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Chemistry (intrinsic) and inclusion (extrinsic) effects on the toughness and Weibull modulus of Fe-based bulk metallic glasses

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Systematic changes in composition were employed to increase the notch toughness of a variety of Fe-based Bulk Metallic Glasses (BMGs). The $Fe_{50}Mn_{10}Mo_{14}Cr_4C_{16}B_6$ BMG possessed very high hardness (e.g. 12 GPa) but very low notch toughness (e.g. 5.7 MPa m$^{1/2}$) at room temperature, consistent with fracture surface observations of brittle features. Many of the other Fe-BMG variants, created to change the Poisson's ratio via systematic changes in alloy chemistry, exhibited higher toughness but more scatter in the data, reflected in a lower Weibull modulus. SEM examination revealed fracture initiation always occurred at inclusions in samples exhibiting lower toughness and/or Weibull modulus for a given chemistry. Implications of these observations on reliability of BMGs are discussed.

Keywords: Fe-based metallic glasses; mechanical properties; toughness; Weibull modulus

1. Introduction

The success in producing bulk (e.g. >5 mm diameter) rods and plates of a large number of metallic glasses has renewed interest in these systems in the past decade due to their exceptional combination of properties (i.e. strength, hardness, corrosion and wear resistance).

The Fe-based systems are some of the strongest Bulk Metallic Glasses (BMGs) [1–3] with hardness/compressive strengths that exceed 12 GPa/4 GPa, respectively. The damage tolerance/toughness and compressive plasticity of bulk versions of these materials has received considerable attention because of their possible use as coatings and other applications that might benefit from an ultra-hard but malleable and corrosion resistant material. Initial work on some Fe-based BMGs revealed low plasticity in compression [4] and very low damage tolerance/toughness [5,6], while early work on Fe-based metallic glass ribbons revealed higher levels of toughness along with both annealing-induced and low-temperature embrittlement [7].

Improvements to the damage tolerance/toughness of various BMGs have been accomplished by careful chemistry control in order to affect the competition between flow

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and fracture [2,6,8]. Fracture energy correlations with the ratio μ/B (or alternately, ν) for a range of BMG compositions (including Fe-based BMGs [8]) has been demonstrated as well as for annealing-induced embrittlement. Independent work has similarly shown a correlation between ductility and Poisson's ratio for both axial compression [2,9] and bending [10]. While very early work on metallic glasses by Chen et al. [11] suggested a correlation between plasticity and Poisson's ratio based on hardness measurements, more recent work has focused on damage tolerance/toughness obtained under stress states more severe and repeatable than uniaxial compression. These tests have been conducted in order to eliminate the effects of test conditions (e.g. length/diameter ratio, stress concentrations between sample/compression platens, alignment, etc.) shown to affect the strength and compressive plasticity in these materials [12].

This work examines the effects of systematic changes in chemistry on the room temperature notch toughness of various Fe-based BMGs. Multiple notch toughness tests were conducted for each chemistry in order to determine the degree of variability along with detailed SEM fractography in order to investigate possible reasons for such variability.

2. Experimental procedures

Samples of Fe–Mo–C–B, Fe–Cr–Mo–C–B, Fe–Cr–Mo–C–B–Mn, Fe–Cr–Mo–C–B–Er, (Fe, Co)–Mo–C–B–Er and Fe–Cr–Mo–C–B–P glassy systems were produced by arc-melting under argon atmosphere and copper-mold casting as described by Gu et al. [1]. In addition, a Fe–Cr–Mo–C–B–Y was produced at Oak Ridge National Laboratory in the same manner described above. Specific compositions (in at.%) are provided in Table 1, along with elastic constants measured at both Case Western Reserve University and University of Virginia in the manner described elsewhere [8]. Rods of 1.5–4 mm in diameter and 30–40 mm in length were received in the fully amorphous condition, as verified by X-ray diffraction using a Scintag X1 diffractometer with (Cu-Kα) radiation.

Three-point bend notch toughness experiments were conducted at room temperature using a MTS model 810 servo-hydraulic testing rig under displacement control with a rate of 0.1 mm min^{-1}. The cylindrical rods were notched using a slow speed diamond wire saw

Table 1. Notch (110 μm) fracture toughness (K_C) and calculated notch fracture energy (G_C) for different Fe-based glassy systems.

Composition	μ (GPa)	B (GPa)	E (GPa)	ν	Ave. K_C (MPa m$^{1/2}$)	Ave. G_C (kJ m^{-2})
$Fe_{59}Cr_6Mo_{14}C_{15}B_6$	77.3	188	204	0.32	52.8 ± 5.1	12.3 ± 2.4
$Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$	66.5	172	177	0.33	39.3 ± 10.6	8.4 ± 4.2
$Fe_{65}Mo_{14}C_{15}B_6$	73.2	192	195	0.33	38.0 ± 10.8	7.0 ± 3.5
$(Fe_{0.9}Co_{0.1})_{64.5}Mo_{14}C_{15}B_6Er_{0.5}$	74.0	177	195	0.32	26.5 ± 11.2	3.8 ± 3.1
$Fe_{49}Cr_{15}Mo_{14}C_{19}B_2Er_1$	78.8	199	209	0.33	27.1 ± 6.4	3.3 ± 1.4
$Fe_{49}Cr_{15}Mo_{14}C_{15}B_6Er_1$	81.9	200	215	0.32	25.6 ± 4.7	2.8 ± 0.9
$Fe_{48}Mo_{14}Cr_{15}Y_2C_{15}B_6$	81.7	196	215	0.32	12.5 ± 4.5	0.73 ± 0.4
$Fe_{50}Mn_{10}Mo_{14}Cr_4C_{16}B_6$	76.1	180	200	0.31	5.7 ± 1.5	0.15 ± 0.1
$Fe_{51}Mn_{10}Mo_{14}Cr_4C_{15}B_6$	76.1	180	200	0.31	3.5 ± 0.8	0.06 ± 0.02

with a root radius of 110 μm to a depth of approximately half the diameter ($a/w = 0.4$–0.5) of the rods prior to testing. Span to diameter ratios were consistent with ASTM standards. At least three and up to 13 tests were performed to failure on each glassy system. Load versus load point displacement was monitored and the notch toughness at maximum load was calculated for each test using standard K-calibrations for this geometry [13]. A Hitachi S-4500 Scanning Electron Microscope (SEM) was used to examine the fracture surfaces, particularly in the notch root regions. In addition, Electron Dispersion Spectroscopy (EDS) was used in order to quantify the chemistry of any features near obvious fracture initiation sites.

3. Results

All Fe-BMG systems exhibited a broad X-ray spectrum, typical of the lack of long-range order exhibited in bulk amorphous materials. The notched toughness (K_c) values were calculated using the maximum load at fracture, summarised in Table 1. All load-displacement traces were linear to fracture. Included in Table 1 is the fracture energy, G_C, calculated as $G_c = K_c^2(1-\nu^2)/E$ [14] using elastic constants determined at both Case Western Reserve University and University of Virginia, also summarized in Table 2. The plastic zone size at failure for the toughest sample (i.e. 57.9 MPa m$^{1/2}$), was estimated at 24.6 μm using $r_p \approx K^2/6\pi\sigma_0^2$ [15]. This is very small compared to the specimen diameter (i.e. 1.5–4 mm diameter), indicating that nominally plane strain conditions can be assumed. However, values for toughness K_C are not reported as K_{IC} because of the lack of a fatigue pre-crack, shown to be particularly important in BMGs [3,16,17].

Figure 1 provides the correlation between fracture energy and the ratio of shear modulus to bulk modulus (μ/B) as well as Poisson's ratio (ν) for the present Fe-based

Table 2. Summary of features present at suspected failure nucleation sites for different Fe-based glassy systems exhibiting high scatter in notch toughness values.

Composition	K_c (MPa m$^{1/2}$)	Distance from notch (μm)	Defect diameter (μm)	Type of defect
$Fe_{49}Cr_{15}Mo_{14}C_{19}B_2Er_1$	18.7	11.4	0.8	Porosity
		89.3	16.0	Inclusion
	27.4	13.0	0.7	Porosity
		34.6	57.0	Inclusion
	34.4	30.4	5.6	Inclusion
		110.0	24.0	Inclusion
$Fe_{49}Cr_{15}Mo_{14}C_{15}B_6Er_1$	26.2	5.5	1.1	Porosity
		19.1	5.7	Inclusion
		19.8	1.0	Porosity
		28.5	3.5	Inclusion
		42.3	4.4	Inclusion
		95.5	13.5	Inclusion
$Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$	27.4	22.3	8.6	Inclusion
	29.7	5.3	0.8	Inclusion
	28.9	11.4	1.1	Inclusion
	29.4	2.8	1.64	Inclusion

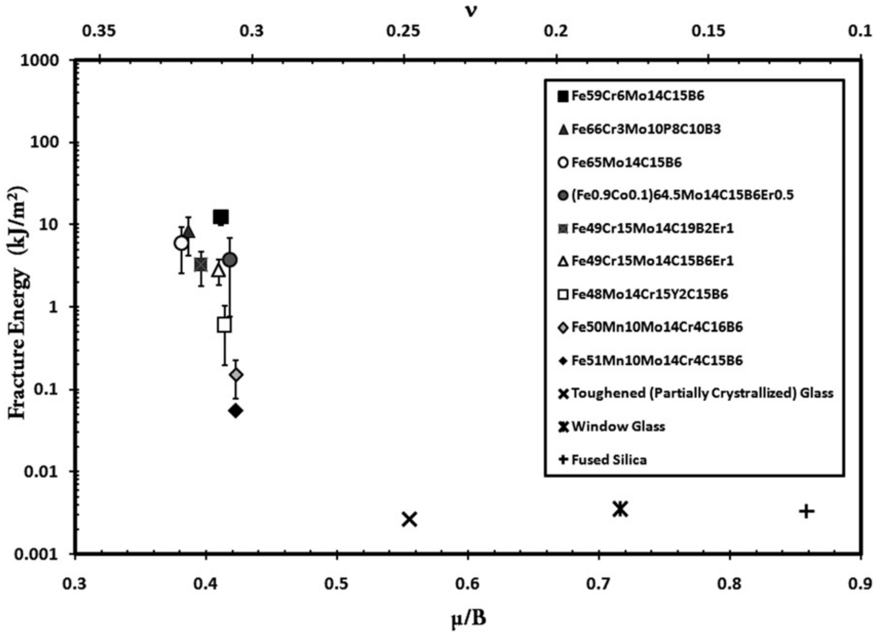

Figure 1. Fracture energy (G_C) *vs.* μ/B for different Fe-based glassy systems. Included are data for nearly ideally brittle systems for comparison.

glassy systems as well as brittle oxide glasses, following approaches developed in other papers [3,6,8]. It is clear that such changes in chemistry can have a significant effect on the fracture energy, with values ranging from $0.06\,\mathrm{kJ\,m^{-2}}$ (i.e. Fe–Mn–Mo–Cr–C–B) to $12.3\,\mathrm{kJ\,m^{-2}}$ (i.e. Fe–Cr–Mo–C–B). These figures also indicate a trend of increasing G (and K) with increasing ν (or decreasing μ/B) with a distinct transition from tougher to more brittle behaviour in the manner reported elsewhere for other bulk metallic systems [6]. The Fe–Mn–Mo–Cr–C–B system exhibits very low toughness, approaching the ideally brittle behaviour associated with oxide glasses. However, replacing Mn with Er and increasing the Cr from 4% to 15% increased the fracture toughness significantly (i.e. from $\approx 5\,\mathrm{MPa\,m^{1/2}}$ to $\approx 26\,\mathrm{MPa\,m^{1/2}}$). In the Fe–Mo–C–B system, the addition of Cr and Er increased in the shear and elastic modulus [1] and reduced the notch toughness by approximately $12\,\mathrm{MPa\,m^{1/2}}$. Furthermore, replacing the Er with P improved the toughness as shown in Figure 1. These results are generally consistent with other work on BMGs [3,6] where systematic changes in chemistry or annealing have been used to change μ/B (or ν) in order to examine the competition between flow and fracture. However, the degree of scatter in toughness for nominally identical materials (within a given chemistry) tested in an identical manner is discussed below.

4. Discussion

The present work also supports the idea that chemistry changes may be used to improve the intrinsic toughness/plasticity of metallic glasses by affecting the elastic constants.

However, close examination of the toughness range for a given chemistry in Figure 1 reveals significant scatter in some systems where up to 13 samples were tested. Recent investigations have begun to investigate the variability in compression [18,19] and tension [20,21] properties of metallic glasses in both ribbon [20,22,23] and bulk [18,19,21] form. The use of notched and/or fatigue precracked samples provides a more direct measure of the flaw/damage tolerance of a material and also provides a more severe stress state than either tension or compression testing. Recent work [12] has also shown significant effects of test geometry, end effects, sample volume, sample preparation and alloy chemistry on the strength and/or plasticity obtained in compression.

Analysis of the present toughness data obtained on notched bend samples which failed in a globally linear-elastic manner under nominally plane strain conditions follows the approach of the Weibull model, which has traditionally been used for brittle/semi-brittle materials to describe the scatter in strength as well as size effects on such properties [24]. The catastrophic nature of damage initiation and growth in BMGs appears to be controlled by the inhomogeneous initiation of shear bands that propagate to failure, consistent with a weakest link type of fracture process. The variability in notch toughness in the present Fe-based BMGs was analysed using the Weibull method which describes the failure probability (P_f) for a given uniaxial stress (σ) via the equation: $P_f = 1 - \exp\{-V[(\sigma - \sigma_\mu)/\sigma_0]^m\}$ where σ_0 is a scaling parameter, m is the Weibull modulus and V is a normalized volume of the tested sample. The parameter σ_μ denotes the stress at which there is a zero failure probability, and is usually taken to be zero [25] for brittle systems, allowing a 'two-parameter' analysis. Recent other work on the scatter in toughness and fracture strength of conventional structural materials [26] indicates that this assumption may not be good for conventional structural materials that typically exhibit very high-toughness/fracture strength and a non-zero stress with zero failure probability. The present case where the minimum toughness/fracture energy approaches that of ideally brittle solids suggests that a 'two-parameter' analysis may be appropriate, although continued improvements in the intrinsic toughness of such systems may require the use of a 'three-parameter' analysis.

The failure probability P_f for a given notched toughness was calculated using the equation: $P_{f,i} = (i - 0.5)/n$ where n is the total number of samples tested and i is the sample rank in ascending order of notch toughness. The results for some of the most extensively tested chemistries are plotted in the usual double logarithmic form of the Weibull expression: $\ln\{\ln[1/(1 - P_f)]\} = \ln V + m \ln \sigma - m \ln \sigma_0$ in Figure 2, where the notch toughness is plotted on the x-axis.

$Fe_{59}Cr_6Mo_{14}C_{15}B_6$ BMG exhibited the highest average toughness ($52.8 \pm 5.1\,\mathrm{MPa\,m^{1/2}}$) and Weibull modulus (i.e. 12.1). While the notch toughness at this strength level (i.e. 4 GPa) is significantly higher than that obtained for the toughness of conventional structural engineering alloys and ceramics, the Weibull modulus is somewhat closer to the range of more brittle systems. It is initially not clear why there should be such significant scatter to the fracture energy/toughness for a nominally homogeneous amorphous alloy under notched bending conditions, since flow and fracture are known to occur via intense localised shear in the absence of any second phases in such systems [27,28] and the fracture process has been modelled using the Taylor meniscus instability [29]. Earlier work [16,30] on Zr-based glasses tested under nominally identical conditions showed good consistency of both fatigue precracked and notch toughness values for material of identical chemistry and test conditions, although those works did indicate that subtle chemistry changes

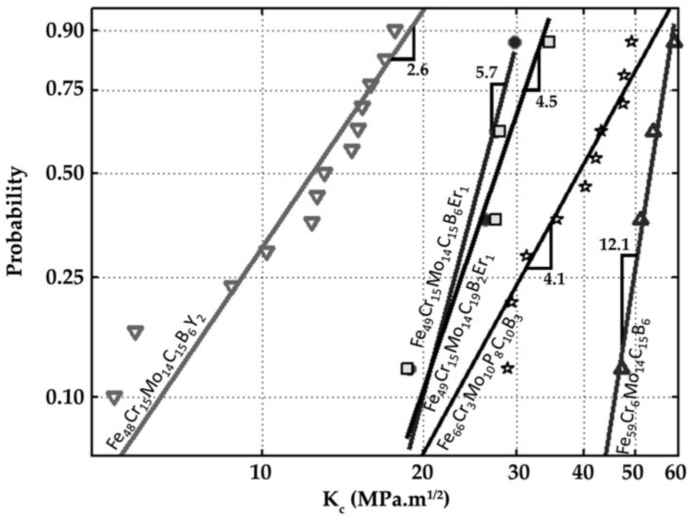

Figure 2. Cumulative probability plot of K_C values obtained for various Fe-BMGs listed in Table 1.

(e.g. oxygen content) could produce significantly different results, as could differences in notch radius [16,30] and loading conditions, as recent work [31] on mixed mode loading has also shown. Furthermore, recent work [32,33] has shown significant detrimental effects of oxygen level on the fracture toughness of the Zr-based glasses (with the strength level in the 1.6 GPa range) via oxide inclusion-initiated fracture in high oxygen containing systems that compromised the toughness values via early initiation of cracks ahead of fatigue precracks.

The Fe-based BMGs tested presently possess hardness in excess of 11 GPa, with compressive strengths in excess of 4 GPa [1,2,8]. The stresses ahead of a notch or fatigue precrack scale with the strength level of the material [34,35], thus the possible stress levels ahead of notches/precracks in these Fe-BMGs (and other higher strength BMGs) can be at least twice as large as those in the Zr-based glasses that exhibit strength levels in the 2 GPa range and are well in excess of the stresses obtained in uniaxial tension or compression. The presence of any secondary phases/particles/inclusions/porosity could severely degrade the damage tolerance under tension/notched/pre-cracked bending conditions.

In order to examine this possibility in the present work, all samples tested were examined using high resolution SEM, with particular attention given to alloy chemistries and samples exhibiting significant scatter in toughness. Figure 3 shows SEM micrographs of the notch region for one of the Fe-BMG samples that clearly reveals inclusion-initiated failure beneath the notch. This sample exhibited a notch toughness value of only 9 MPa $m^{1/2}$, significantly less than those of the same nominal chemistry that did not exhibit inclusion-initiated failure (i.e. 37 MPa $m^{1/2}$). EDS analysis of the inclusion-initiated fracture in Figure 3 reveals Al, Er and O. In contrast, the fracture surface of the Fe–Cr–Mo–C–B–P system exhibited a vein-like pattern that appears to initiate from the notch tip in the absence of any inclusions, Figure 4, and produces much higher toughness (i.e. 49 MPa $m^{1/2}$) with less degree of scatter (and higher Weibull modulus). Table 2 identifies some of the samples that exhibited inclusion/porosity nucleated failure, consistent with their lower toughness numbers, and also provides the location, size and type of defect

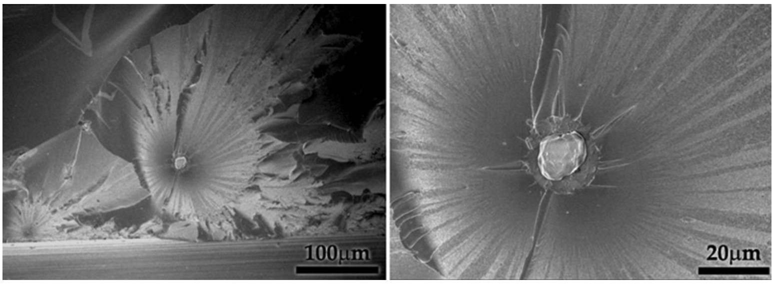

Figure 3. Fracture initiation at inclusion containing Al–Er–O in $(Fe_{0.9}\,Co_{0.1})_{64.5}Mo_{14}C_{15}B_6Er_{0.5}$.

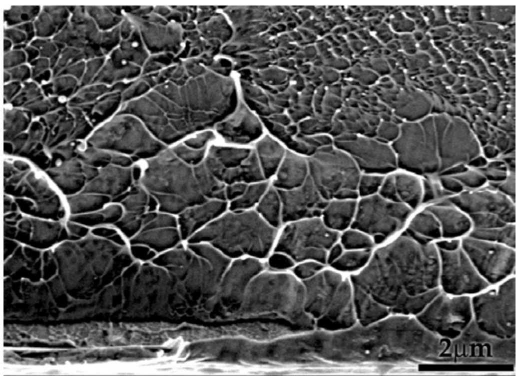

Figure 4. Vein pattern with fracture initiation from notch (bottom of photo) in $Fe_{66}Cr_3Mo_{10}P_8C_{10}B_3$ sample exhibiting high toughness and small scatter.

(inclusion, pore, etc.). The results also suggest that intrinsically tougher BMGs (i.e. due to high ν) may be somewhat more tolerant of defects, although additional testing over a wider range of chemistries, defect populations, and sample volumes is necessary to resolve this. Such work is underway.

The present results continue to indicate that the intrinsic plasticity/toughness of Fe-based BMGs can be tailored via chemistry changes designed to ‘tune’ the elastic constants in the manner outlined previously [2,3,6,8–10]. However, inclusion-initiated fracture can significantly reduce the toughness of these optimised chemistries. Continued efforts on ultra-clean processing of such tailored chemistries should reduce the effects of these extrinsic factors that clearly reduce the toughness, thereby increasing both the toughness and reliability (i.e. Weibull modulus).

5. Conclusions

Alloy modifications designed to change the elastic constants have been shown to affect the notch toughness, with values as high as of 57.9 MPa m$^{1/2}$ obtained under nominally plane strain conditions. While these changes in alloy chemistry appear to have an intrinsic effect on the plasticity/toughness, the large degree of scatter in toughness in some samples was shown to be affected by the presence of processing defects. Both inclusion- and porosity-initiated related fracture were identified in samples exhibiting the largest scatter in toughness, resulting in very low values (e.g. <5) for the Weibull modulus. In addition to toughness improvements via intrinsic (i.e. chemistry) changes, these extrinsic effects must be minimized/eliminated in order to continue to improve the toughness and reliability of such high strength systems.

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