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Tough Fe-based bulk metallic glasses

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The toughness of Fe-based bulk metallic glasses (BMGs) has been significantly improved via systematic changes in chemistry. Chemistry changes were selected based on their likely effects on critical elastic constants shown to affect plasticity/toughness in various BMGs, in addition to their recently discovered effects on chemical bonding in these Fe-based systems. The fracture energy obtained on notched toughness samples tested in mode I was correlated with chemistry-induced changes to Poisson's ratio ν and the ratio of the elastic shear modulus μ to the bulk modulus B, as was the strain energy at fracture for smooth cylindrical compression samples that failed under mode II conditions. Fractographic observations correlate well with the observed increases in toughness. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2890489]

The damage tolerance (toughness) of a structural material is determined by the energy absorbed during deformation and fracture. While this is related to the area under a stress-strain curve conducted in tension or compression, engineering fracture mechanics measurements of toughness typically utilize samples containing a defect (e.g., notch or crack). Bulk metallic glasses (BMGs) are unique as they typically exhibit very high strength, often approaching theoretical values, but generally low global ductility due to the initiation and propagation of bands of intense localized deformation (i.e., shear bands).[1,2] However, the strain in these bands of localized deformation can be very high (e.g., >10). In any case, the competition between flow and fracture will ultimately determine the damage tolerance/toughness of these materials, as has been documented and reviewed for crystalline materials.[3]

Plastic flow and the glide of dislocations on close-packed planes in crystalline metals tested at low homologous temperatures are controlled by the shear modulus μ. Brittle fracture which arises due to the dilatation caused by the hydrostatic stress state present near a crack/defect is controlled by the bulk modulus B. Very early work on crystalline metals showed that high μ/B ratios favor brittle behavior,[3] with more recent rigorous analyses showing the same behavior.[4,5] This same approach has been taken recently on BMGs to rationalize the onset of significant changes to the ductility/toughness that are obtained upon exceeding a critical value of μ/B.[6] Independent works have also shown that metallic glasses with high Poisson's ratio (ν) possess high compressive ductility,[7,8] while the toughness relationship with μ/B has also been correlated with ν.[6]

It has been known for decades that the shear modulus is an important parameter for determining the deformation behavior of metallic glasses. Chen *et al.*[9] first suggested that "it is the high Poisson's ratio which is responsible for the ductile behavior of many metallic glasses," based primarily on microhardness measurements taken on various Pd-based and Pt-based glasses and referencing various fracture experiments on Fe-based glasses, while noting that nonmetallic glasses with $\nu=0.25$ are brittle. Recent discoveries of Fe-based BMGs have enabled quantification of the effects of chemistry changes on elastic constants and their effects on ductility obtained in compression of right circular cylindrical samples that fail in shear under mode II conditions.[10] While most studies to date have focused on the variation of properties with metal contents, the effects of strong chemical bonds inherent to many BMGs have been addressed only very recently[11,12] via combined modeling and experimental approaches. Fe-based BMGs, which consist of both metallic and covalentlike bonds, can potentially provide a unique system on which to study chemical bond effects on properties while also exploring the relationship(s) between critical elastic constants and ductility/toughness. More broadly, the study can also lead to a better understanding of similar effects on intrinsic toughness in other BMG systems.

In this paper, the effects of changes to the chemistry of Fe-based BMGs on toughness are reported. The triaxial tensile stress state present in notch toughness tests conducted under mode I conditions is much more severe than that present in uniaxial compression of smooth cylindrical samples that fail in shear under essentially mode II conditions. Furthermore, compressive ductility is not necessarily a good predictor of toughness. The chemistry changes were selected to systematically vary the elastic constants (i.e., ν, μ, and B) in an attempt to improve the notch toughness, as it has already been shown that annealing-induced changes to the elastic constants affect plasticity and toughness on other metallic glass systems.[6,13] Fe-based BMGs, in the form of 1.5–2 mm diameter rods, were prepared using methods reported elsewhere.[8,10,11] The amorphicity of these BMG samples was confirmed by x-ray diffraction and thermal analysis. Room-temperature compression tests were performed on 1.5 mm diameter by 3 mm long rods using an Instron testing machine at a strain rate of 10^{-4} s^{-1} and are also reported elsewhere.[8,10] Elastic moduli of the BMGs were measured by resonant ultrasound spectroscopy in the manner used previously.[8] Notch toughness experiments were

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TABLE I. Notch toughness and elastic constants (bulk modulus B, shear modulus μ, Young's modulus E, and Poisson's ratio ν) for a variety of Fe-based BMGs.

Alloy	B (GPa)	μ (GPa)	E (GPa)	ν	μ/B	K_c (MPa-$m^{1/2}$)	G_c (kJ/m^2)
$Fe_{50}Mn_{10}Mo_{14}Cr_4C_{16}B_6$	180	76.1	200	0.314	0.423	5.7 ± 1.5	0.15 ± 0.07
$Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$	192	80.8	213	0.316	0.420	12.7 ± 4.1	0.72 ± 0.44
$Fe_{49}Cr_{15}Mo_{14}C_{15}B_6Er_1$	200	81.9	215	0.319	0.410	25.6 ± 4.7	2.8 ± 0.9
$Fe_{49}Cr_{15}Mo_{14}C_{19}B_2Er_1$	199	78.8	209	0.325	0.397	27.1 ± 6.4	3.3 ± 1.5
$(Fe_{0.9}Co_{0.1})_{64.5}Mo_{14}C_{15}B_6Er_{0.5}$	177	74.0	195	0.317	0.417	26.5 ± 11.2	3.8 ± 3.0
$Fe_{65}Mo_{14}C_{15}B_6$	192	73.2	195	0.331	0.382	38.0 ± 10.8	7.0 ± 3.5
$Fe_{59}Cr_6Mo_{14}C_{15}B_6$	188	77.3	204	0.320	0.410	52.8 ± 5.1	12.3 ± 2.4
$Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$	172	66.5	177	0.330	0.387	46.7 ± 6.0	11.1 ± 2.9

conducted in three-point bending on an MTS model 810 servohydraulic testing machine operated under displacement control at 0.1 mm/min. Notches of 220 μm in diameter were placed to a depth nearly half the rod diameter via the use of a slow-speed diamond impregnated Well saw. At least three, and up to ten, experiments were conducted for each chemistry prepared. Notch toughness values (i.e., K_c) were calculated by using standard references for this geometry. Scanning electron microscopy (SEM) on a Hitachi S-4500 operated at 5 kV was utilized to examine the fracture surfaces.

The notch toughness values (i.e., K_c) of the present BMG alloys are listed in Table I along with the measured elastic constants. The very high strength (e.g., >3 GPa) places even the toughest of these samples in the plane strain regime, while the testing geometry produces failure under mode I loading conditions. Table I also includes the fracture energy G_c, calculated in the manner conducted previously,[6] which uses the relationship $G_c = K_c^2(1-\nu^2)/E$, where E is Young's modulus. Figure 1 plots the fracture energy from the mode I notch toughness tests versus μ/B, while Fig. 2 plots the same fracture energy versus ν. Included in Figs. 1 and 2 are regimes of "brittle" and "tough" from previous correlations of this type.[6] From the figures, decreasing ratios of μ/B (or increasing ν) increase the fracture energy of these Fe-based metallic glasses, despite their very high strength levels (e.g., >3 GPa compressive strength). SEM fractography revealed fracture surfaces with features characteristic of locally viscous flow (Fig. 3). The spacing and size of the fracture surface features shown in Fig. 3 are also consistent with recent similar analyses that have related the magnitude of toughness to the scale of fracture surface features.[6,14]

Recent works[8,10,11] have demonstrated similar benefits to the ductility obtained during compression testing of right circular cylinders of the present Fe-based BMGs by systematically varying the elastic constants via chemistry changes. However, shear-induced fracture of a cylindrical compression sample can be viewed as fracture under mode II conditions. While mode II toughness/fracture energy cannot be calculated under these conditions because of the lack of a notch/precrack, it is possible to calculate the strain energy at fracture (from the compression tests on the cylindrical samples) by a knowledge of the compressive stress-strain histories and the measured elastic constants.[8,10] Figure 4 plots the strain energy at fracture obtained from the compression tests versus ν for the Fe–Mo–C–B, Fe–Mo–C–B–Er, Fe–Mo–C–B–Dy, $Fe_{59}Cr_6Mo_{14}C_{15}B_6$, $Fe_{49}Cr_{15}Mo_{14}C_{15}B_6Er_1$, $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$, and $Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$ BMGs. While it is not possible to directly compare the fracture energies obtained from the notched experiments in Figs. 1 and 2 with the strain energies at fracture obtained from the compression experiments in Fig. 4 (because of the significant differences in test technique, loading mode, and stress state), the same general trends are observed. An increase in fracture energy (i.e., from mode I notch toughness tests) and strain energy at fracture (i.e., from compression tests failing in mode II) accompanies an increase in ν (or decrease in μ/B) obtained via systematic alloying strategies for Fe-based BMGs.

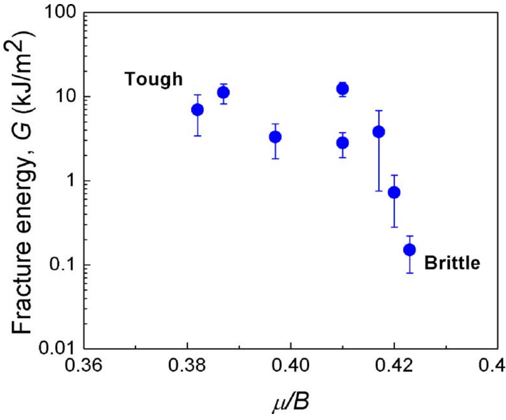

FIG. 1. (Color online) The correlation of fracture energy G (obtained from notched toughness tests) with elastic modulus ratio μ/B for a variety of Fe-based BMGs listed in Table I.

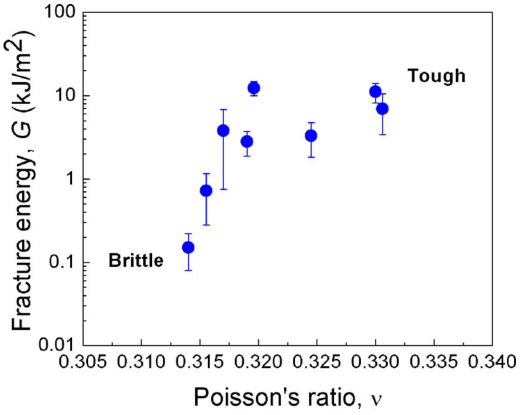

FIG. 2. (Color online) The correlation of fracture energy G (obtained from notched toughness tests) with Poisson's ratio ν for a variety of Fe-based BMGs listed in Table I.

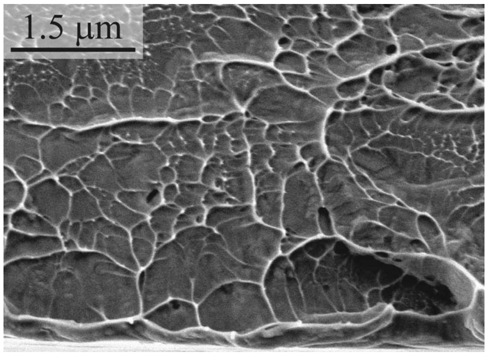

FIG. 3. Typical fracture surface of a notched $Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$ BMG.

While the present work clearly shows that the toughness of Fe-based BMGs can be significantly improved by chemically tuning the elastic properties, these chemistry-induced changes to the elastic constants are determined by the amorphous structure and chemical bonding that result from such modifications.[11,12] Ongoing work utilizing first-principles electronic structure calculations illustrate that these improvements result from partially replacing the elements that create ionic and covalent bonds with other elements that favor metallic cohesion. Covalency strongly influences the shear elastic modulus, while ordinary metallic bonding mainly contributes to the bulk modulus. The present chemistries were selected to chemically tune the strengths and local arrangements of the interatomic interactions in the amorphous network by selecting appropriate combinations of metal and metalloid elements, thereby reducing the shear modulus and increasing Poisson's ratio. In the case of the P containing alloy, recent electronic structure calculations reveal that replacing the B and C metalloids with P produces more metallic bonding and reduces the shear modulus with more subtle changes to the bulk modulus, thereby increasing Poisson's ratio and compressive ductility. It has also been shown in other recent work[8] that the addition of Er causes embrittlement. The embrittlement is attributed to the strong Er-metalloid bonds that are present in the alloys.[12] In the present paper, these chemistry effects are reflected in the higher fracture energy obtained in mode I notch toughness experiments, in addition to a higher strain energy at fracture in the compression experiments, which failed in shear (i.e., mode II conditions).

In summary, the toughness of various Fe-based BMGs was varied via an alloying strategy that would systematically change the elastic constants, leading to improved ductility/toughness. The fracture energy under mode I notched tensile loading, as well as the strain energy at fracture in compression tests that failed in shear (i.e., mode II conditions), was shown to correlate well with increases in ν (or decreases in μ/B). Additional work is focusing on other alloying variants to further improve the toughness/strength relationships in these ultrahigh strength materials.

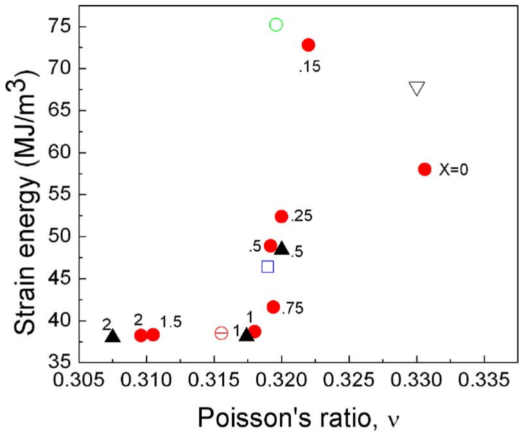

FIG. 4. (Color online) Plot of compressive strain energy at fracture (obtained from compression tests on smooth cylindrical samples) vs Poisson's ratio ν: $Fe_{65-x}Mo_{14}C_{15}B_6Er_x$ (●), $Fe_{65-x}Mo_{14}C_{15}B_6Dy_x$ (▲), $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$ (⊖), $Fe_{49}Cr_{15}Mo_{14}C_{15}B_6Er_1$ (□), $Fe_{59}Cr_6Mo_{14}C_{15}B_6$ (○), and $Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$ (▽).

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