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Homogeneous deformation of metallic glass at room temperature reveals large dilatation

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Room-temperature uniaxial compression of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass at 80% of the yield stress leads to homogeneous viscous flow. The flow in this apparently elastic regime reveals large increases in volume associated with local shearing events in the glass. The extent of this dilatation is masked in more usual tests by significant relaxation of the glass structure during and after shear. The dilatation in deformed metallic glasses can no longer be attributed only to free-volume generation at shear bands.

Keywords: Acoustic methods; Anelastic behavior; Bulk metallic glass; Creep; Elastic behavior

Glassy alloys (metallic glasses) exhibit a high elastic strain limit of about 2% and plastic-deformation mechanisms quite different from those of their crystalline counterparts [1–3]. At relatively low stress and high temperature approaching the glass-transition temperature (T_g), the deformation is homogeneous, each volume element of the material exhibiting similar strain. Well below T_g the deformation is inhomogeneous, the flow occurring in a small volume fraction of the material, localized on very thin shear bands [4]. It is expected that deformation induces disordering and dilatation of the glassy structure, and that relaxation acts to reduce such effects [5–7]. In inhomogeneously deformed samples, there is evidence for structural change in the shear bands, resulting from the very high local shear, and possibly also linked to local heating and rapid cooling [8]. However, homogeneous deformation typically occurs and is studied at high temperatures where relaxation dominates, and the effects of deformation are correspondingly difficult to detect in the final structure. Recent work [9,10] shows that, given sufficient time, homogeneous deformation can be detected under 'elastostatic' (i.e. at a stress less than the yield stress σ_y) loading at room temperature (RT). In the present work we exploit elastostatic compression, at RT to suppress thermal relaxation, to study the changes in volume and in elastic moduli accompanying homogeneous deformation. Remarkably, clear effects are found even for very low plastic strains (down to 2×10^{-5}).

For crystalline alloys at low homologous temperature, loading well below σ_y induces strains considered to be purely elastic. For glasses, however, it has long been noted in atomistic simulations that loading in the elastic regime, can induce irreversible structural changes [11]. A clear experimental demonstration, by Lee et al. [9], showed that uniaxial elastostatic compression of a Ni-Nb glass (at 95% of σ_y for 30 h at RT) induced homogeneous flow (creep), accompanied by an increase in the stored heat of relaxation (taken to be a measure of structural disorder or free volume), and a marked increase in compressive plasticity when subsequently tested beyond σ_y. These features have been verified in several later studies, mostly focused on model binary Cu–Zr glasses showing a range of atomic packing density. Park et al. [10] noted that a higher packing density is associated with a higher σ_y and lower plasticity. Increases in heat of relaxation and in plasticity resulting from elastostatic loading (at 90% of σ_y for 12 h at RT) are much larger in glasses with higher initial packing density, and the increases appear to be associated with destruction of dense atomic clusters with icosahedral

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configuration [10]. At longer loading times, the heat of relaxation saturates, suggesting that under given conditions there is a maximum allowable degree of disorder or free volume. As emphasized in recent work [12], a particular reason for interest is that the structure changed by homogeneous flow at RT may be closely related to that in shear bands.

In the extensive work on elastostatic loading of Ni–Nb and Cu–Zr glasses [9,10,12–14], the structural changes have been indirectly quantified only by measuring the heat of relaxation. In the present work, we extend these studies by attempting a direct measurement of the volume change accompanying deformation, thus permitting a link with models, such as that of Spaepen [4], in which shear-driven atomic motion creates free volume.

Park et al. [10] showed that elastostatic loading reduced the Young modulus of Cu–Zr glasses. But, as discussed for example by Cheng and Ma [15], different elastic moduli vary enormously in their sensitivity to structural changes, the extremes being the shear modulus G (sensitive) and the bulk modulus B (insensitive). In this work we attempt a more complete appraisal of the effects of elastostatic loading on elastic moduli and thereby aim to better elucidate the nature of the induced structural changes.

The bulk metallic glass (BMG) chosen for this study is $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy 4, composition in at.%), an easy glass-former that is expected to have a high atomic packing density, and therefore (according to Ref. [10]) to show larger changes in structure on homogeneous deformation. Its glass-transition temperature T_g is 623 K [16], and room temperature (298 K) thus corresponds to a reduced temperature (T/T_g) of 0.48, very well within the regime in which plastic deformation is expected to be inhomogeneous [4]. This glass is brittle at room temperature, showing no plastic strain prior to failure in typical tests. It was prepared by arc-melting the elemental components under a Ti-gettered argon atmosphere. A cylinder, 5 mm in diameter and 50 mm long, was cast in a water-cooled copper mold. Two samples 14 mm long were cut from this by diamond saw. The ends of the samples were carefully polished flat and normal to the longitudinal axis, as required for uniform loading in compression and for subsequent ultrasonic measurement. The samples were uniaxially loaded at a strain rate of $1 \times 10^{-4}\ s^{-1}$ (Instron electromechanical testing system 3384) up to a limiting compressive stress at which they were held for periods of several hours. All the compression treatments were at RT, loading at 80% of the metallic-glass yield strength (σ_y = 1.83 GPa [16]), a lower fraction than used in previous works on elastostatic loading [9,10]. An extensometer between the upper and lower SiC platens of the testing machine recorded the strain response of the samples during the loading–unloading cycle. After the cycle, the samples were held at RT to recover the anelastic strain. Then, acoustic velocities were measured (MATEC 6600 ultrasonic system) parallel to the rod axis using a pulse-echo-overlap method with a carrier frequency of 10 MHz and a resolution of 0.5 ns. The density of the samples was measured using Archimedes' method to 0.1% accuracy. Values of the Young modulus E, shear modulus G and bulk modulus K were derived from the acoustic velocities [17,18], assuming that the glass is isotropic. The measured properties of the as-cast glass are: density = 5998 ± 4 kg/m^3; E = 93.30 ± 0.07 GPa; G = 34.53 ± 0.03 GPa; K = 104.44 ± 0.08 GPa.

The stress–strain curve of a sample loaded for 5 h, and then unloaded (Fig. 1) shows creep and strain recovery. Just as seen in earlier studies of elastostatic loading [9,10], the total strain has three components. Upon removal of the stress, the elastic strain ε_e is instantaneously recovered, and the anelastic strain ε_a (caused by recoverable atomic adjustments in response to an applied stress) is recovered gradually. In contrast, the viscoplastic strain ε_v reflects permanent, irrecoverable deformation (Fig. 1b). However long the loading, no shear bands are observed: the deformation is homogeneous.

Although near the measurement limit, there are clearly detectable changes (Fig. 2) in density, acoustic velocities, and elastic moduli with compression time within the apparently elastic region. These properties, measured after recovery of the anelastic strain, can be taken to vary linearly with time. The saturation in heat of relaxation seen by Park et al. [10], set in at a viscoplastic strain of $(5\text{–}10)\times10^{-4}$. The present measurements extend up to $\varepsilon_v = 2.3 \times 10^{-4}$, and so are expected to be within the linear regime seen at low strains in the previous work.

The density decreases with elastostatic loading time (Fig. 2a), indicating that dilatation induced by the deformation outweighs any densification from the hydrostatic component of the applied stress. This dilatation is consistent with the disordering and the creation of free volume inferred from increases in the heat of relaxation measured in earlier studies on elastostatic loading [9,10]. Earlier work [10] has discounted the possibility of detection of density change, but the present results allow the change to be quantified.

The relative changes in longitudinal (V_l) and shear (V_s) acoustic velocities (Fig. 2b) can be used to calculate

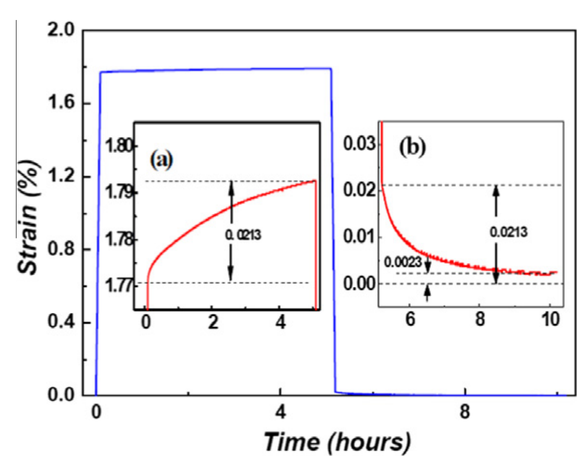

Figure 1. Stress–strain curve for a Vitreloy 4 sample elastostatically compressed at RT at 80% of the yield stress for 5 h and then unloaded. The insets show close-ups of the anelastic (a) compression and (b) recovery.

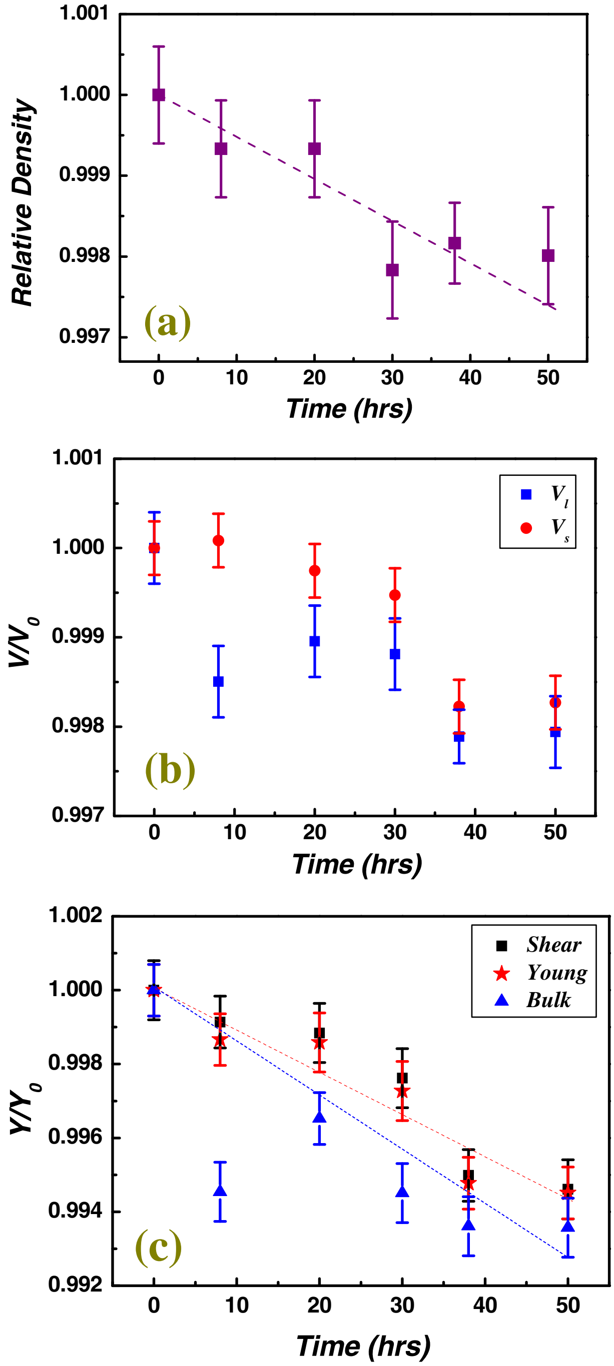

Figure 2. Variation of (a) relative density, (b) acoustic velocities and (c) elastic moduli for Vitreloy 4 elastostatically loaded at 80% of σ_y at RT. The dashed lines show linear-regression fits to the data to guide the eye.

the relative changes in elastic moduli. The Young modulus (E) and shear modulus (G) decrease by similar small amounts, while the bulk modulus (K) decreases rather more (Fig. 2c). The relative decrease in E is roughly 25 times the viscoplastic strain, less than the relative decrease noted in Ref. [10], which is at least $\sim 80\varepsilon_v$ for the most densely packed Cu–Zr glass and even higher for the others. The Young's modulus measurement in Ref. [10] was by nanoindentation, and may therefore not be directly comparable with the acoustic measurements in the present work. The bulk modulus, representing the response to hydrostatic loading is expected to be directly related to density [15], decreasing as the sample dilates. The relative decrease in K is nearly three times the relative decrease in density, however. The surprise in the present results is that the relative change in G (and in E) is so small relative to the change in K. Studies of structural relaxation in metallic glasses [19–22] show that the elastic moduli increase, the changes in K being much smaller than the changes in G or E [15,23]. Thus, while the elastostatic loading gives changes of opposite sign to those induced by annealing, the relative magnitudes of the changes for the different moduli suggest that the effect of elastostatic loading (which could be thought of as 'rejuvenation') is clearly not a simple reversal of relaxation.

Homogeneous deformation of a metallic glass may induce structural changes that can be interpreted as bond-orientational ordering, leading to anisotropy [24,25]. In the present work, the modulus values have been calculated from the measured acoustic velocities on the assumption that the glass remains isotropic. Any induced anisotropy would leave trends unaffected, but could affect the modulus values. To determine the possible effects of the elastic anisotropy, we measured the acoustic velocities parallel and perpendicular to the loading direction of a sample elastostatically compressed for up to 50 h. Within the experimental error of up to 0.04%, there was no detectable anisotropy, possibly because the viscoplastic strain induced by the elastostatic loading is so small (up to 2.3×10^{-4}).

Earlier studies showed that elastostatic compression, to viscoplastic strains of $(2–4)\times10^{-3}$, can give dramatic increases in plasticity in subsequent testing [9,10]. In contrast the Vitreloy 4 glass in the present work is still brittle under uniaxial compression, even after elastostatic loading for 38 h; this may be because the viscoplastic strain is roughly one order of magnitude lower than in the earlier work. However, the fracture of the Vitreloy 4 is affected by the elastostatic loading, becoming more symmetric, consistent with the pre-loading inducing flow and thereby giving a more uniform stress distribution in the test sample.

We now focus on the magnitude of the dilatation induced by elastostatic compression. Loading for 50 h, the viscoplastic strain is 2.3×10^{-4}, associated with a fractional density decrease (Fig. 2a) of 2.6×10^{-3}. The density change though large, roughly ten times the viscoplastic strain, is broadly consistent with the observed fractional decreases in elastic moduli of $(6–7) \times 10^{-3}$ (Fig. 2c).

In randomly packed structures, such as in soils and granular media in general, shear often induces dilatation [26,27]. The phenomenon is well known in the deformation of metallic glasses [6,28,29]. Cahn et al. [6] cold-rolled $Pd_{77.5}Cu_6Si_{16.5}$ BMG to reductions of 30–40% in thickness and showed that this led to a density decrease of 0.15%, reversible by annealing. Attributing this to a change in the shear bands alone, gives a dilatation in the bands of some 15%, a figure that Cahn et al. suggest is too high to be likely. They concluded that free volume created in the bands must diffuse away from them into the matrix. Argon et al. [30] conducted RT compression tests on the same BMG up to strains of 66%. At that strain they estimated that only one third of the deformation was attributable to the operation of shear bands. They measured a density decrease, and by attributing it entirely to the shear bands, they concluded that the dilatation in the bands was 54%. They assumed that such a high value is possible through the formation of nanocavities [29].

Thus earlier work, though recognizing that there may be homogeneous deformation accompanying shear-band operation at RT, assumed that free-volume production is only in the shear bands. And while recognizing that there may be dilatation of the matrix between shear bands, this was attributed only to the diffusion of free volume from the bands.

In contrast, our results suggest that free volume can be generated very effectively in a matrix with no shear bands. For inhomogeneous deformation, it is considered that free volume is created when misfitting atoms enter coordination shells, forcing their expansion [4]. The fundamental unit of deformation in metallic glasses, proposed by Argon [30], is the shear transformation zone (STZ). Local shear in an STZ is activated under load, and coordinated activation of STZs can lead to the development of shear bands. Much attention has been paid to the generation of free volume in shear bands, where the associated strain softening is the origin of the sharp localization of shear. There has been less work on the effects of homogeneous deformation. Following Argon [30], we take the simple shear strain (ε_{12}, when $\varepsilon_{21} = 0$) associated with an STZ to be of order 0.1; this corresponds to a pure shear ($\varepsilon_{12} = \varepsilon_{21}$) of 0.05. The activated STZs in the sample occupy a volume fraction that we denote as F. The pure shear of the overall sample can be estimated as the volumetric average strain $0.05F$; this corresponds to a normal uniaxial strain $0.1F$. Taking the uniaxial strain to be ε_v, and taking the value 2.3×10^{-4} after 50 h of loading, we have $F = 2.3 \times 10^{-3}$. At this point, the fractional increase in sample volume is 2.6×10^{-3}. Attributing this entirely to free-volume production within STZs, and again using a volumetric average, the fractional increase in volume of an STZ is $(2.6 \times 10^{-3})/F \approx 1$ (i.e. a dilatation coefficient of order 1 [31]). Thus, for each atom in an activated STZ the free volume generated is roughly an atomic volume. This is a large increment in volume, yet appears consistent with the significant decreases in measured values of elastic moduli.

In summary, the effects of elastostatic loading reported in Refs. [9,10] are not restricted to model binary metallic glasses, but can be found in the multicomponent BMG Vitreloy 4. This shows plastic deformation at RT (less than 50% of T_g) under uniaxial compression at 80% of the yield stress σ_y. This RT creep is homogeneous and leads to decreases in density (measured directly for the first time) and in elastic moduli. It is inferred that the local volume increase associated with each atom in a shear transformation zone, even after relaxation to remove anelastic strain, is of the order of one atomic volume. Dilatation has long been associated with plastic flow in metallic glasses, but such a strong effect has previously been masked by structural relaxation, either in higher-temperature studies of homogeneous flow, or locally in shear bands where there may be self-annealing associated with heating. The large dilatation associated with homogeneous flow forces reinterpretation of earlier results on volume changes in metallic glass samples deforming inhomogeneously: it is no longer safe to assume that free volume generation occurs only in shear bands.

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