The onset of plasticity of a Zr-based bulk metallic glass

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Abstract

The onset of plasticity of a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glassy alloy under step-controlled tensile loads has been studied *in-situ* and systematically using scanning electron microscopy and synchrotron X-ray diffraction. A circular hole, as a stress concentrator, was introduced in the middle of the gauge length of the sample to facilitate the creation of shear bands in a controllable way at the edge of the hole, and therefore *in-situ* imaging and diffraction studies can be carried out at the identical loads in a quasi-steady state manner. A pair distribution function was used to calculate the strains of different atomic coordination shells and different atomic pairs. The combined imaging and diffraction studies revealed that (1) the nucleation of shear bands is the resulting dilatation of solvent-solvent (Zr-Zr) atomic pairs under tension, and (2) the propagation of shear bands can be controlled by the stress field around them, and a compressive stress field of ~-0.5 GPa can effectively slow down the rate of shear band propagation.

Keywords: Bulk metallic glasses; Shear bands; Electron microscopy; Plasticity; Synchrotron radiation

1.   Introduction

Amorphous metals, or metallic glasses, have attracted a great deal of scientific interest from physics, materials and engineering communities since the first discovery in a rapidly quenched $Au_{75}Si_{25}$ alloy in 1960 (Klement et al., 1960, Fornell et al., 2009). Intensive research has been carried out continuously around the world to design and develop amorphous alloy systems that have a combination of exceptionally high strength, wear and corrosion resistance, and other functional properties (Inoue and Takeuchi, 2011; Axinte, 2012). Breakthroughs in alloy design and development were made when the bulk metallic glasses (BMGs) concept was introduced and empirical rules for alloy design were established in the 1990s (Inoue and Takeuchi, 2011; Chen and Lin, 2010; Jiang et al., 2008a). Hundreds of new glassy alloys have been found or developed in the past 50 years. However, fundamental issues remain for almost all metallic glassy systems developed so far: (1) very low global plasticity especially under tensile loads, and (2) lack of practical solutions to improve the global plasticity (Schuh et al., 2007; Greer, 1995; Wang et al., 2004; Jiang et al., 2008b; Wu et al., 2011). It is therefore essential to study the fundamentals of plasticity of BMGs and identify the mechanism which enhances plasticity for different alloy systems.

It is commonly known that plastic deformation in BMGs is highly localized within shear bands of $10\sim20$ nm thick (Zhang et al., 2003; Li et al., 2013), and the plastic flow is preferably along the narrow shear bands (Huang et al., 2007; Huang et al., 2012), causing catastrophic failure along those shear bands, and near zero global plasticity for most of BMGs systems (Pan et al., 2011; Jiang and Dai, 2011; Kuzmin et al., 2012a,b). The near zero plasticity makes it very difficult to capture the onset of plasticity and study the subsequent dynamics of shear bands.

The development of third generation synchrotron light sources has made high energy, high flux,

and tunable X-ray beams suitable for studying *in-situ* the deformation of materials (Hendrickson, 1991; Pfeifer et al., 2006; Yavari et al., 2005; Poulsen et al., 2005; Wang et al., 2009; Wang et al., 2007; Ott et al., 2005). Using synchrotron X-ray diffraction to study the deformation of BMGs, Hufnagel *et al.* (Hufnagel et al., 2006) first reported that the strains measured in a metallic glass by synchrotron X-ray diffraction agreed with macroscopic measurements. Wang *et al*. (Wang et al., 2012) found that atomic reorientation takes place in the first atomic shell. Chen *et al*. (Chen et al., 2013) established the relationship between the stress-induced structure change and the tension-compression asymmetry of plasticity of a Zr-based BMG; and Qu *et al.* (Qu et al., 2013) explored the structural origins of the high plasticity of a ZrCuNiAl BMG. The above studies confirmed that synchrotron X-ray diffraction is an effective method for studying strain evolution and structural evolution during the deformation of BMGs. Over the approximately same period of time, high resolution electron microscopy, including scanning electron microscopy (SEM) (Li et al., 2003; Cao et al., 2010; Bouzakher et al., 2007) and transmission electron microscopy (TEM) (Chen et al., 2012; Wang et al.,2012), were also used to study *in-situ* the deformation behaviors of metallic glasses. For example, Li *et al*. (Li et al., 2003) investigated the formation and growth of shear bands in two Zr-based metallic glasses and suggested that the normal stress plays an important role in shear band evolution. Hajlaoui *et al*. (Hajlaoui et al., 2006) observed the shear band evolution of a metallic glass containing nanoparticles inside a TEM and found that nano-scale crystals grow in shear bands, and blunt cracks. Using TEM, Chen *et al*. (Chen et al., 2010) performed compressive tests on metallic glass pillars with different diameters and concluded that the deformation is nucleation-controlled in larger pillars but becomes propagation-controlled in smaller pillars. Deng *et al*. (Deng et al., 2011) studied the tensile deformation of a binary glass inside a TEM and attributed its uniform tensile elongation as large as 12 % to the suppression of shear banding

instability. However, it should be pointed out that most of the previous *in-situ* work either used electron microscopy to perform imaging studies, or used synchrotron X-ray diffraction to obtain the strain/stress information. Complementary studies using both electron microscopy and synchrotron X-ray diffraction establish the links between the atomic strains, and the observed shear band nucleation and propagation have not been widely reported.

In this research, we studied *in-situ* the tensile deformation behaviors of Zr-based metallic glass samples using both electronic microscopy and synchrotron X-ray diffraction techniques. A circular hole was drilled at the middle of the gauge length of the dog-bone shaped BMG samples to create a stress concentration, which facilitates shear band nucleation and propagation when controlled load steps are applied. The atomic shell and relative bond lengths were calculated from the X-ray diffraction patterns acquired using pair distribution function (PDF) analysis, and were linked with the nucleation of shear bands. The effect of stress fields on the propagation of the shear bands was also investigated and revealed, for the first time, that the compressive stress field ahead of the shear bands can effectively slow down the rate of shear band propagation.

2. Experimental

A Zr-based bulk metallic glassy alloy, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at. %), was selected as the experimental alloy because of its high glass forming ability (Peker and Johnson, 1993). The master alloy ingots were made by arc melting a mixture of Zr, Ti, Cu, Ni, and Be elemental button ingots (each with a purity > 99.9 %) in a Ti-gettered argon atmosphere. The master alloys were remelted four times to homogenize the composition and then cast into a copper mold to form plate-shaped samples with a dimension of $3\times30\times60$ mm^3. Dog-bone shaped tensile samples with a gauge length of 6.75 mm, a thickness of 0.5 mm and a width of 1.5 mm were electrical discharge machined from

the as-cast alloy plates as shown in Fig. 1a. For some of the BMG samples tested, a 400 μm diameter hole was drilled at the middle of the gauge length, and this geometrical feature proved to be very effective in controlling the nucleation of shear bands and their subsequent propagation due to the creation of a stress gradient near the hole during the tensile tests. The onset of plasticity in the Zr-based BMG is a highly transient and often uncontrollable phenomenon. The use of a stress-concentrating hole to localize shear band nucleation enabled the onset of plasticity to be studied in a much more controllable manner during *in-situ* imaging and diffraction experiments. The samples to be tested were firstly ground using SiC grind papers (400, 800 and 1200 grit sizes) and then sequentially polished using diamond suspensions of 6, 3 and 1 μm, respectively, and finally 0.025 μm colloidal silica suspension. Tensile tests were carried out using a multi-purpose micromechanical straining rig, Deben MICROTEST module 2000 with load-step control mode until sample failure. Fig. 2 shows schematically the *in-situ* acquisition of synchrotron X-ray diffraction at each load step during the tensile tests at the Joint Environmental, Engineering and Processing beamline (I12) of Diamond Light Source, Oxfordshire, UK. Monochromatic X-ray beams (98.856 keV, 0.25×0.25 mm^2 spot size) and a two-dimensional (2-D) detector, Pixium RF4343 were used to acquire *in-situ* diffraction patterns at the three locations marked by P1, P2, and P3 shown in Fig. 1b. NIST 674b Cerium Oxide powders were used to calibrate the X-ray energy, and the sample-to-detector distance was set at 472.85 mm to achieve a high value (~ 20 Å^{-1}) for the scattering vector Q ($Q = 4\pi \sin\theta / \lambda$). At each load step, thirty diffraction patterns were acquired (4 seconds for each pattern) at each location and the experimental procedure can also be found in (Huang et al.,2013). Complementary *in-situ* image studies of the tensile deformation under identical load conditions were also performed inside a Zeiss Evo60 environmental scanning electron microscopy (SEM) operated at 20 keV. At each load step, painstaking imaging studies were made to

observe and record the nucleation and propagation of shear bands near the edge of the hole in order to correlate the deformation showed in the SEM images at each load step to the strain/stress field obtained from the diffraction experiments. Fig. 3 shows the average tensile stress (the applied load divided by the effective cross section area) versus the average strain (the average strain for the gauge length of the sample) for the tested samples with and without hole (the two curves were put into one plot for easy comparison). The microscopic strain/stress fields around the hole were calculated using a commercial finite element based software, COMSOL Multiphysics V4 to complement the measurements obtained using X-ray diffraction technique.

3.   Results and analyses

3.1. In-situ x-ray diffraction study of the evolution of atomic strains

Fig. 2 shows a typical 2-D synchrotron X-ray diffraction pattern acquired for the Zr-based BMG tensile sample before any load applied, exhibiting a diffuse scattering halo, and typical of glassy materials. Under a uniaxial tensile load, the concentric diffraction halo becomes elliptical, expanding in the loading direction and contracting in the transverse direction (Wang et al., 2007; Wang et al., 2012). The changes in shape of the diffraction rings under different loads can be used to calculate the strains for the locations where the diffractions are acquired using the following procedure. Firstly, each of the thirty 2-D diffraction patterns acquired at each stress level were normalized by subtracting the background using software ImageJ (Hammersley et al., 1996) and then integrated. Secondly, each integrated 2-D pattern was segmented anticlockwise into 36 sections in the φ range of 0 to π using Fit2D program (Schneider et al., 2012), and then the scattering intensity within each segment was integrated by using the following equation (Stoica et al., 2008):

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$$I_i(Q, \varphi_i) = \int_{\varphi_i - \pi/72}^{\varphi_i + \pi/72} I[Q(\varphi), I] Q \ d\varphi \qquad (1)$$

with i=1….36, where $Q=Q(s)$ can be defined as (Stoica et al., 2008),

$$Q(s) = \frac{4\pi}{\lambda} \ sin\ [\ arctan(D) \qquad (2)$$

where λ is the X-ray wavelength, D is the sample-to-detector distance, s is the distance from the

origin of the polar coordinate system. In this way, a 1-D scattering intensity spectrum, $I(Q)$, in any

particular φ direction (in this paper, every 5° in the φ direction) was extracted from the 2-D

diffraction rings. Fig. 4 shows a series of $I(Q)$ curves of the tested sample in the loading direction (φ

= 0°) at different applied stresses. It can be seen that the first peaks of the $I(Q)$ curves shift towards

lower Q values when the applied tensile stresses increase (more clearly shown in the inset in Fig. 4).

This azimuthal angle (φ) dependent relative shift of the first peaks of $I(Q)$ in reciprocal space can be

used to calculate the strains for the locations where diffraction patterns are acquired as first

proposed by Poulsen $et\ al.$ (Poulsen et al., 2005) and later used by other researchers (Hufnagel et al.,

2006; Wang et al., 2012; Mattern et al., 2009):

$$\varepsilon_i(\varphi_i, \sigma) = Q(\varphi_i, 0) - Q(\varphi_i, \sigma)] / Q \qquad (3)$$

where $Q(\varphi_i, 0)$ and $Q(\varphi_i, \sigma)$ are the positions of the first peaks of $I(Q)$ curves in the in reciprocal

space at zero stress and σ, respectively. φ_i is the azimuthal angle shown in Fig. 2, for example, in the

tensile loading direction $\varphi_i = 0°$, while in the transverse direction, $\varphi_i = 90°$. The Q value in peak

position was calibrated by using Origin software with Gaussian fitting.

Fig. 5a shows the $Q(0°, \sigma) \sim \sigma$ and $Q(90°, \sigma) \sim \sigma$ relationships for location P1 as shown in Fig.

1b. The shift of $Q(0°, \sigma)$ to a lower value (in Å^{-1}) with the increase of tensile stresses clearly

indicates that interatomic distances increase along the tensile direction. On the contrary, $Q(90°, \sigma)$

moves to a higher value at the same stress level, and therefore interatomic distances decrease in the

transverse direction. The almost perfect linear relationships of $Q(0°, \sigma) \sim \sigma$ and $Q(90°, \sigma) \sim \sigma$ allow

the Poisson ratio to be calculated at 0.352 for this alloy, and later used in the finite element simulation. Similar phenomena were also reported in other BMG alloy systems (Hufnagel et al., 2006; Wang et al., 2012; Mattern et al., 2009).

Using Eq. (3), the angular variations of the strains at P1 produced by the different stresses were calculated and shown in Fig. 5b. The strain distribution shows a clear line symmetry characteristics with the symmetry line lying at $\varphi = 90°$. Although at different stress levels, the strains change from a maximum tensile at $\varphi = 0°$ to a maximum compressive at $\varphi = 90°$, there exist unique strain free angles at $\varphi = 61.5°$ and $118.5°$ for all the cases calculated.

The local strains at P1, P2 and P3 in the $\varphi = 0°$ direction produced by the different average stresses applied during the tests were also calculated using Eq. (3) and shown in Fig. 5c. Although all strain profiles show a linear relationship with the applied average stresses. The presence of a hole in the middle of the gauge length produced variations in the local strains for the locations P1, P2, and P3 with the absolute stain values of P1 > P2 > P3. The variations of strains caused by the hole in the middle of the samples inevitably create local stress variations in P1, P2 and P3 as detailed discussed later.

Based on the 1-D scattering intensity spectrum, $I(Q)$, we calculated the total structural factor $S(Q)$ according to the Egami-Billinge procedures (Egami and Billinge, 2003), using the open source software, PDFgetX2 (Qiu et al., 2004), and then the reduced pair distribution function (PDF), $G(r)$ by Fourier transformation of $S(Q)$ using the following equation (Stoica et al., 2008):

$$G(r) = \frac{2}{\pi} \int_0^{Q_{max}} Q(S(Q)-1)\sin(rQ)dQ \tag{4}$$

$$S(Q) = \frac{I_e(Q) - [\sum_{i=1}^{n} c_i f_i^2(Q)]}{[\sum_{i=1}^{n} c_i f_i^2(Q)]^2} + 1 \tag{5}$$

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where r is the radial distance, $I_e(Q)$ is the normalized elastically scattered intensity, and c_i and $f_i(Q)$ are the atomic concentration and the scattering factor of the ith atom in the alloy, respectively. The pair distribution function, $g(r)$, can be calculated from $G(r)$ by (Stoica et al., 2008):

$$g(r) = \frac{G(r)}{4\pi\rho_0 r} + 1 \tag{6}$$

where ρ_0 is the average atomic number density.

Fig. 6a shows a series of $g(r)$ curves at different applied stresses for location P1, calculated from the corresponding $S(Q)$ data by using Eqs. (4), (5) and (6), with an inset showing an enlarged view of the peak positions of the 1st atomic coordination shell (the 1st peaks marked A in the $g(r)$ curves). Clearly when the applied stresses increase, the first maxima of the $g(r)$ shift towards larger r. The 2nd and the 3rd atomic coordination shells (the 2nd and 3rd peaks marked B and C respectively on Fig. 6a) exhibit the similar trends, indicating that the atomic distance within the atomic shells increase under the tensile stresses applied. Analogous to Eq. (3) (commonly known as Q-space method), the atomic strains can be determined from the shifts of the peak positions according to the following formula (commonly known as real space or direct space method):

$$\varepsilon_j = (r_{j,\sigma} - r_{j,0}) / r_{j,0} \tag{7}$$

where j=A, B, or C, as marked in Fig. 6a, and $r_{j,0}$ and $r_{j,\sigma}$ represent the peak positions of the $g(r)$ curves at zero stress and σ, respectively. The calculated strains for the 1st, 2nd and 3rd atomic shells are shown in Fig. 6b. An almost linear relationship between the applied average stresses and the atomic shell strains are demonstrated along both the tensile and transverse directions. However, the strains for different atomic shells at different stresses are different with the absolute value of $\varepsilon_A < \varepsilon_B < \varepsilon_C$. More interestingly, Fig. 6b shows that the strains calculated using the Q-space method is almost identical to those of the strains of the 3rd atomic shell calculated using the real space method

in both tensile and transverse directions.

In order to study the changes of atomic structure of the Zr-based BMG under different loads, especially the contributions from individual atomic pairs, we obtain the partial pair distribution functions using the following decomposition procedure (Ma et al., 2007; Yang et al., 2004b; Jiang et al., 2008a):

$$g(r) = \sum_{ij} \omega_{ij} g_{ij}(r) \tag{8}$$

where i and j denote the ith and jth atoms, $g_{ij}(r)$ is the partial pair distribution function between the i-j atom pair, and ω_{ij} is the weight factor of i-j atom pair (Yang et al., 2004b), and it can be calculated by:

$$\omega_{ij} = c_i c_j f_i f_j / \left(\sum_i c_i f_i\right)^2 \tag{9}$$

where c_i and f_i are the atomic concentration and scattering factor (referenced from (Waasmaier and Kirfel, 1995)) of the ith atom in the alloy, respectively.

For a multi-component system with five alloy elements, there is no straight forward or commonly accepted procedure to calculate $g_{ij}(r)$ because of the mutual coupling effects of the multi-elements (Yang et al., 2004b), although Ma *et al*. demonstrated a simple case for how to decompose a PDF (Ma et al., 2007). Consequently, we followed the procedure suggested by Jiang *et al*. (Jiang et al., 2008a) and calculated the weight factor ω_{ij} directly by using Eq. (9) (Yang et al., 2004b). Then from the calculated ω_{ij}, the bond length, *i.e.* the atomic pair distance, of each individual atomic pair at different applied average stresses can be extracted using the PDFgetX2. Table I lists the weight factors and the bond lengths for all 15 possible nearest-neighbor atomic pairs for the BMG alloy studied. It can be seen that the weight factors of 7 partials, namely Be-Be, Cu-Be, Cu-Cu, Ni-Be, Ni-Ni, Ti-Ti, and Ti-Be are negligibly small (about 0.02 or below) because of the combined effects of low concentrations and relatively weak scattering powers. Therefore, we

can ignore the contributions of these 7 partials without incurring significant error. At each load step during the tensile tests, the atomic pair distances for the remaining 8 atomic pairs were calculated, and the relative change in distance for each atom pair, namely relative bond length, ε_{ij}, can be calculated:

$$\varepsilon_{ij} = \frac{r_{ij,\sigma} - r_{ij,0}}{r_{ij,0}} \tag{10}$$

where $r_{ij,\sigma}$ and $r_{ij,0}$ refer to the bond length of i-j atom pair under σ and zero stress, respectively.

Fig. 7a presents the relative bond lengths for the Zr-Zr pair in locations P1, P2 and P3 as a function of the applied average stresses. For the three diffraction locations at each load step, the Zr-Zr relative bond length, $\varepsilon_{\text{Zr-Zr}}$, are P1 > P2 > P3. It is also interesting to note that, as the applied stress increases, $\varepsilon_{\text{Zr-Zr}}$ in P2 and P3 increases almost linearly; while $\varepsilon_{\text{Zr-Zr}}$ in P1 firstly increases approximately linearly, and then rapidly towards the final deformation stage, $i.e.$, when the applied global stress is >1321 MPa and shear bands were noticeably observed in the $in\text{-}situ$ imaging study at the identical loading conditions. The evolution of the relative bond lengths in P1 at different applied average stresses for the 8 selected atomic pairs is shown in Fig. 7b. It shows that, for all atomic pairs, the relative bond lengths firstly increase linearly with the increase of average stresses, and toward the final stage of tensile deformation, the increase in relative bond lengths accelerate, especially for the five dominant atomic pairs, $i.e.$ Zr-Zr, Ni-Cu, Zr-Ti, Zr-Cu, and Zr-Ni; and $\varepsilon_{\text{Zr-Zr}} > \varepsilon_{\text{Ni-Cu}} > \varepsilon_{\text{Zr-Ti}} > \varepsilon_{\text{Zr-Cu}} \approx \varepsilon_{\text{Zr-Ni}} > \varepsilon_{\text{Ti-Cu}} \approx \varepsilon_{\text{Ti-Ni}} > \varepsilon_{\text{Zr-Be}}$. According to the peak positions obtained from the decomposition of the 1$^{\text{st}}$ atomic coordination shell, the actual bond lengths are: Zr-Zr = 3.196±0.004, Ni-Cu = 3.146±0.005, Zr-Ti = 3.138±0.005, Zr-Cu = 3.111±0.004, Zr-Ni = 3.109±0.003, Ti-Cu = 3.057±0.004, Ti-Ni = 3.054±0.003, and Zr-Be = 3.040±0.003 Å, respectively, as also listed in Table I. Apparently, the atomic pairs with shorter bond length underwent less

deformation during the tensile tests, which is consistent with the theory that the bond length increases as equilibrium bond length decreases (Wrinch and Harker, 1940). Therefore, among the 8 selected dominant atomic pairs, the Zr-Be pair has the shortest bond length and also the stiffest bond, which is most resistant to the applied tensile deformation.

3.2. Finite element modeling of strains and stresses distribution

To further study the effects of the hole on the distribution of stresses and strains in the BMG samples tested, and to compare with those measured by diffractions at locations P1, P2 and P3, we used commercial finite element based commercial software, COMSOL Multiphysics (version 4.2) to calculate the stresses and strains in the area near the hole at different applied loads. The 2-D model geometry and the mesh are shown in Figs. 1a and 1b, and the elastic modulus (101.2 GPa) and the Poisson's ratio (0.352) are obtained from the data shown in Fig. 3 and Fig. 5a respectively. The alloy density is 6.125 g/cm^3. Triangle meshes, as can be seen in Figs. 1a and 1b, were used in the simulation and much smaller meshes with the minimum mesh size of ~20 micron were used in the area near the hole to study the stress concentration there. Fig. 1c shows the tensile (left half) and compressive stress tensors (right half) near the hole under an applied average stress of 647 MPa. Apparently, the stresses concentrate at the upper and the lower edges of the hole. Using this model, the strains in locations P1, P2, and P3 were calculated at each applied load, and then compared with the measured values using diffraction technique. For example, at the applied stress of 1604 MPa (the final load step before the sample fractured), the simulated strains at P1, P2, and P3 are 1.90 %, 1.28 %, and 0.60 %, respectively, while the strains measured by the Q-space method are 1.92 %, 1.33 %, and 0.59 %, respectively as shown in Fig. 5c. The differences between the simulated and the measured values are 1 % ~ 4 %.

3.3. In-situ SEM imaging study of the onset of plasticity

To complement the diffraction measurements of strain and further elucidate the link between the atomic strains and the nucleation and propagation of the shear bands, we observed the initiation and evolution of shear bands near the hole in the BMG sample using identical loading conditions inside a scanning electron microscope. A series of SEM images captured at different stress levels are shown in Figs 8a, 8b and Figs. 9a-9j. When the applied average tensile stress reached 647 MPa, very fine shear bands were observed to nucleate at the upper edge of the hole as marked by the arrows in Fig.8b inset, indicating clearly the onset of plastic deformation, and from the superimposed simulated tensile stress contours (Fig. 8b), it can be clearly seen that the local tensile stress at the upper edge of the hole is ~3 GPa, much higher than the average fracture stress (2.008 GPa) for this alloy showed in Fig. 3. When the applied average tensile stress reached 755 MPa, three shear bands with a spacing of ~30 µm apart were observed to nucleate at the upper edge of the hole, and grew upwards as marked by the arrows in Fig. 9f. One shear band, marked AB, is selected for tracking of its evolution during subsequent increasing load steps. It can be seen that, at 1132 MPa, shear band AB propagated further (from 85 µm at 755 MPa, to 103 µm at 1132 MPa), and became wider. The three original shear bands tended to branch during propagation and changed directions, but their length remained approximately the same, and three new shear bands were formed at the adjacent locations as shown in Fig. 9g. At 1321 MPa, the six existing shear bands propagated even further with two new shear bands marked CD and EF and marked by the red arrows appeared in Fig. 9h. At this stress level, shear band AB had just propagated onto the edge (highlighted by the dash lines in Fig. 9h) of location P1 where a diffraction pattern was acquired in an identical sample. At 1509 MPa (Fig. 9i), all shear bands propagated into P1 and shear bands CD

and EF overtook the other shear bands. At 1604 MPa (Fig. 9j), shear bands CD and EF grew much faster than the rest, and CD developed into a visual crack with numerous fine shear bands nucleated at the hole edge, causing a catastrophic fracture along its propagation path when the load was increased a little further. It was interesting to find out that, based on this study and hundreds of other SEM observations of the deformation behaviors of this BMG alloy, the propagations of the few shear bands that were nucleated first always slowed down at some points. Then new shear bands nucleated and propagated faster and overtook the original ones to cause the final catastrophic failure. For locations P2 and P3, no shear bands were observed during the whole series of tensile tests.

To quantify the correlation between atomic strains and shear bands, we carefully measured the total line length of all shear bands observed within area P1. Fig. 7b also shows the shear band density in area P1 (the total line length of shear bands observed in area P1 divided by its area) as a function of the applied average stresses. Clearly, when the applied average stresses are larger than 1321 MPa, and the shear band density in P1 increases dramatically, and the relative bond lengths of the dominant atomic pairs, e.g. Zr-Zr, and Ni-Cu, increase more rapidly, indicating clearly that the dilatation of dominant atomic pairs is an essential part of the plastic deformation, and a key mechanism to nucleate a shear band and drive it to propagate.

4.   Discussion

4.1. Control of the nucleation of shear bands

It is commonly known that a shear band of a few tens of nanometers thickness is the basic element for plastic deformation of BMGs (Inoue and Takeuchi, 2011; Schuh et al., 2007). To understand precisely the deformation mechanism of BMGs and explore practical solutions to

improve their plasticity, it is vital to study and understand fully the mechanism for shear band nucleation and propagation, and find suitable engineering solutions to control them. Although a great deal of research has been conducted on this aspect (Li and Li, 2006; Ritter and Albe, 2012; Shi and Falk, 2006; Takeuchi and Edagawa, 2011; Delogu, 2011), no consistent and reliable experimental techniques have been seen reported so far to produce shear bands in BMGs, especially under a tensile load, in a controllable ways and allow their real time nucleation and propagation to be studied *in-situ* and in a systematic and repeatable manner. The majority of previous experimental studies were either carried out *ex-situ* or in an *ad hoc* manner, capturing a few shear bands in real-time just by chance, because the nucleation and propagation of shear bands are an inherently highly transient and inhomogeneous process. It is very difficult to predict where and when shear bands start in a plain sample, let alone to capture and track their propagation. Very recently, researchers, including ourselves (Huang et al., 2013), introduced some artificial defects, such as cracks, holes, and notches into the studied BMG samples (Qu et al., 2012a,b; Tandaiya et al., 2013; Yang et al., 2004a; Xu et al., 2010; Sarac and Schroers, 2013; Demetriou et al., 2011), and tried to capture the shear bands produced around the defects. For instance, stable shear bands round notches have been indeed observed in toughness tests (Tandaiya et al., 2013; Yang et al., 2004a; Xu et al., 2010). In this study, we introduced a circular hole in the middle of the gauge length of the tested BMG tensile samples. Apparently, the introduction of a hole decreases the average fracture stress of the BMG sample from 2008 MPa down to 1722 MPa as shown in Fig. 3, and this is due to the effect of stress concentration near the hole (Pilkey, 1997) as shown in Fig. 1c. Fig. 8b shows that when the applied average stress reached 647 MPa, the simulated local stress at upper edge of the hole is ~3 GPa, much higher than the fracture strength of the sample (2008 MPa as shown in Fig. 3), and therefore shear bands are nucleated there. Furthermore, the tensile stress concentration at the upper

and lower edges of the hole (Fig. 9k ~o) facilitates the nucleation of multiple shear bands, a phenomenon rarely seen in the tensile tests of any BMG samples without artificially introduced or naturally occurring stress concentrators (Sobieraj et al., 2005; Zheng et al., 2003; Qu et al., 2012a). This is because, compared to the very narrow shear band, the area that has the concentrated stresses is at least 10^4 orders of magnitude larger (~ 300 µm long and 250 µm wide in this study), easily producing multiple shear bands. Away from the upper and lower edges of the hole, stresses are far below the fracture strength of the alloy, and therefore shear bands are not produced. On the other hand, compared to the whole cross section area of the tested BMG tensile sample, the areas that have a concentrated stress higher than the fracture strength are relatively small, and the propagation of this small area with higher stress can be controlled by fine tuning the applied load steps and the rate of loading. In this way, we have successfully implemented an experimental strategy that can nucleate shear bands in a very repeatable manner at specifically designed locations on tensile samples under controllable load conditions. More importantly, the nucleated shear bands can be held in a steady state, allowing detailed imaging and diffraction studies to be carried out *in-situ*. The combined advantage of *in-situ* imaging and X-ray diffraction studies allow the dynamics of the shear band nucleation and propagation to be related directly with the micro and atomic strain information, a link that is essential for an in-depth understanding of the onset of plasticity of BMGs.

4.2. Inhomogeneous atomic strain and its effect on shear band formation

Fig. 6b shows that the atomic strains of the studied BMG samples depends strongly on the atomic coordination shells with the 3rd atomic shell having higher strain than the 1st and the 2nd shells, and asymptotically approaching the strain calculated using the *Q*-space method. Similar phenomena were reported in other metallic glassy systems subjected to uniaxial compression and

tension tests (Poulsen et al., 2005; Hufnagel et al., 2006; Dmowski et al., 2010). Some researchers have argued the causes of this inhomogeneous deformation at atomic level. For example, Poulsen *et al*. (Poulsen et al., 2005) postulated that this additional compliance results from structural rearrangement at the medium-range scale of $4\sim10$Å, whereas Hufnagel *et al*. (Hufnagel et al., 2006) proposed that it is due to local atomic rearrangements in topologically unstable regions of the glassy structure. Dmowski *et al*. (Dmowski et al., 2010) went even further, and proposed that about 25 % volume fraction of an amorphous metal is anelastic which represents residual liquidity. The above debates indicate that a precise understanding of the deformation of BMGs at atomic-level remains unclear. For the BMG alloy studied, Zr is the solvent and Be is the major solute. Fig. 7b shows the relative bond lengths for the solvent-solvent (Zr-Zr), solvent-solute (Zr-Be), and the solute-solute (Be-Be) pairs, and clearly the relative bond lengths are Zr-Zr > Zr-Be > Be-Be for each applied average stress. Hence, Be-Be is "stronger" than Zr-Be, and Zr-Zr pair is the "softest" pair. Apparently, the softest Zr-Zr pair contributes most to the elastic deformation during the tensile test. Ma *et al*. (Ma et al., 2012) studied *in-situ* a number of BMGs using neutron diffraction to determine the response of local atomic structures to the stresses applied, and found that the Young's modulus E and shear modulus G of the glasses studied were almost equal to their solvent species. For example, $E = 101.2$ GPa for $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ BMG, just about 3% higher than that of pure Zr (98.0 GPa), and much smaller than those of other species, *i.e*., 120.2 GPa, 129.8 GPa, 199.5 GPa, and 318 GPa for Ti, Cu, Ni, and Be, respectively. Because the elastic modulus reflects the inherent stiffness of atomic bonds, the solvent-solvent bonds are essentially responsible for the elasticity of BMGs (Wang, 2012a,b).

Although lacking a long-range ordered atomic structure, BMGs may still have short-range order (SROs) in the nearest-neighbor atoms and nanoscale medium-range orders (MROs), which would

affect their elastic properties (Wang, 2012a b,; Zeng et al., 2011). The SROs are basically solute-centered clusters surrounded by solvent atoms with atomic distances <5 Å, while the MROs are structured superclusters consisting of interconnected smaller clusters with atomic distances >5 Å. The SROs represent very strong solute-solvent bonds, while the MROs are much weaker solvent-solvent bonds, and this hierarchical atomic arrangement has been verified by Ma *et al*. (Ma et al., 2012). Compared with the stiffer SROs, MROs are the more elastically deformable structure, leading to structure rearrangement when subjected to elastic deformation.

Fig. 6a shows that the 1st and 2nd atomic coordination shells are in the range of < 5 Å, and on the short-range scale while the 3rd one is on the medium-range scale, suggesting that MROs are the main atomic structure for the 3rd shell. For the BMG alloy studied, Zr-Zr is the solvent-solvent pair and belongs to MROs, whereas Be-Be is the solute-solute pair, and belongs to SROs. Apparently, the strongly bonded SROs experience less elastic deformation than that of the MROs. For this alloy, it is striking to find that the atomic strain of the 3rd shell is almost identical to the microscopic strains measured using the *Q*-space method, indicating that the elastic properties of this BMGs are mainly attributed to the solvent species.

Compared Fig. 7b with Fig. 9h-j, it can be seen that, once shear bands propagated into location P1, the relative bond lengths at P1 increases dramatically, indicating that the creation of shear bands are closely linked with the sudden increase in the local relative bond lengths. Shear bands in BMGs can accommodate shear plastic strain as high as 10^4 % (Chen et al., 1994; Jiang et al., 2007; Wu et al., 2007; Kuzmin et al., 2012a; Greer and De Hosson, 2011). Such extremely high strain in shear bands would give a measureable contribution in the diffraction measurement. Spaepan (Spaepen, 2006) suggested that plastic deformation in BMGs is the process of deformation induced strain softening by mechanical dilatation. The dilatation, or increase in excess free volume, dramatically

increases the distribution of bond lengths. In this situation, the atomic bond length would rapidly increase along the loading direction. Therefore, shear-induced dilatation of the randomly close-packed atomic configuration (Klaumünzer et al., 2011) gives rise to a sudden increase for the atomic pair distance at area P1, as shown in Fig. 7b.

4.3. Control of the propagation of shear bands

Assuming a plane stress condition, the simulated color maps for the tensile stress tensor, σ_{xx}, and compressive stress tensor, σ_{yy}, at the areas near the upper edge of the hole are shown in Figs 9k-9o, and 9p-9t respectively. The corresponding shear bands images obtained at those areas and the contour lines of the compressive stress tensor were superimposed onto the colour stress maps for comparison. Fig. 9k clearly shows that, at an average stress of 755 MPa, the stress concentration due to the presence of the hole made the local tensile stress at the area near the upper edge of the hole ~4 GPa, much higher than the fracture strength of the alloy (2.008 GPa), three shear bands are therefore clearly visible there. As the average stress increased to 1132 MPa (the local stress increase too), three more shear bands nucleated and together with the previous three shear bands, and all shear bands propagated approximately at the same rate and reached ~130 μm long. Fig. 9q shows that the tips of the shear bands entered a region with a compressive stress of ~-0.5 GPa. At the next few load steps (Fig. 9q~t), the area of the region that has a compressive stress of ~-0.5 GPa increases as the average stress increased. However, it seemed that the existing shear bands were confined within the ~-0.5 GPa compressive stress region and cannot grow outside the region. While the two new shear bands CD and EF that were nucleated just outside the ~-0.5 GPa compressive stress region propagated very faster and overtook all the previous shear bands and developed into visible crack as clearly shown in Fig. 9m-9o and Fig. 9r-9t. This indicates that the propagation of

shear bands is strongly dependent on the nature of the stress field ahead, and all evidence obtained in this study indicates to that a compressive stress field of > -0.5 GPa can hold or slow down the propagation of shear bands.

5.   Conclusions

The plasticity of a Zr-based metallic glass under step-increased tensile loads was studied *in-situ* using complementary scanning electron microscopy and synchrotron X-ray diffraction experiments. . These experiments were designed to establish the link between shear band nucleation and growth observed in the SEM, and the atomic and microscopic strains/stresses measured using X-ray diffraction, or simulated using the finite element method. Normally, in plain samples, the shear band nucleation and propagation are highly transient and uncontrollable events. A sample design with a circular hole at the middle of the gauge length was used, so that the stress concentration caused by the hole created well-defined regions where shear bands nucleated and propagated. This sample design and stepped loading enabled study of the shear bands in a controllable and quasi-steady state manner, providing quantitative understanding of the mechanisms of shear band formation and their role in the onset of plasticity of BMGs.

Pair distribution function analysis reveals that the nucleation of shear bands is actually the result of the dilatation of the weakest atomic pairs, normally the solvent-solvent atomic pairs (in this case the Zr-Zr pair) and they are also the main atomic bond between the medium range order atomic cluster.

The propagation of shear bands is strongly dependent on the nature of the stress field ahead of the shear bands. A compressive stress field of a certain level (in this case >~ −0.5 GPa) ahead of the shear bands can effectively slow down or pause the propagations of shear bands.

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Table I. The 15 nearest-neighbor atom pairs in the Zr-based BMG studied, the weighting factors ω_{ij}, and the bond length, r_{ij}, for each atom pair at stress-free state

ij	r_{ij}, Å	ω_{ij}	ij	r_{ij}, Å	ω_{ij}	ij	r_{ij}, Å	ω_{ij}
Zr-Zr	3.196	0.3949	Ti-Ti	3.073	0.0106	Ni-Cu	3.146	0.0297
Zr-Ti	3.138	0.1300	Ti-Ni	3.054	0.0218	Ni-Be	3.011	0.0045
Zr-Ni	3.109	0.1330	Ti-Cu	3.057	0.0290	Cu-Cu	3.049	0.0197
Zr-Cu	3.111	0.1750	Ti-Be	3.034	0.0044	Cu-Be	3.011	0.0060
Zr-Be	3.040	0.0298	Ni-Ni	3.045	0.0111	Be-Be	2.972	0.0005

Figure Captions

Figure 1 (a) A dog-bone shaped Zr-based BMG tensile sample with the right half showing the 2D triangular meshes used in the finite element strain/stress analysis, (b) an enlarged view of the region with hole and the three locations, P1, P2, and P3, where diffraction patterns were acquired; and (c) the simulated tensile stress tensor (left half) and compressive stress tensor (right half) around the hole under an applied average stress of 647 MPa.

Figure 2 The experimental setup for the *in-situ* synchrotron X-ray diffraction measurement during tensile tests.

Figure 3 The tensile stress-strain curves of the tested Zr-based BMG samples with and without a hole.

Figure 4 A series of x-ray diffraction intensity curves of the tested samples obtained at different applied average stresses with an inset highlighting the positions and shifts of their first peaks.

Figure 5 (a) The changes of the first peak positions with the applied average stresses in the tensile ($\varphi = 0°$) and transverse directions ($\varphi = 90°$), (b) the angular dependence of the strains measured at different applied average stresses, and (c) the relationships of the applied stresses as functions of the local strains in the $\varphi = 0°$ and $\varphi = 90°$ directions for the samples with a hole. The calculated local strains using finite element method in the $\varphi = 0°$ directions are also superimposed for comparison.

Figure 6. (a) The radial pair distribution function, $g(r)$, calculated for location P1 at different applied stresses with an inset highlighting the 1st coordination shell positions, and (b) the strains derived from the shifts of the three first peaks (A, B, and C) in $g(r)$ at different applied average stresses. The calculated strains for P1 (shown by the black squares) using

Q-space method are also plotted for comparison with those calculated from the 3rd atomic shell (peaks C).

Figure 7 (a) The relative bond lengths of Zr-Zr pair in locations P1, P2 as functions of the applied average stresses, and (b) the relative bond lengths of the 8 selected dominant atomic pairs and the Be-Be pair and the shear band density in area P1 as functions of the applied average stresses.

Figure 8. (a) The SEM images of the tested Zr-based BMG sample taken at the applied average stresses of 647 MPa, (b) the higher magnification of the rectangle area shown in Fig. 8(a) at the upper edge of the hole, with an inset showing the nucleated shear bands at the hole upper edge with the simulated tensile stresses contour superimposed.

Figure 9. A series of SEM images of the tested Zr-based BMG sample taken at the applied average stresses of (a) 755 MPa, (b) 1132 MPa, (c) 1321 MPa, (d) 1509 MPa, and (e) 1604 MPa. (f) ~ (j) are the higher magnification of images (a) ~ (e) at the upper edge of the hole respectively, highlighting the shear bands at the areas above point Y. (k) ~ (o) and (p) ~ (t) are the simulated tensile stresses, σ_{xx} and compressive stresses, σ_{yy} for the areas shown in (f) ~ (j) respectively. The red dash lines in (h) ~ (j) indicate the lower boundary of location P1. In order to clearly link the shear band formation and the stress distribution, the shear bands are also superimposed in Fig. 9(k) ~ (t).