



## **Metallic Glasses I:**

Overview of mechanical properties

A. L. Greer

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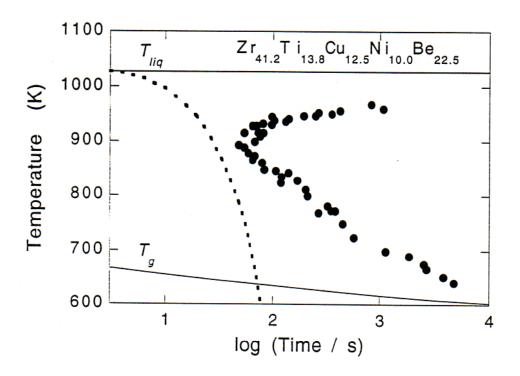
School on Glass Formers and Glasses JNCASR, Bengaluru, 4–20 January 2010

#### **Outline**

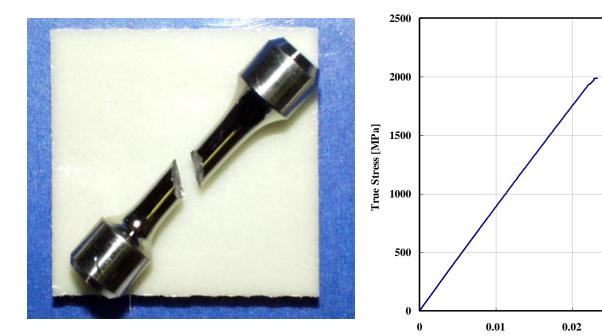
- elasticity
- yield strength
- formability
- elastic strain limit
- elastic energy storage
- losses
- toughness
- shear bands and work softening
- brittleness and plasticity
- effects of plastic deformation on structure
- and overall a look at applications



#### **Bulk Metallic Glasses**



- multicomponent compositions aid glass formation
- the critical cooling rate is low (~1 K s<sup>-1</sup>)
- glasses can be formed in bulk (maximum diameters mm up to a few cm)



Vitreloy 0.1 MPa Hydrostatic Pressure

Yield/Fracture Strength = 1986 MPa  $\epsilon_f = 0\%$ 

0.04

0.05

0.06

0.03

True Strain

J.J. Lewandowski

— can perform macroscopic mechanical tests

# Measuring strain distributions in amorphous materials

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#### AMORPHOUS MATERIALS

#### **NEWS & VIEWS**

## Characterizing amorphous strain

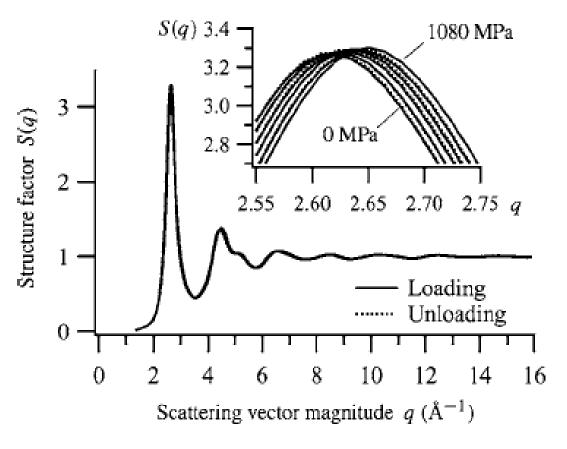
The engineering performance of materials is controlled to a large extent by their elastic stress/strain response. The first X-ray strain measurements in amorphous metals allow for new understanding of complex glassy materials.

GENE ICE is at the Oak Ridge National Laboratory, Bethel Valley Rd, Oak Ridge, Tennessee 37831-6118, USA. e-mail: IceGP@ornl.gov

- can measure elastic strain from *g*(*r*)
- linear elasticity
- can map the strain distribution
- stiffness of nearest-neighbour shell is
- 2.7× that of the bulk

<sup>4</sup> ISIS Rutherford Appleton Laboratory, Oxfordshire OX11 OQX, UK

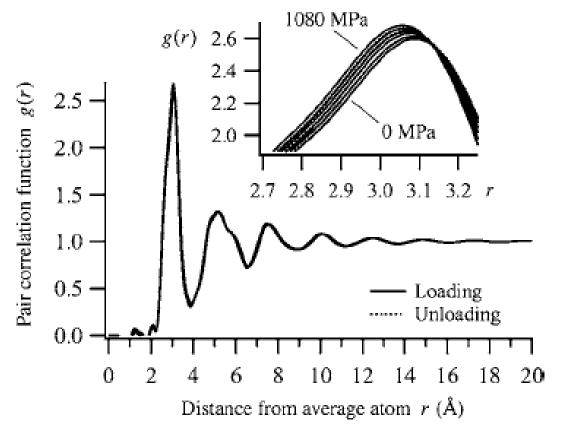
<sup>\*</sup>e-mail: henning.friis.poulsen@risoe.dk



- shifts of first peak give a good measure of elastic strain
- can use *l*(*q*)

FIG. 1. Structure factor S(q) parallel to the loading direction from 11 scattering patterns collected during incremental loading and unloading. Inset: top of the main peak, showing the shift of the peak in S(q) to larger q with increasing compressive stress.

Hufnagel et al. *Phys. Rev. B* **73** (2006) 064204



 elastic strain can also be obtained from the pair distribution function g(r)

FIG. 3. Pair correlation functions g(r) calculated from the S(q) data in Fig. 1 (parallel to the loading direction). Inset: shift in the first peak in g(r) to smaller r with increasing compressive stress.

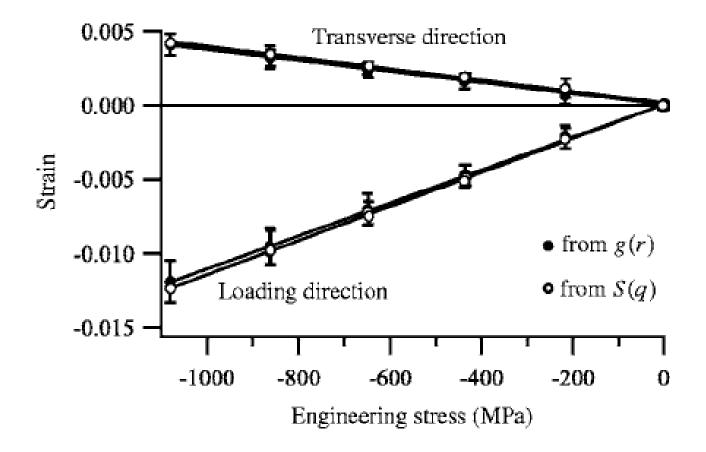
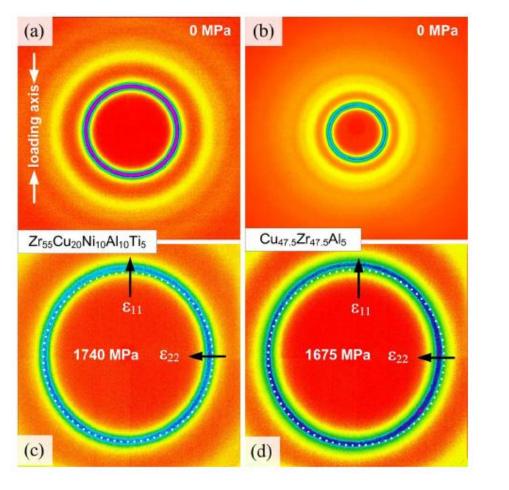


FIG. 2. Strain determined from the structure factor S(q) in reciprocal space and from the pair correlation function g(r) in real space.



## Compressive loading of BMG samples

Das et al. *Phys. Rev. B* **76** (2007) 092293.

FIG. 1. (Color online) The diffraction patterns of  $Zr_{55}Cu_{20}Ni_{10}Al_{10}Ti_5$  and  $Cu_{47.5}Zr_{47.5}Al_5$  before [(a) and (b)] and after employing stress [(c) and (d)] near plastic yielding, showing a very clear change from circular to elliptical shape. A dotted circle is shown to reveal that the average interatomic spacing decreases along the loading axis ( $\epsilon_{11}$ ) and increases along the transverse direction ( $\epsilon_{22}$ ).

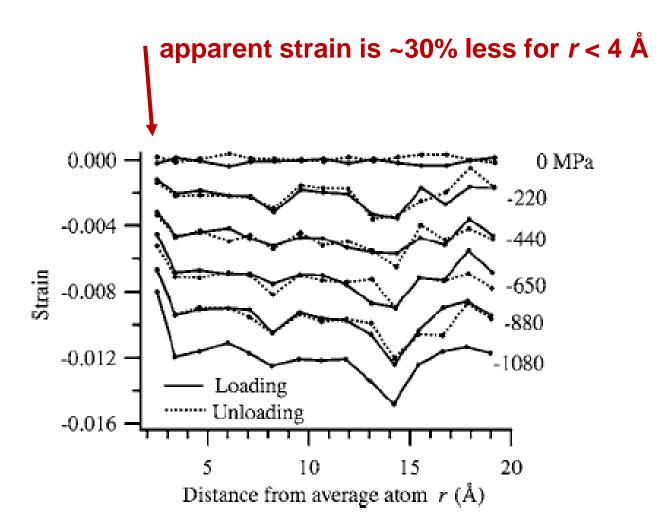


FIG. 4. Strain determined from pair correlation functions g(r) at several stresses.

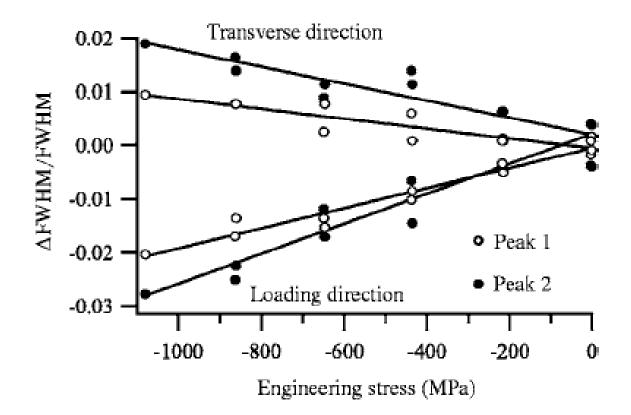
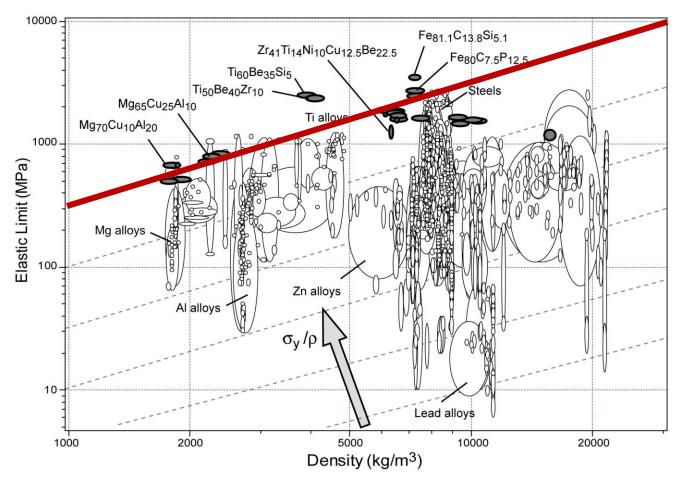


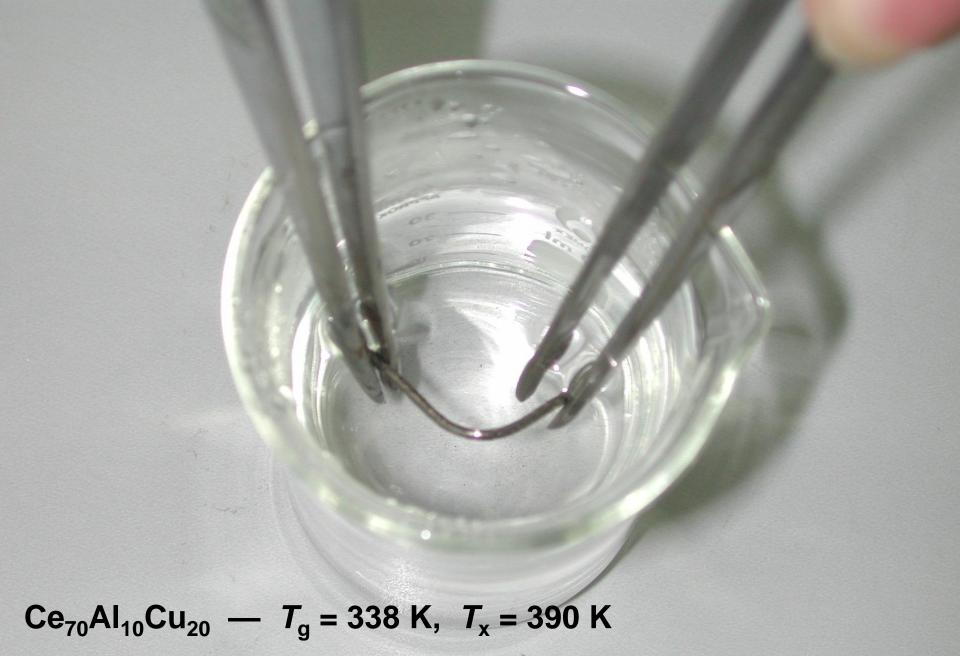
FIG. 7. Change in the widths (FWHM) of the two overlapping peaks in the RDF (Fig. 5).

- overall peak narrowing under stress
- stressed sample has lower entropy
- analogous to "entropy spring" familiar for polymers

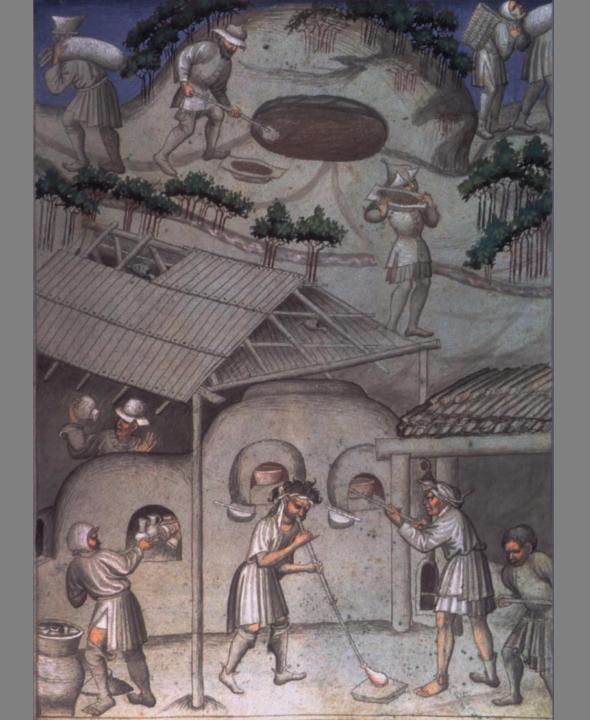
#### Metallic glasses for structural applications



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



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

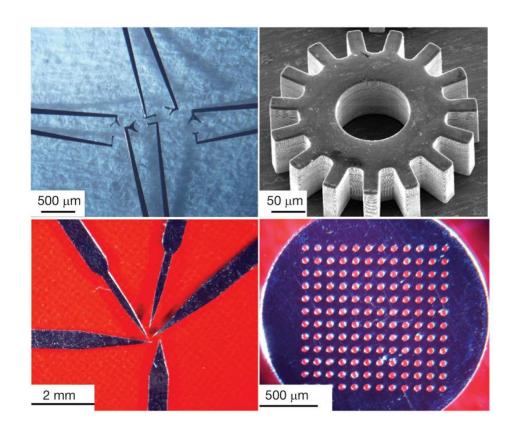






## Nanomoulding with amorphous metals

Optical and scanning electron microscope images of three-dimensional microparts, including tweezers (top left), scalpels (bottom left), a gear (top right) and a membrane (bottom right).

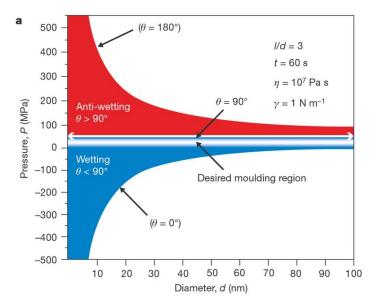


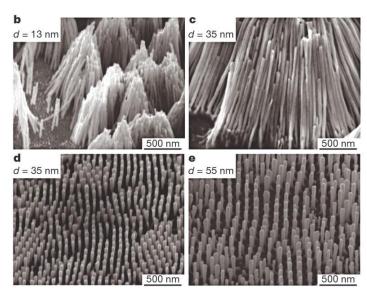


### Nanomoulding with amorphous metals

Controlling metallic glass moulding on scales smaller than 100 nm

Pt-based BMG



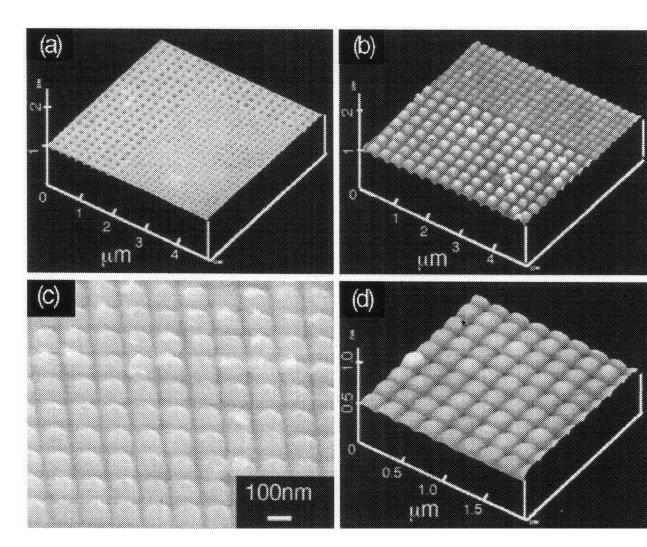




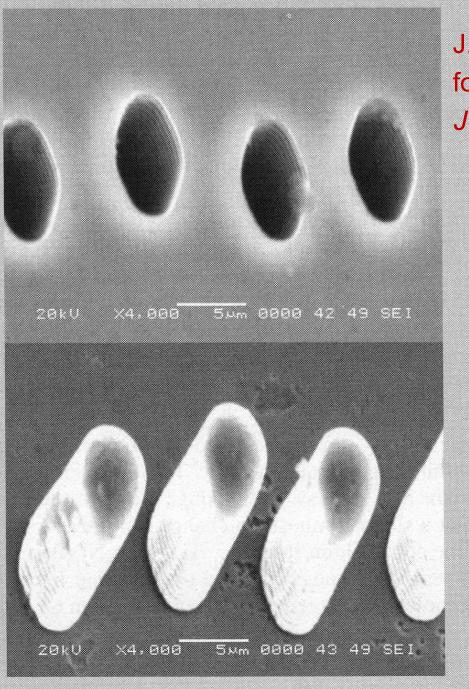
## **Microformability of BMGs**

of interest for micro ano-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)

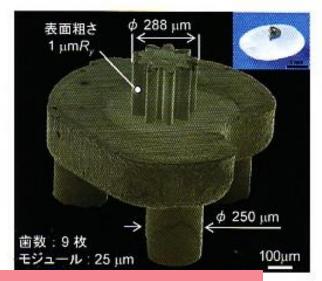


Y. Saotome et al. "The micro-nanoformability of Pt-based metallic glass and the nanoforming of three-dimensional structures", *Intermetallics* **10** (2005) 1241.



J. Schroers: "The superplastic forming of bulk metallic glasses", *JOM* **57**(5) (2005) 35.

Figure 5. A micro-replication of protrusions from a silicon mold (top) by SPF of Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub> at 270°C for 300 s at a pressure of 30 MPa. These processing parameters enable the replication of features in the 100 nm range.

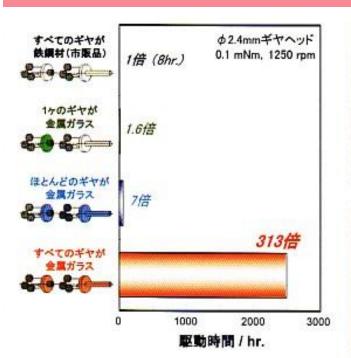




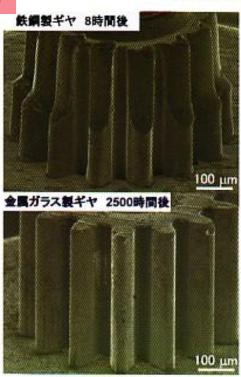
金属ガラス製超精密歯車を組み込んだ世界最小マイクロギヤードモータ

連絡先: RIMCOF Tel: (03)3459-6900

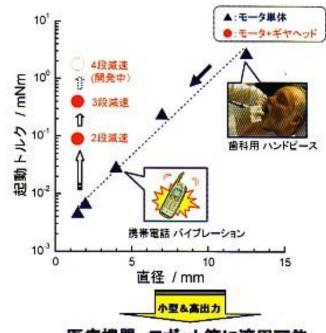
#### The world's smallest motor



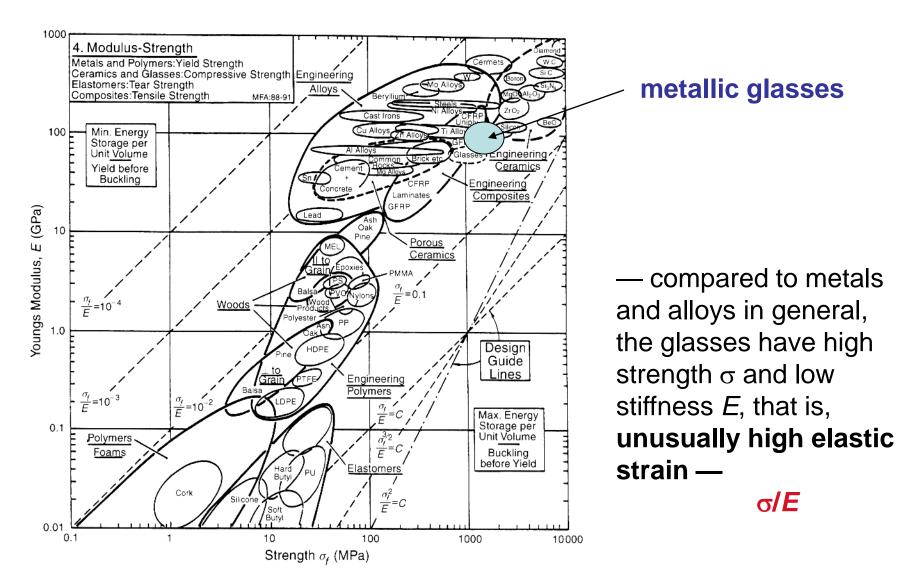
直径2.4 mmギヤヘッド(従来品)を用いた駆動時間比較



駆動試験後の歯車摩耗状況



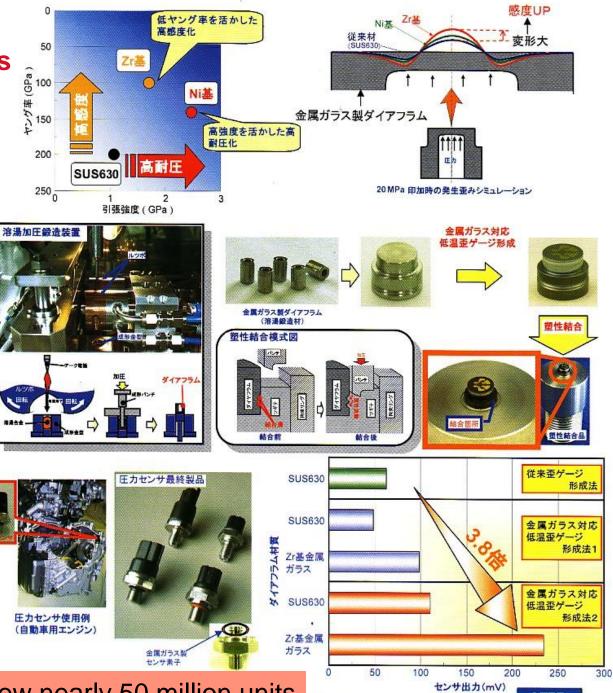
医療機器、ロボット等に適用可能



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

#### **Pressure Sensors**

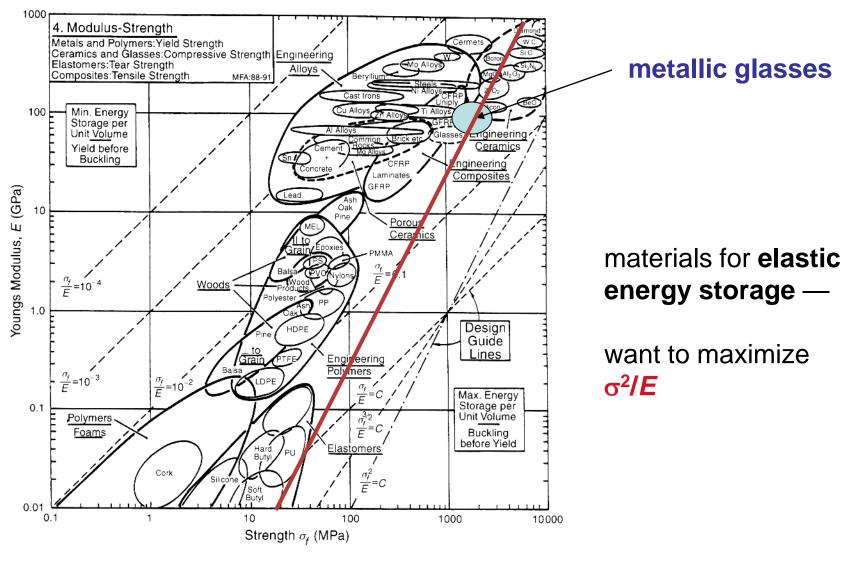
#### **Diaphragms**



Annual production now nearly 50 million units

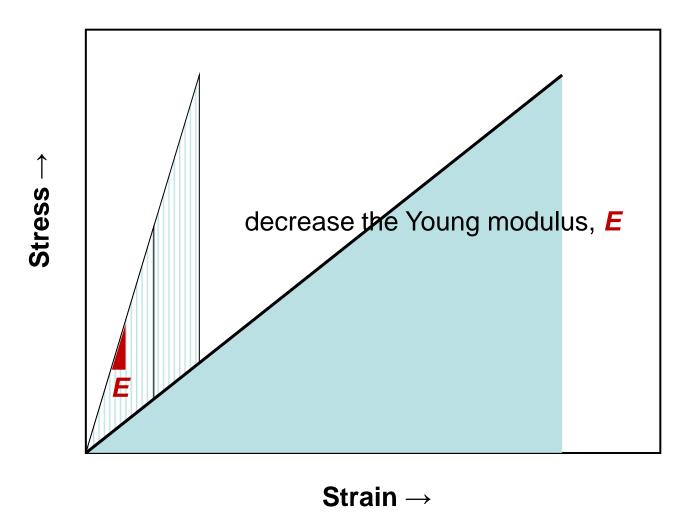
連絡先: RIMCOF Tel: (03)3459-6900

NEDO



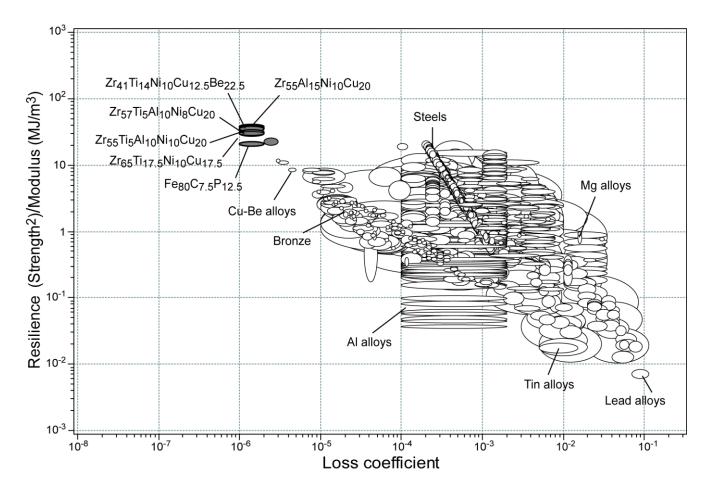
from *Materials Selection in Mechanical Design* (2nd ed.) M. F. Ashby, Butterworth-Heinemann, 1999

#### to increase the elastic stored energy —





Golf clubs .... and tennis-racket frames, baseball bats, skis ...

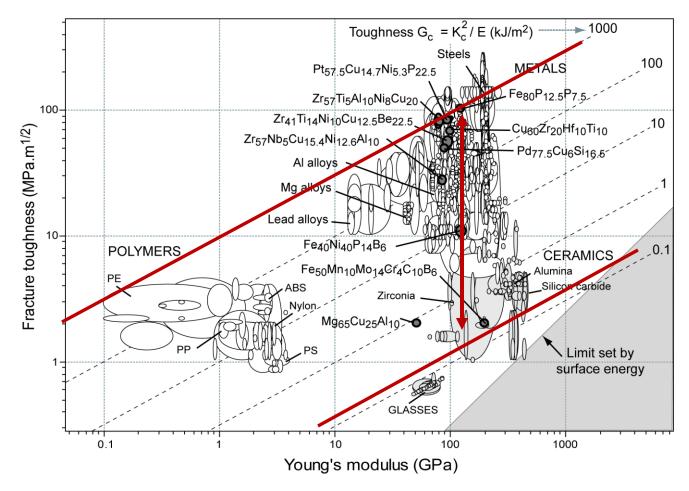


Resilience  $\sigma_y^2/E$  and loss coefficient  $\eta$  for 1507 metals, alloys, metal-matrix composites and metallic glasses.

Conventional glasses are brittle —

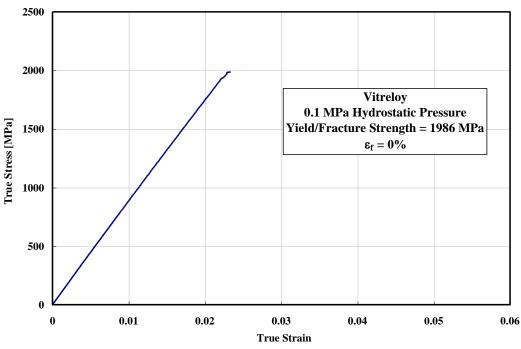
What about metallic glasses?



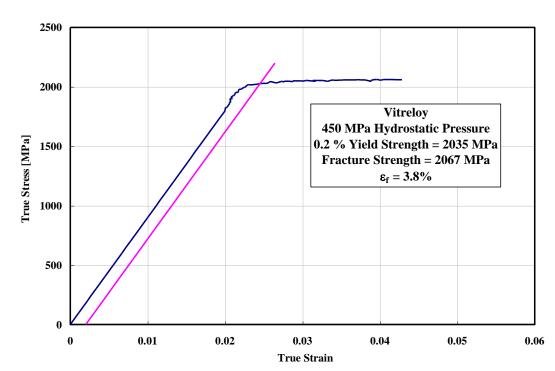


**Fracture toughness** and **Young's modulus** for metals, alloys, ceramic, glasses, polymers and metallic glasses. The contours show the **toughness**  $G_c$  in kJ m<sup>-2</sup>.



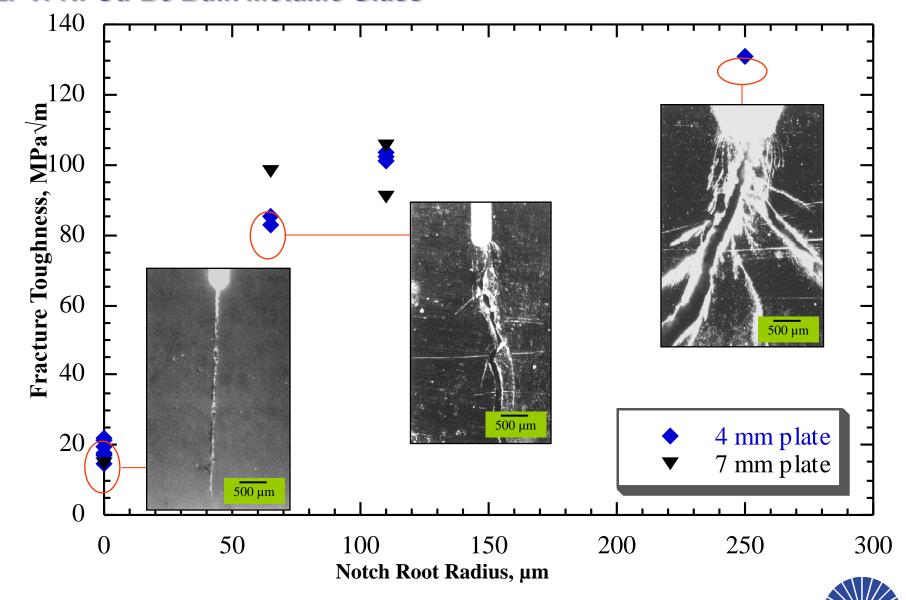


At ambient temperature metallic glasses in tension appear macroscopically brittle. There is plastic flow, but it is localized into shear bands, a sign of work softening.

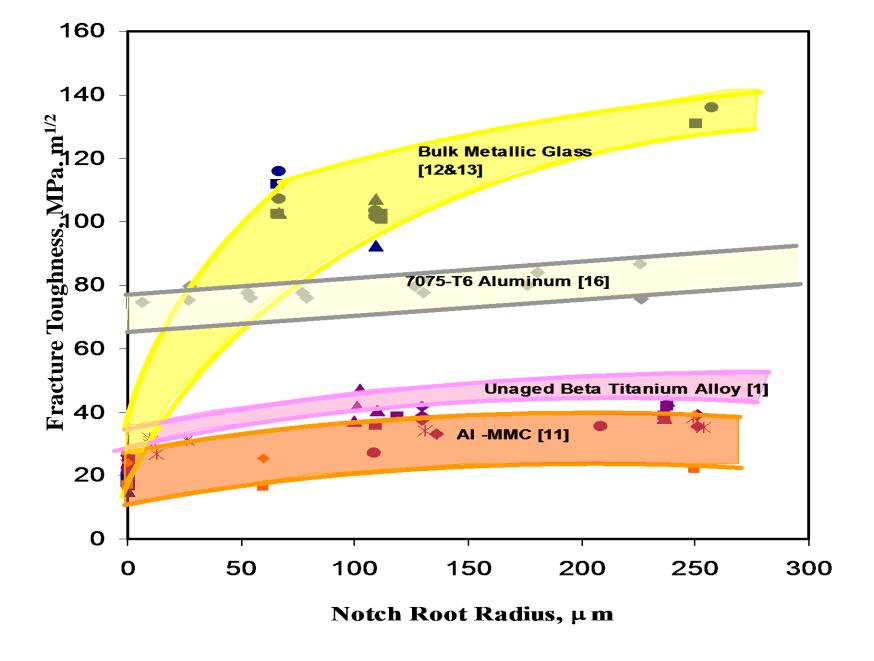


#### J. J. Lewandowski

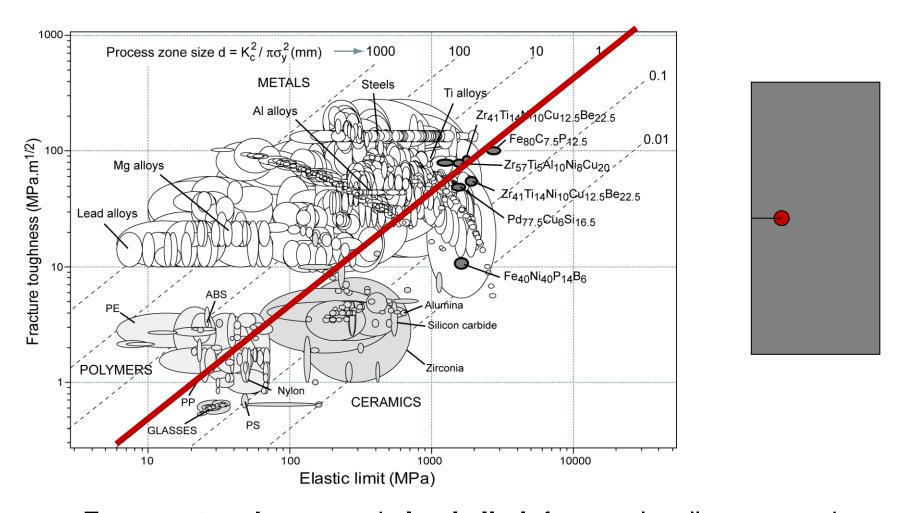
## Effects of Notch Root Radius on Fracture Profile and Toughness of Zr-Ti-Ni-Cu-Be Bulk Metallic Glass



P. Lowhaphandu & J.J. Lewandowski, *Scripta Mater.* **38** (1998) 1811. J.J. Lewandowski – DAAD19-01-0525



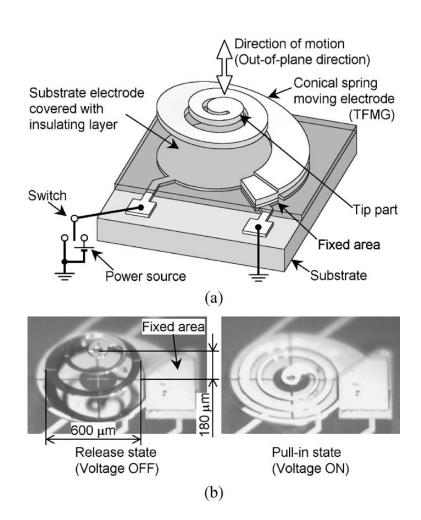
J.J. Lewandowski, Mater. Trans. JIM, 42 (2001) 633.



**Fracture toughness** and **elastic limit** for metals, alloys, ceramic, glasses, polymers and metallic glasses. The contours show the **process-zone size** *d* in mm.

## **MEMS Applications**

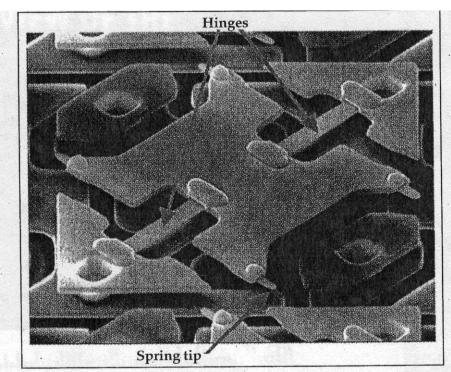
A conical spring microactuator with a long stroke of 200  $\mu$ m normal to the substrate. The spring is a 7.6  $\mu$ m thick film of Pd<sub>76</sub>Cu<sub>7</sub>Si<sub>17</sub> metallic glass.



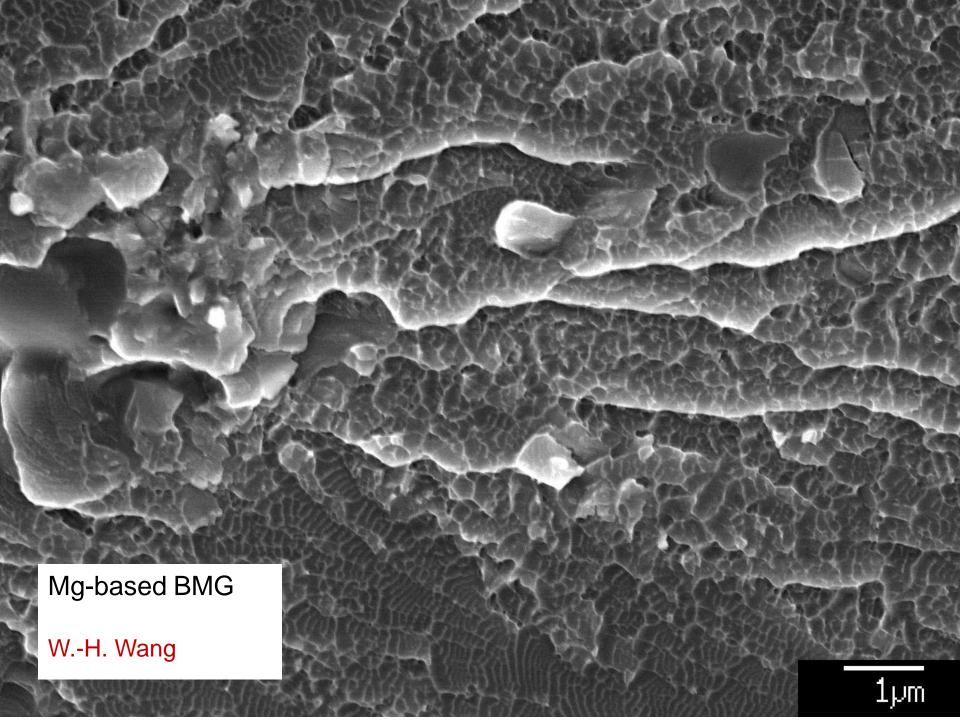
### **MEMS Applications of Metallic Glasses**

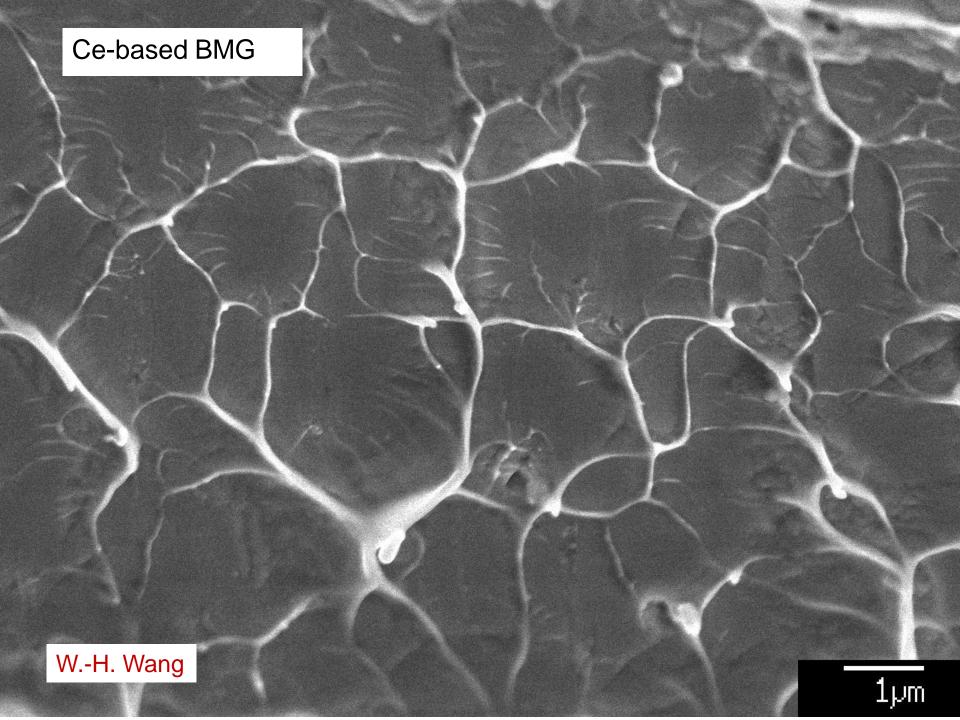
The Texas Instruments Digital Light Processor (DLP) data projector technology is based on mirrors supported by amorphous Ti-Al hinges. DLP devices with >1.3 x 10<sup>6</sup> addressable mirrors are in production, and the hinges still show no fatigue failures after 10<sup>12</sup> cycles.

J.H. Tregilgas, "Amorphous titanium aluminide hinge" *Adv. Mater. Proc.* **162** (Oct. 2004) 40.



This diagram shows a close-up view of the hinges. This is an early digital light processor without the aluminum mirrors, to show the underlying structure with amorphous Ti-Al hinges and spring tips that allow for mirror rotation.





## **Metals: Plasticity or Brittleness?**

- the plastic flow stress in shear is proportional to the elastic shear modulus — thus the shear modulus is a measure of the difficulty of plastic flow
- similarly the bulk modulus is a measure of the difficulty of cracking
- thus high values of the shear-to-bulk modulus ratio μ/B should favour brittleness and vice versa
- proposed by Pugh in 1954, and developed by others —
- S.F. Pugh, *Philos. Mag.* **45** 823 (1954).
- A. Kelly, W.R. Tyson and A.H. Cottrell, *Philos. Mag.* **15** 567 (1967).
- J.R. Rice and R. Thomson, *Philos. Mag.* **29** 73 (1974).
- A.H. Cottrell, in *Advances in Physical Metallurgy*, edited by J.A. Charles and G.C. Smith (Institute of Metals, London, 1990), pp. 181–187.

- For polycrystalline metals there is a scale from ductile, low  $\mu B$  (Ag, Au, Cd, Cu) to brittle, high  $\mu B$  (Be, Ir)
- for fcc metals  $(\mu/B)_{crit} = 0.43-0.56$  or 0.32-0.57
- for hcp metals  $(\mu/B)_{crit} = 0.60-0.63$
- for bcc metals  $(\mu/B)_{crit} = 0.35-0.68$
- thus critical modulus ratio  $(\mu B)_{crit}$  is **not** very well defined even for one structure type
- $(\mu/B)_{crit}$  is affected by anisotropy
- most detailed theory for  $(\mu B)_{crit}$  concerns dislocation emission from a crack tip

# What will happen for metallic glasses?

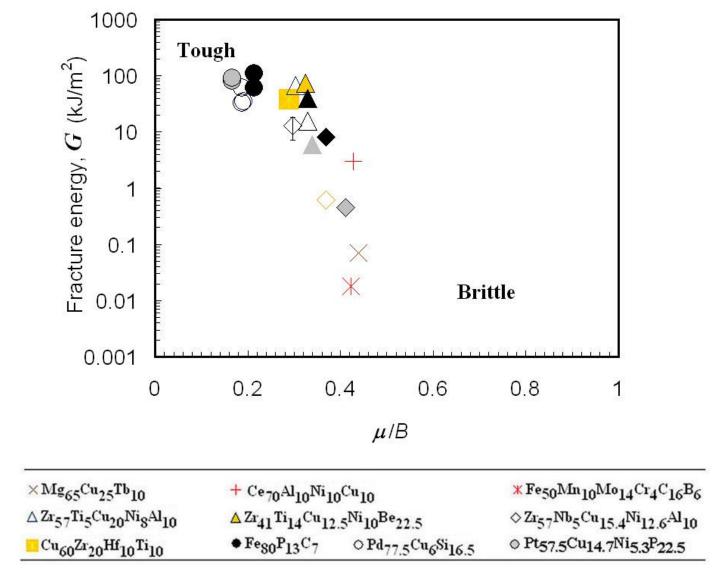
- no anisotropy
- no dislocations
- no clearly different structures

# With BMGs, good data are now available

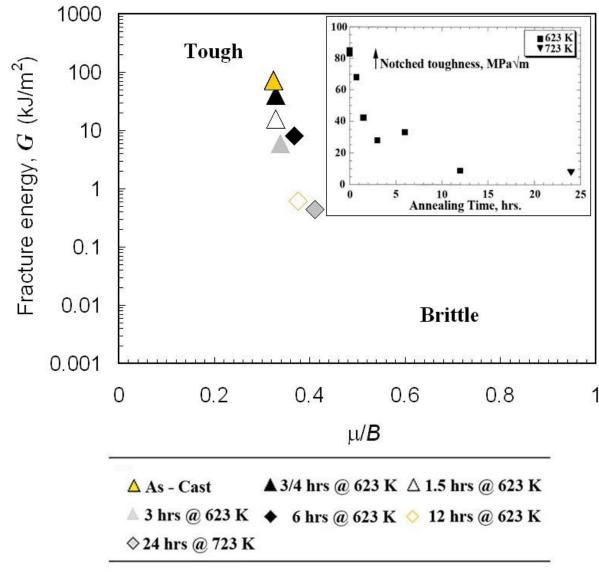
Fracture data are presented in terms of the energy of fracture

$$G = K^2/E(1 - v^2)$$

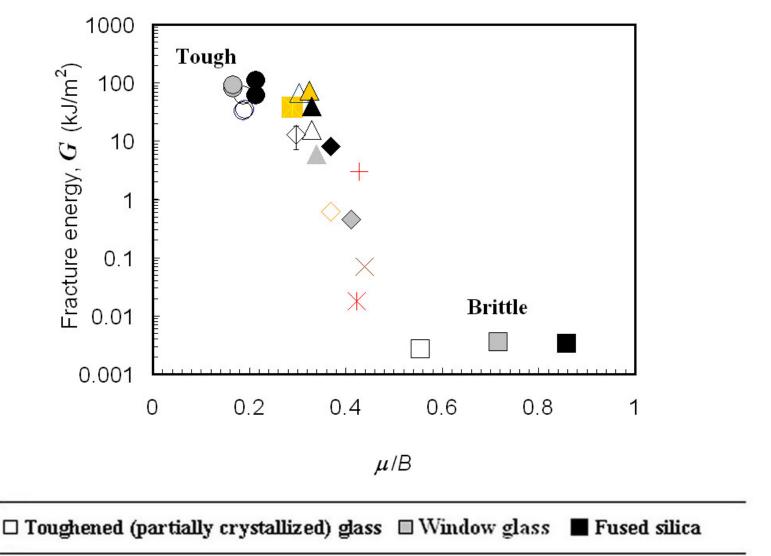
where K is the toughness (stress intensity at fracture) and  $\nu$  is Poisson's ratio



Compilation of **all** relevant and available data on **as-cast** (unannealed) metallic glasses (mostly, but not all BMGs)



The inset shows the decrease in toughness as a function of annealing time for Vitreloy 1. The main figure shows a good correlation of embrittlement with the changing  $\mu B$ .

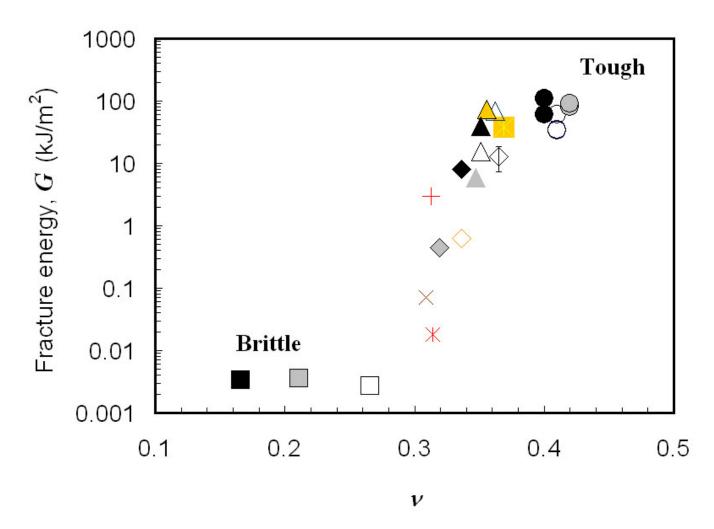


All the data superposed, together with data on oxide glasses for comparison. Overall,  $(\mu B)_{crit} = 0.41-0.43$ 

#### Poisson's ratio

- J. Schroers & W. L. Johnson, [*Phys. Rev. Lett.* **93** (2004) 255506] show that —
- a Pt-rich glass (Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub>) has exceptionally good plasticity and exceptionally high Poisson's ratio  $\nu$ . This is the same correlation because  $\mu B$  and  $\nu$  are related by

$$\frac{\mu}{B} = \frac{3(1-2\nu)}{2(1+\nu)}$$



The same data presented in terms of Poisson's ratio. The critical value corresponding to  $(\mu/B)_{crit} = 0.41-0.43$  is  $v_{crit} = 0.31-0.32$ .

# Alloy design

To avoid intrinsic brittleness and to have greater resistance to annealing-induced embrittlement —

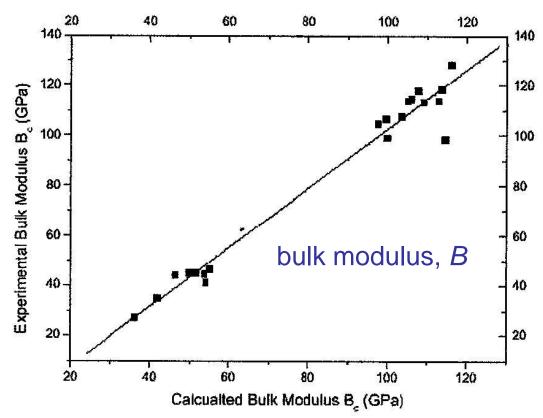
• we need to choose component elements with small  $\mu/B$  or, equivalently, high  $\nu$  (ideally  $\nu$  should tend towards 0.5, which is the value for liquids)

plastic brittle

	Au	Nb	Pd	Pt	Hf	Al	Cu	Zr	Ti	Ni	Ca	Со	Fe	Mg	Nd	La	Pr	Υ	Tb	Gd	Се	Ве
μ/Β	0.12	0.22	0.24	0.27	0.27	0.35	0.35	0.39	0.42	0.43	0.44	0.45	0.48	0.49	0.50	0.52	0.52	0.54	0.57	0.58	0.61	1.02
ν	0.44	0.40	0.39	0.38	0.37	0.34	0.34	0.33	0.32	0.31	0.31	0.30	0.29	0.29	0.28	0.28	0.28	0.26	0.26	0.26	0.25	0.03

For metallic glasses containing only metals, elastic moduli can be predicted surprisingly well by simply taking a weighted average of the moduli of the constituent elements. The weighting here is by volume fraction —

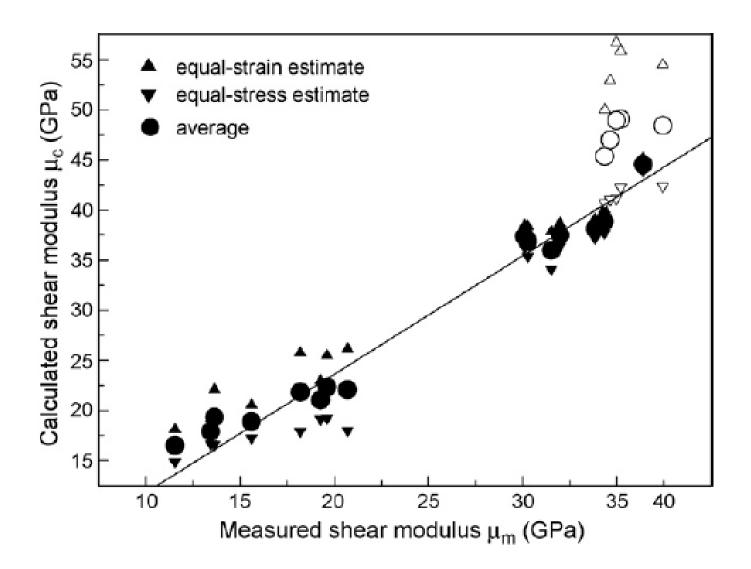
B scales with the number of valence electrons per unit volume
[J.J. Gilman: Electronic Basis of the Strength of Materials, CUP, Cambridge, 2003]



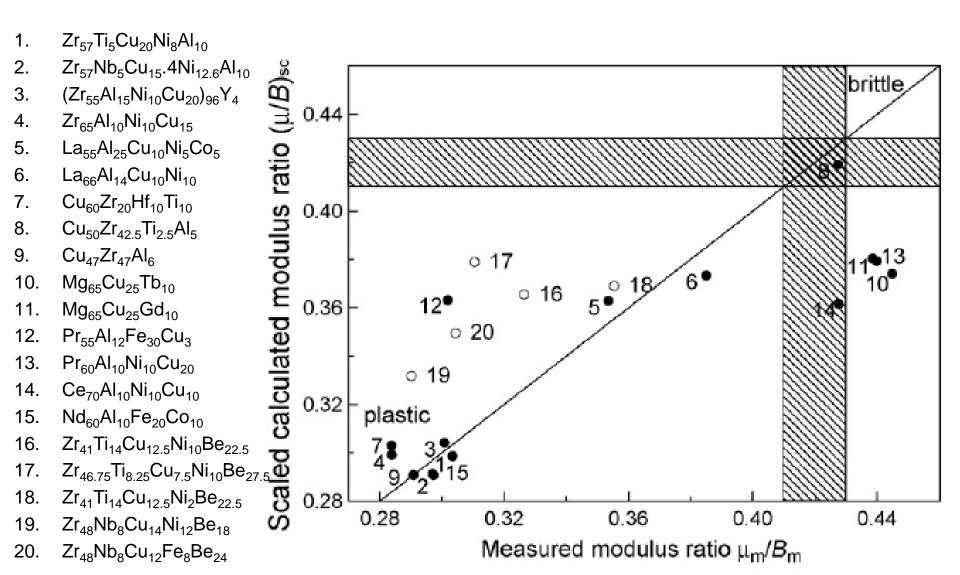
Since both  $\mu$  and B can be predicted moderately well, we should be able to choose compositions to maximize plasticity.

**ISMANAM 2005:** (proceedings to be published in *J. Alloys Compounds*)

Y. Zhang & A.L. Greer, "Correlations for predicting plasticity or brittleness of metallic glasses"

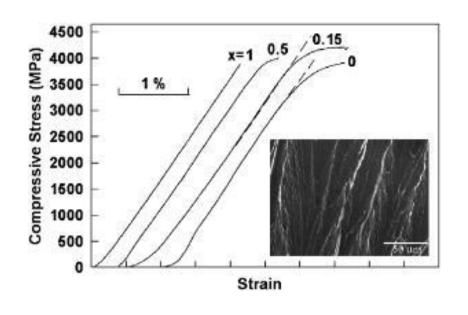


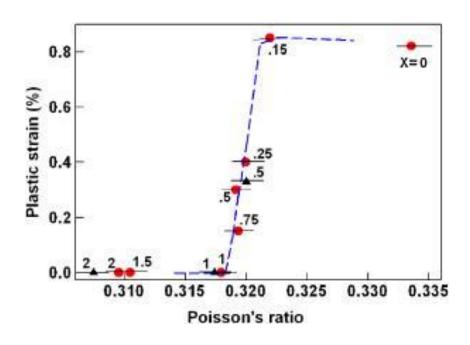
Y. Zhang & A.L. Greer: "Correlations for predicting plasticity or brittleness of metallic glasses", *J. Alloys Comp.* **434-435** (2007) 2.



Y. Zhang & A.L. Greer: "Correlations for predicting plasticity or brittleness of metallic glasses", *J. Alloys Comp.* **434-435** (2007) 2.

# Use of doping to improve plasticity



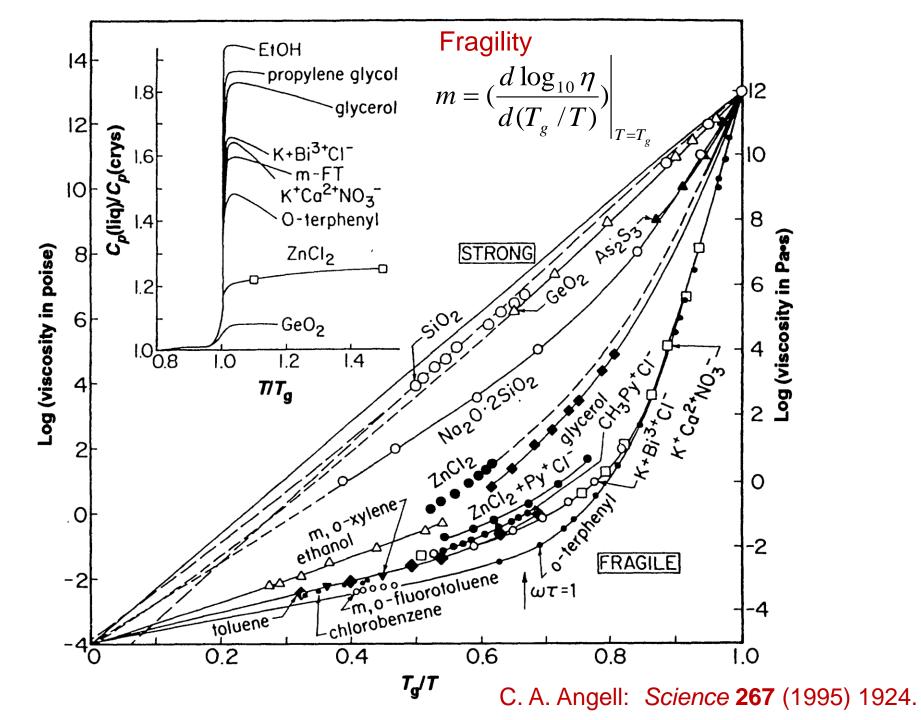


Compression tests on Fe<sub>65</sub>Mo<sub>14</sub>C<sub>15</sub>B<sub>6</sub> show improved plasticity on doping with Er or Dy.

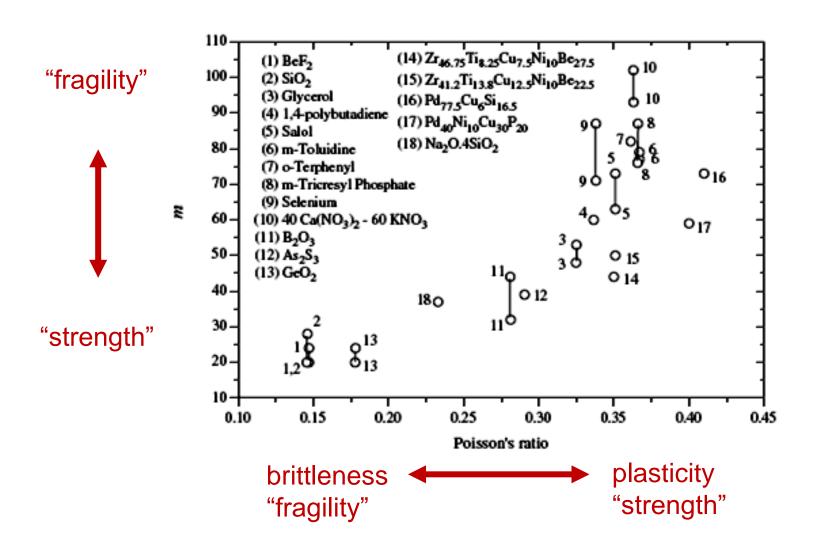
$$Fe_{65-x}Mo_{14}C_{15}B_6Er_x$$
 (circles)  
 $Fe_{65-x}Mo_{14}C_{15}B_6Dy_x$  (triangles)

The critical  $\nu$  is again ~0.32

X.J. Guo, A.G. McDermott, S.J. Poon & G.J. Shiflet, Appl. Phys. Lett. 88 (2006) 211905.

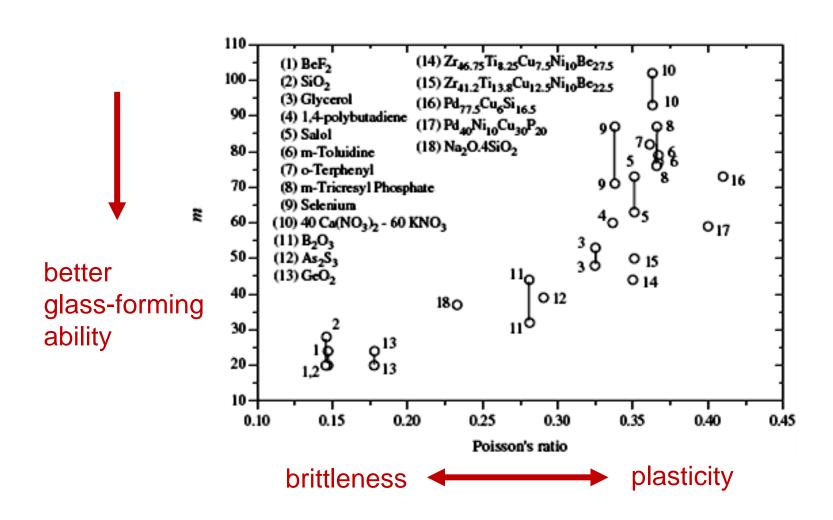


Angell's "fragility" of liquid: 
$$m = \left(\frac{d \log_{10} \eta}{d(T_g/T)}\right)\Big|_{T=T_g}$$



G. P. Johari: *Philos. Mag.* **86** (2006) 1567.

#### The better the glass-forming ability, the more likely to be brittle!



#### **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.

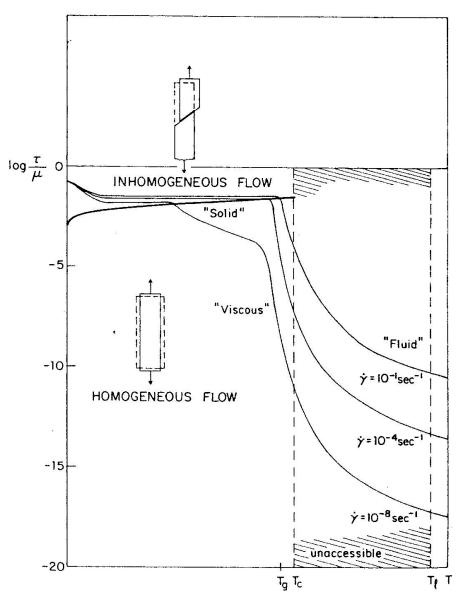
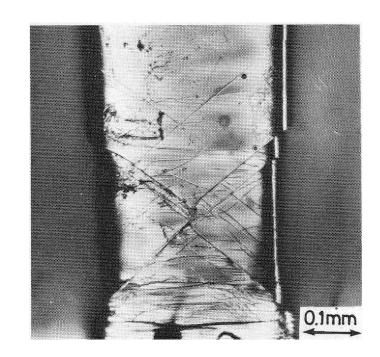


Fig. 2. Schematic deformation map of a metallic glass. The various modes of deformation are indicated.

#### The flow in shear bands does change the structure

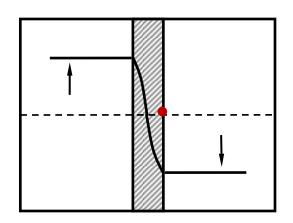
—and the structural change can be erased by annealing



preferential etching at shear bands:
 C.A. Pampillo, Scripta Metall. 6 (1972) 915

preferential shear on existing bands:
 K.D. Krishnanand & R.W. Cahn, Scripta Metall. 9 (1975) 1259

#### Quench rate associated with shear bands?



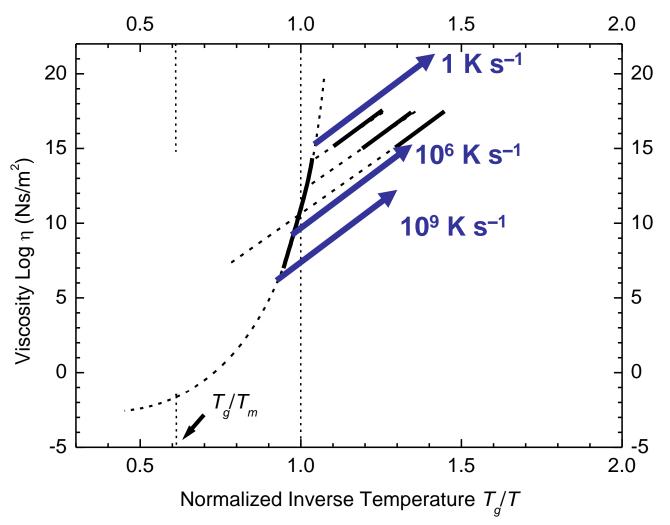
For a typical shear band in Vitreloy 1:

10 nm from centre plane

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

→ the cooling rate is ~10° K s<sup>-1</sup>

#### Variability in the metallic glassy state



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.

# L. Battezzati et al. *J. Non-Cryst. Solids* **61-62** (1984) 877.

heat of relaxation is affected by quenching rate

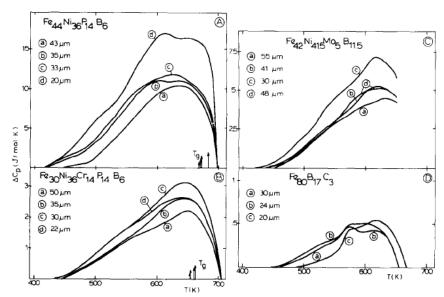


TABLE 1 Enthalpy of relaxation of metallic glasses prepared with different quenching rates. Ribbon thickness is given in brackets ( $\mu m$ ).

Alloy	Enthalpy of crystallization	Enthalpy of relaxation (kJ/mol) at wheel velocity (m/s)							
	(kJ/mol)	20	25	30	40	50			
Fe <sub>44</sub> Ni 36 <sup>P</sup> 14 <sup>B</sup> 6	7.9	2.6 (43)	3.5 (35)	3.6 (33)		5.5 (20)			
Fe <sub>30</sub> Ni <sub>36</sub> Cr <sub>14</sub> P <sub>14</sub> B <sub>6</sub>	4.3	1.0 (50)		1.3 (35)	1.6 (30)	1.5 (22)			
Fe <sub>42</sub> Ni <sub>41.5</sub> Mo <sub>5</sub> B <sub>11.5</sub>	4.4		1.1 (55)	1.2 (41)	1.8	1.2			
Fe <sub>80</sub> B <sub>17</sub> C <sub>3</sub>	3.0		, ,	0.7 (30)	0.6 (24)	0.6 (20)			

#### **The Stored Energy of Cold Work**

Early work by H.S. Chen

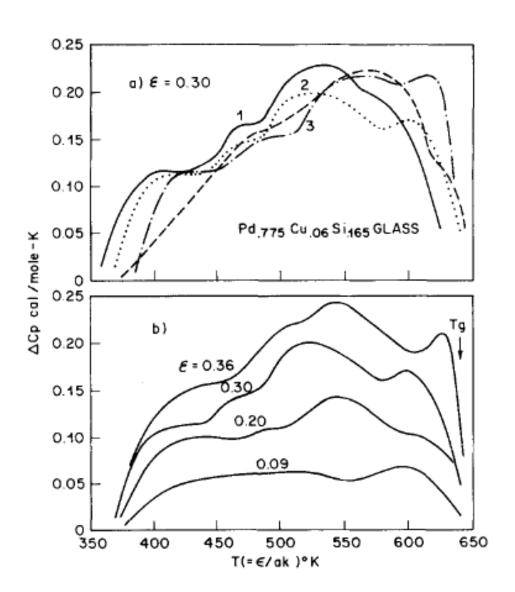
Appl. Phys. Lett. 29 (1976) 328.

Melt-spun Pd<sub>77.5</sub>Cu<sub>6</sub>Si<sub>16.5</sub> coldrolled to a maximum reduction of 36%.

Heat of relaxation measured in DSC —

Maximum stored energy

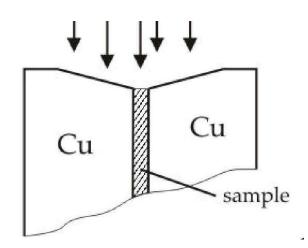
209 J mol<sup>-1</sup>



## Relaxation spectrum of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub>

#### Shot-peening of end-face of the metallic-glass rods

- at liquid-nitrogen temperature
- at dry-ice temperature, or
- at room temperature

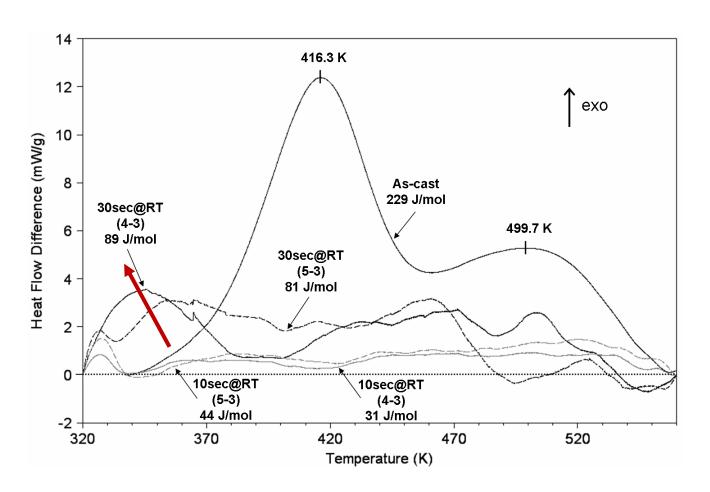


— can store up to ~7% of the cold work at RT.

F.O. Méar, B. Lenk, Y. Zhang & A.L. Greer, "Structural relaxation in heavily cold-worked metallic glass" *Scripta Mater.* **59** (2008) 1243-1246.

#### Shot-peening of annealed glass (30 min at 593 K)

- restores some heat of relaxation
- implies a **less relaxed** state at lower temperature
- does not simply reverse the effect of annealing



F.O. Méar et al., *Scripta Mater.* **59** (2008) 1243.

# Phase Changes Induced by Shot Peening

Studies of Zr<sub>55</sub>Al<sub>10</sub>Cu<sub>30</sub>Ni<sub>5</sub>

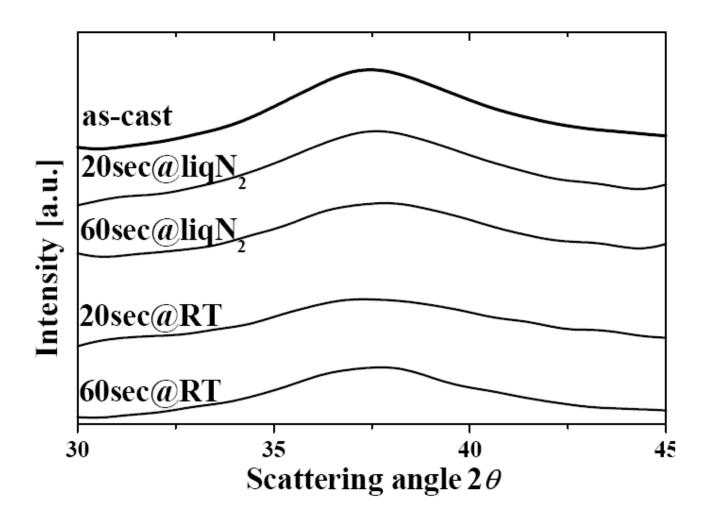
2 mm thick plate, as-cast fully glassy 3 mm diam. rod, as-cast partially crystalline

shot-peened at • room temperature

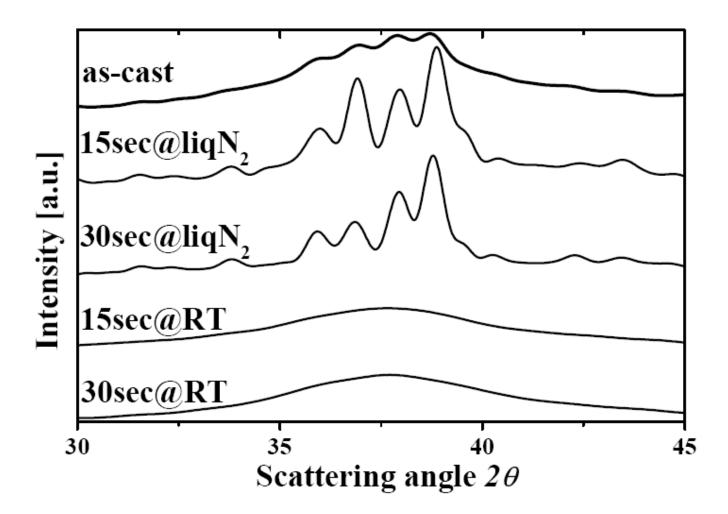
• liquid nitrogen temperature

— 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.



Fully glassy samples stay fully glassy on shot-peening, independent of temperature

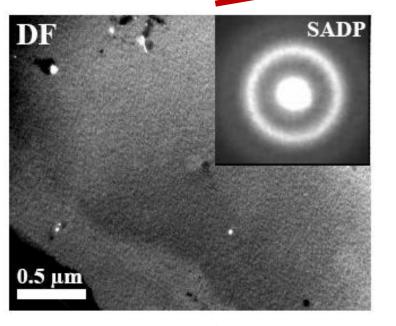


Partially crystalline as-cast samples —

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

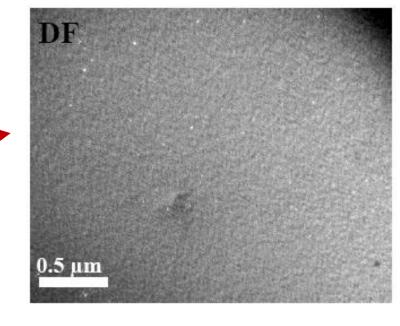
shot-peening at room temp.

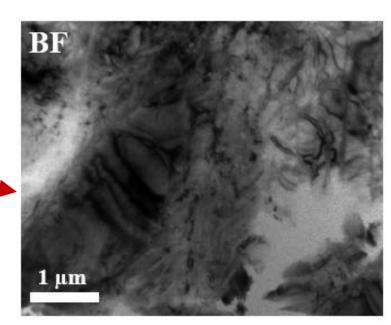
→ AMORPHIZATION

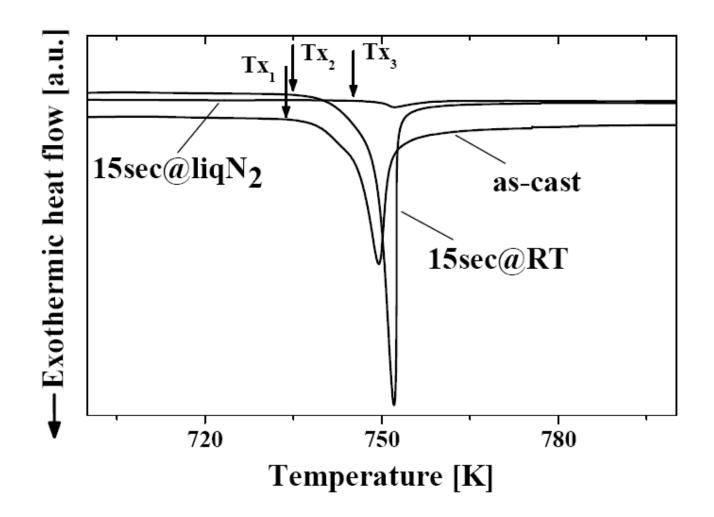


shot-peening at 77 K
→ CRYSTALLIZATION

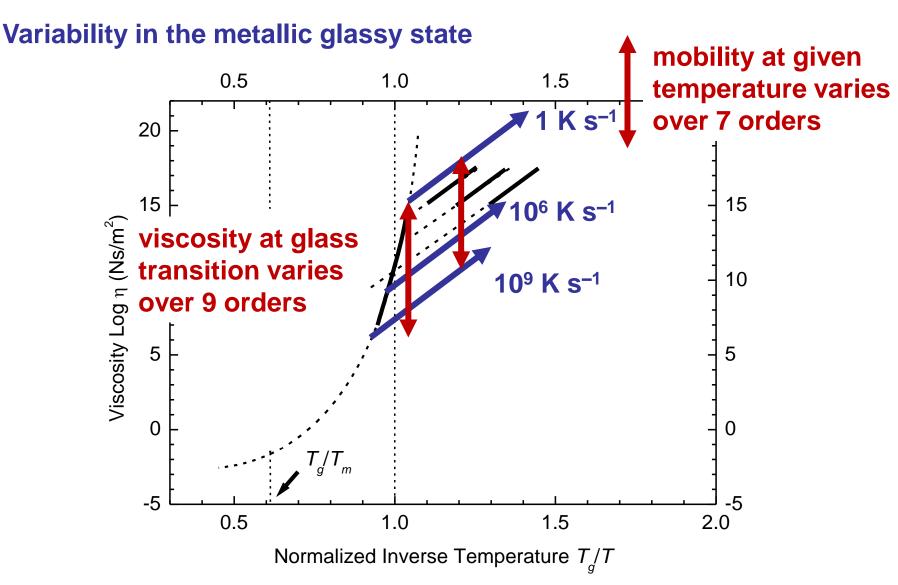
F.O. Méar et al., *J. Alloys Comp.* **483** (2009) 256.







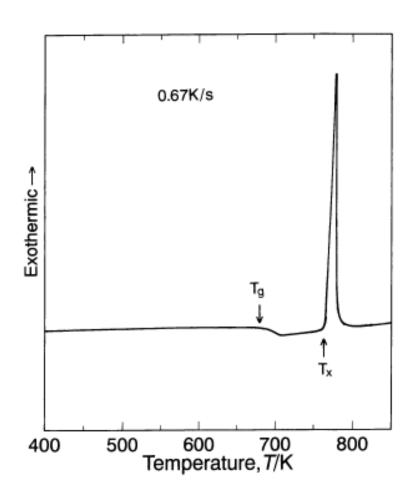
F.O. Méar et al., *J. Alloys Comp.* **483** (2009) 256.



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.

On heating a metallic glass, we expect to see the glass transition before crystallization:

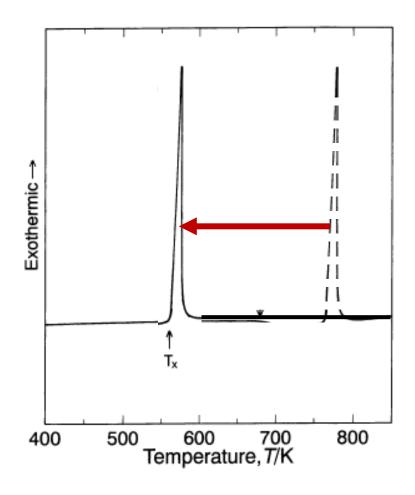
— the crystallization is always of a relaxed sample.



DSC of Zr<sub>55</sub>Al<sub>10</sub>Cu<sub>30</sub>Ni<sub>5</sub>

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

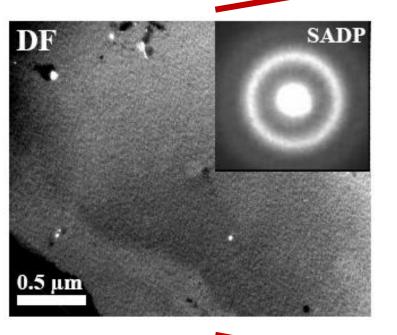
Applying a typical activation energy for crystallization, a change in mobility by a factor of 10<sup>7</sup> is equivalent to a temperature shift of ~200 K



Therefore, on heating a highly unrelaxed sample, we may see crystallization before relaxation.

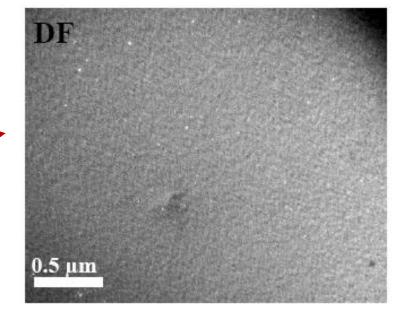
shot-peening at room temp.

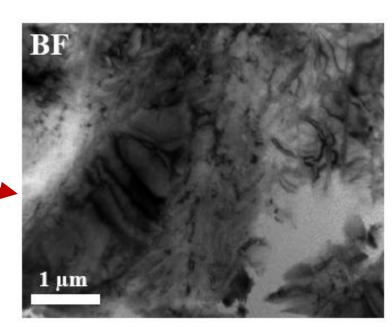
→ AMORPHIZATION



shot-peening at 77 K
→ CRYSTALLIZATION

F.O. Méar et al., *J. Alloys Comp.* **483** (2009) 256.





# **Summary**

- elasticity moduli low compared to crystalline counterparts
- yield strength highest known for metallic materials
- formability excellent, especially at fine scale
- elastic strain limit exceptionally high
- elastic energy storage exceptionally high
- losses exceptionally low
- toughness extremely variable
- shear bands and work softening more in Part II
- brittleness and plasticity can be related to elastic properties
- effects of plastic deformation on structure stored energy of cold work
- and overall a look at applications many niche applications

### **Conclusions**

Metallic glasses are difficult to compare with conventional structural materials — their low process-zone size suggests that they are best suited to small components.

Their high elastic limit and structural uniformity suggest a number of applications

A basis has been established for selection of component elements — a low  $\mu B$  (or high  $\nu$ ) favours plasticity rather than brittleness, by facilitating shear-band initiation.

The ability to plastically deform at RT permits highly unrelaxed states to be reached.

Work softening and the associated shear-banding are the biggest fundamental obstacle to a wider range of structural applications