Effects of Annealing and Changes in Stress State on Fracture Toughness of Bulk Metallic Glass

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The effects of annealing and changes in stress state on the toughness of both 4 mm thick and 7 mm thick plates of a Zr–Ti–Ni–Cu–Be alloy have been determined. In the amorphous state, both notched and fatigue precracked specimens have been tested. The effects of changing the notch root radius from a fatigue precrack to that of a blunt notch on the fracture toughness are dramatic. The toughness increases from approximately 17.9 ± 1.8 MPa√m in the fatigue precracked specimens to in excess of 130 MPa√m in the notched specimens. These results are compared to similar tests on a range of structural materials, including aluminum alloys, steels, Ti alloys, and metal matrix composites. The increased toughness obtained by increasing the notch root radius in this bulk metallic glass far exceeds that typically observed in other structural materials. Possible reasons for this are presented. In addition, the effects of changes in loading rate and various annealing treatments on the toughness are presented and rationalized via both crack path and fracture surface observations. Annealing of this bulk metallic glass at temperatures below Tg produces increases in strength/hardness, rapid decreases in toughness, and a corresponding change in the fracture morphology. Changes in loading rate did not have a significant effect on the toughness for either notched or fatigue precracked specimens.

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1. Introduction

Recent successes in producing bulk amorphous alloys (*i.e.*, metallic glasses)\(^1\)–\(^4\) have resulted in extensive investigations on the processing techniques/parameters, the decomposition/crystallization process,\(^5\)–\(^7\) as well as the effects of nanocrystalline phase formation on the mechanical properties. A few studies have been conducted on the mechanical properties of fully amorphous materials.\(^8\)–\(^17\) Previous and ongoing work at CWRU work has investigated the effects of changes in stress state, conducted via utilizing different loading configurations (*e.g.*, compression, tension, torsion) and superimposed hydrostatic pressure, on the flow behavior.\(^13\)–\(^14\),\(^16\) It was shown that the superposition of pressure did not measurably change the flow/fracture stress, in contrast to various models of deformation for amorphous systems,\(^18\)–\(^21\) although perhaps the use of higher pressures would produce different behavior. Hydrostatic extrusion of bulk metallic glass has also been reported.\(^13\) In addition, the effects of changes in notch root radius from fatigue precracked to 250 μm on the fracture toughness of a bulk Zr–Ti–Ni–Cu–Be alloy were determined for 4 mm plate.\(^15\) The intent of the present paper is to report on additional toughness data obtained on both 4 mm plate as well as 7 mm plate in both the amorphous state as well as after annealing for various times near Tg. In particular, the effects of changes to the notch root radius on the toughness of the amorphous bulk metallic glass is compared to other data obtained on a range of structural materials where identical studies have been conducted.\(^22\)–\(^35\) This has important implications on the engineering usefulness of such materials as has been demonstrated on the range of structural materials presented previously.\(^22\)–\(^35\) In addition, the effects of changes in loading rate on the toughness are reported presently for both notched and fatigue precracked specimens.

2. Experimental Procedures

2.1 Materials

The materials used in this investigation were supplied by Amorphous Technologies International, Inc., Laguna Niguel, California. Three plates of bulk amorphous Zr–Ti–Ni–Cu–Be alloy (Vitreloy™) were received: two 4 mm-thick plates and one 7 mm-thick plate. The composition of the as-received plates were subsequently analyzed via wet chemistry technique (by Stork Herron Testing Laboratory, Inc., Cleveland, OH) to contain in at%: 12.9Ti, 9.5Ni, 12.0Cu, 23.8Be, and Balance Zr for 4 mm-thick material and 12.0Ti, 9.3Ni, 11.9Cu, 26.5Be, and Balance Zr for 7 mm-thick material. Separate oxygen analyses revealed 1600 ppm and 1350 ppm oxygen for 4 mm and 7 mm materials, respectively. The general processing details have been summarized elsewhere.\(^13\) The structure of the as-received materials (*i.e.* 4 mm plate, 7 mm plate) were confirmed to be amorphous via X-ray diffraction on a Scintag X1 apparatus using CuKα radiation and differential scanning Calorimetry (DSC) on a TA Instrument DSC 2920 using a heating rate of 20 K/min.

2.2 Mechanical testing

2.2.1 Fracture toughness tests

Fracture toughness testing was conducted in general accordance with ASTM E399-90 on single edge notch bend specimens of nominal dimensions 85 mm × 12 mm × 4 mm or 40 mm × 8 mm × 4 mm for specimens taken from plate that was 4 mm thick and 95 mm × 14 mm × 7.5 mm for specimens taken from plate that was 7 mm thick. Notches with the following root radii were utilized: 65 μm, 110 μm, and 250 μm in addition to testing fatigue precracked specimens. In the notched toughness specimens containing notches with root radii of either 65 μm or 110 μm, the notches were placed to a depth of a / W = 0.3–0.5 using a slow speed Verti- diagonal wire saw. The 250 μm root radius notches were
placed to a depth of $a/W = 0.3$ using a 45° V-notch cutter coated with TiN. The outside surfaces of the bend bars were polished through the various grit papers and diamond paste polished to a mirror finish. Up to 250 $\mu$m of material was removed from each surface on some of the specimens. This was conducted in order to facilitate crack path monitoring as well as remove any regions of surface residual stress which may have resulted from the processing. Fatigue precracks roughly 500 $\mu$m in length were initiated from specimens with a notch root radius of 110 $\mu$m, to a depth $a/W = 0.5$. Fatigue precracking was generally conducted at relatively high $\Delta K$ (e.g., 10–15 MPa$\sqrt{\text{m}}$) in the investigations reported presently.

The fracture toughness tests were performed according to ASTM E399-90. The specimens were loaded in three-point bending on a 20 Kip MTS servohydraulic machine operated at a constant displacement rate of 0.1 mm/min, although some tests were conducted at 100 mm/min in order to document any effects of loading rate on the magnitude of toughness. Load, load point displacement (LPD) and, in some specimens, crack opening displacement (COD) were monitored during the test. In the latter case, a clip gage was placed across the crack mouth in order to instantaneously measure the COD. A storage oscilloscope was utilized to capture the load-LPD data for the high rate tests.

### 2.2.2 Annealing studies

The annealing studies were performed on some of the 4 mm plate prior to machining/polishing the bend bars to final dimensions. The materials were annealed in Ar at 623 K for the following times: 45 min, 1.5 h, 3 h, 6 h, 12 h, 24 h. In addition, full crystallization was obtained by annealing at 723 K for 24 h. Both XRD and DSC analyses were performed on the as-received and annealed materials and are summarized elsewhere.  

Toughness tests were conducted on specimens notched to contain a root radius of 65 $\mu$m, to a depth $a/W = 0.5$, enabling direct comparison to the data generated on the as-received amorphous materials. The toughness tests were conducted in the manner summarized above.

### 2.3 Fractography

Fractured specimens were examined both macroscopically and microscopically. The macroscopic fracture path was documented with a Leica Wild M8 zoom stereomicroscope. The fracture surfaces of all specimens were examined using a Hitachi S4500 Field Emission Scanning Electron Microscope (SEM).

### 3. Results and Discussion

#### 3.1 Fracture toughness—effects of changing the notch root radius

All of fracture toughness tests exhibited essentially linear load vs. load point displacement/COD traces, while the effect(s) of changes in the notch root radius on the fracture toughness for specimens taken from both 4 and 7 mm thick plate thicknesses are shown in Fig. 1. Included in Fig. 1 are macroscopic views of the outside (polished) surfaces of the fractured bend bars, revealing the macroscopic crack path under the conditions tested. The fracture toughness, $K_{IC}$, of the bulk metallic glass obtained from seven fatigue precracked specimens comprising both plate thicknesses is $17.9 \pm 1.8$ MPa$\sqrt{\text{m}}$. The yield strength obtained from tension specimens tested at 1 atm was $1978 \pm 20$ MPa, providing a calculated plane-strain plastic zone size of less than 4.3 $\mu$m which is well within the thickness requirements for a valid $K_{IC}$ measurement. However, the fracture toughness data obtained on specimens containing fatigue precracks are reported as $K_{Q}$ instead of $K_{IC}$ because the $\Delta K$ levels used during fatigue precracking exceeded those specified by ASTM E-399-90 and thus the toughness data obtained on the fatigue precracked specimens do not strictly conform to the $K_{IC}$ standard, as indicated in an earlier paper on the 4 mm plate material. The toughness values reported in Fig. 1 for the notched

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**Fig. 1** Effects of notch root radius on fracture profile and toughness of Zr–Ti–Ni–Cu–Be bulk metallic glass.
specimens are similarly reported as \( K_C \) due to the lack of a fatigue precrack. The notched toughness data obtained on specimens taken from both 4 mm thick and 7 mm thick plate was essentially identical.

The crack path profile summarized in Fig. 1 was also significantly affected by the notch root radius. The precracked specimens fatigued under the present conditions exhibited a very planar crack front while the notched specimens exhibited extensive shear banding at the notch as well as significant crack bifurcation once the crack propagated. Both processes (i.e., multiple shear banding, crack bifurcation) should absorb more energy than the planar fracture mode exhibited by the fatigue precracked specimens. This is consistent with the relative differences in the measured toughness for the bulk metallic glass obtained for fatigue precracked specimens compared to those containing somewhat blunter notches as shown in Fig. 1. The stress concentration and the stress state ahead of a fatigue precrack is also more severe than that obtained ahead of a blunter notch.

Such observations of the effects of changes in notch root radius on toughness are consistent with much previous work on structural materials, as indicated previously.\(^{15,16}\) However, the magnitude of the effect (of changing the notch root radius on the toughness) in the present bulk metallic glass materials far exceeds that previously reported for a range of structural materials tested at CWRU as well as at other laboratories around the world.\(^{22-35}\) The effects of changing the notch root radius from a fatigue precrack to that of a rounded notch on the toughness data for a range of different structural materials is presented in Figs. 2–5. Relatively modest increases in toughness are shown in Fig. 2 for a high strength aluminum alloy,\(^{39}\) a Ti alloy\(^{22}\) and an aluminum metal matrix composite\(^{32}\) except for the dramatic results obtained for the bulk metallic glass tested presently. Figures 3–5 summarize similar data obtained for a range of steels. Although significant toughness increases are recorded by increasing the notch root radius for a number of the steels listed, the effects demonstrated by the bulk metallic glass (cf. Figs. 1, 2) far surpass those illustrated for the other structural materials listed. As demonstrated in the previous work on structural materials,\(^{22-35}\) the stress concentration and stress state ahead of a fatigue precrack is more severe than that obtained

![Fig. 2](image-2.png)  
Fig. 2 Effects of changes in notch root radius on toughness.

![Fig. 3](image-3.png)  
Fig. 3 Effects of changes in notch root radius on toughness of a variety of steels (24, 29, 30, 31).

![Fig. 4](image-4.png)  
Fig. 4 Effects of changes in notch root radius on toughness of a number of high strength steels (24, 34).

![Fig. 5](image-5.png)  
Fig. 5 Effects of changes in notch root radius on toughness of low carbon steels (26, 27, 28).
ahead of a blunter notch. This should affect the magnitude of load/toughness required to fracture a material, and might affect the micromechanisms of fracture. Less severe stress states may promote more ductile fracture modes in conventional crystalline materials, thereby increasing the energy absorbing capabilities of the material. In the case of the amorphous materials tested presently, changing the notch root radius significantly affects the amount of shear banding present at the notch and along the fracture plane. No obvious change in the fracture micromechanisms/fracture surface appearance accompanied the change in notch root radius/toughness.\(^{14,16}\) This strongly suggests that the increase in toughness obtained in the bulk metallic glass tested presently results from the initiation, propagation, and interaction of multiple shear bands. In this case, the multiplicity of shear banding is facilitated by changing the notch root radius, while Johnson and co-workers have also shown that composite approaches may also be effective in increasing the degree of shear banding.\(^{57}\)

3.2 Fracture toughness—effects of changing the loading rate

Figure 6 illustrates that changing the loading rate from 0.1 to 100 mm/min produced minimal effects on the magnitude of toughness measured for both the fatigue precracked and notched specimens. Fracture path and fracture surface analyses failed to reveal any differences between the tests conducted at slow versus fast testing rates. In particular, the amount of shear banding present at the notch was not significantly affected by changes in the loading rate, over the range tested.

3.3 Fracture toughness—effects of annealing

Figure 7 summarizes the effects of annealing on the notch toughness of the material tested presently. Significant decreases to the notch toughness are obtained after relatively short annealing times at 623 K, while complete crystallization similarly produced severe embrittlement, consistent with much previous work on similar materials. In the materials tested presently, annealing was shown to significantly change the fracture path and mode, as illustrated in Fig. 8. Significantly less shear banding at the notch was exhibited by the annealed materials in comparison to the as received amorphous materials (cf. Figs. 1, 8). Distinct changes to the fracture surface features accompanied the annealing treatments and large decrease in toughness shown in Fig. 7. While such annealing treatments are clearly detrimental to the fracture properties of the presently tested metallic glass, other metallic glass systems appear to show somewhat different behavior after controlled amounts of devitrification.\(^{38}\) In those cases, partial devitrification may promote multiple shear banding, although the detailed understanding of the mechanisms and optimization of such phenomena will require much additional work.

4. Conclusions

(1) The effects of changes in notch root radius on the toughness of both 4 mm and 7 mm plates of Zr–Ti–Ni–Cu–Be bulk metallic glass have been determined and compared to that of conventional structural materials. The toughness

Fig. 6 Fracture Toughness (\(K_c\)) of Vireloy\(^{TM} 1\) as a function of loading rate (\(\dot{K}\)).

Fig. 7 Effect of annealing treatment on notched fracture toughness (65 \(\mu m\) notch root radius).

Fig. 8 Crack path profile of partially crystallized alloy containing 64% crystalline fraction (3 hrs @ 623 K).
increased from $17.9 \pm 1.8 \text{ MPa}\sqrt{\text{m}}$ in the fatigue precracked specimens to in excess of $130 \text{ MPa}\sqrt{\text{m}}$ in the notched specimens of the bulk metallic glass. The magnitude of this effect far exceeds that exhibited by most conventional structural materials and potential reasons for this were discussed.

(2) Changes in loading rate from 0.1 to 100 mm/min did not significantly affect the toughness of either fatigue precracked or notched specimens of the bulk metallic glass tested presently. There were no noticable effects of these changes in loading rate on the fracture path/morphology over the range of loading rates tested.

(3) Annealing of the bulk metallic glass at 623 K produced a significant decrease in notch toughness. Changes to both the fracture path and morphology were exhibited in the annealed materials.

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