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OSTI**ABSTRACT**

The fracture behavior of a Zr-based bulk amorphous alloy, Zr-10 Al-5 Ti-17.9 Cu-14.6 Ni, was examined by transmission electron microscopy (TEM) and x-ray diffraction for any evidence of crystallization preceding crack propagation. No evidence for crystallization was found in shear bands in compression specimens or at the fracture surface in tensile specimens. In-situ TEM deformation experiments were performed to more closely examine actual crack tip regions. During the in-situ deformation experiment controlled crack growth occurred to the point where the specimen was approximately 20  $\mu\text{m}$  thick at which point uncontrolled crack growth occurred. No evidence of any crystallization was found at the crack tips or the crack flanks. Subsequent scanning microscope examination showed that the uncontrolled crack growth region exhibited ridges and veins that appeared to have resulted from melting. Performing the deformations, both bulk and in-situ TEM, at liquid nitrogen temperatures ( $\text{LN}_2$ ) resulted in an increase in the amount of controlled crack growth. The surface roughness of the bulk regions fractured at  $\text{LN}_2$  temperatures corresponded with the roughness of the crack propagation observed during the in-situ TEM experiment, suggesting that the smooth-appearing room temperature fracture surfaces may also be a result of localized melting.

**INTRODUCTION**

In 1989, amorphous alloy compositions based on La-Al-TM were found that could be produced in a bulk form by casting into water cooled copper molds.<sup>1</sup> These materials have some unusual mechanical properties that are attractive for a number of applications. One related alloy developed by Lin, Johnson and Rhim<sup>2</sup> with a composition of Zr-10 Al-5 Ti-17.9 Cu-14.6 Ni exhibits a fracture stress<sup>3</sup> of 1680 MPa at an elastic elongation of ~2%. The Young's modulus is 89 GPa with fracture toughnesses<sup>4</sup> that exceed 50  $\text{MPa}\sqrt{\text{m}}$ . While previous reports have described the appearance of shear bands and the melted-appearing regions on fracture surfaces<sup>3,5,7</sup>, no detailed analysis has appeared concerning the fracture process itself and what happens at the tips of propagating cracks. Transmission electron microscopy (TEM) was used here to examine shear bands in compression specimens, fracture surfaces in tensile specimens, and the actual crack tips in propagating cracks by performing in-situ deformation experiments.

**EXPERIMENTAL PROCEDURE**

Ingots of a bulk amorphous alloy with a composition of Zr-10 Al-5 Ti-17.9 Cu-14.6 Ni that was developed at Caltech<sup>2</sup> were cast at Oak Ridge National Laboratory. The alloys were prepared by arc melting in inert gas and drop casting into 7 mm diam by 72 mm long Cu molds. Further details regarding alloy preparation and bulk tensile and compressive tests are given in reference 3. Specimens for TEM examinations of bulk deformed tensile specimens were pre-

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pared by slicing perpendicular to the fracture surface, mechanical grinding and ion milling this fracture edge in a manner that would sharpen this edge while preserving the area of interest. TEM specimens were made from the shear band regions in compression specimens. TEM examinations and the in situ TEM deformation experiments at both room temperature and liquid nitrogen temperatures were performed at 300 kV using previously described deformation stages.<sup>3</sup> XRD was performed in a powder diffractometer with Cu K $\alpha$  radiation. Bulk deformation experiments were performed on bars 5  $\times$  5  $\times$  40 mm with a chevron notch<sup>9</sup> with the specimen immersed in liquid nitrogen.

## RESULTS AND DISCUSSION

TEM specimens were prepared from bulk deformed material to examine the shear bands that form during bulk tensile or compressive deformation (see Fig. 10a in ref. 3). No evidence of any crystallization was found. In addition, specimens were prepared from the fracture surface and again no evidence of any crystallization was found. Because of the difficulty in preparing specimens that were certain to retain the areas of interest, TEM in situ deformation experiments were initiated to examine the region in front of a stressed propagating crack.

Previous successful in situ deformation experiments on brittle intermetallics such as the Li<sub>2</sub> trialuminide, Al-8 Cr-25 Ti, with toughnesses around 2 MPa $\sqrt{m}$ , suggested that these experiments would be possible for amorphous alloys.<sup>10</sup> Several design features of the TEM stage were incorporated to make the stage as stiff as possible. The stiffness of the pull rod, relative to the cross sectional area of the tensile specimen where the crack initiates, maximizes the chance for controlled crack growth. The lack of triaxiality in the stress state could change some characteristics of the fracture process in thin sections. However, the TEM deformation experiments have followed bulk fracture behavior remarkably well for a wide range of material, from a low stacking fault energy material such as stainless steel, with a rather planar slip and narrow crack opening; to aluminum, with extensive dislocation cross slip and wide crack openings; to a bcc material such as molybdenum, with jerky dislocation motion ahead of the crack tips. In the case of the brittle trialuminide, dislocation generation was profuse with lots of cross slip and wide crack openings which agrees with the low indentation hardness. While the trialuminides are brittle with low toughness but are rather soft, the bulk amorphous alloys examined here are brittle in the sense of no measurable plastic deformation during a tensile test but with high toughness and high indentation hardness.

Figure 1 shows a sequence of TEM micrographs of an actual crack propagating during an in-situ deformation at LN<sub>2</sub> temperature. The arrow marks the same area in each micrograph. No evidence of crystallization was found at the crack tip or along the crack flank. The cracks started and propagated at approximately 90° to the tensile axis. However, on a microscopic scale the crack propagated in a zigzag manner leaving rough crack flanks. While the crack propagated in a controlled manner for quite some time, at some point the crack would propagate in an uncontrolled manner. The original electropolished hole provided the stress concentrator and the crack initiating site. The cracks start in a thin region and propagate into thicker material similar to the chevron notch toughness test.

A scanning electron microscope (SEM) examination of the fracture surface of a TEM specimen fractured at room temperature showed a distinct difference between the controlled crack growth region and the uncontrolled crack growth region. Figure 2 shows that the thicker area has a melted appearance on the ridges and veins on the surface as described by others.<sup>11</sup> The explanation for the prior observations concluded that the high level of stored energy in a

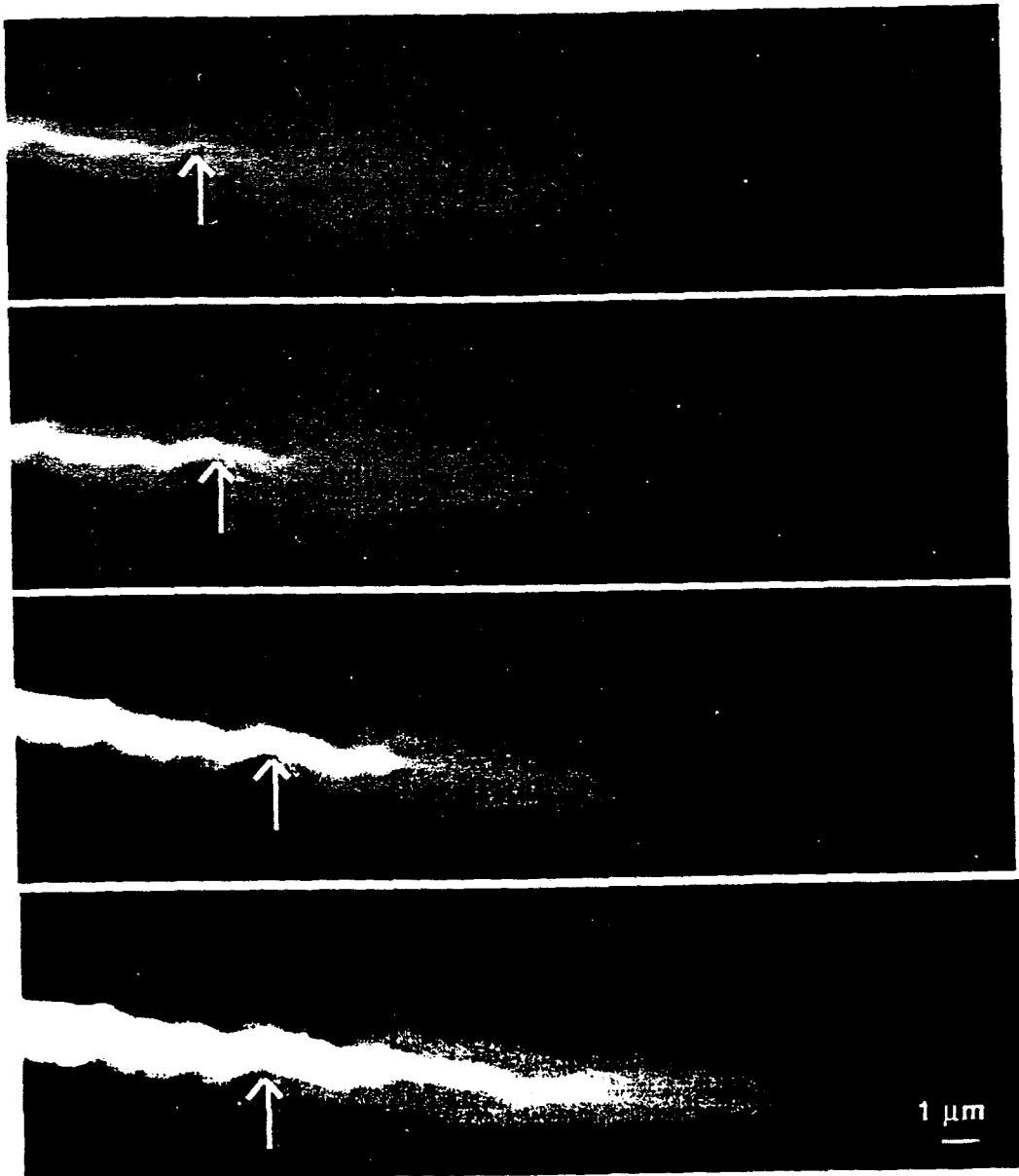
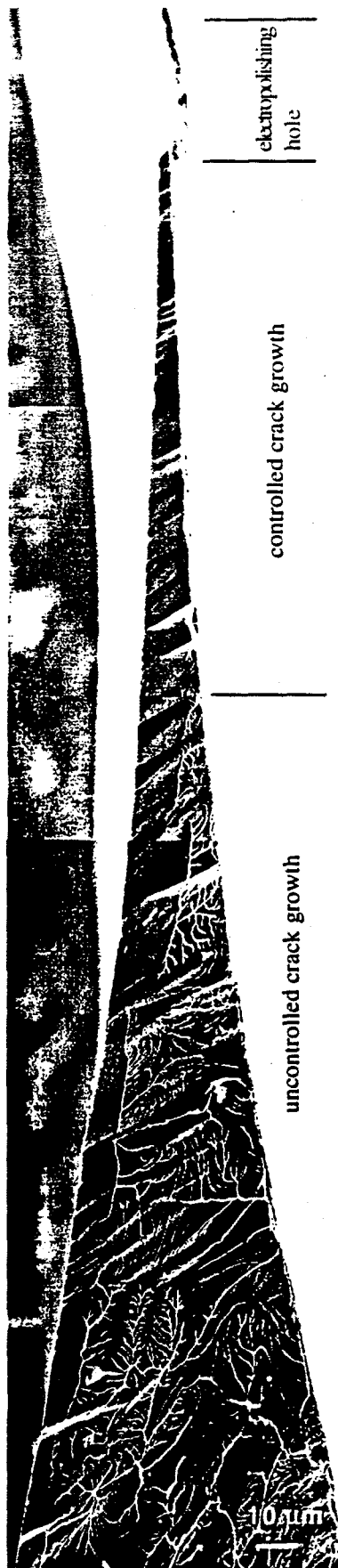


Fig. 1. TEM micrographs of a propagating crack during an in situ deformation at  $LN_2$  temperature in a bulk amorphous alloy. The arrows point to the same spot in each image. No crystalline areas were found in front of or along the crack flanks. Tensile axis was also in line with the arrow. Crack propagation was slow and easily controlled.

material which elastically strains 2% is dumped into heat which results in partial melting of the surface. Bruck actually measured temperature rises during fracture of a similar bulk amorphous alloy and concluded that no heating was found before crack propagation and substantial heating occurred after failure.<sup>5</sup> The crack growth was controlled until the specimen was approximately 20  $\mu m$  thick. The serrations on the fracture surface correspond to the crack jumps during the in situ deformation. While the sequence shown in Fig. 1 was very smooth, as the material got thicker, the crack actually tended to propagate in small jumps and then self arrest.

If the released heat causes in partial melting of the surface then the question is whether this acts as an aid to allowing a crack to propagate along heated material. If this were true then



the toughness might be higher at lower temperatures. Both TEM in situ experiments and bulk chevron notch bend tests were conducted at liquid nitrogen temperatures. The smooth sequence shown in Fig. 1 was performed at  $LN_2$  temperature. Some increase in the area of the fracture surface that did not have the melted ridges was observed in both TEM and bulk specimens but no quantifiable results came out of the chevron notch tests. Within the limits of the experimental setup for the bulk test the crack growth was still largely uncontrolled.

However, differences were noted in the fracture surface appearance. Figure 3 shows two typical fracture surfaces from the in-situ TEM experiments. The cold fracture surface (Fig. 3b) is much rougher than that obtained at room temperature (Fig. 3a). The roughness corresponds with the roughness suggested by the TEM in-situ deformation experiment. In Fig. 3b the particular specimen was fractured in the TEM and allowed to warm inside the ion pumped out liquid nitrogen cold trapped vacuum until the specimen reached room temperature. So no external surface water vapor reaction was expected. The heating phenomena that results in the ridges and veins of Fig. 3b may also "smooth" the surface between the ridges, and the rougher fracture surface in Fig. 3b is a more accurate representative of the actual crack propagation than the faster more uncontrolled fracture surfaces as seen in Fig. 3a.

A confirmation of this correlation between crack growth rate and appearance of the melted surfaces is shown in Fig. 4 from ref. 4 in this proceedings. In Fig. 4a the crack starts at the apex of the triangle at c, is briefly controlled according to the load displacement curve, then in region d is uncontrolled and finally becomes controlled again in region e as the relative compliance of the the specimen/load train increases

Fig. 2. Fracture surface of a specimen fracture inside the TEM at room temperature. The thinnest area underwent controlled crack growth and corresponds to the area here without the melted appearing ridges. The crack did often incrementally advance in the TEM and apparently this corresponds to the serrations seen here.

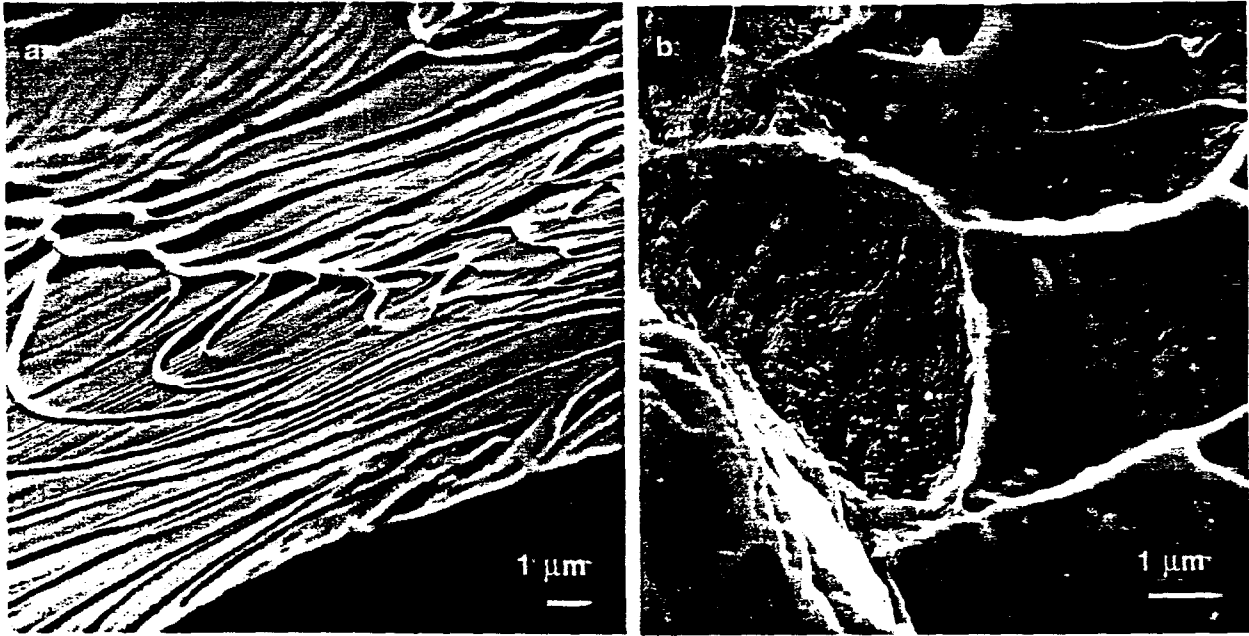


Fig. 3. Fracture surfaces of BAA-11, both from in-situ TEM experiments, (a) room temperature uncontrolled crack growth and (b) fracture at liquid nitrogen temperature in vacuum, also uncontrolled crack growth. The cold specimen was allowed to warm in the vacuum. While the supposed melted ridges looked similar, the room temperature specimen shows a smooth fracture surface otherwise while the LN<sub>2</sub> specimen shows a roughness on a similar scale to the TEM in situ observations.

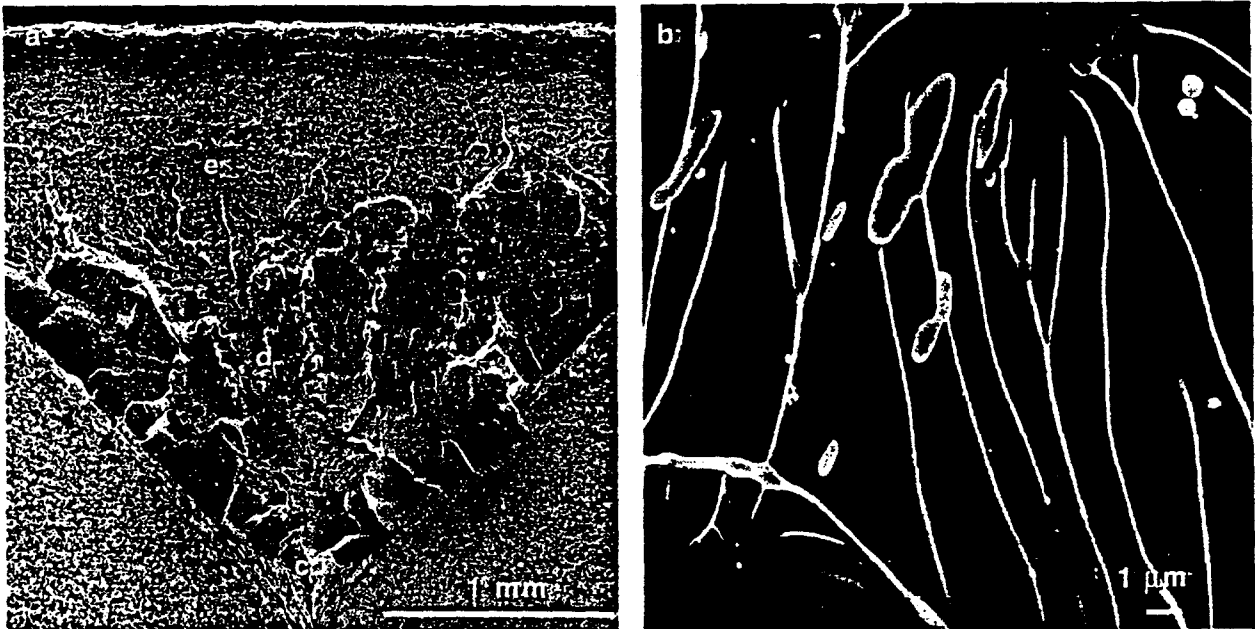


Fig. 4. (a) Fracture surface of a chevron notch bend test specimen. Region (c) and (e) showed controlled crack growth, while region (d) was uncontrolled crack growth. The crack starts at (c). Figure 4b shows an enlargement of region (d) showing how the uncontrolled crack region exhibits the melted appearance while the rougher controlled crack growth region (e) is similar to Fig. 3b. After ref 4.

tive to the specimen geometry. In the uncontrolled fast crack growth region, droplets with a melted appearance were seen on the surfaces (Fig. 4b).

X-ray diffraction was performed on these fracture surfaces with the melted ridges and veins and no evidence of crystallinity has been found, suggesting that the molten material resolidifies again as amorphous material.

## CONCLUSIONS

In bulk amorphous alloys, post failure analysis of fracture surfaces have often found melted appearing features suggesting that the heat dump from the 2% stored elastic energy could be contributing to fast crack propagation by allowing the crack to propagate along a hotter or even molten path. No evidence was found for any crystallization in shear bands or at fracture surfaces in bulk deformed specimens. In situ TEM deformation tests also showed no evidence of any crystallization at the crack tip or along the crack flank. In specimen regions thinner than 20  $\mu\text{m}$ , the cracks propagated in a controlled fashion and left fracture surfaces without any evidence of melting. In thicker areas the crack propagation was uncontrolled and the fracture surface contained the molten veins and ridges. Fracture at liquid nitrogen temperatures partially suppressed this phenomena and increased the amount of controlled crack growth. Furthermore, the smooth appearance to the fracture surface between the ridges is also apparently a result of localized melting since the fracture surface of the specimens fractured at liquid nitrogen temperatures were rough and corresponded to the rougher crack flanks produced during the in situ TEM deformation experiments.

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