Deformation of metallic glasses: insight from in-situ high-energy x-ray diffraction

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Abstract. The most notable property of bulk metallic glasses is their ultrahigh (near theoretical) strength and hardness. Because many of known BMGs miss tensile plasticity and thus exhibit catastrophic failure upon tension it is of great importance to understand deformation mechanisms involved and thus improve their performance. Time-resolved in-situ x-ray diffraction experiments may nowadays be performed at high-brilliance synchrotron radiation sources for a variety of conditions. An example is provided, concerning mapping of the strain distribution in tensile stressed Zr-based BMG by in-situ hard x-ray diffraction.

1. Introduction

Recently, after the discovery of several families of multi-component alloys exhibiting a large supercooled liquid region before crystallization, bulk metallic glass (BMG) formation has become a common phenomenon [1]. Samples with dimensions in the mm range have been prepared by simple mould casting. With the increase of the critical size of BMGs, current research work has focused on their mechanical properties [2]. Although some BMGs exhibit pronounced plasticity under uniaxial compression [3] or bending conditions, they are generally destroyed with catastrophic failure upon tension at room temperature with slow strain rate [4]. It has been proven that high-energy x-ray scattering can be used to in-situ monitor the structural changes of BMGs during compression [5,6] and/or tension [4,7]. The main aim of the current work is to map the macroscopic and microscopic strain distributions in tensile stressed Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ BMG using in-situ x-ray diffraction.

2. Experimental details and description of methods

A BMG plate with nominal composition Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ was prepared by arc melting and suction casting. The as-cast plate was machined by spark erosion method in order to obtain dog-bone shaped specimen with 10 mm x 2 x 1 mm$^2$ reduced section (see inset in figure 2). The dog-bone shape specimen was strained using a tensile module from Kammrath and Weiss GmbH. The room temperature in-situ x-ray diffraction experiments were performed on the wiggler beamline BW5 at the DORIS positron storage ring (Hamburg, Germany) using monochromatic synchrotron radiation of 103.8 keV ($\lambda$=0.0119 nm). The diffraction experiments were carried out in the transmission geometry. For each load, seven independent points (with 1 mm steps along the 10 mm long gauge) in the middle part of the specimen were sequentially scanned. Selected parts of the strained sample were exposed for 10 s to the incident monochromatic beam having a cross section of 1 x 1 mm$^2$.

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Figure 1. Two-dimensional diffraction pattern of amorphous Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ BMG prior deformation. The polar coordinates $(s, \phi)$ and axis of deformation are depicted.

Figure 2. Measured (points) and fitted (lines) stress-strain curves for tensile and transversal direction obtained by in-situ x-ray diffraction. The inset shows dog-bone shape sample.

Diffracted photons were collected using a two-dimensional (2300 x 2300 pixels, 150 x 150 µm$^2$ pixel size) MAR345 imaging plate detector, carefully mounted orthogonal to the x-ray beam. The diffraction pattern from LaB$_6$ was used to calibrate the sample-to-detector distance and tilting of the imaging plate detector with respect to the beam axis. The strain determination of metallic glasses from x-ray diffraction data is based on concepts previously reported by Poulsen et al [5]. Determination of structure factor $S(Q)$ and pair distribution function $g(r)$ from elastically scattered intensities was done using standard procedures described in reference [8].

3. Results and discussion

3.1. Analysis in reciprocal space

Figure 1 shows diffraction pattern of the as-cast Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ sample prior to applying tensile load. The characteristic diffuse scattering pattern confirms the fully amorphous nature of the specimen. After increasing the tensile load $\sigma$, the initially circular symmetric diffraction pattern becomes more elliptical. To describe these changes more quantitatively it is useful represent diffraction patterns with respect to the polar coordinates $s, \phi$ (see figure 1). Dividing the $\phi$-range of 0 to $2\pi$ into 36 segments, we obtain so called “cakes”, each having equal opening of $\pi/18$. The radial integration of such cakes using FIT2D [9] yielded intensity distribution functions $I(Q(s), \phi, \sigma)$, where $Q$ denotes the wave vector transfer. The procedure was repeated for all diffraction patterns acquired from different parts of the strained sample and at different loads $\sigma$. According to the previous work of Hufnagel et al [6] the macroscopic strain $\varepsilon$ can be directly calculated from the relative change of the principal peak position $q$ appearing in $I(Q(s), \phi, \sigma)$ with respect to the unloaded situation $q_0$ by equation $\varepsilon = (q - q_0)/q_0$. A Pseudo-Voigt function has been used to fit the principal peak. Fitting the angular variation of the strain to the following expression [10]

$$\varepsilon(\phi, \sigma) = \varepsilon_{11} \cos^2 \phi + \gamma_{12} \sin \phi \cos \phi + \varepsilon_{22} \sin^2 \phi$$

axial $\varepsilon_{11}$, transversal $\varepsilon_{22}$ and in-plane shear component $\gamma_{12}$ can be derived. Figure 2 shows the stress dependence of axial $\varepsilon_{11}$ and transversal $\varepsilon_{22}$ strain tensor components obtained by scanning the middle point of the specimen. Almost perfect linear response of $\sigma=\sigma(\varepsilon_{11})$ reveals the elastic regime of tensile deformation. The sample fractured at a stress of about 1500 MPa and did not provide any hint for
yielding, despite the fact that the compressive yield strength of this BMG was reported to be 1690–1851 MPa [3]. The maximum axial strain $\varepsilon_{11}$ achieved is $1.51\pm0.01\%$. The elastic modulus determined in tensile mode is $E_{11}=94\pm1$ GPa, and the experimentally determined Poisson’s ratio $\eta$ is $0.30\pm0.01$. The analysis of seven independent scans performed with 1 mm steps along the gauge length indicates that the spatial distribution of macroscopic strain is rather homogeneous within the region of interest. The average values and standard deviations of elastic modulus $E_{11}$ and Poisson’s ratio $\eta$ obtained from seven independent scans along the gauge length are $92.6\pm1.3$ GPa and $0.284\pm0.01$, respectively.

3.2. Analysis in direct space
To map the strain distribution within the local and medium range atomic order we calculated the pair distribution function $g(r)$ by Fourier transformation of structure factor $S(Q)$ by the following equation

$$g(r) = 1 + \frac{1}{2\pi \rho_0 r} \int_0^\infty Q(S(Q) - 1)\sin(rQ)dQ$$

in which $\rho_0$ denotes the average atomic number density. Figure 3 shows the first two coordination shells of $g(r)$'s observed along the tensile direction. One can see that increasing tensile load shifts $g(r)$'s towards higher $r$-values thus indicating an increase of average atomic distances. Due to concentration and different scattering powers of the constituent elements in Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ alloy, it is clear that Zr-Zr and Zr-(Cu, Ni) are the dominant atomic pairs which constitute the first coordination shell of $g(r)$'s. In the light of the first three columns in table 1(a), the maximum strain determined from the relative change of the center of Zr-(Cu, Ni) and Zr-Zr partials is $1.11\pm0.19\%$ and $1.27\pm0.14\%$, respectively. Such values of strain are somewhat smaller than the value of maximum tensile strain ($1.51\pm0.01\%$) obtained by analysis in reciprocal space. Further we were interested what the strain distribution is over longer length scales. The tails of $g(r)$'s, which describe medium range order MRO (range 10-20 Å), were according work to [11] fitted to the equation

$$g(r) - 1 = \frac{A}{r} \exp(-r/A)\sin(2\pi r / D + \Phi)$$

where $A$ is the amplitude, $A$ is the screening length, $\Phi$ is the phase shift and $D$ is the oscillation period associated with MRO. Figure 4 shows perfect agreement between experimentally determined $g(r)$’s and corresponding fits using equation (3). The results of fitting procedure are listed in the table 1(b).
Table 1. Numerical results of two fitting procedures: a) Best-fit peak positions obtained from the decomposition of the first coordination shell (range 2-4 Å) assuming Gaussians distributions for Zr-(Cu,Ni) and Zr-Zr partials. b) Amplitude $A$, screening length $\Lambda$, phase shift $\Phi$ and period of oscillations $D$ as obtained by fitting medium range order (MRO) part (10-20 Å) of experimentally determined $g(r)$’s to the equation (3). $\varepsilon_{\text{MRO}}$ means average MRO strain determined from the expansion of fitted curves, observed along $r$-axis for a given stress with respect to the load-free state.

| $\sigma$ [MPa] | $r_{Zr-(Cu,Ni)}$ [Å] | $r_{Zr-Zr}$ [Å] | $A$ [Å] | $\Lambda$ [Å] | $D$ [Å] | $\Phi$ [-] | $\varepsilon_{\text{MRO}}$ [%] |
|----------------|----------------------|-----------------|---------|-------------|--------|---------|-----------------|
| 0              | 2.68±0.01            | 3.14±0.01       | 5.89±0.12 | 4.88±0.05   | 2.471±0.002 | 0.46±0.02 | -               |
| 800            | 2.70±0.01            | 3.16±0.01       | 6.15±0.13 | 4.79±0.05   | 2.490±0.002 | 0.43±0.02 | 0.83±0.01      |
| 1400           | 2.71±0.01            | 3.18±0.01       | 6.35±0.13 | 4.71±0.05   | 2.506±0.002 | 0.43±0.02 | 1.50±0.02      |

Since the fitted curves perfectly match the MRO part of the $g(r)$’s we used them to determine the average MRO strain $\varepsilon_{\text{MRO}}$ by calculating the expansion of the fitted curves, observed along the $r$-axis for a given stress with respect to the load-free state. We found that expansion along $r$-axis can be described by $r=r_0(1+\varepsilon_{\text{MRO}})$ in which $r$ and $r_0$ are the domains of fitted curves for stress and stress-free state, respectively. Comparing the values of $\varepsilon_{\text{MRO}}$ with the values of macroscopic tensile strain determined from analysis in reciprocal space, one observes perfect matching.

4. Conclusions

The presented experiments clearly demonstrate the advantage of in-situ high-energy x-ray diffraction over conventional methods for studying deformation of BMG’s. The strain analysis based on tracing the position of principal diffuse peak in reciprocal space yielded strain tensor components revealing elastic regime of tensile deformation. Scanning along the gauge length indicates rather homogeneous spatial distribution of the macroscopic strain within the region of interest. The strain calculated from $g(r)$ for the first nearest-neighbour is somewhat smaller than that for longer length scales. Similar results, however on elastically compressed BMG, were reported in [6]. They concluded that such differences are due to anelastic atomic rearrangements in topologically unstable regions of the glass.

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