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Crack-resistance curve of a Zr–Ti–Cu–Al bulk metallic glass with extraordinary fracture toughness

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Abstract

For the emerging bulk metallic glasses (BMGs), damage tolerance is a key mechanical property needed for their practical applications. To reach a fracture toughness on a par with, or even better than, conventional engineering alloys, the only route reported so far is to compositionally base the BMG on high-cost palladium (Pd), which has a very high Poisson's ratio (~0.42). Here we report the discovery of a $Zr_{61}Ti_2Cu_{25}Al_{12}$ (ZT1) BMG that has a toughness as high as the Pd-based BMG, but at the same time consists of common engineering metals and has robust glass-forming ability. The new BMG, while having an unimpressive Poisson's ratio of 0.367, derives its high toughness from its high propensity for crack deflection and local loading-mode change at the crack tip due to extensive shear band interactions. The crack-resistance curve (*R*-curve) of this BMG has been obtained from fatigue pre-crack samples, employing standard "single-specimen" and "multiple-specimen" techniques.

Keywords: Metallic glasses; Fracture toughness; *R*-curve; Crack growth; Zirconium alloys

1. Introduction

As a new class of advanced materials, bulk metallic glasses (BMGs) exhibit large elasticity (~2%) and impressive yield strength on the GPa level, making them promising for structural applications [1,2]. Meanwhile, high fracture toughness is arguably the most crucial property for BMGs, because an adequate damage tolerance is essential for such quasi-brittle materials [3–10]. So far, however, few monolithic BMGs are able to exhibit subcritical crack growth and substantial crack propagation resistance (in terms of measured crack resistance curve or *R*-curve), due to the lack of microstructural variation (such as the dendritic crystals in composites based on BMGs [11,12]). In this regard, an exciting breakthrough was recently reported [10]: a monolithic BMG ($Pd_{79}Ag_{3.5}P_6Si_{9.5}Ge_2$) was demonstrated to rival the best known crystalline alloys in terms of damage tolerance. Unfortunately, this BMG is compositionally based on high-cost palladium and suffers from a rather limited glass-forming ability (GFA). These deficiencies severely limit this BMG for mass-production/application in bulk form. Therefore, whether highly damage-tolerant BMGs can be developed with low-cost metals remains a challenge.

In this work, we report a new Zr–Ti–Cu–Al BMG that combines all the desirable properties above: it is as damage-tolerant as the Pd-based BMG [10], and at the same time consists of common engineering metals of reasonable cost and has robust GFA. We report a reliable *R*-curve measurement that follows the standard ASTM *J–R* curve test procedures [13,14]. Our approach reveals two distinct and sequential regimes, i.e., shear-off and stable crack growth, in the course of the apparent crack opening displacement (COD). Moreover, it is shown that, at the microscopic level, profuse multiple shearing induces

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additional loading modes on the main crack, resulting not only in macrocrack deflections but also a loading mode transformation at the crack tip.

2. Experimental

Fabrication of the as-cast BMG plates (~3 mm in thickness) has been described elsewhere, together with the discussion of a general strategy for locating tough BMGs [9]. Two compositions, $Zr_{61.6}Ti_{4.4}Cu_{24}Al_{10}$ and $Zr_{61}Ti_2Cu_{25}Al_{12}$ (denoted as ZT3 and ZT1, respectively), are selected, due to their robust GFA and based on preliminary results of their (bending) malleability or fracture toughness [9,15]. The materials are monolithic BMGs, without any noticeable heterogeneities (such as phase separation and nanocrystals) when observed under a high-resolution transmission electron microscope. After machining and polishing, the dimensions of toughness testing specimens are at a ratio of 1:2:8 for B (thickness = 3 mm):W (width):S (span). A straight, through-thickness notch was made using a diamond wire saw, with a notch root radius of 150 μm and a length of ~0.25W. The fatigue pre-cracking of the specimens was conducted on a 2.5 kN MTS fatigue test machine, at a frequency of 30 Hz under a constant load ratio of minimum to maximum of 0.1 with the stress intensity factor ΔK of 30–45 MPa m$^{1/2}$. The notch plus the fatigue pre-crack amounted to a length of 0.5–0.7W after 10,000–100,000 fatigue cycles, conforming to the ASTM standards. Three-point bend (3 PB) tests of the fatigue pre-cracked specimens were carried out on a 5 kN Instron 8871 testing machine at a constant displacement rate of 0.3 mm min^{-1}. The crack opening displacements (CODs) were monitored across the crack mouth using a clip gage, mounted between knife edges and affixed to the front of the 3 PB specimen.

To measure the R-curve, both "single-specimen" and "multiple-specimen" techniques were used [13,14]. For the single-specimen technique, the fatigue pre-cracked specimen was first loaded monotonically at a rate of 0.3 mm min^{-1}. When the nonlinear part of the load vs. load line displacement (LLD) curve was observed at an LLD of ~0.3–0.55 mm, the specimen was unloaded by 20–30% of the current load at a rate of 0.15 mm min^{-1}, followed by reloading at 0.3 mm min^{-1}. The number of load–unload sequences depends on the original crack length (10–30 runs were used in the current cases). After completing the final unloading, the load was returned to zero without additional cross-head displacement.

For the multiple-specimen technique, the first specimen was unloaded at the appropriate displacement to produce Δa in a desired position on the J–R curve. The subsequent specimens were unloaded at desired displacements (distributed uniformly), less than the displacement of the first specimen. After unloading, the specimens were heat-tinted at 300 °C for 60–90 min, then re-fatigued on a 2.5 kN MTS fatigue test machine at the frequency of 30 Hz under a constant load ratio (minimum to maximum) of 0.1 until the ultimate fracture. In this way, the physical crack length in fractured samples can be accurately determined by using a Quanta 600 scanning electron microscope (SEM) and a three-dimensional (3-D) measuring laser microscope (LEXT OLS4000).

Using the following standard equations, the J value (nonlinear strain-energy release rate) was calculated from load vs. COD curves:

$$J = \frac{K^2(1-\nu^2)}{E} + J_{pl} \quad (1)$$

$$J_{pl} = \frac{1.9A_{pl}}{Bb} \quad (2)$$

$$K = \frac{PS}{BW^{3/2}} \cdot f\left(\frac{a}{W}\right) \quad (3)$$

$$f\left(\frac{a}{W}\right) = 3\sqrt{\frac{a}{W}} \cdot \frac{1.99 - \left(\frac{a}{W}\right)\left(1-\frac{a}{W}\right)\left[2.15 - 3.93\frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right]}{2\left(1+2\frac{a}{W}\right)\left(1-\frac{a}{W}\right)^{3/2}} \quad (4)$$

where A_{pl} is the area under the load (P) vs. COD record, a is the instantaneous crack size, and b is the ligament length equal to $W - a$. E is the Young's modulus and ν the Poisson's ratio. For the ZT1 BMG, E and ν are 83 GPa and 0.367, respectively [9], whereas the T_g (glass transition temperature), E, and ν of the ZT3 BMG are 633 K, 80 GPa and 0.372, respectively [15].

With the following equations, the length of crack extension (Δa) for the single-specimen technique can be estimated based on the measured specimen compliance:

$$\frac{a_i}{W} = \left[0.999748 - 3.9504u + 2.9821u^2 - 3.21408u^3 + 51.51564u^4 - 113.031u^5\right] \quad (5)$$

$$u = \frac{1}{\left[\frac{BWEC_i}{S/4}\right]^{1/2} + 1} \quad (6)$$

where a_i is the crack length and C_i is the changing compliance during the sequence of multiple unloading/reloading. The calculated Δa is then calibrated by the physical crack growth observed on the (re-fatigued) fracture surface, after the last unloading.

To examine the sample-size dependence of fracture toughness, two additional groups of specimens with thicknesses of 4 and 2 mm were tested as well for the ZT1 BMG. To confirm the reproducibility of the results, at least five specimens were tested for each condition.

3. Results

3.1. R-curve characterization

Fig. 1 shows a representative load vs. COD curve for the ZT1 BMG. The curve does not follow linear-elastic fracture behavior [6,9,16–18]. Besides the pronounced curve bending, the maximum load (P_{max}) is reached at a COD of ~0.74 mm. Beyond the P_{max}, the applied load gradually