Extraordinary Plasticity of Ductile Bulk Metallic Glasses

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Shear bands generally initiate strain softening and result in low ductility of metallic glasses. In this Letter, we report high-resolution electron microscope observations of shear bands in a ductile metallic glass. Strain softening caused by localized shearing was found to be effectively prevented by nanocrystallization that is *in situ* produced by plastic flow within the shear bands, leading to large plasticity and strain hardening. These atomic-scale observations not only well explain the extraordinary plasticity that was recently observed in some bulk metallic glasses, but also reveal a novel deformation mechanism that can effectively improve the ductility of monolithic metallic glasses.

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The most notable property of bulk metallic glasses (BMGs) is their ultrahigh strength and hardness [1,2]. Nevertheless, BMGs generally suffer from low ductility at low temperatures. Room-temperature plastic deformation of metallic glasses has been known to be accomplished through shear bands in which plastic flow driven mainly by shear stresses is localized within a nanoscale zone [3–6]. Because of structural and/or thermal softening, these bands are preferential sites for further plastic flow and lead to the final failure that typically breaks a sample along a single shear band [3,6]. Therefore, the highly localized shearing and resultant strain softening are responsible for the low ductility of BMGs. It has been widely recognized that the ductility improvement of BMGs virtually depends on the suppression of the localized strain softening caused by shear bands. A straightforward strategy is to introduce crystalline phases into BMGs to form BMG-based composites. The crystalline phases can provide dislocation-related work hardening to suppress the strain softening of a single shear band and to promote the generation of multiple shear bands in glassy matrixes. In fact, enhanced plasticity has been observed in a number of BMG-based composites [7–9]. However, as the expenditure of the improved plasticity, the crystalline phases generally cause more or less reduction in strength [8,9]. More recently, extraordinary plasticity and work hardening were observed in Pt- and Cu-based monolithic BMGs with high strength [10,11]. Although a number of explanations have been suggested, including high Poisson's ratio [10] and structure inhomogeneity [12,13], the underlying physical mechanism, in particular, microscopic explanation, remains a mystery. In this Letter, we report atomic-level observations of shear bands in a ductile $Zr_{50}Cu_{50}$ BMG and uncover a new mechanism on enhanced plasticity and work hardening in amorphous materials.

The binary $Zr_{50}Cu_{50}$ BMG used in this study has been found to have very high plasticity and ~50% compression strain has been obtained at room temperature [11], which is much higher than that ($< 2\%$) of most BMGs. Although this alloy has very good glass forming ability and glassy bars with a diameter of about 2 mm can be fabricated [14], to ensure that the as-prepared alloy is fully glassy, melt-spun ribbons with a thickness of about 30 μm were selected in this study to explore the deformation mechanism of the ductile BMG. Transmission electron microscope (TEM) specimens were prepared by electrochemical polishing at low temperatures [15]. Figure 1(a) shows a high-resolution electron microscope (HREM) image of the as-spun $Zr_{50}Cu_{50}$ alloy. Mazelike clusters, which are the typical feature of metallic glasses, can be widely observed [16]. In addition, a halo pattern obtained by fast Fourier transform (FFT) combining with a Fourier-filtered image [Fig. 1(b)] further demonstrate that the as-spun ribbons are fully amorphous without any visible nanocrystalline particles.

The plastic deformation was introduced by manually bending the ribbons to ~180° and then straightening them to approximately flat [17–19]. It was found that the ribbons are very ductile and cracks have not been seen after the bending tests, apart from multiple shear bands on the surfaces. In contrast, $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Ag_{10}$ ribbons were broken when subjected to the same deformation. After the bending tests, deformed regions, about 1–2 mm in width, were thinned to electron transparence by electrochemical polishing for subsequent TEM observations. A number of shear bands with widths ranging from 2 to 20 nm and lengths of several microns can be easily found in the plastically deformed specimens. Figure 2(a) shows an example imaged by bright-field TEM at a low magnification. A 3–10 nm wide shear band spans the thin region of a TEM sample and gradually loses its contrast in the thick region. In both bright-field TEM and HREM [Fig. 2(b)], the shear bands appear lighter than the regions outside the bands, which may come from the mass-contrast difference produced by either less thickness or the lower density of the shear bands [20]. The detailed structure of the shear bands was examined using HREM [Fig. 2(c)]. Sub-nanometer-sized maze structures within the shear band appear slightly coarser than those in the region outside. These structures may correspond to the shear transformation

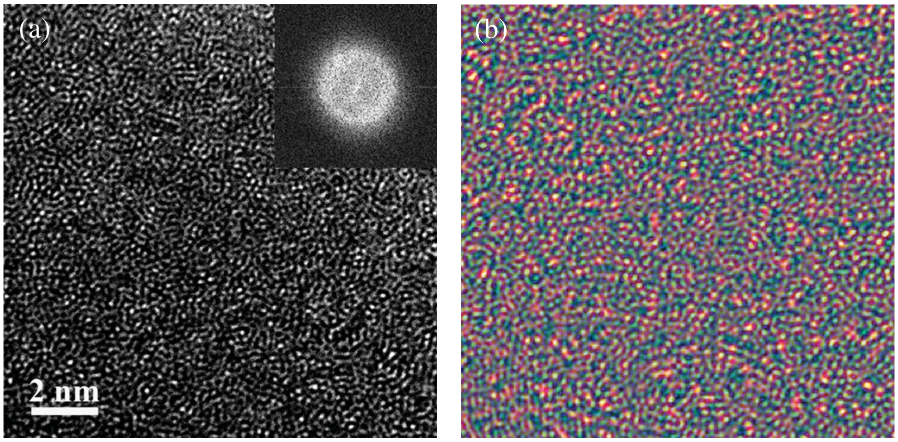

FIG. 1 (color). (a). HREM image and FFT pattern of the as-spun $Zr_{50}Cu_{50}$ BMG. (b). Fourier-filtered HREM image that was reconstructed by a series of images produced with a different aperture sizes.

zones predicted by prevailing theory [4,5] and atomistic simulations [21,22]. However, except these qualitative observations, the structure changes are too small to be quantitatively described.

Interestingly, a number of nanocrystallites that have not been seen in the as-spun ribbons were observed within shear bands in the plastically deformed $Zr_{50}Cu_{50}$ metallic glass [Fig. 2(b)]. The sizes of these nanocrystallites are about 5–20 nm in diameter, close to the width of shear bands. The formation of the nanocrystallites appears to be induced by plastic deformation because nanocrystallites were only observed within the shear bands and cannot be found in the regions outside the bands. Although the underlying mechanism of the deformation—induced nanocrystallization has not been entirely understood, it is highly possible that both the temperature rise and the mass transportation produced by significant plastic flow promote the formation of nanocrystals within the narrow shear bands [18,19,23,24]. Intrinsically, the precipitates of nanocrystallites may be more associated with the low stability of the $Zr_{50}Cu_{50}$ BMG because the crystalline phase was not found in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Ag_{10}$ samples deformed by the same manner. Additionally, a large number of nanocrystallites, which have not been found in the as-prepared

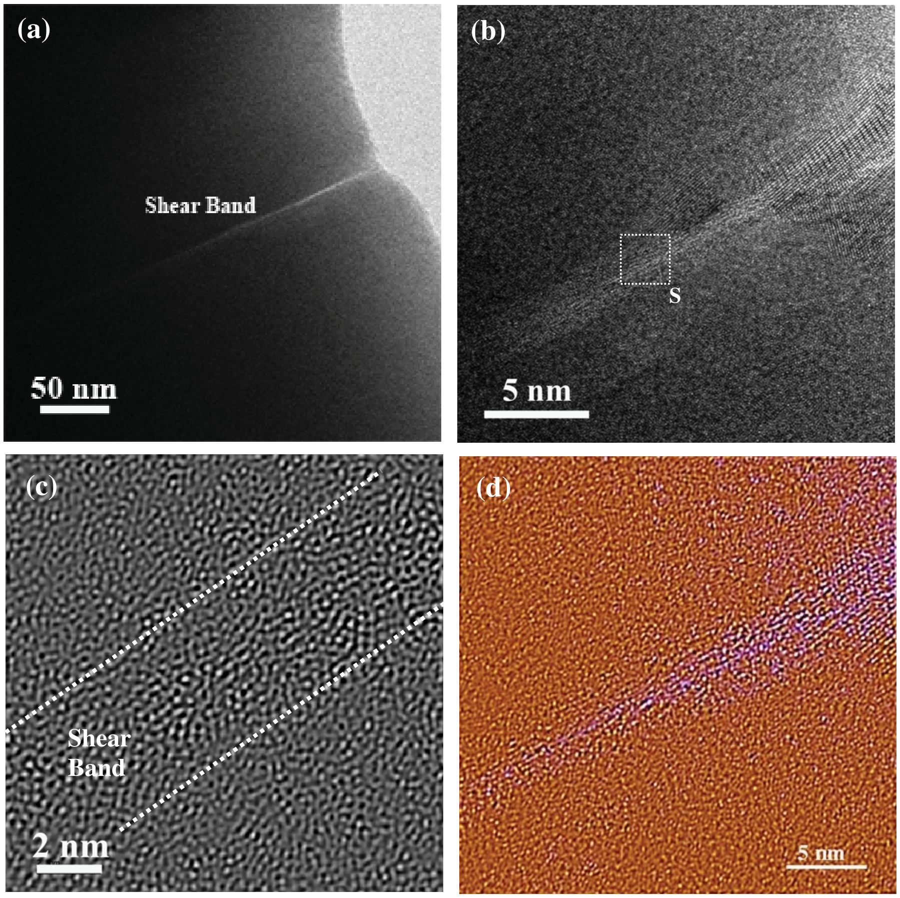

FIG. 2 (color). TEM observations of shear bands in the deformed $Zr_{50}Cu_{50}$ BMG. (a) Bright-field TEM image of a narrow band with lighter contrast across the thin region of the TEM specimen. (b) Low-magnification HREM image of a shear band with precipitate nanoparticles. (c) HREM image of the shear band, taken from the region S in Fig. 2(b). Slightly coarser maze clusters within the shear band can be seen. (d) Fourier-filtered HREM image showing that a shear band gradually becomes wider as approaching a nanoparticle.

$Zr_{50}Cu_{50}$ BMG bars with an initial diameter of ~1 mm, have been observed in the cold-rolled samples. Quantitative HREM measurements and FFT analysis suggest that the deformation-induced nanocrystalline phase is a monoclinic CuZr that is metastable at room temperature [25]. The unit cell of this phase is about $0.52 \times 0.26 \times 0.53$ nm and the β angle is ~105°. The chemical composition difference between the nanophase and glassy matrix cannot be detected by x-ray energy-dispersive spectrometry and electron energy-loss spectroscopy. It is worthy of noticing that the deformation-induced nanophase is different from all the reported crystalline phases produced by thermal processing in the $Zr_{50}Cu_{50}$ alloy, including orthorhombic $Cu_{10}Zr_7$ [26], hexagonal intermediate compound $Cu_{51}Zr_{14}$ [14], and complex cubic Cu_5Zr [11]. In comparison with those equilibrium phases with compositions significantly different from the glassy matrix, the monoclinic CuZr that has the same composition as the parent glass can be formed much easier by a polymorphic transition without the requirement of long-range composition redistribution.

Strong interaction between shear bands and nanocrystallites can be witnessed from the morphology changes of shear bands and the generation of crystal defects in the nanocrystals. Figure 2(d) shows that a shear band gradually becomes wider from 2 nm to about 5 nm when the band approaches a nanocrystal. Both elastic shear stress (τ) and shear strain (γ) are in inverse proportion to the shear-band width (ω), i.e., $\gamma = \Delta\omega/\omega$, and $\tau = \boldsymbol{G}\gamma$, where $\boldsymbol{G}$ is shear modulus and $\Delta\omega$ is elastic displacement along shear bands. For constant $\Delta\omega$ and $\boldsymbol{G}$, the width increase of a shear band reduces the elastic shear stress and strain in the vicinity of the nanoparticles, and thereby impedes the further propagation of the shear band because higher applied force will be required to maintain the shear stress that can keep the shear flow continuously along the band.

The plastic deformation of the nanocrystallites embedding in the shear bands is evidenced by the appearance of crystal defects that are the deformation carriers in crystalline solids. Dislocations, stacking faults, and deformation twins have been witnessed in deformation-produced nanocrystallites [Fig. 3(a)], similar to the heavily deformed nanocrystalline metals [27]. The Burgers vector of the dislocations was measured to be $\langle 001 \rangle$ and $\langle 1\bar{1}0 \rangle$, and the line directions are along $\langle 110 \rangle$ [Fig. 3(b)], suggesting that they are edge dislocations. The slip planes of deformation twins and stacking faults were determined to be on $\{001\}$ and partial dislocations can be identified at the twin interfaces and the tail of the stacking faults [Fig. 3(c)]. These defects are believed to be produced by the strong interactions between the shear band and the nanocrystal because extensive microscopic observations have demonstrated that the nanocrystallites produced by annealing are generally perfect crystals and free of various crystal defects [28]. These observations indicate a transition of deformation mode from shear bands in glass matrix to twinning and dislocation gliding in the nanocrystals. Definitely, these crystal defects generated in the nanocrystals produce strain hardening that can compensate for the strain softening of shear bands, and thereby effectively suppress the autocatalystic plastic flow and catastrophic failure along a single shear band. Moreover, the extensive crystal defects in the nanocrystals suggest that the *in situ* formed nanocrystalline phase is ductile and can be plastically deformed, which is believed to be an important factor to achieve the extraordinary plasticity.

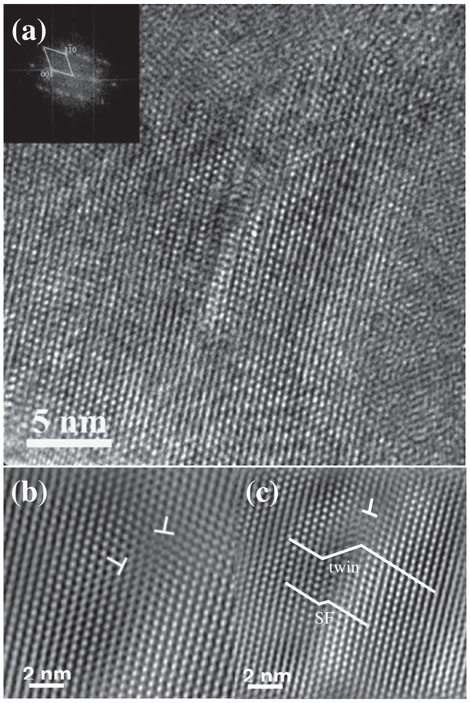

FIG. 3. Crystal defects in the nanoparticles shown in Fig. 2(b). (a). Heavily distorted crystal lattices with dislocations and twins. These crystal defects associated with the plastic deformation were highlighted by the Fourier-filtered images in (b) and (c). (b) Two edge dislocations with Burgers vectors of $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$, respectively; and (c) deformation twins, stacking faults, and partial dislocations.

It has been reported that severe bending and nanoindentation testing can induce the formation of nanocrystallites in Al-based and Zr-based metallic glasses [18,19,23]. Although the formation of nanocrystals is apparently associated with localized shearing flow, the influence of deformation-induced nanocrystallization upon the mechanical performance, in particular, plasticity, has not been discussed before. Interestingly, according to our observations, the deformation-induced nanocrystals are found to prevent the plastic flow within the shear band as shown in Figs. 2 and 3 and the aforementioned discussion. To sustain a plastic deformation rate in a specimen during mechanical testing, new shear bands need to be generated when an active shear band is blocked due to the formation of nanocrystallites. Generally, the nucleation of shear bands prefers to occur at weak sites, such as casting defects (porosity and inclusions) and surface flaws, where high concentrated stresses are easily generated [29]. The critical stresses to drive the formation of new shear bands will gradually increase from easy to difficult nucleation sites. During this deformation process, the applied force is required to progressively increase to keep continuous plastic deformation, which results in "work hardening" and the formation of multiple shear bands as has been observed in compression experiments [10–12]. Apparently, this type of work hardening is different from the classical one that results from the interaction among defects, such as dislocations, deformations twins and grain boundaries, in crystalline materials [30].

Although partially nanocrystallized BMGs produced by thermal annealing have been reported to exhibit enhanced plastic strains (for examples Ref. [7]), the improvement in plasticity is still much limited in comparison with the monolithic BMGs that own "self-locked" shear bands. To effectively prevent the work softening of shear bands that initiate at random sites, a high density of nanoparticles are required to uniformly distribute in the annealed alloys. Because shear bands are the only plastic deformation manner in BMGs, in addition to preventing work softening caused by autocatalystic plastic flow of shear bands, the high density of nanoparticles also affect the nucleation of shear bands and limit their propagation and thereby plasticity. This opinion is supported by the fact that the partially nanocrystallized $Zr_{50}Cu_{50}$ BMG that is prepared by annealing, or casting to a large size (3 mm in diameter), dramatically loses its plasticity from ~30%–50% compression strain to below 5%. In contrast, the self-locked shear bands are highly advantageous because a large amount of plastic shearing can occur prior to the precipitation of nanocrystallites that block further plastic flow along shear bands. Therefore, the deformation-induced *in situ* nanocrystallization allows the nucleation and propagation of shear bands, but prevents runaway localized plastic flow due to work softening and hence catastrophic failure along a single shear bands. Therefore, the novel work hardening and deformation process in $Zr_{50}Cu_{50}$ BMG uncovered by our HREM observations has important implications for developing monolithic BMGs that have both high strength and excellent ductility [31].

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