On the shear-affected zone of shear bands in bulk metallic glasses

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1. Introduction

Metallic glasses (MGs) are principally of great interest as structural materials since they exhibit high strength and hardness. However, most MGs lack ductility, especially under tension where zero ductility prevails. However, in recent years, progress has been made in developing bulk metallic glasses (BMGs) exhibiting respectable ductility during cold rolling, bending and compression tests. Upon inhomogeneous deformation, that is at low temperatures and high stresses, the plasticity is manifested by a macroscopic sliding along a localized region called a shear band (SB) having a thickness of about 15 nm or less. It has been found that such SBs contain alternating density changes accompanied by structural changes in the medium range order (MRO) [12–14].

2. Methods

FEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed with a Thermo Fisher Scientific FEI Themis 300 G3 transmission electron microscope (TEM) operated at 300 kV. Nanobeam diffraction patterns (NBDPs) were acquired with parallel illumination using a probe size of 1.3 nm at full width half maximum (FWHM) in μProbe-STEM mode operated at spotsizes 8 with a 50 μm C2 aperture giving a semi-convergence angle of 0.8 mrad. The probe size used for the acquisition of the NBDPs was measured directly on the Ceta camera prior to the FEM experiments using Digital Micrograph plugins by D. Mitchell [16]. A beam current of 15 pA and a camera length of 77 mm were used for the acquisition in combination with an US 2000 CCD camera (Gatan) at binning (512 × 512 pixels). Data sets consisting of 60 × 200 (Fig. 2) or 80 × 200 (Fig. 1) individual NBDPs were performed across SBs from tensile and compressive sides of 3-point bending tests. From either 60 or 80 individual NBDPs containing the spatially resolved diffracted intensity \( I(\mathbf{r}) \) at a fixed distance \( r \) from the SB, the normalized variance \( V((\mathbf{k}), \mathbf{r}) \) was calculated in the form of the annular mean of variance image (\( \Omega_{V\text{Image}}(\mathbf{k}) \))

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using

\[ V(|k|, R = 1.3 \text{ nm}) = \frac{\langle P^2(k, R, r \rangle}{\langle I(k, R, r \rangle^2} - 1 \]  

where \( \langle \rangle \) indicates the averaging over different sample positions \( r \) or volumes and \( R \) denotes the FWHM of the probe and thus the reciprocal space resolution. Since the normalized \( V(|k|, R) \) scales with \( 1/t \) \([18, 19]\), a thickness correction was made using the slope of the HAADF signal across the SB \([20]\). The individual normalized variances were subsequently plotted against their position. The peak height of the first normalized variance peak was taken as a measure of the MRO volume fraction.

3. Results

3-point bending test of notched bars were carried out (see supplementary video in Appendix A). A more detailed description is given in reference \([21]\). During such deformation tests, the area around the notch is dominated by tensile strain whereas the side opposite to the notch is mainly under compressive strain. In this paper these specific regions are referred to as the tensile and compressive sides, respectively. FIB lamellae containing SBs from each side (tensile and compressive) of the deformed samples were prepared perpendicular to shear steps penetrating through the surfaces. Fig. 1 shows representative examples of normalized variance profiles from as-cast and deformed matrix states (compressive and tensile side) of \( \text{Pd}_{40}\text{Ni}_{40}\text{P}_{20} \) (a, b) and Vit105 (c, d) showing a reduction in peak height due to deformation.

![Figure 1: Normalized variance profiles of as-cast and deformed states](image1)

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This behavior was also observed for severely deformed \( \text{Pd}_{40}\text{Ni}_{40}\text{P}_{20} \) \([22, 23]\). The immediate environments of SBs were inspected by acquiring NBDPs over larger areas. Fig. 2a and Fig. 2c show HAADF-STEM images of the FIB-prepared lamellae. Since the contrast from the SBs is very faint, their positions are indicated by white dashed lines, ending at the surface steps. The FEM analyses were performed for SBs of the tensile sides in \( \text{Pd}_{40}\text{Ni}_{40}\text{P}_{20} \) and Vit105 corresponding to the red rectangular areas shown in Fig. 2a,c. The results; that is, the normalized variances mapped parallel to the dashed grey line are shown in Fig. 2b and Fig. 2d. A shallow continuous gradient is observed for both BMGs running from one side to the other (Fig. 2b and Fig. 2d). The peak height, which is taken as a measure for the MRO
leading to the greatest reduction of MRO. The lateral exten-
sifies the highest stress concentration in the shear band
for Vit105, the dip minimum for $Pd_{40}$ $Ni_{40}P_{20}$ with a clear minimum at the SB position is observed

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ension to be in the range of several microns.
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peak height visible, it is difficult to estimate the lateral
thickness. Since there is no plateau level in the variance
showing that there is hardly any influence from the foil
the case of Fig. 2b the HAADF intensity is almost flat
potentially influencing these gradients in the variance peak
heights, were eliminated by a thickness correction [24]. In
significant differences between the tensile and compressive
volume fraction, was reduced by a factor of about 2 after
deformation (cf. Fig. 1). It is worth noting that thickness
effects (see red HAADF profile in Fig. 3a and Fig. 3b), poten-tially influencing these gradients in the variancepeak heights, were eliminated by a thickness correction [24]. In
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extension of such shallow gradients. Fig. 2d suggests the
extension to be in the range of several microns.

In like manner, the regions around the SBs from the
compressive side were investigated. Fig. 3a and Fig. 3b de-
pict HAADF-STEM images of SBs from the compressive
side. The results of the FEM analyses are shown in Fig. 3b
and Fig. 3d. In contrast to the tensile side, the measure-
ments of the compressive side display for both BMGs a
pronounced dip in the peak height of the normalized vari-
ance $V(k, R)$ in the vicinity of the SB. While a symmetric
dip with a clear minimum at the SB position is observed
for Vit105, the dip minimum for $Pd_{40}Ni_{40}P_{20}$ is displaced
with respect to the SB position. The dip minimum iden-
tifies the highest stress concentration in the shear band
leading to the greatest reduction of MRO. The lateral ex-
tension of the MRO curve is larger than 1 µm. The influence
of the foil thickness is shown by the HAADF signal
(red curves in Fig. 3b and Fig. 3d). Since a thickness cor-
rection was carried out on the variance peak heights, the
dips in the MRO curves are not thickness artifacts.

4. Discussion

In the following we discuss the robustness of this anal-

ysis.

4.1. Error assessment of FEM analysis

FEM analyses reveal differences in the absolute peak
height of the normalized variance $V(k, R)$ in the vicinity
of SBs [1] with respect to the undeformed "as-cast" matrix
by a factor of up to about 2 (Fig. 1). Thus, by consid-
ering the absolute peak height of the normalized variance as
a measure for the MRO volume fraction, changes in the
MRO of the SB environment are detectable. Thickness
gradients along the SB (parallel to the scan direction) are
also an error source since the calculation of the normal-
ized variances results from the averaging of the individual
NBDPs along this direction. An error estimation due to
such thickness effects (parallel to the SB) can be obtained
from the match of very small or high k-values (see 3D plots
in the Supplementary Material (Fig. S2)). These errors
can be estimated to a maximum of $V = 0.005$ and are
thus far below the observed absolute differences in peak
height of the normalized variance $V(k, R)$. As the thick-
ness effects perpendicular to the scan direction (across
the SB) were already corrected using the HAADF intensities
shown in Fig. 2 and Fig. 3, the obtained MRO profiles are
free from thickness artifacts.

4.2. Variance peak height: variations and shapes

The detected peak height variations of $V(k, R)$ reveal
significant differences between the tensile and compressive
side of the sample; that is, a pronounced dip of $V(k, R)$
at the SBs of the compressive side. For the tensile side
a continuous shallow gradient seems to be characteristic.
No clear minimum is visible. While a pronounced $V(k)$-
dependence with a clear minimum at the SB position is
observed for the compressive side of Vit105, the shape of
the $V(k)$-relation for the compressive side of the SBs in
$Pd_{40}Ni_{40}P_{20}$ is asymmetric, showing no overlap between
the location of the SB and the minimum of the data. In-
tuitively, one would expect the minimum to overlap with
the position of the SB since the MRO reduction in the SB
should be highest. Hidden SBs explain the shift of the dip
minimum since two more surface shear steps (see white
arrows in Fig. 2b) clearly indicate the presence of more SBs
within the inspected SB area.

Different structural changes due to the tension-compression
asymmetry in BMGs have also been measured using high-
energy synchrotron x-ray scattering [25]. An explanation
for the difference in shape of the $V(k)$ curves between compressive and tensile sides may be found in the anharmonicity of the interatomic potential so that atoms or clusters are differently affected at a given stress, i.e. pulling them apart is easier than pushing them together. This fits to the observation that the SBs formed earlier and more abundantly on the tensile side (see Supplementary Video).

Another point that needs to be discussed in connection with the shape of the $V(k)$ curves is the amount of deformation (material flow) carried by each individual SB. This can be estimated by the heights of the shear steps at the surface after deformation. Tab. 1 lists the heights of the shear steps of each SB investigated in this study. By comparing these data with the FEM results shown in Fig. 2 and Fig. 3 there seems to be no correlation between the shear offset heights and the impact on the SB environment.

Next, we discuss the influence of the testing geometry on the observed deformation behavior. The different geometrical constraint for tension and compression loading defines the complex stress states in the deformation experiments of BMGs (here notched 3-point bending test) and has thus great influence on the deformation behavior (ductile-brittle) [26, 27]. Since similar deformation signatures (MRO gradients in Fig. 2 and Fig. 3) were found for both tested BMGs showing either ductile or brittle behavior, we believe that the observed MRO gradients represent characteristic stress states for the compressive and tensile side of notched 3-point bending tests. In fact, finite element simulations of BMGs under tensile load [28, 31] showed Von Mises stress distributions which correspond to the shapes of the $V(k)$ curves observed for the tensile side (Fig. 2). This means in conclusion that the MRO memorizes the impact of the stress field.

Table 1: Shear step height originating from the investigated SBs.

| Sample / location | Shear offset height at surface |
|-------------------|-------------------------------|
| Pd$_{40}$Ni$_{40}$P$_{20}$ [tensile side] | 130 nm |
| Vit105 [tensile side] | 40 nm |
| Pd$_{40}$Ni$_{40}$P$_{20}$ [compressive side] | 1.7 μm |
| Vit105 [compressive side] | 200 nm |

4.3. Shear-affected zones

Our results, including previous strain analyses [32] on individual SBs, show that the SB affected zones are in the range of a few microns as an upper limit. However, shear band environments probed by nanoindentation (hardness), Youngs modulus measurements or changes in magnetic domains were reported to extend to 10 – 160 microns [7, 11]. Moreover, these experiments also showed an increase in the lateral extension of the affected zones with in-creasing deformation [8, 9, 33]. We see two reasons for this discrepancy: Firstly, the fact that the measurement scales (lateral resolution) are not comparable to each other. Secondly, deformation frequently leads to (hidden) multiple shear banding with SBs branching off the primary one [33]. Such shear band branches do not always penetrate through the surfaces and thus often remain undetected by more indirect methods (nanoindentation, atomic or magnetic force microscopy). In conclusion our results, having a very good lateral resolution with the ability to visualize the individual SBs, strongly suggest a lateral extension of shear-affected zones in the range of a few microns as an upper limit.

5. Conclusions

Fluctuation electron microscopy revealed a detailed structural picture of the interplay between deformation and MRO structure obtained from two representative BMGs (Pd$_{40}$Ni$_{40}$P$_{20}$ and Zr$_{52.5}$Cu$_{17.5}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$) performed under 3-point bending conditions. (i) Prior to deformation, the amount of MRO was observed to be higher for Vit105 than for Pd$_{40}$Ni$_{40}$P$_{20}$. The degree of MRO was reduced after deformation. Profiling the MRO of shear band environments from compressive and tensile sides revealed characteristic gradients which seem to be material-independent and thus displaying the impact of the local stress state on the MRO. Our results show a lateral extension of shear-affected environments of shear bands in bulk metallic glasses with an upper limit of a few microns.

6. Acknowledgments

We gratefully acknowledge financial support by the DFG via SPP 1594 (Topological engineering of ultra-strong glasses, WI 1899/27-2 and GE 1106/11) and WI 1899/29-1 (Coupling of irreversible plastic rearrangements and heterogeneity of the local structure during deformation of metallic glasses, projekt number 325408982). Moreover, DFG funding is acknowledged for TEM equipment via the Major Research Instrumentation Programme under INST 211/719-1 FUGG.

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