Nanometallic Glasses: Size Reduction Brings Ductility, Surface State Drives Its Extent

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ABSTRACT: We report tensile experiments on Ni80P20 metallic glass samples fabricated via a templated electroplating process and via focused ion beam milling, which differed only in their surface energy states: Ga-ion-irradiated and as-electroplated. Molecular dynamics simulations on similar Ni80Al20 systems corroborate the experimental results, which suggest that the transition from brittle to ductile behavior is driven by sample size, while the extent of ductility is driven by surface state.

KEYWORDS: Metallic glass, electroplating, NiP, brittle-to-ductile, molecular dynamics

Bulk metallic glasses have garnered a significant amount of attention since their inception in 1960.1 High strength and corrosion resistance render metallic glasses as attractive structural materials, but their brittle failure under tension is a key reason that prevents the wide insertion of metallic glasses into commercial applications. Tensile deformation of metallic glasses is typically marked by elastic loading followed by catastrophic failure via shear localization within a narrow region called a shear band.2 Substantial efforts have been made to alleviate brittle behavior by various toughening mechanisms.3–5 One possibility is to reduce the specimen size to below some critical dimension on the order of ∼100 nm, where metallic glasses have been reported to undergo a size-induced brittle to ductile transition in compression6–8 and in tension.9,10 The origin of this transition is still being pursued because the experimental results are inconsistent with some literature reporting this transition to occur at 400,6 200,6 and 100 nm11–15 or not seeing any suppression of catastrophic failure even for sample sizes down to 150–300 nm11–14 Most of the existing literature on nanomechanical deformation of individual metallic glass nanostructures describes experiments on samples fabricated using a focused ion beam (FIB). This milling technique irradiates the sample surface with a relatively high-energy ion beam, which can potentially lead to a modification of the local atomic arrangements or even to surface crystallization.15–17 Molecular dynamics (MD) simulations by Xiao et al. revealed that ion bombardments suppressed shear band formation in 106.4 eV-irradiated Zr-based metallic glass nanowires (7.8 nm in diameter and 17.7 nm in length).18 An alternate synthesis of individual nanosized metallic glasses suitable for mechanical testing is necessary to ascertain whether the size-induced brittle-to-ductile transition is a real physical phenomenon and to shed further light on understanding the deformation mechanisms in metallic glasses at small scales. To date, there has been a paucity of “FIB-less” fabrication methods to produce individual nanoscale metallic glass specimens for nanomechanical testing. Vertically aligned cylindrical nanowires have been synthesized by nanomolding from bulk samples14,19 (Figure 1a) and thin metallic glass films have been electroplated onto indium–tin-oxide-coated (ITO) glass substrates20 (Figure 1b) and deposited using radio frequency magnetron sputtering.21 None of these methods are well-suited for measuring the mechanical properties of individual nanosized samples. Selectively removing individual molded nanowires is one possibility for producing such samples, and tensile experiments on removed Pt57.5Cu14.7Ni5.3P22.5 nanowires revealed that for samples ranging from ∼100–150 nm in diameters and ∼1–3 μm in gauge lengths, ion irradiation was able to induce a brittle-to-ductile transition, while subsequent annealing reversed it.14

We report the fabrication of Ni58P42 metallic glass nanotensile samples with ∼100 and 500 nm diameters and ∼650 nm and 2 μm heights. This synthesis was carried out by electroplating the metallic glass into a poly(methyl methacrylate) (PMMA) template, which was spin-coated onto a presputtered Au seed layer on a Si chip and patterned via e-beam lithography (Figure 1d). In addition, a 2 μm thick film was separately electroplated directly onto another substrate by following the same procedure, and nanotensile samples with...
identical geometries were FIB-carved into the film. The two sets of samples, electroplated and FIB-carved, were virtually identical to each other, both in composition and geometry (see Table 1 for chemical composition analysis, Table 2 for electroplating conditions, and Figure 3 for the SEM images of representative samples). Experiments on these samples allowed for a direct comparison between the mechanical responses of otherwise the same metallic glass nanostructures with irradiated versus as-fabricated surface states. A Ni–P system was chosen because it lends itself well to electroplating. NiP metallic glasses may have different short-range order (SRO) compared with the more common binary glass, CuZr, which has more metallic-like bonding (see Supporting Information for more discussion). Tensile results revealed catastrophic failure in 500 nm diameter samples and postelastic deformability in 100 nm diameter samples fabricated by both techniques. The extent of tensile ductility was nearly a factor of 3 greater in FIB samples, which suggests that a less relaxed (irradiated) surface state may facilitate homogeneous plastic flow via activation of numerous debris bands.

Results. Figure 2 shows an array of electroplated pillars (Figure 2a), tensile (Figure 2b) and compressive (Figure 2c) samples, dark-field transmission electron microscopy (TEM) image (Figure 2d), X-ray diffraction (XRD) pattern (Figure 2e), and energy-dispersive X-ray spectrum (EDX) (Figure 2f). TEM and EDX analyses were performed on a representative nanopillar, while the thin metallic glass film was characterized by XRD and EDX. XRD was not performed on the nanopillars because they are smaller than the X-ray beam spot size. The feature-less dark field TEM image and the corresponding diffuse-ring electron diffraction pattern of a 500 nm electroplated nanotensile sample (Figure 2d) confirm the amorphous microstructure of these electroplated alloys. The EDX analysis (Figure 1f) of relative concentrations of Ni and P revealed that the concentrations of phosphorus, ≈14.9 wt % in the nanopillars and ≈14 wt % in the thin film, were virtually identical. The substantial amount of carbon (≈4.5 wt %) and oxygen (≈4 wt %) on the surface of the electroplated samples was likely a result of the residual organic solvents used to remove the PMMA. The FIB-machined samples also contained a considerable amount of carbon (≈3.4 wt %) and oxygen (≈1.2 wt %), typical of most metallic surfaces exposed to air. The effect of these surface impurities on the mechanical properties is likely negligible because they do not form continuous layers and hence are not able to bear any load (see Supporting Information for additional discussion on surface contamination). XRD spectra of the electroplated thin film, shown in Figure 2e, reveals the presence of three strong peaks: two for the Si substrate (100) and the seed Au layer ([420]). The broad peak at 2θ = 20° stems from the glass slide onto which the sample was mounted. No known peaks for nickel (2θ = 45°, Ni [111]) were observed, instead a broad weak peak (indicated by the blue arrow) was present near 2θ of 45°. These observations imply that the electroplated Ni–P metallic alloy was amorphous, consistent with literature.

Figure 3 shows tensile engineering stress vs engineering strain data for typical 100 nm diameter samples fabricated by both techniques as well as the progressions of the corresponding in situ SEM images during each experiment, which coincide with the same letter-labeled points in the data. The strain was calculated from the displacement using the strain data for typical 100 nm diameter samples fabricated by both techniques as well as the progressions of the corresponding in situ SEM images during each experiment, which coincide with the same letter-labeled points in the data. The strain was calculated from the displacement using the signal from the nanoindenter, a method which has been shown to be more accurate in nanomechanical experiments (see Supporting Information for additional information).

Evidently, both the FIB and EP samples with 100 nm diameters deformed plastically prior to failure. The red dotted lines drawn
from the origin serve to emphasize the deviation from linear elastic regime (to guide the eye), which occurred at the strain of 2.6 ± 0.7% for the FIB-machined samples and of 2.9 ± 0.5% for the EP samples. The yield strengths of FIB-machined samples were slightly lower, 1553 ± 365 MPa versus 1663 ± 291 MPa for EP samples. The total elongation at failure was 5.0 ± 1.2% for FIB-machined samples and 4.0 ± 0.9% for the EP ones. The samples presented are representative of the overall results across 10 samples (5 of each type), and the average moduli of FIB and EP samples were similar: 63.56 ± 13.38 GPa and 60.26 ± 17.69, respectively. The SEM image in the inset of Figure 3b displays necking in a 100 nm diameter Ni−P metallic glass nanocylinder fabricated by focused ion beam, a behavior highly atypical for metallic glasses, which is consistent with a previous report on similarly conducted experiments on Zr-based metallic glass nanostructures.10 Necking was less observable in the electroplated samples (Figure 3b) likely because of the limited ductility and poorer image contrast. Although both the EP and FIB samples with 100 nm diameters exhibited some deformability, the final failure always commenced via shear banding in all samples. These observations are equivalent to those of the tensile experiments on the FIB-fabricated Zr-based metallic glass nanosamples, which showed deformation and necking leading to final failure by shear banding.10 The stress−strain data (Figure 3) indicates that the FIB and the EP samples had the same average tensile strength of ~1.9 GPa (±0.36 for FIB, ± 0.37 for EP), but on average the FIB specimens were capable of sustaining nearly three times greater plastic strain prior to failure of ~2% compared to ~0.76% for the electroplated samples. Here, plastic strain is defined as the total strain at fracture less the elastic strain, ε_plastic = ε_total − ε_elastic. This dissimilarity in the amount of plastic flow between the two sets of samples may be an indication that the FIB-induced irradiation on the sample surface contributes to the tensile ductility of the sample but is not solely responsible for its presence.

These results are diametrically opposite to the tensile response of the 500 nm diameter electroplated samples, shown in Figure 3, as well as of bulk metallic glasses and FIB-machined metallic glass samples of equivalent diameters from literature,7,8,10,26 which is generally marked by an elastic loading followed by a sudden and catastrophic failure via shear banding with no nominal plastic deformation or necking prior to failure.2 The 500 nm diameter electroplated samples were fabricated via the same electroplating process and had a phosphorus content of ~16.5 wt %. This slight increase in phosphorus content may affect the modulus and strength of the samples, but it is unlikely to be solely responsible for the brittle behavior in these samples. EDX and TEM analysis of the 500 nm diameter samples confirmed that they were also amorphous.
Figure 3. Mechanical behavior of EP and FIB samples under tension. Upper left: Engineering stress—strain for EP 500 nm, EP 100 nm, and FIB samples along with video stills from in situ SEM (A−C, A′−C′). A linear red dotted line is added to emphasize the deviation from elastic loading. The 500 nm EP samples break catastrophically while both 100 nm specimen show tensile ductility. (A, A′) Initial contact between grip and sample, with purely elastic loading. (B, B′) FIB samples show noticeable necking prior to failure, visible in the inset of B′. Necking is less pronounced in EP samples. (C, C′) Fracture of specimen with both types marked by shear banding. Upper right: Ultimate tensile strength and plastic strain for both sample types. EP and FIB samples show identical tensile strength (∼1.9 GPa). FIB specimen are able to sustain nearly three times higher mean plasticity prior to failure ($\varepsilon_p = \varepsilon_f - \varepsilon = 3\%$ versus $1.5\%$), within one standard deviation of EP counterparts. Bulk refers to tensile strength calculated from microhardness values using a Tabor factor of 3.53

The results of these experiments can be summarized with two main observations. First, tensile ductility in the 100 nm diameter and a lack thereof in the 500 nm diameter electroplated Ni−P metallic glass samples suggests that the brittle-to-ductile transition is a result of the size effect in metallic glasses rather than of any irradiation effects. Second, surface irradiation with low-energy Ga ions appears to tune the amount of deformability in the metallic glasses whose external dimensions are below a certain critical length scale, that is, a more pronounced necking and increased plastic strain prior to failure in the FIB-fabricated samples with identical chemical composition as the electroplated ones. These results suggest that the microstructural disorder in the vicinity of the free surface may contribute substantially to the mechanism of shear band formation and propagation.

Discussion. Postelastic deformation in metallic glasses is generally carried by the spontaneous motion and coalescence of shear transformation zones (STZs) via collective rearrangements of atomic clusters (on the order of ~100 atoms) ubiquitously populating the microstructure of the amorphous metals. At yield stress, some of the STZs coalesce and assemble into large planar bands, generally called shear bands. Shear band formation and propagation is a highly localized deformation mechanism in metallic glasses strained at room temperature. Homogeneous deformation in bulk metallic glasses has typically been observed only at temperatures above or near the glass-transition point. In contrast to the room-temperature experiments in this work, the high-temperature tensile response in metallic glasses has a peak stress close to the elastic limit of the material and subsequent work softening with failure occurring only when the sample gauge section draws down to a point. Both sets of the EP and FIB-fabricated samples with 100 nm diameters in this work showed considerable differences in their behavior under tension as compared with their bulk counterparts: ultimate tensile strength extended beyond the elastic regime, which is an earmark of work hardening, and failure occurred via shear banding rather than by drawing-to-a-point. These outcomes imply that the size- and/or surface-effect in nanosized metallic glasses may delay the onset of shear banding.

These findings differ from those reported by Magagnosc et al. on uniaxial tension of molded Pt-based metallic glass nanowires with diameters of ~100−150 nm, which compared FIB-irradiated samples to the as-molded ones.14 The FIB-exposed samples in that work also showed extended plasticity of ~2%, qualitatively similar to the results of this work, but they failed by necking down to a tip rather than by shear banding. The as-molded samples in Magagnosc et al.14 did not display enhanced plasticity even at ~100 nm. A possible reason for this difference is that the ~1−3 μm-long gauge sections of the Pt-based metallic glass samples in Magagnosc et al. were 2−5 times longer than those in the Ni-based samples in this work. Large-scale MD simulations on Cu nanowires under uniaxial tension demonstrated that the sample length plays a significant role in determining brittle or ductile behavior. In that work, the simulated 20 nm diameter single crystalline Cu nanowires with lengths of 188, 376, and 751 nm exhibited ductility and necking while the 1503 nm long nanowire failed by unstable shear localization and abrupt failure when pulled in tension to ~7% strain. The authors explained this phenomenon by the higher stored elastic energy in longer wires, which in their work meant that the longer sample had highly concentrated dislocation activity on mainly the same slip systems and in a localized shear region. Although no dislocations are present in
metallic glasses due to a lack of crystallographic order, the analogous line of reasoning that a higher stored elastic energy in longer samples may lead to shear banding is applicable because the deformation process occurs via shear in both cases.

To elucidate the specific role of the irradiation on the mechanical response of metallic glass nanopillars, molecular dynamics simulations were conducted on Ni80Al20 binary alloy. This particular system was examined rather than a replica NiP system because of the limited availability of appropriate Ni–P interatomic potentials. The mechanical properties of Ni80Al20 should be comparable with those of the Ni–P metallic glasses used in the experiments, which have compositions close to Ni80P20. Both types of samples are Ni-rich metallic glasses, and the inclusion of P or Al should play similar roles in increasing the glass forming ability in both cases. All the simulations were carried out using LAMMPS,\textsuperscript{33} and the energies and forces were determined using an embedded-atom method (EAM) potential for Ni–Al binary alloys.\textsuperscript{34} Further details on these simulations can be found in the Supporting Information.

In the simulations, two sizes of nanopillars (400 436 atoms, 10 nm diameters and 66.9 nm lengths; and 7 210 516 atoms, 30 nm diameters and 134.2 nm lengths) were cut from replicated Ni80Al20 liquid configurations. The liquid pillars were then quenched to room temperature at a cooling rate of 1Kps\textsuperscript{−1}, resulting in a material system similar to the EP pillars used in the experiments. A reflective potential wall is applied outside the pillar during quenching to confine its shape, similar to the simulated casting method developed by Shi.\textsuperscript{35} To emulate the FIB pillars, we implanted Al atoms randomly outside the cylinder with a fluence of 0.0625/nm\textsuperscript{2}, a value calculated using the experimental irradiation conditions. An inward velocity corresponding to 1 keV was then applied to all of the inserted Al atoms. Since the fluence was very small compared to the number of atoms in the system, the resulting increase in relative Al content in the irradiated samples was negligible. Uniaxial tension was then applied to both pillar types at a constant strain rate of 0.0001 ps\textsuperscript{−1}. Figure 4 shows the stress–strain response of these pillars: FIB samples transition from elastic to plastic flow at slightly earlier strains, and the yield strengths of FIB samples are also slightly lower, but the overall difference becomes more subtle as the pillar diameter increases. The strengths of all simulated samples were significantly higher than those obtained in the experimental values. This can be attributed to the high strain rates, a limitation imposed by the large size of our simulations and increasing computational time.

The observed size-induced emergence of ductility in nanosized metallic glasses can be rationalized in terms of energetics. Since samples produced by both fabrication techniques ultimately failed by shear banding, the total elastic strain energy stored in a sample with a characteristic dimension \(d\) scales as \(d^3\). The surface energy that a fractured surface or a shear band would have to surmount to propagate scales as \(d^2\), where \(d\) is the diameter. Thus, at sufficiently low sample sizes the surface energy term dominates over the elastic strain energy, and it becomes progressively unfavorable for catastrophic failure to occur at smaller deforming volumes (see Figure S2 in Supporting Information). Within this shear band-dominated framework, there is a critical diameter at which the two energies coincide, and the experiments described here suggest that this length scale is between 100 and 500 nm for this particular metallic glass. Consistent with the experimental results presented here, the theoretical work of Thamburaja on the strained small-scale metallic glasses with fixed diameter-to-length aspect ratios of 1:2 and diameters ranging from 8.5 to 136 nm also revealed shear band suppression.\textsuperscript{36} In that work, the nonlocal, continuum-based theory and classical thermodynamic arguments were incorporated within the finite element framework, which revealed that sample size reduction delayed and diminished the severity of shear localizations such that the samples smaller than the shear band nucleus size on the order of 28 nm deformed homogeneously only.\textsuperscript{36} Albeit compression results cannot be directly compared to ones obtained in tension due to the apparent tension-compression asymmetry in metallic glasses in plasticity,\textsuperscript{37} there have also been numerous observations of size-induced shear band suppression in taper-free pillars under in situ compressive loading.\textsuperscript{38,39}

The differing amount of postelastic deformation observed in the samples fabricated by FIB versus by EP may be explained by the surface modification-induced by Ga ion bombardment. During FIB milling, the ion beam knocks the metallic glass atoms out of their native positions and generates free volume that may disrupt local icosahedral symmetries (see Figure S2 in Supporting Information). Such displaced atoms have higher potential energies, which increases their probability of participating in plastic deformation via a shear transformation because the energy cost of moving such atoms is lowered, akin to the free volume driven mechanism for homogeneous flow (see Figure 4).\textsuperscript{31} This is corroborated by the observation that our FIB samples began plastic deformation at a slightly earlier strain (∼2.6% versus ∼2.9% in EP), and thus at a lower strain energy. As expected, we also see a marginal decrease in yield strength for FIB samples (∼1550 MPa versus ∼1660 MPa for EP), which lie within their mutual error bars. Plastic deformation at lower strain energies in this case may be a sign of the movement of FIB-displaced, high-potential energy atoms. The presented arguments are also supported by the work of Raghavan et al. on Ni ion-irradiated Zr-based metallic glasses, which shows free volume generation leading to enhanced plasticity in fabricated micropillars\textsuperscript{40} and irradiation-induced transition to homogeneous flow under nanoindentation.\textsuperscript{41} In addition to the size effect, this surface effect may further deter crack initiation at the free surface and stifle catastrophic failure. This would allow the formation of

![Figure 4. Stress–strain curves of EP and FIB samples for the binary Ni80Al20 binary alloy system simulated via molecular dynamics using LAMMPS. Results for 10 and 30 nm pillars deformed at strain rates of 0.0001 ps\textsuperscript{−1} are presented. Atomic local strain analysis is provided at 3 and 8% strains for both EP and FIB samples with color-coded mapping of strain intensity ranging from 0.0 (blue) to 0.7 (red). A pair of strain mappings is shown for each combination of sample type and strain with the left ones corresponding to pillar surfaces and right ones corresponding to pillar cross sections.](image-url)
instabilities, such as necking or drawing to a point to take place prior to fracture, which is supported by the results in the uniaxial tensile experiments presented here and in Magagnosc et al., as well as by the nanoindentation experiments on a magnetron-sputtered Zr-based metallic glass by Liu et al. and a bulk Zr-based glass by Raghavan et al. mentioned above. It is reasonable that the surface state with more free volume and higher potential energy per atom may suppress catastrophic shear banding and explain the experimental observations presented here.

To reveal physical mechanisms of deformation as a function of surface energetics, we calculated the atomic local strain at 3 and 8% strains for the 10 nm pillars to visualize and quantify regions with pronounced plasticity and atomic activity. These are depicted in the inset of Figure 4 and show that the surface atoms (left mapping in each pair) carry most of the plasticity at 3% strain, while the pillar cores (right mapping) show little activity. FIB samples also display more strain activity on the surface compared to EP samples. Shear localizations emerge at 8% strain in the pillar cores and span the entire sample diameters. In this case, the FIB samples have slightly more diffuse shear regions, whereas these regions appear more concentrated in the EP samples. The main observations from the simulations are (1) the surface atoms carry most of the early plasticity and (2) the FIB pillars contain more diffuse shear localizations. These findings corroborate our experimental observations and proposed phenomenological theory.

We developed an electroplating-based nanofabrication methodology to create isolated metallic glass nanostructures, which does not utilize ion irradiation. In situ uniaxial tensile experiments on such-fabricated Ni–P metallic glass nanostructures and on the nominally identical ion-irradiated (FIB) ones revealed that samples with 100 nm diameters produced by both fabrication techniques displayed postelastic deformability and necking at room temperature. This is in contrast to the immediate failure via a single sample-spanning shear band of 500 nm diameter nanostructures tested and fabricated by the identical electroplating methodology, as well as of FIB-produced and bulk metallic glasses. These findings demonstrate that the brittle-to-ductile transition in Ni-based metallic glasses is likely size-induced and is not a sole effect of ion irradiation. The irradiated samples exhibited a factor of 3 greater plastic strain-to-failure than the electroplated ones. The lower elastic strain in FIB samples suggests that ion irradiation perturbs the surface energy state to produce atoms with higher potential energies and lower icosahedral symmetries, which are more likely to participate in shear transformations. This provides a plausible explanation for the surface-state effect in irradiated metallic glasses, and it is well-supported by our simulations results, which show that surface atoms carry the early plastic strain, an effect that is more pronounced in the simulated FIB samples, and that shear transformations are more diffuse in simulated FIB samples. Experimental observations such as those in this work further our understanding of the underlying deformation mechanisms in amorphous metals, which have generally been difficult to study and are not well understood.

**ASSOCIATED CONTENT**

* Supporting Information
Supporting figures, methods, and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**
D.Z.C. carried out the in situ tensile experiments, EDX, XRD, and SEM analysis. D.J. performed TEM analysis and trained D.Z.C on various techniques. D.Z.C. and D.J. fabricated samples using FIB. Q.A. developed and performed the MD simulations with input from D.Z.C. and W.A.G. D.Z.C. and K.M.G. developed the electroplating process, and K.M.G. electroplated samples. D.Z.C., D.J., and J.R.G. interpreted of the results, and D.Z.C. wrote the manuscript with input from D.J., Q.A., K.M.G., J.R.G., and W.A.G. D.Z.C., D.J., and J.R.G. designed the experiments and J.R.G. supervised the project. Q.A. designed the simulations with input from D.Z.C. and W.A.G.

**Notes**
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### REFERENCES