Structural heterogeneity and plasticity of a Zr-based metallic glass modulated by high-temperature deformation

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I. INTRODUCTION

Metallic glasses (MGs) are a type of disordered alloys with high strength, large toughness, but poor plasticity. When they are deformed at low temperatures (T), catastrophic failure occurs with the development of shear bands (SBs) and cracks due to the highly localized shear,1,2 which limits their applications as engineering materials. According to free volume (FV) theory3 and shear transformation zone (STZ) theory,4,5 shear localization initiates in the regions with a higher concentration of free volume or larger configurational entropy. It expands quickly because of shear- or heat-induced softening in front of and inside SBs.6 The low-T plasticity of MGs can be improved by altering their heterogeneous structure.7–9 With finite-element analysis, Chen et al. reported that the yield strength and plasticity of MGs depend on the concentration and distribution of FV, respectively.10 Zhong et al. observed size-independent homogeneous deformation in MGs with shear-band-like structures using molecular dynamics (MD) simulation and suggested that the plasticity of MGs can be improved by increasing the uniformly distributed FV concentration.11 Tang et al. reported uniform deformation and large plasticity of MGs quenched with a high cooling rate in MD simulation and attributed the phenomenon to uniform dispersion of strain energy into local atomic shear.12 Wang et al. found that the plasticity of (Zr56Cu38Fe7Al10)94Nb6 bulk MGs increases to 17.3% with annealing for 30 min due to the work-hardening and decreases with further annealing.13 Zhu et al. discovered that the plasticity of MGs can be enhanced without decreasing its strength after deep-cooling treatment as the internal stress generated by cooling contraction activates atomic motions in weakly bonded regions and leads to the formation of icosahedral short-range ordering.14 Liu et al. reported that the nanoscale heterogeneity of Pd82Si18 MG can be enhanced by plastic deformation due to phase segregation and SB interaction as demonstrated by high-energy synchrotron x-ray small-angle scattering and diffraction experiments.15 Tao et al. showed that the plasticity of MGs can be improved by severe deformation due to lower energy barriers and more nuclei for shear transformation in the deformation-induced rejuvenated heterogeneous structure.16 Pan et al. revealed that triaxial compression at room temperature (RT) increases FV in MGs, promoting strain hardening during deformation and significantly enhancing their plasticity.17 Wu et al. introduced nonmetallic elements as dopants into MGs and found that the regions surrounding these solute atoms are more prone to plastic deformation with elevated critical stress.18 Tong et al. discovered that FV concentration and structural inhomogeneity of
MGs can be tuned by high-temperature deformation and the plasticity of the studied MGs can also be enhanced. However, it is still unclear how the structural heterogeneity of MGs evolves under high-\( T \) deformation and how plasticity is affected by such treatments. We explore the evolution of the heterogeneous structure of a Zr-based MG during deformation under different stresses (\( \sigma \)) near the glass transition temperature (\( T_g \)) and investigate its influence on the MG’s plasticity at RT.

II. METHODS

Master ingots of the composition \( \text{Zr}_{64.13}\text{Al}_{10}\text{Ni}_{10.12}\text{Cu}_{15.75} \) were prepared by arc-melting elemental metals with purity better than 99.9\% in Ar atmosphere. MG ribbons were produced by melt-spinning the ingots in argon atmosphere with a rotation speed of the copper roller as 30 m/s. The ribbons were heated to 579 K (0.9\( T_g \), \( T_g = 643 \) K) and cooled for 30 min under different stress levels (0, 40, 80, 120, 160, 200, and 240 MPa) in a dynamic mechanical analyzer (DMA, TA Q850) in the nitrogen atmosphere for preventing oxidation. Then, the ribbons were cooled to RT with a cooling rate of 10 K/min.

The morphology of SBs in the bent MG ribbons was analyzed by AFM (Bruker) in an ambient environment. To achieve an atomic frictional image (AFM, Bruker) in an ambient environment. To achieve a cooling rate of 10 K/min. The local elastic modulus (\( E \)) of the ribbons were measured in an area of \( 50 \times 50 \mu \text{m}^2 \) by nanoindentation (KLA-iMicro) with a Berkovich diamond tip using the method developed by Oliver and Pharr. The distance of neighboring detected positions is 5 \( \mu \text{m} \). For each nanoindentation, the loading rate is 0.2 mN/s and the peak load is held for 10 s at 20 mN. The viscoelastic behavior was investigated with atomic force microscopy (AFM, Bruker) in an ambient environment. To achieve high spatial resolution, an AFM tip with a radius of 8 nm was used, which possesses a spring constant \( k \) of 24.5 N m\(^{-1} \) and a damping factor \( Q \) of 359. During AFM scanning, the amplitude-modulation (AM) or tapping mode was employed at a pre-defined setpoint amplitude \( A \) as 100 mV and a frequency \( \omega_0 \) as 300 kHz. The MG ribbons pretreated by high-\( T \) deformation were bent at RT by compressing them in the length direction with an initial length of 300 mm and a displacement-changing rate of 1.5 mm/s in DMA. The morphology of SBs in the bent MG ribbons was analyzed using scanning electron microscopy (SEM, ZEISS GeminiSEM 300).

III. RESULTS AND DISCUSSION

Figures 1(a), 1(c), 1(e), 1(g), 1(i), 1(k), 1(m), and 1(o) show the AM-AFM phase-shift (\( \delta \)) images of the as-spun MG and those deformed with \( \sigma \) as at 579 K. Figures 1(b), 1(d), 1(f), 1(h), 1(j), 1(l), 1(n), and 1(p) show the distributions of \( \delta \) angle for the studied MGs. The surface of the studied MGs is clean and no apparent oxide surficial layer appears in the optical and scanning electron microscopic images even after they were deformed at 579 K (Figs. S1 and S2 in the supplementary material). Oxidation was well prevented in the nitrogen atmosphere during the deformation process, which could show little influence on the \( \delta \) images. As the surface topography of the MGs does not overlap with the \( \delta \) image (see Fig. S3 in the supplementary material), the \( \delta \) variation at the surface of the MG mainly originates from the viscoelastic behavior. A larger \( \delta \) value indicates larger energy dissipation in the detected area and the phase-shift spatial distribution reflects nanoscale dynamic heterogeneity of the MGs. With \( \sigma \) increasing from 0 to 120 MPa, the \( \delta \) value of the as-spun MG successively decreases and the \( \delta \) angle distribution moves to low \( \delta \) values, which is probably being induced by structural aging at high \( T \). With further increasing \( \sigma \) to 240 MPa, \( \delta \) increases and the \( \delta \) angle distribution moves to high \( \delta \) angles, suggesting structural rejuvenation, which could be caused by high-\( T \) deformation at large \( \sigma \).

Figure 2(a) shows the value \( P(\delta) \) of \( \delta \) correlation function calculated via

\[
P(\delta) = [P(\delta) - P(0)]^2,
\]

where \( P(\delta) \) and \( P(0) \) are the \( \delta \) values at the coordinate (x, y) and the reference position (\( x_0 \), \( y_0 \)), respectively. The r-dependent \( P(\delta) \) can be fitted with

\[
P(\delta) = 2\sigma_\delta^2[1 - \exp(-r(\xi)^2)],
\]

where \( \sigma_\delta \) is the root mean square \( \delta \), \( \alpha \) is the phase shift exponent, and \( \xi \) is the correlation length. \( \xi \) of the as-spun MG decreases from 1.81 to 0.95 nm with deformation under 0 MPa at 579 K. \( \xi \) is larger for the area along the thickness direction with larger residual stresses induced by the thermal gradient (S1 and Fig. S4 in the supplementary material). Thus, the decrease of \( \xi \) at the surface after annealing could be due to the removal of residual stresses and surficial irregularities from the as-spun MG. \( \xi \) gradually increases to 1.37 nm when \( \sigma \) increases to 160 MPa. With \( \sigma \) further increases to 240 MPa, \( \xi \) decreases to 1.09 nm suggesting structural evolution different from that at small \( \sigma \).

The phase shift \( \delta \) can be converted to the local energy dissipation induced by the interaction between the tip and the sample using the equation

\[
E_{\text{dis}} = \frac{\pi k A_0}{Q} \left[ \sin \left( \frac{\pi}{2} - \delta \right) - \frac{\omega \cdot A}{\omega_0 \cdot A_0} \right],
\]

where \( \omega \) is the drive frequency, \( \omega_0 \) is the resonant frequency of cantilever, \( A \) is the vibration amplitude during testing, \( A_0 \) is the free amplitude without tip-sample interaction, \( k \) is the spring constant of cantilever, and \( Q \) is the quality factor. During the test, \( \omega_0 \) is chosen as 300 kHz, \( k \) is 24.5 N m\(^{-1} \), \( Q \) is 359, \( A_0 \) is 500 mV, \( A \) is 100 mV. With Eq. (3), we have calculated the local energy dissipations \( E_{\text{dis}} \) from the phase shift images which are shown in Fig. 2(b). Figure 2(b) shows that energy dissipation initially decreases and then increases with the gradual increase of \( \sigma \), which is consistent with the phase shift variation. The decrease of \( E_{\text{dis}} \) at low stresses indicates structural relaxation. The increase of \( E_{\text{dis}} \) at large stresses is due to the structural rejuvenation induced by high stress in metallic glass, resulting in the formation of more defect regions within the structure exhibiting increased "liquid-like” behavior, and consequently higher energy dissipation.

Figures 3(a)–3(h) show the spatial distributions of the detected local \( E \) for the as-spun MG and those deformed with \( \sigma \) as 0, 40, 80, 120, 160, 200, and 240 MPa at 579 K. During nanoindentation, the adhesion between the indenter and the sample can mainly arise from the capillary force of the narrow layer of liquid at the surface, which is about three orders of magnitude smaller than the peak load. The nonuniform distributed local \( E \) in the detected area
indicates microstructural heterogeneity of the studied MGs at the micrometer. The distributed local $E$ tend to increases with $\sigma$ increasing to 120 MPa. When $\sigma$ reaches 160 MPa, the local $E$ decreases with $\sigma$. The corresponding count distributions of the detected local $E$ for the studied MGs are shown in Fig. S5 in the supplementary material. The count distributions can be fitted with the Gaussian function

$$P(E) = \frac{1}{\sigma_E \sqrt{2\pi}} e^{-\frac{(E-E_\text{av})^2}{2\sigma_E^2}}, \quad \text{(4)}$$

where $E$ is the average local $E$, $\sigma_E$ is the standard deviation of the local $E$. The fitting $E_\text{av}$, $\sigma_E$ and $\sigma_E/E_\text{av}$ are listed in Table S1 in the supplementary material. With increasing $\sigma$, $E$ reaches the largest value of 93.6 GPa at $\sigma$ of 120 MPa and then decreases to 84.8 GPa at

FIG. 1. $\delta$ images [(a), (c), (e), (g), (i), (k), (m) and (o)] and the distributions of $\delta$ angles [(b), (d), (f), (h), (j), (l), (n) and (p)] for the as-spun MG and those deformed under 0, 40, 80, 120, 160, 200, and 240 MPa at 579 K.
σ of 240 MPa, being consistent with the δ change in Figs. 1(a)–1(h). The increase of $E$ under small $\sigma$ should be due to the $\sigma$-enhanced atomic diffusion and structural aging, and the decrease of $E$ might be caused by the fast generating rate of FV under large $\sigma$. At low stresses, due to the enhanced atomic diffusion at high temperatures (579 K, 0.9$T_g$), structural relaxation dominates leading to the increase of the local elastic modulus. When the stress reaches a critical value, shear transformation occurs in a large number of local regions inducing the increase of free volume due to shear dilation. With the stress further increasing, more shear transformation zones are created and shear dilation overwhelms the relaxation effect. Thus, rejuvenation of the microstructure happens resulting in the decrease of local elastic modulus. In addition, the high-temperature creep under large stresses can also introduce large

FIG. 2. (a) $\delta$ correlation function for the as-spun MG and those deformed under 0, 40, 80, 120, 160, 200, and 240 MPa at 579 K, (b) the distribution of energy dissipation for the MGs deformed under 0, 40, 80, 120, and 240 MPa at 579 K. The solid line is the Gaussian fit of the experimental data points.

FIG. 3. The spatial [(a)–(h)] distributions of the detected local $E$ for the as-spun MG and those deformed under 0, 40, 80, 120, 160, 200, and 240 MPa at 579 K.
residual anelastic strains.27 The anelastic sites might also lead to the decrease of the local elastic modulus, which needs to be further researched. The apparent inhomogeneous distribution of $E$ corresponding to the large $\sigma_r/E$ at $\sigma$ of 40 and 240 MPa (see Table S1 in the supplementary material) indicates more heterogeneous structure at the micrometer scale which could be induced by the inhomogeneous relaxation and SB nucleation, respectively.28

It is noticeable that a $\sigma$ threshold value exists, above which shear dilation overwhelms the relaxation effect for the studied MGs3 Thus, rejuvenation of the microstructure happens under large $\sigma$. In addition, high-temperature deformation under large $\sigma$ can also introduce large residual anelastic strains.27 The anelastic sites might also lead to the increase of $E_{\text{dis}}$ and the decrease of $E$, which needs to be further researched. Besides the variation of $\delta$ and $E$, the transition from structural relaxation to rejuvenation under large $\sigma$ at high $T$ can also be verified by the change of the isotropic part $G_0^0(r)$ of the pair distribution function detected with synchrotron x-ray diffraction. As reported, the first principle peak of $G_0^0(r)$ sharpens for MGs after being annealed at high $T$ without $\sigma$, indicating structural relaxation.29,30 With creeping at high temperatures under large $\sigma$, the main peak of $G_0^0(r)$ hardly changes or weakens suggesting structural relaxation is overwhelmed by the rejuvenation effect.19,31

Subsequently, the as-spun and deformed sample MGs were bent in the DMA under the same condition, resulting in the formation of SBs on the surface. The stress–strain curves are shown in Fig. 4 (To present the result clearly, the curves are moved vertically with different values.). For each ribbon, with reducing the distance of their two clamped ends, the detected strain (i.e., the distance change of the two ends divided by the initial distance value) becomes larger and the bending angle appears larger. The detected compressive stress also increases. A kink (as marked by the arrows) exists in the stress–strain curve with the strain reaches a critical value. Similar to the pop-in in the load–displacement curve of nanoindentation,32 the kink should be associated with the process of shear banding. It can be seen that the strains corresponding to the first kinks (marked by black arrows) for ribbons pre-deformed at 0, 40, 80, and 120 MPa are apparently larger than those (marked by red arrows) for ribbons pre-deformed at 160, 200, and 240 MPa. It suggests that shear banding occurs at a smaller $\sigma$ in the bent

FIG. 4. Strain–stress curves for the as-spun ribbon and those deformed under 0, 40, 80, 120, 160, 200, and 240 MPa at 579 K.

FIG. 5. SEM images of the central areas for the (a) as-spun MG, MGs deformed under (b) 0 MPa, (c) 80 MPa, (d) 160 MPa, (e) 200 MPa, (f) 240 MPa at 579 K.
ribbon pre-deformed under larger $\sigma$. More shear bands can be initiated in the ribbons after the same amount of bending. Thus, the plasticity of the ribbons can be improved if they are deformed under large $\sigma$.

Figures 5(a)–5(f) show the SEM images around the central areas of the bent MGs. As compared to the as-spun MG, the SBs of the MGs deformed below $\sigma$ of 160 MPa at 579 K converges to the central region more apparently suggesting more severe stress concentration during bending. With $\sigma$ increasing to that above 200 MPa, more SBs spread into a much larger area rather than the central region, indicating more uniform distribution of local shear strain and better plasticity. With high-$T$ deformation at small $\sigma$, the heterogeneous structure of the as-spun MG relaxes quickly due to atomic diffusion and a reduction of FV. The local soft potential STZ regions decrease and SBs can only be initiated in the central region of the bent MG with large concentrated stresses. At large $\sigma$, the MG is deformed at a larger strain rate and the FV generation overwhelms the process of atomic diffusion. More potential STZ regions with a larger FV concentration and a large configurational entropy are created in the MG as indicated by Fig. 3. Meanwhile, $\xi$ of the deformed MG becomes smaller (Fig. 2), implying smaller sizes and activation energy of STZs. Thus, STZs can be more easily activated and more SBs form in a larger area leading to the improved plasticity during bending.

IV. CONCLUSION
In summary, $\xi$, local $E$ increase and local $E_{\text{dis}}$ decreases for the studied MGs with deformation under small $\sigma$ at 0.9$T_g$ as structural aging dominates. $\xi$, and local $E$ decrease and local $E_{\text{dis}}$ increases when the MG is deformed above a critical $\sigma$ at 0.9$T_g$ due to the more important role of structural rejuvenation. With high-$T$ deformation under larger $\sigma$, SBs can be initiated at a smaller strain and more SBs form in a larger area in the MGs during bending suggesting improved plasticity. The results could be significant for controlling the plasticity of glassy materials by tuning their heterogeneous microstructures with high-$T$ deformation.

SUPPLEMENTARY MATERIAL
See the supplementary material for the scanning electron microscopic images and distance-dependent phase shift correlation functions of the cross section, the uncorrelated nature of the sample’s phase shift with surface tomography, as well as the distributions and fitting values of the elastic modulus for the as-spun and deformed samples.

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AUTHOR DECLARATIONS
Conflict of Interest
The authors have no conflicts to disclose.

Author Contributions
Wenting Lu: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Methodology (equal); Writing – original draft (lead). Bo Huang: Conceptualization (supporting); Funding acquisition (lead); Resources (lead); Writing – original draft (supporting); Writing – review & editing (equal). Shanshi Liao: Data curation (supporting); Formal analysis (supporting). Penghua Liu: Data curation (supporting). Hui Lv: Data curation (supporting). Jiayi Wu: Data curation (supporting). Jun Yi: Writing – review & editing (equal). Qing Wang: Conceptualization (supporting); Methodology (supporting); Resources (equal); Writing – review & editing (equal).

DATA AVAILABILITY
The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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