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Intrinsic plasticity or brittleness of metallic glasses

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The intrinsic plasticity or brittleness of crystalline metals correlates with the ratio of the elastic shear modulus μ to the bulk modulus B; when the ratio μ/B exceeds a critical value, the metal is brittle. Sufficient data on elastic moduli and toughness are now available to permit an assessment for metallic glasses. We find a similar correlation, with the critical value of μ/B for metallic glasses (0.41–0.43) more sharply defined than for crystalline metals. This critical value applies also for annealing-induced embrittlement of metallic glasses. The clear correlation between mechanical behaviour (plasticity or brittleness) and μ/B assists in understanding flow and fracture mechanisms, and in guiding alloy design to alleviate brittleness of metallic glasses.

1. Introduction

Whether a structural material shows plastic flow or brittle fracture on loading is of clear practical significance. Brittleness in polycrystalline metals can be intrinsic or induced, for example, by impurity segregation to grain boundaries [1]. The factors determining intrinsic plasticity or brittleness have no simple link with interatomic potentials, yet there is a correlation with the ratio of the elastic shear modulus μ to the bulk modulus B [1–4]. That high μ/B favours brittleness and vice versa was first pointed out by Pugh [2] in analysing the competition between plastic flow and brittle (transgranular) fracture in metals. The analysis was made rigorous by Kelly *et al*. [3], and quantitatively analysed by Rice and Thomson [4]. The competition between transgranular and intergranular fracture in polycrystalline metals has similarly been analysed by Cottrell [5]. At low homologous temperatures, plastic deformation in crystalline metals occurs by glide of dislocations on close-packed planes, with the

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resistance to plastic deformation proportional to the shear modulus, μ. In contrast, brittle fracture involves the tensile separation of non-close packed atomic planes via the propagation of cracks through grains (transgranular) or along grain boundaries (intergranular). In either case, the resistance to dilatation caused by the hydrostatic stress state present near the crack is proportional to the bulk modulus, B.

The data on polycrystalline pure metals collected by Pugh [2] provide a qualitative ranking from ductile (e.g. Ag, Au, Cd, Cu) to brittle (e.g. Be, Ir) behaviour as μ/B increases. For cubic close-packed (ccp) metals the critical ratio $(\mu/B)_{\mathrm{crit}}$ dividing the two regimes is in the range 0.43–0.56, and for hexagonal close-packed metals 0.60–0.63. Cottrell [5] has estimated $(\mu/B)_{\mathrm{crit}}$ for transgranular fracture from measured surface energies: 0.32–0.57 for ccp metals and 0.35–0.68 for body-centred cubic metals. The spread in values for each structure type largely blurs the distinction between them. Each structure type, however, includes metals with widely differing degrees of elastic anisotropy. Detailed analysis requires knowledge of the slip and cleavage planes, of the relevant elastic constants and critical stresses for slip and cleavage on those planes, and of the stresses in the vicinity of a crack tip. The definitive analysis by Rice and Thomson [4] quantifies the critical conditions for ductile behaviour in terms of dislocation emission from a crack tip. Glassy or amorphous alloys, in contrast, are normally expected to be elastically isotropic and cannot show dislocation-mediated plasticity.

Metallic glasses were originally made by ultra-rapid quenching of the liquid [6], but by careful selection of composition the glass-forming ability of alloys can approach that of conventional oxide glasses. At such compositions, *bulk metallic glasses* (BMGs), i.e. with a minimum dimension of $\geq 10\,\mathrm{mm}$, can be cast at low cooling rates ($< 10\,\mathrm{K\,s^{-1}}$) [7–9]. The availability of BMG samples has permitted better characterization of the mechanical properties of metallic glasses, in particular the determination of plane-strain fracture toughness K_{Ic} on fatigue pre-cracked specimens [10]. When metallic glasses show plastic flow (e.g. those based on zirconium or palladium), it is localized into *shear bands*. The *local* plasticity (i.e. within the shear band) is very high ($\gg$100% strain) in these cases and forms part of the micromechanism of fracture [11]. The associated fracture surface (figure 1a) shows a very characteristic *vein* pattern and evidence of high *local* plasticity arising from instabilities in the band of lowered viscosity. This shear-softening (in marked contrast to the work-hardening exhibited by crystalline metals) prevents stable (i.e. global) plastic elongation in tension. Thus metallic glasses showing plasticity cannot properly be termed globally *ductile*, though they are *malleable* (capable of plastic compression) and can be bent plastically. Plastic flow occurs at unusually large fractions of the theoretical strength and this combined with the capacity for *local* plastic flow can give high fracture toughness ($K_{\mathrm{c}} > 20\,\mathrm{MPa\,m^{1/2}}$) [10, 12–15]. It is appropriate to use linear elastic fracture mechanics (LEFM) concepts in these cases as the global plastic zone size(s), calculated [10] using standard relations [16], are much smaller than the specimen dimensions reported in those studies [10, 12–15]. In notched samples many shear bands are initiated at and propagate from the notch, leading to $K_{\mathrm{c}} > 60\,\mathrm{MPa\,m^{1/2}}$ [10, 12, 14, 17], although the plasticity is again confined to boundary layers contiguous with the crack faces in which all irreversibilities are confined. In contrast, other metallic glasses (e.g. those based on magnesium) [18] are

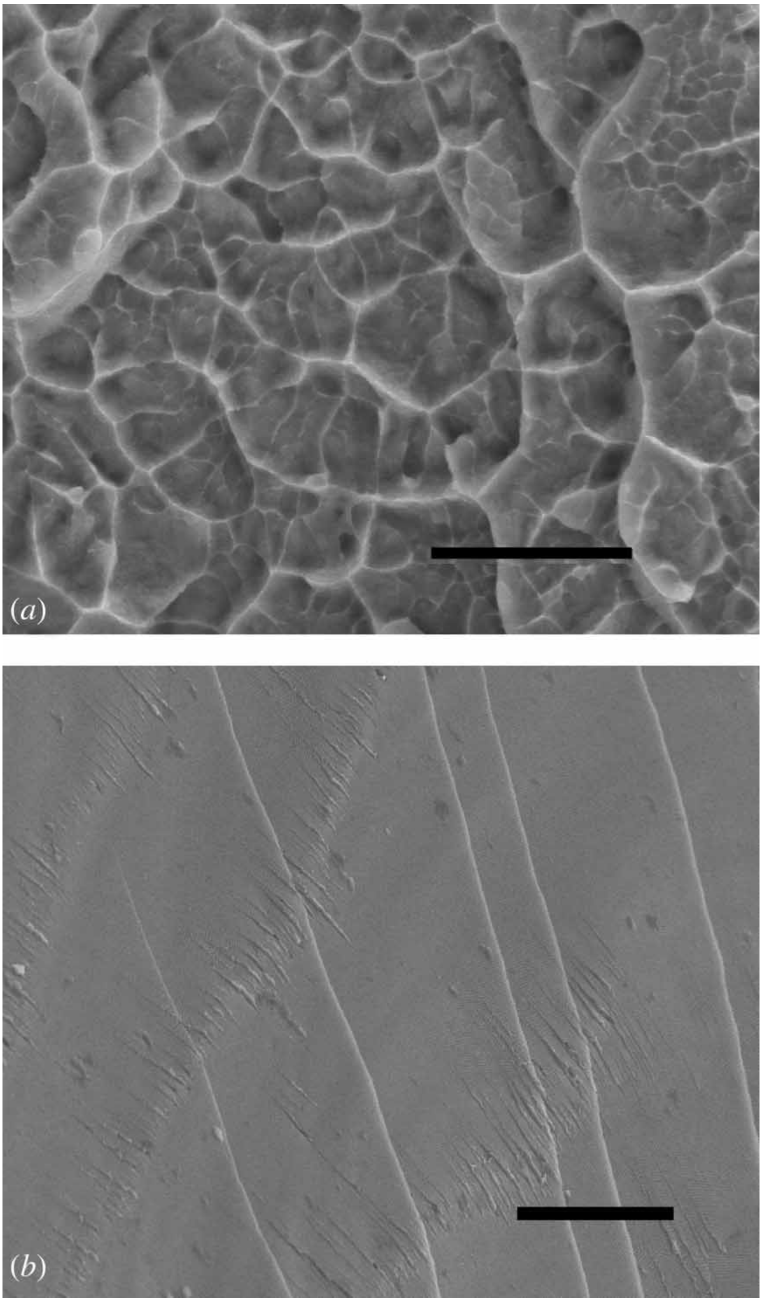

Figure 1. Scanning electron micrographs of fracture surfaces of the bulk metallic glass $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%, Vitreloy 1^{TM}): (a) the as-cast glass shows the vein pattern associated with localized plastic flow in shear bands in materials with significant toughness; (b) the annealed (12 h at 623 K) glass shows the river pattern associated with cleavage fracture of brittle materials. (Scale markers: 5 μm).

both globally and locally brittle, with properties similar to oxide glasses, showing quite different fracture surfaces and notch toughness less than 5 MPa m$^{1/2}$. Also, metallic glasses showing high *local* plasticity can be embrittled by annealing [19, 20]. An example of a locally brittle fracture produced by annealing a Zr-based BMG for 12 h at 623 K is shown in figure 1b [19]. For metallic glasses, through the use of BMG samples, it is only recently that significant amounts of data have been collected on fracture toughness and elastic constants. We now exploit the availability of these data to explore the significance of the ratio μ/B for the mechanical properties of isotropic amorphous metallic structures.

2. Methods

Bulk metallic glasses and their oxide counterparts exhibit isotropic elastic constants that have been measured via ultrasonic [21] and other techniques. The values of the moduli μ and B used in the present work were either obtained directly from literature sources, or calculated from a knowledge of at least two of the elastic constants using standard relations [22]. The experimental accuracy is of the order of 1% for density and 1–2% for acoustic velocity measurements, producing an accuracy better than 5% for the elastic constants. Values of fracture toughness or notch toughness were similarly taken from literature sources. The scatter in toughness data for identical tests on nominally identical crystalline materials is typically less than 10% [16, 23]. Recent tests [10, 19, 24, 25] on Zr-based bulk metallic glasses reveal a similar degree of scatter in toughness when nominally identical materials are tested using standardized test techniques. Because the metallic glasses under comparison have such a wide range of Young's modulus E, it is better not to quantify their mechanical behaviour in terms of toughness but rather in terms of the energy of fracture G; this is the energy required to create two new fracture surfaces and for ideally brittle materials is just 2γ, where γ is the surface energy per unit area. Under plane strain [16, 23], $G = K^2/E(1-\nu^2)$, where K is the stress intensity (MPa m$^{1/2}$) at fracture, and ν is Poisson's ratio.

3. Results

All the data used in the present work are collected in table 1; this includes all available relevant data on as-cast metallic glasses [10, 12–15, 17, 18, 24–28], on an annealed glass [19], and selected data on oxide glasses [29] for comparison.

The data on as-cast metallic glasses, plotted in figure 2, show a clear correlation between fracture energy G and μ/B. With low values of μ/B, the glasses based on palladium, zirconium, copper or platinum, all have fracture energies well in excess of 1 kJ m^{-2}, exhibit extensive shear banding, and have vein-pattern fracture surfaces [10, 12–15, 17, 24–26]. With high μ/B the magnesium-based glass [18] approaches the ideal brittle behaviour ($G \approx 1$ J m^{-2}) associated with oxide glasses. Recent reports [26] of platinum-based glasses with low μ/B and exceptionally high toughness and malleability fit well on the same correlation. This correlation between G and μ/B is similar to that discussed earlier for crystalline metals. Interestingly iron, which as a crystalline metal exhibits borderline ductile–brittle behaviour [4], appears to behave

Table 1. Data collected on metallic glasses (as-cast and annealed), and oxide glasses for comparison.

Material	ρ (g/cm^3)	B (GPa)	μ (GPa)	E (GPa)	ν	μ/B	K_c (MPa m$^{1/2}$)	G_c (kJ/m^2)	Refs.
Fused silica	2.203	36.4	31.3	72.9	0.166	0.858	0.5	0.003	[29]
Window glass	2.421	38.8	27.7	67.2	0.211	0.716	0.2	0.004	[29]
Toughened glass	2.556	61.9	34.4	87.0	0.266	0.555	0.5	0.003	[29]
$Mg_{65}Cu_{25}Tb_{10}$	3.979	44.71	19.6	51.3	0.309	0.439	2	0.07	[9, 18]
$Ce_{70}Al_{10}0Ni_{10}Cu_{10}$	6.67	27	11.5	30.3	0.313	0.427	10	3	[9, 18]
$Fe_{50}Mn_{10}Mo_{14}Cr_4C_{16}B_6$		180	76.1	200.0	0.314	0.423	2	0.02	[28, 30]
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	8.315	128.2	36.9	101.1	0.369	0.288	67	38	[9, 12]
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	6.69	107.7	32.0	87.3	0.365	0.297	27	7	[9, 24]
$Pd_{77.5}Cu_6Si_{16.5}$		167	31.5	88.8	0.41	0.189	51	35	[13, 21, 27]
		175	32.9	92.9	0.41	0.188	29	61	[13, 21, 27]
		180	34.4	93.6	0.41	0.191	67	33	[13, 21, 27]
		164	30.1	85.0	0.41	0.184	50	23	[13, 21, 27]
		170	31.9	89.9	0.41	0.188	50	24	[13, 21, 27]
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	6.52	99.2	30.1	82.0	0.362	0.303	80	68	[9, 24]
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	6.12	114.7	37.4	101.3	0.353	0.324	86	72	[10, 19, 34]
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	6.12	114.7	37.4	101.3	0.341	0.324	86	74	[10, 19, 34]
Annealed 0.75 h @ 623 K		114	37.5	101.6	0.351	0.329	68	40	[19, 34]
Annealed 1.5 h @ 623 K		114	37.5	101.6	0.351	0.329	42.5	16	[19, 34]
Annealed 3 h @ 623 K		114.4	38.8	107.5	0.347	0.339	27	6	[19, 34]
Annealed 6 h @ 623 K		114.4	42.1	111.4	0.336	0.368	32	8	[19, 34]
Annealed 12 h @ 623 K		115	43.2	113.3	0.333	0.376	9	0.6	[19, 34]
Annealed 24 h @ 623 K	6.192	118.6	48.8	128.7	0.319	0.411	8	0.4	[19, 34]
$Fe_{80}P_{13}C_7$		228.5	49.0	137.3	0.4	0.214	77	60	[13, 27]
		207	44.3	124.0	0.4	0.214		110	[13, 27]
$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$				94.8	0.42	0.167	79	80	[26]
$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$				94.8	0.42	0.167	84	90	[26]

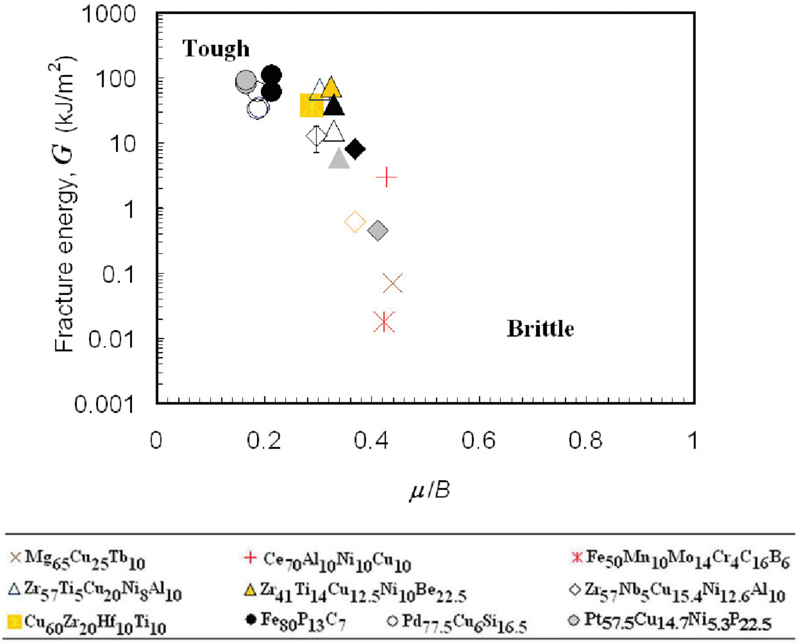

Figure 2. The correlation of fracture energy G with elastic modulus ratio μ/B for all the as-cast (unannealed) metallic glasses for which relevant data are available (all compositions in at.%). Elastic constants [9, 21, 26, 27, 30, 34] were used to convert fracture toughness (K_{Ic}, K_c) [10, 12–15, 17, 18, 24, 26–28] to fracture energy.

similarly in glassy alloys: the Fe–Mn–Mo–Cr–C–B BMG is brittle [28, 30], while the Fe–P–C glass has significantly lower μ/B and greater toughness [27].

To eliminate alloy composition as a variable, it is useful to examine the effects of annealing on a single metallic glass. Annealing-induced embrittlement, in early studies identified as a problem with rapidly solidified iron-based metallic glasses of interest for their soft-magnetic properties, is associated with structural relaxation of the glass and occurs before the onset of crystallization. The structural relaxation involves a densification of the glass (loss of free volume) and can give significant changes in properties [31]. For example, the BMG $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%, Vitreloy 1^{TM}) shows (inset in figure 3) a gradual reduction in notch toughness on annealing [19], associated with a reduction in shear banding, and gradual changes in fracture surface morphology (figure 1a,b). Figure 3 shows that G and μ/B remain correlated as the annealing progresses. The correlation is the same as that found when comparing different glasses, as can be seen when all the data on as-cast and annealed metallic glasses are combined (figure 4). This figure also includes data on oxide glasses which, having high μ/B and low G [32], evidently follow the same behaviour.

For a metallic glass the value of μ/B is typically about two-thirds of the value for the polycrystalline pure metal on which it is based. The glasses might therefore be expected to show more plasticity, but this is offset by the shift in value of $(\mu/B)_{crit}$

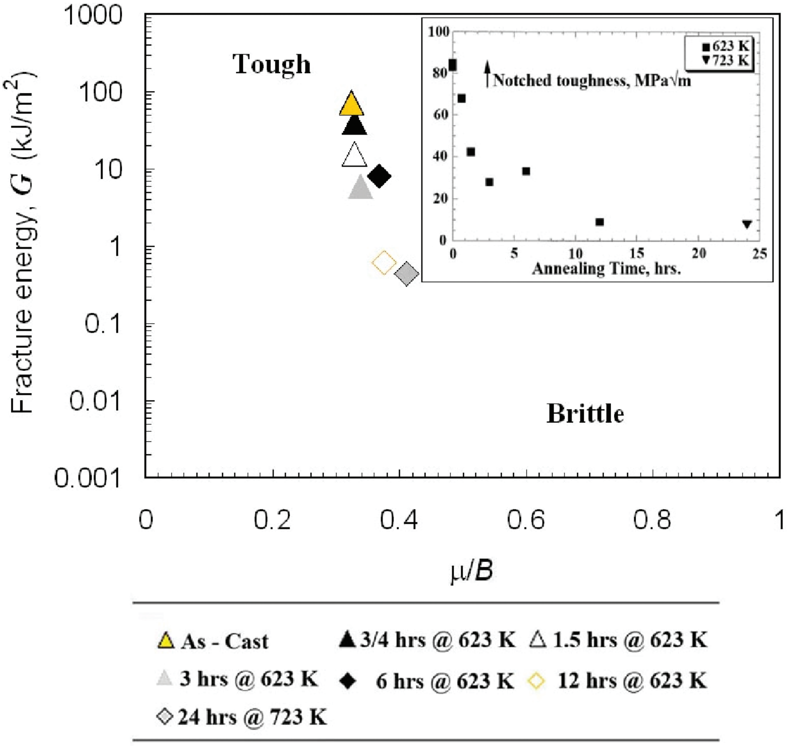

Figure 3. The correlation of fracture energy G with ratio μ/B as the BMG $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%, Vitreloy 1) is annealed. The inset shows the decrease in notch toughness as a function of annealing time [19]. Fracture energies were calculated based on elastic constants reported elsewhere [34].

which divides plasticity and brittle fracture. For metallic glasses (figure 4) $(\mu/B)_{\text{crit}}$ is in the range 0.41–0.43, where there is a large drop in G with increasing μ/B, and G approaches the toughness of oxide glasses. This is lower than the range of values for $(\mu/B)_{\text{crit}}$ reported earlier for polycrystalline pure metals. Overall, it would appear that glassy alloys are slightly more likely than their crystalline counterparts to show brittle behaviour. The correlation between fracture energy and elastic constants can also be expressed in terms of Poisson's ratio. Higher values of ν give higher fracture energy, the transition between brittle and tough regimes where there is a large increase in G beyond the oxide glass values being for $\nu_{\text{crit}} = 0.31$–0.32, as shown in figure 5.

4. Discussion

Comparison of figures 2 and 3 shows that the transition from plasticity to brittleness is more diffuse when a range of glass compositions is considered. This can mostly be attributed to scatter in the G values arising from differences in test technique and in details such as notch radius and specimen thickness. For example, the magnitude

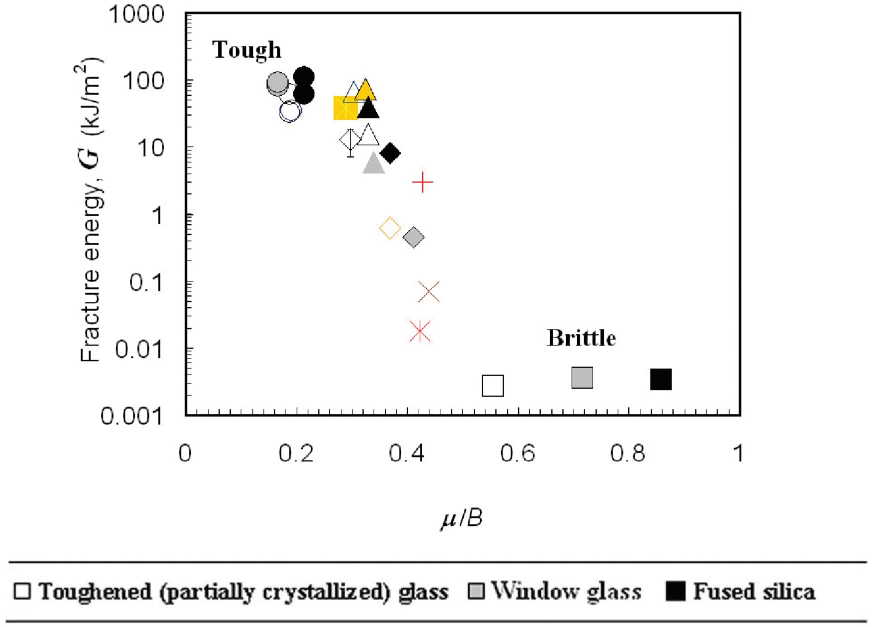

Figure 4. The correlation of fracture energy G with ratio μ/B for all the collected data on metallic glasses (as-cast and annealed, symbols the same as in figures 2 and 3), as well as for oxide glasses. The divide between the tough and brittle regimes is in the range $(\mu/B)_{\text{crit}} = 0.41$–$0.43$.

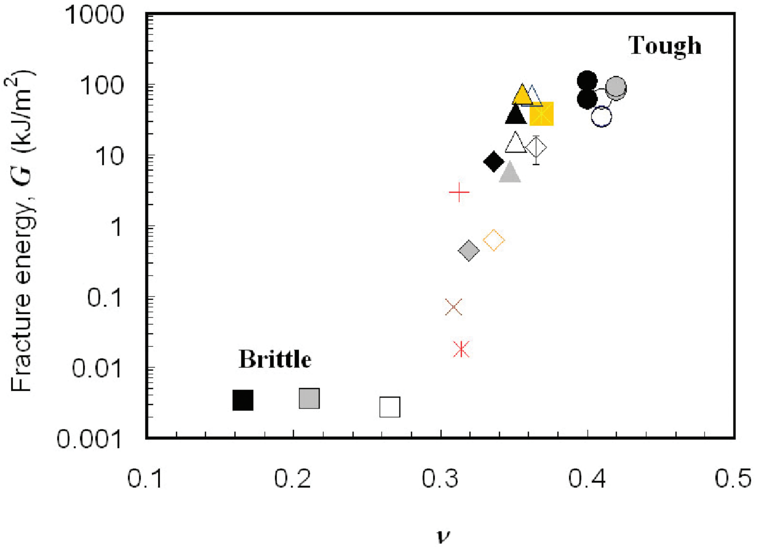

Figure 5. The correlation of fracture energy G with Poisson's ratio ν for all the collected data on metallic glasses (as-cast and annealed) as well as for oxide glasses. The symbols are the same as in figure 4 and earlier figures. The divide between the tough and brittle regimes is in the range $\nu_{\text{crit}} = 0.31$–0.32.

of toughness of a variety of metallic glasses depends on specimen thickness due to associated changes in stress state [13, 27], analogous to those observed in crystalline metals [16]. It has also been demonstrated [10, 19, 25] that decreasing the notch radius to that of a fatigue pre-crack reduces the toughness measured in Zr-based bulk metallic glasses; a similar, though weaker, trend is found for crystalline metals [10, 16, 19]. However, while the magnitude of the measured toughness in these cases is affected by these changes in specimen geometry (i.e. sample thickness, notch radius), the fracture micromechanism and degree of *local* plasticity appear unchanged. There may be some composition-dependent spread in the value of $(\mu/B)_{\mathrm{crit}}$, but it is remarkable that the spread is so small and certainly much less than for the crystalline metals. The existence of a sharp transition for metallic glasses shows that the correlation between fracture energy and μ/B is fundamental for metallically bonded systems and does not depend on there being dislocation-mediated flow as found in crystals.

Annealing-induced embrittlement of metallic glasses could be linked to several of the property changes associated with structural relaxation. That the transition from plasticity to brittleness occurs at the same critical value of μ/B as when as-quenched glasses of different compositions are compared (figure 2) is strong evidence that the embrittlement (figure 3) is most closely connected to the changes in elastic moduli. It has been shown that annealing-induced changes in moduli can be reversed by plastic deformation [33], raising the possibility that deformation could be used to reverse embrittlement.

In parallel with this work, W.L. Johnson (personal communication) and co-workers have studied the flow of metallic glass-forming liquids, and the flow and fracture of metallic glasses, in relation to elastic constants particularly ν. They have demonstrated a link between plasticity and high values for ν for a particular platinum-rich glass [26]. We have focused more narrowly on the correlation between G and μ/B. This correlation may be useful in ranking the embrittlement sensitivity of metallic glasses. For example, BMGs based on palladium and platinum, which have exceptionally low μ/B, are resistant to annealing-induced embrittlement. The elastic constants of metallic glasses (at least those not containing metalloid elements such as B, C, P, Si) show a good correlation with a weighted average of the constants for the constituent elements. Thus consideration of μ/B can assist in selecting alloying additions for alleviating brittleness, a key concern for many BMGs. Finally the well defined values of $(\mu/B)_{\mathrm{crit}}$ and ν_{crit}, uncomplicated by anisotropy, may yet assist in understanding the mechanisms of plastic flow and fracture in amorphous systems.

5. Conclusions

Data from bulk samples show that for metallic glasses there is a clear, universal correlation between the energy of fracture G and the elastic modulus ratio μ/B. Metallic glasses with $\mu/B > 0.41$–0.43 (or, equivalently, with $\nu < 0.31$–0.32) are brittle. This correlation applies equally for as-cast metallic glasses of different compositions and for a given glass embrittling on annealing. The critical μ/B ratio is more clearly defined for metallic glasses than for crystalline metals, and its value 0.41–0.43 is less than the range reported for the latter. The glasses, however, have μ/B ratios approximately two-thirds those of their crystalline counterparts, and overall tend to be more brittle. The correlation between mechanical properties and elastic moduli indicates that brittleness in metallic glasses can be alleviated by alloying with elements with low μ/B (or, equivalently, high ν) as constituents.

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