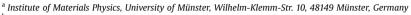Full length article

Shear band relaxation in a deformed bulk metallic glass

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ABSTRACT

Relaxation of shear bands in a $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass was investigated by radiotracer diffusion allowing to determine for the first time the effective activation enthalpy of diffusion along shear bands in a deformed glass. The shear bands relax during annealing below the glass transition temperature and the diffusion enhancement reveals unexpectedly a non-monotonous, cross-over behavior. The development of shear bands and the subsequent relaxation of stresses after the shear had been switched off are characterized on microscopic to mesoscopic length scales by molecular dynamics simulation subjecting a model glass to a constant strain rate. Mean-squared displacements as well as strain maps indicate that the heterogeneity, as manifested by shear bands in the systems under shear, persist after the shear was switched off. We observe a continued relaxation of residual stresses that remain localized in regions where the shear band has been present before, although the system is — different from the macroscopic experiment — homogeneous with respect to the local density. These results indicate that even on a local scale one may expect strong dynamic heterogeneity in deformed glassy solids due to shear banding that correlates with the existence of short-circuit type diffusion on a macroscale. The results thus suggest that plastically deformed metallic glasses present poly-amorphous systems that necessitate descriptions that are analogous to multiphase materials including the presence of heterophase interfaces.

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1. Introduction

Although non-homogenous plastic deformation of bulk metallic glasses (BMGs) via the formation of shear bands attracted increased attention in the past [1,2], it is still far from being resolved, see e.g. the reviews in Refs. [3,4]. As a generally accepted concept, so-called "shear transformation zones" (STZ), i.e. areas in which groups of atoms collectively undergo a local shear transformation, have been introduced [5] as "unit carriers" of plastic deformation in metallic glasses. A cross-over from random 3-dimensional shear events (STZ formation) to correlated 2-dimensional dynamics has been brought forward to explain the observed shear banding in metallic glasses [6]. Although the activation of a single STZ event is not inevitably related to a change of the excess volume, shear bands are often described in terms of excess volume accumulation [3,7]. Recently, we investigated diffusion in deformed $Pd_{40}Ni_{40}P_{20}$ (at. %; in what follows we will use the abbreviation PdNiP) glass, in which almost a single family of shear bands was introduced, and were able to

unambiguously prescribe the observed enormous enhancement of the diffusion rate to an ultra-fast atomic transport along these quasi-2-dimensional pathways [8]. The tracer concentrations in the corresponding concentration profiles, which were related to shear band diffusion, were shown to scale with the number density of the introduced shear bands (that in turn scales with the imposed strain), substantiating the reliability of the measurements. Nevertheless, dedicated TEM measurements revealed strong and probably characteristic changes of the specific volume along shear bands [9,10], with alternating regions of diluted and denser regions.

These results indicate significant modifications of the local structure of the glassy material inside the shear bands compared to the surrounding matrix, which have been revealed by local analyses via fluctuation electron microscopy [9,10], too. Additionally, these results point out that deformed glasses containing shear bands might be treated in analogy to a two-phase material including heterophase interfaces, with the second phase being the shear band phase that has undergone strong structural modifications due to the applied shear. Such structural modifications should also affect characteristic glass properties such as the relaxation dynamics and, potentially, might even affect the structure and properties of the matrix zones surrounding the shear bands via an

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exchange of the excess volume. On the other hand, structural relaxation is a characteristic process of glasses and thus serves as a sensitive probe for analyzing the presence of such an apparent poly-amorphicity in deformed metallic glasses.

In order to address the relaxation behavior of shear bands, in the present paper the diffusion rates in plastically deformed PdNiP glasses are experimentally measured as function of temperature and varying annealing and pre-annealing times. These measurements target the relaxation behavior that is specific of the glassy material inside the shear bands only, which is not possible by macroscopically averaging measurements, since the fraction of matter inside the shear bands is only of the order of 10^{-4} to 10^{-3} in a moderately deformed glass. Such information is, however, vital in order to understand the modifications of the structure of the glass inside the shear bands, as well as the possible coupling of excess volume fluxes and excess volume re-distribution inside the shear bands and within the surrounding matrix.

Complementary to the experiments, shear band relaxation is investigated by molecular dynamics (MD) computer simulations of a simple model of $Ni_{80}P_{20}$, namely a binary glass-forming Lennard-Jones (LJ) mixture, sheared with a constant strain rate. A small shear rate is applied that is associated with the formation of a shear band. Subsequently, the stress relaxation was analyzed by switching off the shear at different strain values. As a matter of fact, the shear stress does not decay to zero after switching off the shear field, but it tends to approach a finite value in the long-time limit and thus the resulting glass structure, albeit not sheared anymore, is established to remain under stress. Different from the response in the supercooled liquid state [11], such residual stress has been found to be the generic case with respect to stress relaxation after switching-off of shear in glassy solids [12]. Furthermore, the residual stresses are found to be *heterogeneously* distributed in the glass sample, thus reflecting the memory of the shear band, as formed in the sheared system. We analyze the formation of shear bands by a methodology that we have recently developed in the context of a sheared soft-sphere mixture in its glass state [13,14]. To this end, maps of the local mean-squared displacements (MSDs) are computed. The simple LJ-type glass-forming system is deliberately chosen in the present case to investigate the generic features of strain localization upon deformation on a well-characterized glass. The results of this approach will be discussed in the context of analyzing the microscopic origin of the observed macroscopic diffusion data, particularly concerning the existence of short circuits for diffusion transport in deformed glasses, namely the shear bands.

The simulations show that on microscopic to mesoscopic length scales the shear bands do not lead to heterogeneities that can be characterized by a significant variation of the local density, as found experimentally on significantly larger scales [9,10]. However, residual stresses are spatially localized in the region where the shear band was created earlier and the simulation can disentangle how these localized residual stresses affect the mechanical properties of the glass. Moreover, the direct comparison between experimental results (which involve macroscopically averaged data) and simulations allows analyzing the unexpectedly complex relaxation behavior of shear bands in metallic glasses that needs to be taken into account for any constitutive description of the plastic response of metallic glasses.

2. Experimental and simulation details

2.1. Material and characterization

PdNiP-based bulk metallic glass with the composition of $Pd_{40}Ni_{40}P_{20}$ (in at.%) was prepared by direct melting of palladium (purity 99.95 %) and Ni_2P powder (purity 99.5 %) in an alumina crucible using an induction furnace in a purified argon atmosphere. The chemical compositions of the samples were confirmed by atomic absorption spectroscopy (Mikroanalytisches Labor Pascher, Germany). The crystalline master alloy was re-melted and then chill-cast into a copper mold with a $1 \times 10 \times 30$ mm^3 cavity.

A glassy sample was plastically deformed by cold rolling in one step at room temperature. The deformation degree, ε, was determined by the thickness reduction and the strain rate, $\dot{\varepsilon}$, was estimated at about 5.5 s^{-1}. Cold rolling of the glassy samples led to shear band formation, which was detected by optical microscopy of the shear offset on the specimens surfaces. Plastic deformation to a relatively low strain of about 8% was applied and the resulting shear band density, ρ_{SB}, was estimated at about 0.06 μm^{-1}.

X-ray diffraction was performed using a Siemens D-5000 diffractometer equipped with a Cu cathode, a K_α monochromator, and a rotating sample holder in the $\theta-2\theta$ geometry, using a point detector.

Differential scanning calorimetry (DSC) characterization was performed by a Perkin Elmer Diamond power compensated DSC applying a constant heating rate of 20 K/min in a temperature interval from 303 K to 798 K. The sample mass was about 20—30 mg. The measured signals on crystallized samples were used as baselines.

2.2. Radiotracer diffusion experiments

The ^{110m}Ag radioisotope (half-life of 252 days) with an initial specific activity of about 17 MBq/mg was produced by neutron irradiation of a natural silver chip at the research reactor FRM II, TU Munich, Germany. The activated chip was first dissolved in 20 µl of HNO_3 and dissolved in 20 ml of double-distilled water. A droplet of the highly diluted ^{110m}Ag solution was deposited onto the polished surface of each specimen and dried. The specimens were evacuated in silica ampoules to a residual pressure less than 10^{-4} Pa, sealed, and annealed. The annealing temperatures were chosen well below the calorimetric glass transition temperature. After the annealing treatments, the samples were reduced in diameter to remove the effect of lateral and/or surface diffusion.

The penetration profiles were determined by the serial sectioning technique using a precision parallel grinder. As a key point we mention that a second γ-isotope, ^{59}Fe, was further applied just before sectioning in order to check for the possible existence of micro-cracks (not seen by optical microscopy) and to guarantee the absence of any artifacts related to mechanical sectioning. The relative radioactivity of each section was measured with an intrinsic Ge γ-detector. The penetration profiles represent the plots of the measured relative specific radioactivity of the sections with subtracted background (which is proportional to the layer concentration of solute atoms) against the penetration depth, y, squared (according to the solution of the diffusion equation for the present boundary conditions). It was proven that the intensity of the ^{59}Fe isotope decreases below the detection limit already after several sections, thereby validating the reliability of the penetration profiles measured for ^{110m}Ag diffusion.

The relaxation behavior of shear bands at 498 K was investigated applying the radiotracer diffusion measurements as a sensitive probe of the shear band state. To this end, the diffusion sample, once annealed at 498 K for 3 days, was re-grinded and polished to background radioactivity, the ^{110m}Ag tracer was deposited again, and the diffusion annealing at 498 K was repeated for 3 more days. This step was repeated 3 times, so that the sample was finally annealed in total for 12 days. In parallel, DSC scans were performed after each heat treatment on a similar (non-radioactive) sample.