2014 Spring

"Advanced Physical Metallurgy" - Bulk Metallic Glasses -

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1

8.2 Deformation Behavior



- high temp. (>0.7T_g) and in the SCLR/
 high strain rate
- Viscous flow → significant plasticity
 : achieve net-shape forming capability
- Newtonian (high temp. & low stress) VS non-Newtonian (high temp. & applied stress) : associated with the precipitation of nanocrystals



Low temp. $(<0.5T_g)$ / high stress

- Localized shear band/ 45° to the loading axis
- Strain softening: deformed at lower stress and higher rate



Flow Mechanisms



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

3

Homogeneous deformation: Liquid Flow

Liquid Region (above and near T_α)

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

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

Newtonian Viscous Flow









Extended elongation in a 3mm diameter BMG rod of La₅₅Al₂₅Ni₂₀ alloy superplastically deformed in the supercooled liquid region at 500K and a strain rate of 10⁻¹ s⁻¹.

Inhomogeneous deformation: Deformation-induced Softening

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



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



SB nucleation and propagation : <u>Multiple serrations</u>, observed only at slow strain rates



FIGURE 8.1

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

8.4 Temperature rise at shear bands

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



FIGURE 8.9

Scanning electron micrograph of the surface of Zr_{41.2}Ti_{13.8} Cu_{12.5}Ni₁₀Be_{22.5} BMG, which was originally coated with a tin coating. During deformation, the "fusible coating" had melted near the shear bands. The round shape of the tin beads clearly suggests that the coating had melted due to the temperature rise as a result of deformation and had resolidified. The bar in the micrographs corresponds to 1 µm. (Reprinted from Lewandowski, J.J. and Greer, A.L., *Nat. Mater.*, 5, 15, 2006. With permission.)

8.4.1 Nanocrystallization near Shear Bands



Atomic bond topology



T. Egami

Atomic bond topology

- Network of atomic connectivity / ٠ topology of the atomic structure
- Bond-exchange mechanism of ٠ shear deformation



A. S. Argon



Deformation maps for metallic glasses



Thermal T_g vs Mechanical T_g for metallic glasses



Limited Plasticity by shear softening and shear band

Microscopically brittle fracture

→ Death of a material for structural applications





(a) Variation of strength with glass transition temperature, T_g for a number of BMGs. (b) Relationship between the calculated fracture strength from a free-volume model and the ratio of $\Delta T_g/V$ for a variety of BMGs. (Reprinted from Yang, B. et al., *Appl. Phys. Lett.*, 88, 221911-1, 2006. With permission.)



Relationship between (a) tensile strength and Young's modulus and (b) Vickers hardness and Young's modulus for some typical BMGs. The data for crystalline alloys are also shown for comparison. (Reprinted from Inoue, A., *Acta Mater.*, 48, 279, 2000. With permission.)



Scanning electron micrograph of the fractured surface of a bulk metallic glass alloy specimen. Note the vein pattern, which is typical of many metallic glasses that fracture along a shear band. Such microstructures are obtained both in tension and compression.



Comparison of the fracture surfaces of Zr₅₉Cu₂₀Al₁₀Ni₈Ti₃ BMG alloy that has failed under (a) compressive loading and (b) tensile loading. Notice that the specimen that has failed under compressive loading exhibits vein-like pattern while the specimen that had failed in tension shows round cores with vein-like features radiating outward from their centers. The arrow in (a) shows the shear direction, while the arrows in (b) indicate the location of the round cores. (Reprinted from Zhang, Z.F. et al., *Acta Mater.*, 51, 1167, 2003. With permission.)

What governs plasticity in metallic glasses?

Plastic deformation in metallic glasses

Plastic deformation in metallic glass

- No dislocation / No slip plane
- Inhomogeneously localized plastic flow in the shear band

interrupt the localization of stress and deformation

- Prevent propagation of single shear band composites
- Multiple shear band formation





BMG matrix

Ex-situ BMG matrix composites

1) Casting : hard/ductile particle







200µm (Johnson et al., Acta Mater, 1999)



In-situ BMG matrix composites

1) Solidification : formation of primary ductile phase





(Johnson et al., Acta Mater., 2001)

2) Solidification : precipitation of ductile phase



Size of heterogeneity

Shear bands are ~20 nm in width



• Prevent propagation of single shear band

Micro- or nanometer scale heterogeneity

Size of heterogeneity

Selementary flow event in an metallic glasses



Flow governed by localized defect (~10 atoms) and creates defects

atomic scale heterogeneity

$$\eta = \eta_0 \exp\left\{A\frac{V_0}{V_f}\right\}$$



Plastic deformation in metallic glasses

- Flow governed by localized defect (~10 atoms)
- Flow creates defects



Amorphous: dilatation

• Shear bands form by accumulation of defects

Understanding how shear bands form and propagate in metallic glasses

Fragility

Fragility ~ extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state



Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at

Correlation between fragility and plasticity

Correlation between elastic constants and plasticity



Correlation between fragility and plasticity



* Appl. Phys. Lett., 91, 031907.

Enhancement plasticity in BMGs with atomic scale heterogeneity a) Effect of quenched-in quasicrystal nuclei

Effect of secondary phase in amorphous matrix 3 mm rod



β-Zr dendrite in amorphous matrix

I-phase particle in amorphous matrix

Effect of secondary phase in amorphous matrix

* unpublished (2008)



Continuous interface between amorphous and I-phase



Role of icosahedral particle on the propagation of SB









shear band

- Shear band passes through icosahedral particle.
- Icosahedral particle splits across with the plastic deformation of metallic glass matrix
 - **W** No distribution of icosahedral particle to blocking the propagation of shear band.
 - **IF** No enhancement of plasticity in MGMC with icosahedral particle

Effect of quenched-in quasicrystal nuclei

2 mm rod

(a) $Zr_{63}Ti_5Nb_2Cu_{15.8}Ni_{6.3}AI_{7.9}$



 β -Zr particle (~70 nm) in amorphous matrix

(b) $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}AI_{7.5}$



I-phase particle in amorphous matrix

Effect of quenched-in quasicrystal nuclei



Effect of quenched-in quasicrystal nuclei

Activation E : driving force for nucleation


Effect of quenched-in quasicrystal nuclei

Isotherm in DSC



Effect of quenched-in quasicrystal nuclei

EXAFS analysis

(b) *Zr₅₇Ti₈Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}*



Enhancement plasticity in BMGs with atomic scale heterogeneityb) Effect of element having positive enthalpy of mixing among constituent elements

Improvement of plasticity in monolithic BMGs

* Enhancement of plasticity in monolithic BMGs

 \longrightarrow No clear explanations so far.

* Reports for enhancement of plasticity in monolithic BMGs

	Compressive plastic strain, ε _ρ (%)	
Zr ₅₉ Ta ₅ Cu ₁₈ Ni ₈ Al ₁₀ ¹	~ 6.1	
Zr ₅₇ Ti ₅ Cu ₂₀ Ni ₈ Al ₁₀	~ 1.1	
Ni ₅₉ Zr ₁₆ Nb ₇ Ti ₁₃ Si ₃ Sn ₂ ²	~ 6.2	
Ni ₅₉ Zr ₂₀ Ti ₁₆ Si ₂ Sn ₃	~ 2.1	1 Xing et al., Phys. Rev. B (2001)
Cu ₄₇ Ti ₃₃ Zr ₇ Nb ₄ Ni ₈ Si ₁ ³	~ 4.1	2 Lee et al., Intermetalics (2004), BMG III
Cu ₄₇ Ti ₃₃ Zr ₁₁ Ni ₈ Si ₁	~ 1.5	3 <u>Park et al., J. Non-cryst. Sol. (2005)</u>
Cu ₄₃ Ag ₇ Zr ₄₃ Al ₇ ⁴	~ 4.1	4 Sung et al., Met. Mater. –Int (2004) and
Cu ₅₀ Zr ₄₃ Al ₇	~ 1.5	Oh et al., Scripta Mater. (2005)

(Ta-Zr: +13KJ/mol, Nb-Zr: +17KJ/mol, Nb-Ti: +9KJ/mol,Cu-Ag: +5 KJ/mol)

- Previous results on the effect of micro-alloying on plasticity
 - : Effect of elements having positive heat of mixing

Alloy design

* Substitution of Zr with Y in Cu-Zr-Al system



D. Xu, G. Duan and W.L. Johnson, Phys. Rev. Lett. 92, 245504 (2004)

* Acta Materialia, 54, 2597 (2006)

Thermal analysis : DSC results



Exothermic peak which exhibit that Y rich amorphous phase crystallize

Structural analyses : TEM results

As-melt-spun



- With increasing Y content, Compositional inhomogeniety

Phase separation







 $Cu_{35.7}Zr_{12.8}Y_{44.3}Al_{7.2}$ (CuY-rich)

Compression test in Cu-Zr-Al-Y alloy system



► A larger amount of strain along the shear band led to localized melting before fracture

Measurement of viscosity using TMA



Structural analyses: HRTEM

$Cu_{46}Zr_{42}Al_7Y_5$

As-melt-spun

Heated up to 480 ℃



: nanocrystallization of Y rich amorphous phase due to relatively lower GFA

* Acta Materialia, 54, 2597 (2006)

In-situ WAXS analysis of Cu₄₆Zr₄₂Al₇Y₅ during heating



Effect of element having positive enthalpy of mixing

Abnormal behavior of supercooled liquid region



Effect of element having positive enthalpy of mixing

Atom probe concentration depth profiles in Ni₆₁Zr₂₂Nb₇Al₄Ta₆



easy crystallization

Effect of element having positive enthalpy of mixing



Ordering in supercooled liquid region

Enhancement plasticity in BMGs with atomic scale heterogeneity c) Effect of element having significantly different enthalpy of mixing among constituent elements

Cu-Zr-Be ternary alloy system

* Acta Materialia, 56 3120 (2008)







a 3DAP-FIM results



(a) FIM image and (b)-(d) composition depth profile of the as-spun $Cu_{47.5}Zr_{40}Be_{12.5}$ ribbon sample

Visualization of Atoms by FIM



Analysis of atoms by 3DAP





Energy-compensating reflectron lens



NIMS 3DAP



Complementary structural analysis

Local Chemical Composition



Local Structure

r (Å) σ^2 N Total N Cu-Cu Cu-Zr Cu-Cu Cu-Zr Cu-Cu Cu-Zr Cu₆₀Zr₄₀ 2.49 2.69 3.0 0.0116 0.0233 3.7 6.7 0.0227 Cu_{47.5}Zr₄₀Be_{12.5} 2.70 2.5 0.0107 2.51 4.8 7.3 Zr-Cu Zr-Zr Zr-Cu Zr-Zr Zr-Zr Zr-Cu 6.9 11.3 0.0124 Cu₆₀Zr₄0 3.10 2.68 4.4 0.0263 Cu_{47.5}Zr₄₀Be_{12.5} 3.12 6.2 0.0130 2.69 3.5 9.7 0.0257





Atoimic diameter in Å: Cu-Cu = 2.56, Cu-Zr = 2.88, Zr-Zr = 3.20.

EXAFS analysis

Cargill-Spaepen short-range order parameters, η

	Z _{AB}	<z></z>	Z * _{AB}	Z ** _{AB}	η	
Cu ₆₀ Zr ₄₀	3.7	8.540	3.416	3.546	0.043	
Cu _{47.5} Zr ₄₀ Be _{12.5}	4.8	7.348	2.939	3.855	0.245	

	n > 0					

Cargill-Spaepen SRO parameter $\eta = Z_{AB} / Z_{AB}^{**} - 1$ $Z_{AB}^{**} = x_B Z_B Z_A / \langle Z \rangle$

chemical ordering between AB nearest-neighbor pairs

Enhancement plasticity in BMGs with atomic scale heterogeneity d) Effect of atomic scale heterogeneity on SB nucleation

Effect of alloy composition on SB nucleation *Ni-Nb-Zr ternary alloy system -167 Ni₆₀Nb₄₀ and Ni₆₀Nb₂₀Zr₂₀ alloys Ni Nb -143 Ni-Nb Ni-Zr Ni₆₀Nb₄₀ Zr addition 2 nm **Compositional inhomogeniety** (conformed by EXAFS)

Experimental equipment



Normal camera 25 frames per sec Interval : 0.04 sec



Effect of local favored structure on SB nucleation



100 µm

Effect of local favored structure on SB nucleation



Si₆₀Nb₂₀Zr₂₀: amorphous phase with local favored structure

- Increased nucleation sites of shear bands
 - ; evaluate the local heterogeneity in amorphous phase

Tailoring of structural inheterogeneity

Alloy design + Process control

atomic scale inhomogeneity generation

Solidification under appropriate conditions

 \Rightarrow Enhanced plasticity in Ni₆₀Nb₃₂Zr₈, Ni₆₀Nb₃₀Zr₁₀ BMGs (σ_{max} : 3.2 GPa, ϵ_{p} : 2.5 %)



Comparison of Work-hardenability depending on 2nd Phases



Comparison of Work-hardenability depending on 2nd Phases



Higher strain hardening of SMA, then larger work hardenability of BMGMCs

Strain hardening(2nd)

Work hardening

(SMA > S.C. > H.C.)

(SMA > S.C. > H.C.)

Mechanism of Work-hardening in BMGC with transformable 2nd phase

"Strain hardening of 2nd phase contributes to work hardening behavior of BMGC."



Deformation behaviors of BMGMC under compression depending on 2nd phase



MATERIALS SCIENCE

Shape Memory Bulk Metallic Glass Composites

Douglas C. Hofmann

10 SEPTEMBER 2010 VOL 329 SCIENCE

Glass-forming and shape memory metals may provide a route to fabricating materials with enhanced mechanical properties.



LETTERS

1) Work softening behavior by ductile secondary phase



High fracture toughness: > 10 % plastic strain in tensile test


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NATURE MATERIALS | LETTER

Stress-induced phase transformation of secondary phase

Transformation-mediated ductility in CuZr-based bulk metallic glasses

S. Pauly, S. Gorantla, G. Wang, U. Kühn & J. Eckert Affiliations | Contributions | Corresponding author

Nature Materials 9, 473–477 (2010) | doi:10.1038/nmat2767 Received 17 November 2009 | Accepted 09 April 2010 | Published online 16 May 2010



Figure 3: Microstructure of a $Cu_{47.5}Zr_{47.5}AI_5$ specimen deformed to fracture.











Materials

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Figure 2. Engineering tensile stress-strain curves of the BMG composites. Dashed lines indicate the unloading process. Top inset shows the outer appearance of the tensile samples pre-strained at the different stages and the lower inset shows the true tensile stress-strain curves, indicating a significant strain-hardening behavior.

Z.P. Lu, et al. Adv. Mater. 2010, 22, 2770-2773



COMMUNICATION