Tracer Measurements of Atomic Diffusion inside Shear Bands of a Bulk Metallic Glass

Joachim Bokeloh,* Sergiy V. Divinski, Gerrit Reglitz, and Gerhard Wilde
Institute of Materials Physics, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm Strasse 10, 48149 Münster, Germany

(Received 7 September 2011; published 30 November 2011; corrected 6 December 2011)

Atomic diffusion in deformed $Pd_{40}Ni_{40}P_{20}$ bulk metallic glass containing a single family of deformation-induced shear bands was measured by the radiotracer technique. The significant, by orders of magnitude, enhancement of the diffusion rate with respect to that in the untransformed matrix suggests that the shear bands represent short-circuit diffusion paths. Correlations between diffusivity, viscosity, and the excess free volume distribution inside of shear bands are discussed.

DOI: 10.1103/PhysRevLett.107.235503 PACS numbers: 61.43.Dq, 66.30.Pa, 68.35.bj, 72.15.Cz

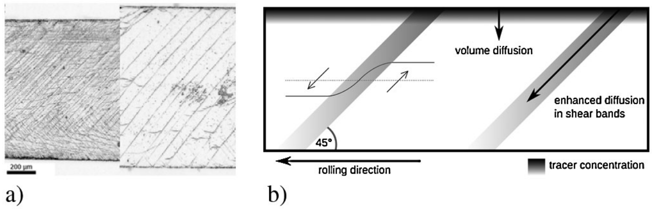
In the past two decades, the underlying mechanisms of shear banding in metallic glasses during plastic deformation has been subject to intensive research [1–3] because of the interesting mechanical properties of metallic glasses in general [4]. While the near theoretical strength of metallic glasses makes them immediately attractive for structural applications, this benefit is hampered by the low plasticity and—even more significant—the work softening observed in most cases [5], especially under tensile loading conditions. Only a few exceptions to this behavior have so far been reported, e.g., [6]. It is widely accepted that the work softening and the low plasticity are a consequence of the localization of the plastic deformation in shear bands, once the elastic limit has been exceeded [2,5] and that in the few cases where considerable plasticity is observed, this is caused by a hindrance of the propagation of shear bands [7]. Considerable effort has been undertaken to investigate the formation and propagation of shear bands [2,3] in order to understand the origin and the formation kinetics of this mesoscale defect. However, due to the inherent difficulties faced when investigating features that are only 10 to 50 nm in width [8], experiments are generally restricted to macroscopic probing and the atomistic details are mostly investigated by theoretical modeling and atomistic simulations [9–11], without input from experiments on the same microscopic scale. A few experiments that come near to probing the microscopic properties of shear bands were made by acoustic emission spectroscopy [12] and transmission electron microscopy [13,14].

Ever since the first publications on metallic glasses, a reduced viscosity as a key factor in the response of metallic glasses to an external mechanical stress has been repeatedly hypothesized. The first theoretical models for the observed flow softening rely on assuming an enhanced free volume inside the shear bands [2,5]. Some metallic glasses show preferential crystallization that has been strictly confined to the shear bands. While some researchers argue that this is caused by adiabatic heating of the glass during the deformation [15], the confinement of the crystallization to the shear bands [16] and the fact that the preferential crystallization also occurs in the postdeformed state and represent a thermally activated process [14] indicate already that the crystallization is largely due to an enhanced atomic mobility inside the shear bands.

The diffusion properties of bulk metallic glasses are considered to be investigated in detail and to a great extent to be well understood [17,18]. However, it is surprising that diffusion in a deformed glass so far was practically not investigated. To the best of our knowledge, in the only study available [19], a distinct but moderate enhancement of Au diffusion in a Ni-Zr glass was reported at relatively high temperatures near the corresponding glass transition point. However, no correlation has been drawn between the diffusion enhancement and the deformation-induced structure modification.

In the present study, for the first time, the diffusion measurements are performed on deformed metallic glasses at relatively low temperatures addressing directly the diffusion properties of shear bands. Since diffusion is extremely sensitive to the atomistic energy landscape of the (fastest) diffusion pathways, it is ideally suited to probe the changes in plastically deformed metallic glasses.

The radiotracer measurements were performed on the bulk metallic glass former $Pd_{40}Ni_{40}P_{20}$ that had been deformed by cold rolling in a controlled way to produce a single family of uniform shear bands [see Fig. 1(a)]. This



a) b)

FIG. 1. Optical image of cross sections of the deformed $Pd_{40}Ni_{40}P_{20}$ glasses (a) and the schematics of diffusion fluxes under the present experimental conditions (b). In (a), the images that were obtained for a sample reduced from 1.01 to 0.99 mm (true strain $\varepsilon_1 = 0.02$; on the right) and a sample reduced from 1.02 to 0.91 mm ($\varepsilon_2 = 0.1$; on the left) are combined for a better comparison. In (b), local shearing across a shear band is depicted schematically.

system is one of the best-studied bulk metallic glasses [20] and extensive experimental diffusion data for the as-prepared, undeformed state are also available [18,21]. Volume diffusion in this glass was already measured for ^{198}Au [21] and ^{103}Pd [18]. In the present study the ^{110m}Ag radiotracer was chosen for the investigation of localized diffusion in shear bands due to several reasons: (i) silver has a similar atomic radius to gold and palladium studied before and similar bulk diffusivities can be expected [22]; (ii) the β decays of the ^{110m}Ag isotope can be detected more precisely over the background by γ spectrometry that is a prerequisite for reliable measurements of localized diffusion.

The $Pd_{40}Ni_{40}P_{20}$ samples were prepared by melting pure Pd and Ni_2P powders in an induction furnace. Amorphous sheets with dimensions of $20 \times 10 \times 1$ mm^3 were then produced by copper mold casting. The samples appear fully amorphous in x-ray diffraction and transmission electron microscopy (TEM) including high resolution TEM. Differential scanning calorimetry was used to determine the glass transition temperature (585 K; half c_p) and the crystallization onset temperature (667 K). Further experiments show that annealing the samples for several hours at temperatures of up to 623 K does not cause discernible crystallization, in line with previous investigations [13]. The diffusion temperature of 473 K was chosen in order to guarantee the absence of crystallization during the diffusion annealing.

For the diffusion measurements, disc-type specimens were machined from the original samples and polished to a mirrorlike finish. Two radioisotopes, ^{110m}Ag and ^{59}Fe were applied. The ^{110m}Ag radioisotope was produced by neutron irradiation of a natural silver chip at the research reactor GKSS, Geesthacht, Germany. The irradiated chip was first dissolved in a small amount of HNO_3 which was then highly diluted by double-distilled water. The ^{59}Fe radioisotope was purchased as a 0.1 M HCl solution and diluted by double-distilled water.

First, the ^{110m}Ag tracer was applied by dropping few microliters of the corresponding solution and drying under an infrared lamp. The diffusion annealing treatment was carried out at 473 K for three days.

In order to ensure that the measured concentration profiles are the "fingerprints" of diffusion and were not induced by experimental artifacts such as cracks that might have been introduced by the deformation step or "grinding in" of the tracer during the sectioning process, the second tracer, ^{59}Fe, was deposited by the same drop-and-dry method on the polished surface after the diffusion anneal. Then, without any further diffusion annealing, the sectioning was performed by a high precision parallel grinding device.

A well-type intrinsic Ge γ detector with very low background has been used to measure the intensities of radioactive decays. The tracer concentration in a section is proportional to the measured intensity of the γ lines (with 656 and 1099 keV for ^{110m}Ag and ^{59}Fe, respectively) divided by the section mass. Further details on the technique can be found elsewhere [23].

The differences between the concentration profiles of ^{59}Fe and ^{110m}Ag measured on the undeformed sample are negligible (Fig. 2). The profiles represent solely the "device function" of the mechanical sectioning technique used. Thus, Ag diffused negligibly in the undeformed glass after annealing at 473 K for 3 days. This result agrees very well with the diffusion coefficients of Au and Pd measured previously in the $Pd_{40}Ni_{40}P_{20}$ glass. Extrapolating the given data [18,21], a bulk diffusivity of the undeformed glass of $D_V = 10^{-25}$ m^2/s is obtained as an estimate for the Ag volume diffusion coefficient D_V at 473 K. This value limits the penetration depth of the tracer in the bulk to 0.2 nm at this temperature for the given annealing time, which is well below the resolution limit of the mechanical sectioning method used.

The comparison of the obtained diffusion profiles of an undeformed sample and the samples deformed to different strains ($\varepsilon_1 = 0.02$ and $\varepsilon_2 = 0.11$) is shown in Fig. 2.

Most importantly, this result shows that under the given conditions, practically no detectable diffusion transport is observed in the undeformed $Pd_{40}Ni_{40}P_{20}$ glass, whereas a pronounced tracer penetration is obvious in the deformed samples that contain shear bands.

In the case of the deformed samples, the concentration profiles, Fig. 2, clearly indicate that the ^{110m}Ag tracer penetrated much deeper than the ^{59}Fe tracer, thus confirming that diffusion occurs due to the annealing treatment and is not related to, e.g., a hypothetical liquid penetration along a network of deformation-induced microcracks, as

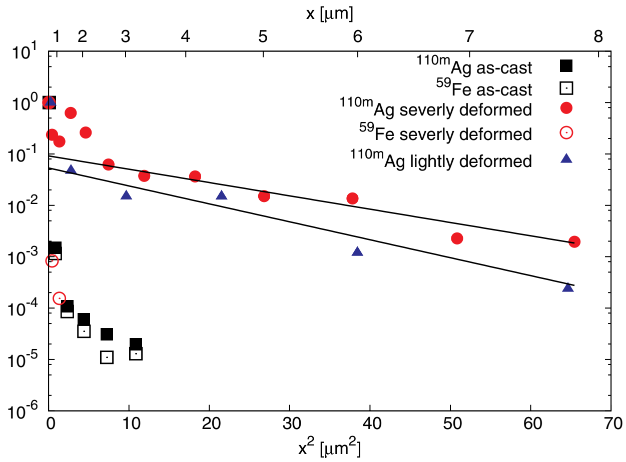


FIG. 2 (color online). Diffusion profiles of ^{110m}Ag (closed symbols) at 473 K in deformed samples compared to diffusion in an undeformed sample. The ^{59}Fe tracer (open symbols) was applied after the diffusion anneals and monitors experimental artifacts. Clearly, the diffusion in deformed samples is largely accelerated.

it was found, e.g., in severely deformed copper [24]. For both deformed samples, the tracer concentration profiles plotted against the square of the penetration depth can be fitted by the Gaussian solution and the following diffusion coefficients of ${D_{\mathrm{sb}}}^1 = 1.13 \times 10^{-17}\ \mathrm{m}^2/\mathrm{s}$ and ${D_{\mathrm{sb}}}^2 = 1.96 \times 10^{-17}\ \mathrm{m}^2/\mathrm{s}$ for the diffusion in the shear bands are obtained for the samples deformed to different strains, respectively (Fig. 2).

Since the plastic deformation is essentially localized to shear bands, it is reasonable to assume that the diffusion properties of the untransformed matrix are not significantly modified and that the zone of enhanced diffusivity is localized to the shear bands. Thus, the shear bands act as short-circuit diffusion paths in the glass [Fig. 1(b)] and thus diffusion in a deformed glass can be treated analogously to diffusion in a polycrystalline material with the shear bands corresponding to the grain boundaries. Since bulk diffusion is assumed to be frozen, the formal conditions of the C-type kinetics regime [25] are applied and the estimated effective diffusivities represent the rates of atomic transport within the shear bands. (The used assumption about the value of the bulk diffusion coefficient of Ag in the untransformed matrix of the deformed $\mathrm{Pd}_{40}\mathrm{Ni}_{40}\mathrm{P}_{20}$ glass is not very restrictive. Only if the true bulk diffusivity of the untransformed matrix is enhanced by 4 and more orders of magnitude with respect to the initial value, the formal B regime conditions [25] would apply and a different treatment of the diffusion problem would be required.)

A note is due here. The diffusion measurements in the C-type kinetics regime are not sensitive to the thickness of the short-circuit paths and it is an assumption that the zone of enhanced diffusion is related to the localization zone of plastic deformation. The diffusional width of the short-circuit paths could hypothetically be both larger as well as smaller than the shear band width.

The obtained diffusion coefficients are more than 8 orders of magnitude higher than the volume diffusion coefficients measured by [18,21]. This unexpectedly large difference cannot be explained in terms of a less relaxed glassy state of the matrix. The relaxation dependence of the diffusivity in metallic glasses is well studied [21,26] and the effect on diffusivity is usually within 1 order of magnitude. Thus, the present measurements verify unambiguously that the atomic diffusivity in shear bands is largely enhanced and remains to be significantly enhanced even after the external stress field has ceased.

Since diffusion is closely linked to the microstructure, such a drastic change of the diffusion coefficient also implies that the atomic structure of the shear bands differs considerably from the structure of the matrix. According to Rätzke *et al.* [18], the Stokes-Einstein equation is valid for the largest constituent—in this case Pd—even at temperatures of more than 100 K below the glass transition point. We may assume that this relation holds also in the present case and that it is applicable for silver diffusion, too, since the atomic radii of Ag and Pd are similar. Then applying the Stokes-Einstein equation,

$$D = \frac{k_B T}{6\pi\eta a},$$

where η is the viscosity, k_B the Boltzmann constant, and a the atomic radius, the measured short-circuit diffusion coefficients D_{sb} are translated into a hypothetical viscosity of the shear bands of about 10^5 Pa s.

A viscosity of this magnitude prompts several issues. A viscosity of 10^5 Pa s is much too low for a glassy state and is typical for the undercooled liquid region. Literature values of the viscosity of $\mathrm{Pd}_{40}\mathrm{Ni}_{40}\mathrm{P}_{20}$ show that 10^5 Pa s are reached at around 700 K—more than 100 K above the glass transition [27,28]. In this state, instantaneous relaxation can be expected and therefore it should be expected that no enhanced diffusion should be measurable. In addition, it also seems highly unrealistic that mechanical integrity could be maintained with sheets of low-viscosity material of considerable thickness (10–50 nm) present inside the otherwise almost unchanged matrix material: a viscosity of 10^5 Pa s translates into a shear rate of the order of 1 s^{-1} under the shear force of the samples' own mass.

In the case that the Stokes-Einstein equation is indeed valid for the short-circuit paths in question, the enhancement of D_{sb} with respect to the matrix diffusivity is quite spectacular in terms of the viscosity η. On the other hand, the relation between the magnitudes of bulk and grain boundary diffusion in crystalline solids falls into a similar range. According to Wolf [29], general high-angle grain boundaries, which represent typically the fastest short-circuit diffusion paths in a polycrystalline metal, contain about 10% extra free volume with respect to the crystalline bulk. The diffusion enhancement in general high-angle grain boundaries in metals is generally explained in terms of a less ordered and more open structure of the interfaces with respect to the crystalline bulk. Such structure arguments are at least not straightforward for shear bands with approximate widths of a few tens of nanometers while quantitatively similar diffusion enhancement is observed. This discrepancy indicates that the mobility distribution might not be represented by assuming uniform characteristics for the entire shear band.

Instead, the observed diffusion profiles can be explained by diffusion mediated through free volume accumulated—for example—at or near the interfaces between the shear band and the matrix. The underlying physical picture may conceptually resemble the situation of a two-component single phase material that has undergone the so-called prewetting phase transition, as, e.g., in polycrystalline copper-based alloys where the grain boundaries under particular conditions are covered by 2D quasiliquid bismuth-rich layers, even in the single phase region of the corresponding phase diagram [30]. Extremely high grain boundary diffusion coefficients of the order of 10^{-8}

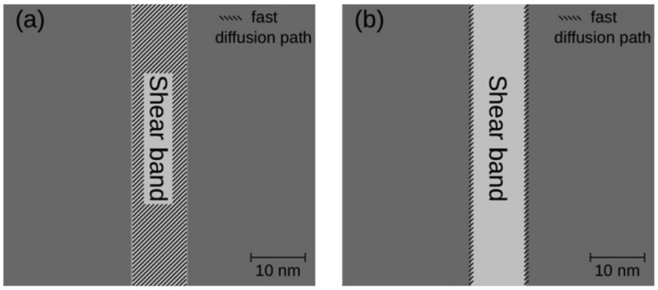


FIG. 3. Schematic drawing of constitutive models of shear bands in deformed metallic glasses. The shaded areas represent the fast diffusion pathways and would correspond to a locally increased free volume fraction. Both scenarios—an enhanced diffusion across the whole shear band (a) or an enhanced diffusion limited to the boundary between shear band and amorphous matrix (b)—would be compatible to the measured diffusion profiles.

to 10^{-9} m^2/s, which do correspond to diffusion transport in a liquid, were measured for 1 nm thin interface layers in Cu-Bi alloys under such conditions, while the samples remain structurally integer [31]. In analogy to those findings, the current results suggest the possible existence of similar high-mobility pathways at the interfaces between shear bands and matrix or even the appearance of "2D confined liquid" layers in deformed bulk metallic glasses.

A schematic drawing of the hypothetical location of the fast diffusion paths and the corresponding accumulation of the excess free volume across a shear band, according to our hypothesis, is given in Fig. 3. The previous semiquantitative arguments prefer the model (b) in Fig. 3 with interfacelike localization of the free volume in shear bands. The exact nature of the localization is pure speculation. The fast diffusion path may as well run through the center of the shear band or even follow a more complex route, running back and forth across the shear band in a zigzag manner.

Let us assume now that the Stokes-Einstein relation is not valid in the present conditions. Evidence that the Stokes-Einstein relation is not necessarily valid in dense liquids was, for example, recently given by Brillo *et al.* [32].

Then, the possible reasons for the enhanced diffusivity can be found in a significant change of the energy landscape of the shear band as compared to the undeformed matrix. An increase of the diffusivity by 8 orders of magnitude corresponds formally to a decrease of the energy barriers by about 0.7 eV. For example, a significant shift (0.4 eV) in the distribution of transition energies was reported by Rodney *et al.* for a Lennard-Jones $Cu_{50}Zr_{50}$ model glass after simulated deformation [33]. Such a change in the energy landscape can also explain the change in diffusivity without relying on the structural modifications that would lead to the drastically decreased viscosity and the connected problems of instantaneous relaxation and structural integrity.

Comparing the present experimental results to simulations is difficult at best, since direct molecular dynamics simulations at such relatively low temperatures are absent so far. Additionally, in the present set of experiments, the postdeformed state was examined, which is not easy to perform by simulations, since the simulated glasses after deformation are at very high fictive temperatures [34] and instantaneous relaxation is expected. In their very recent atomistic study, Albe and Ritter observed a moderate, but distinct enhancement of the Cu and Zr diffusivities inside of a shear band with respect to that of the untransformed matrix in a $Cu_{64}Zr_{36}$ glass [11].

In summary, by the radiotracer measurements we established that the atomic diffusion in the shear bands of the metallic $Pd_{40}Ni_{40}P_{20}$ glass is enhanced by more than 8 orders of magnitude with respect to that in the untransformed matrix. This fact agrees well with reports of a less dense atomic structure of the shear bands and can explain the occurrence of highly localized crystallization inside shear bands. The localization and mechanical stability of the excess free volume inside shear bands represent a nontrivial issue. In fact, it remains unclear how a highly nonrelaxed state could remain for extended times, even at temperatures considerably below the glass transition. Additionally, an even distribution of the excess free volume throughout the shear band would challenge the structural integrity of the material. We thus suggest that the excess free volume inside the shear bands is not homogeneously distributed, but tends to accumulate at or near the interfaces between unmodified matrix and shear band, which in this sense resemble grain boundaries in polycrystalline materials. Conceptually, this picture is similar to Gleiter's suggestions concerning "nanoglasses" and their kinetic stability [35]. Severe deformation of a metallic glass under high (quasi-)hydrostatic pressure that has also been shown to introduce enhanced number densities of nanocrystals [36] may introduce such interfaces in the glassy matrix and transform it to a "fine-grained" glass state. A conceptually different explanation might be given by changes of the energy landscape of the glass inside the shear bands. Further investigations are necessary to distinguish between these different scenarios.

The authors would like to acknowledge the support by Research Center Geesthacht for tracer activation and the financial support by DFG. In addition, we like to thank the reviewers for their constructive suggestions and for bringing Ref. [33] to our attention.

---

[*] Corresponding author.
joachim.bokeloh@uni-muenster.de

[1] C. A. Pampillo, Scr. Metall. **6**, 915 (1972).
[2] A. S. Argon, Acta Metall. **27**, 47 (1979).

[3] C. A. Schuh, Acta Mater. **55**, 4067 (2007).
[4] W. H. Wang, C. Dong, and C. H. Shek, Mater. Sci. Eng., R **44**, 45 (2004).
[5] F. Spaepen, Acta Metall. **25**, 407 (1977).
[6] J. Schroers and W. L. Johnson, Phys. Rev. Lett. **93**, 255506 (2004).
[7] C. C. Hays, C. P. Kim, and W. L. Johnson, Phys. Rev. Lett. **84**, 2901 (2000).
[8] Y. Zhang and A. L. Greer, Appl. Phys. Lett. **89**, 071907 (2006).
[9] K. Brinkmann and H. Teichler, Phys. Rev. B **66**, 184205 (2002).
[10] M. L. Falk and J. S. Langer, Phys. Rev. E **57**, 7192 (1998).
[11] Y. Ritter and K. Albe, Acta Mater. **59**, 7082 (2011).
[12] A. Y. Vinogradov and V. A. Khonik, Philos. Mag. **84**, 2147 (2004).
[13] Y. M. Chen, T. Ohkubo, T. Mukai, and K. Hono, J. Mater. Res. **24**, 1 (2009).
[14] G. Wilde and H. Rösner, Appl. Phys. Lett. **98**, 251904 (2011).
[15] A. A. Csontos, G. J. Shiflet, Nanostruct. Mater. **9**, 281(1997).
[16] R. J. Hebert, J. H. Perepezko, H. Rösner, and G. Wilde, Scr. Mater. **54**, 25 (2006).
[17] F. Faupel *et al.*, Rev. Mod. Phys. **75**, 237 (2003).
[18] A. Bartsch, K. Rätzke, A. Meyer, and F. Faupel, Phys. Rev. Lett. **104**, 195901 (2010).
[19] D. Akhtar, B. Cantor, and R. W. Cahn, Bull. Mater. Sci. **7**, 3 (1985).
[20] G. Wilde, G. P. Görler, R. Willnecker, and G. Dietz, Appl. Phys. Lett. **65**, 397 (1994).
[21] P. A. Duine, J. Sietsma, and A. van den Beukel, Phys. Rev. B **48**, 6957 (1993).
[22] A.van den Beukel, Acta Metall. Mater. **42**, 1273 (1994).
[23] S. V. Divinski, G. Reglitz, and G. Wilde, Acta Mater. **58**, 386 (2010).
[24] J. Ribbe, D. Baither, G. Schmitz, and S. V. Divinski, Phys. Rev. Lett. **102**, 165501 (2009).
[25] L. G. Harrison, Trans. Faraday Soc. **57**, 1191 (1961).
[26] W. Dorner and H. Mehrer, Phys. Rev. B **44**, 101 (1991).
[27] G. Wilde, G. P. Görler, R. Willnecker, and H. J. Fecht, J. Appl. Phys. **87**, 1141 (2000).
[28] I.-R. Lu, G. Wilde, G. P. Görler, and R. Willnecker, J. Non-Cryst. Solids **250–252**, 577 (1999).
[29] D. Wolf, Curr. Opin. Solid State Mater. Sci. **5**, 435 (2001).
[30] L.-S. Chang *et al.*, Acta Mater. **47**, 4041 (1999).
[31] S. V. Divinski, M. Lohmann, C. Herzig, B. Straumal, B. Baretzky, and W. Gust, Phys. Rev. B **71**, 104104 (2005).
[32] J. Brillo, A. I. Pommrich, and A. Meyer, Phys. Rev. Lett. **107**, 165902 (2011).
[33] D. Rodney and C. Schuh, Phys. Rev. Lett. **102**, 235503 (2009).
[34] T. Egami, V. A. Levashov, J. R. Morris, and O. Haruyama, Metall. Mater. Trans. A **41**, 1628 (2010).
[35] D. Sopu, K. Albe, Y. Ritter, and H. Gleiter, Appl. Phys. Lett. **94**, 191911 (2009).
[36] N. Boucharat *et al.*, Scr. Mater. **53**, 823 (2005).