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ABSTRACT

The fracture and plastic deformation mechanisms of a Zr-Ti-Ni-Cu-Be bulk metallic glass and a composite utilizing a crystalline reinforcement phase are reviewed. The relationship between stress state, free volume and shear band formation are discussed. Positron annihilation techniques were used to confirm the predicted increase in free volume after plastic straining. Strain localization and failure were examined for a wide range of stress states. Finally, methods for toughening metallic glasses are considered. Significant increases in toughness are demonstrated for a composite bulk metallic glass containing a ductile second phase which stabilizes shear band formation and distributes plastic deformation.

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INTRODUCTION

The recent development of *bulk* metallic glasses allows the mechanical behavior of these unique materials to be studied and modeled under a variety of loading conditions and stress states. Although bulk metallic glasses have shown potential as structural materials, applications are currently limited by the lack of any significant plastic deformation. Bulk metallic glasses fail by forming intense shear bands which propagate catastrophically due to the lack of grain structure and work hardening [1].

In this work, we review our examination of the relationship between free volume and deformation of a Zr-based bulk metallic glass. In particular, the effect of mean stresses on free volume and flow localization was examined. Flow processes in metallic glasses are associated with a dramatic increase in free volume. To address this issue directly, positron annihilation techniques were used to characterize the free volume of the bulk metallic glass before and after straining and after crystallization. Additionally, the issue of shear band stabilization is discussed. A dendritic Zr-Ti-Nb phase precipitated *in situ* [2] is used to reinforce the bulk metallic glass matrix, leading to stable crack growth at stress intensities nearly double the fracture toughness of the monolithic alloy.

EXPERIMENTAL

Positron lifetime and Doppler broadening of the associated annihilation γ-rays were used to study the open volume defects in a $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass. The sample thickness of 6 mm was sufficient to completely block the positron beam. Details of the techniques are available elsewhere [3-5]. Samples were prestrained in compression for the positron annihilation experiments. Additional samples were cathodicly charged with hydrogen as described previously [6].

To examine the effect of stress state on flow localization, notched bars with notch radii between 0.25 and 2.50 mm (10 mm diameter gauge section) were machined and tested on an electro-servo-hydraulic system with a crosshead displacement rate of 5 μm/s. Elongation across the notch was monitored with a clip gage. An elastic analysis of the stress state in the notched region was performed to determine the mean and effective stresses. Further details are described elsewhere [7].

The Mode I crack growth behavior of a bulk metallic glass reinforced with a ductile dendritic Zr-Ti-Nb phase formed *in situ* was studied [2]. Compact tension (C(T)) samples were machined from plates and fatigue precracked. Fracture testing was performed on a high resolution electro-servo-hydraulic test system operating under displacement control according to ASTM-E399 standards.

RESULTS

Positron lifetime results for the prestrained samples together with data for samples which had been hydrogen charged are shown in comparison with an as-received sample in Figure 1(a). Compared to the control sample, the prestrained samples have slightly longer (~1 ps) positron lifetimes, consistent with the notion of an increase in free volume associated with shear band formation. The hydrogen charged samples, in which hydrogen occupies some of the free volume sites, exhibited shorter positron lifetimes than the reference. While the differences in the positron lifetimes are small, Doppler broadening data confirm these results. A comparison of the contribution of core and valence electrons to Doppler broadening of the annihilation γ-ray spectra is shown in Figure 1(b). The prestrained samples have a smaller contribution from core electrons, indicating a smaller energy shift and therefore more open volume. Conversely, the hydrogen charged samples exhibit a larger contribution from core electrons than the reference sample, consistent with positron trapping in smaller open volume sites and interactions with the hydrogen atoms themselves. Further results using a low energy positron source also indicated that very heavy hydrogen charging causes an increase in open volume defects, possibly due to the opening of subsurface cracks or flaws. This is consistent with observations of surface flaking [6].

The annihilation γ-ray momentum spectra obtained from the bulk metallic glass samples were compared with a composite spectrum of the individual components, obtained from pure (>99.9%) reference samples. The experimental and theoretical spectra for the alloy in the as-received condition are shown in Figure 2(a), where the theoretical composite spectrum includes the constituents in their atomic percentages. Similar results were obtained for the prestrained and crystallized samples. Obviously, the positron trapping sites are not distributed evenly among all the constituents. By adjusting the fractional contribution of each of the pure spectra, a better fit to the actual results is obtained. Only three components, Zr, Ti, and Be, were required for a good fit. The adjusted fractions are compared with the stoichiometric fractions in Figure 2(b). It is apparent that the annihilation spectrum has a larger contribution from Zr and Ti at the expense of Ni, Cu, and Be. This implies that the Zr and Ti sit in more open volume regions, while the smaller atoms are more closely surrounded by their neighbors, as has been noted in a similar metallic glass alloy [4]. Note that the strained samples consistently exhibited a slight 2-4% increase in the contribution of Zr and a corresponding decrease in Ti, suggesting some chemical reordering associated with plastic flow. The Zr contribution increased dramatically in the crystallized sample, while the Ti contribution again showed a complimentary decrease. This significant reordering is expected during the crystallization process.

In the stress state study, all tensile bars failed in the notch region with a cup and cone type morphology similar to that found in ductile metals. Fractographic evidence suggests that failure initiated at some point in the interior of the notched region of the bar, rather than at the notch tip. The crack front propagated radially on a plane perpendicular to the tensile axis, followed by the formation of ~45° shear lips. Equiaxed voids were noted near the initiation point, while the remainder of the failure surface exhibited typical vein patterns with smeared voids and molten droplets on the shear lip surface [7]. Although the failure surfaces exhibited significant softening, the plastic strain as measured from the change in bar diameter at the root of the notch was negligible.

The effective and mean stresses at the failure initiation site were compared as functions of the stress state at failure as shown in Figure 3. For the stress states used in this study, the mean stress remains relatively constant with stress state, with an average value of 0.95 ± 0.13 GPa, while the effective stress decreases with increasing triaxiality. This suggests that a critical mean stress was attained at failure for the tensile stress states examined. This is contrasted with results from other studies utilizing compressive means stresses [1, 8].

Shear band stabilization has been observed in the bulk metallic glass fracture toughness experiments utilizing the SEN(T) geometry [9]. A more consistent method for shear band stabilization is the incorporation of a ductile crystalline second phase. In this case, the second phase blocks and redirects shear bands, leading to a distributed damage zone at the crack tip as shown in Figure 4. This damage zone also gives rise to stable crack growth over a range of up to 2 mm, in contrast to the unstable crack growth observed in the monolithic alloy. The resistance curve behavior of the composite is shown in Figure 5. Final failure occurred at an applied stress intensity of up to 35 MPa√m, almost double the fracture toughness of the unreinforced bulk metallic glass. While the second phase distributed the plastic damage, no evidence of crack bridging was observed.

DISCUSSION

Positron annihilation results confirm the increase in free volume associated with even small plastic strains in metallic glasses. Direct evidence of short range reordering of the metallic glass structure following straining was also apparent. The role of adiabatic heating in the softening evident on fracture surfaces remains unresolved [10-12]. Direct measurements of heating associated with stable crack growth indicate relatively small temperature increases [13]. Alternatively, shear band formation appears to be significantly effected by the mean stress. The effect of a wide range of stress states on the initiation of failure is shown in Figure 3 [1, 8]. For a range of stress state parameters from -0.33 to 0.33 (uniaxial compression to uniaxial tension), a von Mises based criterion predicts the onset of failure. Results can also be predicted using a flow localization model which has been modified to include the effect of the mean stress elastically changing the initial free volume [7, 14, 15] as shown in Figure 3. On the other hand, a von Mises criterion is inappropriate for tensile mean stresses, since the effective stress at failure varies markedly with stress state. Again, the mean stress modified flow model captures the effect of large tensile mean stresses on free volume dilatation and subsequent failure.

The above observations support the notion that tensile mean stresses may increase the free volume, and thereby lower the activation energy required for shear processes. Spaepen [16] has compared the free volume dilatation associated with mean stresses to that associated with thermal expansion between room and the glass transition temperature. For the present composition, a mean stress of 0.95 GPa causes a dilatation equivalent to increasing the temperature by 274 K, to about 51 K below the glass transition temperature of 625 K [7]. This alone would be sufficient to significantly lower the viscosity of the metallic glass, possibly giving rise to the obviously softened appearance of the fracture surface.

The stabilization of shear bands is a key requirement if bulk metallic glasses are to be used in structural applications. The ductile particle reinforcement was shown to effectively distribute plastic damage and increase the toughness of the alloy. However, further toughness increases are expected if the reinforcement phase actually bridges the crack, shielding the crack tip from the applied loads. This could be accomplished with larger crystalline particles.

CONCLUSIONS

Positron annihilation experiments confirm the increase in free volume associated with plastic strains in metallic glass. Doppler broadening results provide an indication of short range reordering during plastic flow. Studies of the effect of stress state on the flow process indicate that a large tensile mean stress could cause a critical dilatation, decreasing the glass viscosity and giving rise to strain localization and failure. Mean stress modified flow relationships provide an accurate prediction of this behavior.

Toughening in composite microstructures was examined. A ductile crystalline reinforcement phase blocked and redirected shear bands in a bulk metallic glass matrix composite, giving rise to a large crack tip damage zone and significant stable crack growth at stress intensity values nearly double that of the monolithic alloy.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Positron lifetime data for prestrained and hydrogen charged bulk metallic glass samples are shown in (a). The longer lifetime in the strained samples is consistent with a free volume increase relative to the control sample. Doppler broadening results obtained with a high energy positron beam, plotted as W (core electron contribution) versus S (valence electron contribution) is shown in (b). All beam energies are 2.8 MeV except as noted.

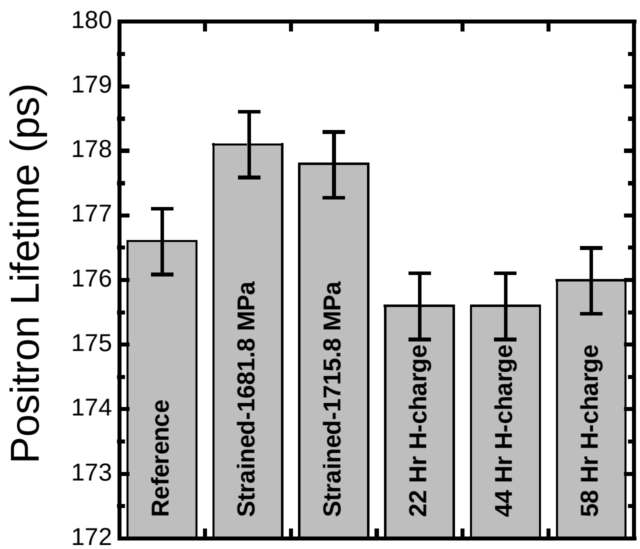
Figure 2. The momentum spectrum from the bulk metallic glass in the as-received state is compared in (a) with a theoretical spectrum in which the components contribute in their atomic percentages. The best fit curve was determined by adjusting the individual component contributions. The distribution is weighted with p_L^2 to emphasize the high momentum features. The elemental contribution to the momentum spectra are compared with the atomic composition of the alloy in (b). Note that nickel and copper were not needed to achieve a good fit to the experimental spectra.

Figure 3. The effective and mean stresses at the initiation site are compared with those found in other studies [1, 8]. The curves result from a mean stress modified flow localization model [7].

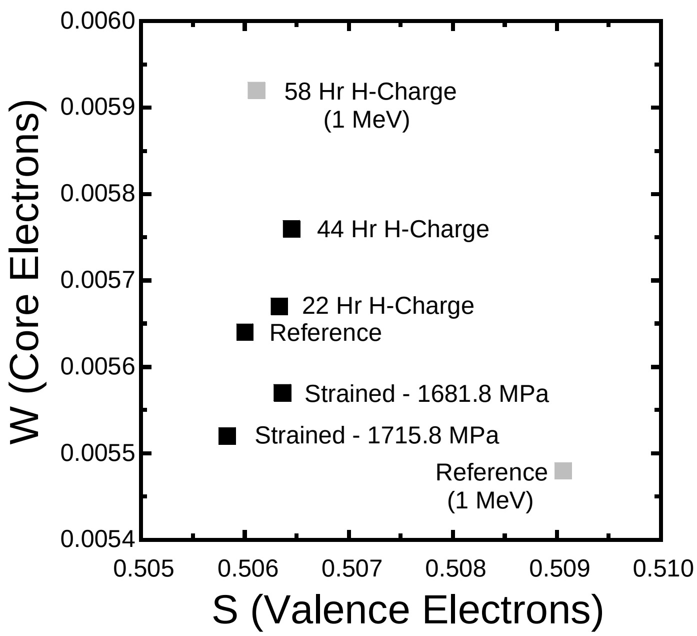
Figure 4. Backscatter SEM fractography of the crack profile near the fatigue precrack tip is shown after fracture. Note the branching, evidence of significant plastic deformation at the crack tip.

Figure 5. Fracture resistance curves for the monolithic bulk metallic glass and its composite. One composite sample exhibited stable crack growth up to a stress intensity of 35 MPa√m. A second exhibited less stable growth, fracturing unstably at 26 MPa√m after 0.45 mm of crack growth.

FIGURES



(a)



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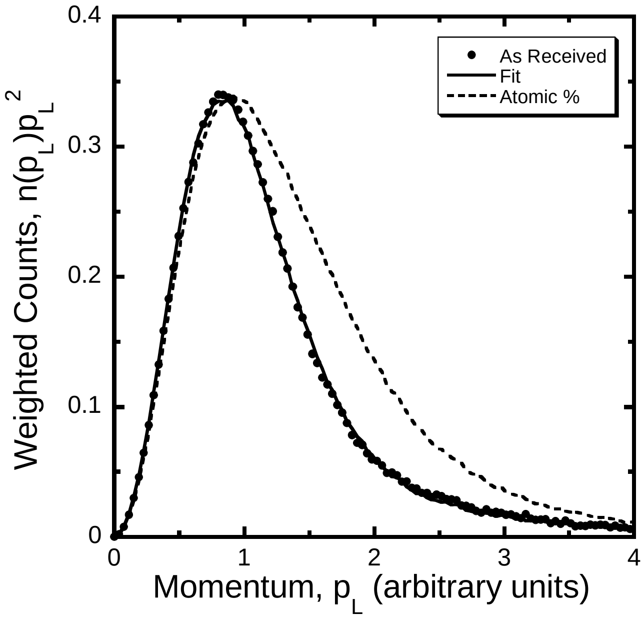

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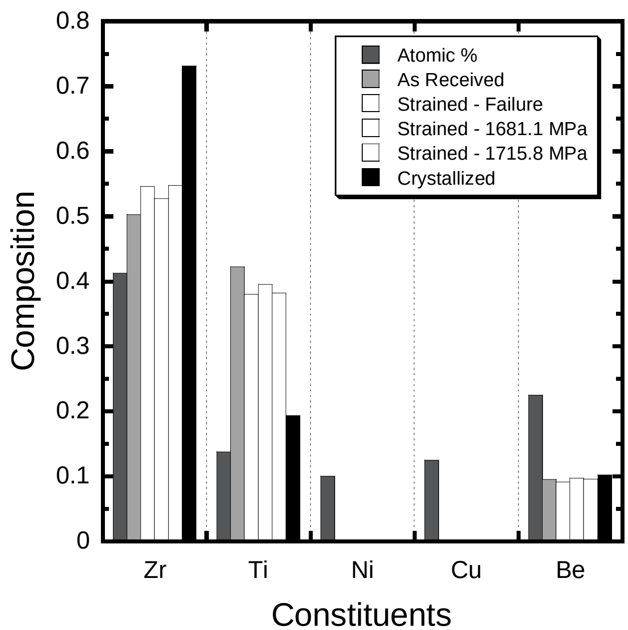

(b)

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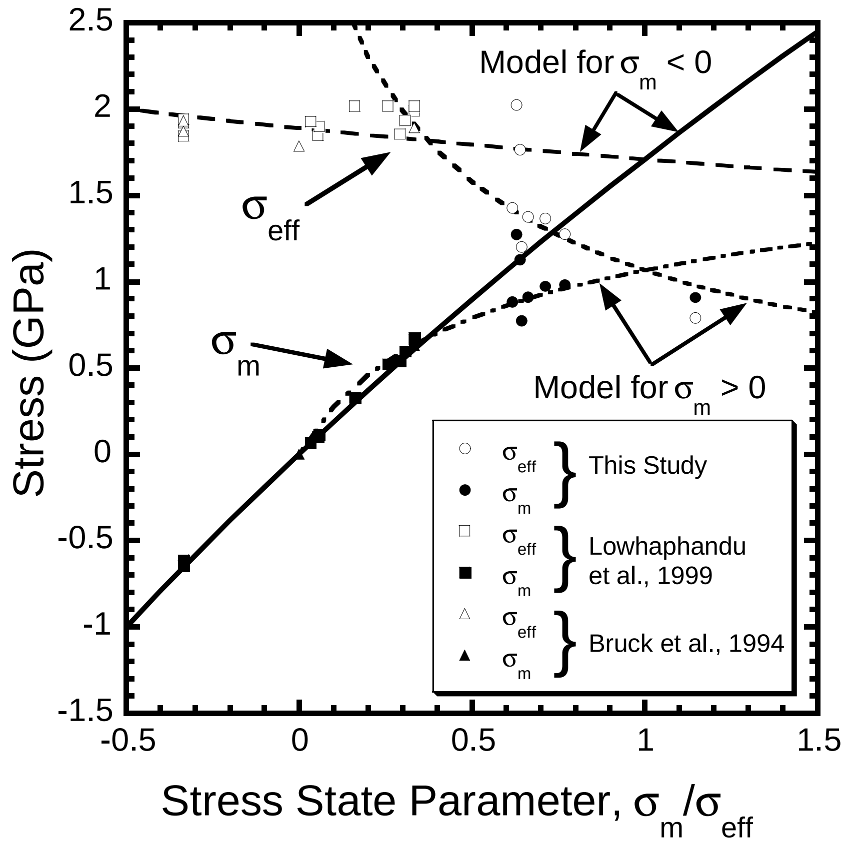

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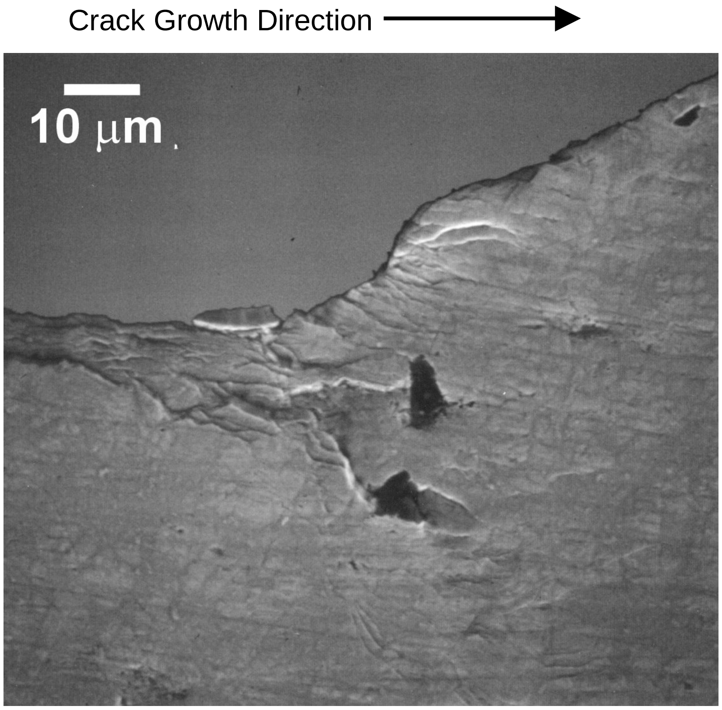

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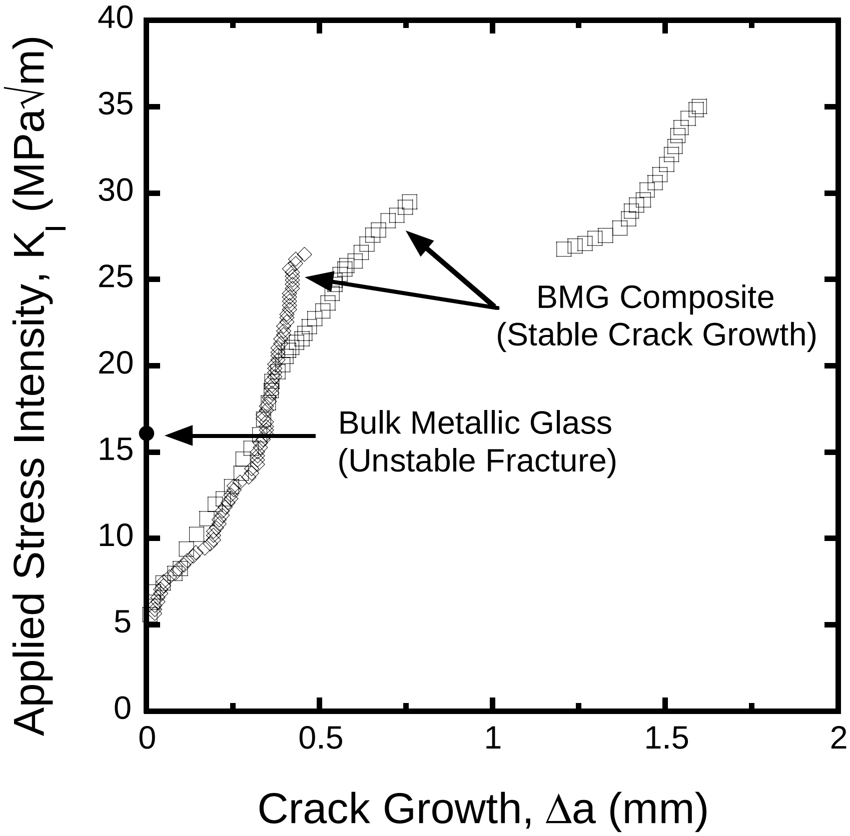

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