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6. AUTHORS
John J Lewandowski

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Case Western Reserve University
10900 Euclid Ave.

Cleveland, OH 44106 -4919

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14. ABSTRACT
The funded work has investigated the effects of confinement on the flow/fracture behavior of metallic glass. In addition, metallic glass wires in size scales ranging from the micro- to nano-scale have been prepared, followed by tension testing to determine the effects of changes in size scale on plasticity. Confinement effects on the plasticity were investigated by testing bulk metallic glasses under superimposed pressure, while micro-and nano-scale wires were also machined via FIB. Materials were characterized via DSC, SEM, and TEM. Significant effects of confinement and changes in size scale on the plasticity of metallic glasses were observed for the first time

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Final Report: Size Scale and Confinement Effects on Metallic Glasses

ABSTRACT

The funded work has investigated the effects of confinement on the flow/fracture behavior of metallic glass. In addition, metallic glass wires in size scales ranging from the micro- to nano-scale have been prepared, followed by tension testing to determine the effects of changes in size scale on plasticity. Confinement effects on the plasticity were investigated by testing bulk metallic glasses under superimposed pressure, while micro-and nano-scale wires were also machined via FIB. Materials were characterized via DSC, SEM, and TEM. Significant effects of confinement and changes in size scale on the plasticity of metallic glasses were observed for the first time.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/19/2015	7	Jun Yi, Wei Hua Wang, John J Lewandowski. Sample Size and Preparation Effects on the Tensile Ductility of Pd-based Metallic Glass Nanowires, Acta Materialia , (01 2015): 1. doi:
05/19/2015	16	Henry J Neilson, Alex S Peterson, Andrew M Cheung, S Joseph Poon, Gary J Shiflet, Mike Widom, John J Lewandowski. Weibull Modulus of Hardness, Bend Strength, and Tensile Strength of Ni-Ta-Co-X Metallic Glass Ribbons, Materials Science and Engineering A, (03 2015): 176. doi:
05/19/2015	15	Henry J Neilson, Jennifer LW Carter, John J Lewandowski. An Improved Method for Estimation of Elastic Constants of Metallic Glasses, Materials Science and Engineering A, (03 2015): 183. doi:
05/19/2015	14	Jun Y, Wei Hua Wang, John J Lewandowski. Guiding and Deflecting Cracks in Bulk Metallic Glass to Increase Damage Tolerance, Advanced Engineering Materials, (09 2014): 1. doi:
05/19/2015	13	S Mohsen Seifi, Jun Yi, Wei Hua Wang, John J Lewandowski. A Damage Tolerant Bulk Metallic Glass at LN2 Temperature, Journal of Materials Science and Technology, (09 2014): 627. doi:
05/19/2015	8	Luciano O Vatamanu, John J Lewandowski. Pressure and Temperature Effects on Tensile Strength and Plasticity of Metallic Glasses, Mechanics of Materials, (02 2013): 86. doi:
08/28/2014	3	John_ Lewandowski. Modern Fracture Mechanics, Philosophical Magazine, (10 2013): 3893. doi:
08/28/2014	4	Jun Yi, S. Mohsen Seifi, Weihua Wang, John J. Lewandowski. A Damage-tolerant Bulk Metallic Glass at Liquid-nitrogen Temperature, Journal of Materials Science & Technology, (06 2014): 0. doi: 10.1016/j.jmst.2014.04.017
08/28/2014	5	Luciano O. Vatamanu, John J. Lewandowski. Pressure and temperature effects on tensile strength andplasticity of metallic glasses, Mechanics of Materials, (12 2013): 0. doi: 10.1016/j.mechmat.2012.11.011

TOTAL: **9**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received   Paper

TOTAL: **3**

Number of Papers published in non peer-reviewed journals:

(c) Presentations

** Denotes Invited Presentation

1. “EBSD Analysis for Microstructure Characterization of Zr-based Bulk Metallic Glass Composites”, J. Booth, J. Lewandowski, J.W. Carter, Microscopy and Microanalysis Meeting, Hartford, CT, August 7, 2014.

2. “Fracture Toughness of BMG Composites”, J. Booth, J.W. Carter, and J.J. Lewandowski, MS&T, Pittsburgh, PA, October 14, 2014.

3. “Processing and Size Scale Effects on Plasticity of Metallic Glass Fibers”, H.J. Neilson, J. Yi, W.H. Wang, and J.J. Lewandowski, MS&T, Pittsburgh, PA, October 15, 2014.

4. “Weibull Modulus of Hardness, Bend Strength, and Tensile Strength of Ni-Ta-Co-X Metallic Glass Ribbons”, H.J. Neilson and J.J. Lewandowski, MS&T, Pittsburgh, PA, October 15, 2014.

5. “Novel Manufacturing Techniques of Metallic Glass Fibers”, H.J. Neilson, J. Yi, and J.J. Lewandowski, MS&T, Pittsburgh, PA, October 15, 2014.

6. **“Unique Flow, Fracture and Fatigue Behavior of Metallic Glasses – Potential Applications”, J.J. Lewandowski, GE Global Research, Niskayuna, NY, October 23, 2014.

7. “Processing and Size Scale Effects on Plasticity of Metallic Glass Fibers”, H.J. Neilson, J. Yi, W.H. Wang, and J.J. Lewandowski, MRS Fall Meeting, Boston, MA, December 3, 2014.

8. “Fracture Toughness of Bulk Metallic Glasses and Metallic Glass Composites”, J.J. Lewandowski, J. Booth, and J.W. Carter, MRS Fall Meeting, Boston, MA, December 4, 2014.

9. **“Effects of Pressure on Flow and Fracture of Materials”, J.J. Lewandowski, TMS Annual Meeting, Orlando, FLA, March 17, 2015.

10. “Hot Microhardness Testing for Rapid Assessment of Mechanical Behavior, Microstructure Evolution, and Processing Windows”, J.J. Lewandowski, TMS Annual Meeting, Orlando, FLA, March 19, 2015.

Number of Presentations: 10.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

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(d) Manuscripts

Received Paper

08/16/2012 1.00 John Lewandowski, Luciano Ovidiu Vatamanu. Pressure and Temperature Effects on Plasticity of Metallic Glasses,
Mechanics of Materials (07 2012)

08/30/2013 2.00 John J Lewandowski. Modern Fracture Mechanics,
Philosophical Magazine (03 2013)

TOTAL: **2**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

1. Visiting Professor - NTU, Singapore (2015)
2. TMS Leadership Award (2014)
3. ASMI Cleveland Chapter Award of Distinction (2013)
4. Invited Paper-Modern Fracture Mechanics: Sir Alan Cottrell Special Issue in Philos. Mag. (2013)
5. Arthur P. Armington Professorship in Engineering II (2013-Present)
6. Nominee - Srinivasa P. Gutti Memorial Teaching Award (2014)
7. Numerous Invited Talks - International Conferences and Universities

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Henry Neilson	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Jun Yi	0.30
FTE Equivalent:	**0.30**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
John J Lewandowski	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Mark Lewandowski	0.05	Mechanical Engineering
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME	
Jesi Booth	
Henry Neilson	
Total Number:	**2**

Names of personnel receiving PHDs

NAME	
Total Number:	

Names of other research staff

NAME	PERCENT_SUPPORTED
Chris Tuma	0.05
Rich Tomazin	0.05
FTE Equivalent:	**0.10**
Total Number:	**2**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Our early work on this grant focused on determining the effects of superimposed hydrostatic pressure and test temperature on the plasticity of two
different bulk metallic glasses. The use of superimposed hydrostatic pressure relates to the classic Bridgman experiments for which he won the Nobel Prize. In our experiments, it has been shown that the effects of superimposed hydrostatic pressure on the global tensile plasticity at test temperatures well below the Tg of the metallic glass are negligible, consistent with the minor effects of superimposed pressure on the elastic constants at these temperatures. However, increasing the test temperature produces tensile strength reductions and an increase in the global plasticity at 0.1 MPa. Superposition of hydrostatic pressure produces significant increases in strength and reduced ductility at temperatures approaching Tg for both a Zr-based and La-based bulk metallic glass. Potential source(s) of the pressure-induced changes in strength and global plasticity of the bulk metallic glasses include pressure-induced increases to the viscosity of the glass. The results have significant implications on the flow and fracture behavior of such materials, particularly under deformation processing conditions. The paper published in Mechanics of Materials details this work while multiple oral presentations at national and international conferences have been given on this work.

Other more recent work on this grant has successfully prepared micro and nano sized metallic glass wires for subsequent tension testing. The work uniquely obtained metallic glass micro- and nano-wires via a unique deformation process that no one else has used. In addition, unique tension testing experiments were conducted whereby samples were never exposed to an electron beam (in order to minimize damage) prior to or during testing. A size-induced brittle to ductile transition was obtained whereby nano-wires necked to a point and exhibited uniform tensile plasticity while larger diameter samples simply failed in shear similar to that obtained on bulk metallic glasses. The effects of sample preparation and test techniques were shown to significantly affect the results which were published in Acta Materialia and multiple oral presentations have been given on this work. The observations have significant implications on the flow and fracture behavior of micro- and nano- metallic glass systems.

Technology Transfer

1. PI has visited ARL and presented a seminar.
2. PI has visited AFRL, NSWC, and NRL at various times to deliver seminars on topics contained herein.
3. PI has ongoing collaborations with Innovare, Inc. regarding the design and construction of next generation high pressure extrusion devices for various advanced metalworking operations.
4. PI has presented a number of invited seminars, including one at the most recent BMG-X meeting in China, in addition to a number of invited lectures at US Universities.
5. PI has had individual discussions with Profs. Frans Spaepen, Ali Argon, Lindsay Greer, and Takeshi Egami regarding both the results and interpretation of these results.

Sample size and preparation effects on tensile ductility of Pd-based metallic glass nano-wires

Jun Yi[a,*], Wei Hua Wang[b] and John J. Lewandowski[a]

[a]Department of Materials Science and Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, USA.

[b]Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.

Abstract

Glass materials, including metallic glasses, typically fracture in tension at room temperature in a globally elastic manner. Although homogeneous tensile plasticity and necking of nanoscale metallic glasses have been reported, controversy exists regarding possible contributions from specimen preparation and testing techniques. Here, we show the separate effects of sample size reduction and extrinsic effects on the homogeneous tensile plasticity and necking of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy wires tested at room temperature. An intrinsic transition from catastrophic shear fracture to plasticity and necking was obtained in this glass when its diameter approaches estimations of the length scale of the shear-band nucleus size (i.e. 500 nm). Further reduction of the wire diameter to 267 nm produces homogenous flow and complete ductile necking, with a true fracture strain in excess of 2.0. Our theoretical analysis shows that the plasticity of nanoscale metallic glassy wires with diameters smaller than a critical length scale is mediated by shear transformations catalyzed by local shear dilatation, and the predicted critical length scale for the brittle-to-ductile transition of the glassy wires is consistent with our experimental results. Extrinsic effects introduced during sample preparation and/or testing produce entirely different results and are reviewed in the light of previous work.

Keywords: Nanoscale metallic glasses; Catastrophic shear; Complete ductile necking; Shear transformation; Homogeneous plasticity

1. Introduction

Unlike crystalline metals that deform via mobile dislocations and exhibit uniform plasticity prior to necking, glasses without mobile flow defects have no tensile ductility at room temperature (RT) [1-3]. Bulk metallic glasses (MGs) often exhibit compressive plasticity because of their metallic bonding [4], but fracture in tension occurs via catastrophic shear at the elastic limit [5]. Recent reviews have shown that the ductility of crystalline metals can be further enhanced by reducing sample size from bulk to micrometer ranges [6], and nanoscale oxide glass spheres exhibit compressive plasticity even though bulk oxide glasses fail elastically [1]. It can be concluded that such size reductions are effective in enhancing the ductility of many materials systems.

Considerable recent work has focused on the mechanical behavior of nanoscale metallic glasses (NMGs). A transition from shear banding to homogeneous plastic deformation in NMGs has been observed by some, but not all, research groups [6]. The existence of an intrinsic size-induced plasticity of metallic glasses remains controversial due to possible extrinsic effects introduced during sample preparation and/or testing [6,7]. Typical sample preparation techniques including focused ion beam (FIB) milling of samples [8,9], magnetron-sputtering of metallic glassy films [10-12], and nanomoulding of MG nanowires [13,14] were used to investigate the tensile properties of NMGs. Free volume or gallium ion softening can be introduced by FIB and may also improve the ductility of NMGs [7,13], while heating induced by high speed gallium ions may promote structural relaxation that reduces ductility [15]. The specimen taper that is typically produced by FIB can also affect the mechanical behavior of NMGs [7,9,11] while the structure of magnetron-sputtered MG films is very different from their bulk counterparts, as pointed out by various authors [16], potentially obscuring any intrinsic size effects. Although nanomoulding can be used for fabrication of MG nanowires from bulk counterparts, the exposure of samples to air combined with the compressive stress state and contact of samples to the mold at high temperatures can produce oxidized and/or structurally relaxed samples [17]. Sample manipulation and imaging during in-situ testing in a scanning electron microscope or transmission electron microscope can produce heating that can also cause structural relaxation [18] or surface diffusion that promotes diffusive plasticity [1,19]. Most recently, there has been a report of RT homogeneous plasticity obtained in compression of micrometer-sized MG pillars fabricated by FIB-machining of sputtered PdSi MG films, along with strain rate effects on the behavior. This recent work [11] minimized the top rounding of the pillars and ion irradiation effects, while the authors indicated that no extrinsic effects were introduced during testing [11]. The behavior in tension was not investigated in that work [11].

The size effect in MGs has been depicted by phenomenological models [9,12,20,21]. In these models, a shear band is treated as a crack driven by the release of elastic energy stored in the sample [9,12,20,21]. However, as pointed out by others [22-24], the behavior of a shear band is very different from that of a crack and these models cannot explain some experimental data reported in the literature [22]. A more recent phenomenological model utilized the dependence of shear band spacing and shear offset on sample size to depict the size effect obtained during compression studies of magnetron-sputtered and FIB-machined MGs [11]. However, this model alone cannot explain the observed strain-rate effect on the inhomogeneous-to-homogeneous plastic deformation transition. An empirical law describing the ductile-to-brittle transition in a size-rate deformation map was proposed [11] and invoked rate effects on shear band velocity in samples of different sizes. It will be interesting to explore how this empirical law could be applied to tensile deformation given the differences in stress state and test techniques. At elevated temperatures, the brittle-to-ductile transition of MGs has been described by steady state constitutive flow equations constructed by a free volume model [23] and shear transformation (ST) model [24,25]. The ST model [25,26] has also been used to describe the transition from inhomogeneous to homogeneous deformation induced by high loading rates in nanoindentation [27].

Here, we demonstrate an intrinsic transition from catastrophic shear fracture to complete ductile necking (i.e. ductile rupture, necking to a point), with evidence of homogeneous flow during tension testing at RT of uniform and smooth $Pd_{40}Cu_{30}Ni_{20}P_{20}$ glassy wires [28] produced and tension tested without exposure to FIB and/or electron beam. It is shown that wires with diameters smaller than about 500 nm neck during tension tests at RT, while identical-sized and smaller MG nanowires previously exposed to either an electron beam or ion beam fail predominantly via catastrophic shear when tested with beam-off conditions. The critical diameter of MG nanowire required to produce this brittle-to-ductile transition in the absence of beam exposure is comparable to estimates [26] of the shear band nucleus size for a similar metallic glass. A modified ST theory that incorporates redistribution of the stress and strain fields of STs catalyzed by local shear dilatation is used to explain this transition in deformation behavior of the glassy wires. The effects of various electron- and/or ion-beam exposures on the tensile plasticity of identical nano-wires were determined in order to document any extrinsic effects that may arise in sample preparation and/or testing.

2. Experimental methods

2.1. Preparation of MG wires

$Pd_{40}Cu_{30}Ni_{10}$ ingots were prepared by arc melting Pd, Cu and Ni pieces with purity better than 99.9 wt.% under a Ti-gettered argon atmosphere in a water-cooled copper hearth. The $Pd_{40}Cu_{30}Ni_{10}P_{20}$ ingots were prepared by induction heating a $Pd_{40}Cu_{30}Ni_{10}$ ingot and elemental P crystals with purity better than 99.999 wt.% in a sealed vacuum quartz tube. Because of the evaporation of P during melting, the composition cannot be accurately controlled by melting only once. In the first trial, 1.2 times the weight of needed P was used to make the content of P in the ingot higher than 20 at.%. Then, this ingot and pulverized pieces of $Pd_{40}Cu_{30}Ni_{10}$ with the amount required to produce the desired final composition (i.e. $Pd_{40}Cu_{30}Ni_{10}P_{20}$) were sealed in a vacuum quartz tube with B_2O_3 in order to purify the material using a fluxing technique. $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy rods with a diameter of 1 mm were fabricated by a suction-casting method under a Ti-gettered argon atmosphere in a vacuum chamber maintained at 3×10^{-3} Pa. $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy nanowires were then prepared by drawing the glassy rods in their supercooled liquid region. Details of the fabrication method of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy nanowires can be found elsewhere [28]. The fully amorphous nature of the $Pd_{40}Cu_{30}Ni_{20}P_{20}$ glassy wire was verified as depicted in previous work [28].

2.2. SEM and Ion Beam (FIB) Exposure of Samples

Placement and alignment of the nanowires required some minimal exposure to an electron beam (e.g. 0.17 nA and 5 kV) in the SEM prior to tension testing. The initial tension tests did not additionally expose the nanowires to either an electron- or ion-beam until after failure. Current and voltage of the electron beam for SEM imaging of failed MG wires were 1 nA and 20 kV respectively.

In addition to testing nano-wires that had received minimal electron-beam exposure, separate nano-wires used an FEI Nova Nanolab 200 to manipulate, image, attach, and mill some of the MG wires. Current and voltage of ion beam for both observation and milling were 10 pA and 30 kV. Pt deposition was used to attach the nano-wires to a substrate in some cases, using an electron beam with current and voltage of 4 nA and 15 kV, respectively.

2.3. Tensile testing of MG wires with minimal exposure to electron/ion beam

In order to investigate the intrinsic mechanical behavior of the metallic glassy wires, attempts were made to eliminate artifacts during sample preparation, manipulation, and testing. The samples used here are uniform and smooth $Pd_{40}Cu_{30}Ni_{20}P_{20}$ glassy wires fabricated via fast drawing of metallic glassy rods in their supercooled liquid region [28]. The wires are rapidly cooled during drawing as they exit the heat source and likely provide an unrelaxed sample. Unfortunately, sample size limitations prevent the use of other conventional characterization techniques (e.g. DSC, DMA, etc.). However, the limited heating during preparation of the nanowires should not change the mechanical behavior of the wires, because the critical fictive temperature of the Pd-based glass is higher than its glass transition temperature [29].

Separate MG wires with diameter of 1.48 μm or 2.5 μm and 1 cm gauge length were pulled in tension by the method as depicted in Fig. 1a at RT. In this case, the wire is adhered to two Si substrates by using silver epoxy adhesive in order to avoid Pt-deposition and associated beam exposures. Both Si substrates were on a smooth glass slide and the sample was carefully aligned using fiducial marks on the Si substrates. One Si substrate was fixed to the glass baseplate while the other was manually driven in air at room temperature by a micrometer 20 μm every 3 seconds (i.e. about 1×10^{-3} s^{-1} shear strain rate ($\dot{\gamma} = (1+\nu)\dot{\varepsilon}$) [30]). This arrangement provided good alignment of the sample and no exposure to electron/ion beams during tension testing.

Wires with smaller diameter were pulled as shown in Fig. 1b. These tests used a combination of carbon tape and the strong surface adhesion between the Si substrate and nano-wire to adhere the samples to the Si substrate. These wires all had a larger diameter end and a nano-diameter end. The larger diameter end results from the wire drawing process while the diameter of the wire away from this large end is uniform and of nanoscale with a gauge length of about 1 mm. In order to ensure high alignment during tension testing, a drop of water was first put onto the Si substrate away from the carbon tape. The smaller diameter end of the nano-wire was then placed onto the water drop, followed by the larger diameter end adhered to the carbon tape, as shown in Fig. 1b. The Si substrate was then inclined, permitting the water droplet to slide down and away from the end of the nano-wire, thereby aligning it with the large diameter end. The small diameter end then simply adhered to the Si substrate due to the strong interaction between them [31]. The MG wire was then pulled 2 μm every 3 seconds (the shear strain rate is about 1×10^{-3} s^{-1}) in the direction as indicated by the arrow in Fig. 1b at RT. The Si substrates were again present on a glass substrate to ensure additional alignment and the samples tested in this manner received no exposure to either electron- or ion beams during tension testing.

3. Results

3.1. Brittle-to-ductile transition

SEM images taken after tension testing are shown in Fig. 2. Wires with a diameter of 1.48 μm and 2.5 μm failed in catastrophic shear as shown in Fig. 2b, similar to the behavior of bulk metallic glasses [5]. However, significant differences in mechanical behavior were obtained in samples with smaller diameter. A diffuse shear band exists in the MG wire with a diameter of 715 nm (Fig. 2c). This sample dislodged from the substrate prior to failure during the tension test. Further diameter reduction to 420 nm produces necking at RT (Fig. 2d). An intrinsic brittle-to-ductile transition is shown in Fig. 2a by quantifying the dependence of the reduction of area (A_0 - A_f)/A_0 (A_f is the cross-sectional area at fracture, A_0 is the cross-sectional area far away from the failure) on the sample diameter d normalized with the estimated size of the shear band nucleus S_n (i.e. d/S_n, where S_n = 500 nm [26] for a similar glass). A transition from catastrophic shear to homogeneous plasticity and necking appears to occur for this material when tested in this manner when the sample diameter approaches S_n (i.e. d/S_n approaches 1.0).

3.2. Towards complete ductile necking (i.e. ductile rupture)

The variation of neck appearance with wire diameter was investigated by testing wires with even smaller diameter. Tension testing of wire with diameter of 267 nm produced necking to a point, Fig. 3b. This necking does not appear to be preceded by cavitation which is typically observed in ductile engineering materials [32]. In order to further quantify the level of ductility in such samples, Fig. 3a plots the true strain ε_T ($\varepsilon_T = \ln(d_0^2/d^2)$ at different normalized distances from the failure sites (i.e. L/d_0) along the axis of the wires. d_0 is the diameter of wire far away from the failure site, d is the diameter of wire at the neck. This is not plotted on a linear scale since all samples with diameter greater than 1.48 μm (including bulk samples) are known to fail in catastrophic shear with zero global plasticity.

As shown in Fig. 3a, the 1.48 μm diameter sample that failed in catastrophic shear (Fig. 2b) did not exhibit any change in ε_T along the gage length. The 2.5 μm diameter sample exhibited the same behavior. However, as the initial wire diameter decreased to 420 nm and 267 nm, the

ε_T increased significantly, and the length of the neck normalized by d_0 increased to 0.54 and 6.49 respectively, Fig. 3a. This demonstrates that the MG wires with smaller diameter prepared and tested in this manner have higher resistance to both fracture and instability to homogeneous plastic deformation [32].

3.3. Extrinsic effects introduced during sample preparation and/or testing

3.3.1 Extrinsic effects on tensile behavior of MG wires

The effects of different sample preparation and testing techniques (Fig. 4) on the mechanical behavior were also studied. To reduce the strong interaction between the Si substrate and nanowires in order to enable manipulation of the nanowires, a Si substrate with trenches was used as shown in Fig. 4a. The nanowire was first adhered to the micromanipulator by deposited Pt, cut by FIB (Fig. 4b), transported to the edge of another Si substrate, adhered to that substrate by Pt deposition and then pulled by the micromanipulator with beam off (Fig. 4c). In contrast to the plasticity and necking exhibited by the 420 nm diameter wire in Fig. 2d, the MG wire with a diameter of 418 nm tested in this manner failed in catastrophic shear, Fig. 5a. Although a smaller diameter wire (i.e. 150 nm) tested in this manner produced some local necking (Fig. 5b), the final fracture of this wire was still dominated by shear, unlike the previous results shown in Figs. 2 and 3 that followed the testing method outlined above in Fig. 1. These experimental results appear to be similar to those reported in the literature [9].

The mechanical behavior of smaller diameter samples ion-milled from our larger diameter wires was also investigated. A micro-wire with original diameter 887 nm was milled (by ion beam) to a sample with a thickness of 358 nm as shown in Fig. 6a, and then pulled with the beam off in the manner shown in Fig 4. Although implantation of gallium ions can introduce free volume or create chemical softening [7,13], the FIB-machined NMG with a thickness of 358 nm only exhibited limited necking with failure in shear, Fig. 6b. Structural relaxation induced by the heating of Pt deposition [33] may contribute to this observation. Experiments to investigate this are underway but beyond the scope of this paper. Figures 5 and 6 are provided to show that extrinsic effects introduced into our samples produce experimental results similar to those reported in the literature [6] on a range of metallic glasses prepared and/or tested in this manner.

3.3.2 Damage caused by electron beam irradiation

Figure 7 further shows the self-bending of an originally straight and free-standing MG nanowire caused by irradiation of the electron beam with the same current density and voltage used for Pt deposition. These results indicate that the damage induced by electron beam exposure under these conditions is strong. The lack of bending of FIB-prepared samples reported in the literature [7,9,12] as well as that shown in Fig. 6a, could arise due to the symmetric ion beam exposure used to machine the samples. However, samples that are restricted [8,10] in any manner (e.g. Fig. 6a) are also not permitted to bend, although residual stresses may develop as a result. While these effects may not be visible on the machined sample, they will affect the subsequent mechanical behavior.

4. Discussion

The following is an attempt to explain our observations of a size-induced brittle-to-ductile transition based on the original shear transformation theory [34]. Both the local stress and strain field of catalyzed STs (CSTs) are different from isolated STs (ISTs) at low stresses due to the local shear dilatation [26,34,35]. The critical yield stress of CSTs (τ_0') would be larger than that of ISTs (τ_0) [26,34]. According to the cooperative shear model, the critical yield stress of an ST $\tau_c = \pi\phi_0/4\gamma_c$, where γ_c is the critical shear strain and the total barrier energy density $\phi_0 = (8/\pi^2)\,\mu\gamma_c^2$ (where μ is shear modulus) [36]. Then, $\tau_c = 2\mu\gamma_c/\pi = \sigma_y/\pi$, where σ_y is the yield stress of MGs, that is, the critical yield stress of an ST is proportional to the yield strength of MGs. Therefore, $\tau_0'/\tau_0 = \sigma_I/\sigma_0$, where σ_I is the strength of MG nanowire, σ_0 is the bulk strength. Because $\sigma_I^2 - \sigma_0^2 = \Psi/d$ (where Ψ is the materials constant regarding Young's modulus and shear band energy density) [22],

$$\tau_0' = \tau_0(1 + \Psi/d\sigma_0^2)^{1/2}. \qquad (1)$$

The operation of CSTs rearranges the atoms of adjacent transformed volume elements. Such rearrangement releases the strain of the seeding shear transformations [26,34]. The average local shear strain of CST can be written as

$$\gamma_0' = \frac{1}{2}\gamma_0, \qquad (2)$$

where γ_0 is the local shear strain of an IST. According to ST theory [26,35], the Helmholtz free energy required to operate the CST

$$\Delta F_0' = \left[\frac{7-5\nu}{30(1-\nu)} + \frac{2(1+\nu)}{9(1-\nu)}\beta^2 + \frac{1}{2\gamma_0'}\cdot\frac{\tau_0'}{\mu}\right]\cdot\mu\cdot\gamma_0'^2\cdot\Omega_f, \qquad (3)$$

where ν is Poisson's ratio, β is the dilatation factor which is about unity for metallic glasses [35], T is temperature and $\Omega_f = \frac{4}{3}\pi(2.5D)^3$ is the volume of an individual ST (D is the nearest neighbor distance corresponding to the first peak position in the radial distribution function) [34].

The shear strain rate of a metallic glassy sample subjected to a shear stress τ resulting from the superposition of many individual STs is written as

$$\dot{\gamma} = \alpha_0 \gamma_0' \nu_G \cdot \exp(-\frac{\Delta F_0'}{kT}) \cdot \sinh(\frac{\tau \gamma_0' \Omega_f}{kT}), \qquad (4)$$

where k is the Boltzmann constant, α_0 and ν_G are pre-exponential coefficients [35] as listed in Table I. The transition between homogeneous and inhomogeneous deformation can be taken as the critical stress level of $\tau = 0.6\tau_0'$ in equation (4) [24]. Incorporating parameters given in Table I, $\Psi/\sigma_0^{\ 2}$, where σ_0 = 1.7 GPa [36], is estimated to be 670 nm by fitting the experimental data (i.e. dependence of strength on size) of Pd-based glass [37] using equation $\sigma_I^2 - \sigma_0^2 = \Psi/d$.). This leads to the relation between $\dot{\gamma}$ and d/S_n plotted in Fig. 8 that delineates the transition between homogeneous and inhomogeneous deformation. At the present shear strain rate of approximately 1×10^{-3} s^{-1}, this transition is predicted to occur at about 470 nm, roughly consistent with our experimental results and the calculated shear band nucleus size of 500 nm [26]. Therefore, it appears that the size-induced plasticity of MG nanowires observed presently is mediated by CSTs in the shear band nucleus. In the shear band nucleus, STs are catalyzed by the local dilatation in the vicinity of previous shear transformed sites [26]. During the operation of such STs, free volume is redistributed, and the memory of the initial unstressed state is lost [26,35]. Therefore, the material inside the shear band nucleus can undergo plastic deformation. As the sample size approaches the size of the shear band nucleus, shear banding should be preceded by homogeneous plastic deformation since the shear band nucleus cannot percolate to form a shear band as in bulk metallic glasses [38].

5. Concluding Remarks

In summary, we show a room temperature intrinsic transition from catastrophic shear failure to more uniform plasticity and complete ductile necking of a metallic glass when the sample diameter is reduced to below 500 nm when prepared and tested in a manner to avoid extrinsic effects. This sample dimension is on the order of the shear band nucleus size [26] calculated for a similar metallic glass. According to our theoretical analysis, the plasticity of NMGs is mediated by the STs catalyzed by the local dilatation. The prediction of our theoretical analysis on the critical length scale of the brittle-to-ductile transition is consistent with our experimental results. In order to further reveal deformation mechanisms in NMGs, more effort should be made to investigate the behavior of the plasticity carriers (CSTs) in NMGs. Extrinsic effects introduced during our sample preparation and/or testing produce entirely different results.

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Figure captions

Fig. 1. Tension testing of MG wire. (a) The large diameter (e.g. 1.48 μm, 2.5 μm) MG wire is adhered to two Si substrates by silver epoxy adhesive. One Silicon substrate is fixed onto the

underlying glass slide, while the other one is driven manually by a micrometer. (b) Tension test technique of smaller diameter wires used a combination of carbon tape and the strong surface adhesion between the Si substrate and nano-wire to adhere the samples to the Si substrate. In order to ensure high alignment during tension testing, a drop of water was first put onto the Si substrate away from the carbon tape. The smaller diameter end of the nano-wire was then placed onto the water drop, followed by the larger diameter end adhered to the carbon tape, as shown in Fig. 1b. The Si substrate was then inclined, permitting the water droplet to slide down and away from the end of the nano-wire, thereby aligning it with the large diameter end. The small diameter end then simply adhered to the Si substrate due to the strong interaction between them [31]. The same underlying glass slide is used during the tension test, performed by using micrometers to pull in the direction indicated by the arrow.

Fig. 2. Transition from catastrophic shear fracture to ductile necking of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy wires with reduction in sample diameter. (a) Relationship between the reduction of area $(A_0 - A_f)/A_0$ and diameter of the wires normalized by shear band nucleus size S_n (i.e. 500 nm) for a similar glass [26]. The reduction of area increases rapidly from 0 to nearly 1 with decreasing diameter of the wires in the range from d/S_n = 1.6 to 1.0. (b) Catastrophic shear failure of a MG wire with a diameter of 1.48 μm or 2.5 μm. (c) Diffuse shear banding of a 715 nm diameter MG wire that dislodged from the Si substrate prior to tensile failure. (d) Necking of a MG wire with a diameter of 420 nm.

Fig. 3. (color online) Towards complete ductile necking of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy wires. (a) Variation of the true strain with distance along the axis of the wire starting with the failure location. As the starting wire diameter decreases from 1.48 μm (or 2.5 μm) to 267 nm, the length of neck normalized by d_0 increases from zero to 6.49. (b) SEM image of MG wire with a diameter of 267 nm that has necked to a point. The black solid lines in (a) are eyesight guides.

Fig. 4. Procedure for tension testing of MG nanowires using micromanipulator in scanning electron microscope. (a) A metallic glass wire positioned for manipulation on a Si substrate with trenches. The width and depth of the trenches are 10 μm and 1 μm respectively. The distance between trenches is about 10 μm. (b) Pt deposition used to adhere the metallic glass wire to micromanipulator. The wire was then cut by ion beam about 20 μm away from the Pt deposition. (c) The metallic glassy wire is transported to the edge of another Si substrate, adhered to the second Si substrate by deposition of Pt and then pulled in tension by the micromanipulator. The micromanipulator was moved 0.2 μm in about 15 s. The shear strain rate was estimated to be about 1×10^{-3} s^{-1}.

Fig. 5. Fractured $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy wire tested using the method as shown in Fig. 4. (a) Catastrophic shear fracture of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy with a diameter of 418 nm. (b) Tensile failure of a MG nanowire with a diameter of 150 nm. Although there is indication of very local necking, shear dominates the final failure.

Fig. 6. Effect of ion beam irradiation on tensile fracture of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glassy wire.(a) MG nanowire with a reduced thickness of 358 nm milled by mild ion beam with current and voltage of 10 pA and 30 kV, respectively, from a MG wire with an original diameter of 887 nm. (b) Catastrophic shear failure of the 358 nm NMG in (a) with minimal local necking.

Fig. 7. Self-bending of pristine and originally straight MG nanowire with a diameter of 422 nm caused by electron beam irradiation. The electron beam with 4 nA current and 15 kV voltage is focused in a 1×1 μm^2 area for 10 s at the right end of an initially straight pristine nanowire. The current and voltage used here is the same as that of electron beam used for Pt deposition. This

illustrates that such conditions clearly cause damage and likely affect subsequent mechanical behavior.

Fig. 8. The transition between homogeneous deformation and inhomogeneous deformation of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glass at room temperature, plotting the shear strain rate $\dot{\gamma}$ during tension versus normalized diameter d/S_n of the MG wire. The transition was calculated using equation (4) and the parameters listed in Table I. This transition at 1×10^{-3} s^{-1} was estimated at a sample diameter of $0.94S_n$, close to the experimental data shown in Fig. 1 and the size of shear band nucleus.

TABLE I. List of material constants of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ glass at RT.

Parameter	Value	Reference
$\alpha_0\gamma_0\nu_G$	10^{11} s^{-1}	[26,34]
γ_0	0.125	[26,34]
ν	0.394	[36]
β	1	[26,35]
μ	33 GPa	[36]
D	2.77×10^{-10} m	[39]
σ_0	1.7 GPa	[36]
τ_0/μ	0.03	[26,34]
T_g	593 K	[36]

TABLE I, J. Y. *et al.*