Locating bulk metallic glasses with high fracture toughness: Chemical effects and composition optimization

Qiang He\textsuperscript{a}, Yong-Qiang Cheng\textsuperscript{b}, Evan Ma\textsuperscript{b}, Jian Xu\textsuperscript{a,*}

\textsuperscript{a} Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China
\textsuperscript{b} Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD 21218, USA

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\textbf{Abstract}

We have developed new bulk metallic glasses (BMGs) with optimized glass-forming ability (GFA), in ternary Zr–Cu–Al and quaternary Zr–Ti–Cu–Al systems. The relatively large dimensions of these BMGs permitted fracture toughness tests, leading to the discovery of Zr\textsubscript{61}Ti\textsubscript{2}Cu\textsubscript{25}Al\textsubscript{12} (ZT1) that has a toughness among the highest for monolithic BMGs (fatigue pre-cracked fracture toughness, \(K_{\text{max},\text{in}}\), excess of \(\approx 100\) MPa.m\(^{1/2}\)). This BMG also has a nonlinear-elastic fracture behavior as seen in the resistance curve. We have also measured the toughness for Zr–TM–Al (TM = Co, Ni) BMGs, which have previously been optimized for GFA. Comparing the BMGs studied, in conjunction with literature data on Zr-based BMGs, we have identified trends in chemistry effects on BMG fracture toughness, in particular the role of Al as well as the effects of Cu when substituting Ni (or Co). These trends are explained in terms of not only the internal atomic packing structure, but more importantly the electronic structure and nature of bonding in light of the first-principles calculations. A strategy is then outlined to locate BMG compositions with high toughness. The correlations of the BMG toughness with the shear banding behavior, the Poisson’s ratio (\(\nu\)), the product of shear modulus and molar volume (\(\mu V_m\)), and the glass transition temperature (\(T_g\)), are also discussed.

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\section{1. Introduction}

Without long-range order in their internal structure, bulk metallic glasses (BMGs) exhibit much higher yield/fracture strength than their polycrystalline counterparts. However, the BMGs exhibit almost zero global plastic tensile strain at failure. For such materials, fracture toughness is a particularly critical property for them to find practical applications [1–4]. The search for BMGs with decent fracture toughness is therefore of high priority in the field of amorphous alloys.

From the alloy design perspective, there are at least two major issues to consider for locating useful BMGs with high toughness. First, the alloy must first have a high glass-forming ability (GFA), such that samples with sufficiently large sizes can be obtained. Such samples are needed to approach conditions for the evaluation of plane-strain fracture toughness, using standard (such as fatigue pre-cracked samples) and reliable tests. Only then can the measured toughness be compared with those of other engineering structural materials such as high-strength steels and titanium alloys. So far, such data are rarely available, and those in the literature for BMGs are mostly for Zr-based alloys, such as Zr\textsubscript{41.25}Ti\textsubscript{13.75}Cu\textsubscript{12.5}Ni\textsubscript{10}Be\textsubscript{22.5} (trade name Vitreloy 1\textsuperscript{e}/LM 1) and Zr\textsubscript{55}Cu\textsubscript{30}Ni\textsubscript{5}Al\textsubscript{10} (denoted as Z2) [5–11], primarily because these BMGs have the robust GFA to fabricate large-section samples, making them popular for investigations of potential applications and for meaningful toughness testing [12,13]. Also, without a high GFA, the small-sized BMGs are unlikely to be
amenable to applications, even if the material is intrinsically tough.

Second, in a given BMG family such as the Zr-based one, fracture toughness is composition-dependent. The constituent elements and sometimes even micro-alloying can induce major differences. As shown recently by Kim et al. [9], the fracture toughness of quaternary Ni-free Zr_{65.5}Ti_{12.5}Cu_{15}Be_{27.5} (Var1) and Zr_{44}Ti_{17}Cu_{20}Be_{25} (Var2) BMGs exceeds 80 MPa m^{1/2} (even though the data are not the valid mode I plane-strain fracture toughness, K_{IC}), significantly higher than that of the popular Vitreloy 1, which is also Zr-based but Ni-containing. In addition, it was shown that minor addition of Fe (0.5 at.%) into Vitreloy I results in appreciable degradation in fracture toughness of the BMG. Therefore, one needs to learn which element is beneficial (or detrimental) for enhancing the toughness, and how to adjust the composition for optimization in a given alloy system. For example, it has been demonstrated from the glass structure perspective that ductile ternary Zr/Cu/Ni-Al BMGs should have a high concentration of Zr/Cu [14], correlating with a lower shear modulus (μ) or higher Poisson’s ratio (ν).

Therefore, locating practically useful high-toughness BMGs requires concerted efforts that simultaneously take into account the two considerations above. Both of these two aspects involve strong chemistry effects, such that the composition has to be optimized in such a way that both high GFA and toughness can be reached at the same time. This paper reports a study in this direction, resulting in some insights into how to adjust the alloy chemistry to reach the targeted combination of GFA and toughness. Specifically, with focus on the Zr-rich side, we revisit the compositional dependence of the GFA in the ternary Zr–Cu–Al system [15,16]. Starting from alloy Zr_{60}Cu_{26}Al_{10} [14] and using the “3D pinpointing approach” [17], alloys with the optimal GFA have been located in the ternary Zr–Cu–Al and quaternary Zr–Ti–Cu–Al system, yielding sufficiently large as-cast BMG plates that can be made into fatigue pre-cracked samples in accordance with ASTM standards for fracture toughness testing. The new BMGs, together with other known Zr–TM–Al (TM = transition metal) BMG formers, Zr_{56}Co_{28}Al_{16} [18], Zr_{60}Ni_{21}Al_{19} [19] and Zr_{48}Cu_{45}Al; [15], are used to investigate the chemistry effects on toughness. All these alloy compositions have optimal GFA in their respective system. Meanwhile, Co, Ni and Cu have similar atomic sizes (atom radius of Co, Ni, Cu is 0.125, 0.125, 0.128 nm, respectively), making the size effect insignificant and chemistry effect more prominent. The available toughness data for Zr-based BMGs have been summarized to critically assess the validity of the previously suggested correlations between the fracture toughness and ν or μ [20–22]. This work not only lands a BMG with high GFA and record-high toughness simultaneously, but also provides insights that allow us to propose a strategy for locating high-toughness BMGs, which will be summarized in the last section of this paper.

2. Experimental procedures

Elemental pieces with purity better than 99.9 wt.% were used as starting materials. The master alloy ingots with the nominal composition (in at.%) were prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper hearth. The alloy ingots were re-melted several times to ensure compositional homogeneity. The glassy rod/plate samples were fabricated by using vacuum suction casting or copper mold casting of the arc-melted alloys. The amorphous feature of as-cast samples was characterized by X-ray diffraction (XRD), taken from the cross-section surface of the as-cast rods. Glass transition temperature (T_g) and crystallization behavior of the as-cast BMGs were examined in a Perkin–Elmer differential scanning calorimeter (Diamond-DSC) at a heating rate of 20 K min^{-1}.

Samples for the notch toughness tests were taken from the as-cast BMG plates that had a dimension of 3.2 mm × 9 mm × 60 mm. The sample dimensions were B (thickness) = 3 mm, W (width) = 6 mm, S (span) = 24 mm, achieved by electro-discharge machining and polishing. The oxygen content in the as-cast BMG plates was determined to be as low as 90–130 ppm using inert-gas fusion analysis. For the single edge notched bend (SENB) specimen, a straight-through notch with a notch root radius of 150 μm and a length of 0.43–0.55W was made using a diamond wire saw. To confirm the reproducibility of the experimental results, at least five samples were tested for each alloy.

For the fracture toughness tests using the fatigue pre-cracked specimens, the sample dimensions were set to be B = 4 mm, W = 8 mm, S = 32 mm, respectively, again using electro-discharge machining and polishing from as-cast BMG plates (4.2 mm × 11.5 mm × 60 mm). In both cases of the notched and fatigue pre-cracked samples, a surface layer of ~0.2 mm in thickness was removed for each plate to reduce the effects of the residual stresses introduced during the casting process. The fatigue pre-cracking of the samples was conducted on a 5 kN Shimadzu EHF-FB05 fatigue test machine at the frequency of 30 Hz under a constant load ratio of minimum to maximum of 0.1 with the stress intensity factor AK of 17–25 MPa m^{1/2}. The notch plus the fatigue pre-crack were obtained with a length of 0.45–0.55W after 210,000–520,000 fatigue cycles, strictly conforming to ASTM standards. Three-point bending (3 PB) tests of the samples were carried out on a 10 kN MTS A/T 858 testing machine at a constant displacement rate of 0.3 mm min^{-1} at room temperature. 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 SENB and fatigue pre-cracked samples.

The side/fracture surfaces of the fractured samples were examined in a Quanta 600 scanning electron microscope (SEM). The elastic constants of the BMGs, including Yong’s modulus (E), bulk modulus (K), μ and ν, were measured using resonant ultrasound spectroscopy (RUS).
Cylindrical samples of 3 or 4 mm in diameter with known volume and mass were placed between the piezoelectric transducers. Two independent elastic constants $C_{11}$ and $C_{44}$ from the average of three samples for each alloy were obtained, and used to calculate the elastic modulus. The mass density ($\rho$) of the BMG samples was measured using the Archimedes method (at least three measurements for each alloy).

3. Results

3.1. Optimizing glass-forming ability of Zr(Ti)–Cu–Al alloys with high Zr content

The best glass former known before in the ternary Zr–Cu–Al system is Zr$_{48}$Cu$_{45}$Al$_7$ [15]. Here we demonstrate another one on the Zr-rich side that possesses comparable GFA. Fig. 1a illustrates a composition map of BMG formation in the Zr-rich region. Monolithic glassy rods of 3 mm in diameter can be fabricated within a range of 10–16%Al, 24–36%Cu and 51–66% Zr. The best BMG-forming compositions are located at Zr$_{60}$Cu$_{28}$Al$_{12}$ and Zr$_{58}$Cu$_{30}$Al$_{12}$, where the critical diameter ($D_c$) for fully glassy cylinders is 6 mm, see square symbol in Fig. 1a. The $D_c$ of Zr$_{60}$Cu$_{28}$Al$_{12}$ is large enough for toughness testing using the designed sample dimensions.

To further improve the GFA, Ti was incorporated into the base alloy, due to its chemical similarity with Zr but different atomic size ($r_{Ti} = 0.146$ nm, $r_{Zr} = 0.160$ nm), which is expected to enhance the topologically dense atomic packing in the glass, thereby promoting the GFA. The quaternary Zr–Ti–Cu–Al alloy was treated as the pseudo-ternary (ZrTi)–Cu–Al. The “3D pinpointing approach” we established previously [17] was used, with Zr$_{60}$Cu$_{28}$Al$_{12}$ as the starting point. Fig. 1b shows a composition map of $D_c$ for BMG-rod formation on the composition plane of Zr:Ti = 58:2. In comparison with the ternary Zr–Cu–Al, the GFA is significantly enhanced: the $D_c$ of as-cast rods increases from 6 mm at Zr$_{60}$Cu$_{28}$Al$_{12}$ to 10 mm at compositions near (Zr$_{0.97}$Ti$_{0.03}$)$_{64}$Cu$_{25}$Al$_{11}$. At least nine compositions have a capability of $D_c$ = 10 mm (with a composition interval of 1%). Among them, Zr$_{61}$Ti$_{2}$Cu$_{25}$Al$_{12}$ (denoted as ZT1) alloy exhibits the best GFA, as it has the longest length of fully amorphous structure from the bottom of the as-cast 10 mm-diameter rod.

3.2. Notch toughness of Zr–TM–Al (TM = Co, Ni, Cu) and ZT1 BMGs

To observe how toughness changes with alloying elements and composition, ternary Zr–TM–Al alloys with different TM elements (Co, Ni or Cu), including Zr$_{58}$Co$_{28}$Al$_{16}$, Zr$_{60}$Ni$_{21}$Al$_{19}$, Zr$_{60}$Cu$_{28}$Al$_{12}$ and Zr$_{48}$Cu$_{45}$Al$_{7}$, as well as the quaternary ZT1, were tested for notched fracture toughness, using identical configurations of the sample and notch. These compositions have the best GFA in the respective ternary [15,18,19] or quaternary system. Fig. 2 shows the typical curves of load vs. COD for these notched BMG plates under 3 PB (mode I) loading. In the case of Zr$_{58}$Co$_{28}$Al$_{16}$, the BMG fails in the form of complete linear-elastic deformation, see curve A in Fig. 2. According to ASTM standard [12], the notch toughness ($K_Q$) of Zr$_{58}$Co$_{28}$Al$_{16}$ BMG is calculated to be 77 ± 8 MPa$\sqrt{m}$. For Zr$_{60}$Ni$_{21}$Al$_{19}$, slightly visible

Fig. 1. Composition maps of BMG formation for the alloys with high concentrations of Zr in: (a) ternary Zr–Cu–Al and (b) pseudo-ternary (Zr$_{0.97}$Ti$_{0.03}$)–Cu–Al. Different symbols indicate the different critical diameters ($D_c$) of complete glass formation for as-cast rods fabricated using copper mold casting.

Fig. 2. Load vs. crack opening displacement (COD) curves for the five investigated Zr-based BMGs, obtained from notch toughness test.
deviation from linearity prior to failure is observed, see curve
B in Fig. 2. However, significant nonlinear-elastic curves are
shown for the three Cu-bearing BMGs, see curves C, D and
E. In such a scenario, the maximum toughness \( K_{\text{max}} \) is a
better measure than \( K_Q \) for fracture toughness evaluation,
based on ASTM standard E399. The \( K_{\text{max}} \) can be calculated
using Eqs. (1) and (2)

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

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

where for the calculation of \( K_{\text{max}} \), \( P \) is substituted by \( P_{\text{max}} \), i.e. the peak force loaded on the samples, \( S \) is the span be-
tween the two support rollers, \( B \) is the specimen thickness,
\( W \) is the specimen width, and \( a \) is the initial crack size.

For the purpose of comparison, the \( K_{\text{max}} \) values of the investigated BMGs are summarized in Table 1. Among the ternary Zr–Al-based BMGs, the \( K_{\text{max}} \) decreases from the Cu-bearing alloys, 101 MPa m \(^{1/2} \) for Zr\(_{48}\)Cu\(_{45}\)Al\(_{7}\) and 93 MPa m \(^{1/2} \) for Zr\(_{50}\)Cu\(_{28}\)Al\(_{12}\), down to 89 and 77 MPa m \(^{1/2} \) for Zr\(_{60}\)Ni\(_{21}\)Al\(_{19}\) and Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\), respectively. The \( K_{\text{max}} \) of the quaternary ZT1 (Zr\(_{60}\)Ti\(_{5}\)Cu\(_{23}\)Al\(_{12}\)), \( K_{\text{max}} = 96 \) MPa m \(^{1/2} \), is comparable to that of Zr\(_{60}\)Cu\(_{28}\)Al\(_{12}\) and Zr\(_{48}\)Cu\(_{45}\)Al\(_{7}\), while about 20% higher than Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\) and Zr\(_{60}\)Ni\(_{21}\)Al\(_{19}\) BMGs. The roles of the elements and compositions in influencing the toughness will be discussed in the next section.

As shown in Fig. 2, significant nonlinearity in the load–COD curves is observed for the Zr–Cu-based BMGs, implying that extensive plastic deformation and subcritical cracking have occurred. In this case, single-value measurement with \( K \) as discussed above, is insufficient to characterize the toughness. Consequently, the \( J \)-integral characterization based on nonlinear-elastic fracture mechanics has been employed to capture the contribution from inelastic deformation for the toughness evaluation. In accordance with ASTM standard [13], we calculated the maximum strain-energy release rate \( J_{\text{max}} \) using the following equations:

\[
J = \frac{K^2 (1 - \nu^2)}{E} + J_{\text{pl}}
\]

\[
J_{\text{pl}} = \frac{1.9 A_{\text{pl}}}{B b_0}
\]

where \( J_{\text{pl}} \) is the area under maximum force (\( P_{\text{max}} \)) vs. dis-
placement record, \( b_0 \) is the ligament length equal to \( W - a \), and \( E \) is the Young’s modulus of the materials. For the calculation of \( J_{\text{max}} \), the value of \( K_{\text{max}} \) is used for \( K \) in Eq. (3).

The calculated \( J_{\text{max}} \) values are also listed in Table 1. Note that among the five investigated alloys, the ZT1 shows the largest \( J_{\text{max}} \) value, 235 ± 63 kJ m \(^{-2} \). For a comparison, Fig. 3 illustrates the relative toughness for these BMGs tested using notched samples, normalized by the \( J_{\text{max}} \) value of ZT1. The toughness of Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\) and Zr\(_{60}\)Ni\(_{21}\)Al\(_{19}\), with their \( J_{\text{max}} \) less than 100 kJ m \(^{-2} \), is only 20\% and

\(~40\%\) of that of the toughest ZT1, respectively, whereas the \( J_{\text{max}} \) of Zr\(_{48}\)Cu\(_{45}\)Al\(_{7}\) and Zr\(_{60}\)Cu\(_{28}\)Al\(_{12}\) (around 200 kJ m \(^{-2} \)) is about 90\% and

\(80\%\) of that of the ZT1, respectively. It is interesting to note that minor alloying with Ti (2\%) into the Zr–Cu–Al alloy has enhanced both the toughness and the GFA.

Fig. 4a–e shows a group of SEM images observed for the side surface of fractured BMG samples after 3 PB test, in front of the notch tip. As the representative, we focus on the two extreme cases, the least-tough Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\) and the toughest ZT1 BMGs. In the case of Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\) (see Fig. 4a), a few shear-band offsets emanating from the notch are observed, accompanied by a small plastic zone size of

\(~0.2\) mm. The crack initiating from the notch tip

\begin{table}[h]
\centering
\caption{Glass transition temperature, mass density, elastic properties and notch toughness for the investigated Zr–TM–Al (TM = Co, Ni, Cu) BMGs.}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
\textbf{Alloy Composition (at.\%)} & \textbf{\( T_g \) (K)} & \textbf{\( \rho \) (g cm\(^{-3}\))} & \textbf{\( E \) (GPa)} & \textbf{\( \mu \) (GPa)} & \textbf{\( \beta \) (GPa)} & \textbf{\( \gamma \)} & \textbf{\( K_Q \) (MPa m\(^{1/2} \))} & \textbf{\( K_{\text{max}} \) (MPa m\(^{1/2} \))} & \textbf{\( J_{\text{max}} \) (kJ m\(^{-2} \))} \\
\hline
1 & Zr\(_{56}\)Co\(_{28}\)Al\(_{16}\) & 753 & 6.5 & 92.4 ± 0.1 & 33.9 ± 0.1 & 113.1 ± 2.2 & 0.364 ± 0.003 & 77 ± 8 & 56 ± 11 \\
2 & Zr\(_{60}\)Ni\(_{21}\)Al\(_{19}\) & 723 & 6.3 & 91.2 ± 0.6 & 33.5 ± 0.2 & 109.0 ± 0.5 & 0.361 ± 0.001 & 89 ± 9 & 88 ± 26 \\
3 & Zr\(_{48}\)Cu\(_{45}\)Al\(_{7}\) & 708 & 7.1 & 90.1 ± 0.1 & 33.0 ± 0.1 & 112.8 ± 1.6 & 0.367 ± 0.002 & 101 ± 9 & 208 ± 32 \\
4 & Zr\(_{50}\)Cu\(_{28}\)Al\(_{12}\) & 666 & 6.6 & 84.0 ± 0.2 & 30.7 ± 0.1 & 106.5 ± 0.2 & 0.360 ± 0.001 & 93 ± 7 & 188 ± 30 \\
ZT1 & Zr\(_{60}\)Ti\(_{5}\)Cu\(_{23}\)Al\(_{12}\) & 652 & 6.5 & 82.8 ± 0.5 & 30.2 ± 0.2 & 101.4 ± 0.8 & 0.367 ± 0.001 & 96 ± 5 & 235 ± 63 \\
\hline
\end{tabular}
\end{table}
propagates in a straightforward manner along the direction nearly perpendicular to the loading stress, indicating a low fracture resistance of the material. In contrast, the ZT1 BMG exhibits an extended and much larger plastic zone size of $\sim 0.9$ mm along the crack propagation direction. A number of shear-banding offsets emanating from the notch tip are present, indicating proliferation of shear banding, as seen in Fig. 4e. The crack propagation path is significantly deflected and bifurcated, reflecting a high crack growth resistance. The situation of the remainder BMGs (Zr–Ni–Al and Zr–Cu–Al) is in the middle between the two ends of the spectrum, Zr–Co–Al and Zr–Ti–Cu–Al.

Fig. 4. SEM images showing multiple shear bands near the notch root and crack deflecting, after fracture of the: (a) Zr$_{56}$Co$_{28}$Al$_{16}$, (b) Zr$_{60}$Ni$_{21}$Al$_{16}$, (c) Zr$_{48}$Cu$_{45}$Al$_{7}$, (d) Zr$_{60}$Cu$_{28}$Al$_{12}$ and (e) Zr$_{61}$Ti$_{2}$Cu$_{25}$Al$_{12}$ (ZT1) samples. The crack extension direction is from bottom to top.
It can be concluded from the observations above that the population of shear bands and the magnitude of the plastic zone size ahead of the notch tip scale with the magnitude of the measured toughness, \( J_{\text{max}} \) (\( K_{\text{max}} \) as well). Evidently, the toughness response for BMGs is directly related to whether the formation of shear bands in front of the crack tip is easy and populous, which leads to extensive plastic shielding and increased energy absorption.

### 3.3. Correlation between toughness and elastic properties

To examine the validity of using \( \mu \) or \( v \) as the indicator for BMG property [20–23], the correlation between \( v \) or \( \mu \) and notch toughness (using \( J_{\text{max}} \) here) was examined for the current five Zr–TM–Al BMGs. The measured \( T_g, \rho, E, \mu, \beta \) and \( v \) are summarized in Table 1, as well as the \( K_Q, K_{\text{max}} \) and \( J_{\text{max}} \). Fig. 5a displays a plot of \( J_{\text{max}} \) vs. \( v \), showing two distinct groups. The group consisting \( \text{Zr}_{48}\text{Cu}_{45}\text{Al}_{7}, \text{Zr}_{60}\text{Cu}_{28}\text{Al}_{12} \) and ZT1 has simultaneously higher \( v \) and \( J_{\text{max}} \), while the less-tough group (\( \text{Zr}_{56}\text{Cu}_{28}\text{Al}_{16} \) and \( \text{Zr}_{60}\text{Ni}_{21}\text{Al}_{19} \)) exhibits a relatively lower \( v \) value. This is consistent with the general trend that BMGs with a higher \( v \) have higher toughness [22]. Within each group, however, the trend is not obvious as the differences in \( v \) (or \( J_{\text{max}} \)) are close to being within experimental error.

Fig. 5b plots \( J_{\text{max}} \) vs. \( \mu \) multiplied by molar volume \( (V_m) \) for the investigated BMGs. The physical significance of the \( \mu V_m \) will be addressed later in Section 4.2. Similar to the scenario of the \( v \), the Zr–Cu-based BMG group (three alloys) with higher \( J_{\text{max}} \) exhibits lower \( \mu V_m \), and vice versa for the Zr–Co and Zr–Ni-based alloys. This suggests that the higher toughness of the BMGs is intrinsically associated with their lower energy barrier for shear events.

Furthermore, since the \( T_g \) is also a measure of the energy barrier for shear transformation in BMGs that scales with \( \mu \) [24–26], the relationship between the \( J_{\text{max}} \) and homologous temperature \( (T_R/T_g, \text{normalized with respect to room temperature } T_R = 298 \text{ K}) \) is plotted in Fig. 5c. As expected, a higher \( T_g \) has a negative effect on the toughness of BMGs. In other words, the higher the \( T_g \) (equivalent to a lower homologous temperature) of the BMG is, the more brittle the BMG. Our finding is also consistent with the previous report [27] that the toughness increases with increasing the testing temperature for Vitreloy 1 (higher homologous temperature).

### 3.4. Fatigue pre-cracked fracture toughness of ZT1 BMG

As shown in Section 3.2 using notched samples, \( \text{Zr}_{61}\text{Ti}_{2}\text{Cu}_{25}\text{Al}_{12} \) (ZT1) exhibits the highest toughness among the investigated Zr–TM–Al BMGs, based on the measured \( J_{\text{max}} \) value and observed crack path, as seen in Table 1 and Fig. 4e. While the notch toughness, when measured in the same way and in the same geometry, is useful to compare the toughness of different BMGs (as we have done in some plots in this paper), to measure more rigorously the intrinsic material fracture toughness one needs to exclude the blunting effect of the notch root radius [7,29]. The ZT1 BMG was therefore further tested using
fatigue pre-cracked samples. The sample thickness was increased to 4 mm, in an effort to meet the requirement of plane-strain conditions. This increase was possible for ZT1, since its GFA is high enough (the critical diameter for fully glassy rods is 10 mm, such that plates with \( B = 4 \) mm, \( W = 8 \) mm, \( S = 32 \) mm can be made). Similar to the notched samples (see curve E in Fig. 2), a significant nonlinearity in the load–COD curve is observed also for fatigue pre-cracked thicker samples, as shown in Fig. 6 with a typical example. As seen in the curve, the ratio of \( P_{\text{max}}/P_Q \) is \( \sim 1.38 \), which fails to pass a major validity requirement for \( K_{1c} \): \( P_{\text{max}}/P_Q \leq 1.10 \) (see ASTM E399). As discussed earlier, in such cases \( K_{\text{max}} \) and \( J_{\text{max}} \) better evaluate the elastic–plastic fracture toughness. The \( K_{\text{max}} \) and \( J_{\text{max}} \) values of ZT1 BMG are calculated using Eqs. (1) and (3).

\[ J_\text{max} = \left[ \frac{J \cdot E}{1 - v^2} \right]^{0.5} \]

As an inset in Fig. 6, a nominal “R curve” of ZT1 BMG is displayed. As indicated, stable crack growth is sustained up to about 0.4 mm before failure. Meanwhile, as the crack extends, the \( K_J \) increases, saturating at \( \sim 132 \) MPa m\(^{1/2} \). The crack-initial toughness, \( K_0 \), at \( \Delta a = 0 \), is \( \sim 40 \) MPa m\(^{1/2} \). Such “R curve” behavior indicates the high crack resistance of the new ZT1 BMG we developed. We should point out, however, that even though the ZT1 BMG exhibits somewhat nonlinear fracture behavior, its plastic displacement (for \( \Delta a \)) in the test record remains too small/short for a valid \( J_{1c} \) measurement with \( J-R \) testing as in tougher BMG composites [4].

Fig. 7a displays an SEM image of the fracture surface of a typical sample after 3 PB test, showing the pre-notched (A), fatigue pre-cracked (B) and overloaded (C) regions. Fig. 7b is a high-magnification image for the crack tip area inside the box shown in Fig. 7a. Within the fatigue pre-cracked region, “striation-like” features are observed (see Fig. 7b), as often seen in the case of fatigue-induced failure of BMGs [5,7]. In contrast, in the overloaded region, a rough zone caused by a significant crack bifurcation is observed, suggesting that the advancing crack is slowed down in this region. Furthermore, zooming in the rough zone, randomly-distributed dimple patterns associated with local viscous flow are present, which is a feature often observed in less-brittle BMGs [2,22].

The plastic zone size in plane-strain state can be estimated to be \( r_p = 1/6\pi (K_Q/\sigma_y)^2 = 0.2 \) mm, where \( K_Q \) is taken to be 102 MPa m\(^{1/2} \). This \( r_p \) value is about one third of that in the plane-stress state (\( \sim 0.6 \) mm). Fig. 7c shows the surface of a fractured sample after 3 PB loading. One observes extensive shear banding at the crack tip and significant crack bifurcation during crack propagation. The emanated shear bands ahead of the crack tip extend to about 1.2 mm, which is comparable to the estimated plastic zone size in plane-stress state. Consequently, the high fracture toughness of ZT1 BMG is associated with significant plastic deformation ahead of the crack tip and crack path deflection. Locally extended shear bands and branched cracks form an energy dissipating damage zone at the crack.

Moreover, the crack growth behavior of ZT1 BMG with a high fracture toughness can be characterized with a nominal resistance curve (R curve), showing a trend of stable crack growth under loading. Based on the ASTM standards [12,30], the effective crack lengths (\( \Delta a \)) can be approximated by measuring the compliance during loading, although they are not real physical crack lengths. With this simple way, the \( \Delta a \) value can be obtained through drawing secants to the test curve from the origin to arbitrarily selected points on the load vs. COD records. Ignoring the history of crack extension, \( J \) value is calculated using Eqs. (3) and (4). The correspondent fracture toughness \( K_J \) value is obtained by the \( J-K \) equivalence.

\[ K_J = \left[ \frac{J \cdot E}{1 - v^2} \right]^{0.5} \]
In addition, the plastic zone size of fatigue pre-cracked samples is slightly smaller than that of the notched sample with more proliferation of shear bands, as seen in Fig. 4e. The latter case is due to the less severe stress state caused by the blunted notch.

4. Discussion

4.1. Correlation between elastic properties and toughness

We visit again the correlation between elastic properties and toughness, because this correlation has been of considerable interest and under intense debate recently for BMGs [9,22,23,31]. As is well documented, fracture processes ahead of a crack tip are largely controlled by two competing factors: shear flow of the material and dilatation of the material caused by the opening of the crack. While the shear modulus, \( \mu \), captures the resistance to the former, the bulk modulus, \( \beta \), embodies the latter. Therefore, it was suggested that the \( \mu/\beta \) ratio should broadly indicate the fracture resistance of metallic glasses, with a lower ratio favoring higher toughness [22]. Such a statement is equivalent to the concept employing Poisson’s ratio, since \( \mu/\beta = (3/2)(1-2v)/(1+v) \) for isotropic materials. Moreover, based on the “cooperative shear model” [32], the shear-flow energy barrier \( W \) relates to the \( \mu \) for a metallic glass frozen at \( T_g \), expressed as \( W(T_g) \propto \mu(T_g)\nu_m(T_g) \). Meanwhile, \( T_g \) scales with \( \mu \) and is thus also a measure of \( W(T_g) \), and the requirement for the liquid viscosity at \( T_g \) \( (10^{22} \text{ Pa s}) \) gives \( W(T_g) \approx 37RT_g \) [26]. Therefore, a higher \( \mu \) implies a higher energy barrier for shear flow, i.e., a higher resistance of the glass to the relaxation of stress by undergoing shear transformations [33].

In the present work with the Zr–TM–Al glasses, as a general trend the tough BMGs do correspond to higher \( m \) or lower \( \mu \) and \( T_g \) (equivalent to a higher homologous temperature), as shown in Fig. 5a–c. Our findings further support that the \( \nu, \mu \) and \( T_g \) can be used as a guideline for alloy design of tough BMGs.

4.2. Chemistry effects on the optimization of toughness of Zr–TM–Al BMGs

To find high-toughness BMGs that are practically useful and conducive to standard property measurements comparable with other materials, the first requisite is to produce BMGs sufficiently large. As presented in previous studies [15,18,19], in the ternary Zr–TM–Al (TM = Co, Ni, or Al) systems, the GFA of alloys is strongly composition-dependent. Optimizations of the GFA have to rely on systematical work and “trial and error”. For the three systems we studied, only the compositions with the highest GFA in each system can allow the fabrication of samples with adequate dimensions for standard fracture toughness testing (usually, minimum thickness of 2 mm with \( B:W:S = 1:2:8 \) for SENB samples). The three constituent elements have to be simultaneously adjusted in composition optimization.
to arrive at the best GFA. Fig. 8 shows the ternary Zr–TM–Al (TM = Co, Ni, or Cu) BMGs with the optimal GFA, in a composition map. It is obvious that simple mutual substitution between TM elements does not lead to the best BMG formers. While the GFA optimization is necessary to land BMGs suitable for toughness tests, the resulting compositions in Fig. 8, with the contents of all three elements changed simultaneously, add difficulty to the assessment of the chemistry (composition) effect on the toughness.

However, useful insight can still be gained by comparing these BMGs that have been studied. The following directions have been found to optimize the toughness: high Zr, low Al, and substitution of Ni/Co with Cu. We now set out to explain these observations, based on our understanding of the atomic and electronic structure in Zr–TM-based BMGs.

Let us first focus on the atomic-level structure. Recent studies [23, 24] have suggested that the icosahedral order in Zr–TM-based BMGs may play a key role in the structure-property relationship. Specifically, icosahedral clusters in these alloys are found to be the structural unit with highest stability and shear resistance. Therefore, a higher population and better connection of these clusters in the BMG may lead to higher $T_g$, higher $\mu$, lower $\nu$, more severe shear softening and strain localization [23], and thus lower toughness. The degree of icosahedral order can be tuned by changing the composition, and in Zr–TM–Al alloy, it is found that higher Zr concentration corresponds to lower icosahedral fraction, while higher TM and/or Al leads to more icosahedral clusters. Particularly, the effect of Al addition is two-fold: it favors the formation of both TM-centered and Al-centered icosahedra. From the perspective of the atomic-level structure, therefore, it is expected that high Zr and/or low Al would be the direction for improved toughness.

In fact, one can monitor the changes in the elastic properties of the BMGs at different Al contents to reflect the effect of increasing Al concentration on the structure (and hence on the mechanical properties, because of the strong correlation of the latter with the elastic constants discussed earlier). To this end we use molecular dynamics (MD) simulations employing the newly developed embedded-atom-method potentials we reported [28]. In Fig. 9, the $\mu$ or $\nu$ of the MD-generated Zr$_{47-x}$Cu$_{46}$Al$_x$ ($1 \leq x \leq 9$) glasses are plotted as a function of Al content. Details of the simulation method and the procedures to calculate elastic constants can be found in Ref. [23]. We observe a monotonic increase in shear modulus (the bulk modulus changes much less) and decrease in Poisson’s ratio with increasing Al content. Again, compared with the experimental finding in Table 1, the MD simulations in Fig. 9 vary only the Al content (in substitution of Zr), and as such better accentuate the role of Al. On the experimental side, available data are for the measured $T_g$ for the Zr$_{74-x}$Cu$_{26}$Al$_x$ ($8 \leq x \leq 16$) series BMGs, as plotted in Fig. 10. The $T_g$ increases as the Al concentration increases from 625 K at
Al = 8 at.\% to 685 K at Al = 16 at.\%, at a rate of \(~7.5\) K at.\%\(^{-1}\). This trend is consistent with what is shown in Fig. 9, not only for \(T_g\) but also for the elastic modulus because \(T_g\) is correlated with the elastic constants and the toughness, see Fig. 5. All the above trends are further corroborated by Fig. 11, which shows the \(J_{\text{max}}\) measured with notched samples as a function of Al concentration in the five investigated Zr-based BMGs. The general trend is that increasing the Al content in the alloys leads to significant degradation in toughness.

In addition to the atomic-level (packing) structure, the electronic structure and chemical bonding are also important in determining the mechanical properties. The environment around Al in Zr\(_{47}\)Cu\(_{46}\)Al\(_7\) metallic glass has been revealed before using first-principles calculations, see supplementary information II in Ref. [28]. The electron charge density distribution is more polarized around Al. The bonding electrons tend to be localized in between Cu and Al as the \(sp\) orbitals of Al hybridize with the \(d\) orbitals of Cu, in contrast to the spherical charge density distribution around Cu when it is surrounded by Zr. In other words, Al brings in certain degree of covalent bonding with directionality. It is expected that the more covalent nature of the bonding due to the addition of Al would make the alloy more brittle.

The effects of Ni or Co, in comparison with Cu, can be assessed in a similar manner. Cu has a low-lying \(d\) band (3–4 eV below the Fermi level), which is almost filled, while the \(d\) band of Ni (or Co) is partially filled and much closer to the Fermi level. As a result, the \(d\) electrons of Ni/Co are expected to have stronger interaction with the \(sp\) electrons of Al (e.g., stronger hybridization) than the more localized \(d\) electrons in Cu. This is demonstrated in Fig. 12, where the site- and orbital-projected electron density of states (DOS) of Zr–Cu–Al and Zr–Ni–Al is compared, and the different position of the \(d\) band are clearly shown. Specifically, the majority of the high-lying \(d\) band of Ni is better aligned with the Al \(p\) band (compared to the low-lying Cu \(d\) band), indicating stronger interaction and orbital hybridization, and consequently higher degree of covalent bonding. Similar mechanism of the covalent-like bonding is also expected between TM and Be, but should not work between TM and heavier metals like Zr. This is because the valence electrons are less screened in Al and Be, such that Al and Be atoms (in their elemental crystals, fcc Al and hcp Be) retain certain degree of anisotropy and directionality. For heavy metals with a large number of core electrons, however, the screening effect renders the \(sp\) valence electrons more free-electron-like and more isotropic, and the bonding is therefore almost non-directional. The covalent-like character associated with Al and Be appears to be particularly salient when their \(sp\) orbitals hybridize with the narrow and intense \(d\) band of TM (where electron interaction is strong). To summarize, from the perspective of chemical effects, a low Al and Ni/Co-free environment would suppress the \(sp–d\) electron interaction between TM and Al, reduce the covalent-like character of the bonding, and thus elevate the toughness. This rationalizes the trend observed in Fig. 11.

As an alternative approach, one can evaluate the chemical affinity between the constituent elements using the chemical mixing enthalpy of alloys, \(\Delta H_{\text{chem}}\). As suggested in Ref. [34], the \(\Delta H_{\text{chem}}\) of a given ternary alloy in liquid state can be estimated with the following equation:

\[
\Delta H_{\text{chem}} = \sum_{i=1}^{3} 4\Delta H_{\text{mix}}^{i\text{AB}} c_i c_j
\]

where \(\Delta H_{\text{mix}}^{i\text{AB}}\) is the mixing enthalpy between alloying elements, for which estimates can be obtained using Miedema’s macroscopic model for binary liquid alloys. \(c_i\) is the...
composition of the 8th component. The $\Delta H_{\text{chem}}^i$ value for $Zr_{60}Ni_{21}Al_{19}$, $Zr_{56}Co_{28}Al_{16}$, $Zr_{60}Cu_{28}A1_{12}$ and $Zr_{48}Cu_{45}A1_{7}$ BMGs was calculated to be $-48$, $-45$, $-28$, and $-26 \text{kJ mol}^{-1}$, respectively. Apparently, the order here scales with the Al content discussed above, and the Ni/Co-bearing alloys have more negative values. The use of this $\Delta H_{\text{chem}}^i$ indicator is therefore consistent with the electronic structure analysis present above. As seen in Fig. 13 for the relationship between $J_{\text{max}}$ and $\Delta H_{\text{chem}}^i$, the more negative the $\Delta H_{\text{chem}}^i$, the lower the toughness.

Of course, the change in the bonding nature also affects the packing of atoms. For example, Zr–Cu–Al and Zr–Ni–Al (at the same composition) may not have the same structure, as suggested by the pair distribution functions (PDFs) measured by Antonowicz et al. [35]. In any case, the difference in toughness of the Zr–TM-based BMGs has its origin in both the atomic-level structure and electronic interactions.

In fact, previous investigations [9] have also indicated that Ni has adverse effects on the ductility and toughness of BMGs. Here we re-examine this postulation in the context of chemical effect discussed above, using a set of available data of fatigue pre-cracked fracture toughness for Zr-based BMGs. The previously tested BMGs include Vitreloy 1, Var1, Var2, $Zr_{52.5}Ti_{17.9}Ni_{14.6}Al_{10}$ (Vitreloy 105) and $Zr_{55}Cu_{30}Ni_{5}Al_{10}$ (Z2). In the previous studies, only linear-elastic fracture happened for fracture toughness testing of these BMGs. Therefore, for the purpose of comparison, we converted their $K_{Q}$ values into $K_{\text{max}}$ assuming $K_{\text{max}} = 1.10K_{Q}$, as the upper-bound value to avoid underestimation. In addition, available data of the $T_g$, $p$, elastic modulus, yield strength $\sigma_y$ are collected from literatures [36–40]. The elastic constants and density for Vitreloy 105 and Z2 were re-measured in this work. These data are summarized in Table 2. The error bars are given based on the data statistics reported in the literature. Our new ZT1 BMG exhibits the lowest fracture strength but the highest toughness among all these Zr-based BMGs, either Be- or Al-bearing.

Plots are made for these Zr-based BMGs in Fig. 14, in the form of toughness $K_{\text{max}}$ as a function of elastic constants. Fig. 14a plots the $K_{\text{max}}$ vs. $v$. For the three Be-bearing BMGs, the toughness of the Ni-free Var1 and Var2 is appreciably higher than that of the Ni-containing Vitreloy 1, even though they have a comparable $v$ value ($\sim 0.355$). Presumably, the $sp$–$d$ electron interaction that affects toughness in these (Al-free) cases happens between TM (Cu or Ni) and Be. Similarly, in the case of Al-bearing BMGs without Be, the current Ni-free ZT1 has a toughness obviously higher than the Ni-containing Vit105 and Z2, while all having $v \sim 0.369$. This plot confirms the general trend that the Ni-free BMGs are tougher than Ni-containing ones with similar $v$. Meanwhile, when comparing BMGs within the same group, i.e., those containing Ni (or those without Ni), it is seen that the toughness increases with increasing $v$ value (see the two dashed lines in Fig. 14a). In Fig. 14b, the $K_{\text{max}}$ vs. $\mu V_m$ for these Zr-based BMGs is plotted. Similar to the correlation with $v$, the increase in toughness correlates with a reduction of $\mu V_m$. Such a correlation is present again only when the comparison is made separately for the BMGs with and without Ni, with the Ni-free ones constituting the higher toughness group.

These additional examples reaffirm that, in addition to increasing the Zr content and limiting the Al content, Ni appears to be detrimental to toughness and should be substituted with Cu. A general guideline can then be drawn from these discussions to locate tough BMGs, as will be presented in Section 5.

Table 2
Glass transition temperature, mass density, elastic properties, yield strength and fracture toughness measured with fatigue pre-cracked samples for the Zr-based BMGs.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (at.%)</th>
<th>$T_g$ (K)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$E$ (GPa)</th>
<th>$\mu$ (GPa)</th>
<th>$\beta$ (GPa)</th>
<th>$\nu$</th>
<th>$\sigma_y$ (GPa)</th>
<th>$K_{\text{max}}$ (MPa$\sqrt{\text{m}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitreloy 1</td>
<td>$Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$</td>
<td>623</td>
<td>6.06</td>
<td>95.8</td>
<td>35.3</td>
<td>110.2</td>
<td>0.356</td>
<td>1.36</td>
<td>65 ± 26</td>
</tr>
<tr>
<td>Var1</td>
<td>$Zr_{52.5}Ti_{17.9}Ni_{14.6}Al_{10}$</td>
<td>606</td>
<td>5.58</td>
<td>99.6</td>
<td>36.8</td>
<td>113</td>
<td>0.353</td>
<td>1.75</td>
<td>91 ± 15</td>
</tr>
<tr>
<td>Var2</td>
<td>$Zr_{60}Cu_{28}Al_{12}$</td>
<td>613</td>
<td>6.03</td>
<td>95.8</td>
<td>35.3</td>
<td>112.2</td>
<td>0.356</td>
<td>1.8</td>
<td>93 ± 13</td>
</tr>
<tr>
<td>Z2</td>
<td>$Zr_{55}Cu_{30}Ni_{5}Al_{10}$</td>
<td>669</td>
<td>6.6</td>
<td>87.2</td>
<td>31.8</td>
<td>111.4</td>
<td>0.370</td>
<td>1.77</td>
<td>54 ± 21</td>
</tr>
<tr>
<td>Vitreloy 105</td>
<td>$Zr_{55}Cu_{30}Ni_{14.6}Al_{10}$</td>
<td>658</td>
<td>6.8</td>
<td>86.8</td>
<td>31.7</td>
<td>109.9</td>
<td>0.369</td>
<td>1.82</td>
<td>58 ± 12</td>
</tr>
<tr>
<td>ZT1</td>
<td>$Zr_{60}Cu_{28}Al_{12}$</td>
<td>652</td>
<td>6.5</td>
<td>82.8</td>
<td>30.2</td>
<td>104.1</td>
<td>0.367</td>
<td>1.60</td>
<td>112 ± 6</td>
</tr>
</tbody>
</table>

\[ a \] Data from Refs. [5–9,36–39].
\[ b \] Data from Ref. [9].
\[ c \] Data for $T_g$, $\sigma_y$, and $K_{Q}$ from Ref. [11].
\[ d \] Data for $T_g$, $\sigma_y$, and $K_{Q}$ from Refs. [10,40].
It is worth noting that for biomedical implant applications [41,42], such as orthopedic devices and hard tissue prostheses, Ni is also a bad element that should be left out as it causes allergic reaction to the human body and toxic effects to tissues. Several groups are developing Ni-free Zr-based BMGs [43,44]. In comparison with previous Ni-free Zr-based BMGs, our Zr$_{61}$Ti$_2$Cu$_{25}$Al$_{12}$ (ZT1) BMG has a significant advantage, not only in higher GFA but also in higher fracture toughness.

4.3. Elastic–plastic fracture behavior of Zr(Ti)–Cu–Al BMGs

As shown in Section 3.4, even in the case of fatigue pre-cracked samples, our ZT1 BMG manifests a visible nonlinear–elastic fracture (R curve) behavior, as seen in Fig. 6. This behavior, indicating high toughness, is rarely observed at room temperature in monolithic BMGs, except at a high temperature near $T_g$ [27]. In a recent study [4] on monolithic Vitreloy 1 BMG and metallic glass–matrix composites, the R curve testing was performed. Comparison of fracture behavior between ZT1 and Vitreloy 1 indicates that, when the stress intensity increases to 54 MPa$\sqrt{m}$, Vitreloy 1 exhibits immediate unstable fracture behavior, whereas in the case of ZT1, the stable crack extension proceeds without immediate failure, when a similar intensity of about 50 MPa$\sqrt{m}$ is reached. Even though in comparison with the metallic glass composites such as DH1 ($J_{\text{RE}} = 96$ kJ m$^{-2}$, $K_{\text{RE}} = 91$ MPa$\sqrt{m}$) and DH3 ($J_{\text{RE}} = 282$ kJ m$^{-2}$, $K_{\text{RE}} = 157$ MPa$\sqrt{m}$) [4], such stable crack extension of ZT1 BMG is not as sustainable, our ZT1 appears to be the toughest among monolithic BMGs. Also, we noted that the length of $\Delta a$ is actually in the range of 0.4 mm, which remains well within the size of the plastic zone of ZT1. This implies that local plastic deformation in the area of plastic zone is mainly responsible for the stable crack extension.

As is well known, the $K_{\text{IC}}$ properly defines the toughness of nominally brittle materials such as most monolithic BMGs, based on linear-elastic fracture mechanics (LEFM), which do not account for the energy associated with plastic deformation. However, our findings indicate that the $K$ measurements are not always sufficient for toughness characterization of BMGs, especially for the tough ones with a sizable plastic zone (such as near 1 mm). In many cases, thicker BMG materials (typically $>5$ mm) are not achievable owing to the limitation of the GFA. Appropriate section sizes for the $K_{\text{IC}}$ tests are thus not available. Therefore, $J$-based toughness values and $R$ curves are more appropriate to characterize the fracture toughness. To meet the requirement of plane-strain condition, the section size of the test samples required for $J$ measurements is much less than that required to determine a valid $K_{\text{IC}}$ [45]. In the current case, it is certain that $J_0$ should be less than $J_{\text{max}}$ of ZT1 (148 ± 22 kJ m$^{-2}$). Therefore, we can take $J_0 = 148 \pm 22$ kJ m$^{-2}$ to conservatively estimate the sample thickness $B$ required to satisfy the size-independent condition for a valid $J_{\text{IC}}$. According to $B \geq 10 J_0/\sigma_y$, the $B$ is required to be larger than 0.9 mm. Such a relatively small thickness makes $J$ determination feasible for more BMGs with modest GFA, if they are indeed tough that the $J$–$R$ test can be operative.

5. Concluding remarks

The main outcomes of this study are two-fold. First, in terms of alloy development, we have discovered a Ni-free Zr$_{61}$Ti$_2$Cu$_{25}$Al$_{12}$ (ZT1) BMG that possesses simultaneously high GFA and high toughness. The ZT1 shows a detectable nonlinear–elastic fracture (resistance curve) behavior and a fatigue pre-cracked fracture toughness ($K_{\text{IC}}$) in excess of 100 MPa$\sqrt{m}$, which is the highest for all the monolithic Zr-based BMGs reported to date. We observed that the toughness for the Zr–TM–Al BMGs scales with the population of shear bands formed in front of the notch tip. Therefore, the high fracture toughness and elastic–plastic fracture behavior observed in our tough BMGs are believed to result from the extensive plastic deformation mediated by proliferation of multiple shear bands, which
lead to extensive plastic shielding, and the resultant deflection of crack paths. The toughness of these BMGs shows a general correlation with the Poisson’s ratio ($\nu$), the product of shear modulus and molar volume ($\mu V_m$), and homologues temperature ($T_R/T_g$). These indicators can be used to guide the search for high-toughness BMGs.

Second, in terms of physical insight, we have uncovered significant chemistry effects on the fracture toughness of Zr-based BMGs, by investigating selected ternary Zr–TM–Al (TM = Co, Ni, Cu) BMGs that have optimal GFA in their respective systems. The insight is useful for understanding the BMG properties and can guide future alloy development. We will therefore summarize the chemical effects again in the following when the general strategy is proposed.

Based on the success achieved and the insight gained in the investigations of the two aspects above, a strategy can be outlined as follows to locate the BMG compositions with high fracture toughness.

(i) In each system (such as Zr–Cu–Al), only limited compositions can provide the required GFA to yield sufficiently large samples for near-standard $\mathcal{K}_0$-based (linear-elastic) fracture toughness testing that can be compared with existing engineering materials. The first step is therefore to search for high GFA compositions.

(ii) From the perspective of atomic-level structure, higher toughness is expected at relatively high Zr contents and low Al contents, as this is the regime where the internal structure contains lower fraction of the rigid icosahedral clusters. Also, from the perspective of chemical interactions: (a) the introduction of Al results in hybridization of the Al-$sp$ orbitals and the Cu-$d$ orbitals, giving rise to covalent-like features in the bonding and (b) the substitution of Cu with Ni/Co elevates the TM-$d$ band to interact more strongly with the $sp$ valence electrons of Al, and enhances the degree of covalency. Both lead to decreased toughness. Therefore, in the search for high toughness BMG, the second step is to find a system in which the highest GFA occurs at a relatively high Zr and low Al concentrations. Zr–Cu–Al is such a case, compared with Zr–Ni–Al and Zr–Co–Al systems: for Zr–Cu–Al there are best GFA alloys at 7% and 12% Al, much lower than the 16% and 19% Al required for the other Zr–TM–Al systems. Meanwhile, one prefers to stay away from TM elements with high-lying partially-filled $d$ band and stronger orbital hybridization with Al (or Be), which would be detrimental to toughness. Higher toughness is thus expected when Ni (Co) is replaced. In this regard the Ni(Co)-free Zr–Cu–Al emerges again as the winner, as it satisfies this requirement as well. It is the simultaneous presence of a relatively high Zr content, relatively low Al concentration and Ni(Co)-free environment that imparts to Zr–Cu–Al BMGs a toughness superior to the other systems.

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