Hardening of shear band in metallic glass

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Strain hardening, originating from defects such as the dislocation, avails conventional metals of high engineering reliability in applications. However, the hardenability of metallic glass is a long-standing concern due to the lack of similar defects. In this work, we carefully examine the stress-strain relationship in three bulk monolithic metallic glasses. The results show that hardening is surely available in metallic glasses if the effective load-bearing area is considered instantly. The hardening is proposed to result from the remelting and ensuing solidification of the shear-band material under a hydrostatic pressure imposed by the normal stress during the shear banding event. This applied-pressure quenching densifies the metallic glass by discharging the free volume. On the other hand, as validated by molecular dynamics simulations, the pressure promotes the icosahedral short-range order. The densification and icosahedral clusters both contribute to the increase of the shear strength and therefore the hardening in metallic glasses.

Strain hardening is a highly desired property for structural materials, especially for high-strength engineering metals and alloys\textsuperscript{1}. It renders the strained material harder and increasingly difficult to deform further in the plastic regime, and therefore enables the material to accommodate the plastic strain globally. This prevents premature strain localization like necking in materials under tension and benefits the materials in terms of mechanical reliability. In general, strain hardening is ascribed to the multiplication, interaction or entanglement of dislocations in conventional crystalline metals\textsuperscript{1}. On the contrary, no crystallographic defects like dislocation have been found to make the strain hardening available in monolithic metallic glasses (MGs) so far\textsuperscript{2–6}. As a result, the plastic strain cannot be spread out in the whole sample; instead, it is often localized into thin shear bands in MGs at room temperature\textsuperscript{7–9}. Worse yet, this localization is self-catalytic, so one primary shear band carries more and more strain and eventually develops into a crack causing the fracture\textsuperscript{7}. One can easily infer that the lack of strain hardening must lead to a low damage tolerance in MGs. Partly for this reason, MGs are hardly employed in engineering applications despite their very high strength\textsuperscript{10–12}.

For the MGs in which the plastic deformation proceeds via shear banding events\textsuperscript{7}, their capability to be hardened substantially depends on the shear band itself\textsuperscript{13}. Recently, Wang \textit{et al.}\textsuperscript{14} have shown that the strain hardening is also possible in MGs. Stretching a Zr-based MG rod deeply notched, they found that the strain hardening indeed happened to the notched part. This hardening was attributed to densification as a net effect of free volume creation and annihilation. It must be noted that no shear band is developed in the plastically deformed material in ref. \textsuperscript{10}. If the shear bands has formed and developed during the plastic deformation of MGs, strain softening was frequently confirmed\textsuperscript{15–18}. The softening was considered to result from shear-induced dilation and nano-void formation and coalescence inside the shear bands\textsuperscript{16,17}. This notion has widely been accepted in the community\textsuperscript{15,16}. However, a work-hardenable Cu\textsubscript{27.7}Zr\textsubscript{47.5}Al\textsubscript{25} MG was fabricated by Das \textit{et al.}\textsuperscript{21}. They achieved ~18% plasticity in the Cu\textsubscript{27.7}Zr\textsubscript{47.5}Al\textsubscript{25} MG under compression. Scanning electron microscope (SEM) observation exhibited multiple branched and wavy shear bands on the surface of failed sample. It means the sample was not subject to a single dominant shear band. Conversely, a large number of shear bands carried a small fraction of strain each. This manner was associated with the atomic-scale inhomogeneity in the sample\textsuperscript{21}. This kind of inhomogeneity has

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also been witnessed in other MGs, e.g. Zr\_{63.8}Ni\_{16.2}Cu\_{15}Al\_{5}\textsuperscript{22} and Zr\_{64.13}Cu\_{15.75}Ni\_{10.12}Al\_{10}\textsuperscript{23}. More interestingly, in the very Zr\_{64.13}Cu\_{15.75}Ni\_{10.12}Al\_{10} MG, Han et al.\textsuperscript{24} demonstrated that there was no strain hardening or strain softening at all, and the critical flow stress was invariant if the instant load-bearing area was taken into account. As such, a controversial issue arises: can the shear band in MG be hardened ever? This is not only a key problem of science but also directly related to the engineering application of MGs as mentioned above.

In this paper, we investigate the operating characteristics of shear bands in three typical Zr-based MGs through compression tests. The shear bands are found to harden indeed during the plastic deformation when the instant effective load-bearing area is considered. Even though the intrinsic shear strength is taken into account, the hardening is still apparently evident. However, the mechanism of hardening is significantly different from that in crystalline materials dominated by dislocations. Instead, we propose that remelting and solidification under a hydrostatic pressure imposed by the normal stress result in the hardening of the shear band material. Applying a hydrostatic pressure during the quenching process, molecular dynamics (MD) simulations reveal that the formed MG is densified as expected. More importantly, the atomic structure is remarkably tuned by the pressure, as identified by the Voronoi tessellation analysis. In particular, we find that the icosahedral clusters increase with the increasing applied pressure and they are responsible for the increase of shear strength in MGs.

Results

Microstructure investigation. To assure the MGs a fully glassy state, microstructure characterization and thermal analysis have been conducted. Figure 1 presents the XRD pattern and DSC trace for Zr\_{50}Cu\_{44}Al\_{6} MG. No any Bragg peaks can be seen in Fig. 1a, while the glass transition (marked by \(T_g\)) and crystallization (marked by \(T_x\)) behaviors are very clear in Fig. 1b. This implies the glass nature of Zr\_{50}Cu\_{44}Al\_{6}. Owing to their excellent glass forming ability, neither Zr\_{65}Cu\_{15}Ni\_{10}Al\_{10}\textsuperscript{25} nor Vit 1 is subject to XRD and DSC\textsuperscript{25,26}. However, nanocrystals are sometimes observed to precipitate in the glassy matrix dominated by dislocations. Instead, we propose that remelting and solidification under a hydrostatic pressure imposed by the normal stress result in the hardening of the shear band material. Applying a hydrostatic pressure during the quenching process, molecular dynamics (MD) simulations reveal that the formed MG is densified as expected. More importantly, the atomic structure is remarkably tuned by the pressure, as identified by the Voronoi tessellation analysis. In particular, we find that the icosahedral clusters increase with the increasing applied pressure and they are responsible for the increase of shear strength in MGs.

Mechanical performance and the intrinsic shear strength. Figure 3 presents the measurement and observation of the deformation behavior in the Zr\_{50}Cu\_{44}Al\_{6} MG. In Fig. 3a, the true stress–strain curve (blue) is calculated according to the engineering one (black), in which the calculation is well known in textbooks as\textsuperscript{2}:

\[
\varepsilon = \ln(1 + \varepsilon)
\]
\[
\sigma = \sigma_0(1 + \varepsilon)
\]

where \(\varepsilon\), \(\sigma\), \(\varepsilon\), and \(\sigma\) are the engineering strain and stress and the true strain and stress, respectively. At the first glance, \(\sigma\) increases with the increasing \(\varepsilon\) in the plastic regime, which is clearer in the inset. In particular, the
Figure 2. The amorphous microstructure of Zr₅₀Cu₄₄Al₆ alloy. (a) TEM with a SAED pattern (inset) and (b) HRTEM.

Figure 3. The investigation on the deformation behavior in Zr₅₀Cu₄₄Al₆ MG under compression. (a) The engineering (black) and true (blue) stress-strain curves and the inset magnifying the plastic regime. (b) The SEM image of the deformed sample in which the primary shear band is marked by the arrows. (c) A schematic illustration of the effective load-bearing area in the rod sample. (d) The real stress (red) calculated using the area A in Eq. (2) showing the hardenability in Zr₅₀Cu₄₄Al₆ MG with a strain hardening coefficient \( n = 0.613 \). (e) The intrinsic shear strength calculated by Eq. (4) shows a hardening behavior also.
valley (marked by the violet arrow) of the serration in the latter part are higher than the peak (marked by the green arrow) for that in the first. It looks like the strain hardening. On the other hand, in the true stress-strain curve, stress almost keeps a constant with strain, which is in line with the conclusion by Han et al. However, the prerequisite for Eq. (1) that is used to calculate the true stress-strain is the constant volume of the sample, which implies that the effective load-bearing area increases with the strain due to the decreasing length of the sample in the compression. Figure 3b shows the SEM image of the deformed sample. As marked by the arrows, only one primary shear band develops and accommodates all the plastic strain. More importantly, one can easily find that the load-bearing area is factually decreasing with the increasing strain, resulting in the invalidity of Eq. (1). As illustrated in Fig. 3c, the horizontal projected area of the instant load-bearing area (shaded region) with a shear angle \( \theta \) is

\[
A = 2r_0^2(\varphi - \sin \varphi \cos \varphi)
\]

where \( \varphi = \arccos \left( \frac{1 - \eta \theta}{2 \eta} \right) \), \( r_0 \) and \( l_0 \) are the radius and length of the rod sample at the elastic limit, and \( \varepsilon_p \) is the plastic strain. As a matter of fact, Han et al. adopted Eq. (2), but a fixed \( \theta = 45^\circ \) was taken. According to the statistics by Zhang et al., \( \theta \) is a variable and usually less than 45° in compression, which holds true in this work (\( \theta = 41^\circ \)). Using \( A \) in Eq. (2), the real stress \( \sigma \) (red) is presented in Fig. 3d, significantly different from \( \sigma \) (blue). Obviously, \( \sigma \) increases with the plastic strain, which firmly demonstrates the characteristics of strain hardening. Along the Ludwik-Hollomon relationship

\[
\sigma = \sigma_y + k \varepsilon_p^n
\]

where \( \sigma_y \), \( k \) and \( n \) are the yield stress, pre-exponential factor and strain-hardening coefficient, respectively, \( n = 0.613 \) is obtained for Zr_{50}Cu_{44}Al_{6} MG by fitting the stress-strain curve in plastic regime, similar to those for steel (0.36) and brass (0.42). Unquestionably, shear band is operating in mode II. Therefore, the shear strength has attracted many attentions. Zhang et al. found that the measured shear stress \( \tau \) depends on the normal stress \( \sigma \) in the shear plane as illustrated in Fig. 3c. Afterwards, Qu et al. formulated the \( \sigma \) dependence of the critical shear stress (or intrinsic shear strength) \( \tau_0 \) as

\[
\tau_0 = \sqrt{\tau^2 + \alpha^2 \beta \sigma_y^2}
\]

in which \( \alpha = 2 (1 - 2\nu)/(1 + \nu) \) proposed by Liu et al. \( \nu \) is Poisson's ratio and \( \beta = -0.5 \) for compression. Figure 3e displays the plot of \( \tau_0 \) with \( \varepsilon_p \). Clearly, \( \tau_0 \) increases with increasing \( \varepsilon_p \), indicating the hardening of shear-band material. This also holds true in Zr_{50}Cu_{35}Ni_{10}Al_{15} and Vit 1 MGs (see Figs S3 and S4). It should be noted that \( \tau_0 \) also increases with \( \varepsilon_p \) as shown in Fig. S2.

Occasionally, inside the shear band precipitate some nanocrystallites in the deformed MG sample, though they are absent in the as-prepared sample. The longitudinal section of the deformed sample in Fig. 3b is...
exhibited in Fig. 4. A region enclosed by the circle is taken as the TEM sample, in which the approximate path of shear band is marked by the dotted line. Then, the TEM observation is performed carefully, and the TEM imaging features (see details in Fig. S5) are extremely similar to those in Fig. 2. No any nanocrystallites can be found, which essentially excludes the involvement of dislocation-induced hardening in Fig. 3. In other words, there should be a different hardening mechanism in MGs.

The role of hydrostatic pressure. Our previous studies showed that the temperature rise is significant inside the shear band during its sliding37, 38. Then they convincingly responded to the argument of no significant temperature rise38–41. Besides, the melted shear-band material is subsequently quenched at an ultrahigh cooling rate of $\approx 10^8$ K/s at the end of a shear-banding event37. On the other hand, the hydrostatic pressure $P$ imposed by the normal stress $\sigma_n$ was found to play an important role, as suggested by Zhang et al.31. Generally, it has

$$P \approx \frac{2}{3} \sigma_n$$

according to the spherical stress tensor1, and $P$ increases due to the increasing $\sigma_n$ during the plastic deformation (see Fig. S2-1). It implies that the effect of hydrostatic pressure will become greater and greater with the plastic strain. Herein, we do propose that the atomic structure of the shear-band material is remarkably mediated during the remelting and the following solidification under a hydrostatic pressure and therefore becomes more resistant to the shear. To validate this proposal, MD simulations were conducted for Zr$_{50}$Cu$_{44}$Al$_6$ MG, but not for Zr$_{65}$Cu$_{15}$Ni$_{10}$Al$_{10}$ MG or Vit 1 owing to their inaccessible interaction potential so far.

Under a hydrostatic pressure, the glass transition happens at an elevated temperature in MGs42. Figure 5a and b show the reduced volume $V_r = V/V_0$ and the reduced potential energy $PE_r = PE/|PE_0|$ ($V_0$ and $|PE_0|$ are respectively the volume and the absolute value of potential energy at 2000 K) against the temperature under various pressures. Clearly, $T_g$ increases with the applied pressure, as marked by the dashed line. It is because the pressure can enhance the viscosity through reducing the free volume in the sample and therefore rendering the atomic diffusion sluggish37. As shown in Fig. S5, the average atomic volume contracts greatly with the increasing pressure at a certain temperature. For instance, it is 17.9 Å$^3$ for 0 GPa at 300 K, for 20 GPa with 14% decrement to 15.4 Å$^3$. Meanwhile, Fig. 5d shows that positions of the first and second peaks in pair correlation function $g(r)$ shift to the smaller radial distance, indicating that the atoms come closer to each other. Obviously, the Zr$_{50}$Cu$_{44}$Al$_6$ MG must be densified by the discharge of the free volume.

The reduction of the free volume can always elevate the shear stress in MGs because of

$$\tau \propto \exp\left(\frac{C}{V_f}\right)$$

in which $C$ is a constant for a given composition and $V_f$ is the average free volume per atom19. Figure 6a shows the shear stress-strain curves for samples prepared under various pressures at 300 K. One can see that the shear strength
increases with the increasing applied pressure. The shear strength here is defined as the peak value of the shear stress in the curve, i.e. $\tau_m$ marked in Fig. 6a. This trend is clearly presented in Fig. 6b. Moreover, the shear modulus $G$ shares the same trend. Accordingly, it comes to a conclusion that the hardening presented in Fig. 3e should be caused by the remelting and solidification of shear-band material under a hydrostatic pressure. This effect is experimentally confirmed in a Zr$_{48}$Cu$_{36}$Al$_8$Ag$_8$ MG prepared though remelting and pressure-casting\textsuperscript{43}.

Atomic configuration. Based on the Voronoi tessellation analysis, the atomic structure has been examined in the as-prepared and deformed Zr$_{50}$Cu$_{44}$Al$_6$ MG. Figure 7a and b schematically present the virginal and 20% shear-strained atomic configurations in the simulation box with a size of about $52 \times 52 \times 52$ Å$^3$. (c) The fraction of Voronoi polyhedra of the five most common atom motifs in the as-prepared samples. (d) The fraction of icosahedron with a Voronoi index $<00120>$ varies with the increasing shear strain.

Figure 6. The MD simulations of the shear deformation in Zr$_{50}$Cu$_{44}$Al$_6$ MG samples prepared under various hydrostatic pressures. (a) The shear stress-strain curves on which the maximum value $\tau_m$ is defined as the shear strength. (b) The shear strength and the shear modulus are enhanced by the increasing pressure.

Figure 7. The examination on atomic structure of Zr$_{50}$Cu$_{44}$Al$_6$ MG via MD simulations. The illustrations of (a) as-prepared and (b) 20% shear-strained atomic configurations in the simulation box with a size of about $52 \times 52 \times 52$ Å$^3$. (c) The fraction of Voronoi polyhedra of the five most common atom motifs in the as-prepared samples. (d) The fraction of icosahedron with a Voronoi index $<00120>$ varies with the increasing shear strain.
The fractions of these motifs vary with the applied pressures. Along with the increasing pressure, \(<0 2 8 1>\) is subject to a slight decrease in fraction, while the four others grow with different increments. In particular, the fraction of \(<0 0 12 0>\) increases from 4.1% for 0 GPa to 9.6% for 20 GPa. In other words, the number of \(<0 0 12 0>\) is doubled in virtue of hydrostatic pressure. In fact, \(<0 0 12 0>\) represents the icosahedral-short-range-order which is a key feature of microstructure in MGs. In simple liquids and MGs, icosahedron is proposed to be preferred even over the FCC and HCP packing due to its lower potential energy. As a result, it needs to exert a larger stress to deform the icosahedra than to deform other clusters. If the number of icosahedra increases in the sample, the yield stress of the material would be enhanced. This is reflected by Figs 6 and 7c. In addition, the evolution of these motifs is examined during the deformation of the sample. As shown in Fig. 7d, the fraction of icosahedra almost keeps constant within the first elastic strain of 4%. This is because the atomic bonding is not broken or rebuilt but just adjusted slightly in the elastic regime. After the strain of 12%, the fraction of icosahedron changes very slightly, but that for high pressure (e.g. 20 GPa) still remains higher than that for low pressure (e.g. 5 GPa). Interestingly, other motifs basically do not vary much and almost keeps the original fraction (see details in Fig. S6). This proves that the icosahedra play a prominent role in the deformation of MG indeed.

Discussion

However, if the hardening is available in the shear-band material as aforementioned, why do then not the secondary shear bands develop at other sites in the sample? In reality, the increasing stress is partly due to the decreasing load-bearing area as illustrated by the shaded region on the shear plane in Fig. 3c, so the shear stress at other sites is not increased so much as that on the shear plane. On the other hand, the first shear band must initiate somewhere with a relatively lower critical shear stress, say \(\tau_1\), compared with that, say \(\tau_2\), for elsewhere. A increment of critical shear stress, \(\Delta \tau\), is caused by the hardening. If \(A(\tau_1 + \Delta \tau) < A_2 \tau_2\) in which \(A_2 = \pi r_s^2\), the secondary shear bands cannot be activated. This is the situation in present work. Once \(A(\tau_1 + \Delta \tau) > A_2 \tau_2\), the secondary and multiple shear bands are probably triggered, which has already been observed by a number of early studies.

For the MGs under uniaxial tension, the multiple shear bands can hardly develop and only one primary shear band dominates always. As a matter of fact, the hydrostatic pressure \(P\) is negative inside the shear band under...
tension. Figure 8 shows the structural and deforming features in Zr_{50}Cu_{44}Al_{6} MG for P = −2 GPa compared with those for P = 0 GPa. As shown in Fig. 8a, the first peak in the g(r) curve shifts towards a larger radial distance r, indicating a lower packing density of atoms. Besides, the fraction of icosahedron characterized by the Voronoi index V0 0 12 0 > is less for P = −2 GPa than for P = 0 GPa (Fig. 8b), consistent with the previous result of binary Cu-Zr MG. Following the discussion above, the shear strength τm for P = −2 GPa should therefore be lower, which is actually verified in Fig. 8c essentially in agreement with the difference between the compressive and tensile strength of MGs. As such, the shear band will carry more and more shear strain and eventually develop itself to a crack. This explains the absence of tensile ductility in MGs. Nevertheless, it cannot help to understand the densification and strain hardening in the notched MG sample under tension in ref. 10 where there was no shear band found at all.

It is sometimes found that the stress drops with the strain even with consideration of Eq. (2), especially in the heavily deformed sample. The SEM observation shows that the micro-voids and/or cracks already appear in the shear band in the MG samples subject to the large plastic deformation. They reduce the effective load-bearing area further and make Eq. (2) invalid. In this work, a small plastic strain less than 3% was therefore applied and no micro-voids or cracks is developed in the shear band as shown in Fig. 4, and therefore the hardening behavior is clearly presented in Figs 3, S3 and S4. Besides, it is sometimes found that the dilatation or cavitation happens to some very local sites in the shear band due to the internal tensile stress. For a MG sample under compression, the shear band is globally subject to compressive stress instead of tensile one. As a result, the shear band must be densified and hardened as a whole, though some local regions may undergo the reverse.

In summary, we have investigated the deformation behavior in three monolithic metallic glasses. The hardening behavior is witnessed in the plastic regime when the effective load-bearing area is taken into account instantly. The hardening mechanism is proposed to originate from the remelting and solidification of the shear-band material under a hydrostatic pressure imposed by normal stress on the shear plane. As expected, the shear-band material is densified during the quenching, confirmed by the molecular dynamical simulations. Meanwhile, MD simulations show that the icosahedral clusters are favored by virtue of the pressure. The densification and icosahedra work together to enhance the strength of the metallic glass and therefore achieve the hardening. Our findings and analyses address the issue of the hardenability in metallic glasses to some degree. They help to understand the unique mechanical property more deeply and evaluate the engineering reliability of metallic glasses in applications.

Methods

Experimental procedure. Three typical MGs with nominal composition of Zr_{50}Cu_{44}Al_{6} (at.%), Zr_{65}Cu_{15}Ni_{10}Al_{10} and Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} (i.e. Vit 1) were prepared by arc-melting and then suction-casting pure metals into a water-cooled copper mold under a Ti-gettered argon atmosphere. The prepared rod-shaped MG samples have a diameter of 2 mm. Their glassy nature was ascertained by XRD method using BRUKER D8 ADVANCE and TEM of TECNAI-F20. Thermal analysis was performed using Perkin Elmer DSC-7 at a heating rate of 20 K/min. As-cast rod samples with an aspect ratio of around 2:1 were compressed using Instron 8562 machine at a strain rate of 10^{-4} s^{-1} at room temperature. In particular, great care was taken to ensure the two ends of sample for compression test flat and parallel to each other and perpendicular to the longitudinal loading axis. The samples were unloaded after ~5% total strain without fracture. The deformed samples were investigated by SEM of Philips XL30 instrument and TEM.

MD simulations. In our work, MD simulations were performed to Zr_{50}Cu_{44}Al_{6} MG due to its accessible embedded-atom method (EAM) potential and details can be found in ref. 56. All the simulations were operated using the LAMMPS package. The cubic box contains 8,000 atoms with periodic boundary conditions in three dimensions. In the preparation, the sample was first equilibrated at 2,000 K for 2 ns and then was quenched to 300 K at a cooling rate of 10^{11} K/s in the isobaric-isothermal (NPT) ensemble, during which the box size was adjusted to give the applied pressure. In the shear deformation process, the prepared sample was sheared at a strain rate of 10^{7} s^{-1} in the canonical NVT ensemble at 300 K. The atomic structure was characterized by Voronoi tessellation.

References

1. Meyers, M. A. & Chawla, K. K. Mechanical Behavior of Materials. (Cambridge University Press, 2009).
2. Cheng, Y. Q. & Ma, E. Atomic-level structure and structure–property relationship in metallic glasses. Prog. Mater. Sci. 56, 379–473 (2011).
3. Schulz, C. A. Hufnagel, T. C. & Ramamurty, U. Mechanical behavior of amorphous alloys. Acta Mater. 55, 4067–4109 (2007).
4. Sun, B. A. & Wang, W. H. The fracture of bulk metallic glasses. Nat. Mater. 74, 211–307 (2015).
5. Miracle, D. B. A structural model for metallic glasses. Nat. Mater. 3, 697–702 (2004).
6. Sheng, H. W., Luo, W. K., Alamgir, F. M., Bai, J. M. & Ma, E. Atomic packing and short-to-medium-range order in metallic glasses. Nature 439, 419–425 (2006).
7. Green, A. C., Cheng, Y. Q. & Ma, E. Shear bands in metallic glasses. Mater. Sci. Eng. A 74, 71–132 (2013).
8. Wu, F. D., Zheng, W. F., Wu, S. D., Zheng, Z. F. & Shen, J. Shear stability of metallic glasses. Int. J. Plast. 27, 560–575 (2011).
9. Rudnicki, J. W. & Rice, J. R. Conditions for the localization of deformation in pressure-sensitive dilatent materials. J. Mech. Phys. Solids 23, 371–394 (1975).
10. Maali, R. & Löffler, J. F. Shear-Band Dynamics in Metallic Glasses. Adv. Funct. Mater. 25, 2353–2368 (2015).
11. Wondraczek, L. et al. Towards Ultrastrong Glasses. Adv. Mater. 23, 4578–4586 (2011).
12. Jang, D., Gross, C. T. & Green, J. R. Effects of size on the strength and deformation mechanism in Zr-based metallic glasses. Int. J. Plast. 27, 858–867 (2011).
13. Zhao, P., Li, J. & Wang, Y. Heterogeneously randomized STZ model of metallic glasses: Softening and extreme value statistics during deformation. Int. J. Plast. 40, 1–22 (2013).
14. Wang, Z. T., Pan, J., Li, Y. & Schuh, C. A. Densification and strain hardening of a metallic glass under tension at room temperature. Phys. Rev. Lett. 111, 135505 (2013).
15. Pan, J., Chen, Q., Liu, L. & Li, Y. Softening and dilatation in a single shear band. *Acta Mater.* **59**, 5146–5158 (2011).
16. Bei, H., Xie, S. & George, E. P. Softening Caused by Profuse Shear Banding in a Bulk Metallic Glass. *Phys. Rev. Lett.* **96**, 105503 (2006).
17. Song, S. X., Bei, H., Wadsworth, J. & Nieh, T. G. Flow serration in a Zr-based bulk metallic glass in compression at low strain rates. *Intermetallics* **16**, 813–818 (2008).
18. Jiang, M. Q. & Dai, L. H. On the origin of shear banding instability in metallic glasses. *J. Mech. Phys. Solids* **57**, 1267–1292 (2009).
19. Spaepen, F. A Microscopic Mechanism for Steady State Inhomogeneous Flow in Metallic Glasses. *Acta Metall.* **25**, 407–415 (1977).
20. Spaepen, F. Must shear bands be hot? *Nat. Mater.* **5**, 7–8 (2006).
21. Das, J. et al. *“Work-Hardenable” ductile bulk metallic glass. Phys. Rev. Lett.* **94**, 205501 (2005).
22. Du, X. H. et al. Two-glassy-phase bulk metallic glass with remarkable plasticity. *App. Phys. Lett.* **91**, 131901 (2007).
23. Liu, Y. H. et al. Super plastic bulk metallic glasses at room temperature. *Science* **315**, 1385–1388 (2007).
24. Han, Z., Yang, H., Wu, W. F. & Li, Y. Invariant critical stress for shear banding in a bulk metallic glass. *App. Phys. Lett.* **93**, 231912 (2008).
25. Peker, A. & Johnson, W. L. A highly processable metallic glass: Zr60Ti13Cu20Ni10Be17. *App. Phys. Lett.* **63**, 2342–2344 (1993).
26. Kawamura, Y., Shibata, T., Inoue, A. & Masumoto, T. Deformation behavior of Zr58Al16Ni10Cu4 alloy with wide supercooled liquid region. *App. Phys. Lett.* **69**, 1208–1210 (1996).
27. Pauly, S., Coranta, S., Wang, G., Kuhn, U. & Eckert, J. Transformation-mediated ductility in CuZr-based bulk metallic glasses. *Nat. Mater.* **9**, 473–477 (2010).
28. Chen, M., Inoue, A., Zhang, W. & Sakurai, T. Extraordinary plasticity of ductile bulk metallic glasses. *Phys. Rev. Lett.* **96**, 245502 (2006).
29. Maass, R., Klaumünzer, D., Preiß, E. I., Derlet, P. M. & Löffler, J. F. Single shear-band plasticity in a bulk metallic glass at cryogenic temperatures. *Scripta Mater.* **66**, 231–234 (2012).
30. Chen, Y., Jiang, M. Q. & Dai, L. H. Collective evolution dynamics of multiple shear bands in bulk metallic glasses. *Int. J. Plasticity* **50**, 18–36 (2013).
31. Zhang, Z. F., He, G., Eckert, I. & Schultz, L. Fracture Mechanisms in Bulk Metallic Glassy Materials. *Phys. Rev. Lett.* **91**, 045505 (2003).
32. Meyers, M. A. Dynamic Behavior of Materials. (John Wiley & Sons, Inc., 1994).
33. Qu, R. T. & Zhang, Z. F. A universal fracture criterion for high-strength materials. *Sci. Rep.* **3**, 1117 (2013).
34. Liu, Z. Q., Qu, R. T. & Zhang, Z. F. Elasticity dominates strength and failure in metallic glasses. *J. Appl. Phys.* **117**, 014901 (2015).
35. Kim, J.-I., Choi, Y., Suresh, S. & Argon, A. S. NanocrySTALLization during nanoindentation of a bulk amorphous metal alloy at room temperature. *Science* **295**, 654 (2002).
36. Yavari, A. R. et al. Crystallization during bending of a Pd-based metallic glass detected by x-ray microscopy. *Phys. Rev. Lett.* **109**, 085501 (2012).
37. Wang, J. G. et al. How hot is a shear band in a metallic glass? *Mater. Sci. Eng. A* **651**, 321–331 (2016).
38. Wang, J. G. et al. Ideal shear banding in metallic glass. *Philos. Mag.*** **96**, 3159–3176 (2016).
39. Ketov, S. V. & Louzguine-Luzgin, D. V. Localized shear deformation and softening of bulk metallic glass: stress or temperature driven? *Sci. Rep.* **3**, 2798 (2013).
40. Wright, W. J., Samale, M. W., Hufnagel, T. C., LeBlanc, M. M. & Florando, J. N. Studies of shear band velocity using spatially and temporally resolved measurements of strain during quasistatic compression of a bulk metallic glass. *Acta Mater.* **57**, 4639–4648 (2009).
41. Slaughter, S. K. et al. Shear bands in metallic glasses are not necessarily hot. *APL Mater.* **2** (2014).
42. Ding, J., Asta, M. & Ritchie, R. O. Anomalous structure-property relationships in metallic glasses through pressure-mediated glass formation. *Phys. Rev. B* **93**, 140204 (2016).
43. Zhang, Q.-D., Wang, L.-F., Yang, Y. Q. & Chen, N. Superductile bulk metallic glass. *App. Phys. Lett.* **88**, 122106 (2006).
44. Yokoyama, Y., Fujita, K., Yavari, A. R., Inoue, A. & Mukherjee, A. K. Shear band formation and ductility in bulk metallic glass. *Phil. Mag.*** **85**, 2671–2687 (2005).
45. Ramamurty, U., Jana, S., Kawamura, Y. & Chattopadhyay, K. Hardness and plastic deformation in a bulk metallic glass. *Acta Mater.* **53**, 705–717 (2005).
46. Zhang, Z. F., Eckert, J. & Schultz, L. Difference in compressive and tensile fracture mechanisms of Zr59Cu20Al10Ti3 bulk metallic glass. *Acta Mater.* **51**, 1167–1179 (2003).
47. Maass, R., Samwer, K., Arnold, W. & Volkert, C. A. A single shear band in a metallic glass: Local core and wide soft zone. *App. Phys. Lett.* **105**, 171902 (2014).
48. Khonik, V. A. The kinetics of irreversible structural relaxation and rheological behavior of metallic glasses under quasi-static loading? *J. Non-Cryst. Solids* **296**, 147–157 (2001).
49. Schmidt, V., Rosner, H., Peterlechner, M., Wilde, G. & Vöyles, P. M. Quantitative Measurement of Density in a Shear Band of Metallic Glass Monitored Along its Propagation Direction. *Phys. Rev. Lett.* **115**, 035501 (2015).
50. Maas, R., Birckigt, P., Borchers, C., Samwer, K. & Volkert, C. A. Long range stress fields and cavitation along a shear band in a metallic glass: The local origin of fracture. *Acta Mater.* **98**, 94–102 (2015).
51. Cheng, Y. Q., Ma, E. & Sheng, H. W. Atomic level structure in multicompontent bulk metallic glass. *Phys. Rev. Lett.* **102**, 245501 (2009).
52. Plimpton, S. Fast Parallel algorithms for short-range molecular dynamics. *J. Comp. Phys.* **117**, 1–19 (1995).

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J.G.W., Y.P. and J.E. designed the research. J.G.W., K.K.S. and G.W. performed the experiments. J.G.W., Y.C.H., P.F.G. and L.W. conducted the simulations. All the authors contributed to the manuscript.

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