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# Surface roughness imparts tensile ductility to nanoscale metallic glasses

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## ABSTRACT

Experiments show an intriguing brittle-to-ductile transition on size reduction on nanoscale metallic glasses (MGs). Here we demonstrate that such phenomena is linked to a fundamental characteristic size effect in the failure mode under tensile loading. Large-scale molecular dynamics simulations reveal that nanoscaled MGs with atomistically smooth surfaces exhibit catastrophic failure via sharp, localized shear band propagation. In contrast, nanosized specimens with surface imperfections exhibit a clear transition from shear banding to necking instability above a critical roughness ratio of $\xi \sim 1/20$, defined as the ratio between the average surface imperfection size and sample diameter. The observed brittle-to-ductile transition that emerges in nanosized MGs deformed at room temperature can be strongly attributed to this roughness argument. In addition, the results suggest that the suppression of brittle failure may be scale-free and be realizable on length scales much beyond those considered here, provided the threshold roughness ratio is exceeded. The fundamental critical roughness ratio demonstrated sheds light on the complex mechanical behavior of amorphous metals and has implications for the application of MGs in nano- and micro-devices.

Bulk metallic glasses (BMGs) represent an attractive class of materials for their outstanding mechanical properties, including high strength, high elastic limit, and high hardness compared with their crystalline counterparts [1–3]. A serious limitation of most monolithic BMGs is that they fail catastrophically when subjected to uniaxial tension with little macroscopic plasticity [2–5]. This is unlike their crystalline analogs that commonly exhibit significant plastic deformation prior to failure. The basic carriers of plastic deformation in metallic glasses (MGs) are shear transformation zones (STZs), and catastrophic brittle failure of BMGs is associated with the collective dynamics of STZs that coalesce to form nanoscale shear bands (SBs) in which intense local plastic strain occurs. In macroscale specimens, strategies proposed to mitigate the brittle failure of MGs and induce tensile ductility involve promoting heterogeneous stress states to control SB propagation. For example, carefully designed BMG composites have been shown to produce a ductile response under tensile loading much like crystalline metals [6]. Inducing stress gradients

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through specimen geometry modification is another approach that increases ductility [7,8]. A third strategy to enhance both the deformability and work hardening of MGs is via reduction of the external dimensions of the samples down to the nanometer range [9–11]. Experiments on nanoscale samples have shown brittle failure via localized SBs and ductile deformation via necking [2,6,9–16]. A brittle-to-ductile transition (BDT) has been reported to occur at a critical sample size, which is a function of the specific processing steps and chemistry of the glass. A catastrophic SB typically characterizes brittle failure above a critical specimen dimension $d_c$, while necking induced plasticity is evident below $d_c$ for various MG compositions [9–11,16]. *In situ* tensile experiments by Guo et al. [9] indicate necking of monolithic MG samples with sizes in the order of ∼100 nm. Jang and Greer [10] reported extendibility in excess of 20% and necking in freestanding Zr-based MG nano-samples with diameters of $d \sim 100$ nm, while larger diameter specimens failed catastrophically via SBs. Tian et al. [11] reported a similar transition at $d \sim 80$ nm in nanoscale tensile experiments on freestanding $Cu_{49}Zr_{51}$ MG samples. Several other recent investigations demonstrate clearly ductility in MG nano-pillars fabricated both by electroplating into a template and focused ion beam (FIB) milling [16–18].

These nanoscale experiments were performed on nominally monolithic materials with nominally uniform specimen geometries. It has been suggested that the traction-free surface as well as the surface energy state may play a role in the ductility observed at the nanoscale [14,16,19–21]. Previous molecular dynamics (MD) simulations [17] suggest that surface STZs may initiate with a lower activation barrier compared to those in bulk MGs; this may result in size dependent response on the nanoscale [17]. The caveat is that the sample size at which the ductility transition occurs in atomistic simulations is typically an order of magnitude smaller than those observed experimentally [16]. Experiments reveal that nanofabrication techniques, such as FIB milling, modify the structural state near the surface in a manner that enhances tensile ductility [16,17,21]. However, this does not explain the observed size dependent transition in nanoscaled specimens fabricated using electroplating and not exposed to ion irradiation [16]. Recently, Zhao et al. proposed a statistically-informed theory that considers the effects of surface and bulk characteristics on size dependent macroscopic responses in MGs through the notion of extended defects [22]. Their work makes broad connections to some of the observed experimental phenomena, but does not explain the mechanics of a size-dependent transition in the deformation mode of MGs.

No clear mechanism exists that can both explain the SB-necking transition in monolithic nanosized MGs and reconcile its apparent insensitivity to both the composition and the extent of ion damage. The question remains—what physical mechanism related to the dimensionality of MGs suppresses catastrophic failure? Tensile ductility of monolithic BMGs has been shown to increase in the presence of external notches, presumably as a result of the local stress triaxiality [7,8,23]. Sample synthesis unavoidably leads to finite surface roughness of different levels. The surface roughness of nanoscale samples is much higher relative to the sample size than that in most macroscale experiments. We speculate that it is the high surface roughness-to-diameter ratio in nanoscale samples that leads to similar notch-induced ductility observed in macroscale samples [4]. The magnitude and geometric characteristics of roughness differ among the various fabrication techniques. During mechanical straining, the topological surface features likely act as stress concentrators, similar to external notches [24]. For example, the stress intensity factor for a surface with normally distributed random roughness is given by $K_t = 1 + 2\sqrt{2}(\bar{a}/\beta)$ where $\bar{a}$ is the RMS roughness and $\beta$ is the autocorrelation length, which is qualitatively similar to that produced by single or multiple notches [24]. Could this nanoscale roughness be partially responsible for the tensile necking in nanoscale MGs? What is the length scale associated with the transition from catastrophic shear banding to necking? Does such dependence span a wide range of length scales? We employ large-scale MD simulations to investigate the effect of roughness on the BDT of MG nanopillars. The results reveal that small, densely populated, surface imperfections roughness play a critical role in determining the failure mode of MGs at the nanoscale. The results of this work suggest that the BDT in deformation of MGs may be valid at length scales well beyond the nanoscale, assuming the samples roughness-to-diameter ratio is above the intrinsic threshold value for the material.

The sample geometries were simulated to resemble those in experimental studies on nanoscale MGs. Fig. 1(a) shows an atomic force microscope (AFM) image of a Ni–P MG surface exposed to FIB irradiation. It shows a valley-to-peak height difference in the 1–3 nm range over an area of 1 $\mu m^2$, with nanoscale ridges parallel to the direction at which the FIB was applied. In comparison, the scanning electron micrograph (SEM) of an electroplated Ni–P MG nanopillar with no FIB exposure indicates a nominally uniform surface along the pillar test section (Fig. S1-a in Supplementary Information). The pillar test section is noticeably smoother than the pillar cap due to the templated fabrication process discussed in the Methods section. Fig. S1-b shows an AFM image of Ni–P MG film surface generated by electrodeposition with no FIB exposure. The surface profile is diffuse with no well-defined peaks or valleys. Motivated by these observations, we performed a series of MD simulations on three closely related sets of cylindrical nanopillars under uniaxial tension: (i) *smooth* (S) specimens prepared by carving from larger bulk systems, (ii) *single-notched* (SN) specimens, which are identical to (i) with an intentional circumferential notch, and (iii) *rough* (R) specimens, which contain multiple densely populated circumferential notch-like imperfections placed along the specimen length. The simulations of SN specimens can help elucidate the role of roughness in the SB-necking transition and can be analyzed in terms of elasto-plastic fracture mechanics. In accordance with earlier experimental studies [12,13,25] and the height profile shown in Fig. 1(a), we introduced notches whose width and depth ($a$) are equal to 1 nm. For S and SN specimens, we systematically varied the specimen diameter in the $5 \leq d_0 \leq 100$ nm range while