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Universal mechanism of thermomechanical deformation in metallic glasses

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We investigated the atomistic structure of metallic glasses subjected to thermomechanical creep deformation using high energy x-ray diffraction and molecular dynamics simulation. The experiments were performed *in situ* at high temperatures as a time dependent deformation in the elastic regime, and *ex situ* on samples quenched under stress. We show that all the anisotropic structure functions of the samples that have undergone thermomechanical creep can be scaled into a single curve, regardless of the magnitude of anelastic strain, stress level, and the sign of the stress, demonstrating universal behavior and pointing to a unique atomistic unit of anelastic deformation. The structural changes due to creep are strongly localized within the second nearest neighbors, involving only a small group of atoms.

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Metallic glasses are known for their high mechanical strength and are promising as structural materials [1]. However, in spite of extensive research over many years, the atomistic mechanisms of mechanical deformation in metallic glasses remains poorly understood. A major cause of difficulty in determining the mechanism is that, at room temperature, deformation in metallic glasses is highly localized in narrow shear bands, and any local structural change induced by deformation is wiped out by subsequent heating [2]. On the other hand, thermomechanical creep deformation, induced when metallic glass is subjected to stress at elevated temperatures approaching the glass transition, is spatially homogeneous and thus easier to study (e.g., Ref. [3]). It is known that creep deformation leaves the sample in a structurally anisotropic state because of anelastic deformation resulting in bond-orientational anisotropy [4,5]. In this Rapid Communication we focus on the structural aspects of the thermomechanical creep deformation by using high energy x-ray diffraction and we show that, when appropriately scaled, the structural anisotropy induced by creep deformation is independent of time and stress, implying that a universal mechanism of creep deformation exists.

In crystalline materials, anelastic and plastic deformation is caused by the movement of lattice defects. In glasses, on the other hand, defects cannot be easily and uniquely identified. Phenomenologically, the creep is explained in terms of formation and interaction of the shear transformation zones (STZs) [6,7]. STZ is an important concept used in explaining mechanical deformation and flow of metallic glasses [8–11]. However, experimental determination of the atomistic details of the STZ has been controversial [12–15]. To shed light on this question we examined the structure of bulk metallic glasses subjected to thermomechanical creep in the anelastic, recoverable regime using high energy x-ray diffraction. Diffraction experiments were performed on samples *in situ* during time dependent deformation at 300 °C, and *ex situ* at room temperature, after quenching down the samples crept at 300–350 °C. The quenched samples were submitted to compression during creep. The *in situ* studies were carried out in tension. All the samples retained a fully amorphous structure.

X-ray diffraction measurements were done at the synchrotron beamlines 1-ID at the APS, Argonne National Laboratory, Argonne, IL and WB5 at the DESY, Hamburg. The incident energy was tuned to 100 keV ($\lambda = 0.1254$ Å). The beam size was $0.2 \times 0.2\ \mathrm{mm}^2$ at 1-ID or $0.4 \times 0.4\ \mathrm{mm}^2$ at WB5. GE and Perkin Elmer area detectors were used in collecting diffracted x rays. We used $Zr_{55}Cu_{30}Ni_5Al_{10}$ (the glass transition temperature, $T_g = 434\,^\circ$C; yield stress, $\sigma_y = 1820$ MPa at 25 °C 1450 MPa at 300 °C, and 1000 MPa at 350 °C, with a strain rate 0.000 1/s; the structure function and pair distribution function of the as-cast sample are shown in the Supplemental Material [16], Fig. S1) metallic glass to examine creep in different conditions, as indicated in the figures. Samples were prepared by melt casting into 8 mm diam rods [17]. Dog-bone shapes, with the central part being 9.6 mm long and $2 \times 0.6\ \mathrm{mm}^2$ cross section, were cut using electrical discharge machining (EDM) and used for the tension experiment. Compression tests were performed on cylindrical rods (2 mm diam × 4 mm tall). After the EDM cuts, the materials were polished to establish precise dimensions and to remove surface contaminations. Samples were placed in load frames with internal heaters and annealed under stress with inert gas flow. The *ex situ* deformation was done up to 7 h at 350 °C under a fixed load of 800 MPa, and up to 1000 MPa for a fixed time of 1 h, while the *in situ* experiment was carried out in tension for 5 h at 800 MPa/300 °C. For each measurement the background due to dark current was subtracted from the data, and then normalized by the incident beam monitor.

The spherical harmonics expansion was performed on the normalized data to determine the anisotropic components of the structure function $S(Q)$ ($Q = 4\pi \sin\theta/\lambda$, where θ is the diffraction angle) and the pair distribution function (PDF) $g(r)$, as described elsewhere [4,18,19],

$$g(\boldsymbol{r}) = \sum_{\ell,m} g_\ell^m(r) Y_\ell^m\left(\frac{\boldsymbol{r}}{r}\right), \quad S(\boldsymbol{Q}) = \sum_{\ell,m} S_\ell^m(Q) Y_\ell^m\left(\frac{\boldsymbol{Q}}{Q}\right), \tag{1}$$

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where $Y_l^m(\mathbf{r}/r)$ are the spherical harmonics. The anelastic deformation is recoverable, therefore, the sample has a memory of the original state which is stored as structural anisotropy. Indeed, the structure of the glass, after high-temperature creep, has anisotropy with $l = 2$ symmetry [4], and the next term with $l = 6$ is much smaller [20]. For cylindrical symmetry, as in the present case, only the terms with $m = 0$ are nonzero [18]. In the present work, the diffraction data are analyzed using only the elliptical ($l = 2, m = 0$) terms of the expansion. It has been shown that for affine deformation the derivative of the isotropic term in the $S(Q)$ or $g(r)$ is proportional to the elliptic component and the proportionality constant is equal to the strain ε_{aff} [4,19],

$$\begin{aligned} g_{2,\text{aff}}^{0}(r) &= -\varepsilon_{\text{aff}}\left(\frac{1}{5}\right)^{1/2}\frac{2(1+\nu)}{3}r\frac{d}{dr}g_0^0(r),\\ S_{2,\text{aff}}^{0}(r) &= -\varepsilon_{\text{aff}}\left(\frac{1}{5}\right)^{1/2}\frac{2(1+\nu)}{3}Q\frac{d}{dQ}S_0^0(Q), \end{aligned} \tag{2}$$

where ν is the Poisson's ratio, and $g_2^0(r)$ and $S_2^0(Q)$ are directly related to each other through the second-order spherical Bessel transformation.

Figure 1(a) shows the data obtained *in situ* during annealing at 300 °C under a constant stress of 800 MPa, which is below the yield point (∼1500 MPa at 300 °C). The magnitude of $S_2^0(Q)$ was found to increase with holding time. The anisotropic patterns shown in Fig. 1(a) are typical for creep in metallic glasses and are distinct from pure elastic deformation [19] or residual elastic stresses [21]. The dashed line in Fig. 1(a) corresponds to the $S_2^0(Q)$ expected for affine elastic deformation, which significantly differs from the experimental result on creep deformation. Similar results were obtained for the samples that underwent thermomechanical deformation in compression at 350 °C/800 MPa for varying time and fixed time (1 h) and varying stress (200-1000 MPa), and were quenched under stress to room temperature (Figs. S2 and S3 in the Supplemental Material [16]). The intriguing feature of the creep strain in metallic glasses is a strong similarity of all of the patterns regardless of the holding time and the stress level. Figure 1(b) shows elliptical terms for the *in situ* creep in tension and *ex situ* creep in compression scaled by some renormalizing constants. The sign of the data for the compression creep is inverted and the data are shifted in Q to adjust for thermal expansion due to different measurement temperatures. Interestingly, the patterns of $S_2^0(Q)$, corresponding to the creep strain, can be scaled very well into the same form factor $S_2^0(Q)$, regardless of duration, stress level, and the sign of the stress, as shown in Fig. 1(b) (separate scaling for each measurement set is shown in Figs. S4–S6 in the Supplemental Material [16]). The constants used in scaling are not exactly proportional to the holding time, but are roughly proportional to the stress level. This scaling behavior clearly confirms that the microscopic mechanism of anelastic creep deformation in metallic glasses is well defined, common, and the same for different modes of deformation (compression and tension) and stress range, contrary to the crystalline materials, where different types of defects can be operational, and relates to the viscoelasticity of a glass [22]. The scaling is weakly affected by temperature because the amount of unrecoverable plastic strain depends strongly on temperature, and it is likely that this slightly affects the scaling behavior. Since $g_2^0(r)$ is related by a simple transformation to $S_2^0(Q)$, the same scaling behavior is observed in real space.

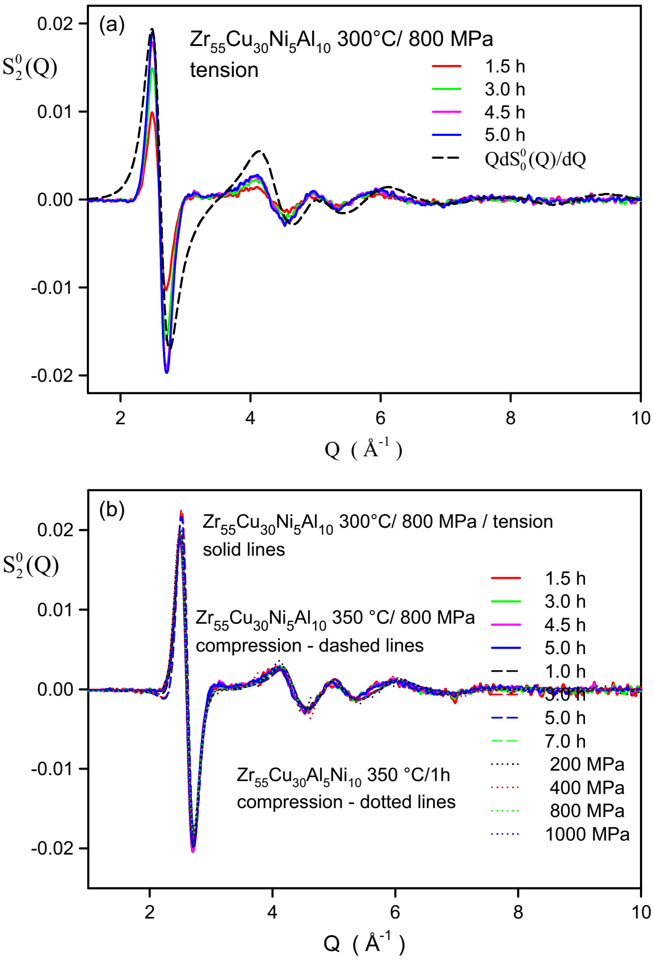

FIG. 1. (Color online) (a) The anisotropic part of the $S(Q)$ resulting from creep during time dependent study at 300 °C, at 800 MPa. The dashed curve corresponds to $S_2^0(Q)$ for purely affine deformation behavior. (b) The anisotropic part of the $S(Q)$ for samples from Figure 1 and for samples that underwent creep at 350 °C at 800 MPa in compression and were later measured at room temperature. The data is scaled by arbitrary constants. In addition the data for compression are inverted to make them look like in tension and scaled in Q to take different measurement temperatures into account. All the $S_2^0(Q)$ can be collapsed into one curve within small deviations. The individual temperature data sets are shown in the supplementary section.

To assess the microscopic mechanism of the creep, we compared the anisotropic component of the PDF, $g_2^0(r)$, against the one expected for affine deformation, $g_{2,\text{aff}}^0(r)$, using Eq. (2), which gives direct insight into the changes in the atomic structure. Figure 2(a) shows the elliptical term of the pair distribution function after creep in compression at 800 MPa for 7 h at ∼350 °C, overlapped with scaled *in situ* tension data, together with the first derivative of the isotropic term. The derivative is scaled such that the three plots match at large r, so that the scaling constant is proportional to the long-range or average internal strain. There is a large difference in the amplitude of $g_2^0(r)$ and $g_{2,\text{aff}}^0(r)$ at short distances. This is very

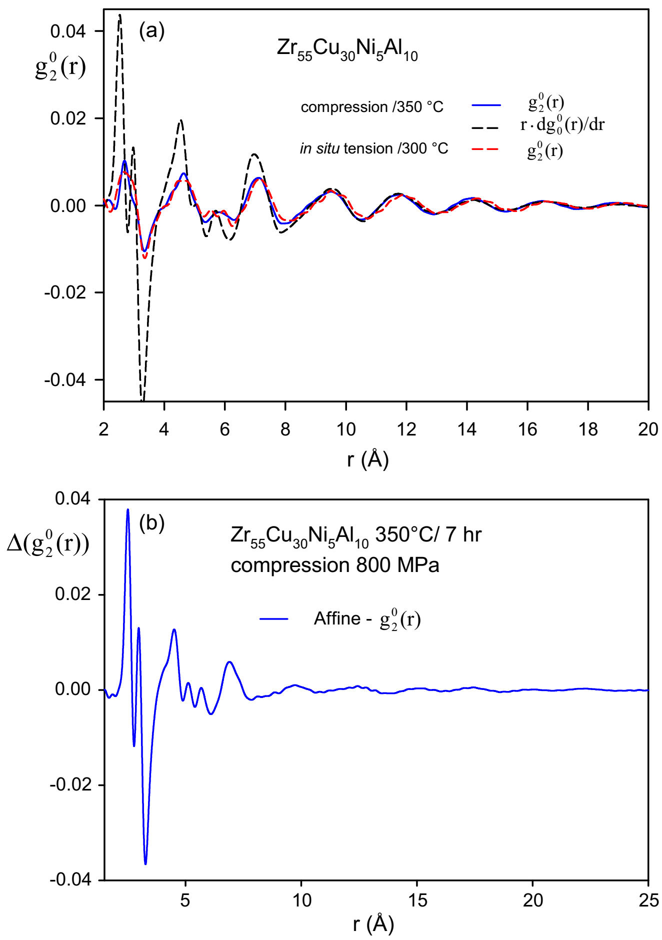

FIG. 2. (Color online) (a) The anisotropic part of the PDF for samples that underwent creep in compression at high temperature and were quenched to RT (measurement is performed at RT) and *in-situ* creep measurement during tension at 300 °C. (b) The difference in $g_2^0(Q)$ between the affine deformation and creep data in compression. It shows that beyond 8 Å strain is essentially elastic and that anelastic relaxation is localized within small group of atoms.

typical of $g_2^0(r)$ for anelastic creep deformation in metallic glasses. Figure 2(b) shows the difference, $g_{2,\mathrm{aff}}^0(r) - g_2^0(r)$. This difference describes the extent of the local atomic rearrangement which occurred during the creep to relax the applied stress. The local relaxation creates a local stress which balances the internal long-range stress field because the total stress is zero. It is seen that the anelastic deformation is localized to a small group of atoms within the first and second neighbors, and beyond ~8 Å the difference is practically zero within experimental resolution. The Supplemental Material also shows data (Fig. S7 [16]) for a glass with a different composition.

Molecular dynamics (MD) studies were performed on a model of amorphous iron [23] with 16 584 atoms to avoid the chemical composition effects. Initially, the structure of a glass was prepared by an instant quench from a liquid at 1500 K to a glass at 700 K, followed by cooling process at 0.2 K/ps. After gradual cooling to room temperature, the system was relaxed for 2 ns under an *NPT* ensemble with pressure set to zero and temperature at 300 K. Initially, the positions of all atoms were homogeneously displaced with a tensile strain of 1% and a Poisson ratio of 0.33. The deformed structure was then relaxed at 300 K. Because computer generated models are quenched at high rates (~10^{11} K/s) they are unstable and show creep behavior even at room temperature. Such elastic heterogeneity was also observed by other molecular dynamics simulations [24,25]. After the creep, each atom in the structure was examined and three groups were identified: the atoms which retained their original neighbors, the atoms which lost at least one of its neighbors that moved to the next neighbor shell (bond breaking), and the atoms which gained at least one new neighbor (bond formation). For each atom in the structure, the anisotropic component of the pair distribution function was calculated and then summed up according to the above classifications. As a result, three $g_2^0(r)$ were obtained: for atoms without local topological change, atoms which lost

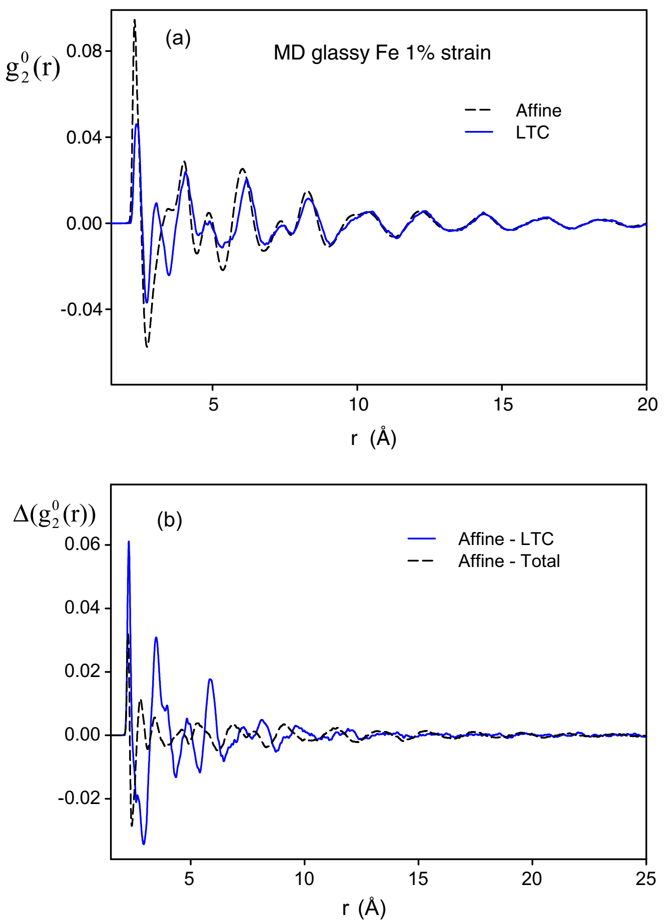

FIG. 3. (Color online) (a) The anisotropic part of the PDF obtained for groups of atoms that underwent local topological change compared to the affine case. Similarly to experiment, data overlap at large *r* but differ at short-range covering first and second atomic shells. (b) The difference between the $g_2^0(r)$ calculated for the affine deformation and that for the LTC atoms (solid line), and that between the $g_2^0(r)$ calculated for the affine deformation and that for the Total (dashed line). The LTC atoms represent atoms that changed its local topology. Total represents all atoms in the sample. The plot shows that local relaxation is caused mostly by atoms that changed their local topology, despite the fact that they represent ~10% of all atoms.

a neighbor (B-B; bond breaking), and atoms which gained a new neighbor (B-F; bond formation). In the simulation ∼10% of all atoms lost or gained a neighbor. Because atoms that have changed their local topology correspond to the shear deformed groups, we have combined these $g_2^0(r)$ (B-B and B-F) into a group that has experienced local topological change (LTC), as shown in Fig. 3(a). The MD result looks qualitatively similar to the experimental data in Fig. 2(a) in spite of the difference in composition and time scale. The PDF for LTC atoms and the PDF expected for affine deformation scale well at large r and differ significantly in the first atomic shells. Figure 3(b) shows the difference, $g_{2,\mathrm{aff}}^0(r) - g_2^0(r)$, between the affine and LTC, and the affine and total (average). Despite the differences in composition and temperature, the result for LTC atoms in Fig. 3(b) is very similar to that in Fig. 2(b). The plot shows that the local relaxation, which is represented by the difference between the affine and the measured $g_2^0(r)$, originates mostly from the atoms that changed their local topology, even though they represent only ∼10% of all atoms, and suggests that the mechanism of thermomechanical creep is local structural relaxation of the applied stress by cutting or forming the atomic bonds. In particular, the bonds are severed in a direction of the applied stress, and new bonds are formed in the perpendicular direction. Such bond-exchange processes produce the bond orientational anisotropy previously proposed to explain the structural change after thermomechanical creep [4].

In this Rapid Communication we have demonstrated that the pattern of change in the structure function induced by thermomechanical creep is independent of the duration, magnitude, and sign of the stress applied during creep, suggesting the presence of a well-defined, unique, universal mechanism. The structural changes described by the anisotropic PDF are strongly localized to within the second nearest neighbors, and are characterized by the cutting and forming of atomic bonds. Even though the exact details of the changes in the structure are different for each occurrence of local deformation, statistically they result in the repeatable changes in the anisotropic PDF. These actions of cutting and forming of atomic bonds are similar to the elementary excitations in the liquid state [26] in spite of the vast differences in time scale and temperature. It is likely that the process of changing the local topology of atomic connectivity by cutting and forming the atomic bonds is the basic process of excitation and structural change, both in the liquid state and in the glassy state. This structural behavior may be related to the basic relaxation mechanism in glasses [27,28]. If the results were to be explained in terms of the STZ, the STZs are strongly localized, and composed of cutting and forming local atomic bonds.

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