MIT 3.071
Amorphous Materials

10: Metallic Glass

Juejun (JJ) Hu

After-class reading list

- Structure of metallic glass
  - D. Miracle, “A structural model for metallic glasses”
- Mechanical properties
  - C. Schuh *et al.*, “Mechanical behavior of amorphous alloys”
- Topical review
  - M. Chen, “A brief overview of bulk metallic glasses”

Metallic glass: the timeline

- **1960**: First report of a metallic glass in binary Au-Si via rapid solidification (RS)
- **1970's**: Study of RS ribbons; commercialization in magnetic applications
- **1980's**: First observation of 'bulk' metallic glass (BMG) formers > 1 mm in size
- **1990's**: Development of 'cheap' bulk glasses (Vitreloy) based on Zr
- **2000's**: First limited commercialization of BMG, rapid increase in number of glass forming alloys, discovery of bulk binary glasses
- **2010's**: Gradual increase in understanding toughness and plasticity

Metallic glass: the timeline

1. Nonferrous alloy systems	
Mg–Ln–M	1988
(Ln = lanthanide metal, M=Ni, Cu, Zn)	
Ln–Al–TM	1989
(TM = VI–VIII group transition metal)	
Ln–Ga–TM	1989
Zr–Al–TM	1990
Ti–Zr–TM	1993
Zr–Ti–TM–Be	1993
Zr–(Ti, Nb, Pd)–Al–TM	1995
Pd–Cu–Ni–P	1996
Pd–Ni–Fe–P	1996
Pd–Cu–B–Si	1997
Ti–Ni–Cu–Sn	1998
Cu–(Zr, Hf)–Ti	2001
Cu–(Zr, Hf)–Ti–(Y, Be)	2001
2. Ferrous alloy systems	
Fe–(Al, Ga)–(P, C, B, Si, Ge)	1995
Fe–(Nb, Mo)–(Al, Ga)–(P, B, Si)	1995
Co–(Al, Ga)–(P, B, Si)	1996
Fe–(Zr, Hf, Nb)–B	1996
Co–(Zr, Hf, Nb)–B	1996
Ni–(Zr, Hf, Nb)–B	1996
Fe–Co–Ln–B	1998
Fe–(Nb, Cr, Mo)–(C, B)	1999
Ni–(Nb, Cr, Mo)–(P, B)	1999
Co–Ta–B	1999
Fe–Ga–(P, B)	2000
Ni–Zr–Ti–Sn–Si	2001

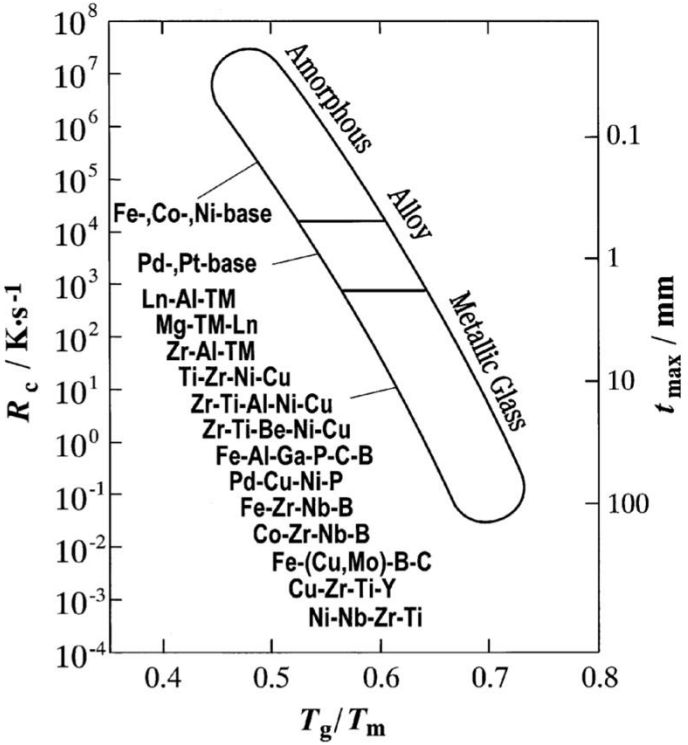


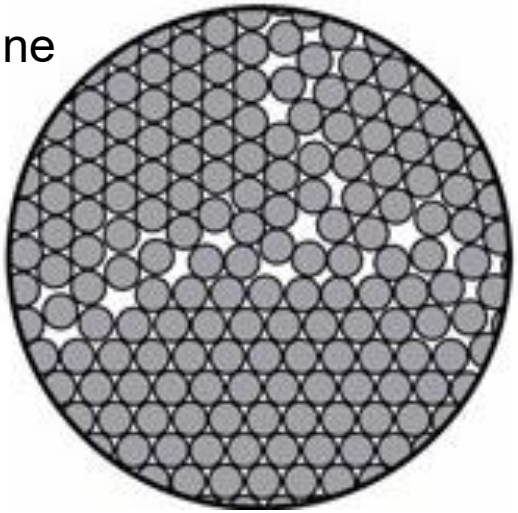
Fig.1 Critical cooling rate (R_c), maximum sample thickness (t_{max}) and reduced glass transition temperature (T_g/T_m) relationship for bulk glassy alloys developed over the last decade, together with the previous data on ordinary amorphous alloys in Fe-, Co- and Ni-based systems and Pd- and Pt-based glassy alloys.

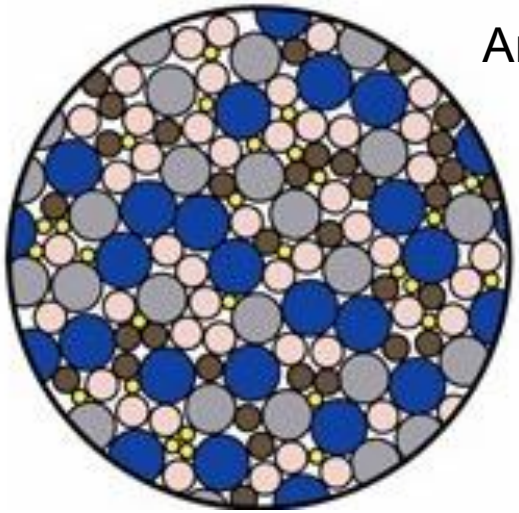
Mater. Trans. **43**, 1892 (2002)

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Metallic glass: structure

Polycrystalline metal



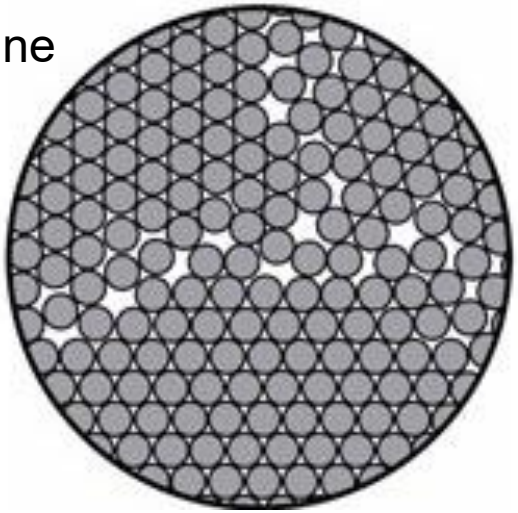


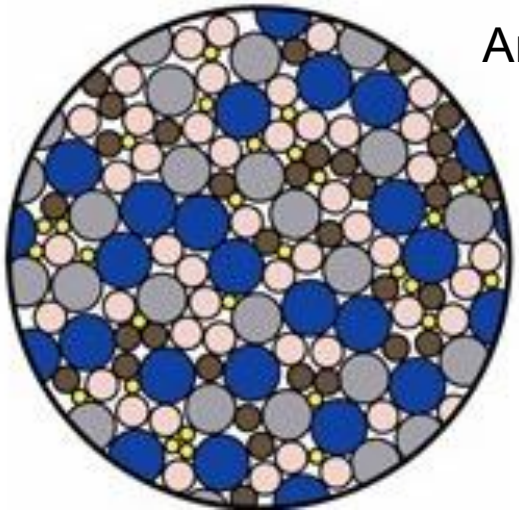
Amorphous metal

Metallic bonding, largely non-directional, is mostly about achieving dense packing

Metallic glass: structure

Polycrystalline metal

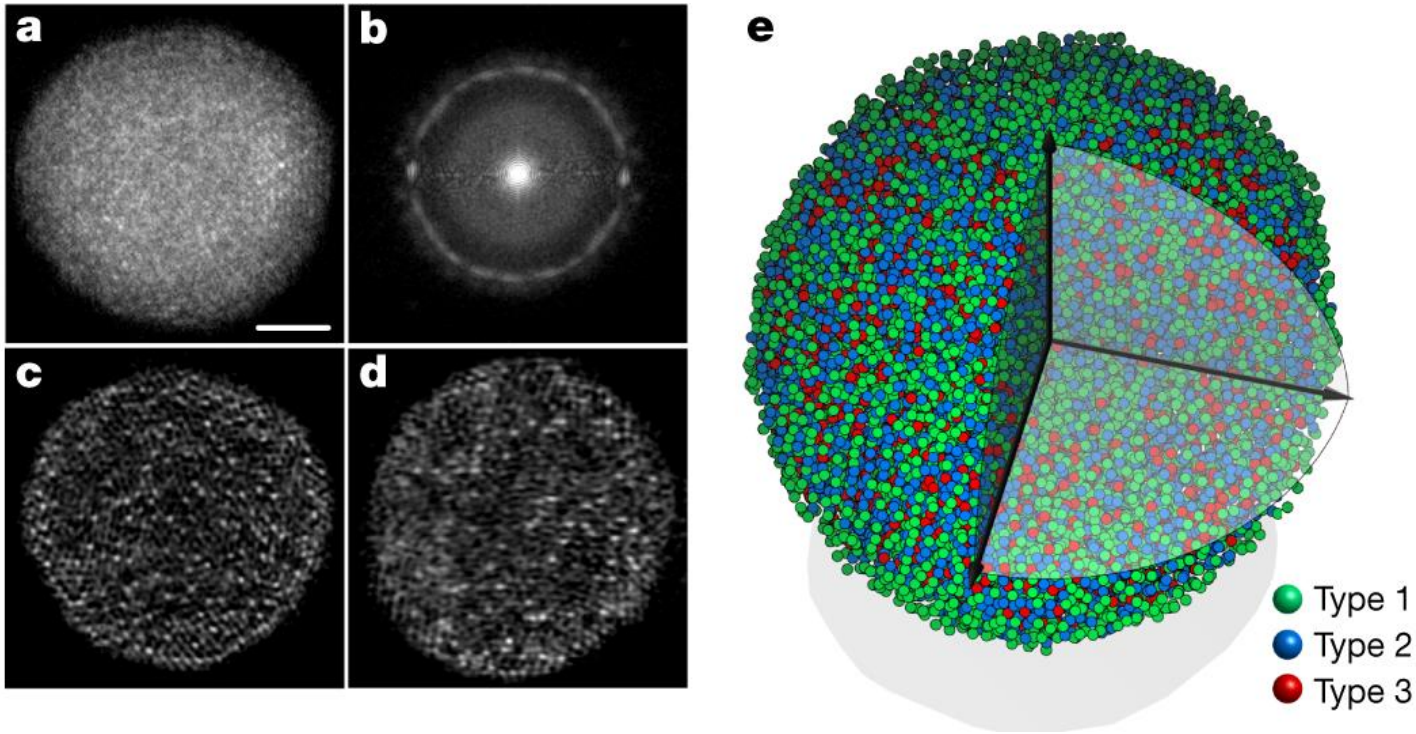




Amorphous metal

- Inoue's empirical rules for bulk metallic glass (BMG) formation
  - Multicomponent systems consisting of three or more elements
  - Significant difference in atomic size ratios (frustration)
  - Negative enthalpy of mixing

3D atomic structure of a multi-component metallic glass nanoparticle

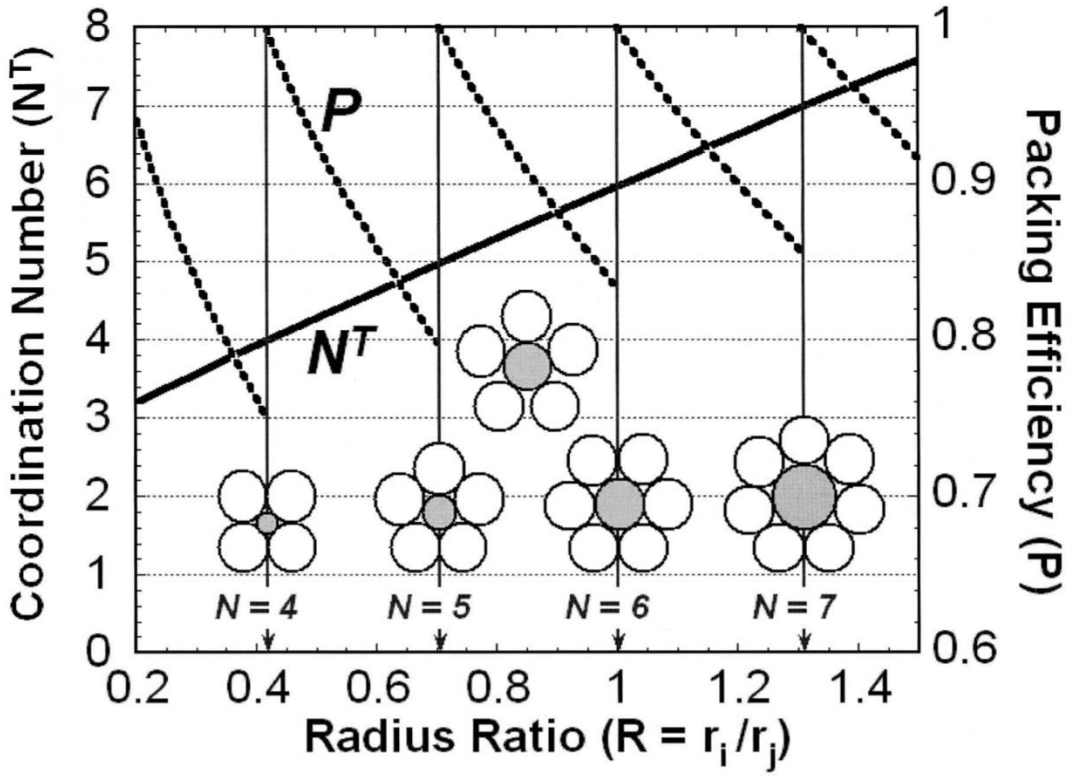


Close-packed structure imaged using atomic electron tomography

Nature **592**, 60-64 (2021)

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Hard sphere packing in 2-D



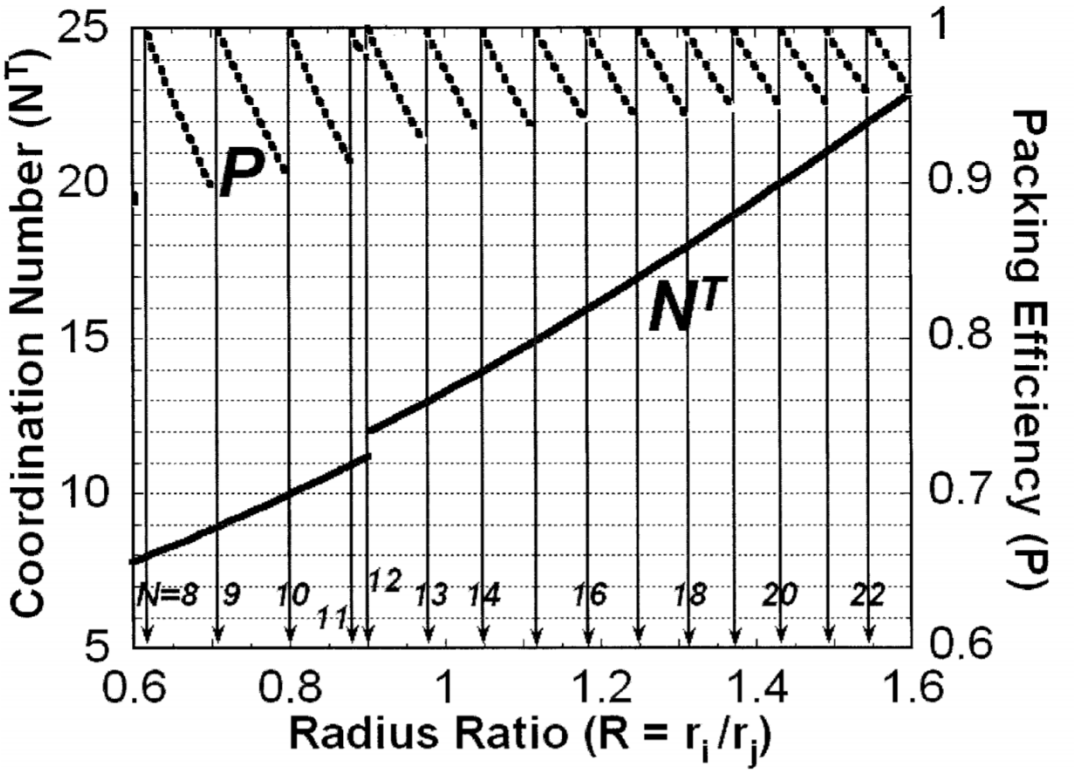
The theoretical coordination number N^T (——) and packing efficiency P (- - - -) as functions of radius ratio R for two-dimensional clusters of circles. Four two-dimensional configurations representing a packing efficiency of 1.0 are shown, with $R_4^* = 0.414$, $R_5^* = 0.701$, $R_6^* = 1.000$ and $R_7^* = 1.305$. A cluster with a packing efficiency less than one is also shown.

Dense packing is only achieved at certain critical radius ratios

Philos. Mag. **83**, 2409 (2003)

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Hard sphere packing in 3-D



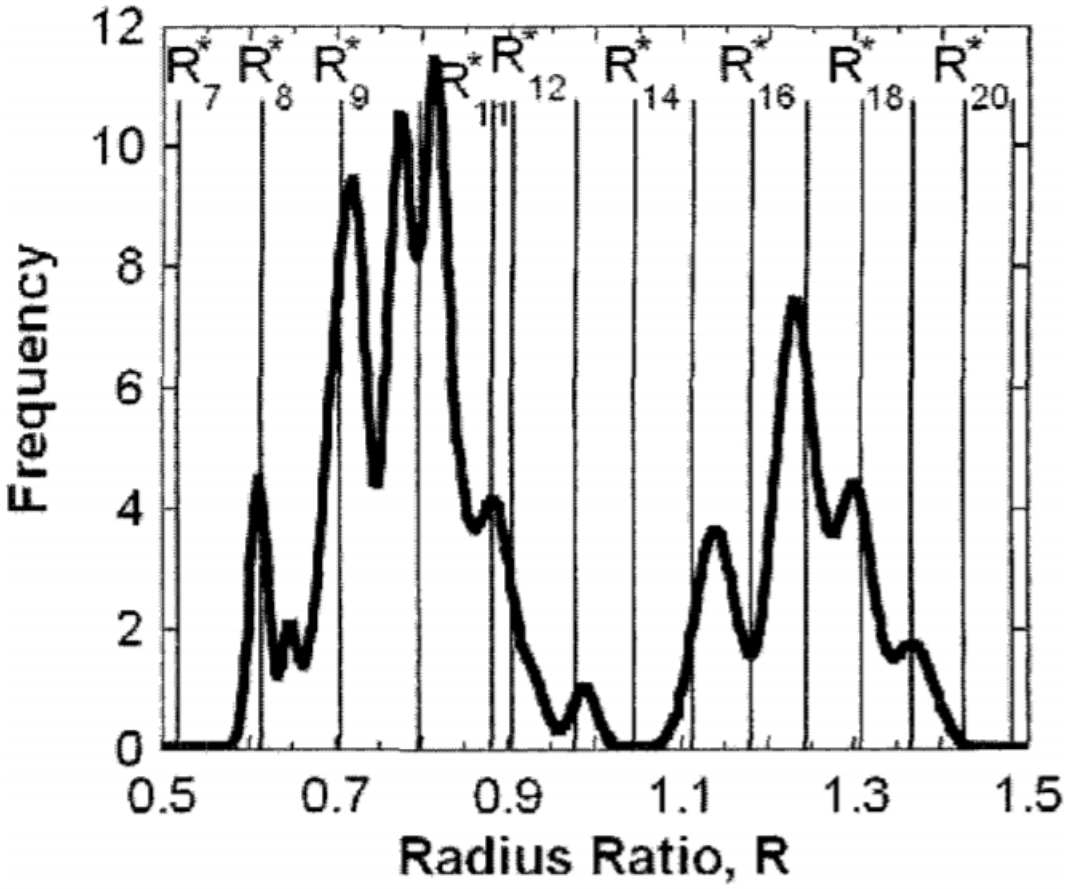
The theoretical coordination number N^T (——) and packing efficiency P (- - - -) as functions of radius ratio R for three-dimensional clusters of spheres. A discontinuity occurs where the maximum surface coordination increases from $q = 4$ for $R < 0.902$ to a maximum surface coordination of $q = 5$ for $R = 0.902$. A maximum packing efficiency occurs for discrete values of R^* where N^T is an integer. These specific radius ratios are shown by the vertical lines, and the associated coordination numbers are also shown.

Local structures of metallic glasses are efficiently packed in systems with critical atomic radius ratios

Philos. Mag. **83**, 2409 (2003)

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Dense packing favors metallic glass formation

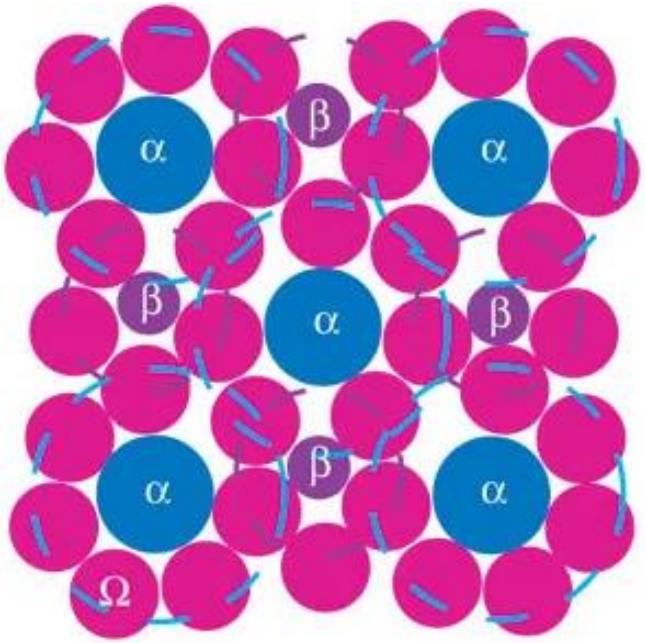


Stable binary metallic glasses tend to form at atomic size ratios corresponding to dense packing

Philos. Mag. **83**, 2409 (2003)

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Beyond nearest neighbors: cluster packing



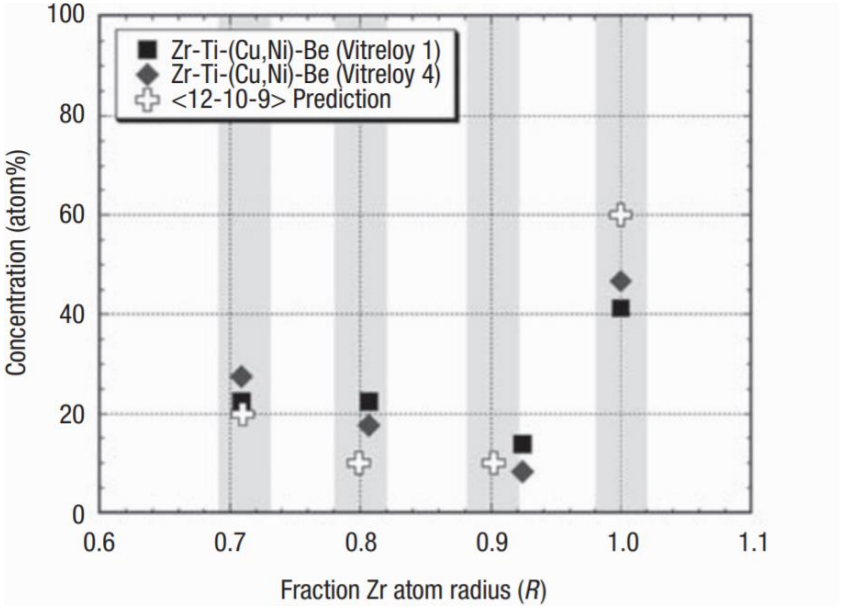


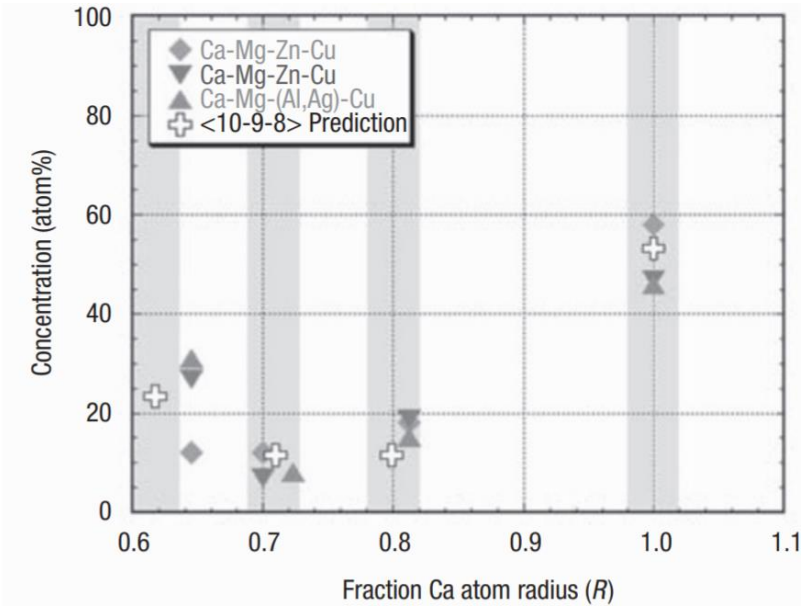
Nat. Mater. **3**, 697 (2004)

- Close-packed clusters sharing faces or edges
- Atoms of different **critical** sizes fulfill different topological roles
- α: center atom of polyhedral; β / γ: filling in interstitials

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Beyond nearest neighbors: cluster packing

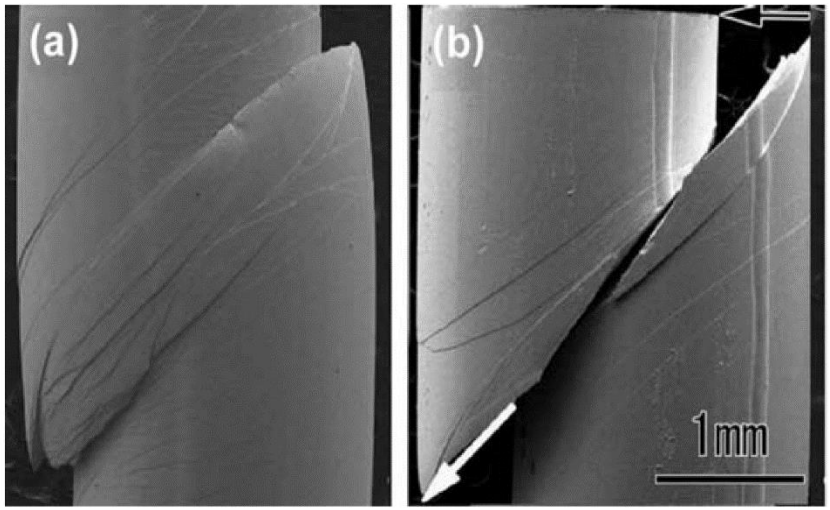


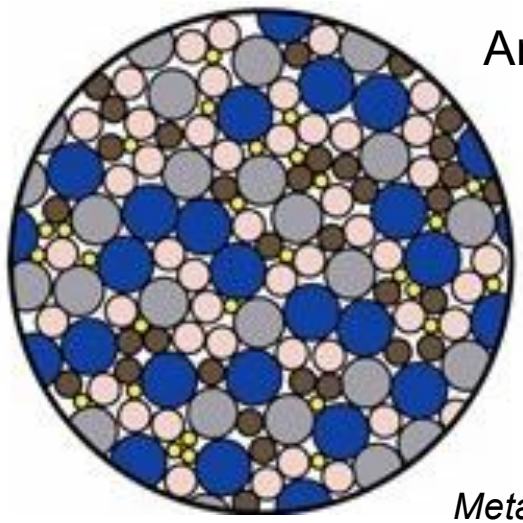


The cluster packing model correctly predicts the atomic size and concentration of stable metallic glasses

D. Miracle, *Nat. Mater.* **3**, 697 (2004)

Mechanical properties of metallic glasses





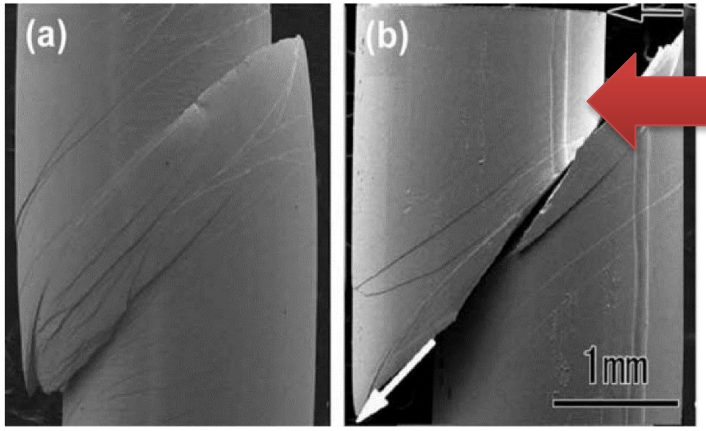
Amorphous metal

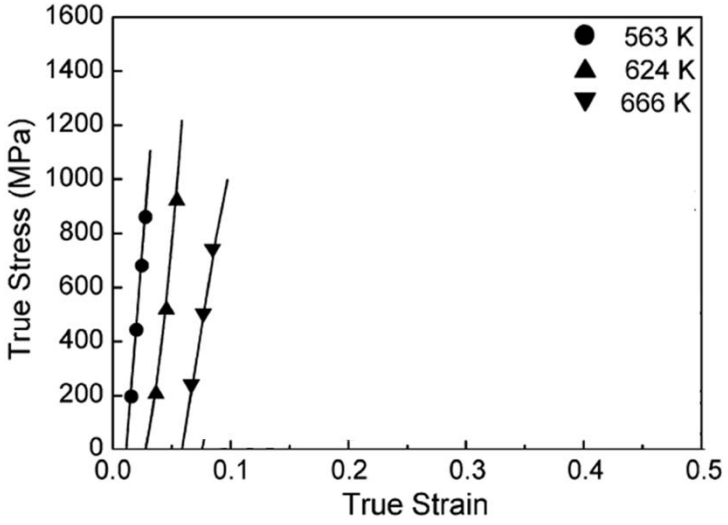
Metals **3**, 1 (2013)

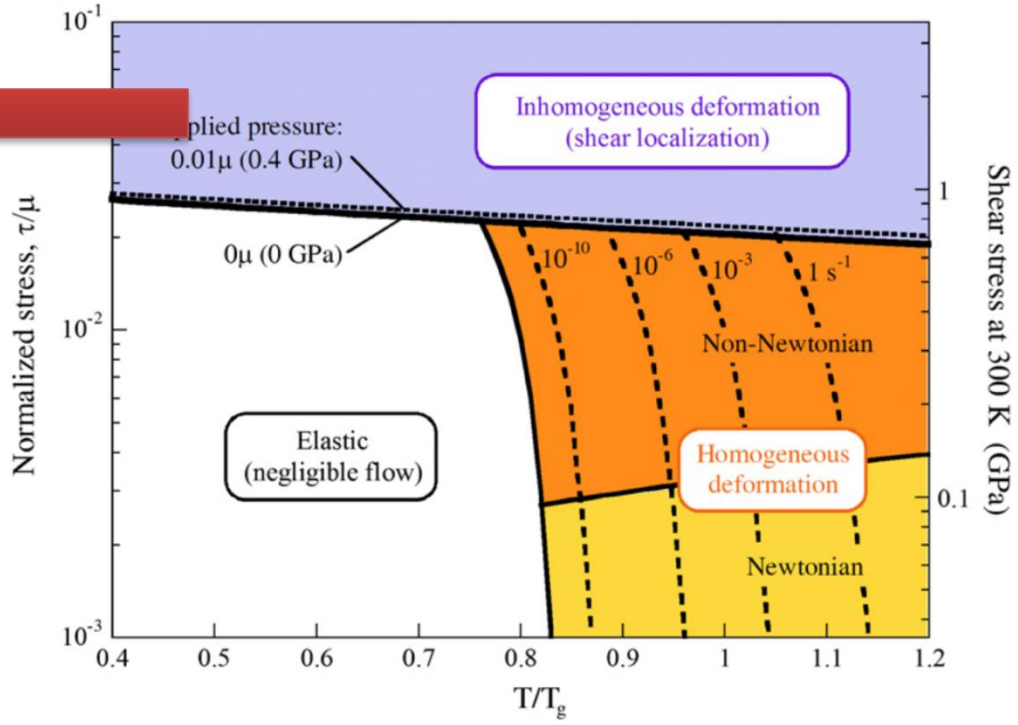
- Absence of dislocations and slip planes/directions in BMG
  - **Large elastic limit** and high yield strength (2% and 2 GPa in Zr-based BMGs)
  - Poor global plasticity: absence of strain hardening, strong tendency towards **shear localization**

Courtesy of Louzguine-Luzgin, Dmitri V., Larissa V. Louzguina-Luzgina, and Alexander Yu. Churyumov. Used with permission. License: CC-BY

A deformation map of metallic glasses





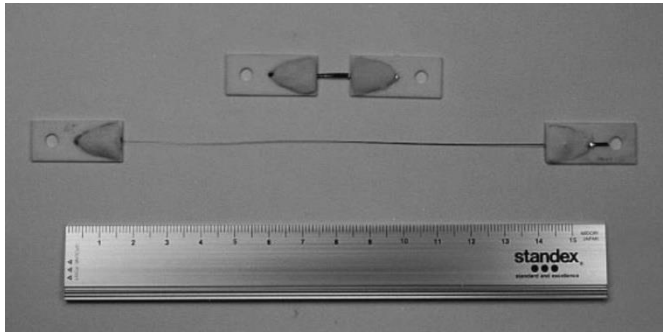


Schuh *et al.*, *Acta Mater.* **55**, 4067 (2007)

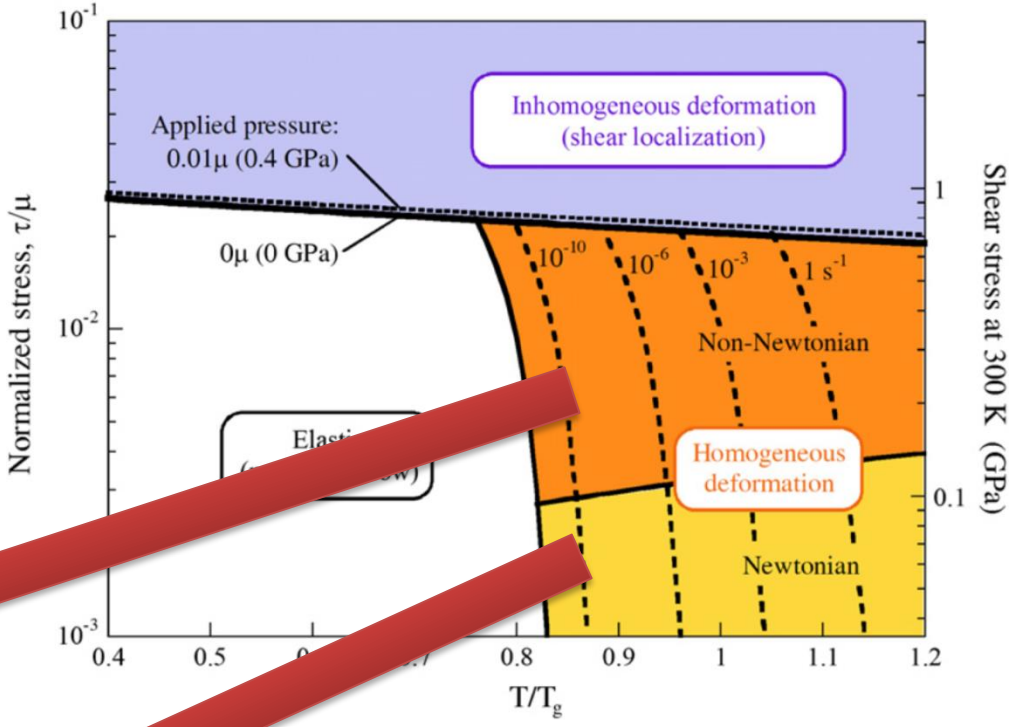
Shear localization at high stresses

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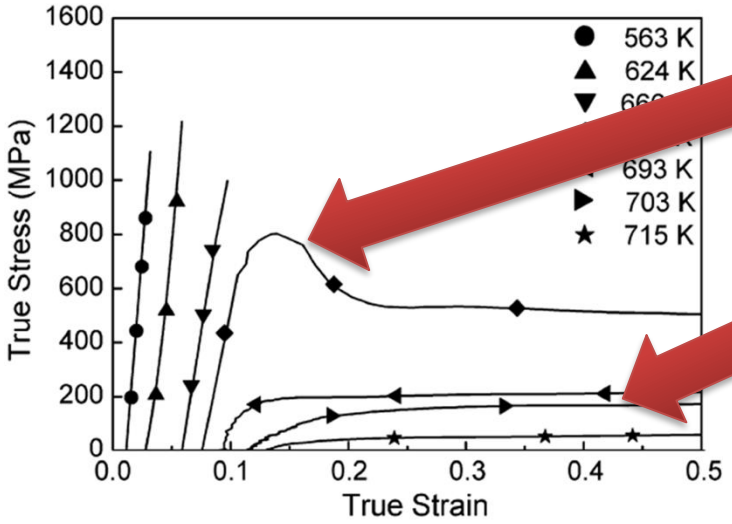
A deformation map of metallic glasses



Scr. Mater. **39**, 301 (1998)



Schuh *et al.*, *Acta Mater.* **55**, 4067 (2007)



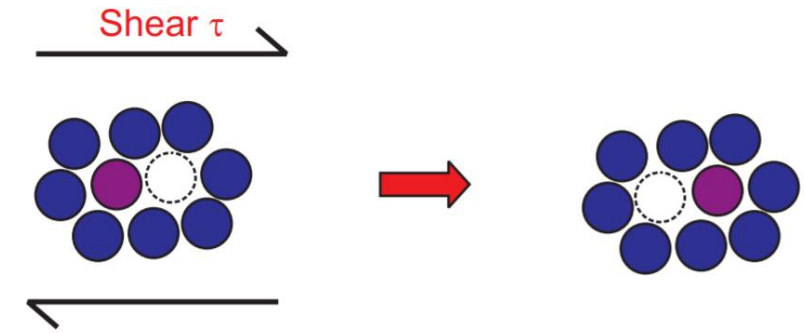
Homogeneous flow at high temperatures

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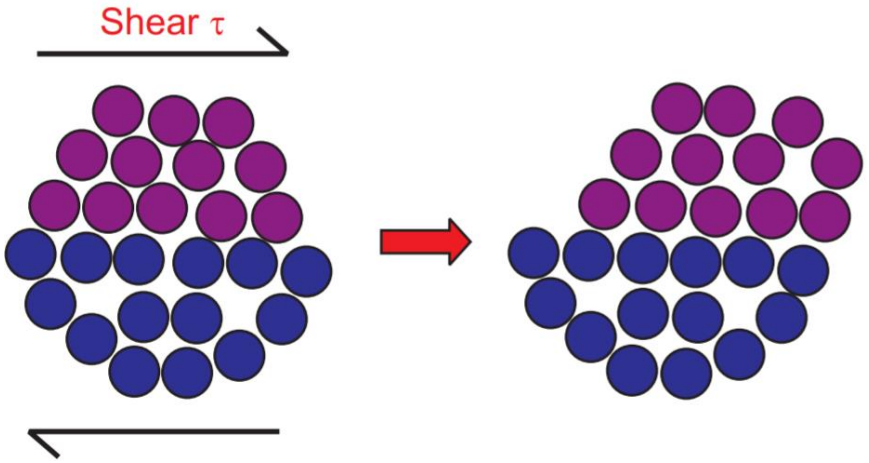
Elastic and anelastic deformation

- Isotropic media
- Bulk modulus: typically ~ 6% smaller than that of the crystalline counterpart
  - Can be accounted for by the less dense packing (presence of free volume) in metallic glasses
- Shear/Young's modulus: ~ 30% smaller than that of the crystalline counterpart
  - In a crystal, all atoms undergo similar displacement defined by the macroscopic strain
  - In metallic glass, non-uniform local displacement takes place, e.g. through STZ

Atomistic mechanisms of deformation



Diffusive atomic jump

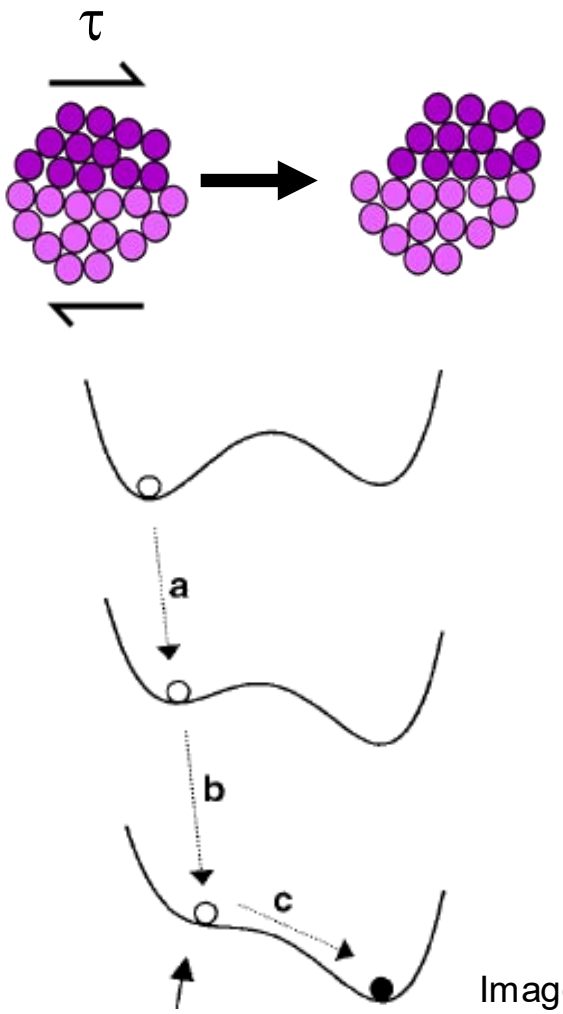


Shear transformation zone (STZ)

Acta Mater. **55**, 4067 (2007)

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Atomistic origin of plastic deformation



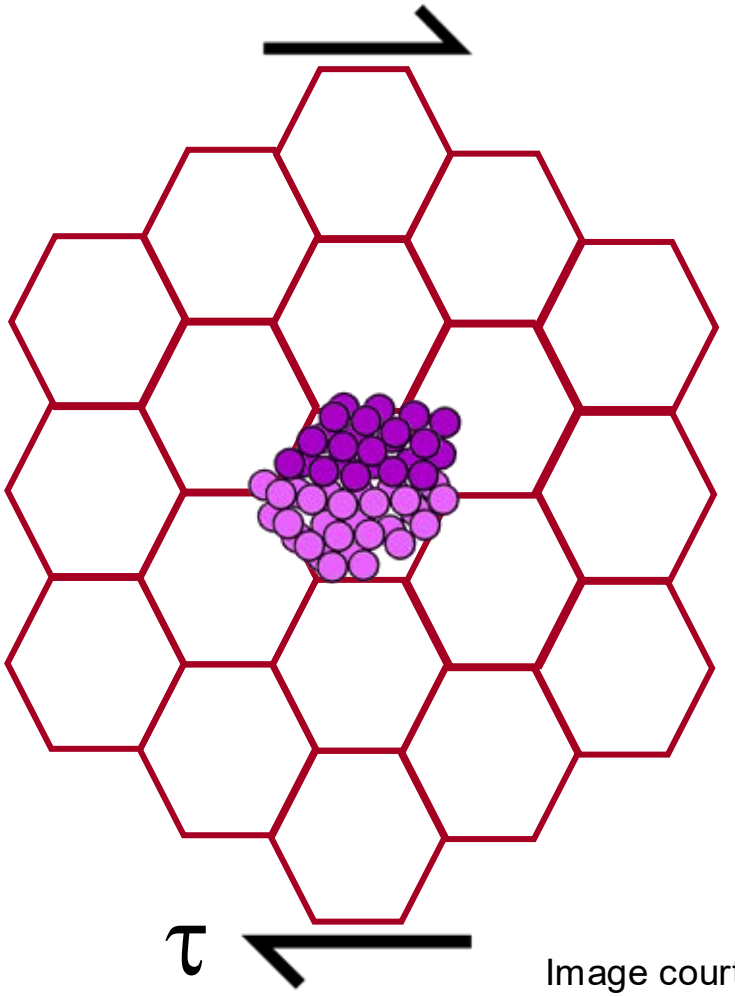
- "The plastic deformation of metallic glasses on the macroscopic scale is essentially a biased accumulation of local strains incurred through the operation of STZs and the redistribution of free volume."

Schuh *et al.*, *Acta Mater.* **55**, 4067 (2007)

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Atomistic origin of plastic deformation



- Once a local deformation occurs in a STZ, its surrounding regions are placed under strain
- The strain catalyzes plastic deformation in surrounding STZs
- STZs "talk" with each other through strain

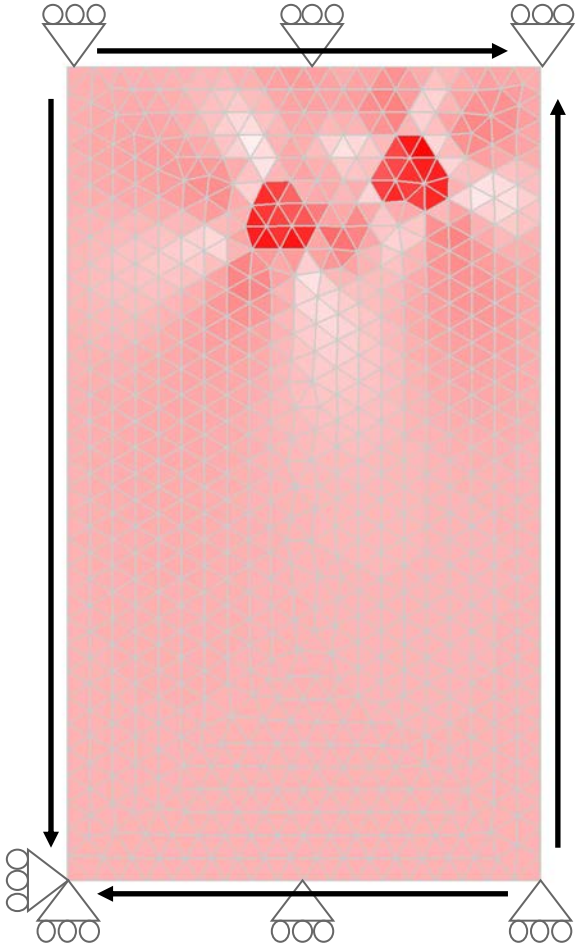
Phys. Rev. B **81**, 064204 (2010)

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The origin of shear localization

- Strain softening
- Homogeneous deformation: at high temperatures, all zones readily deform
- Shear localization: STZs adjacent to the one that has already deformed preferentially deforms due to strain coupling; this effect is most pronounced at high stress levels and reduced temperatures

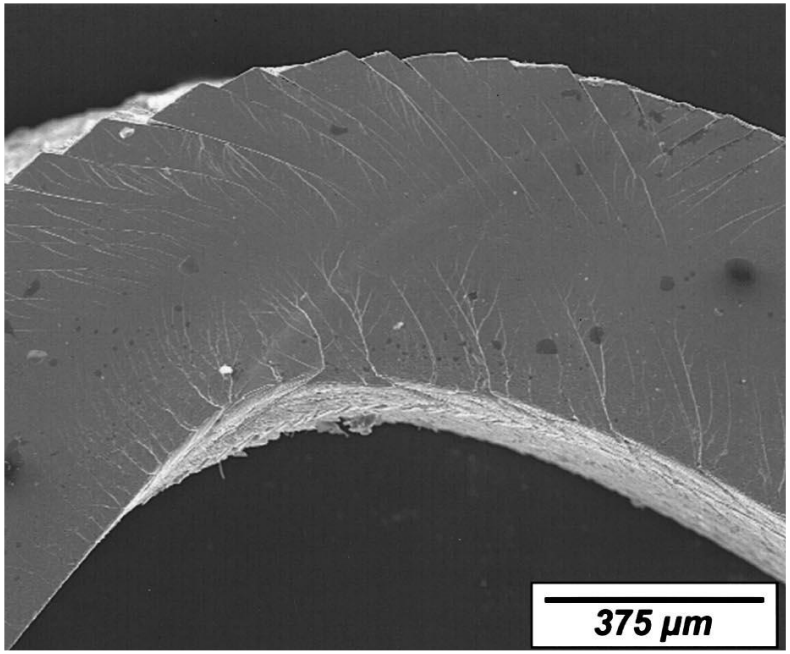


Kinetic Monte Carlo modeling of STZs

Acta Mater. **57**, 2823-2833 (2009)

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Shear localization and shear band formation



Plastic strain concentrated in narrow shear bands in both compressive and tensile regions

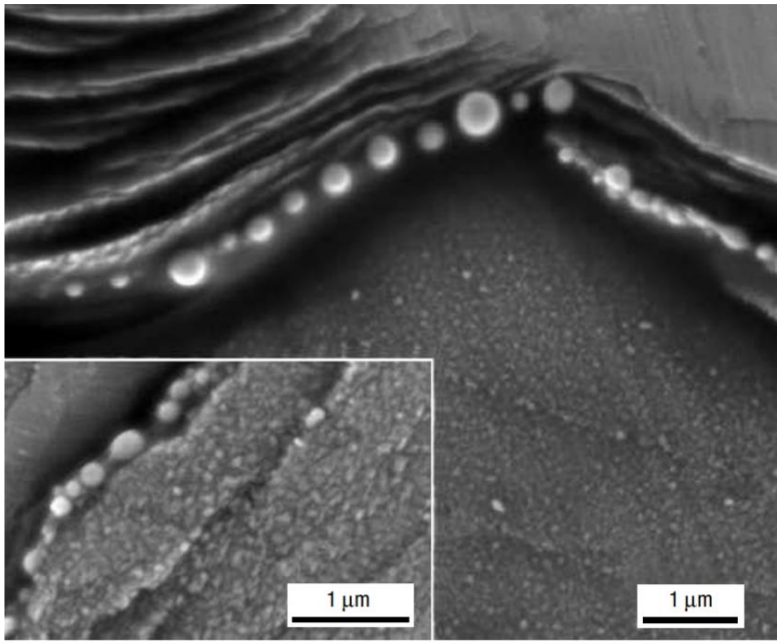


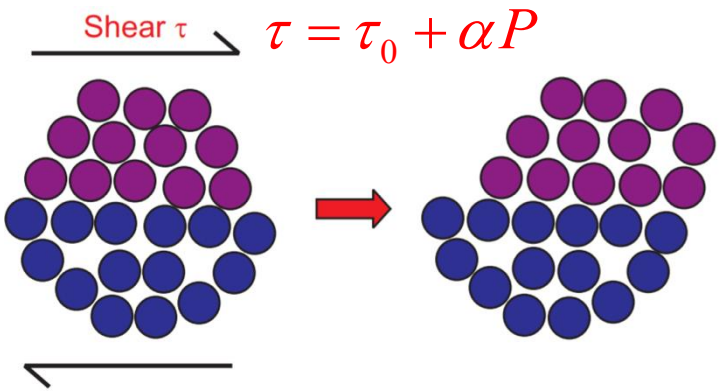
Figure 3 Tin coating formed into spherical beads at shear bands provides evidence of local heating and melting of the coating. Scanning electron micrographs showing details of shear bands after local melting of the tin coating. Near the shear band, the as-deposited island pattern disappears and is replaced by beads of tin. The inset shows the shear-band pattern and tin beads located in regions removed from the large shear offset shown at top of figure.

J. Appl. Phys. **94**, 904 (2003); *Nat. Mater.* **5**, 15 (2006)

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Shear deformation in metallic glass is dilatational

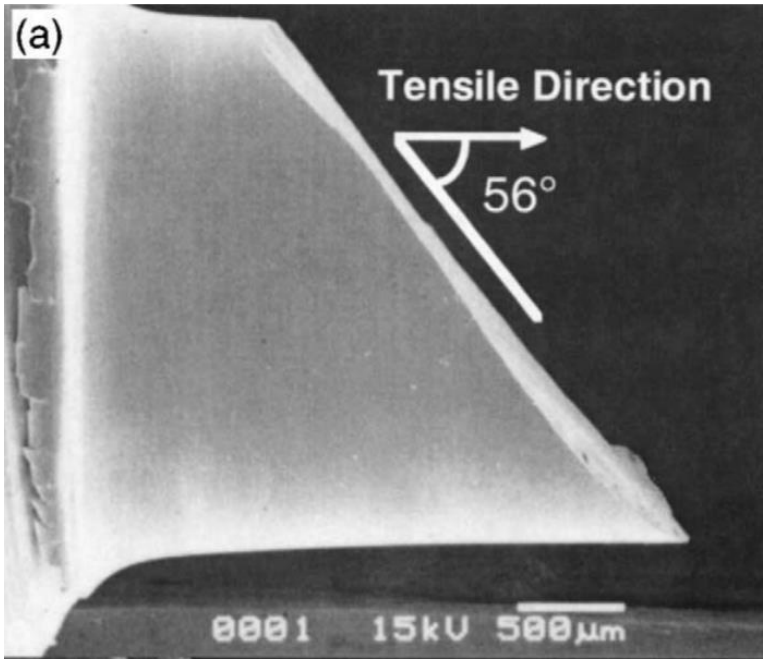


- Free-volume creation: strain softening
- Shear deformation is a pressure-dependent, **frictional** process

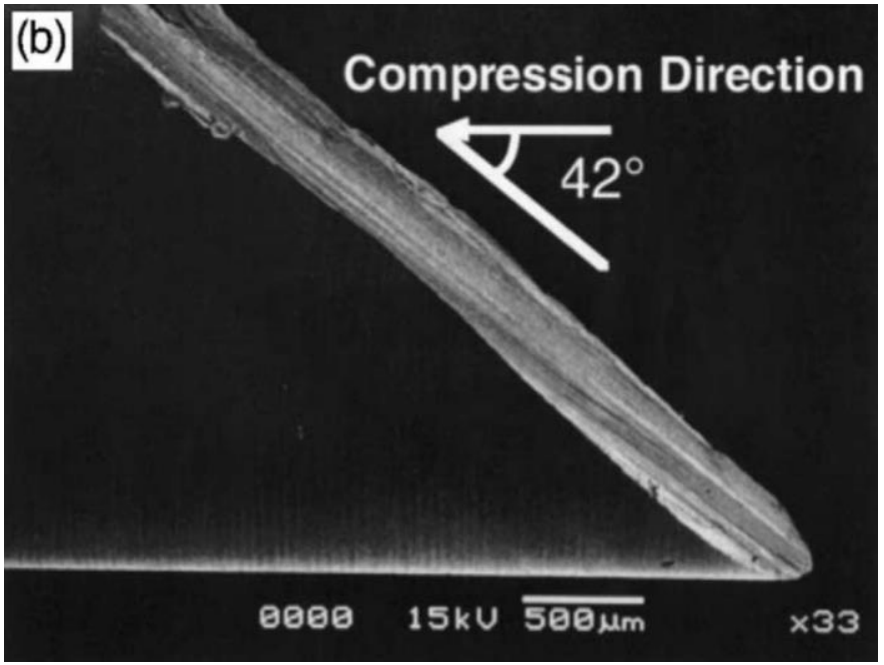


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Shear angles in uniaxial loading tests



Fractured surface in tensile test



Fractured surface in compressive test

Intermetallics **10**, 1071-1077 (2002)

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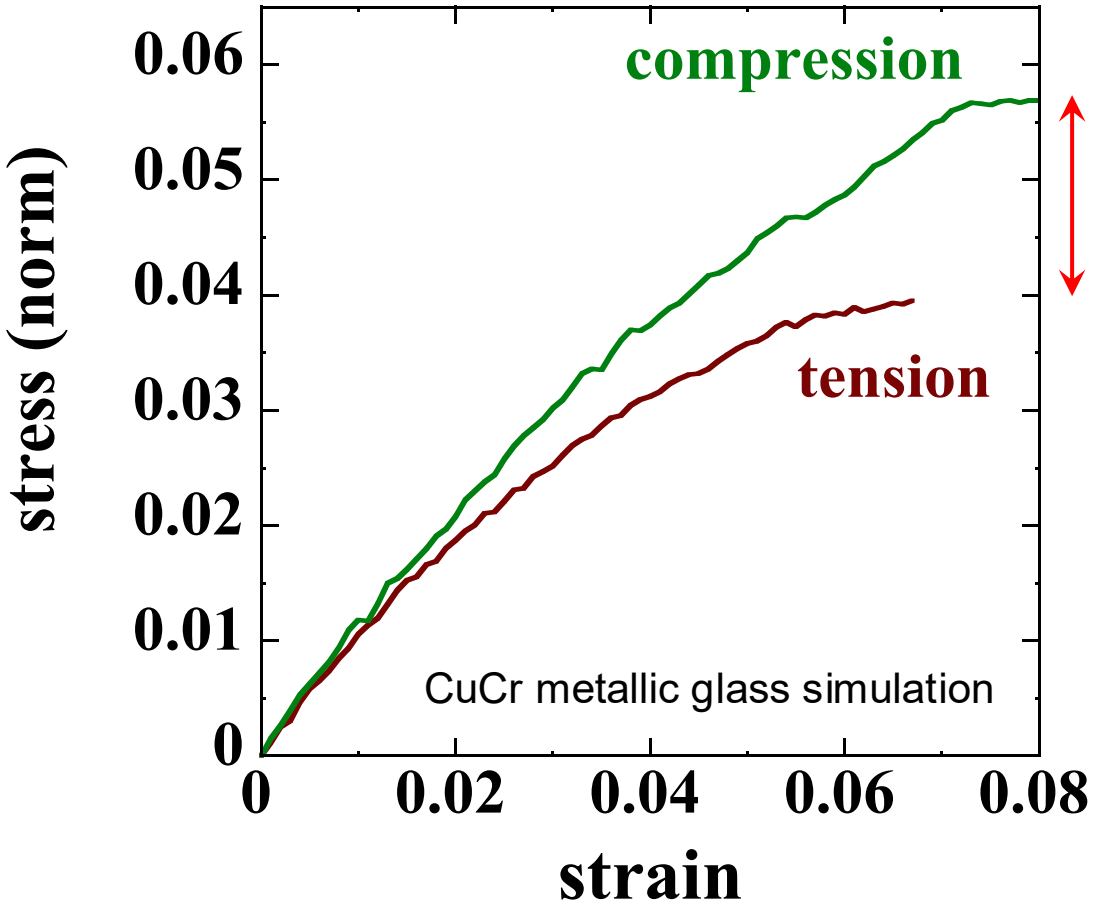
Shear angles in uniaxial loading tests

Investigator	Material	Tension		Compression	
		θ_T	α	θ_C	α
Zhang et al. [48]	$Zr_{59}Ni_8Cu_{20}Al_{10}Ti_3$	54°	0.32	43°	0.07
Liu et al. [2]	$Zr_{55}Ni_5Cu_{30}Al_{10}$	53-58°	0.29-0.49		
	$Zr_{52.5}Ni_{14.6}Cu_{17.9}Al_{10}Ti_5$	54°	0.32	44-46°	0.03-0
Wright et al. [40]	$Zr_{40}Ni_{10}Cu_{12}Ti_{14}Be_{24}$			42°	0.11
Lewandowski and Lohaphandu [9]	$Zr_{63.2}Ni_{9.4}Cu_{13.4}Ti_{9.9}Be_{4.1}$	50-53°	0.18-0.29	39.4-41.4	0.13-0.20
Donovan [7]	$Pd_{40}Ni_{40}P_{20}$			40.7-43.1°	0.15-0.07
Donovan* [7]	$Pd_{40}Ni_{40}P_{20}$	50°	0.18	40°	0.18
Mukai et al. [1]	$Pd_{40}Ni_{40}P_{20}$	56°	0.40	42°	0.11
Megusar et al. [10]	$Pd_{80}Si_{20}$	48-50°	0.11-0.18		
Takayama [11]	$Pd_{77.5}Cu_6Si_{16.5}$	51°	0.21		

Shear angles are larger than 45° in tension and smaller than 45° in compression

Acta Mater. **51**, 5399-5411 (2003)

Tensile/compression asymmetry due to friction



Metallic glass is stronger in compression than in tension

Acta Mater. **51**, 5399 (2003)

Summary

- Metallic glass structure is dictated by close packing requirements
- Large elastic limit, lower elastic moduli compared to crystalline metals
- Plastic deformation
  - Homogeneous flow (important for thermoplastic forming): high temperature
  - Inhomogeneous deformation (strain softening): high stress
- Atomistic mechanisms of plastic deformation
  - Shear transformation zone and STZ coupling
  - Pressure-dependent, frictional shear deformation

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