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Tunable Tensile Ductility in Metallic Glasses

SUBJECT AREAS:
NANOWIRES
STRUCTURAL PROPERTIES
STRUCTURE OF SOLIDS AND LIQUIDS
GLASSES

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Widespread adoption of metallic glasses (MGs) in applications motivated by high strength and elasticity combined with plastic-like processing has been stymied by their lack of tensile ductility. One emerging strategy to couple the attractive properties of MGs with resistance to failure by shear localization is to employ sub-micron sample or feature length scales, although conflicting results shroud an atomistic understanding of the responsible mechanisms in uncertainty. Here, we report *in situ* deformation experiments of directly moulded $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ MG nanowires, which show tunable tensile ductility. Initially brittle as-moulded nanowires can be coerced to a distinct glassy state upon irradiation with Ga^+ ions, leading to tensile ductility and quasi-homogeneous plastic flow. This behaviour is reversible and the glass returns to a brittle state upon subsequent annealing. Our results suggest a novel mechanism for homogenous plastic flow in nano-scaled MGs and strategies for circumventing the poor damage tolerance that has long plagued MGs.

Metallic glasses (MGs) offer a suite of attractive properties such as high strength, large elastic range, low internal friction, high wear and corrosion resistance, and excellent soft magnetic properties, in addition to facile processing and formability owing to the presence of a glass transition temperature (T_g)[1–6]. However, the lack of tensile ductility and inability to offset catastrophic failure has been considered the Achilles' heel of MGs, despite widespread global interest in employing these disordered metals as structural materials[2] since their discovery in 1960[7]. The focus of research on MGs in the last decade, as a consequence, has been on understanding and improving the accommodation of plastic deformation and increasing resistance to shear localization[4,6,8,9]. The three most promising strategies that have emerged to impart capacity for plastic flow are creating a more liquid-like MG structure[4,10], designing a composite structure[11–13], and by decreasing sample or feature sizes to the nanoscale[14]. A more liquid-like structure, and thus behaviour, of MGs can be achieved by designing a MG to approach elastic incompressibility. This is obtained when the Poisson's Ratio is equal to 0.5 (equivalent to a low ratio of shear to bulk moduli) promoting shear band formation and extension over crack formation[4], although this approach in MGs has improved only compressive and bending plasticity. The strategy in the composite approach is to surround a glassy phase by ductile crystallites such that the dimensions of the glassy phase are smaller than the critical crack length required for facile fracture[5,13]. While plastic deformation still proceeds by shear localization, propagating shear bands are absorbed by the ductile phase before they develop into cracks. These two strategies require altering the material composition, whereas reducing a MG specimen or feature below a critical length scale to invoke homogeneous plastic deformation[11,12,14–17] is based on size alone, allowing for the use of diverse MG chemistries. Exploiting length scales has been reported to lead to tensile ductility in MGs[16,18], which coupled with additional property improvements at the nanoscale and ease of processing[1,19], highlights a promising materials design strategy. Indeed, these small length scales are readily accessible via established processing schemes for synthesizing metallic glasses such as thin film vapor deposition, electrochemical deposition, and thermoplastic forming. Micro- and nanoscale applications of MGs hinge on successful tailoring of mechanical behaviour, yet the atomic mechanism(s) responsible for a transition in plastic deformation mode at reduced length scales is elusive and remains subject to debate[14–17,20–24].

Here we describe experiments that reveal a transition from brittle behaviour to tensile ductility and quasi-homogeneous plastic flow in nano-sized metallic glasses that originates from structural changes due to ion irradiation, and not directly from specimen size as previously suggested[14,16–18,23]. The changes in the glassy structure resulting from high-energy ion bombardment coerce the MG into a new state that facilitates an entirely distinct mechanism for accommodating plasticity via quasi-homogeneous flow at room temperature. However,

this altered state is reversed by annealing below T_g, which induces structural relaxation and returns the MG to a brittle state. The notion of structural changes leading to very different underlying atomic mechanisms and ensuing mechanical responses in glasses, initiated by ion irradiation and reversed by thermal processing, suggests new strategies for controlling the ductility of metallic glasses by suppressing shear band formation.

Results

To shed light on whether the propensity for shear localization diminishes in nanoscale metallic glass specimens, we performed microscopic compression experiments on arrays of moulded nanowires, enabling observations of deformation morphology on hundreds of nanowires at once, and *in situ* quantitative tensile tests on individual nanowires. Nanowires of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ MG with diameters ranging from 50 to 200 nm were fabricated by thermoplastic moulding *(1)* in nano-porous alumina templates and subsequently released (Figs. 1a, b).

To assess the plastic deformation mode of arrays of nanowires, a flat punch with a diameter of ~50 μm was brought into contact with the nanowires to apply uniform compression over a collection of specimens (Fig. 1c), and the resulting surfaces were characterized using scanning electron microscopy (SEM). The deformed regions of the arrays could easily be distinguished from intact regions (Fig. 1d), as the nanowires incurred bending stresses beyond their elastic limit leading to characteristic folded orientations. Arrays of nanowires with mean diameters of 100 nm and lengths of 500 nm showed clear signatures of shear banding following compression as manifest by localized surface steps (highlighted in Fig. 1e) in contrast to the relatively smooth surfaces of the as-moulded nanowires. The orientations of the surface steps were near 45° with respect to the nanowire axis, suggesting shear-mediated processes. Such surface features were observed in approximately 90% of nanowires in the deformed regions of the arrays, determined from direct inspection of 78 nanowires where plastic deformation clearly occurred and the full specimen could be imaged. Similar behaviour was observed in yet smaller diameter nanowire arrays (Fig. 1f), indicating that shear localization (heterogeneous plastic flow) is the prevailing plastic deformation mode down to at least 60 nm.

Our statistically significant observations of prominent shear banding in as-moulded nanowire arrays are in contrast to recent experiments showing a transition to quasi-homogeneous plastic flow in MG specimens prepared by focused ion beam (FIB) milling with diameters below approximately 400 nm and specimen lengths of 1 μm[14,16–18,23]. To gain more direct and quantitative insight on the mechanical response and deformation morphology of our MG nanowires, we performed *in situ* tensile testing of individual nanowires at room temperature in a controlled loading geometry. Tensile stress-strain curves for moulded nanowires are shown in Fig. 2a (left panel). The representative tensile behaviour for the as-moulded nanowires involves linear elastic response until final fracture at strengths of 1.6 ± 0.4 GPa (bulk strength, 1.4 GPa)[4], which occurred without any detectable signs of gross plastic flow. Specifically, the mechanical behaviour was characteristically brittle despite the relatively large range of elastic strain, which is common in MGs[25]. The measured tensile response corroborated the fracture morphology, which always occurred heterogeneously (in a localized manner) at angles near 50° with respect to the tensile axis (Fig. 2b), as is consistent with a pressure-augmented shear stress failure criterion[26]. As the cross-sectional areas were fairly constant over the tested lengths of the nanowires, fracture was found to occur at apparently random locations along the gage length, with no correlation between fracture location and strength. Our measurements of brittle tensile response in combination with observations of shear-localized fracture are consistent with the typical tensile response of macroscopic MGs specimens[27], wherein heterogeneous failure driven by shear banding is the predominant deformation mode. However, both our compressive and tensile measurements starkly contrast with numerous reports of homogeneous plastic flow in submicron MG specimens, which in all cases were prepared by FIB milling.

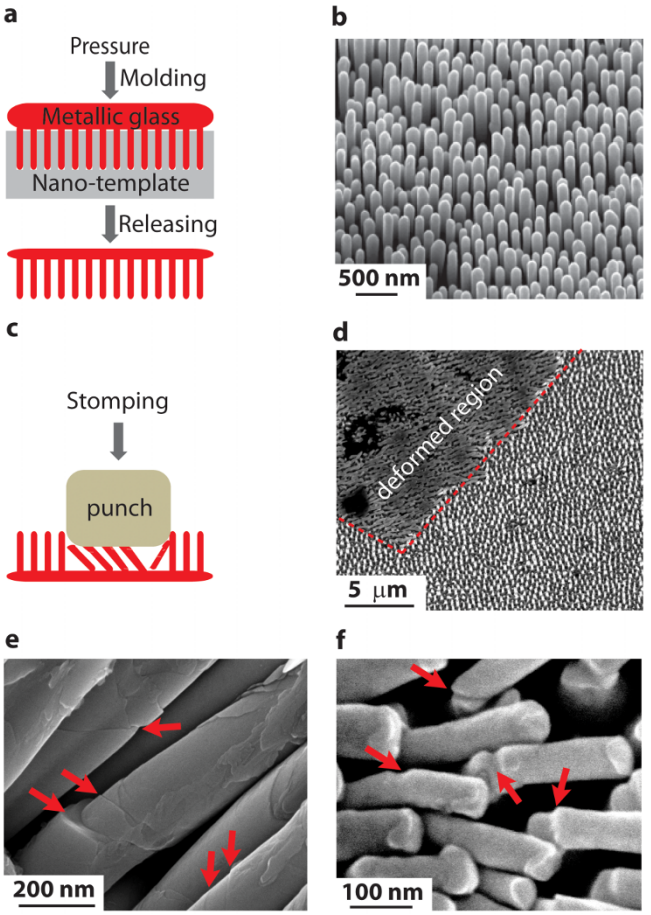

Figure 1 | Fabrication and deformation morphology of nano-moulded $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ MG nanowires. (a), Schematic of MG nanowire moulding approach, wherein a cast MG sample is pressed into a nanoporous template above T_g, which is subsequently etched away to reveal free-standing nanowires. (b), SEM image of an as-moulded nanowire array. (c), Schematic of microscale compression testing of collections of nanowires with a 50 μm flat punch. (d), SEM image of array clearly delineating deformed region. Following compression testing, shear offsets indicating the formation of shear bands are prevalent in majority of deformed nanowires, with diameters of approximately (e), 100 nm and (f), 60 nm.

We then considered the role of ion irradiation in preparing micro- and nano-scaled specimens. High-energy ion irradiation is known to impart structural changes in amorphous metals[28,29], leading to measurable changes in mechanical behaviour and shear band-mediated plastic response[29,30]. This is particularly true in micro- and nanoscale volumes, where the fraction of material altered by ion irradiation is necessarily large. Therefore, we subjected our nano-moulded and mounted tensile specimens to ion irradiation *in situ* in a central portion of the gage section. A key advantage of these experiments is direct comparison of the mechanical response and plastic morphology of irradiated MGs to pristine nanowires of the same material and dimensions. The nanowires were subjected to focused Ga^+ ion irradiation at 30 kV (incident angle 38° with respect to tensile axis) and ion doses varying from approximately 100 – 300 ions/nm^2 over a region approximately 1 μm in length (see Supplementary Information). The tensile response is shown in Fig. 2a (central panel). The measured mechanical behaviour was markedly different from the

as-moulded nanowires, as characterized by clear plastic yielding and inelastic response. In addition to large proportional limits, post-yielding strains were measured to be as large as ~2%. In one case measurable apparent strain hardening occurred, with yielding occurring at ~1.7 GPa and a subsequent fracture stress exceeding 2.5 GPa (green curve in Fig. 2a). While apparent strain hardening has been previously measured and argued on the basis of a sampling of shear band nucleation sites with increasing strength as deformation increases (i.e. extreme statistics)[25], other ion irradiated nanowires that we tested did not demonstrate such strain hardening. Nevertheless, the measurements of tensile ductility clearly contrast with the brittle response of as-moulded nanowires. Most surprisingly, the fractured regions of the ion-irradiated specimens (Fig. 2c, 2d) demonstrated copious plastic flow as shown by thinning of the cross-section down to a fine point. Fracture always occurred in the irradiated section, presumably due to smaller cross-sectional areas resulting from removal of material in these regions via ion sputtering. Transmission electron microscopy images of the fractured regions (Fig. 2d, 2f) confirm that plastic flow occurs over an extended region along the length of the irradiated region (i.e. quasi-homogeneously), often causing profuse necking down to a tip with a radius of ~5 nm. Both fractured ends of the ion-irradiated specimens exhibit such morphology along the entire width of the specimen, which indicates a plastic deformation mechanism distinct from heterogeneous shear banding.

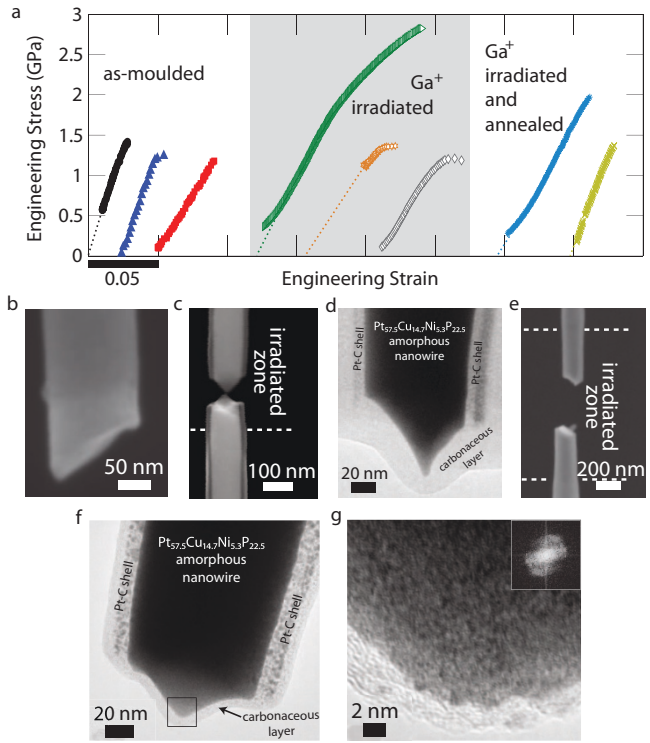

Figure 2 | Mechanical response and deformation morphology of nano-moulded MG nanowires. (a), Representative stress strain curves obtained from *in situ* tensile testing of as-moulded, focused Ga^+ ion irradiated, and irradiated and annealed ($T = 0.96T_g$) nanowires with diameters ranging from ~100–150 nm. Ion irradiation induces changes to the material allowing for tensile ductility, in contrast to the brittle response measured in all as-moulded nanowires. Upon annealing irradiated nanowires below T_g, subsequent tensile testing shows a return to the brittle state, suggesting the mechanical response may be tunable. The measured mechanical response is supported by different morphology for the different preparation conditions, shown in SEM images for: (b), as-moulded, (c), ion-irradiated, and (e), irradiated and annealed fractured nanowires. (d), TEM image of deformed ion-irradiated nanowire, showing clear evidence of plastic flow in the irradiated region. (e), TEM image of the fracture site in a MG nanowire subjected to focused Ga^+ ion irradiation at a dose of 305 ions/nm^2 showing ductile morphology following tensile testing. (g), high resolution TEM image showing heavily deformed ductile zone of fracture surface. No evidence of crystallization is observed, as confirmed by the FFT of the image (inset), suggesting that ductility is accommodated entirely by structural changes to the glass.

The tensile ductility and quasi-homogeneous plastic flow observed in Ga^+ ion-irradiated nano-moulded MGs indicate a clear demarcation from the brittle behaviour of as-moulded specimens that fail by a heterogeneous shear-mediated process. To investigate the underlying deformation mechanisms governing this change in plastic response, we examined the locally necked regions of deformed ion-irradiated specimens using high-resolution TEM. Fig. 2f shows one such nanowire specimen, confirming a quasi-homogeneous plastic deformation mode due to the clear necking morphology. Moreover, closer inspection of the heavily deformed region (Fig. 2g) at many focus and tilt conditions indicates that the material retains its amorphous structure and no evidence of crystallization, as would be detected by lattice fringes, was found. A fast Fourier transform of the high-resolution image in Fig. 2g shows a diffuse band of contrast (indicative of a poorly defined spatial frequency of atomic positions) and no discrete spots that would occur for nanocrystallites present within the glass. Taken as a whole, these observations indicate that the structural or chemical changes incurred by ion irradiation preserve the glassy structure of the moulded nanowires, ruling out both shear band inhibition by crystallites and absorption mechanisms that have been proposed for enhanced ductility in glassy/crystalline composites[8,9].

Considering that the glassy structure of the nanowires can be altered by focused Ga^+ ion irradiation to produce measurable tensile ductility, we next considered if these structural changes are reversible. In the framework of a glassy configuration occupying a metastable state in a potential energy landscape, one can envision activated processes that shift the state to higher or lower energy minima within a larger energy basin. One such process is structural relaxation in glasses leading to annihilation of excess free volume[31,32], which is often accomplished by annealing MGs below the glass transition and has been shown to lead to embrittlement in most MGs (see e.g.[33]). To investigate the reversibility of the irradiation-induced structural changes, we performed annealing of nano-moulded specimens that were ion irradiated to doses shown to facilitate tensile ductility and quasi-homogeneous plastic flow (Fig. 2a). Two nanowires were subjected to Ga^+ irradiation in a central region of the tensile gage sections, and subsequently were annealed at 215°C ($0.96T_g$) for 70 min. The annealing conditions were chosen to achieve complete structural relaxation in a MG of the same nominal composition[34]. As shown in Fig. 2a (right panel), these individual irradiated and annealed nanowires were subsequently tested *in situ*. They exhibited a brittle tensile response, with fracture occurring in the irradiated zone and no indications of measurable plastic flow, reminiscent of the mechanical behaviour of as-moulded nanowires. The absence of tensile ductility was corroborated by fracture morphologies that showed heterogeneous failure along orientations of high shear stresses (Fig. 2e).

Discussion

These experimental results imply that indeed the mechanical response, ductility, and ensuing plastic failure mode can be reversibly transformed by way of structural changes to the glass; a departure from recent reports claiming that size alone is responsible for such transitions. High-energy ion irradiation leads to measurable tensile ductility and quasi-homogeneous plastic flow, while subsequent sub-T_g annealing induces structural relaxation, returning the glass to a brittle state. The effect of fabrication methods and annealing on the MGs' plasticity, which has been correlated with Poisson's Ratio (and

accordingly G/B), has been observed in bending and compression geometries[4,35,36], but never for tensile ductility. Our findings indicate dramatic changes in the structure, beyond a mere reduction in shear localization tendency, to a liquid-like structure[31,37] in the irradiated MG. The salient implications of our findings are twofold. First, interpretation of recent reports of a transition between heterogeneous (shear banding) and homogeneous plastic flow in MGs with specimen sizes below several hundred nanometers is complicated by the influence of ion irradiation during specimen fabrication and is likely not representative of the as-cast structural state of the glass. The prevailing view supporting experimental observations of the suppression of shear localization in submicron MGs is that small volumes do not release sufficient elastic strain energy during shear banding to counter the energy penalty of shear disordering (analogous to Griffith theory for crack propagation). In this framework, the critical stress σ for shear band propagation can be derived to be $\sigma = \sqrt{2^{3/2}\Gamma E/L}$, where Γ is the shear band energy associated with atomic disordering within the small band, E is the Young's modulus, and L is the specimen length[14]. Comparing reports of transitions in plastic deformation mode in FIB-made pillars[14,16,17,20,22–24,27,30,38] with our as-moulded nanowires via the Griffith-like prediction for the onset of homogeneous flow (using the reported flow strengths and elastic moduli, and assuming a maximum shear disordering strain of unity and a 10 nm shear band thickness[27]), the observed deformation modes are consistent with this theoretical prediction (Fig. 3a). However, our ion irradiated nanowires displaying tensile ductility and homogeneous flow (open green symbols) show behaviour contrary to this prediction, well into the regime where heterogeneous behaviour is predicted. Furthermore, changes to E and Γ owing to ion irradiation would likely lower the threshold for shear banding. Therefore, our experiments suggest a distinct mechanism for accommodating plastic flow.

Both liquids and glasses lack long-range structural order, yet liquids differ in their capacity for facile flow. Whereas cooling rates of bulk MGs sufficiently rapid to retain vestiges of the liquid state (known to suppress shear localization in deformed amorphous Si at room temperature[37]) are difficult to attain, ion irradiation of nanoscale volumes could introduce a substantial fraction of liquid-like

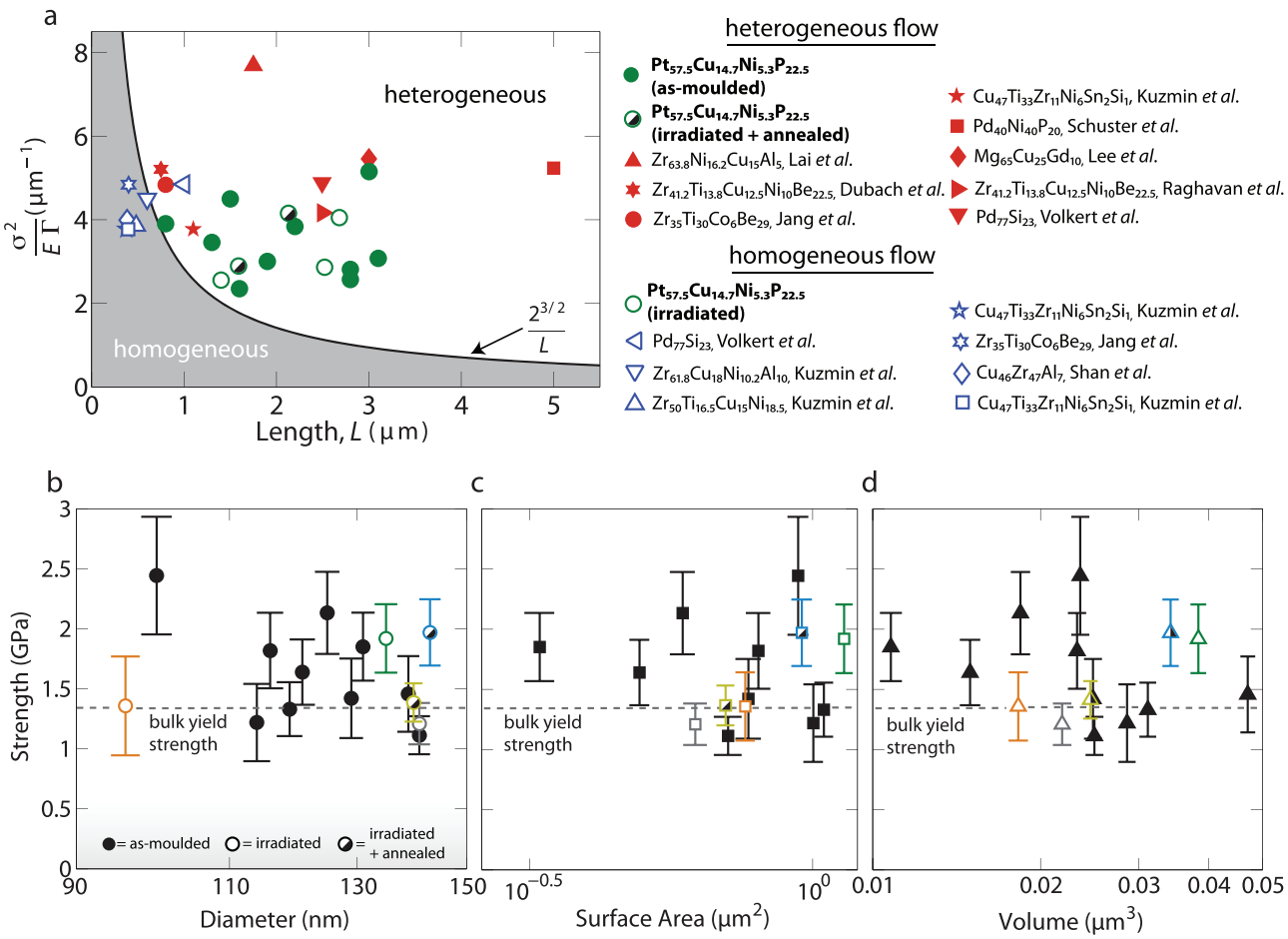

Figure 3 | Effect of size on strength and plastic deformation mode of MG nanowires. (a), Deformation mechanism map giving normalized metric for energy of shear band propagation vs. specimen length for our measurements (green symbols) and various metallic glass small scale experiments[14,16,17,20,22–24,32,38], shown in comparison to the prediction of a size-dependent transition to homogeneous flow[12]. See text for details. While this theory predicts the transition for previous reports (homogeneous flow shown as open symbols), it fails to describe the tensile ductility observed in our ion irradiated moulded nanowires (open green symbols), suggesting a distinct mechanism for accommodating plastic flow. Literature values are estimated by the mean stress for each deformation mode, and lower and upper limits for the length of specimens showing heterogeneous and homogeneous flow, respectively. (b), Measured strength of MG nanowires as a function of size, (c), surface area, and (d), volume. Closed, open, and partially filled symbols represent as-moulded, ion irradiated, and irradiated and subsequently annealed (below T_g) nanowires, respectively. Fracture strength is plotted for nanowires showing brittle response (as-moulded and irradiated and annealed), while 0.2% offset yield strength is shown for ductile nanowires (irradiated). No clear size effect is measured beyond the experimental uncertainty over the tested range (see supplementary information for calculation of error bars), irrespective of the processing condition. Colors of irradiated, and irradiated and annealed data points in (b–d) correspond to those used in the stress strain curves of Figure 2a.

states[31,37] that facilitate homogeneous plastic flow. At ion accelerating energies of approximately 30 kV, the penetration depth of ions was estimated to be approximately 9 nm (compared to 5 nm for glancing ion incidence for pillar fabrication, see Supplementary Fig. S4). Thus, the resulting volume fraction of structurally modified glass would scale with specimen diameter (Supplementary Fig. S5). Provided a structural change leading to a more liquid-like state in our irradiated MGs, the requisite structural contrast between the parent glass and the shear disordering occurring during a localization event would diminish. Thus, plastic flow would manifest more homogeneously, even at testing temperatures below T_g.

This work demonstrates that accurate deconvolution of any true size scale effects with those from irradiation during specimen fabrication requires pristine MG specimens of nano scale dimensions. For instance, incorporation of Ga into the surface of testing samples would cause local changes to chemistry, which could affect the mechanical response. However, the clear transitions in deformation mechanisms and concomitant mechanical behaviour following annealing of our irradiated nanowires back to similar to that measured in as-moulded specimens following both irradiation and annealing suggests that chemical changes are not sufficient to preclude structural relaxation.

Our findings evoke a second key implication. Namely, these insights provide a potential avenue for the design of ductile and tough amorphous metals. In contrast to crystalline metals, where strength and toughness often are sacrificed for one another, glassy materials maintain high strength even in their ductile states. As shown in Fig. 3, neither ion irradiation nor annealing changes the strength of the nanowires beyond the uncertainty of our measurements. Moreover, no clear size, surface area, or volume dependence of strength occurs (Fig. 3). In contrast to previous research that suggests the utilization of nanosize length scales in a MG microstructure as a design tool to achieve tensile ductility, our findings suggest that such ductility can be achieved through structural modifications towards a more liquid-like structure. The present technique is potentially a powerful approach to generate ductility in nano and micron size MG samples and device features, accessible by a variety of established processing schemes in addition to the one presented herein (e.g. vapor deposition, electrochemical deposition, plastic deformation-mediated thinning). Due to the limited depth penetration of ion implantation, modifying the structure of MGs to more liquid-like in bulk samples would require novel processing techniques such as severe plastic deformation[39], shot peening[40], or innovative approaches that would resemble the effects of high cooling rates. Such developments of efficient and economic techniques to achieve tensile ductility in bulk samples may become central to the widespread use of MGs in structural settings.

Methods

Nanomoulding was carried out at 270°C under applied pressures of 130 MPa. Freestanding MG nanowires were exposed by dissolving alumina moulds in a KOH solution (Fig. 1b). Notably, thermoplastic forming as used here for nanowire fabrication does not alter the mechanical properties of the original MG[33]. Specimens were harvested, transferred, and mounted to a custom-built quantitative tensile testing apparatus that was integrated in a dual-beam SEM and focused ion beam (FIB) microscope. This system allows for direct measurements of load, system displacement, and local specimen strain[41] concurrent with direct observation of deformation morphology. All tensile testing was performed at room temperature ($0.59T_g$) and strain rates of approximately 10^{-3} s^{-1}. In experiments on ion irradiated and subsequently annealed nanowires, specimens were exposed to Ga^+ doses of 129 and 142 ions/nm^2 (~30–40% higher than irradiated nanowires shown to exhibit tensile ductility).

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Author contributions

D.S.G., G.K. and J.S. designed the study. D.J.M., R.E. and D.S.G. implemented the *in situ* testing setup and performed tensile experiments. G.K. fabricated samples and performed compression experiments. M.R.H. performed TEM investigations. All authors contributed to discussions and analysis of the data. D.S.G., G.K. and J.S. wrote the manuscript, with support from D.J.M., R.E. and M.R.H.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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