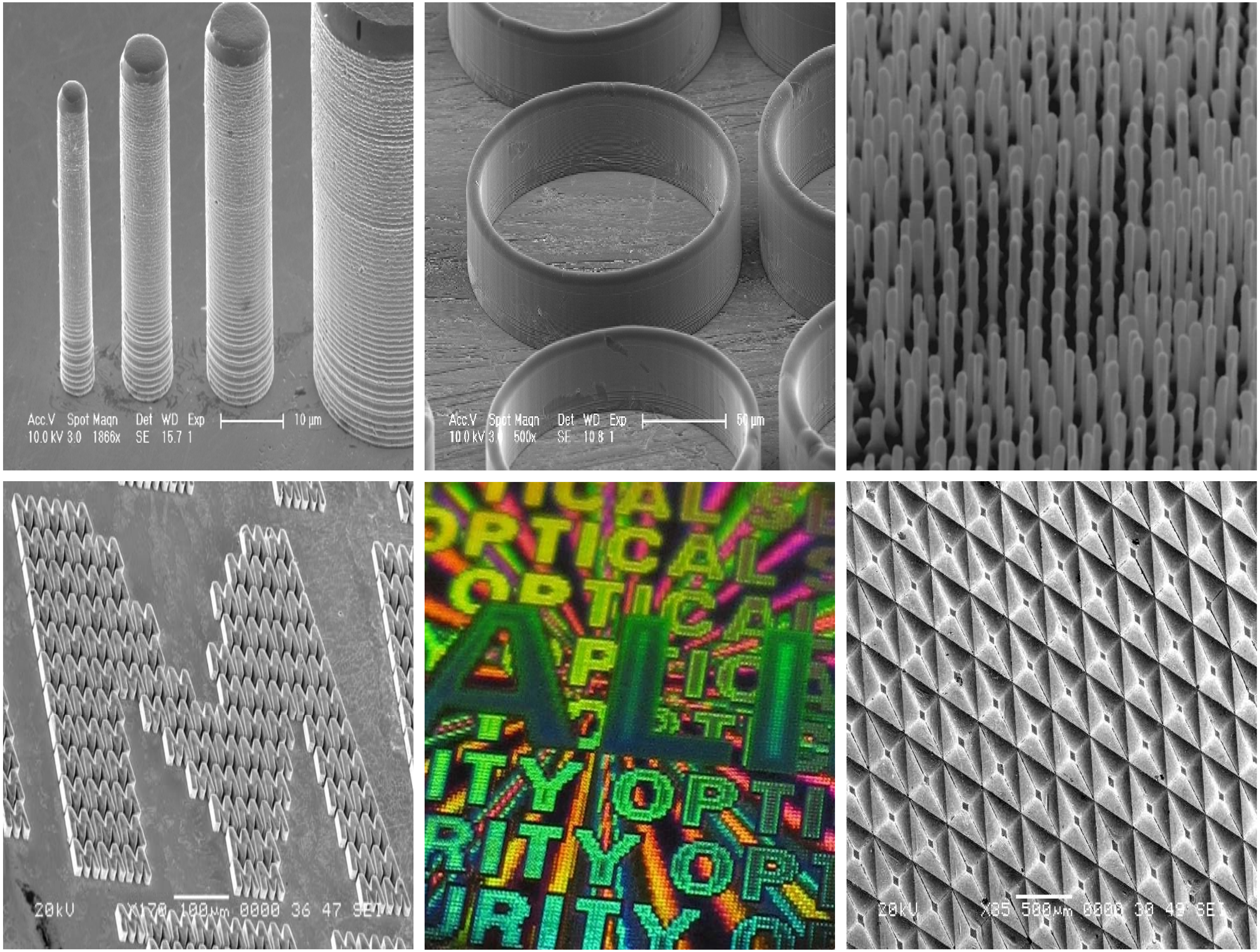
- of interest for micro- & nano-imprinting of surfaces



AFM and SEM images of a patterned (100) Si die and a Pt-based BMG imprinted with the die (10 MPa, 550 K, 300 s)

Y. Saotome et al. “The micro-nanoformability of Pt-based metallic glass and the nanoforming of three-dimensional structures”, *Intermetallics* **10** (2005) 1241.

Surface Replication with BMGs

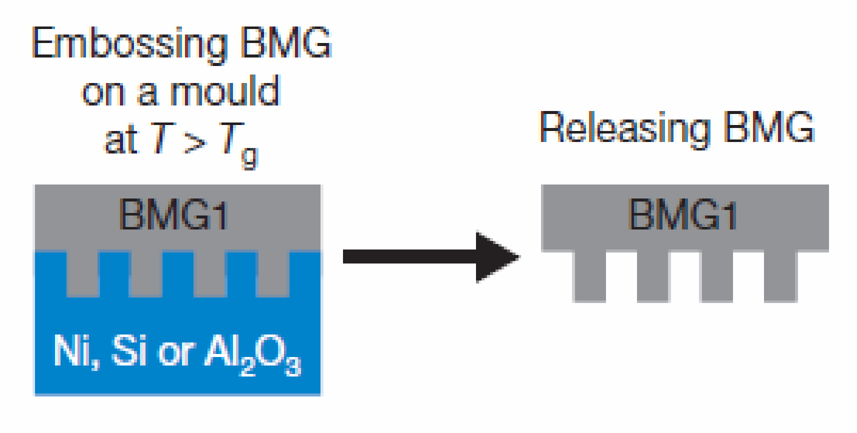


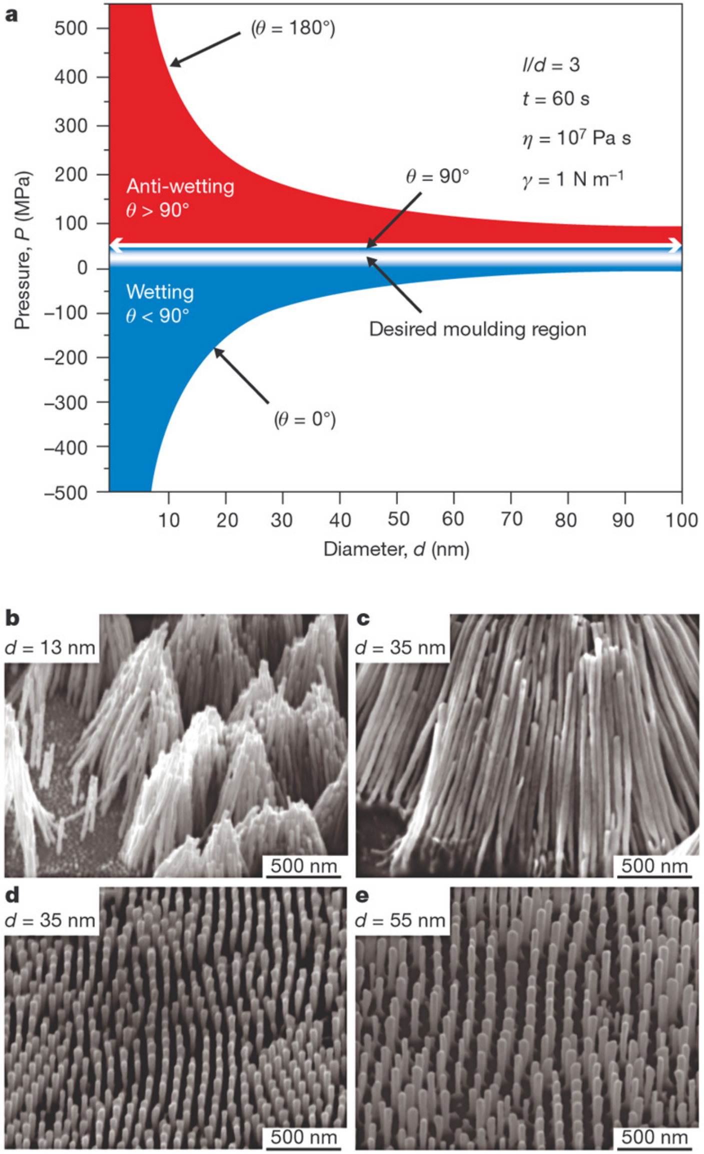
[J. Schroers, *Advanced Materials*, **21** (2010)]

Nanomoulding with amorphous metals

Controlling metallic glass moulding on scales smaller than 100 nm

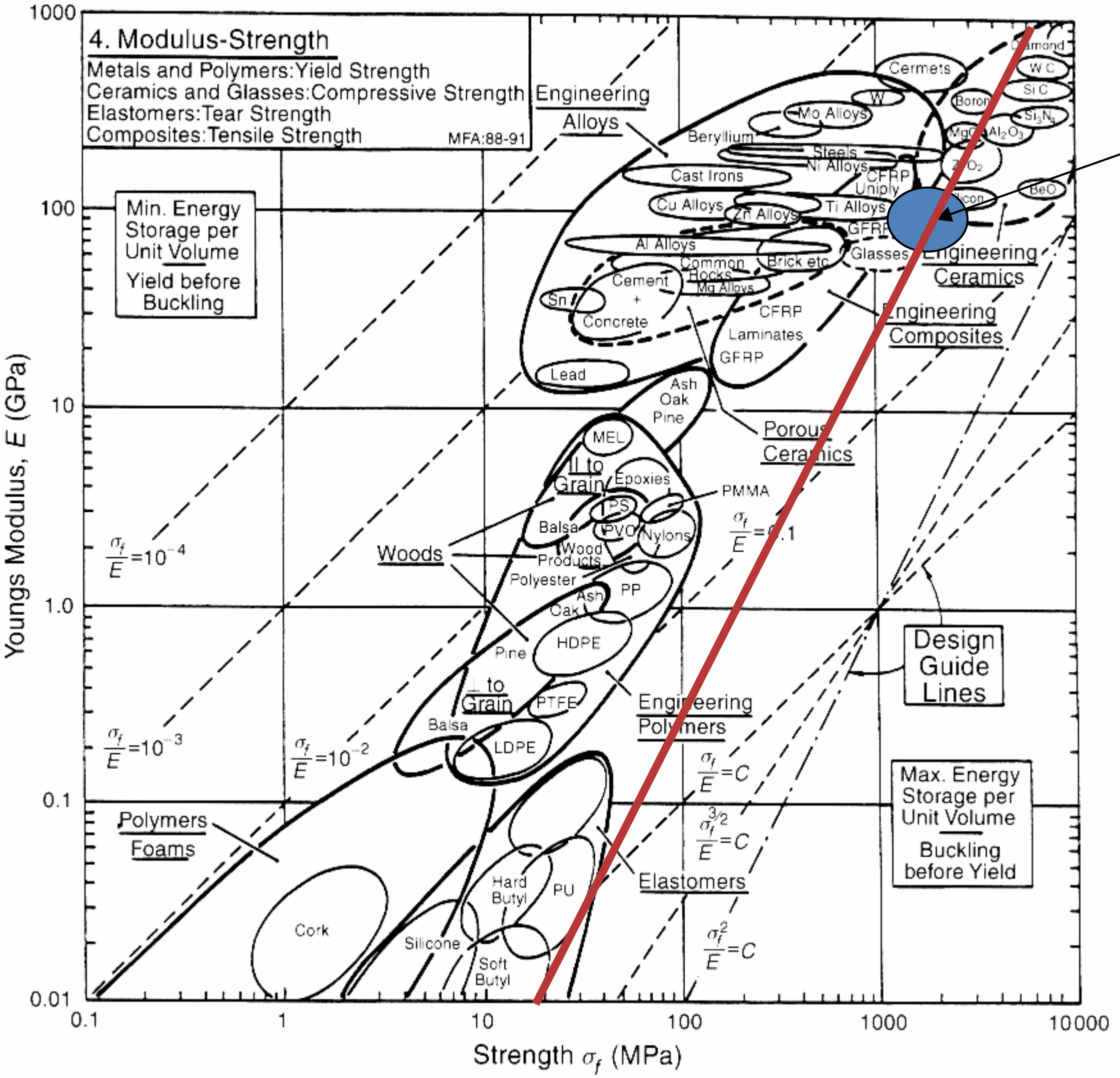
Pt-based BMG





G Kumar, HX Tang & J. Schroers, *Nature* **457**, 868-872 (2009)

nature



metallic glasses

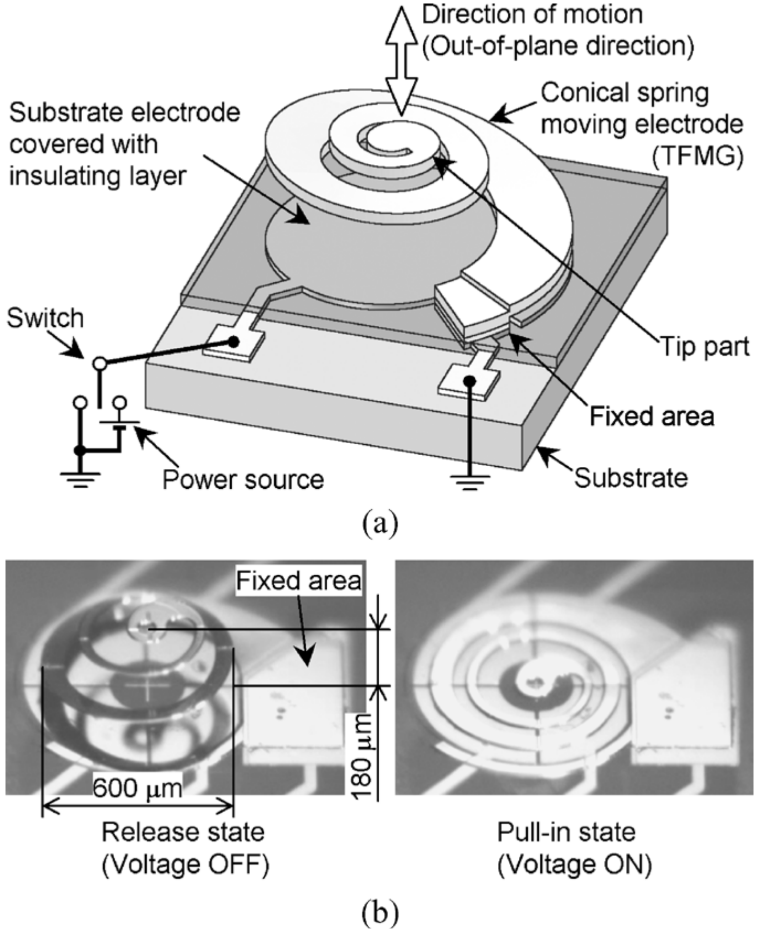
from *Materials Selection in Mechanical Design* (2nd ed.)
M. F. Ashby, Butterworth-Heinemann, 1999

materials for **elastic energy storage** —

want to maximize
σ^2/E

MEMS Applications

A conical spring microactuator with a long stroke of 200 μm normal to the substrate. The spring is a 7.6 μm thick film of $Pd_{76}Cu_7Si_{17}$ metallic glass.



T Fukushige & S Hata, *J. Microelectro. Syst*. (2005) **14**, 243

Plastic Deformation of Metallic Glasses

Ambient temperature / high stress
-- flow localization in shear bands

High temperature / low stress
-- homogeneous viscous flow

F. Spaepen: “A microscopic mechanism for steady state inhomogeneous flow in metallic glasses”, *Acta Metall*. **25** (1977) 407.

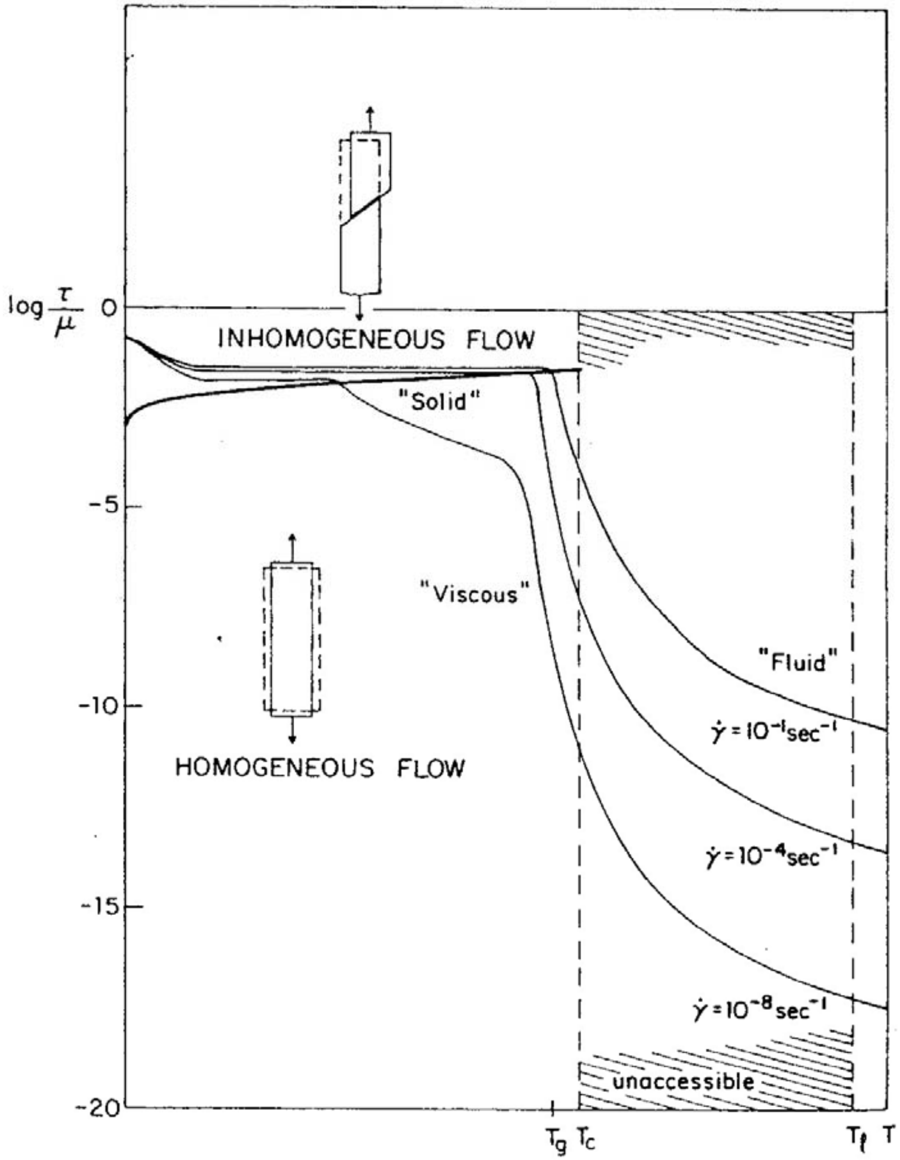
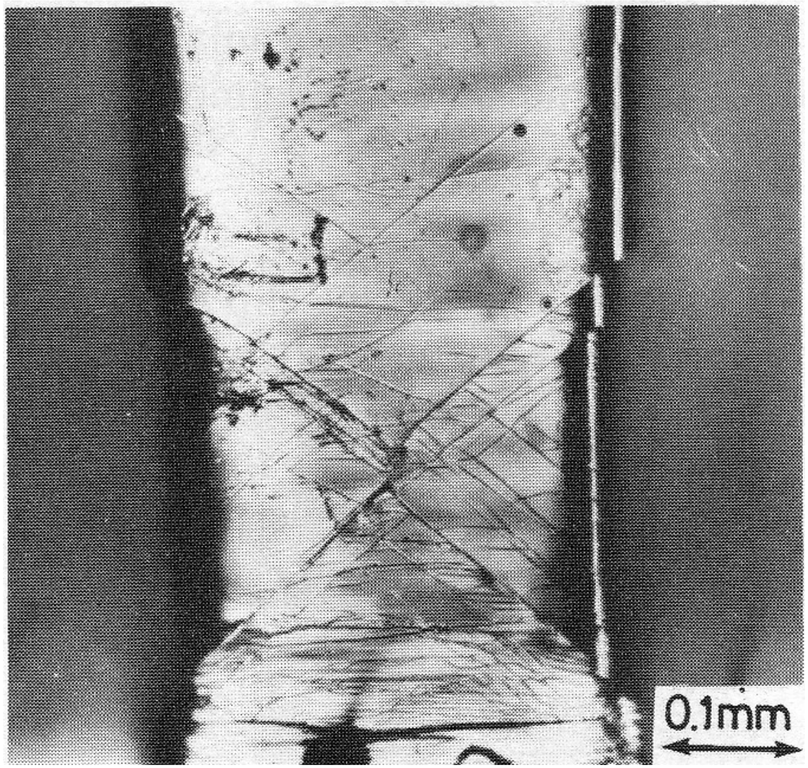


Fig. 2. Schematic deformation map of a metallic glass. The various modes of deformation are indicated.

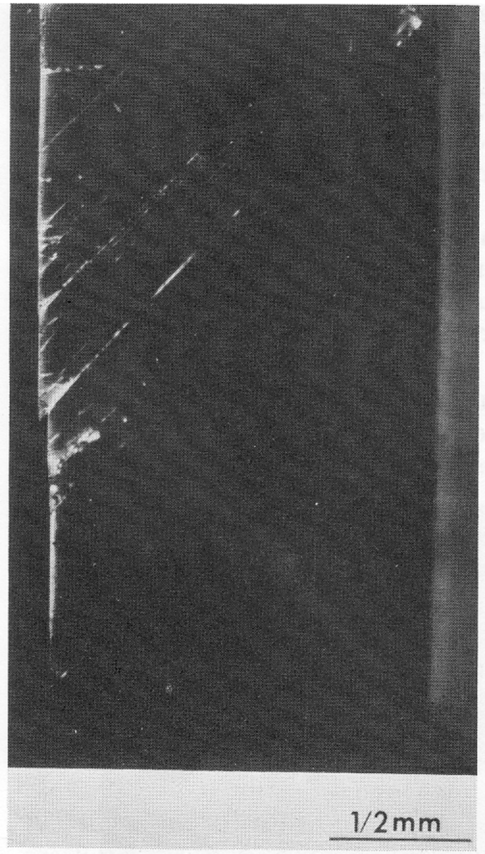
Plastic deformation of a thin plate of a thin plate of $Pd_{77.5}Cu_6Si_{16.5}$ glass in tension. **Shear bands** are consistent with **work-softening**.



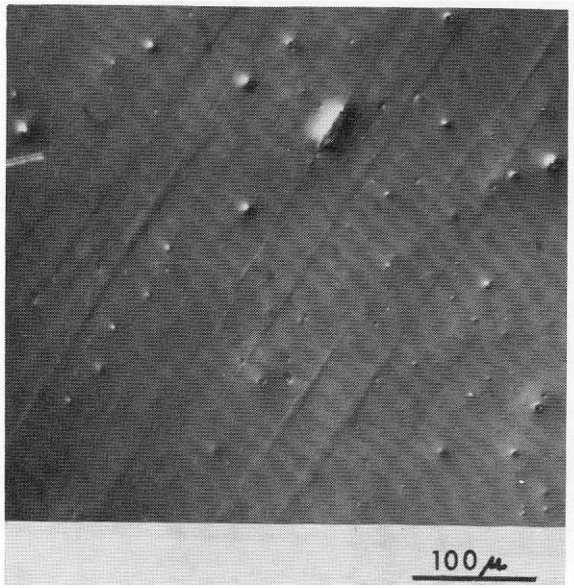
H. Kimura, PhD Thesis (1978) Tohoku Univ.

Shear bands

— residual change of structure after deformation



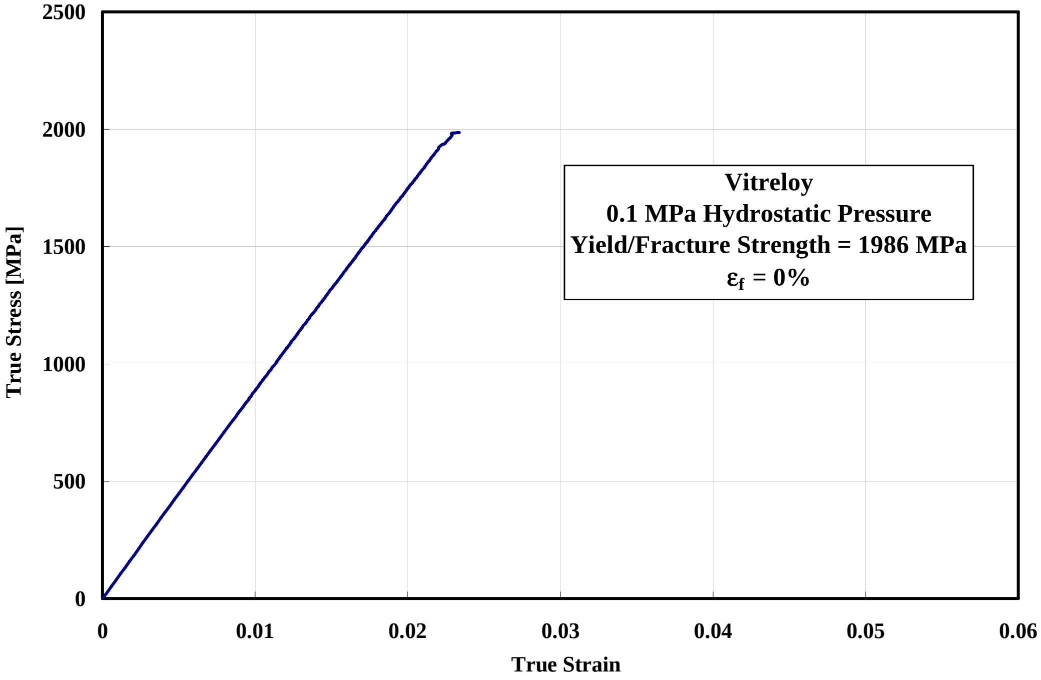
Preferential etching on polished surface



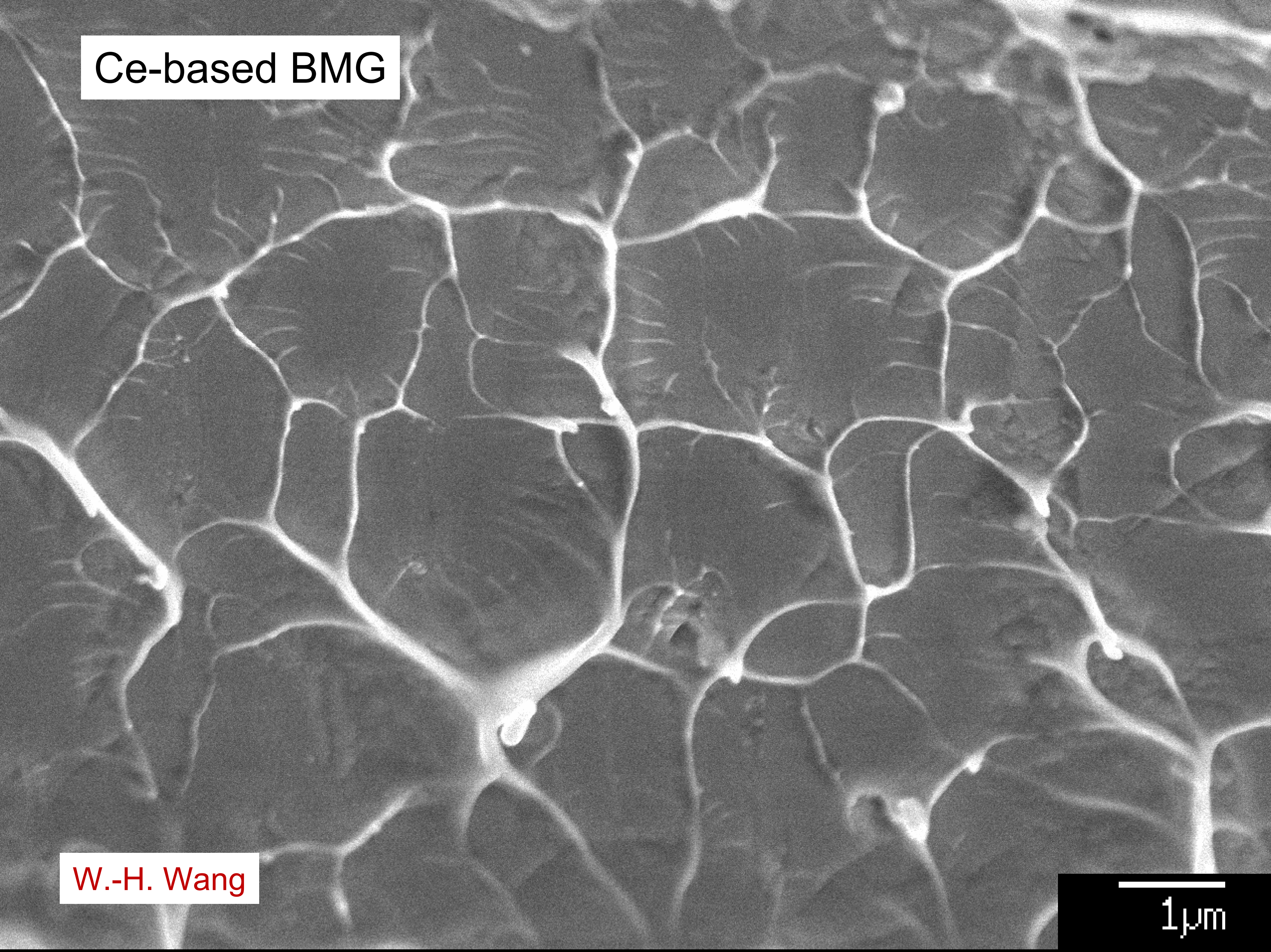
After reshaping and electropolishing, deformation resumes on pre-existing shear bands

C.A. Pampillo & H.S. Chen
Mater. Sci. Eng. **13**, 181-188(1974).

J.J. Lewandowski



At ambient temperature, metallic glasses in tension can **appear macroscopically brittle**, despite extensive local deformation in the shear bands.



Ce-based BMG

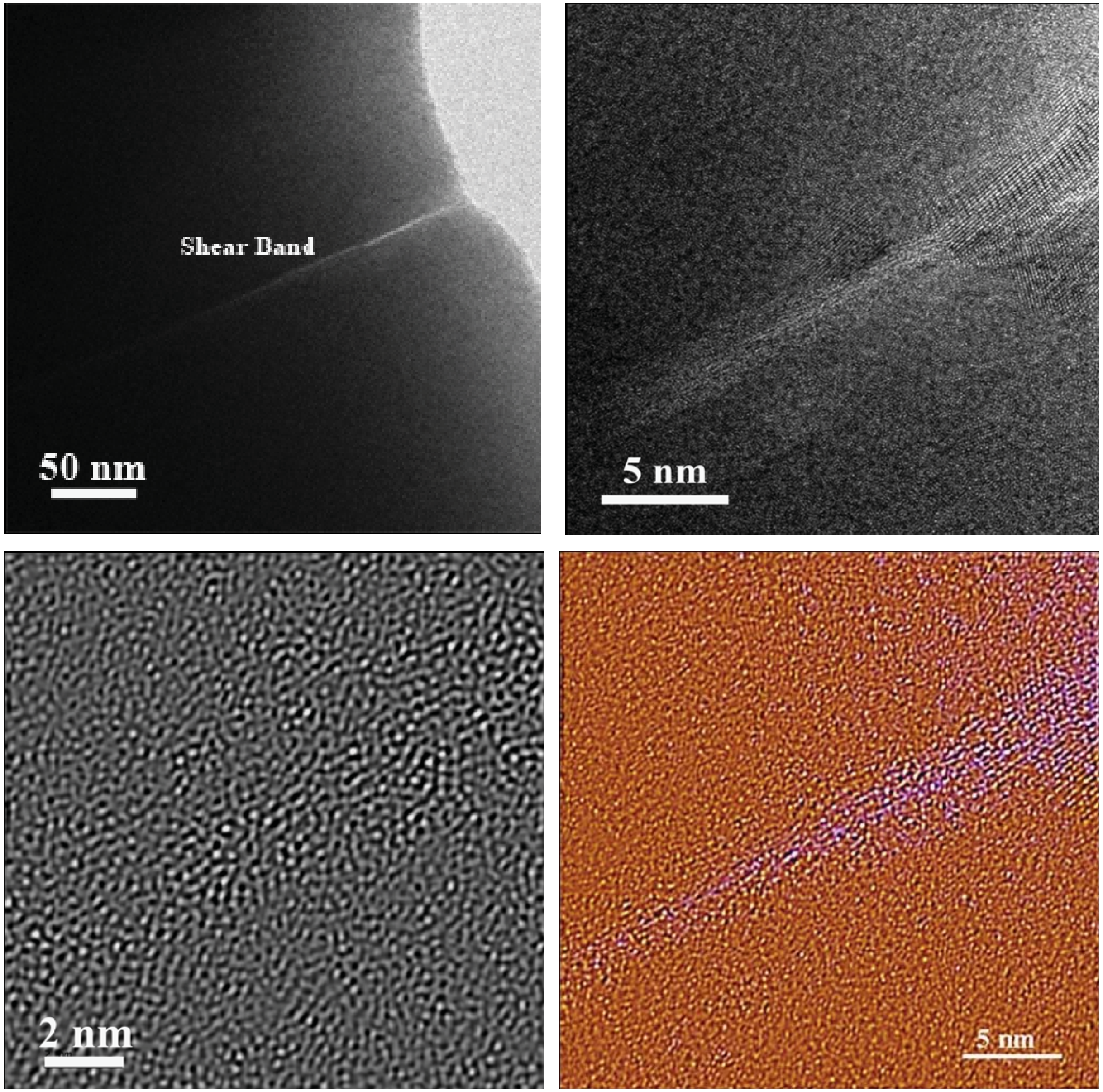
W.-H. Wang

Shear banding

— is a symptom of the **work-softening** that leads to near-zero ductility, and is the major mechanical-property impediment to wider application of metallic glasses.

Questions about shear bands:

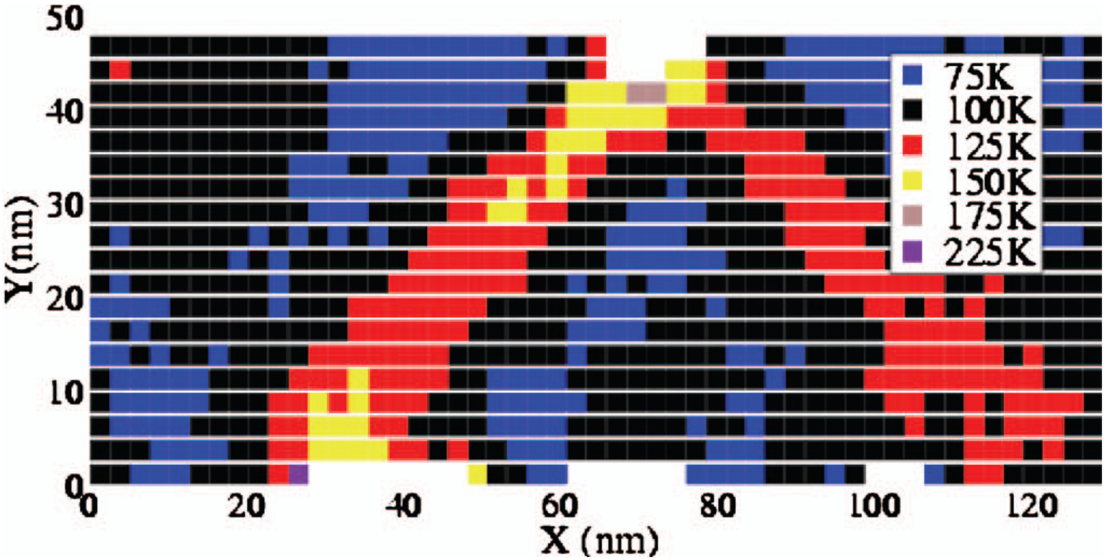
- how thick are the shear bands?
- what is the work dissipated in shear?
- how fast is the shear?
- how large is the hot zone around a shear band?
- what is the state of the material in the bands during/after shear?
- how can shear-banding be controlled to optimize properties?



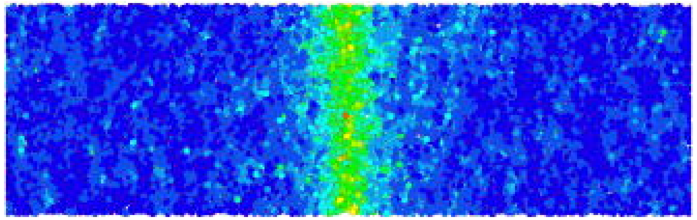
M. Chen, A. Inoue, W. Zhang & T. Sakurai: "Extraordinary plasticity of ductile bulk metallic glasses", *Phys. Rev. Lett.* **96** (2006) 245502.

Molecular-dynamics simulations

— also show a shear-band thickness of ~10 nm



N.P. Bailey, J. Schiøtz & K.W. Jacobsen, *Phys. Rev. B* **73** (2006) 064108.



Q.-K. Li & M. Li, *Appl. Phys. Lett*. **88** (2006) 241903.

Heating at Shear Bands in Metallic Glasses

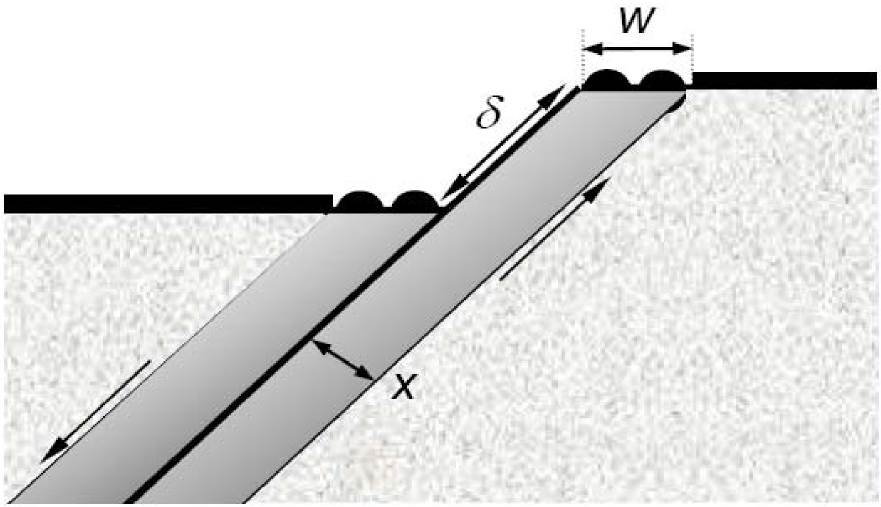
TEM shows that the shear is sharply localized —
— thickness of shear band = 10 to 20 nm

The origins of localization remain controversial — structural change, or temperature rise?

Measurements of temperature rise **0.4 K to 1000 K**

Predictions of temperature rise **40 K to 1000 K**

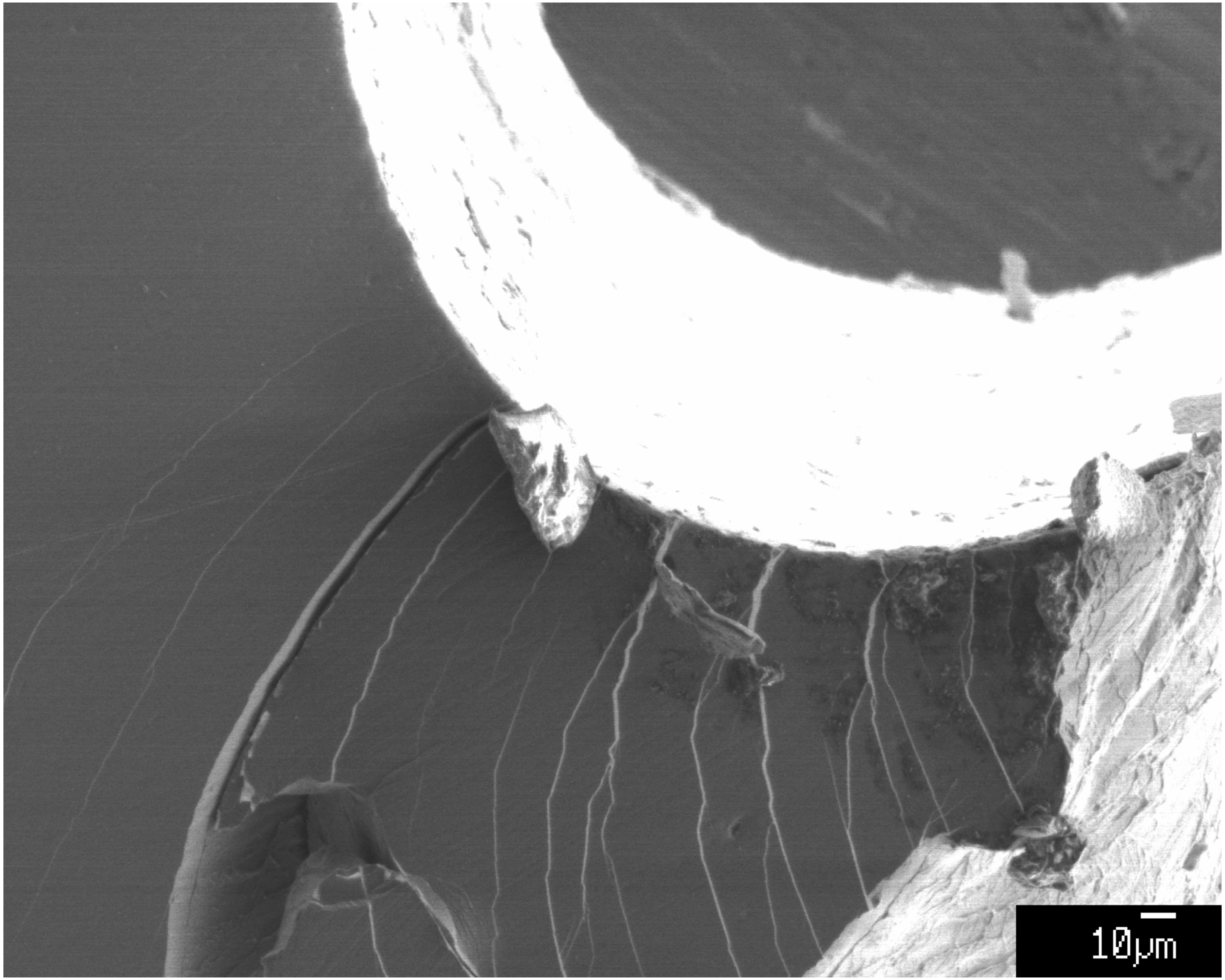
The fusible-coating method



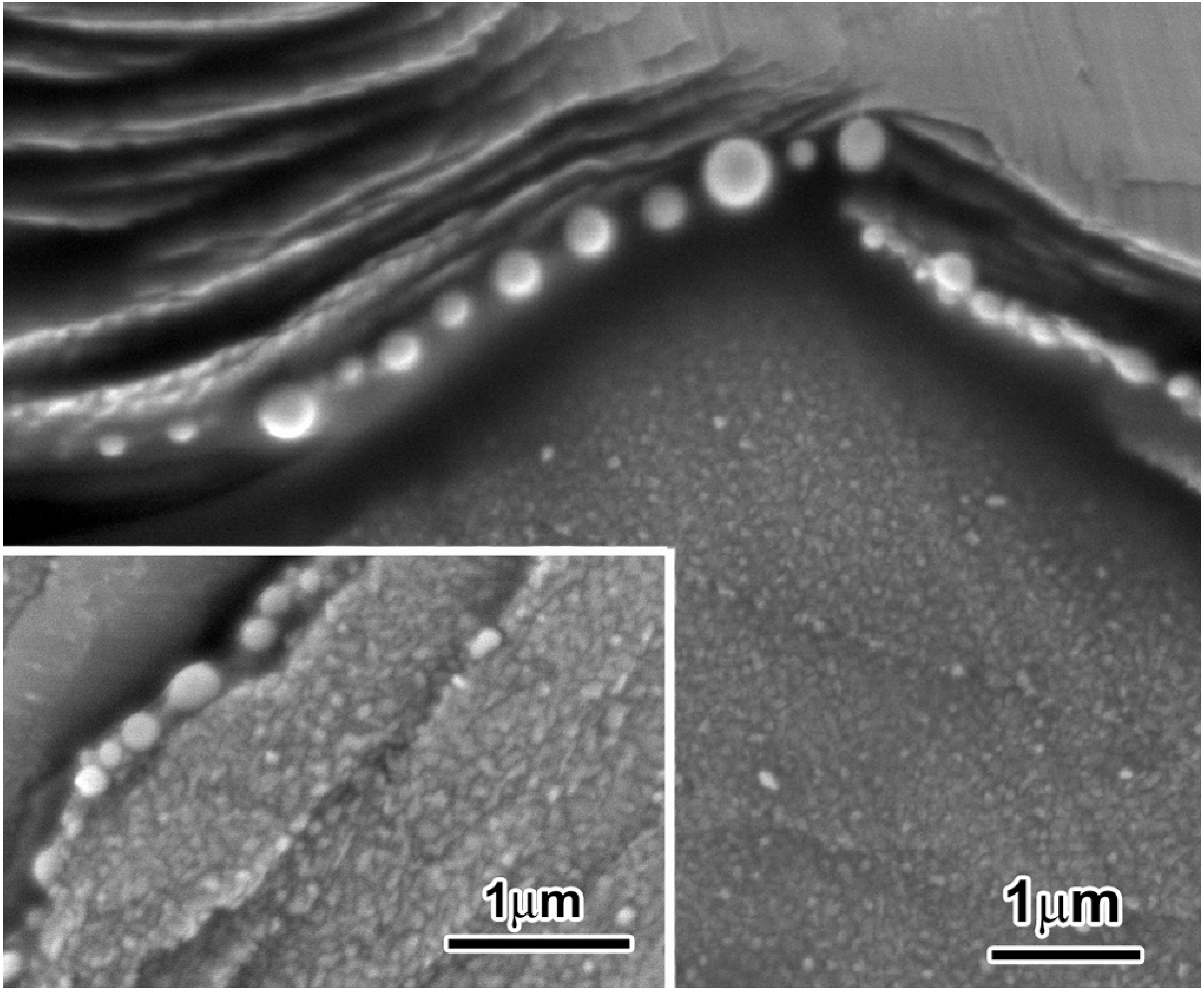
The operation of a shear band in a BMG generates a hot plane and melts the coating (of tin). The total work done by shear is proportional to the offset δ.

J.J. Lewandowski & A.L. Greer: *Nature Materials* **5** (2006) 15.

Test of method on **Vitreloy 1** ($Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$)

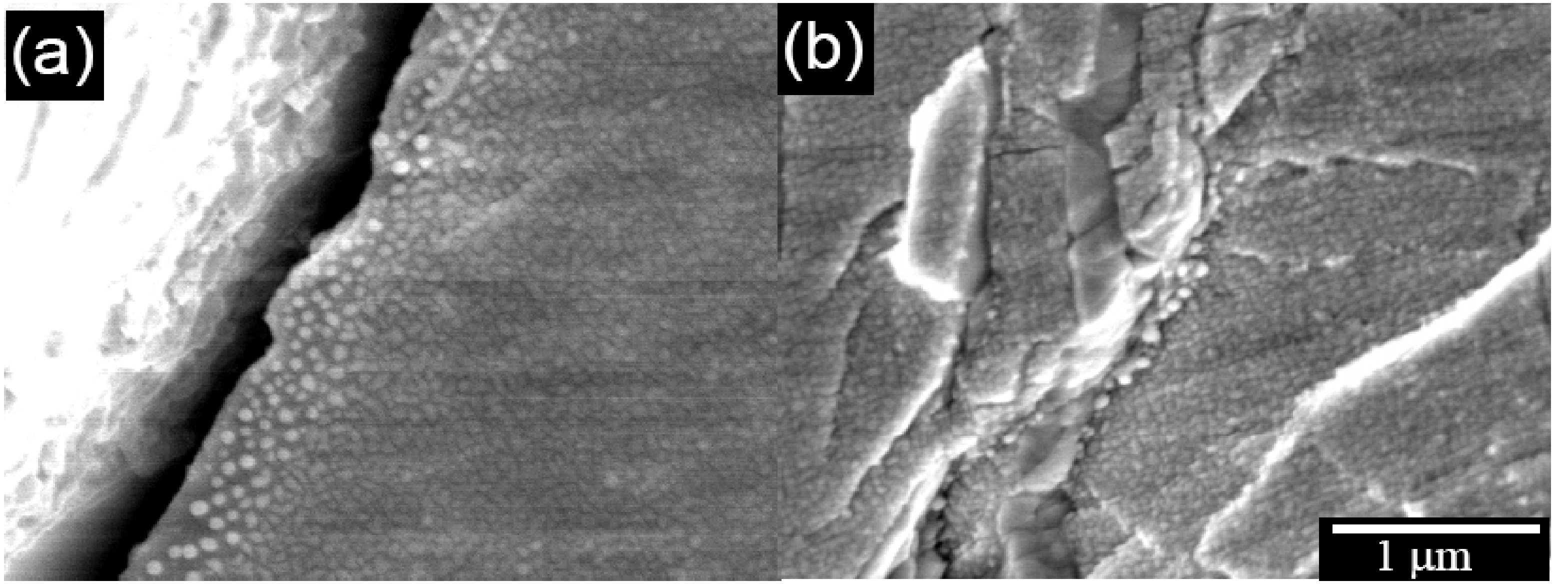


J.J. Lewandowski & A.L. Greer



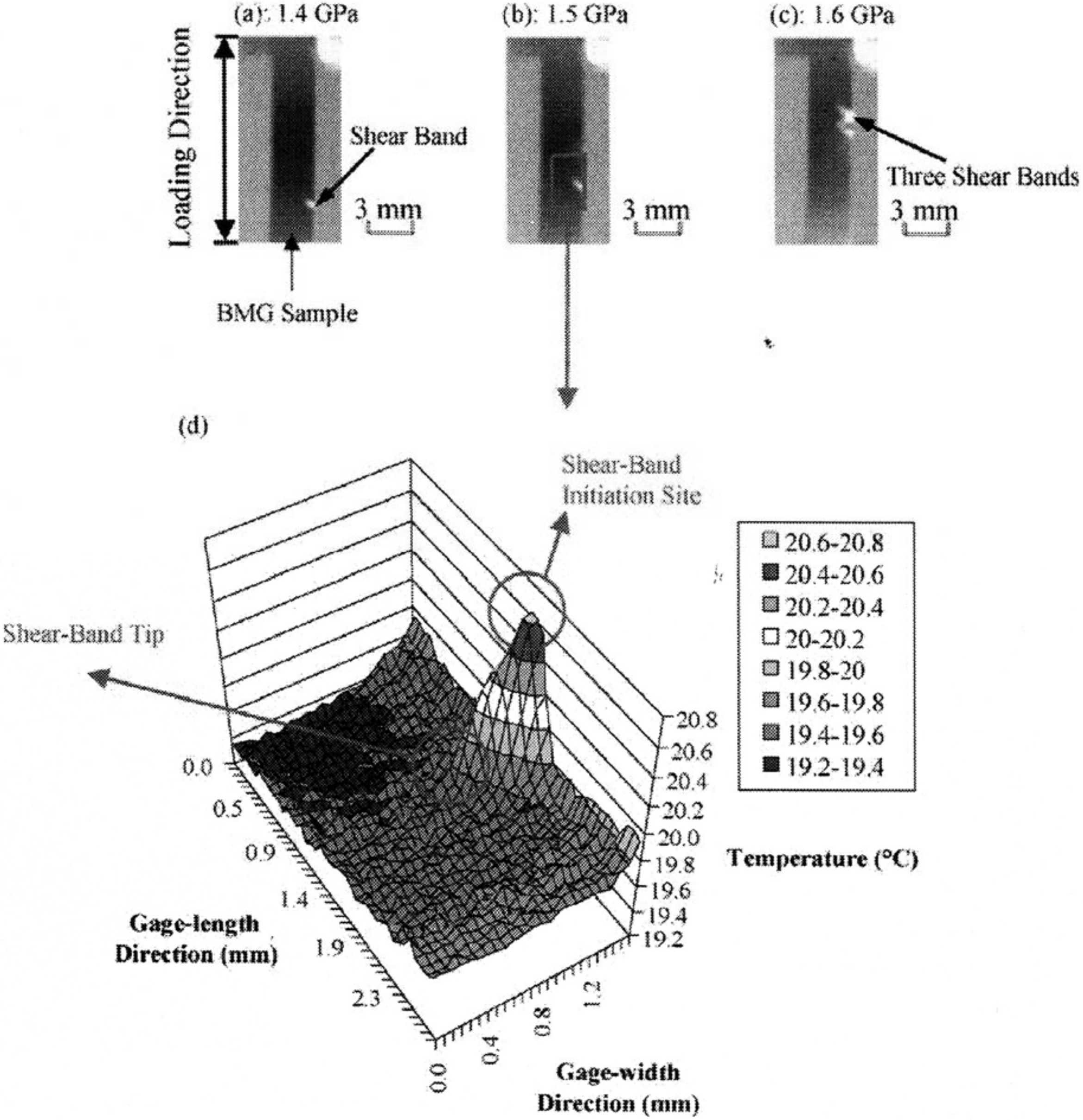
J.J. Lewandowski & A.L. Greer: *Nature Materials* **5** (2006) 15.

Local melting of a tin coating at shear bands in other BMGs



$(Cu_{50}Zr_{50})_{92}Al_8$ $La_{55}Al_{25}Cu_{10}Ni_5Co_5$

Y. Zhang, N.A. Stelmashenko, Z.H. Barber, W.H. Wang, J.J. Lewandowski & A.L. Greer: "Local temperature rises during mechanical testing of metallic glasses", *J. Mater. Res.* **22** (2007) 417.



Average measured temperature rise in shear bands = 0.4 K (for observed width of 0.15 mm)

B. Yang, P.K. Liaw, G. Wang, M. Morrison, C.T. Liu, R.A. Buchanan & Y. Yokoyama: “In-situ thermographic observation of mechanical damage in bulk-metallic glasses during fatigue and tensile experiments”, *Intermetallics* **12** (2004) 1265.

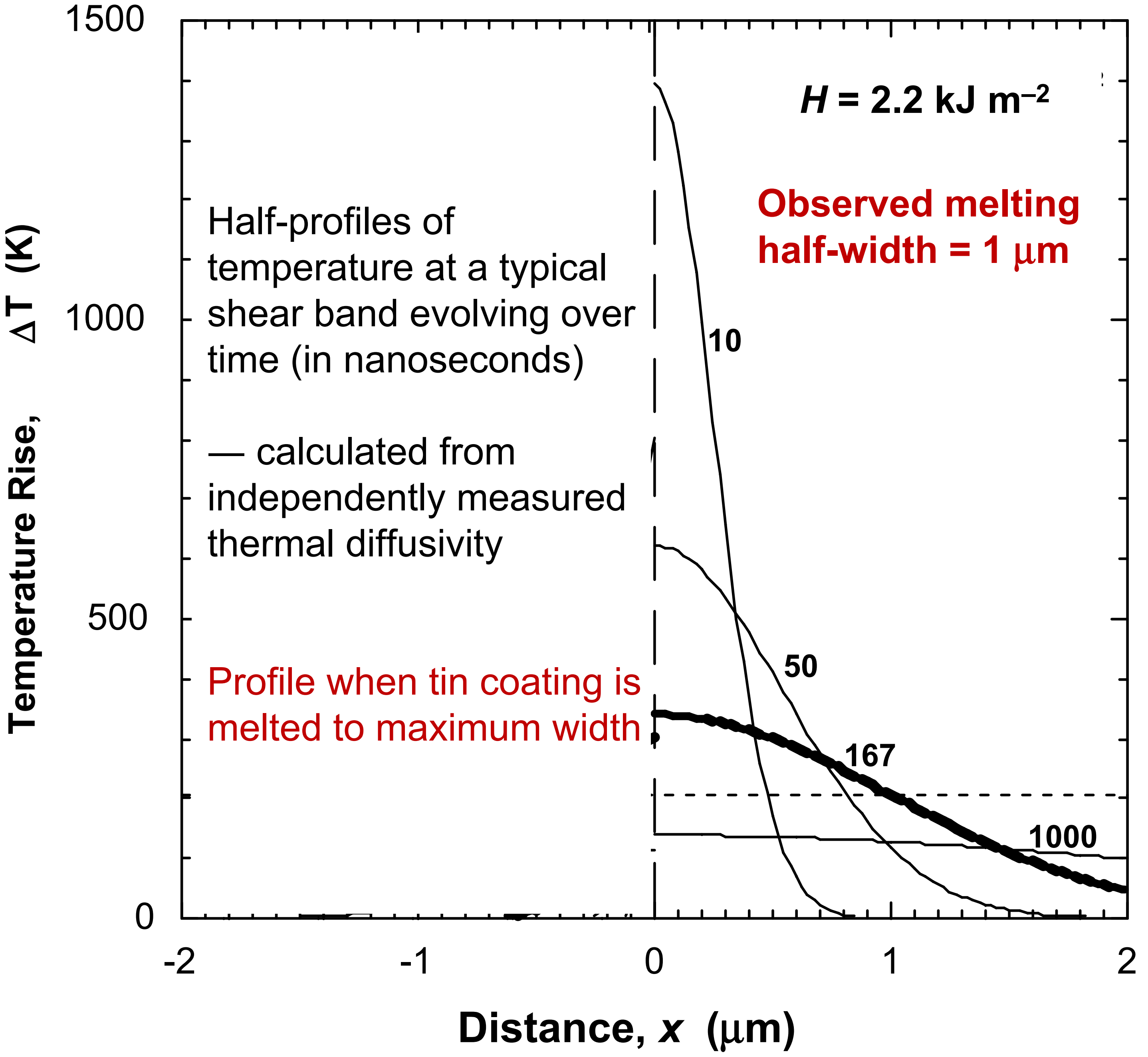
Resolution of the fusible-coating method

- temporal resolution ≈ thermal diffusion time for coating thickness including latent heat of melting, the resolution ≈ **30 ps**

- spatial resolution ≈ scale of islands ≈ **100 nm**

In contrast for direct infrared measurements the best reported resolution combinations are —

• for imaging	**1.4 ms**	**~11 μm**
• for single detector	**~10 μs**	**100 μm**



Observed melting half-width = 1 μm

Half-profiles of temperature at a typical shear band evolving over time (in nanoseconds)

— calculated from independently measured thermal diffusivity

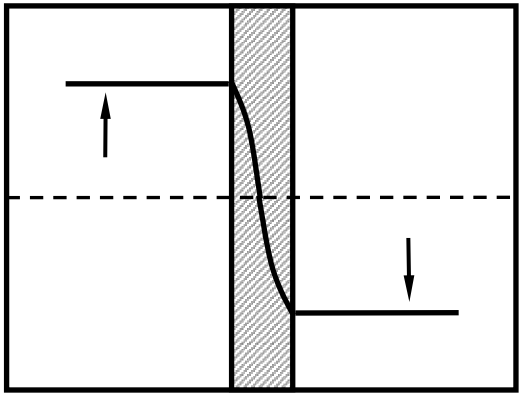
Profile when tin coating is melted to maximum width

Length scales and times associated with shear-band heating

observed half-width of melted zone	**200 nm**	**1 μm**
calculated heat content of shear band, H (**$\mathbf{J\ m^{-2}}$**)	**0.4**	**2.2**
time at melting limit (**ns**)	**7**	**167**
shear offset calculated from H and τ_y (**μm**)	**0.8**	**4.3**
[assumed shear velocity = 206 $\mathrm{m\ s^{-1}}$ (~ 10% transverse sound veloc.)]		
lower-bound estimate of shear duration, δt (**ns**)	**3.9**	**20.9**
upper-bound estimate of temperature rise at shear-band centre (**K**)	**743**	**1990**
thermal diffusion length at end of shear (**nm**)	**500**	**1000**

[measured (from TEM) thickness of shear band = **10 to 20 nm**]

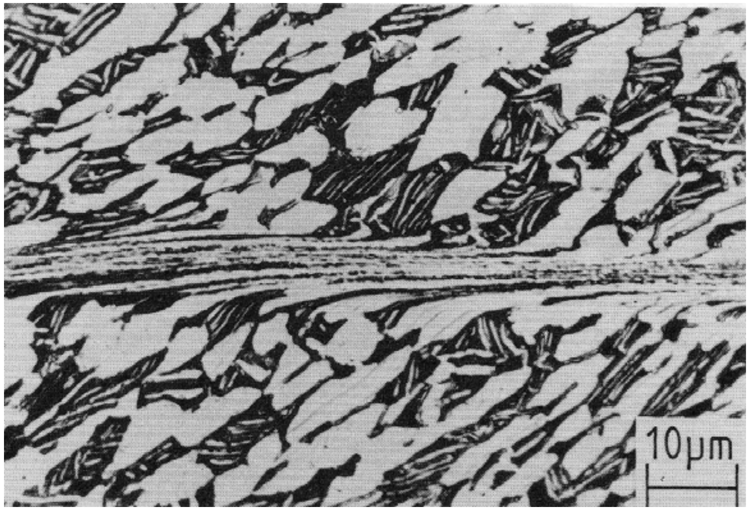
How to understand the thickness of shear bands?



TEM studies consistently suggest a shear-band thickness of ~10 nm

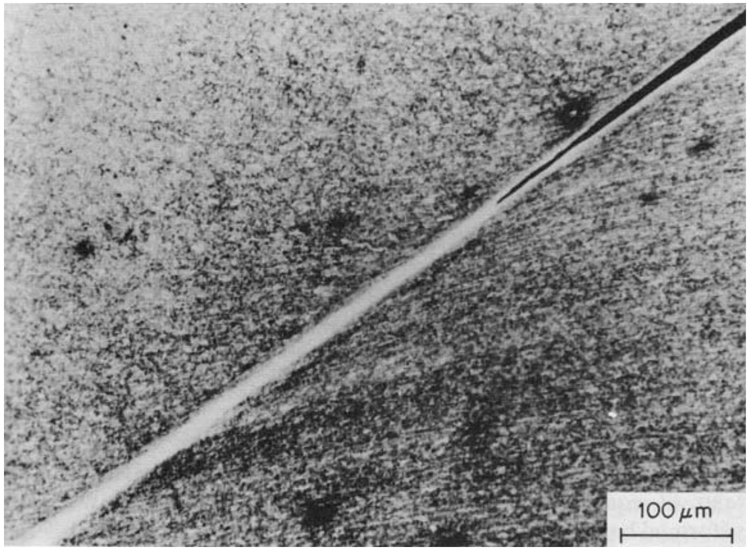
Y. Zhang & A.L. Greer: "Thickness of shear bands in metallic glasses", *Appl. Phys. Lett.* **89** (2006) 071907.

Adiabatic shear bands in conventional (polycrystalline) engineering alloys



α-β titanium alloy

S.P. Timothy & I.M. Hutchings (1984)



martensitic steel

R. Dormeval (1987)

- in conventional adiabatic localization: the harder the material, the thinner the shear band
- in the absence of any hardening as in BMGs, we expect the shear-band thickness to fall to an absolute minimum

Shear Localization in Powders and Soils

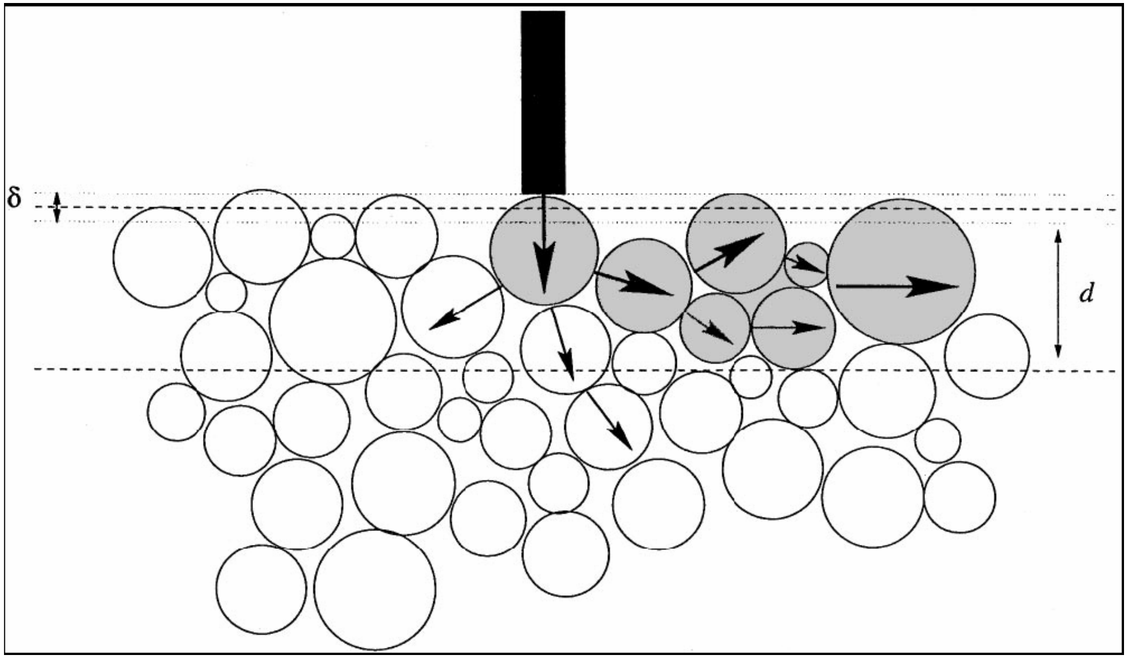
- powders and soils can show unstable dilatation and softening under shear
- no thermal effects
- studies of shear bands in rounded sands show thicknesses ≈ 10 x average particle diameter

[K. H. Roscoe, *Géotechn.* **20** (1970) 129]
[X. B. Lu et al., *Int. J. Numer. Anal. Meth. Geomech.* **28** (2004) 1533]

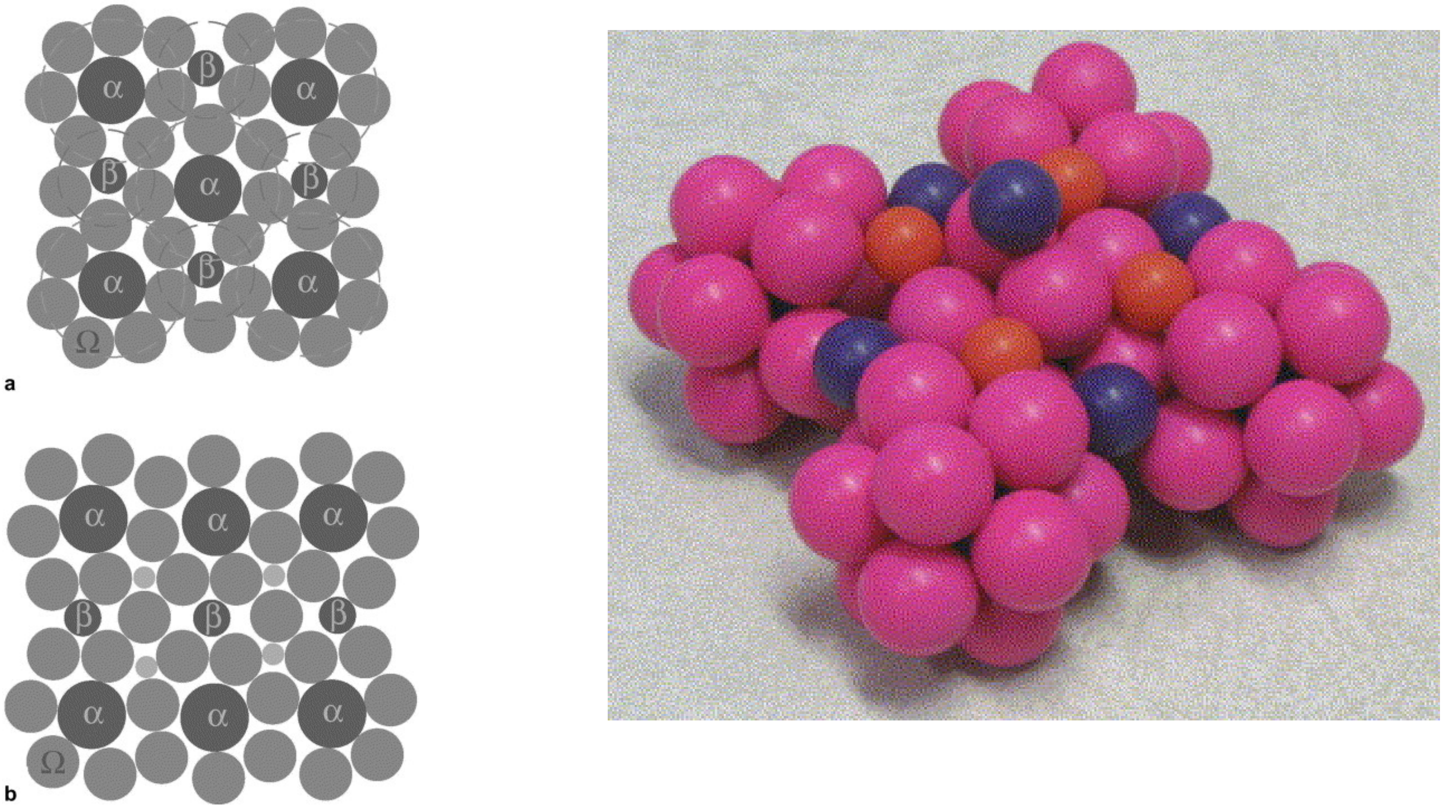
In Metallic Glasses?

- d_{Zr} = 0.31 nm, so predicted shear-band thickness is 3.1 nm
- actual thicknesses are 10 to 20 nm, so perhaps we should consider stable clusters

The finite thickness of shear bands can be analysed in terms of the chain of particle contacts necessary to generate dilatation.

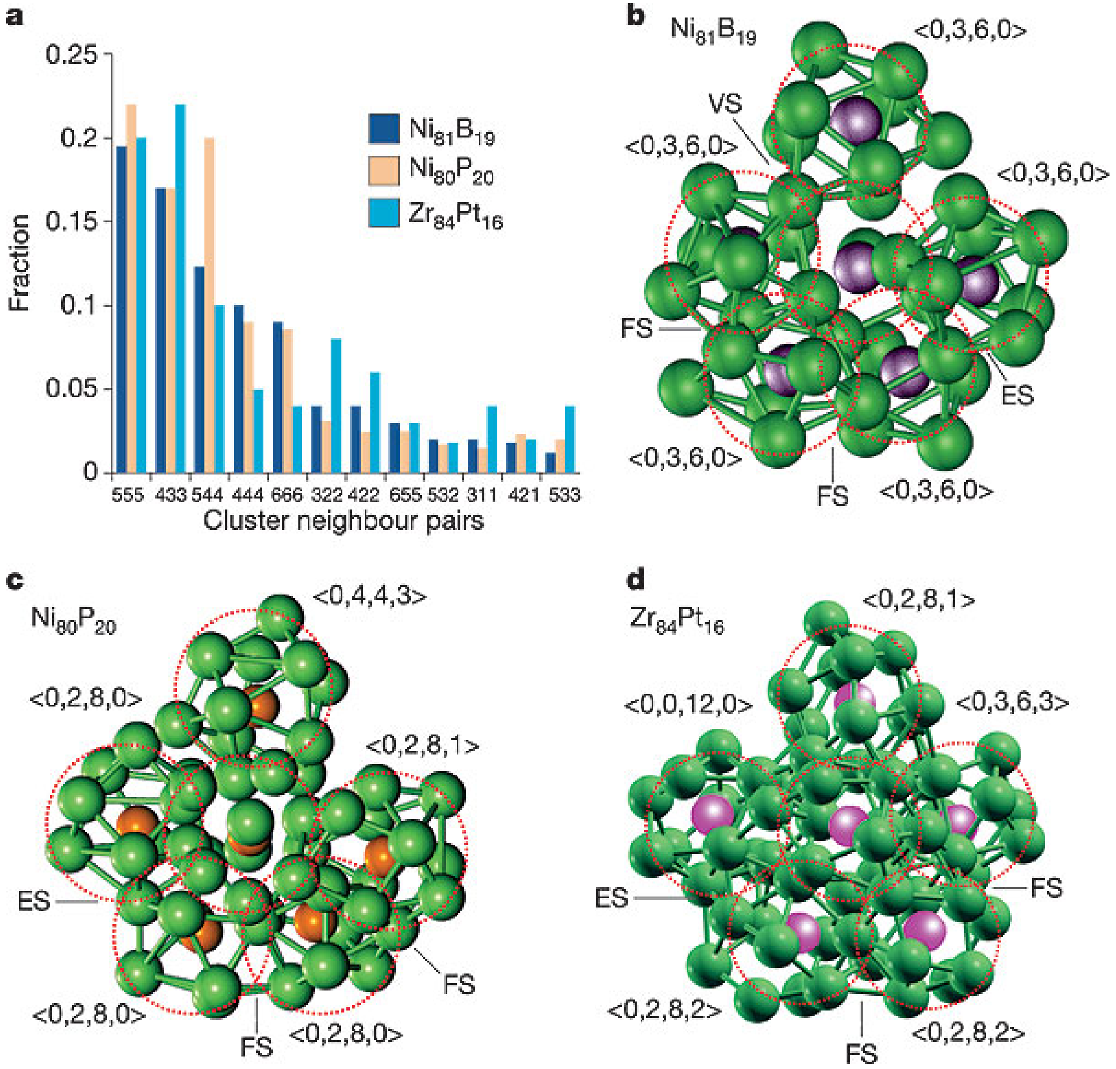


B. Francois, F. Lacombe & H.J. Herrmann, *Phys. Rev. E* **65** (2002) 031311.



Interpenetrating clusters in the efficient cluster packing model of Miracle et al.

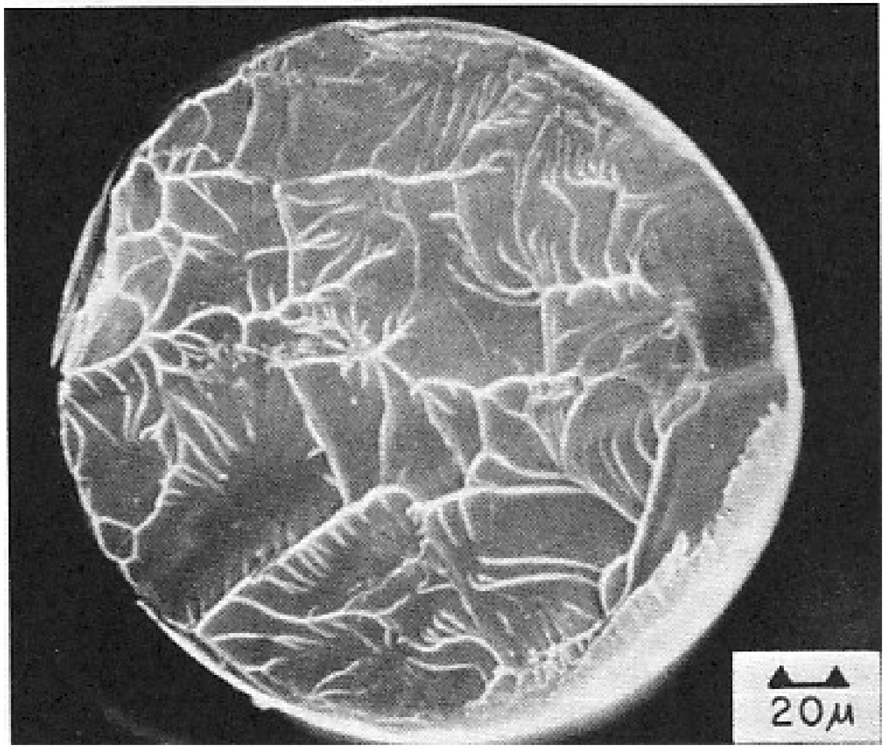
D B. Miracle, *Acta Mater*. **54** (2006) 4317.



Short-to-medium-range order in metallic glasses.

H.W. Sheng, W.K. Luo, F.M. Alamgir, J.M. Bai & E. Ma, *Nature* **439** (2006) 419.

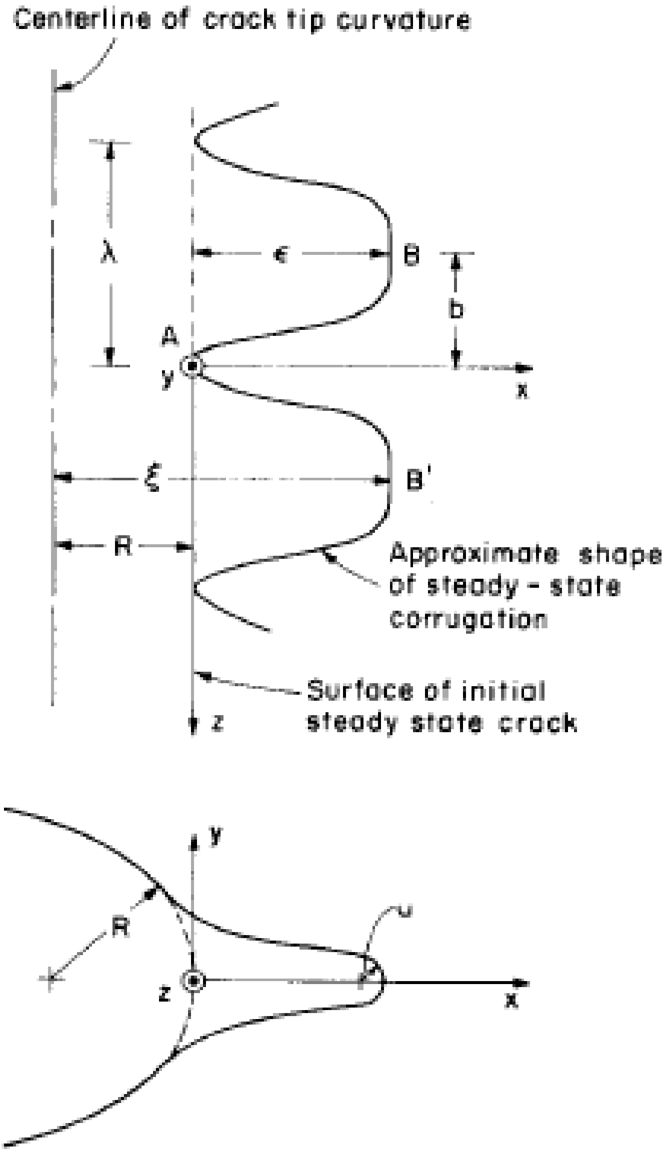
Fracture surface of $Pd_{77.5}Cu_6Si_{16.5}$ — characteristic vein pattern, formed by Saffman-Taylor fingering in a liquid-like layer.



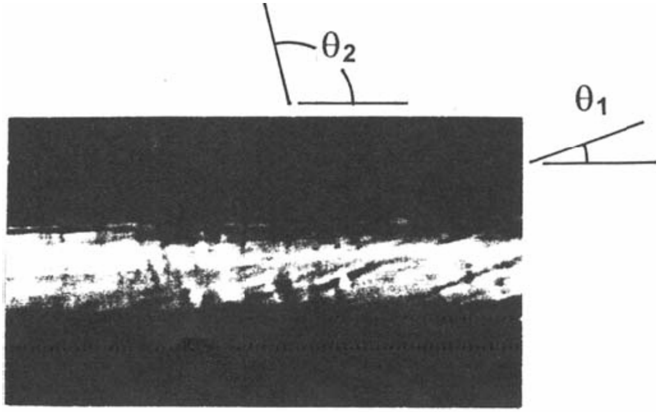
L.A. Davis & S. Kavesh, *J. Mater. Sci*. **10** (1975) 453.

The thickness of the liquid-like layer must be at least several μm.

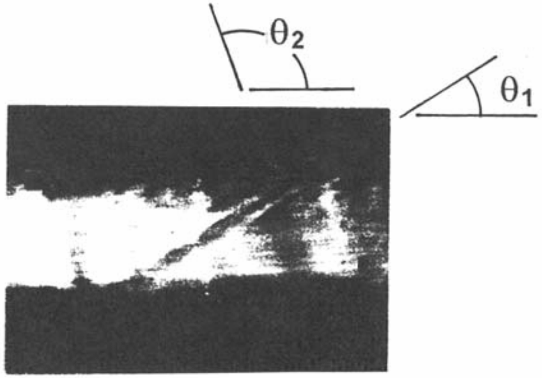
The vein pattern is formed by Saffman-Taylor fingering of air into a liquid-like layer of thickness 2-20 times the vein spacing.



A.S. Argon & M. Salama, *Mater. Sci. Eng*. **23** (1976) 219.



5P4E, p=275MPa, T=38°C



MCS1218, p=241MPa, T=16°C

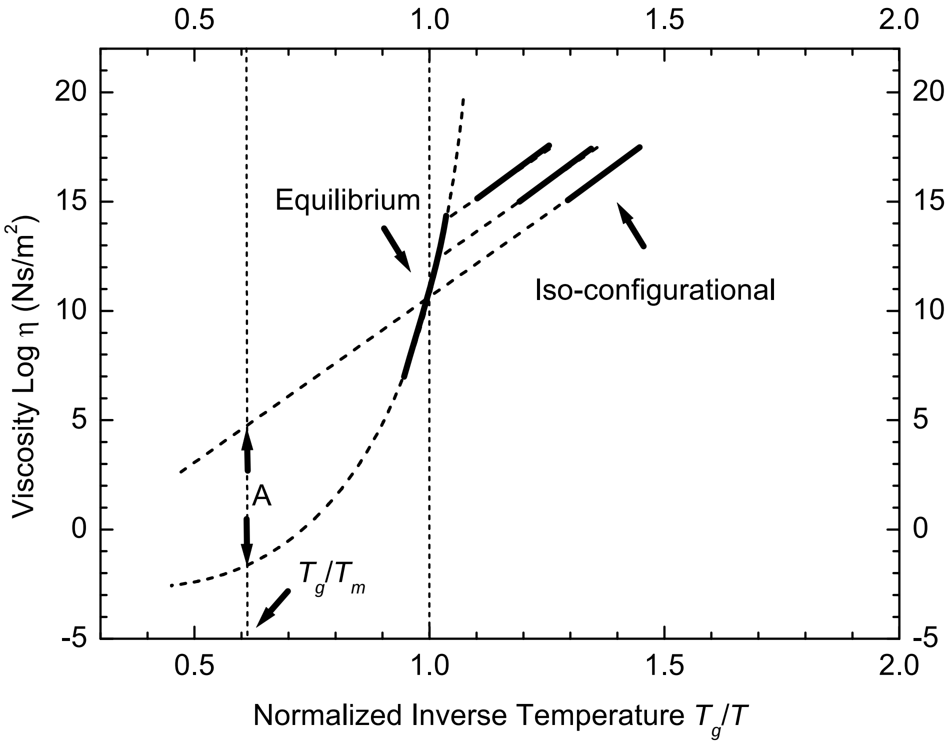
Shear bands can be found even in liquids – for example in liquid lubricants at high pressure, seen here in high-molecular weight organic liquids.

S. Bair & C. McCabe: “A study of mechanical shear bands in liquids at high pressures”, *Tribology Int*. **37** (2004) 783.

Formation of a liquid-like zone at a shear band

Rapid heating is **isoconfigurational**, and the viscosity is not lowered to the equilibrium value.

Data on Pd-Cu-Si and Pd-Si glasses from A.I. Taub & F. Spaepen, *Acta Metall.* **28** (1980) 1781. Isoconfigurational heating shown by C.A. Volkert & F. Spaepen, *Acta Metall.* **37** (1989) 1355.



Y. Zhang & A.L. Greer: "Thickness of shear bands in metallic glasses", *Appl. Phys. Lett.* **89** (2006) 071907.

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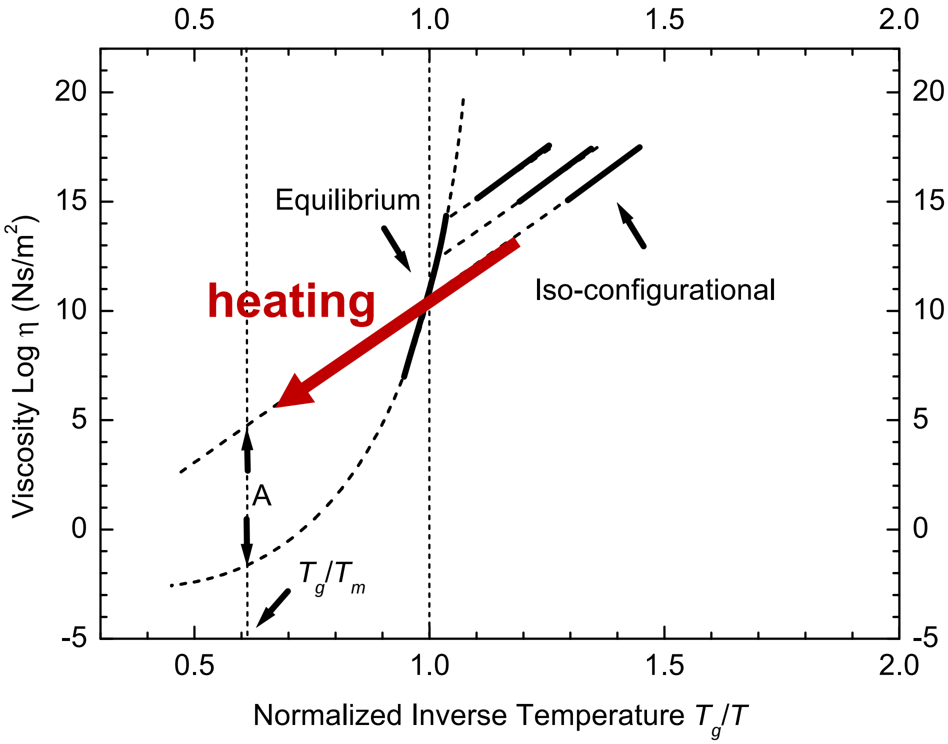

Y. Zhang & A.L. Greer: "Thickness of shear bands in metallic glasses", *Appl. Phys. Lett.* **89** (2006) 071907.

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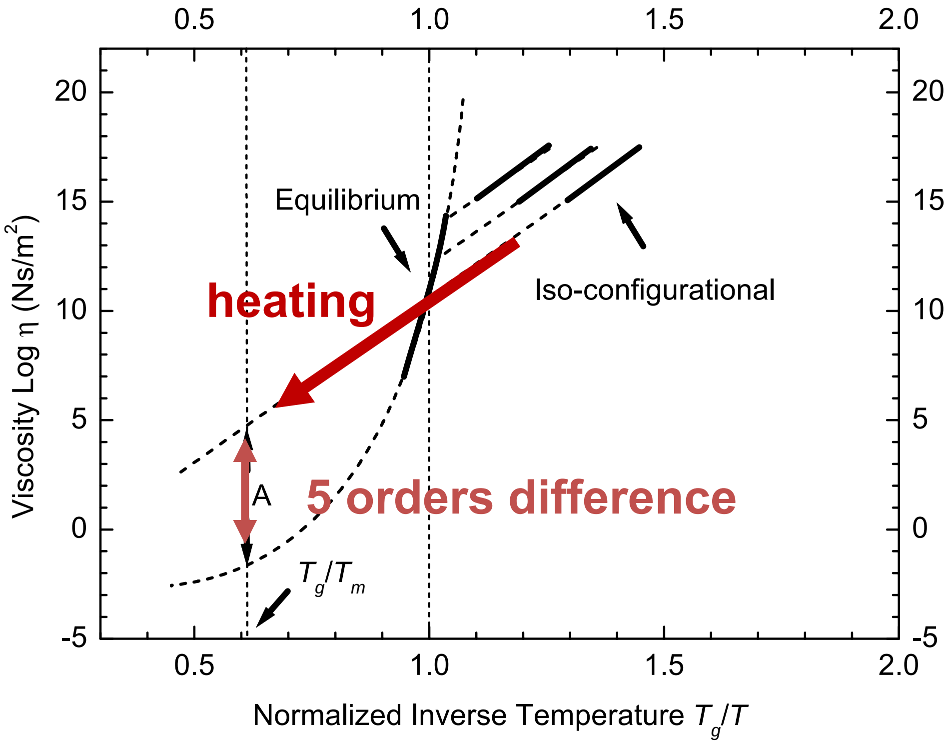
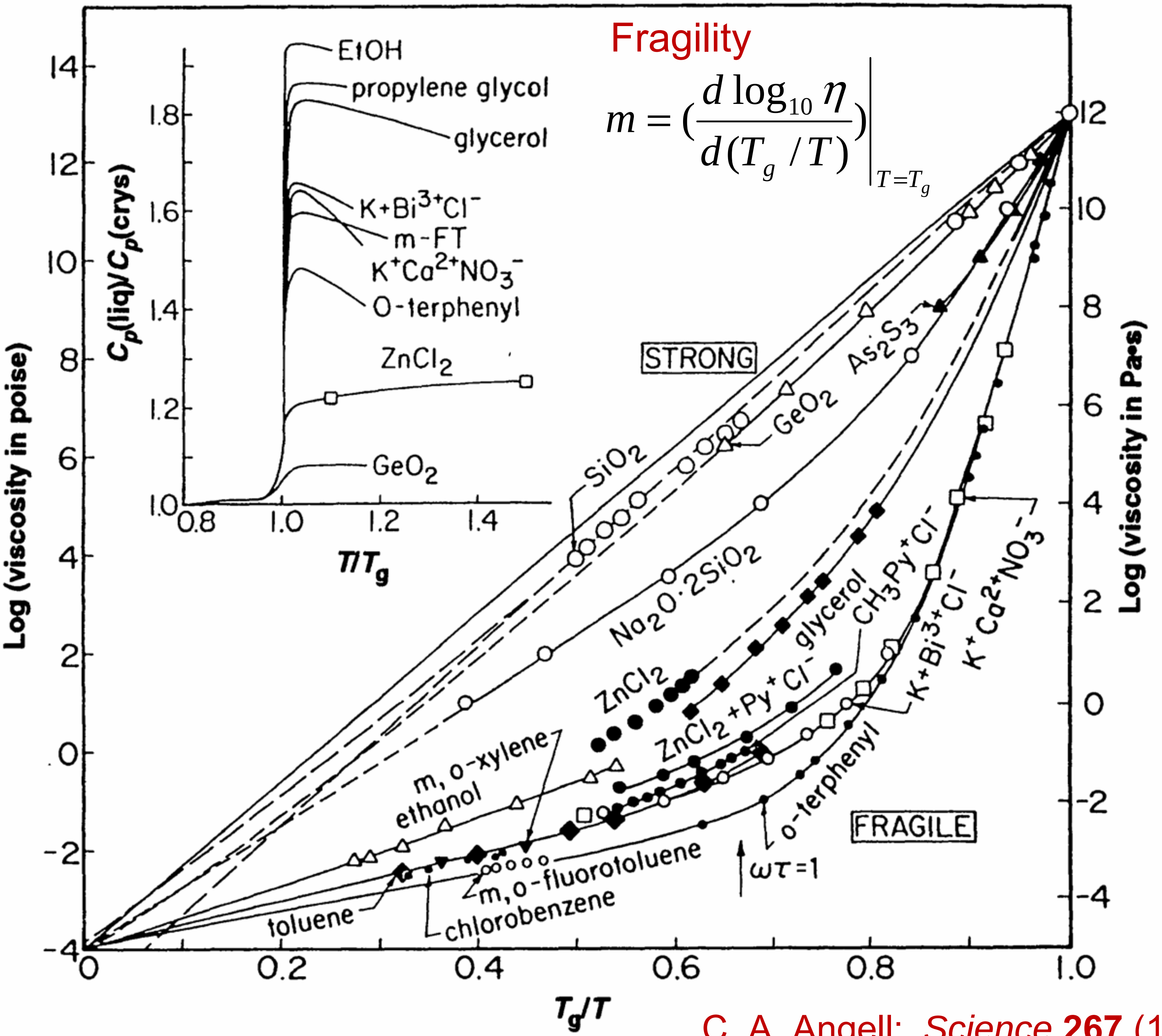


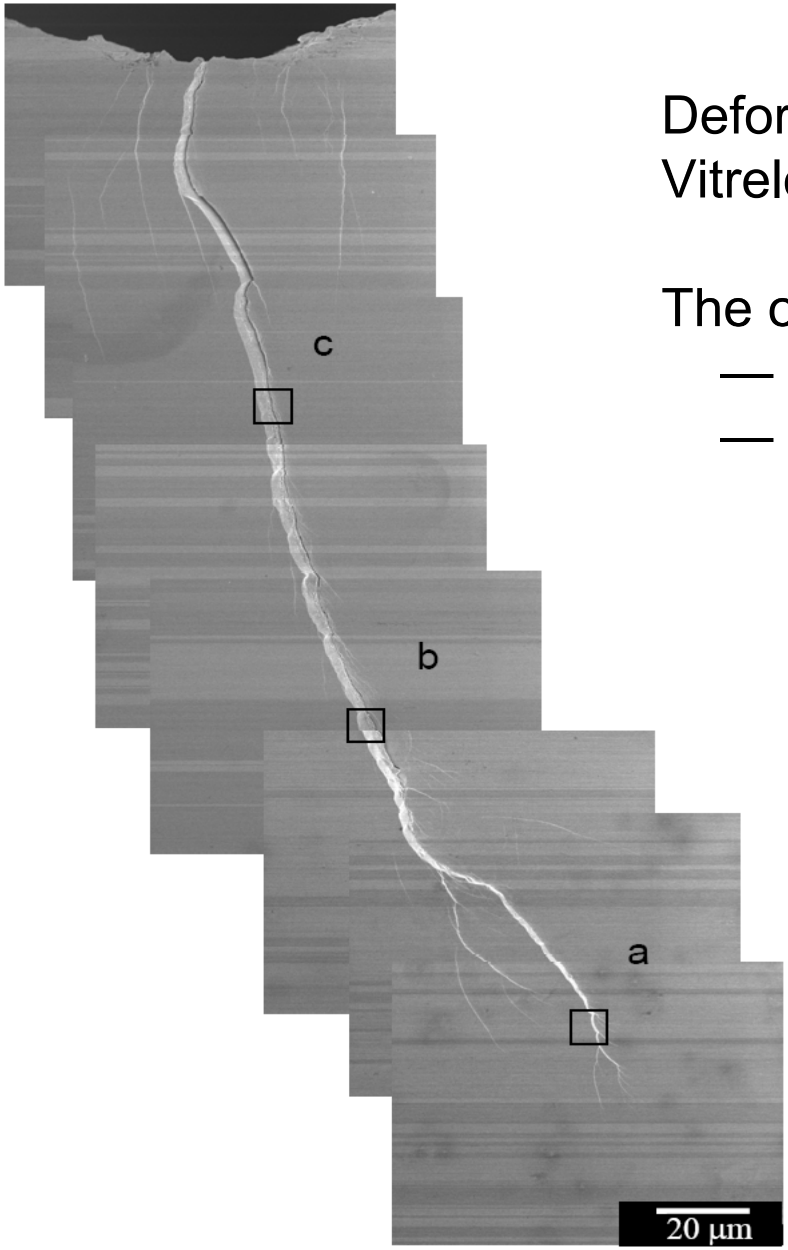
Y. Zhang & A.L. Greer: “Thickness of shear bands in metallic glasses”, *Appl. Phys. Lett.* **89** (2006) 071907.

Fragility

$$m = \left(\frac{d \log_{10} \eta}{d(T_g / T)}\right)\bigg|_{T=T_g}$$



C. A. Angell: *Science* **267** (1995) 1924.



Deformation and fracture at a notch in Vitreloy 1.

The offset δ at shear bands

— varies

— is largest near the notch

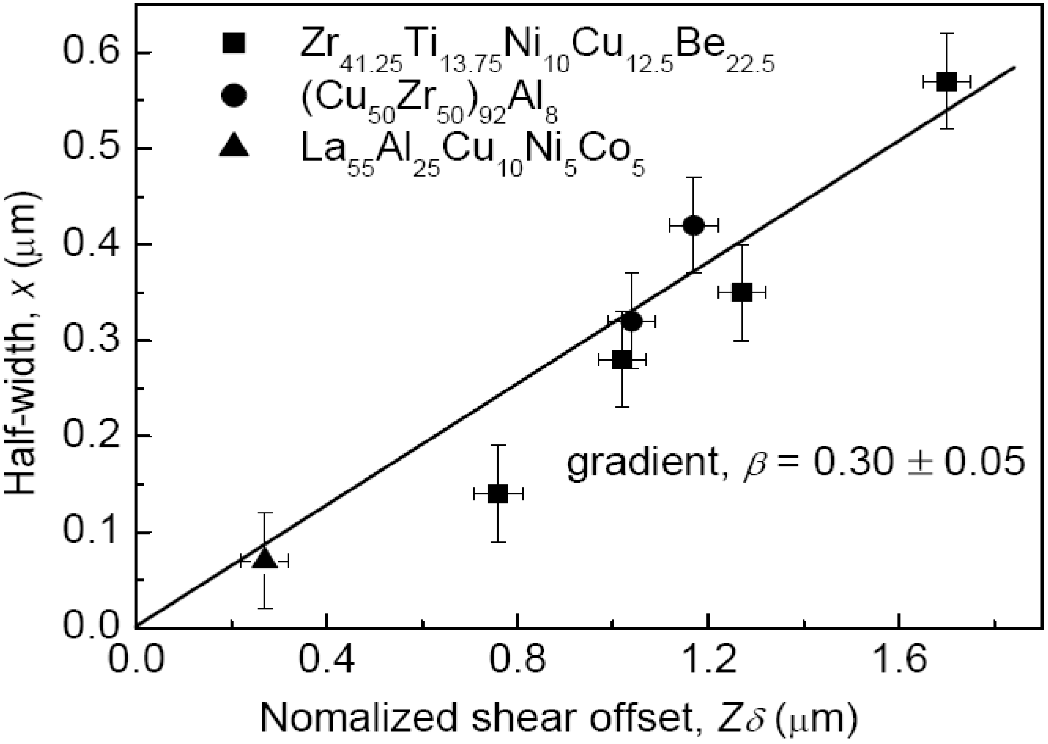
Y. Zhang et al. “Local temperature rises during mechanical testing of metallic glasses ”, *J. Mater. Res.* **22** (2007) 417.

Half-width of hot zone

$$x = \beta Z \delta$$

If work done corresponds to the yield stress of the BMG acting on the shear band throughout its operation, β would be 0.5. Measurement suggests $\beta = 0.3$

$$Z = \frac{1}{\sqrt{2\pi e}\,\Delta T_{\max}^{\text{crit}}}\left(\frac{\sigma_y}{\rho C}\right)$$



From this correlation, it seems that the shear stress acting on a shear band during its operation is 50-70% of the value corresponding to the onset of macroscopic yielding.

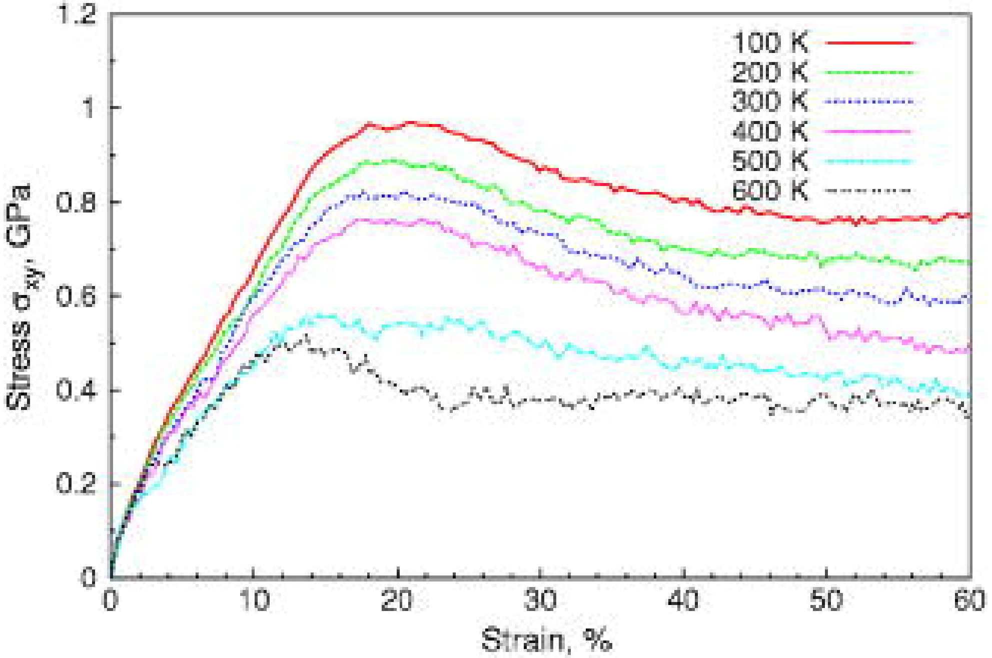
Y. Zhang et al. *J. Mater. Res.* **22** (2007) 417.

Molecular-dynamics simulations

simulated $Cu_{64}Zr_{36}$

up to 288 000 atoms

cooled at 4×10^{12} K s^{-1}



Q.-K. Li & M. Li: "Atomic scale characterization of shear bands in an amorphous metal", *Appl. Phys. Lett*. **88** (2006) 241903

How fast are shear bands?

Estimates of the time of shear vary enormously —

— as short as 0.2 ns

(estimated from the offset and the speed of sound)

— as long as 100 ms

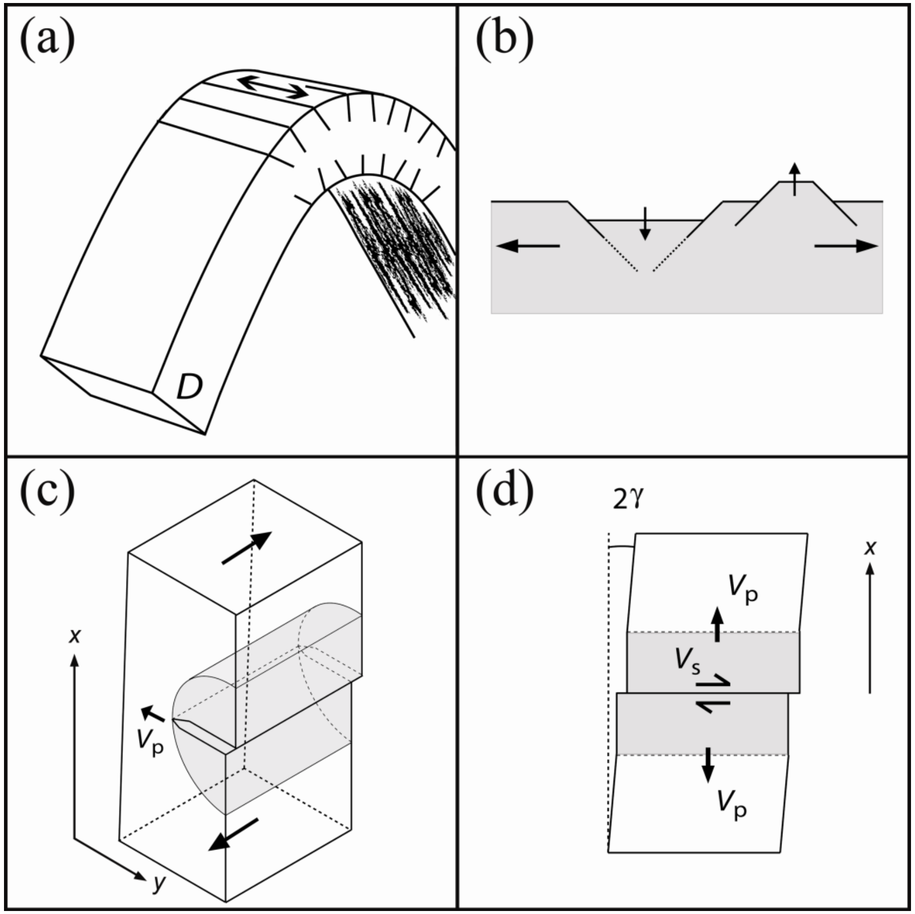
(estimated from serrations on stress-strain curves)

Mode III Shear

velocity of propagation V_p
(velocity of the shear-band front)
≤ 90% of transverse sound speed

shear velocity V_s
(does work and sets local shear time) $V_\mathrm{s} = 4\gamma V_\mathrm{p}$

$\gamma = 0.0267$ (Johnson & Samwer)
$\boldsymbol{V_\mathrm{s} = 0.107\ V_\mathrm{p}}$



Velocities less than ~50% of the maximum would be insufficient to melt tin coatings

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
Thermal profiles around shear bands in metallic glasses

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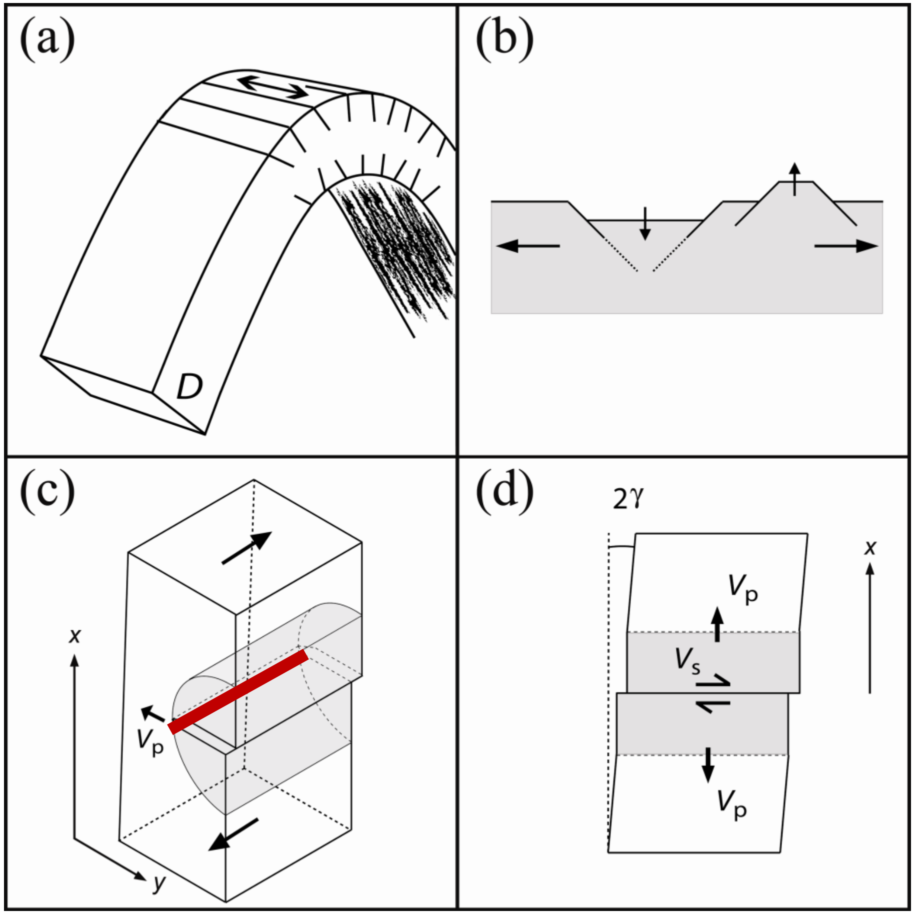

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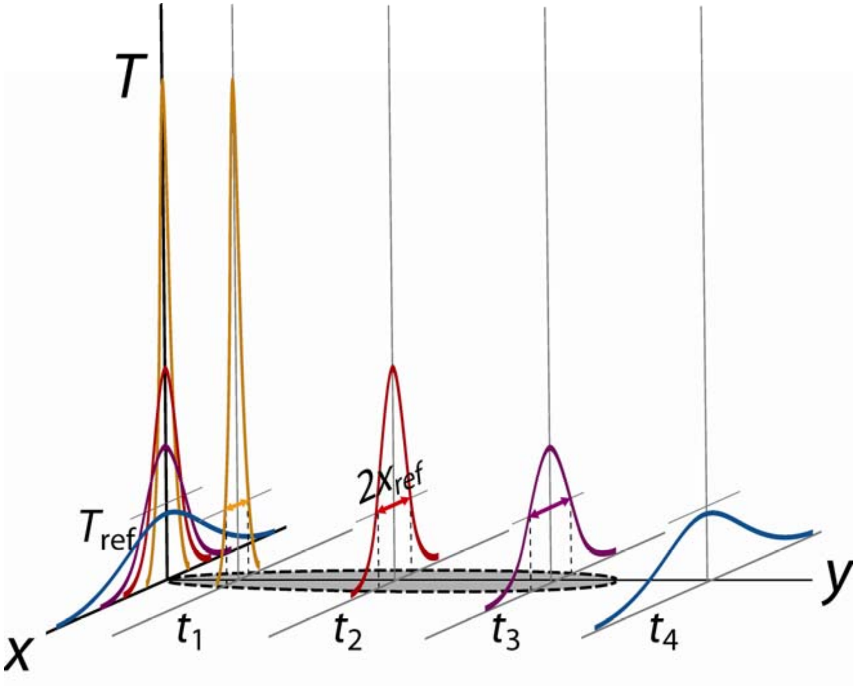

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
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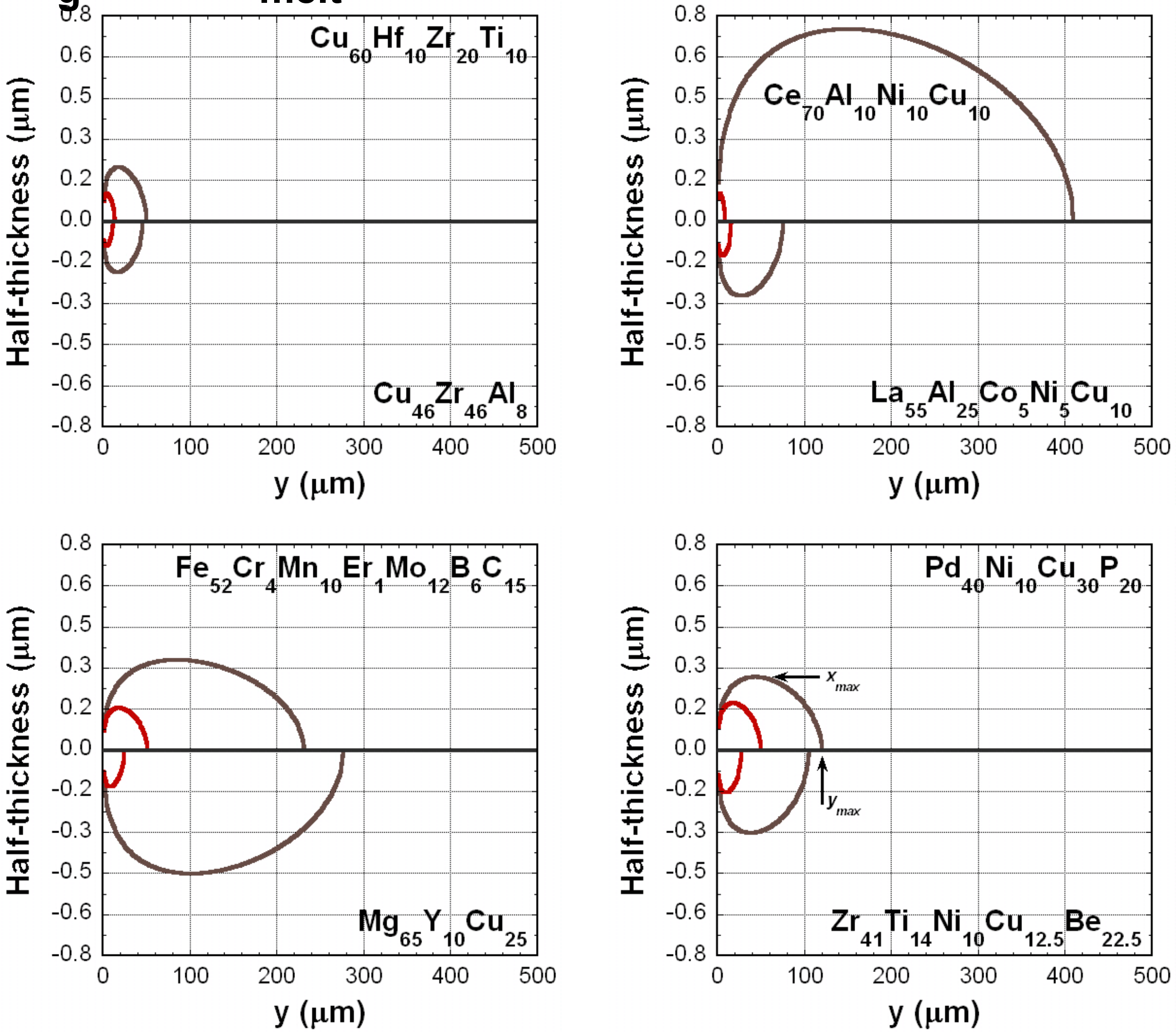
Shapes of thermal profiles — contours of T_g and T_{melt}

constant shear offset = 2 µm



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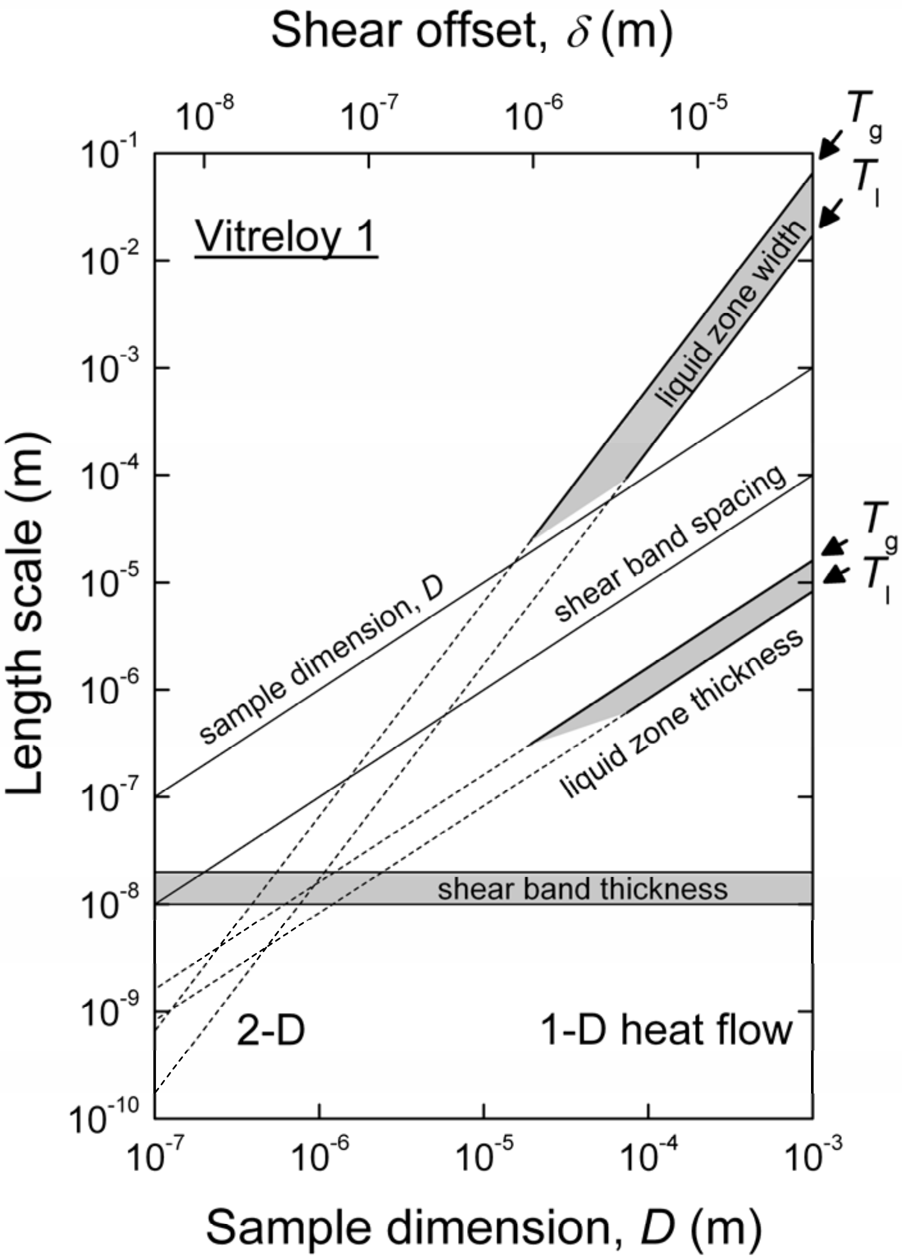

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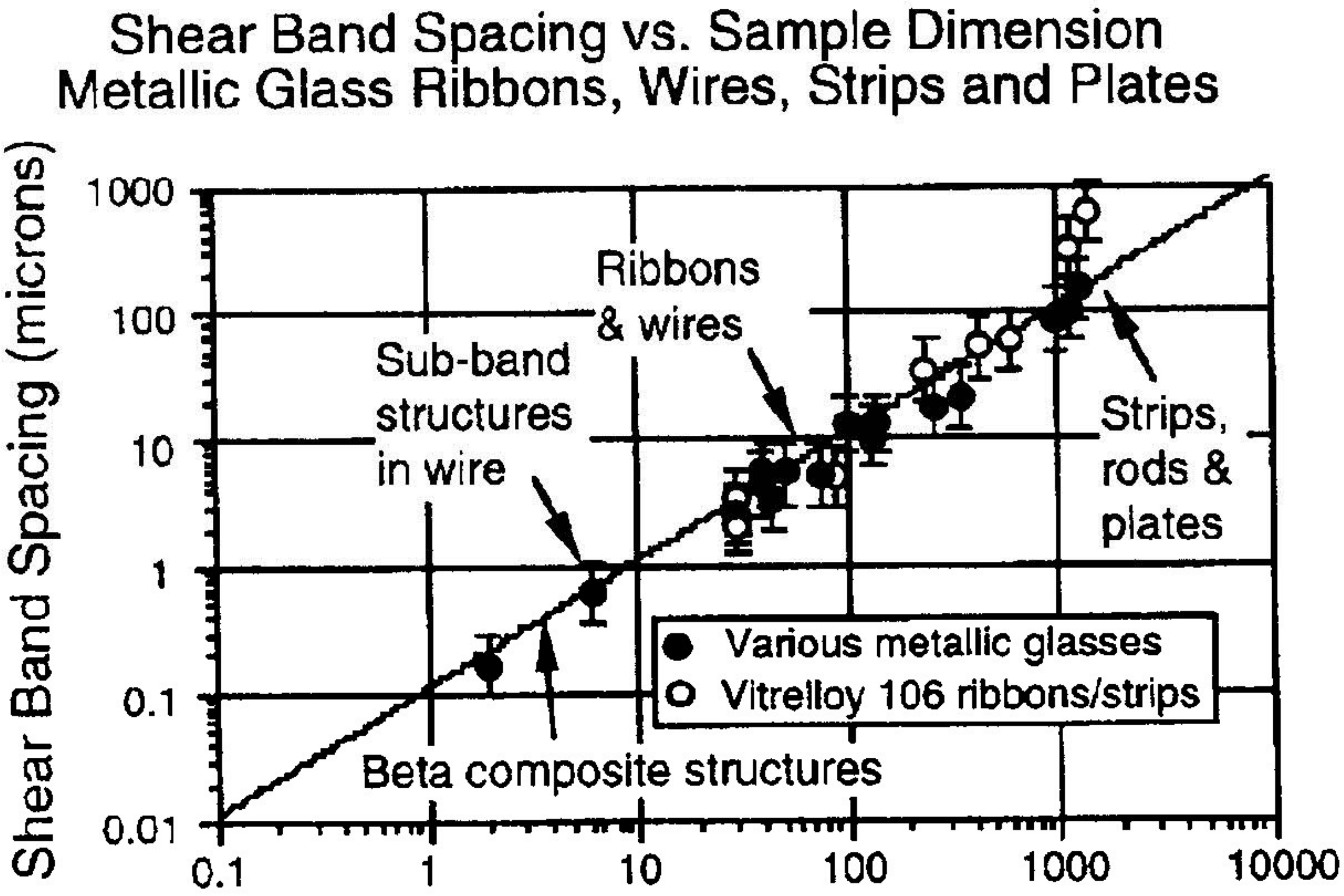
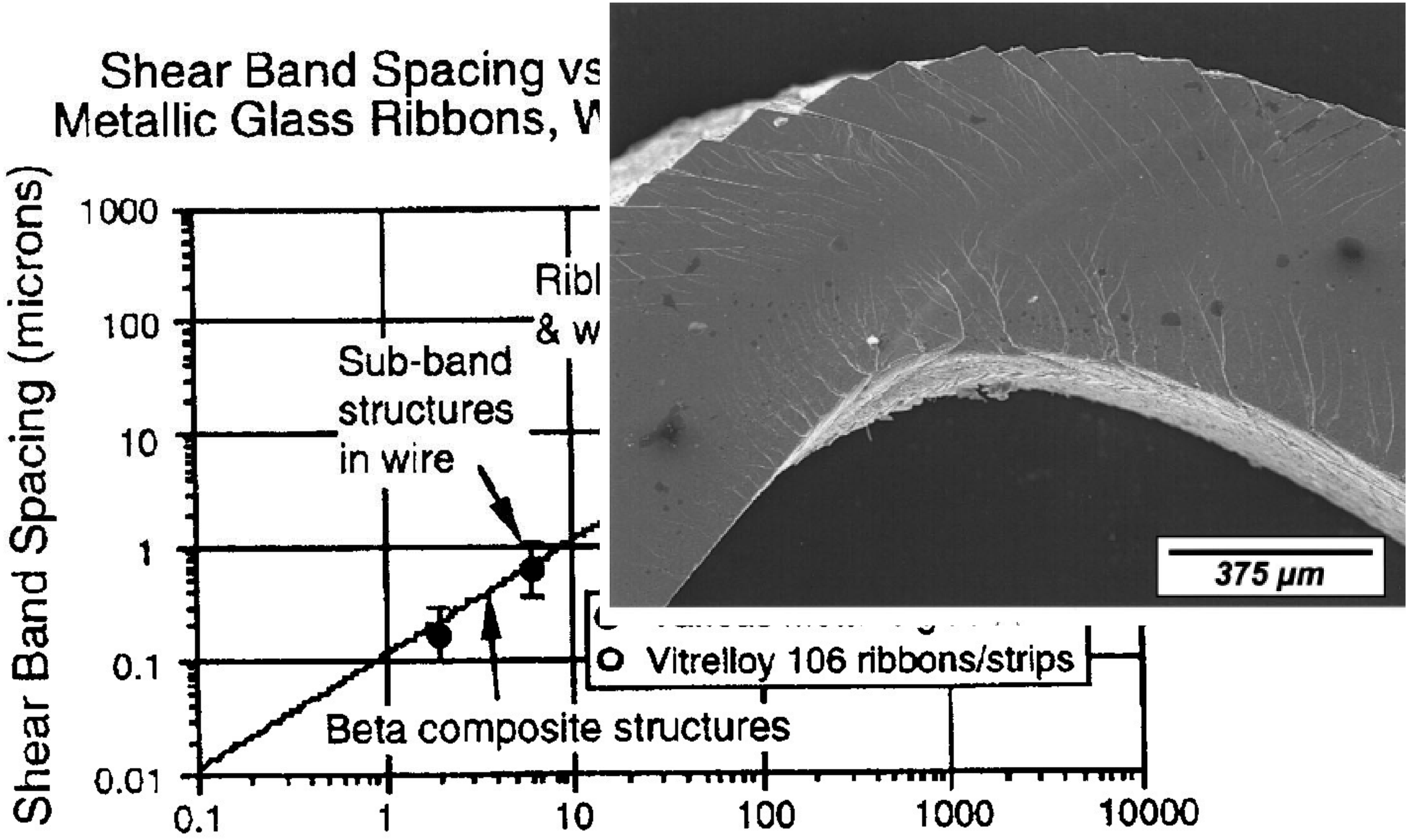


FIG. 3. Shear band spacing as a function of sample size (plate thickness or wire diameter) at the point of fracture for various metallic glasses and Vitreloy 106. The shear band spacing is shown to scale linearly with the sample size. Conner *et al.*[11]

R.D. Conner, W.L. Johnson, N.E. Paton & W.D.Nix: ”Shear bands and cracking of metallic glass plates in bending”, *J. Appl. Phys.* **94** (2003) 904.



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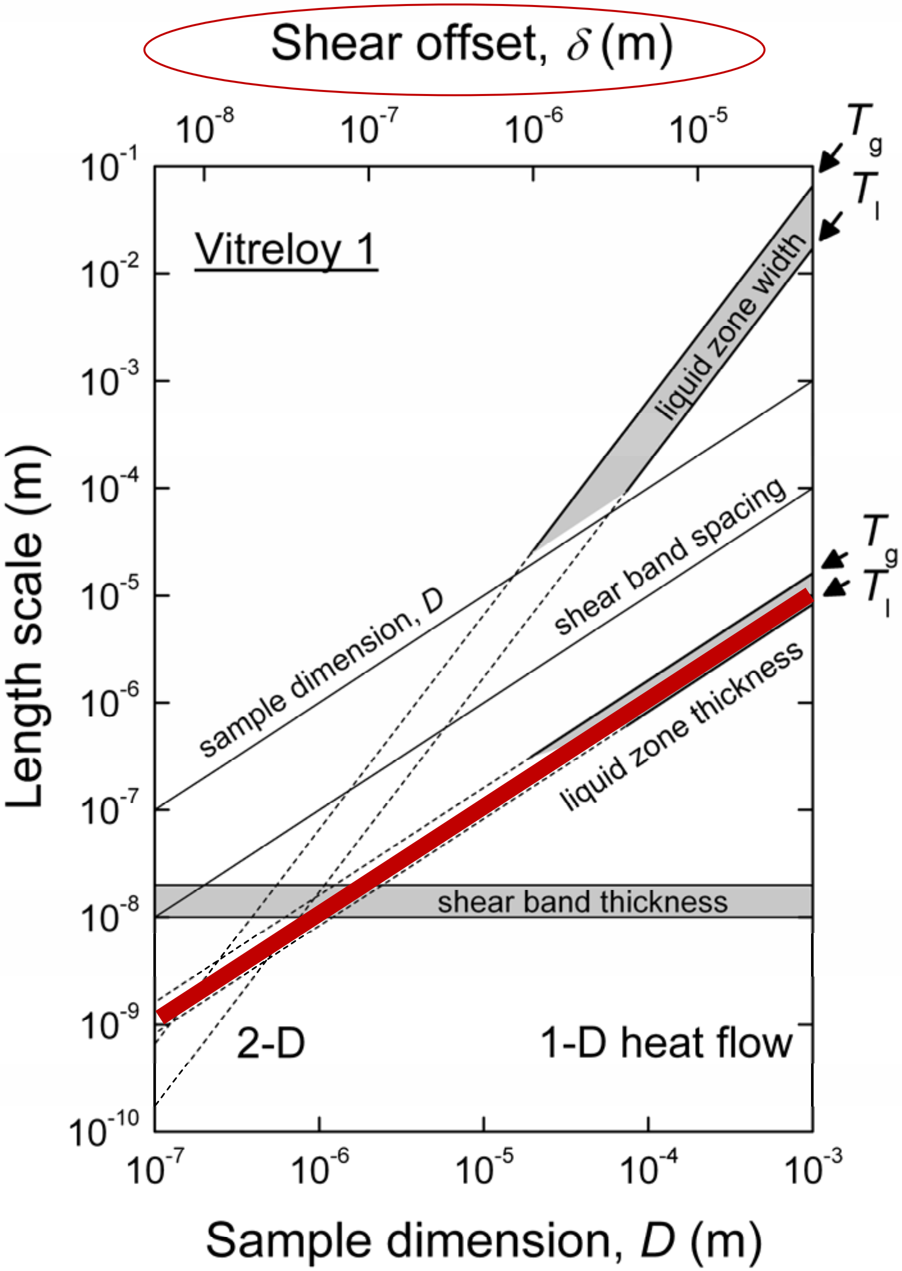

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
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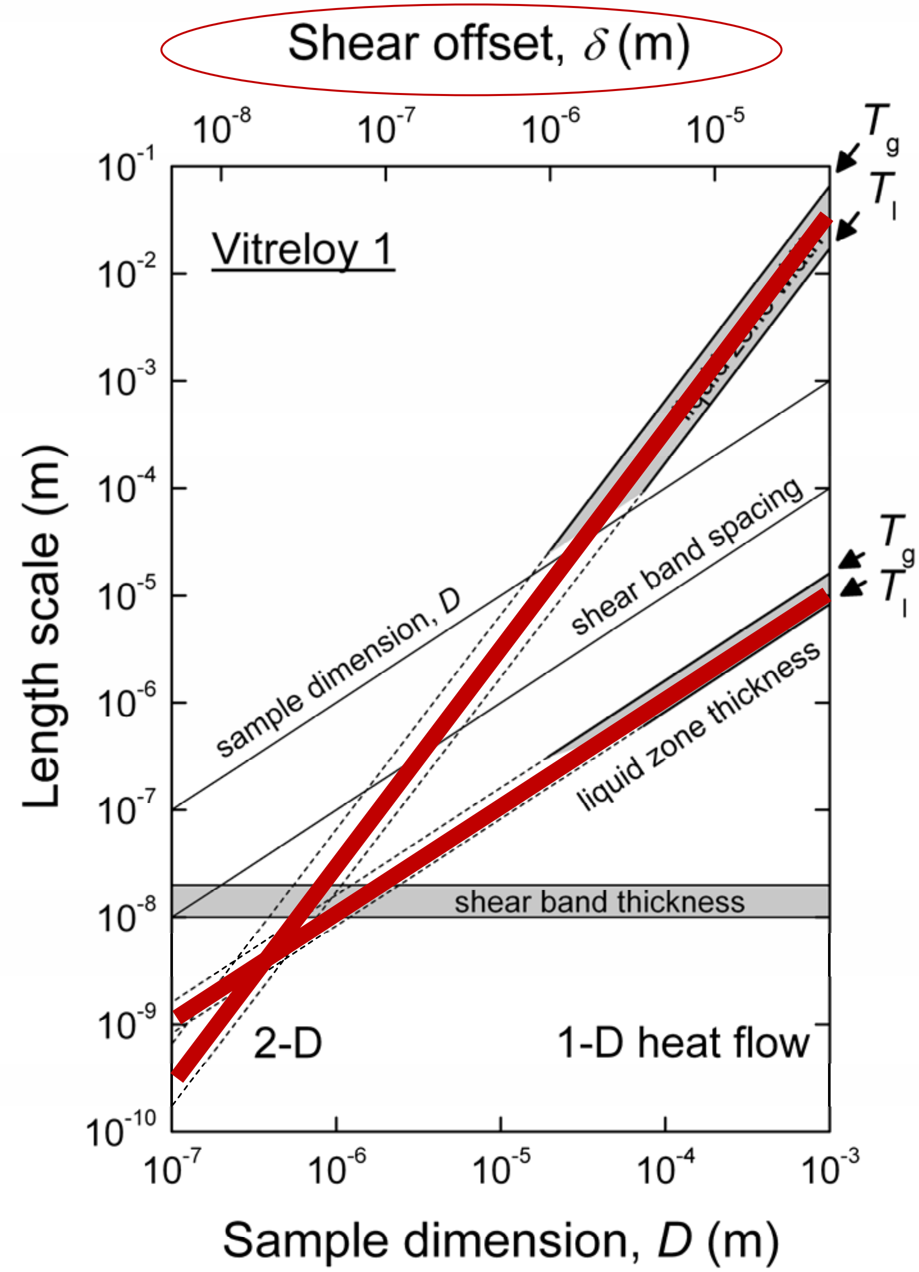

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
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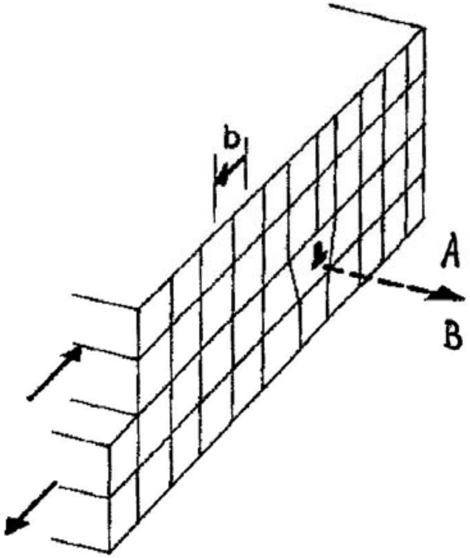
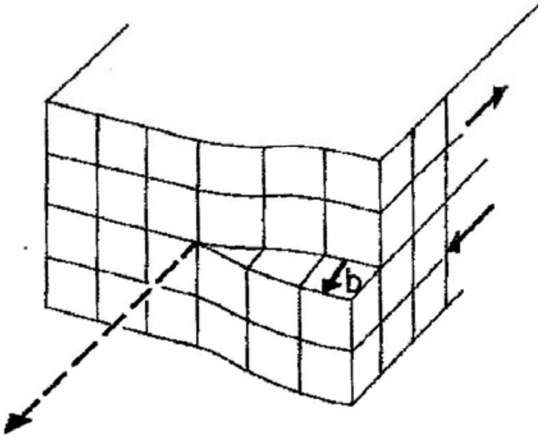
Line Sources of Heat

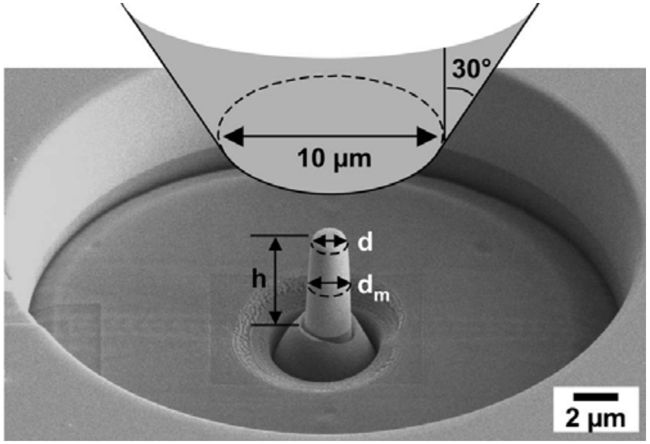
— moving dislocations and crack tips

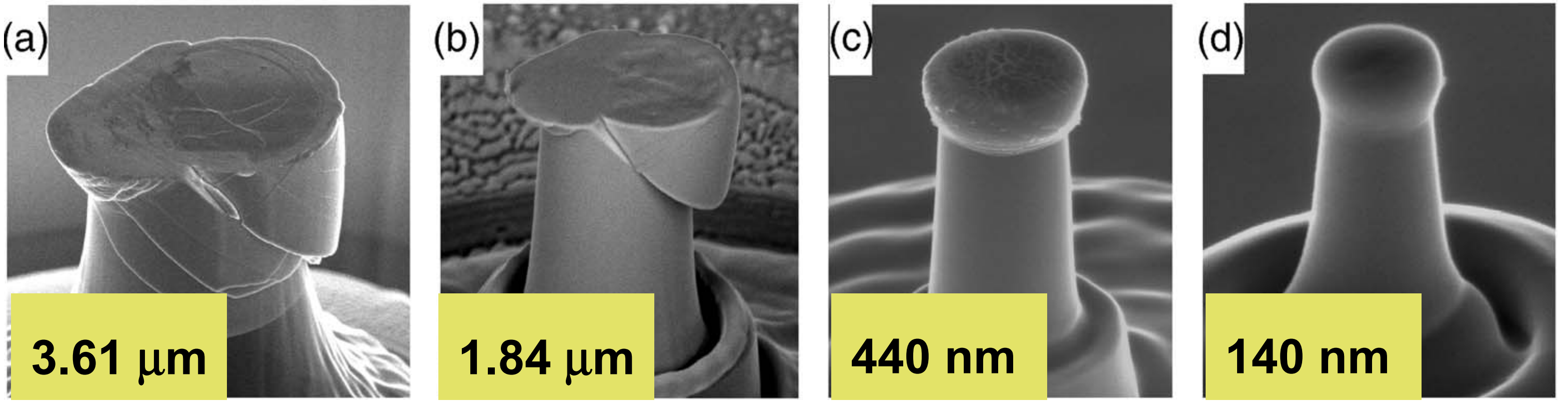




Possibility that shear bands do not operate in small samples

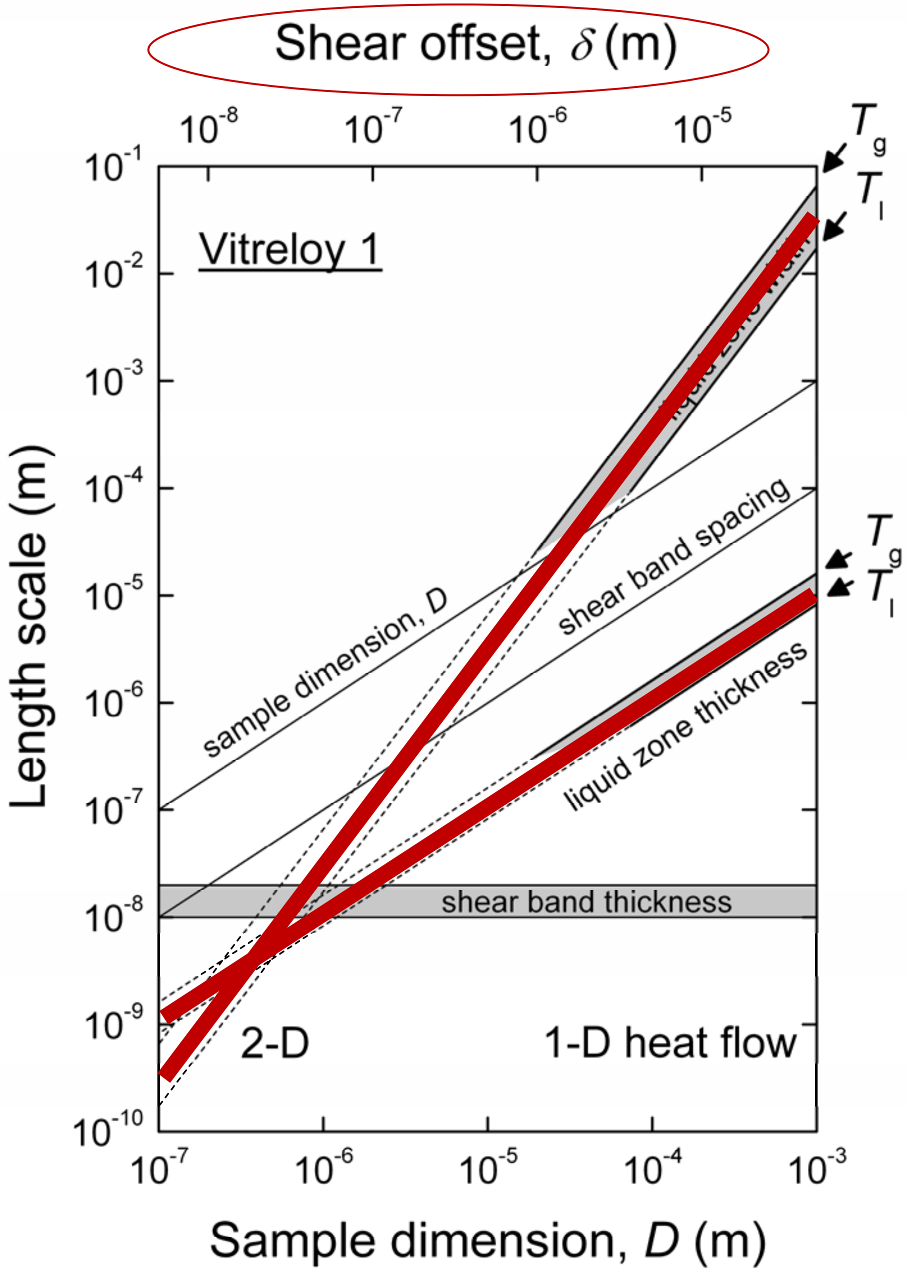
— no bands seen in columns of diameter < 400 nm





— ***still controversial!***

CA Volkert, A Donohoe & F Spaepen:
“Effect of sample size on deformation in amorphous metals”
J. Appl. Phys. **103** (2008) 083539.



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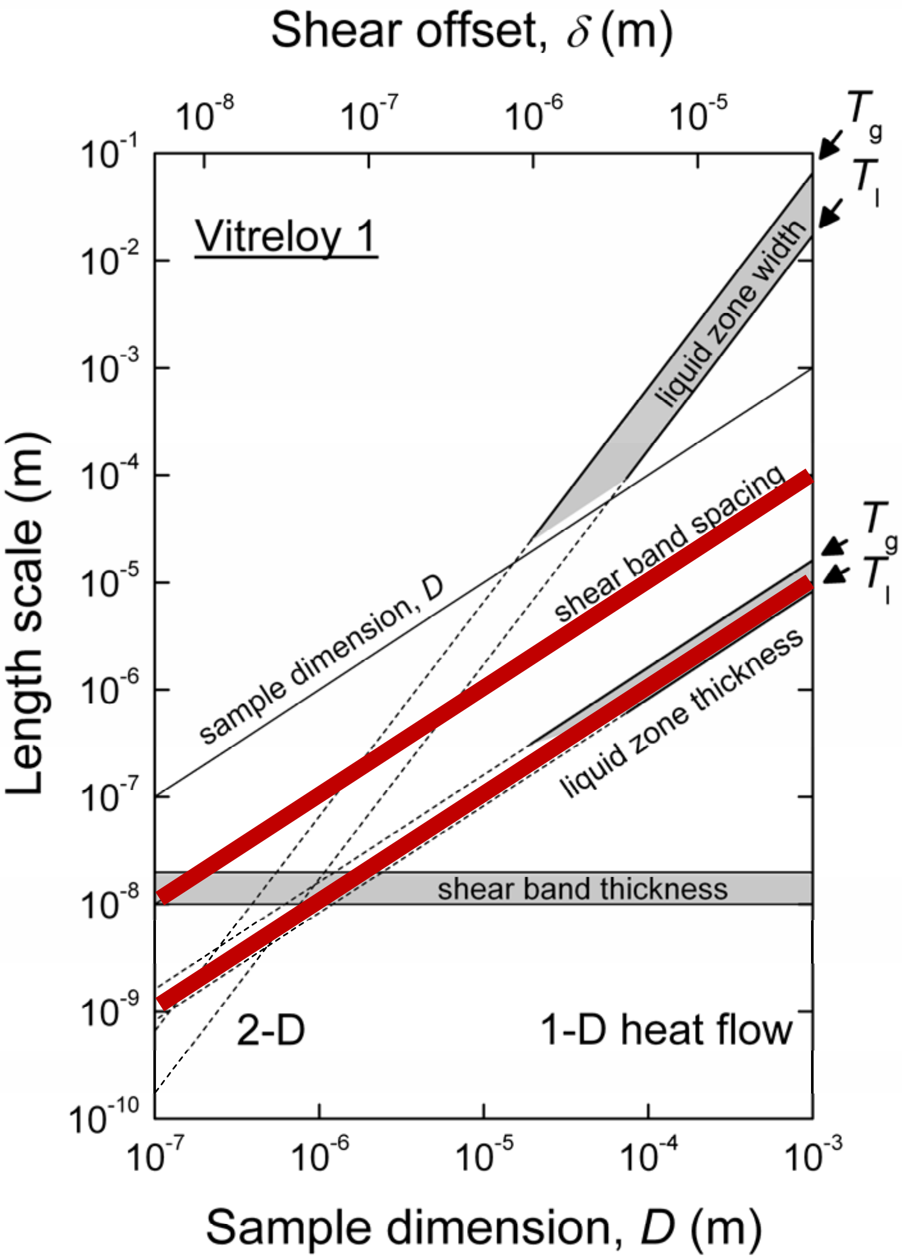

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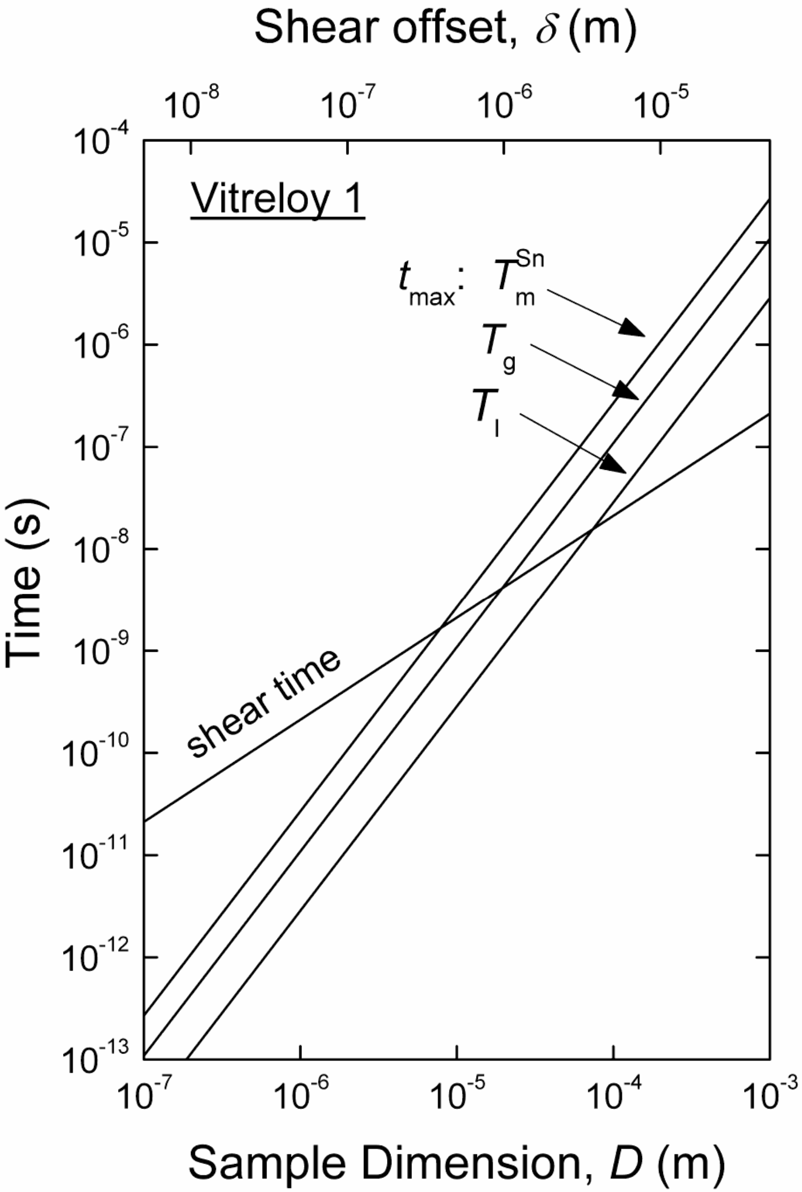

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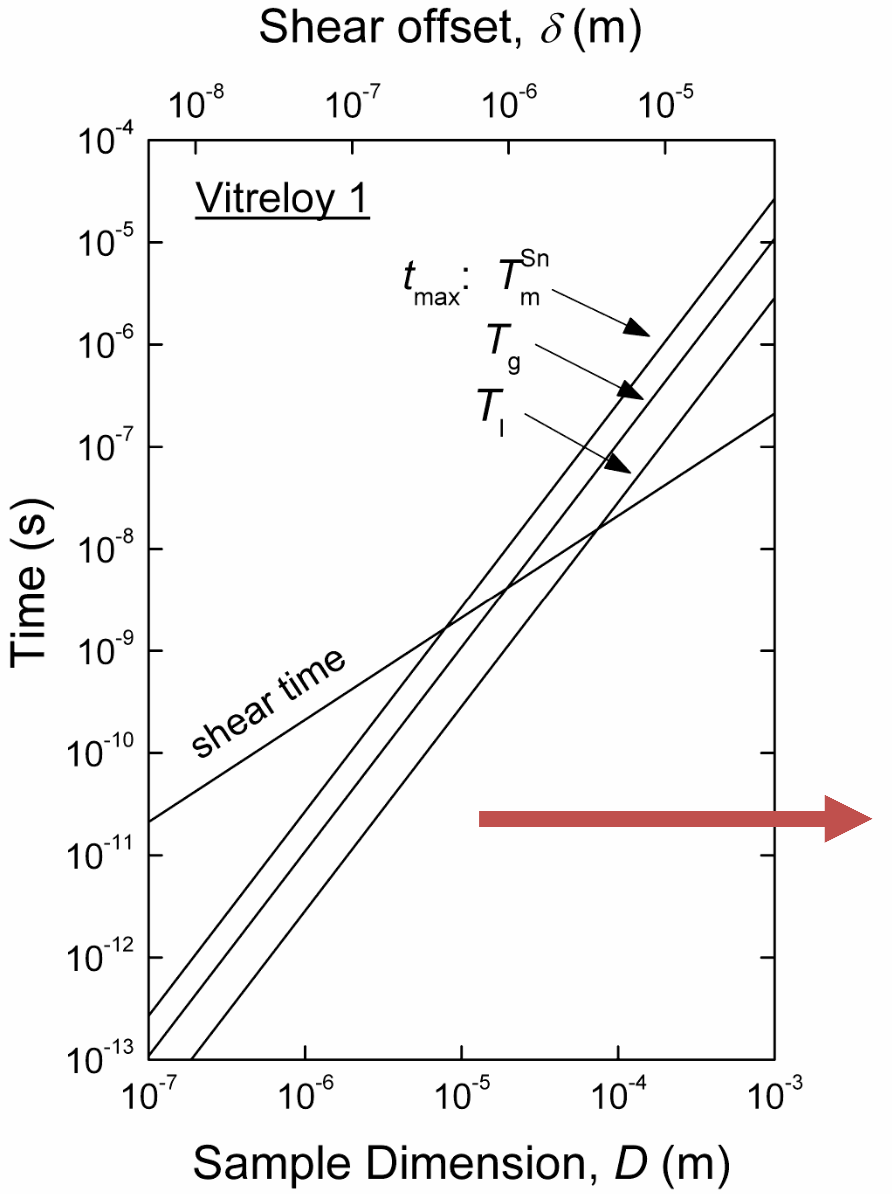
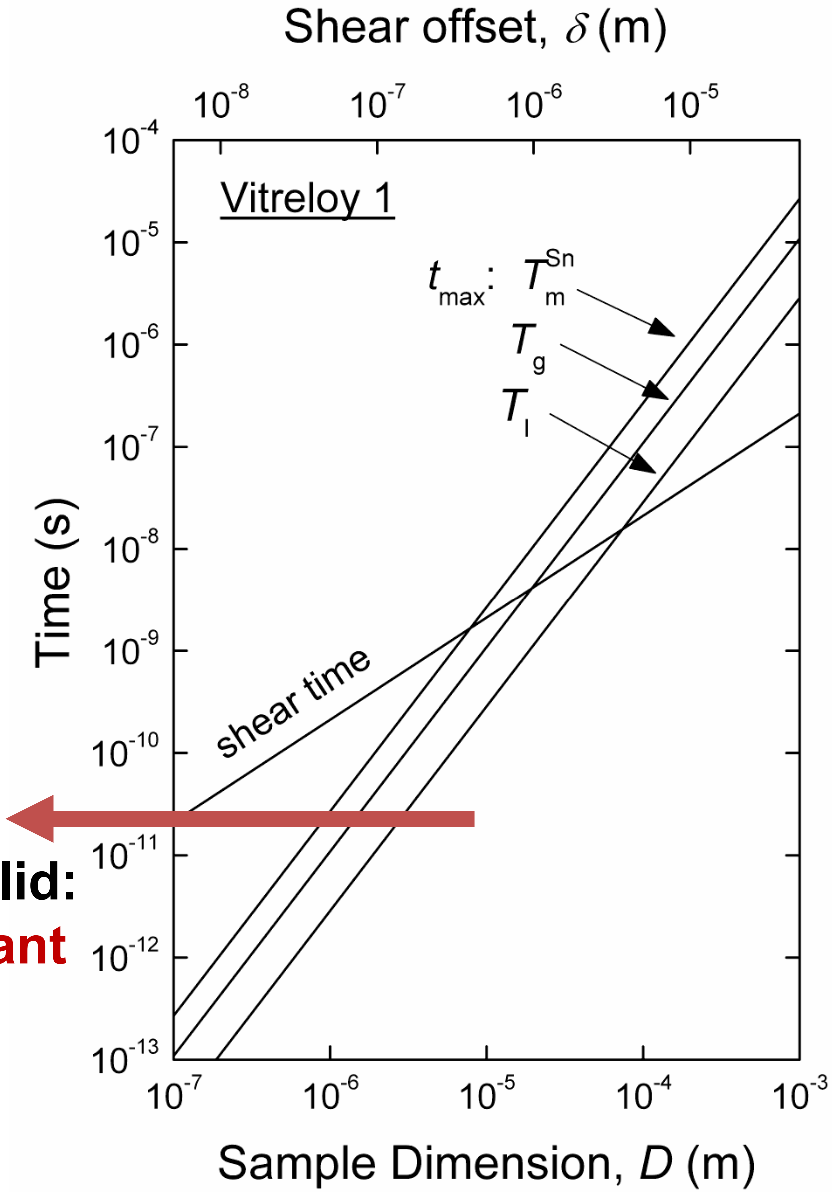


1D heat-flow calculation is valid

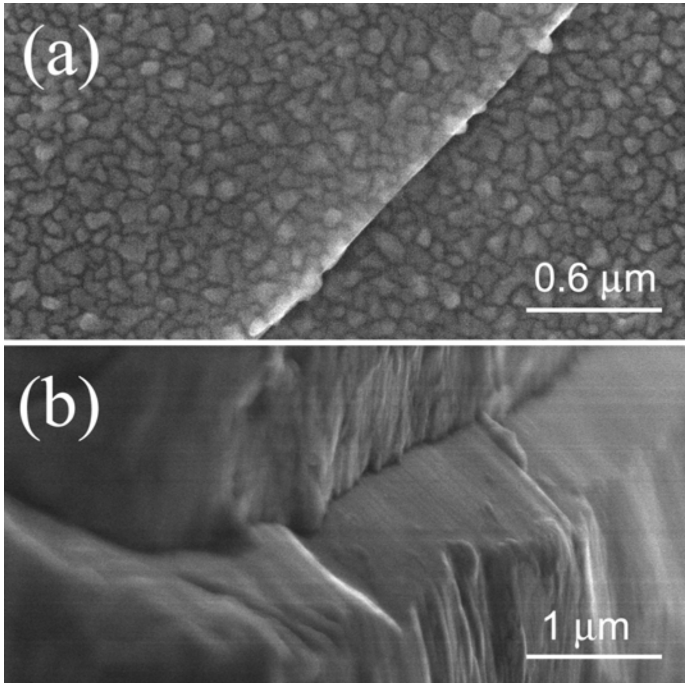
DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
Thermal profiles around shear bands in metallic glasses



calculation not valid:

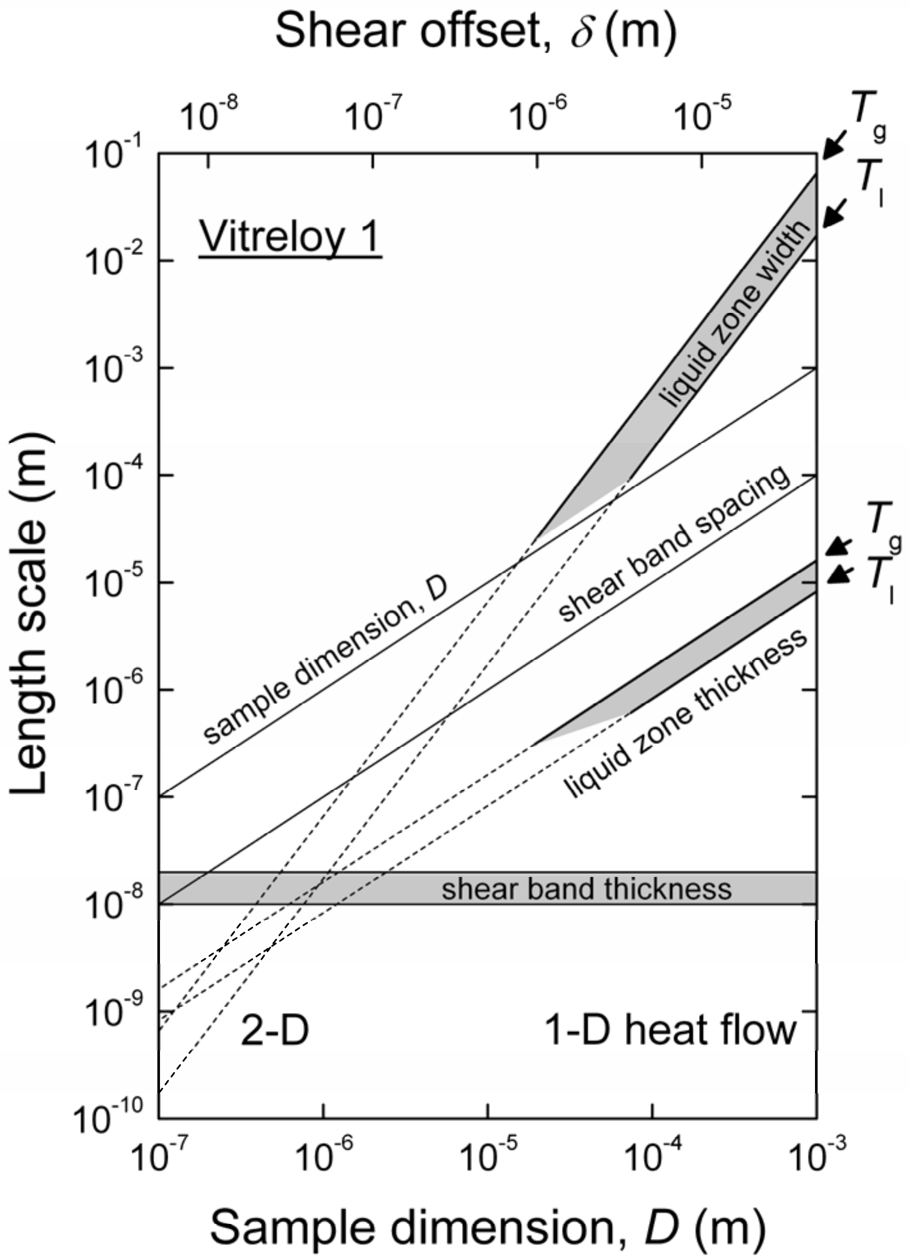
heating insignificant

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
Thermal profiles around shear bands in metallic glasses



$Zr_{65}Cu_{15}Ni_{10}Al_{10}$ metallic glass deformed by 4-point bending — a small shear offset of <1 µm shows no evidence of heating or liquid-like flow.

DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
Thermal profiles around shear bands in metallic glasses



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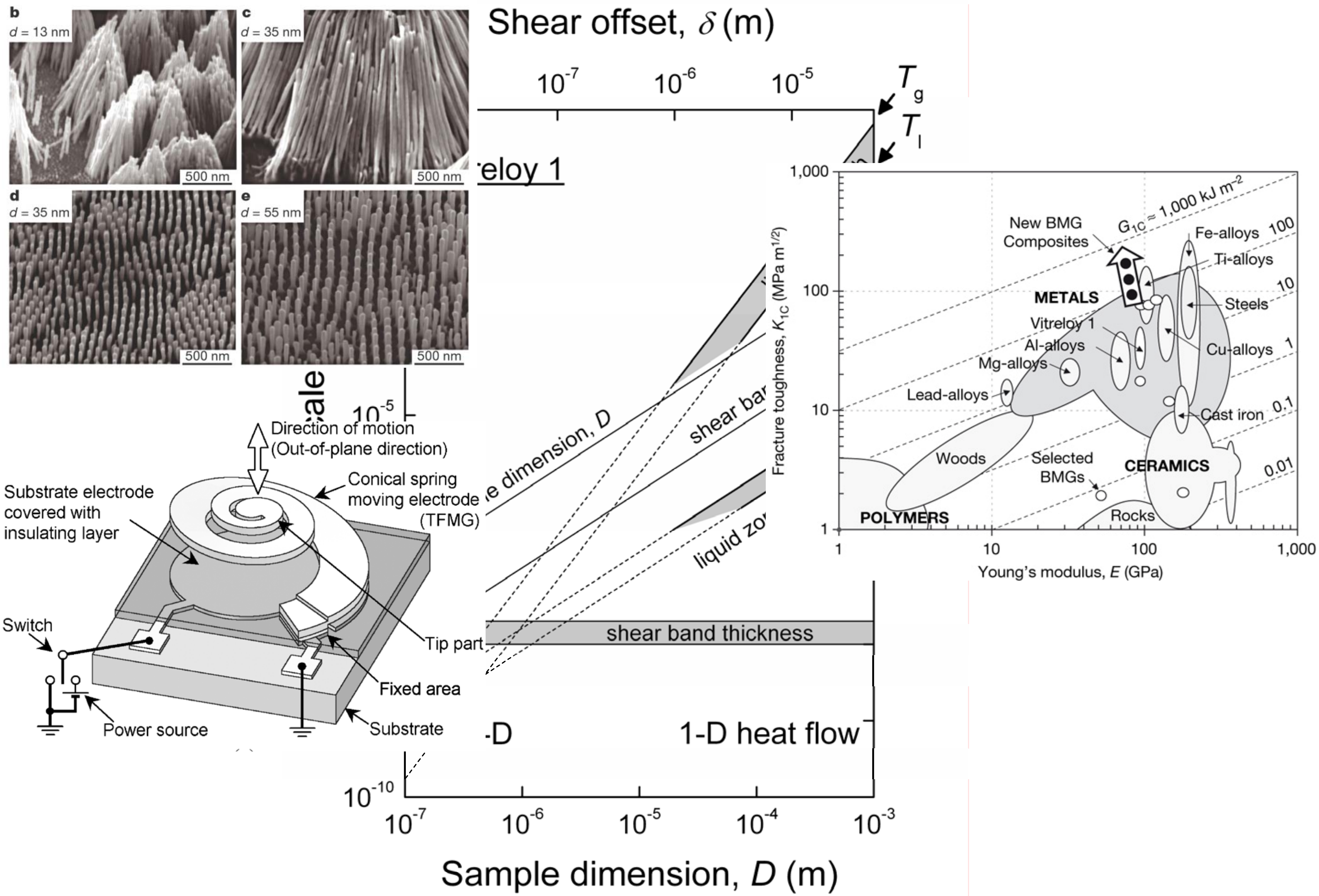
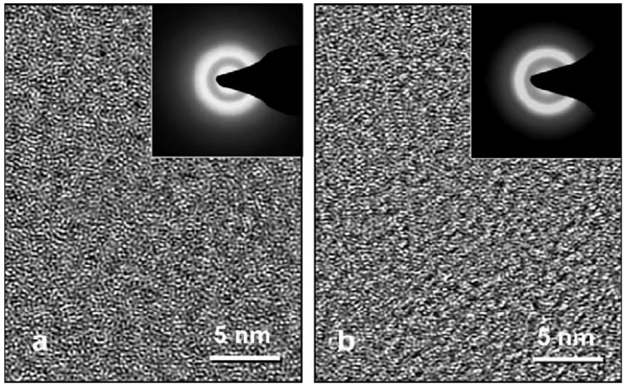


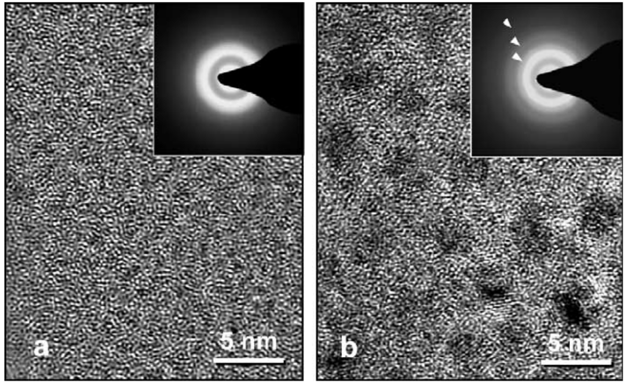
DB Miracle, A Concustell, Y Zhang, AR Yavari & AL Greer:
Thermal profiles around shear bands in metallic glasses

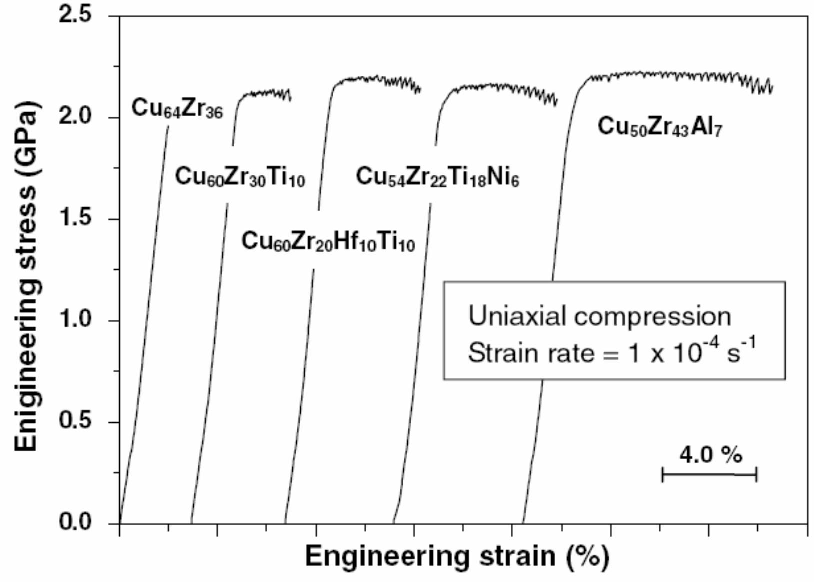
Uniaxial compression

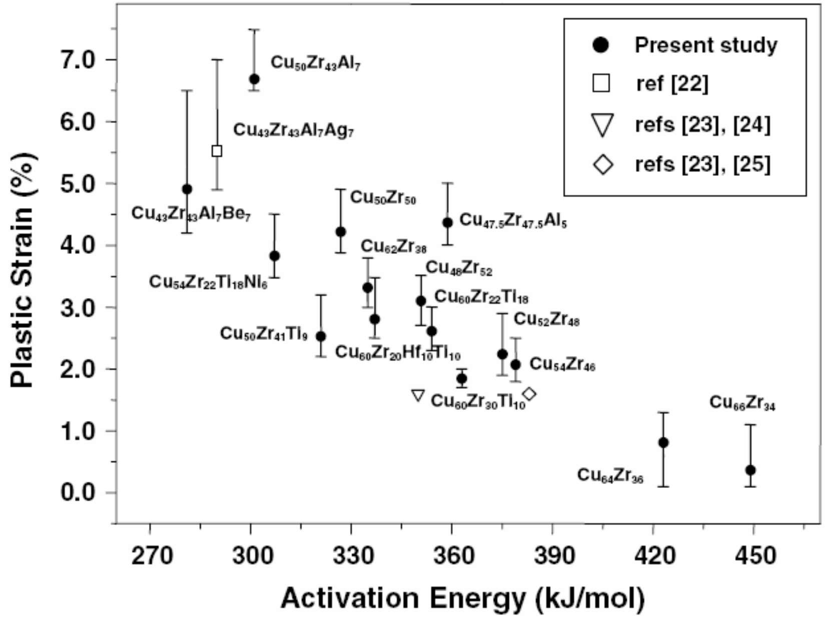


brittle

plastic



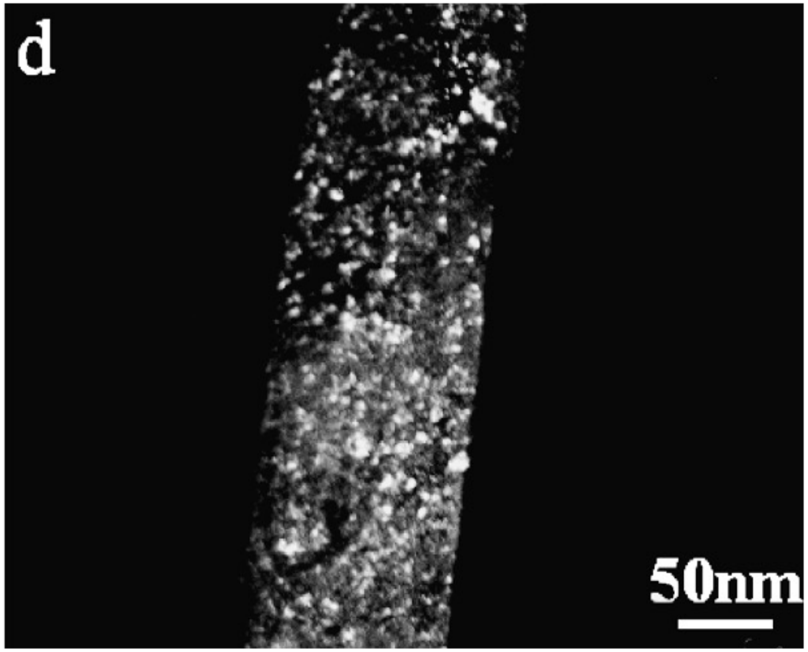


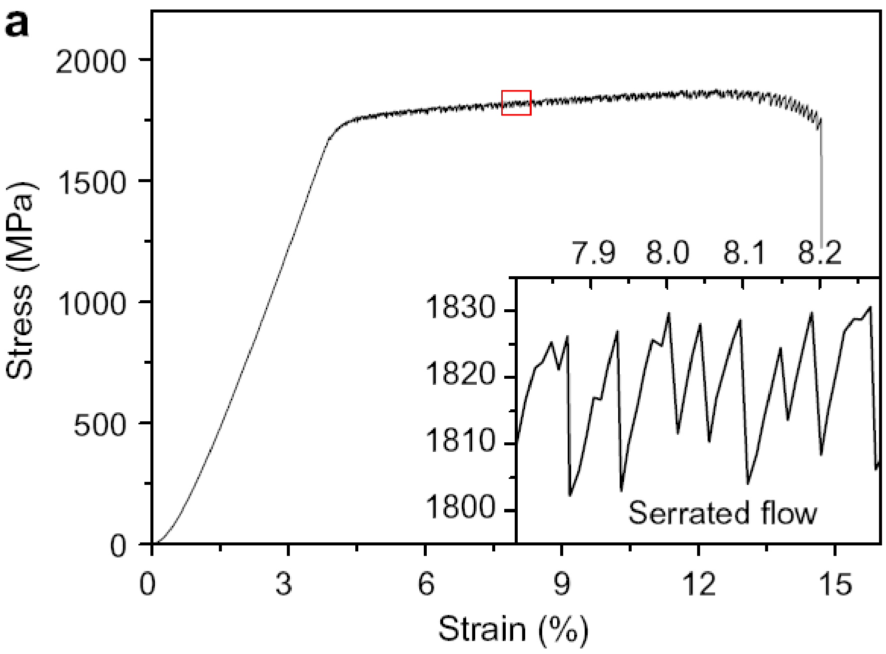


S.W. Lee, M.Y. Huh, E. Fleury & J.C. Lee, Crystallization-induced plasticity of Cu-Zr containing bulk amorphous alloys, *Acta Mater*. **54** (2006) 349.

Nanocrystallization in shear bands is a way of arresting shear bands — a possible origin of serrated flow

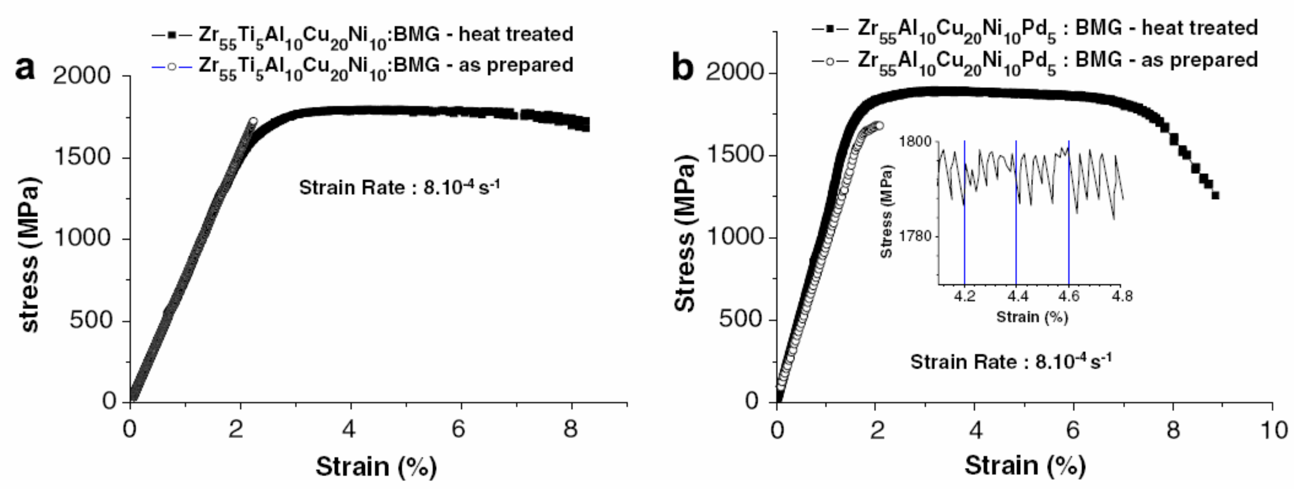
$Ni_{50}Pd_{30}P_{20}$

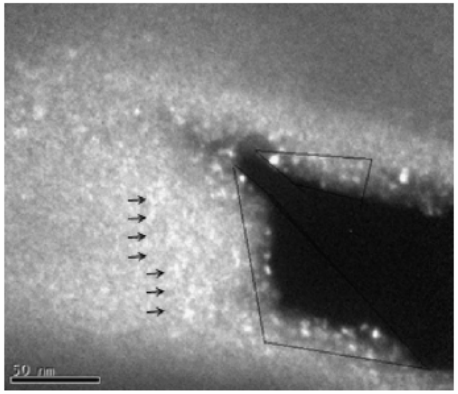


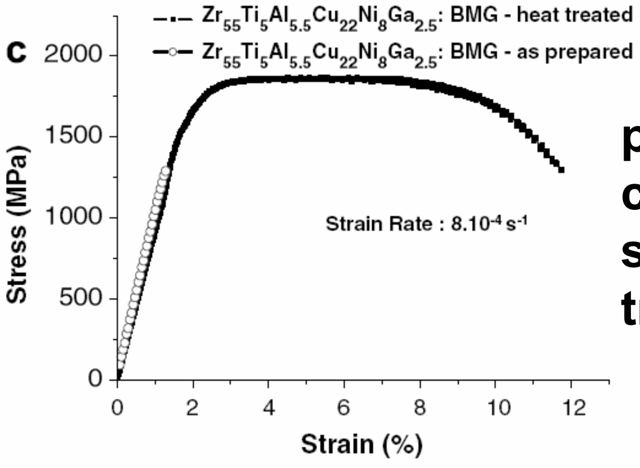


K. Wang, T. Fujita, Y.Q. Zeng, N. Nishiyama, A. Inoue and M.W. Chen, Micromechanisms of serrated flow in a $Ni_{50}Pd_{30}P_{20}$ bulk metallic glass with a large compression plasticity, *Acta Mater*. **56** (2008) 2834.

Nanocrystallization during shear may improve plasticity —



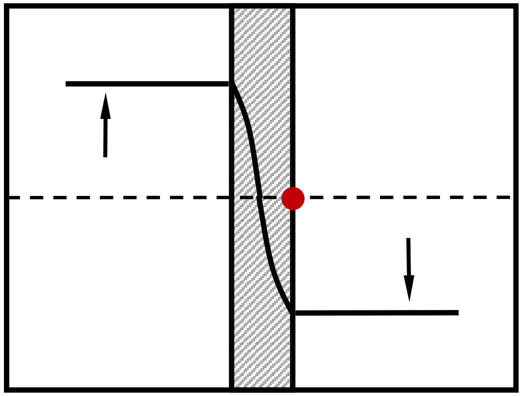




pre-nucleation of crystals facilitates subsequent transformation

K. Hajlaoui, A.R. Yavari, A. LeMoulec, W.J. Botta, G. Vaughan, J. Das, A.L. Greer & Å. Kvick, Plasticity induced by nanoparticle dispersions in bulk metallic glasses, *J. Non-Cryst. Solids* **353** (2007) 327.

Quench rate associated with shear bands?



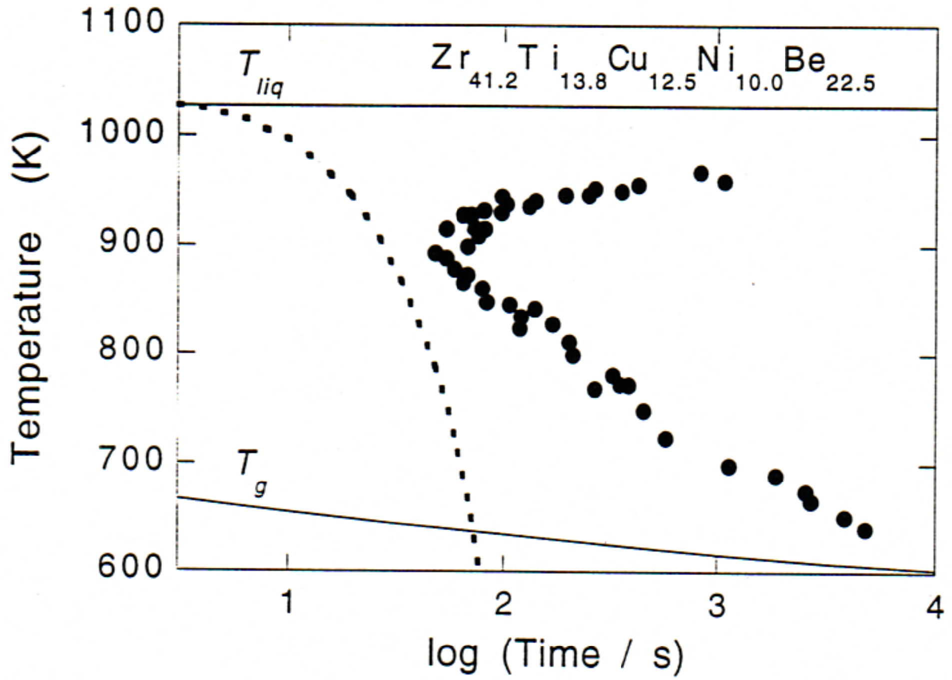
For a typical shear band in Vitreloy 1:

10 nm from centre plane

at T_g (= 613 K)   (occurs at ~190 ns)

→ the cooling rate is **~10^9 K s^{-1}**

Bulk metallic glasses



- multicomponent compositions aid glass formation
- the critical cooling rate is much lower (~1 K s^{-1})
- glasses can be formed in bulk

Changes in glass structure induced by deformation

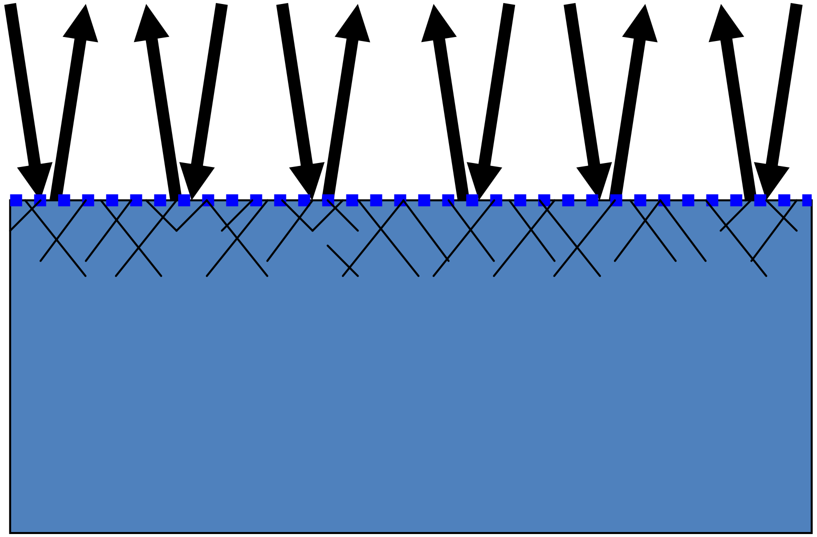
- changes in metallic glasses are difficult to detect because only a limited volume fraction is plastically deformed

- shot-peening is particularly attractive:
  - — high strain, high volume fraction deformed
  - — relatively low contamination

- shot-peening can induce damage or relaxation

- shot-peening can induce amorphization or crystallization

Effects of shot-peening on BMGs



- introduction of shear bands
- induce compressive residual stress in the surface
- gives improved mechanical properties
- plastic deformation also changes the glass structure

Phase changes induced by shot peening

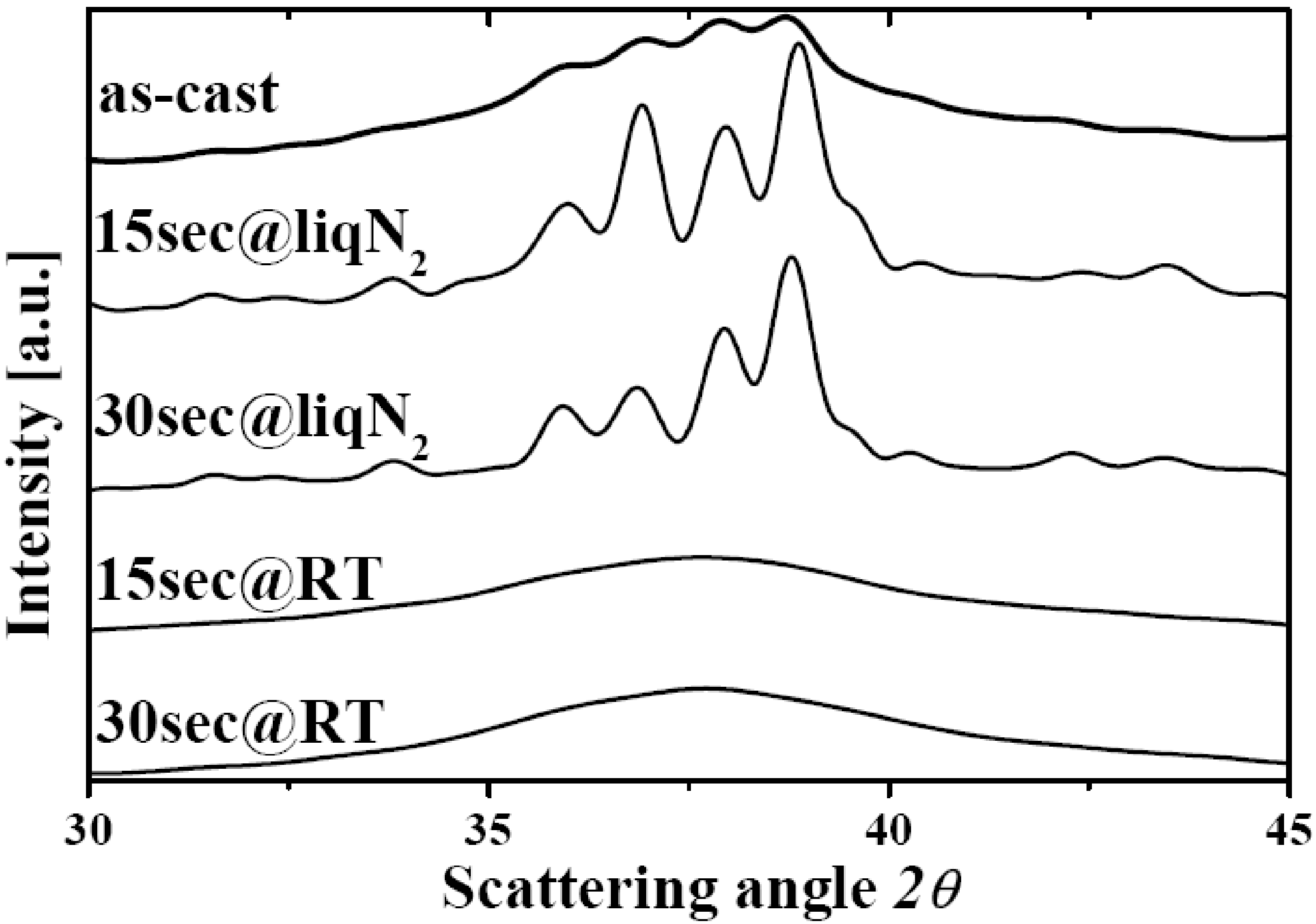
Studies of $Zr_{55}Al_{10}Cu_{30}Ni_5$

2 mm thick plate, as-cast fully glassy
3 mm diam. rod, as-cast partially crystalline

shot-peened at
- room temperature
- liquid nitrogen temperature

— a system already studied by T. Yamamoto et al. [*J. Alloys Comp*. **430** (2007) 97]

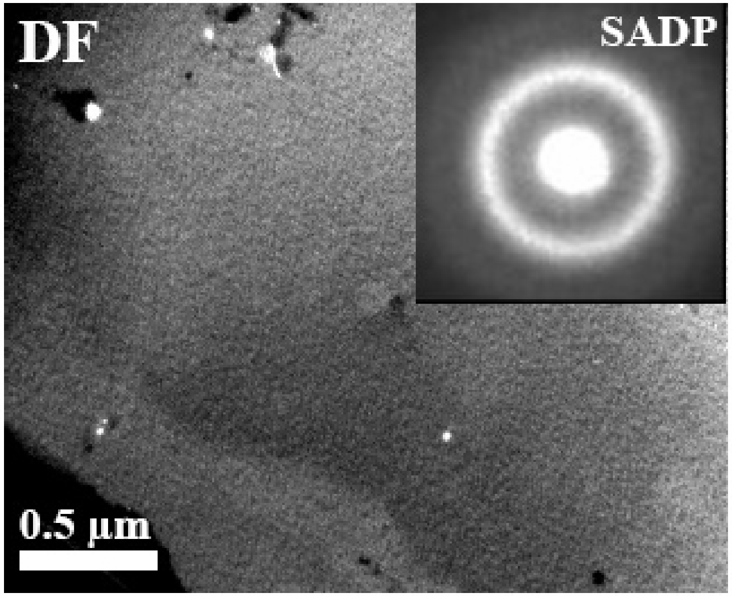
F.O. Méar, B. Doisneau, A.R. Yavari & A.L. Greer, “Structural effects of shot-peening in bulk metallic glasses”, *J. Alloys Comp.* **483** (2009) 256–259.



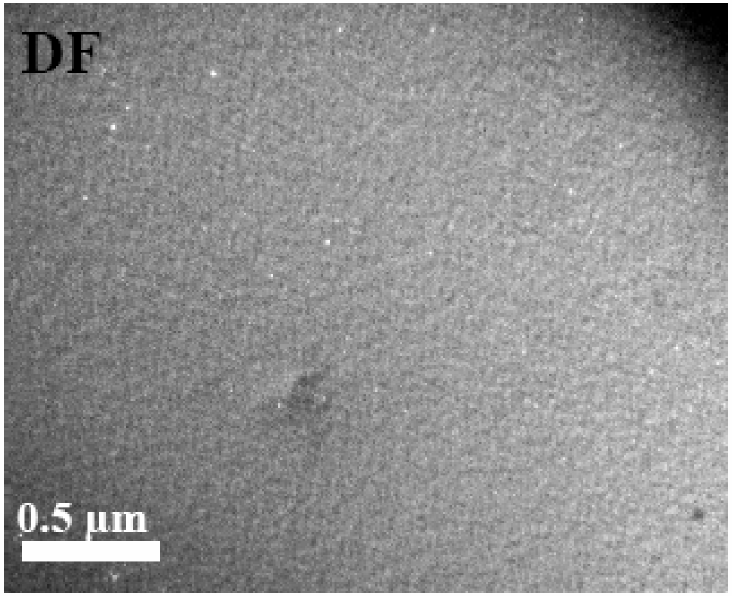
Partially crystalline as-cast samples —

- **amorphized** by peening at **room temperature**
- **crystallized** by peening at **liq. nitrogen temperature**

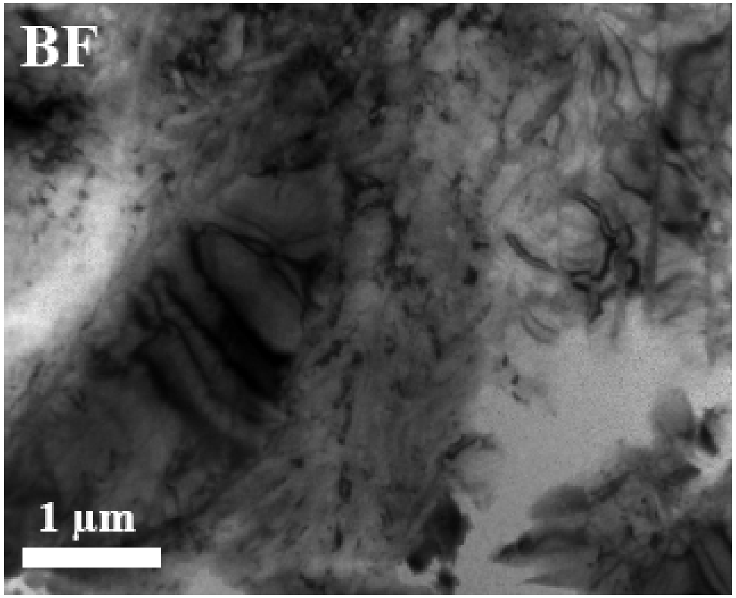
F.O. Méar, B. Doisneau, A.R. Yavari & A.L. Greer, "Structural effects of shot-peening in bulk metallic glasses", *J. Alloys Comp.* **483** (2009) 256–259.



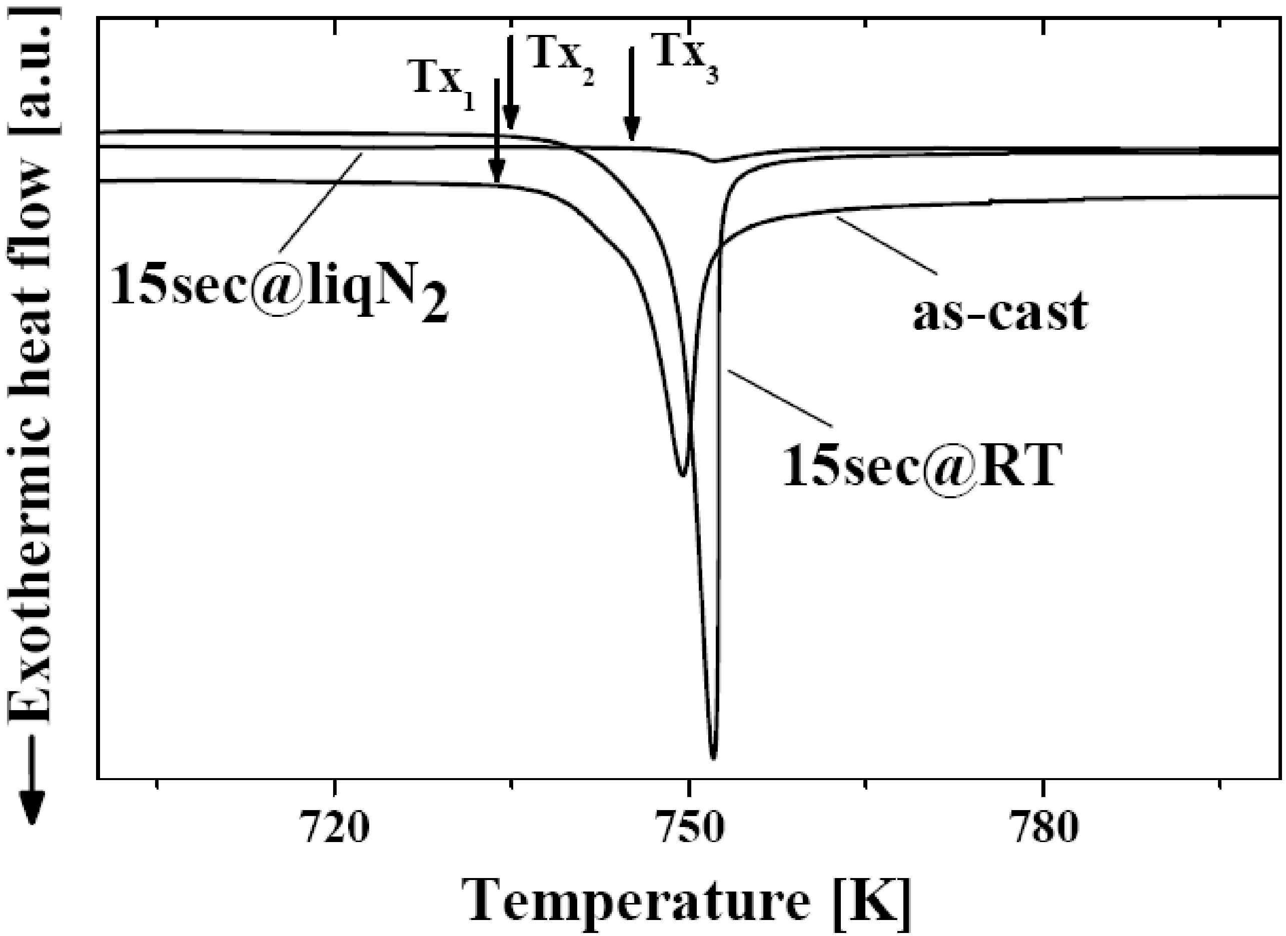
shot-peening at room temp.
→ AMORPHIZATION



shot-peening at 77 K
→ CRYSTALLIZATION

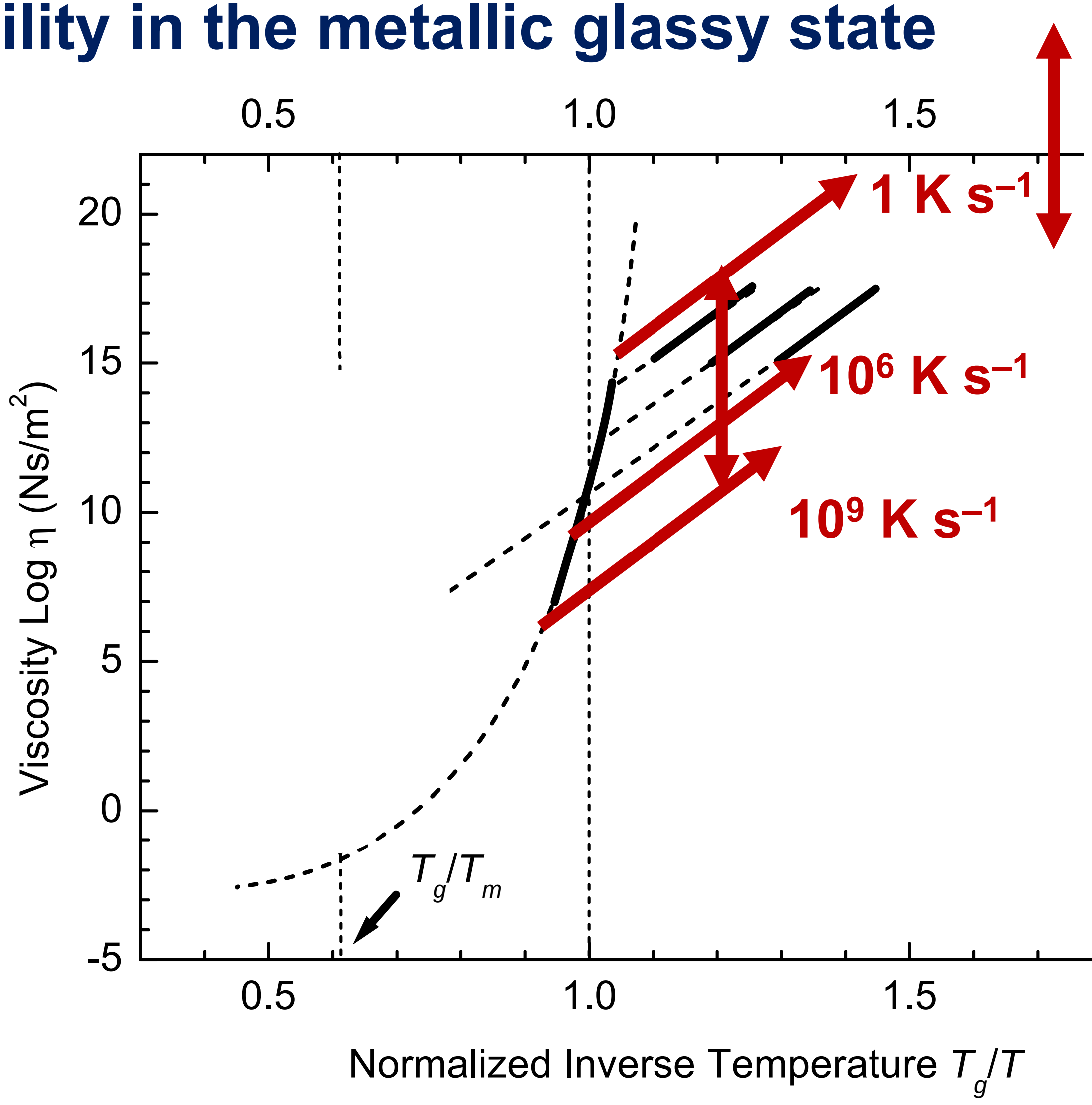


F.O. Méar et al. (2009)



F.O. Méar, B. Doisneau, A.R. Yavari & A.L. Greer, "Structural effects of shot-peening in bulk metallic glasses", *J. Alloys Comp.* **483** (2009) 256–259.

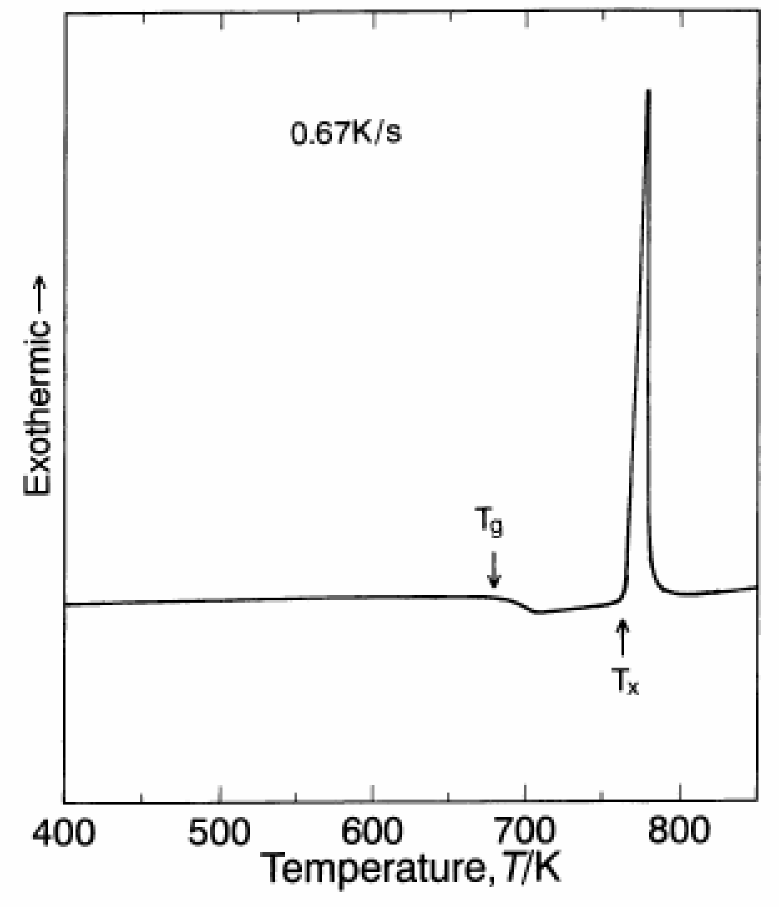
Variability in the metallic glassy state



mobility at given temperature varies over 7 orders

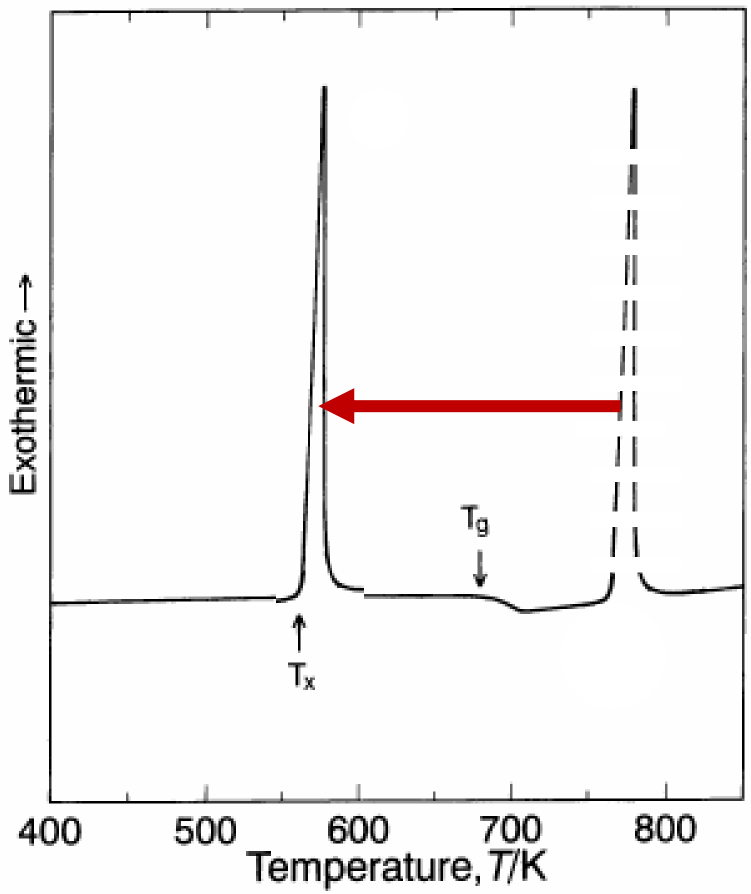
Data on Pd-Cu-Si and Pd-Si glasses from A.I. Taub & F. Spaepen, *Acta Metall.* **28** (1980) 1781. Isoconfigurational heating shown by C.A. Volkert & F. Spaepen, *Acta Metall.* **37** (1989) 1355.

DSC of $Zr_{55}Al_{10}Cu_{30}Ni_5$



A. Inoue & T. Zhang, *Mater. Trans. JIM* **37** (1996) 185.

Applying a typical activation energy for crystallization, a change in mobility by a factor of 10^7 is equivalent to a temperature shift of **~200 K**



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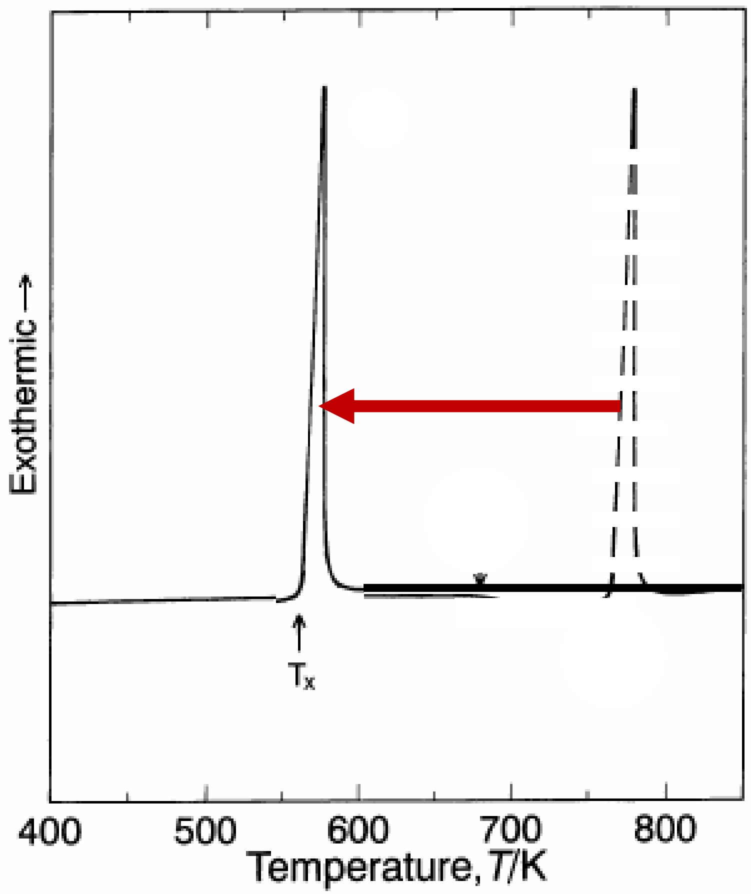

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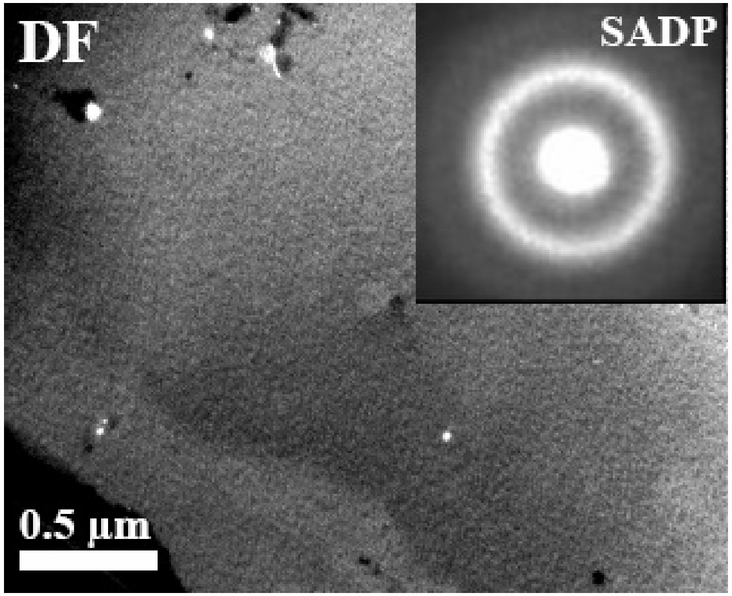
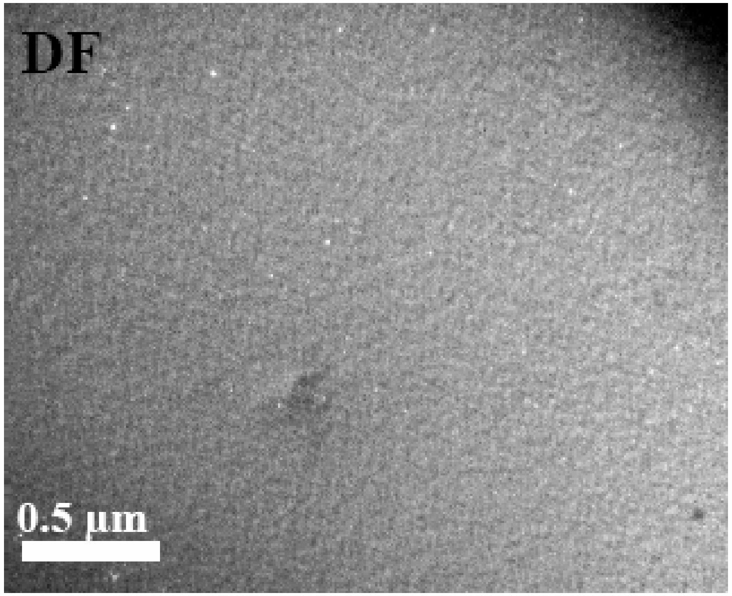
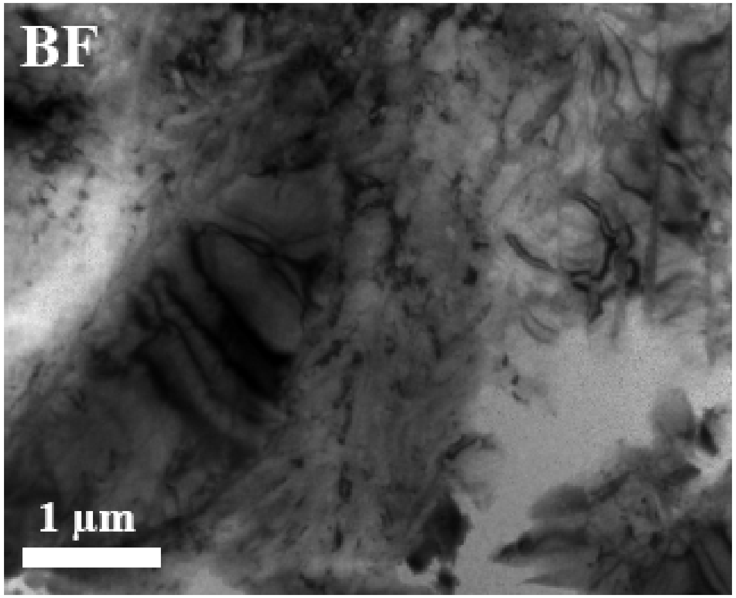


shot-peening at room temp.
→ AMORPHIZATION



shot-peening at 77 K
→ CRYSTALLIZATION



F.O. Méar et al. Proc. ISMANAM 2007

Thermal?

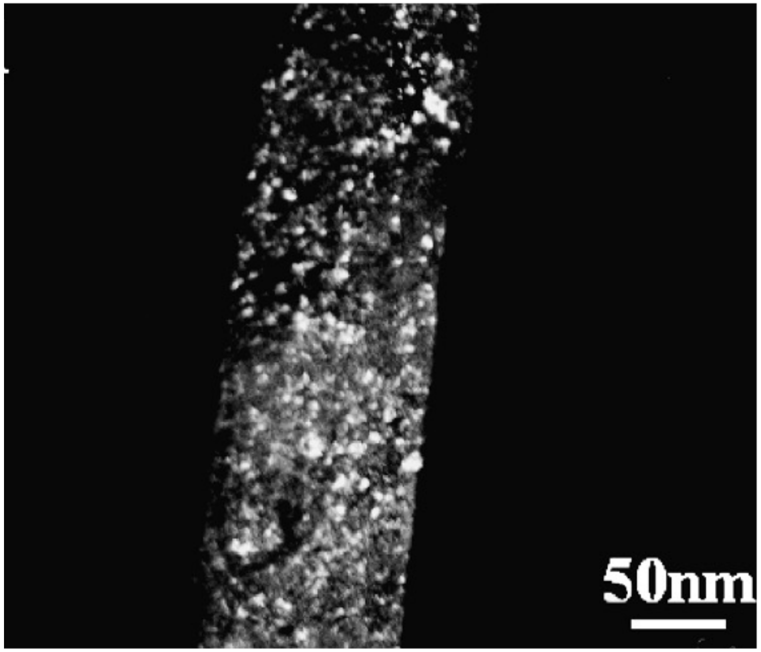
- crystallization often assumed to be thermal
- obvious heating at shear bands
- sometimes same crystals as on annealing or slow quenching
- high-temp. phases found
- observation of diffusion fields around crystals

Non-Thermal?

- often crystallization pathway is different from annealing
- crystallization at sub-ambient temperature
- different composition dependence of stability
- short thermal pulse **($\ll 1\ \mu$s)**
- melting on shear band: high cooling rate **(~10^9 K s^{-1})**
- crystallization is found in, not near, shear bands

Mechanically induced crystallization

- metallic glasses show crystallization as for other glasses
- but metallic glasses can be mechanically deformed
- mechanically induced crystallization and other structural changes
- clear evidence for non-thermal effects
- evidence for crystallization well below T_g



Shear banding

— is a symptom of the **work-softening** that leads to near-zero ductility, and is the major mechanical-property impediment to wider application of metallic glasses.

Questions about shear bands:

- how thick are the shear bands?
- what is the work dissipated in shear?
- how fast is the shear?
- how large is the hot zone around a shear band?
- what is the state of the material in the bands during/after shear?
- how can shear-banding be controlled to optimize properties?