PHYSICAL REVIEW B, VOLUME 64, 180201(R)

Enhanced plastic strain in Zr-based bulk amorphous alloys

L.-Q. Xing
Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218

Y. Li and K. T. Ramesh
Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland 21218

J. Li and T. C. Hufnagel
Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218

(Received 12 June 2001; published 1 October 2001)

Bulk metallic glasses subjected to quasistatic uniaxial compression at room temperature typically display large elastic strains but limited plastic flow of 0–2% before failure. We have developed an amorphous alloy, $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, which experiences an average macroscopic plastic strain of 4.5% before failure. The as-cast alloy shows no evidence for the presence of crystalline phases, and displays a distinct glass transition temperature and a wide supercooled liquid region. Upon compression beyond the yield point, the alloy develops shear bands which show a pronounced tendency for branching. We propose that this shear band branching distributes the plastic strain on the shear band, thereby suppressing crack initiation and allowing the material to experience a large macroscopic plastic strain before failure.

DOI: 10.1103/PhysRevB.64.180201 PACS number(s): 62.20.Fe, 81.05.Kf, 61.43.Dq

The mechanical behavior of bulk metallic glasses at low temperatures (well below the glass transition) is quite different from that of crystalline alloys. The macroscopic behavior under quasistatic loading is approximately elastic-perfectly plastic, with an extended region of elastic strain (2–3%) followed by apparent overall plastic flow at nearly constant stress.[1–3] Plastic deformation is highly localized into shear bands, which initiate and rapidly propagate across the sample at an angle of approximately 45° to the loading axis; a shear band can also initiate a crack which will cause macroscopic fracture. In uniaxial tension, crack initiation and propagation occurs almost immediately after the formation of the first shear band, and as a result metallic glasses tested in tension show essentially zero plastic strain prior to failure.[1]

In compression, in contrast, some overall plastic strain is usually observed. If the specimen geometry is such that the shear bands cannot propagate across the entire width of the sample (that is, if the aspect ratio is less than 1:1), then a large number of shear bands can form and large plastic strains develop. If the specimen length is greater than its width, then shear bands can propagate across the width of the sample, but typically several shear bands still form, causing overall plastic strains of 0–2%. It is also possible to enhance the ductility of metallic glasses by creating a composite material, in which second-phase particles can act both as initiation sites for shear bands and as barriers to shear band propagation. The result is a dramatic increase in the number density of shear bands, which in turn allows for significant ductility even in uniaxial tension.[4]

In this paper, we describe a bulk glass-forming alloy, $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, with enhanced plasticity relative to other bulk metallic glasses. We observe, for instance, a mean plastic strain to failure under quasistatic uniaxial compression of 4.5% for rods 6 mm long and 3 mm diameter (2:1 aspect ratio) of this alloy, as compared to 1.1% for identical samples of the related alloy $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$. The alloy shows no evidence for long range atomic ordering in either x-ray diffraction or high resolution transmission electron microscopy, and retains all of the thermal characteristics of a bulk metallic glass including a distinct glass transition and a wide supercooled liquid region. The enhanced plastic strain of this alloy is apparently due to a strong tendency for the shear bands to branch while propagating. The branching presumably redistributes plastic strain that would promote crack initiation and therefore failure, or makes it difficult for a crack to grow in a single plane.

The alloys described here have the general composition $Zr_aTa_bTi_cCu_dNi_8Al_{10}$, with $45 \leqslant a \leqslant 70$, $0 \leqslant b \leqslant 10$, $0 \leqslant c \leqslant 5$, and $18 \leqslant d \leqslant 20$. (All compositions are stated in atomic percent.) We present a detailed comparison of the properties of one composition, $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ (which has the largest plastic strain of the compositions we have examined), with those of a conventional bulk amorphous alloy $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$. Samples were produced by arc melting the pure elements together under a purified Ar atmosphere into ingots of the desired composition; each ingot was then remelted twice to ensure a homogeneous composition. We then made 3 mm diameter rods of metallic glass by suction casting the molten alloy into a copper mold.

To characterize the structure of the metallic glass samples, we used a Philips x-ray powder diffractometer with Cu Kα radiation and a graphite monochromator in the diffracted beam. Because x-ray diffraction is not capable of revealing the presence of very small crystallites, we also examined sections of the metallic glass rods by high resolution electron microscopy using a Philips CM300 field emission gun transmission electron microscope operated at 300 kV. Samples for electron microscopy were prepared by electropolishing using a solution of 10% perchloric acid in ethanol at a temperature of $-30\,°C$. The resulting electropolished samples have a thin surface oxide, which was removed by subsequent ion beam thinning for one hour.

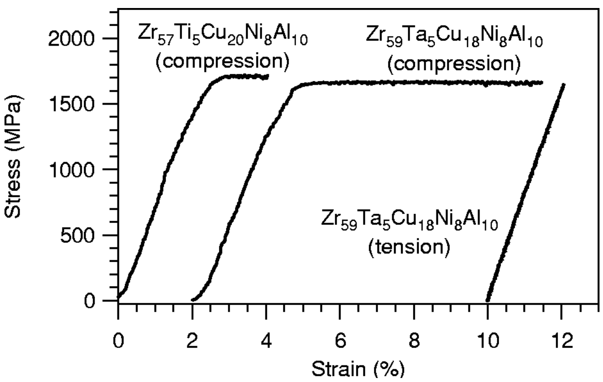

FIG. 1. Stress-strain curves for a conventional bulk metallic glass, $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$, in uniaxial compression, and the alloy $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ in uniaxial compression and tension. The curves have been offset along the strain axis for clarity. Note the extended region of plastic deformation in the Ta-containing alloy.

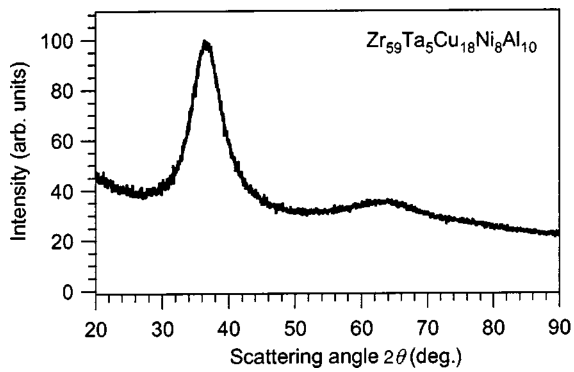

FIG. 2. X-ray diffraction pattern from the as-cast $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ alloy (Cu Kα radiation). There are no sharp diffraction features indicative of crystalline phases.

The uniaxial compression tests were performed on 6 mm long sections cut from the 3 mm diameter cylinders; the samples were lapped in a jig designed to ensure parallelism of the ends. We used a servohydraulic testing machine under displacement control and calculated the strain from the displacement of the machine platens. The platens were lubricated with lithium grease to minimize friction effects. The tensile samples had a gauge section 6 mm long and 2 mm in diameter. For all of the tests described here the strain rate was 1×10^{-4} s^{-1}.

Figure 1 shows a stress-strain curve for a sample of the alloy $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ tested in uniaxial compression, together with that of a conventional bulk metallic glass, $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$. In each case the sample was tested to failure. The mechanical behavior of both alloys is approximately elastic-perfectly plastic, with approximately 2.5% elastic strain and a flow stress of about 1700 MPa. Serrated flow is apparent in the plastic region of both stress-strain curves. $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, however, shows a plastic strain to failure of 6.8%, while that of the conventional glass is only 1.3%. After failure, the fracture surfaces of both samples have the vein pattern morphology characteristic of metallic glasses. Tests on other samples of the same compositions show similar results, although there is some scatter in the plastic strain measurements (Table I). The enhanced plasticity of $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ does not, however, extend to tensile loading; as also shown in Fig. 1, there is essentially zero tensile ductility. This is true for other monolithic bulk metallic glasses as well.

TABLE I. Mechanical properties of bulk amorphous $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ under quasistatic loading. Typical compressive properties of another bulk amorphous alloy, $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$, are shown for comparison.

Alloy	Loading	Flow/fracture strength (MPa)	Plastic strain to failure (%)
$Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$	Compression	1700 ± 60	4.5 ± 1.9
	Tension	1630 ± 110	0
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	Compression	1710 ± 30	1.1 ± 0.4

Enhanced plastic strain to failure has been observed in other Zr-based metallic glasses in which crystalline phases are present, either as reinforcements in metallic-glass matrix composites[5] or as crystalline phases that precipitate out during cooling.[4] We have considered this possibility by carefully examining the structure of our samples. Figure 2 shows an x-ray diffraction pattern from a sample of $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ in the as-cast state. The x-ray diffraction pattern resembles that of a fully amorphous material, with a broad amorphous scattering maximum but no sharp diffraction features indicative of the presence of crystalline phases. Figure 3 shows a high resolution transmission electron micrograph and electron diffraction pattern from the same alloy; again, there is no evidence for any crystalline phases. (A complete through-focus series yields the same conclusion.) The minimum observable crystallite size with this technique is about 2 nm, so we conclude that there are no crystallites larger than this present in the sample.

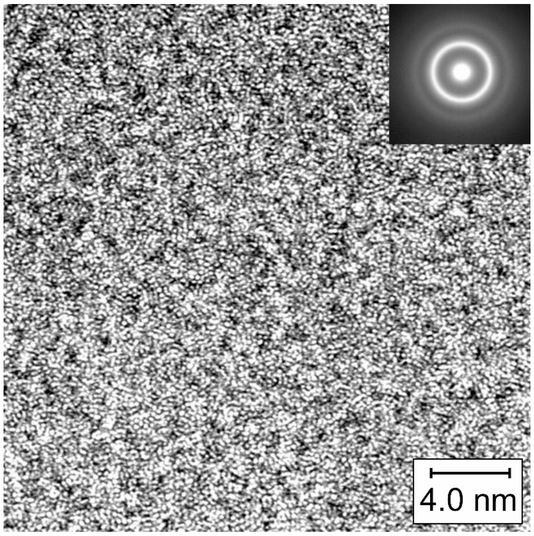

FIG. 3. High resolution TEM image of as-cast $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$. No lattice fringes are visible. Inset: Selected area electron diffraction pattern.

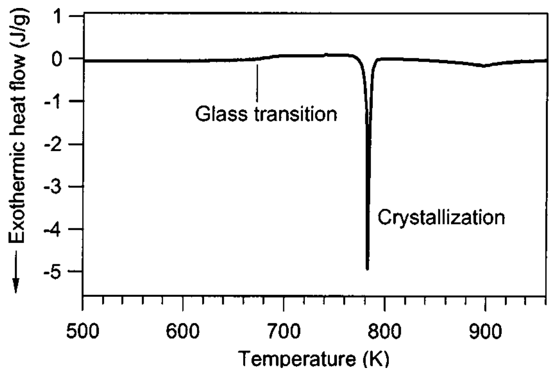

FIG. 4. Differential scanning calorimetry data collected from $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ at a heating rate of 20 K/min. There is a distinct glass transition at 673 K, and the onset of crystallization occurs at 770 K.

Additional confirmation of the amorphous nature of the samples comes from differential scanning calorimetry (Figure 4). The as-cast $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ alloy shows a distinct glass transition at 673 K (for a heating rate of 20 K/min), with an onset of crystallization at 770 K. The supercooled liquid region is therefore 97 K wide; in comparison, $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ has a supercooled liquid region of 52 K.[6]

Based on the structural and thermal characterization, we conclude that the as-cast $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ alloy is fully amorphous with no long-range order and no crystalline phases larger than about 2 nm (the limit of detection). Given that there are no crystalline phases to interact with the shear bands, it is not immediately obvious why the plastic strain to failure should be larger in $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ than in $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$.

To gain a greater understanding of the shear band behavior, we made several compression specimens with rectangular cross sections and polished the surfaces parallel to the loading axis to a mirror finish. When such a specimen is compressed beyond the yield point but unloaded before fracture occurs, slip steps are visible where shear bands intersect the specimen surface. Figure 5 shows slip steps on the surfaces of samples of $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ and $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ loaded in this way. The slip steps in $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ are, for the most part, straight and usually exist as well-separated individual steps. In contrast, the slip steps for $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ are more jagged and typically occur as groups of several slip steps close together. We believe that these features occur due to the branching of individual shear bands as they propagate through the material. Branching can distribute the plastic strains associated with the shear band; furthermore, the shear strain in any one branch may be much smaller than that of a single, unbranched shear band. This makes it more difficult for a propagating shear band to result in a crack that will cause failure, and therefore the plastic strain prior to failure is increased.

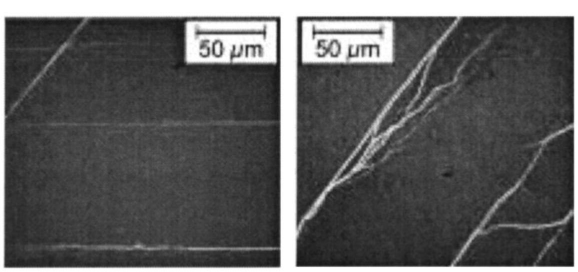

FIG. 5. Scanning electron micrographs of slip steps on the surfaces of samples of $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ (left) and $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ (right) loaded in uniaxial compression beyond the yield point.

If the enhanced plastic strain to failure is due to shear band branching, what is it about the alloy that promotes this branching mechanism? While we are presently examining this question, we propose two possibilities. First, several Zr-based bulk metallic glasses experience phase separation upon annealing;[7–9] it is possible that $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ phase separates into regions of different composition upon cooling from the liquid state. A propagating shear band reaching a region of different composition (and therefore different density) might be forced to branch, analogous to crack deflection in composite materials. A second possibility is that the structure of $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$, while apparently amorphous, has significantly enhanced medium-range order (structure on the 1–2 nm scale), which influences free volume distribution and therefore shear band propagation. Preliminary evidence in support of enhanced medium-range order in $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ is presented elsewhere.[10]

Recent work has shown that annealing some Zr-based bulk metallic glasses can also result in enhanced plastic strain to failure.[11,12] The enhanced plastic strain was attributed to the presence of a small volume fraction ($<20\%$) of nanocrystals that developed upon annealing; it was postulated that the nanocrystals acted as either initiation sites for shear bands or barriers to shear band propagation (or both). It is worth noting, however, that in addition to partial devitrification, annealing can produce changes in the amorphous matrix, such as spinodal decomposition and structural relaxation. Our observation that plastic strain can be enhanced without the production of nanocrystals suggests that these matrix effects may be predominant, and that the nanocrystals themselves may have little effect on the mechanical properties, so long as the volume fraction of nanocrystals is not too large.

In conclusion, we have demonstrated that small changes in composition of fully disordered alloys can have a dramatic effect on mechanical behavior. In particular, $Zr_{59}Ta_5Cu_{18}Ni_8Al_{10}$ has a significantly enhanced plastic strain to failure, probably due to branching of the shear bands. This suggests that the structure and mechanical properties of fully disordered alloys are more complex than has been appreciated, and presents the possibility of developing bulk metallic glasses with even greater plasticity.

We gratefully acknowledge Y. Ding and K. Livi for assistance with the transmission electron microscopy, S.-Y. Hwang and J. Spangler for assistance with mechanical testing, and useful discussions with C. Fan. This work was supported by the U.S. Army Research Laboratory under Grant No. DAAL-019620047; support for the transmission electron microscopy was provided by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

[1] H.A. Bruck, T. Christman, A.J. Rosakis, and W.L. Johnson, Scr. Metall. Mater. **30**, 429 (1994).

[2] L.Q. Xing, C. Bertrand, J.-P. Dallas, and M. Cornet, Mater. Sci. Eng. **A241**, 216 (1998).

[3] A. Inoue, Acta Mater. **48**, 279 (2000).

[4] C.C. Hays, C.P. Kim, and W.L. Johnson, Phys. Rev. Lett. **84**, 2901 (2000).

[5] R.D. Conner, R.B. Dandliker, and W.L. Johnson, Acta Mater. **46**, 6089 (1998).

[6] L.Q. Xing, P. Ochin, M. Harmelin, F. Faudot, J. Bigot, and J.P. Chevalier, Mater. Sci. Eng., A **220**, 155 (1996).

[7] S. Schneider, P. Thiyagarajan, and W.L. Johnson, Appl. Phys. Lett. **68**, 493 (1996).

[8] J.F. Löffler, P. Thiyagarajan, and W.L. Johnson, J. Appl. Crystallogr. **33**, 500 (2000).

[9] T.C. Hufnagel, X. Gu, and A. Munkholm, Mater. Trans., JIM **42**, 562 (2001).

[10] J. Li, X. Gu, and T. C. Hufnagel, Microsc. Microanal., Suppl. 2 **7**, 1260 (2001).

[11] C. Fan and A. Inoue, Appl. Phys. Lett. **77**, 46 (2000).

[12] C. Fan, C. Li, A. Inoue, and V. Haas, Phys. Rev. B **61**, R3761 (2000).