Fatigue endurance limit and crack growth behavior of a high-toughness Zr$_{61}$Ti$_2$Cu$_{25}$Al$_{12}$ bulk metallic glass

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Abstract

We report the fatigue damage behavior of a Zr$_{61}$Ti$_2$Cu$_{25}$Al$_{12}$ (ZT1) bulk metallic glass (BMG), which was known to have a record-high fracture toughness. The ZT1 exhibits the highest fatigue endurance limit among all BMGs, with a normalized fatigue limit of $\sigma_f \approx$ 440 MPa (in four-point bending at a loading ratio of 0.1), or $\sim$0.27 of its tensile strength. The crack-growth resistance in the stress/life tests arises from crack-tip plastic shielding due to prolific shear-banding, as well as deflected crack path following a “zig-zag” pattern. The relation between the range of stress intensity factor ($\Delta K$) and the crack-growth rate ($\Delta a/\Delta N$) was also determined. ZT1 shows a fatigue threshold, $\Delta K_{th}$, of 2.8 MPa$\sqrt{m}$, which appears to be related to the onset of shear band nucleation. Three distinct regimes of fatigue crack growth were observed, with different slopes in the $\Delta a/\Delta N$–$\Delta K$ curve, attributable to different mechanisms. In the Paris regime, each fatigue striation on fracture surface is generated by a number of loading cycles, rather than by a single loading cycle. In general, the $\Delta K_{th}$ of a BMG approximately scales with its fracture toughness. At different levels of $\Delta K$, shear bands appear to play different roles, either facilitating or blunting the crack growth.

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1. Introduction

Bulk metallic glasses (BMGs) exhibit a high yield strength (e.g., $\sim$2 GPa) and large elastic strain limit ($\sim$2%), and are interesting materials potentially useful for structural applications [1–3]. However, most of the available BMGs have been found to be susceptible to cyclic fatigue damage. As for conventional alloys, the stress–life (S/N) approach (Wöhler plots) was used to assess the fatigue endurance limit of BMGs. Against the expectation from their high strength, the reported fatigue endurance limits of BMGs are often disappointingly low [4–11], usually below $\sim$0.2$\sigma_t$ (where $\sigma_t$ is the tensile strength). This has been attributed to the lack of a microstructure that provides local arrest points for newly initiated or pre-existing cracks [4–6,12]. In the meantime, the fatigue limit data are also highly scattered. The reasons responsible for this inconsistency are rather complicated, including the effects of loading modes, sample thermal history, mechanical history, environment, specimen geometries and as-cast defects.

The S/N approach alone is insufficient to reveal the mechanisms responsible for fatigue failure, since the measured fatigue lifetime simultaneously involves a sequence of interdependent processes, from crack nucleation to crack growth to final failure. To examine the fatigue crack growth behavior of the BMGs from near their fatigue threshold and up, crack growth experiments based on fracture mechanics have also been performed, mostly on Zr-based BMGs such as Vitreloy 1 [7,13–18], due to their robust glass-forming ability (GFA) to allow the preparation of sufficiently large samples. It has been reported that the fatigue threshold, $\Delta K_{th}$, is in the range of 1–2 MPa$\sqrt{m}$ (load ratio R = 0.1). The Paris law exponent $m$ falls in the range of 2–3, which is insensitive to BMG composition and comparable to conventional metallic materials ($m$ = 2–4) [19]. The relatively low $\Delta K_{th}$ reflects the fact that once damage has initiated, its growth is difficult to suppress and failure will occur after only a limited number of cycles [5,14]. As such, any respectable endurance limit was most likely related to an increased number of fatigue cycles needed to initiate damage [20].

From the structure perspective, it is generally rationalized that the fatigue crack initiation is associated with the accumulation of “free volume” in the MG and the excessive strains under cyclic loading [21,22]. The mechanically induced free volume, in the fatigue transformation zone [7,22], appears to control the rate of fatigue crack growth. Interestingly, the free volume could exert opposite effects on fracture toughness and on fatigue resistance: the annihilation of free volume by thermal ageing was found to enhance the fatigue resistance, but ruin the toughness [7,23]. In
addition, Tong et al. [24] showed that upon cyclic loading even in the elastic range, the atomic structures of BMGs undergo irreversible changes. When comparing two Zr–Cu–Al BMGs, it was found that the Zr61Cu39Al12 with a higher fracture toughness (110 MPa√m) was more susceptible to fatigue damage than the Zr-less Zr50Cu40Al10 with a lower fracture toughness (51 MPa√m). As such, the correlation between fatigue resistance with toughness remains unsettled for BMGs.

Recently, BMGs characterized by a high crack-growth toughness (crack-resistance curve) have been discovered, firstly a noble Pd-based Pd79Ag3.5Pb55Sn3Ge2 [25], and later a Zr-based Zr61Ti2Cu32Al12 (at.%), denoted as ZT1 [26,27,29,30]. It is encouraging that the Pd79Ag3.5Pb55Sn3Ge2 BMGs manifests a higher-than-normal fatigue resistance, as indicated by the fatigue endurance strength of σf = 360 MPa, or 0.24σU (in four-point bending at R = 0.1), and the ΔKth is at 3.3 MPa√m [28]. A distinct feature for this BMG is that the fatigue crack propagates in a highly “zigzag” manner, creating a rough “stair-like” profile. It is therefore of interest to find out if such a mode is universally functional in other high-toughness BMGs. Furthermore, the fatigue crack growth behavior of such crack-resistant BMGs under fatigue loading has not been well understood yet.

In this work, we systematically investigate the fatigue damage behavior of the Zr61Ti2Cu32Al12 (ZT1) BMG. First, fatigue fracture is characterized following the S/N approach to reveal macroscopic failure mechanism. Second, fatigue crack growth behavior based on fracture mechanics is examined, around the fatigue threshold. The micromechanism of fatigue crack growth is analyzed based on fractography features. The role played by shear banding in both of the two scenarios above is discussed. Finally, combined with data in the literature, the fatigue resistance is correlated with the fracture toughness of the BMGs.

2. Experimental

The robust GFA of Zr61Ti2Cu32Al12 made it feasible to fabricate the relatively large BMG plates needed for toughness and fatigue tests. The sample fabrication method of the as-cast BMG plates has been described elsewhere [26,29]. The material properties of the ZT1 BMG are summarized in Table 1.

To determine the fatigue endurance limit, 3 × 3 × 25 mm3 rectangular beams taken from the BMG plate (3.2 mm × 9 mm × 60 mm) were used. To minimize the residual-stress effect, a surface layer of at least 100 μm in thickness in the as-cast plates was removed via grinding. Four-point bending testings were performed over a range of cyclic stresses, with an inner span, S1, of 10 mm, and an outer span, S2, of 20 mm. Corners of the specimens were slightly rounded to reduce stress concentration along the beam edges. All the surfaces were polished to a 1 μm finish with diamond paste. Cyclic loading tests were conducted under a constant load ratio (the ratio of minimum to maximum loads) of R = 0.1, at a frequency of 20 Hz (sine wave) on a computer-controlled MTS 858 mechanical testing machine. The stress at the tensile surface within the inner span was calculated as

\[ \sigma = \frac{3P(S_2 - S_1)}{2bh^2} \]

where \( P \) is the applied load, \( h \) is the specimen thickness, and \( b \) is the specimen length. To ensure the data reproducibility, at least three specimens were tested at each stress range. The tests were terminated in the cases when failure did not take place after 107 loading cycles.

Tests of fatigue crack growth rate were conducted using three-point bending with a span of 32 mm. In this case the rectangular samples were taken from as-cast BMG plates with a dimension of 4.2 × 11.5 × 60 mm3. Surface layer of ∼100 μm in thickness was removed from each surface to eliminate the residual stress, and the final sample dimensions were B (thickness) = 4 mm, W (width) = 8 mm, L (length) = 40 mm, fabricated via electro-discharge machining and grinding. The single-edge notched bend (SENB) specimens were made using a diamond wire saw, with a straight-through notch (the notch radius was 150 μm and the notch length was 1.5 mm). A pair of knife-edges were machined via electro-discharge machining for supporting the arms of the clip gage.

In general accordance with ASTM-E647 [31], fatigue crack growth is characterized by the stress–intensity factor, \( K \). The tests were performed under a constant load ratio of \( R = K_{min}/K_{max} = 0.1 \) and a frequency of \( f = 20 \) Hz (sine wave) on an Instron E3000 testing machine. In all cases, the pre-cracking procedure was carried out with decreasing ΔK (\( ΔK = K_{max} - K_{min} \)) step by step, until the pre-crack growth rate was about \( 10^{-8} \) m/cycle. Three pre-cracked specimens were fatigued in the K-decreasing procedure for the cases where \( da/dN < 10^{-8} \) m/cycle, where \( a \) is the crack length and \( N \) is the number of fatigue cycle. The crack growth rates and the fatigue threshold \( K_{th} \) were determined. The \( K_{th} \), defined as the applied \( ΔK \) for \( da/dN \) values approaching \( 10^{-10} \) m/cycle, was obtained via stepped reductions of \( ΔK \), which was kept constant at each step. The reduction at each step was smaller than 10% of the previous \( K_{max} \). Two additional pre-cracked specimens were tested under constant-force-amplitude loading to determine faster fatigue crack growth rates when \( da/dN > 10^{-8} \) m/cycle. A clip gauge was affixed to the knife-edges of each sample for monitoring the crack length extension in the specimen.

The morphology of side/fracture surfaces for the fractured samples was examined using Quanta 600 and Supra 55 scanning electron microscope (SEM). A LEXTOLS4000 laser microscope (LOM) was also used to characterize the fracture surface.

3. Results

3.1. Stress–life fatigue behavior

The number of cycles to failure, \( N_t \), measured as a function of cyclic stress amplitude, \( \sigma_f = (\sigma_{max} - \sigma_{min})/2 \), for the ZT1 BMG is plotted in Fig. 1. For all these data, the specimens failed within the inner span of the beam in the four-point bending tests. The endurance limit, defined as the maximum stress amplitude to which the material is subjected for 107 cycles without failure, was determined to be 441 MPa. With the tensile strength of ZT1 at \( \sigma_f = 1600 \) MPa [29], the endurance limit of the ZT1 reaches 27% of its ultimate tensile strength.

As a representative, Fig. 2(a)–(d) shows the fractography observed in SEM for a specimen failed at \( \sigma_f = 652 \) MPa and \( N_t = 5192 \) cycles. The fractured surface shows three distinct areas: zone I as the crack initiation, zone II with the stable crack propagation, and zone III of the final unstable fracture, as shown in

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Selected mechanical properties of fully amorphous Zr61Ti2Cu32Al12 (at.% ) bulk metallic glass (ZT1) [26,27,29,30].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material property</td>
<td>Value</td>
</tr>
<tr>
<td>Glass transition temperature, ( T_g )</td>
<td>652 K</td>
</tr>
<tr>
<td>Ultimate tensile strength, ( \sigma_U )</td>
<td>1600 MPa</td>
</tr>
<tr>
<td>Compressive yield strength, ( \sigma_Y )</td>
<td>1688 MPa</td>
</tr>
<tr>
<td>Vickers hardness, ( H_v )</td>
<td>4.9 GPa</td>
</tr>
<tr>
<td>Young’s modulus, ( E )</td>
<td>82.8 GPa</td>
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<tr>
<td>Shear modulus, ( G )</td>
<td>30.2 GPa</td>
</tr>
<tr>
<td>Bulk modulus, ( B )</td>
<td>104 GPa</td>
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<tr>
<td>Poisson’s ratio, ( \nu )</td>
<td>0.367</td>
</tr>
<tr>
<td>Fracture toughness, ( K_{FC} )</td>
<td>130 MPa√m</td>
</tr>
</tbody>
</table>

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Fig. 2(a). The fatigue crack initiated from the tensile-stressed-side surface of the beam, as shown in Fig. 2(b). No as-cast defects, such as pores and inclusions, were visible at the crack initiation site. The early crack propagation traced a semielliptical region in radial fashion. As shown in Fig. 2(c), typical uniform fatigue striations, perpendicular to the crack growth direction, are obvious on the fracture surface, indicative of stable crack growth. As the crack propagated, the specimen ligament was reduced to below a critical size, and catastrophic fracture occurred. In this latter stage, the typical vein-like patterns appear on the fracture surface, as shown in Fig. 2(d).

To catch the crack initiation event, a specimen was tested under the load of 495 MPa stress amplitude, and the testing was interrupted at regular intervals of 1000 cycles. The tensile-stress surface of the specimen was periodically examined under SEM and LOM. Fig. 3 shows a LOM image of the specimen after 17,000 cycles. A crack with a length of 200 \( \mu m \) was detected. The crack is at an angle about 84° inclined to the stress direction, rather than completely perpendicular. Finally, this specimen failed at 20,761 cycles. Here the period of crack initiation takes up almost 80% of the whole lifetime. In other words, the fatigue lifetime of the material is dominated by the phase of macroscopic crack initiation.

To reveal the crack growth history, Fig. 4(b)–(d) shows the SEM images of the specimen side surface in the vicinity of the main crack. The crack path during stable crack growth is globally perpendicular to the applied loading, as shown in Fig. 4(b). On a more microscopic scale, nevertheless, it exhibits a distinct zigzag feature, as shown in Fig. 4(c). Along the crack wake, profuse shear-banding offsets are generated in the neighboring region, constituting a plastic zone spanning to 170 \( \mu m \) ahead of the crack tip. Furthermore, each short crack segment is deflected at an angle of \( \approx 41° \) from the plane of the main crack, as shown in Fig. 4(d).
3.2. Fatigue crack growth rate

3.2.1. Relationship between \( \frac{da}{dN} \) and \( \Delta K \)

Fig. 5 displays a log–log plot of fatigue crack-growth rate, \( \frac{da}{dN} \), versus a range of \( \Delta K \) applied to the ZT1 BMG. A typical sigmoidal curve containing three distinct regions is observed.

3.2.1.1. Region I: Near-threshold regime (\( \Delta K < 4 \text{ MPa}\sqrt{\text{m}} \)). In this regime, the slope of the curve rapidly increases with decreasing \( \Delta K \), accompanied by a crack growth rate of \(<10^{-9} \text{ m/cycle} \). The value of \( \Delta K_{th} \) is determined to be \( 2.8 \pm 0.2 \text{ MPa}\sqrt{\text{m}} \), which is comparable to aluminum alloys [32]. Note that the ZT1 BMG shows higher \( \Delta K_{th} \) value than Vitreloy 105 (\( \Delta K_{th} = 2 \text{ MPa}\sqrt{\text{m}} \)) [16], but it is \( \sim 15\% \) lower than that of Pd_{79}Ag_{3.5}P_{0.5}Si_{9.5}Ge_{2} BMG (\( \Delta K_{th} = 3.3 \text{ MPa}\sqrt{\text{m}} \)) [28].

3.2.1.2. Region II: The Paris regime (\( 4 \text{ MPa}\sqrt{\text{m}} < \Delta K < 17 \text{ MPa}\sqrt{\text{m}} \)). This regime is characterized by a linear relationship in log (\( \frac{da}{dN} \)) versus log \( \Delta K \), with an intermediate crack growth rate from \( \sim 10^{-9} \text{ m/cycle} \) to \( 3 \times 10^{-8} \text{ m/cycle} \). The steady-state crack growth can be characterized by the Paris law [33],

\[
\frac{da}{dN} = C \cdot \Delta K^m
\]

where \( m \) is the crack-growth exponent and \( C \) is a scaling constant, which were determined from Fig. 5 to be \( 2.3 \pm 0.11 \) and \( (5.8 \pm 1.1) \times 10^{-11} \text{ m} \cdot \text{MPa}^{-0.15} \text{ cycle}^{-1} \), respectively. As usual, an exponent of 2 can be rationalized using a geometric model based on crack-tip blunting and hence cyclic crack tip opening displacement [19]. Additionally, it is noteworthy that the steady-state crack growth can be sustained to a rather high \( \Delta K \) of \( \sim 17 \text{ MPa}\sqrt{\text{m}} \).

3.2.1.3. Region III: High growth rate regime (\( \Delta K > 17 \text{ MPa}\sqrt{\text{m}} \)). In this regime, the crack growth rate reaches above \( 3 \times 10^{-8} \text{ m/cycle} \), and the slope of the curve is estimated to be 3.8, which is obviously higher than that in the Paris regime. But the crack propagation remains relatively stable. It is contrary to previously-investigated Zr-based BMGs, for which the crack growth rate increased drastically at high \( \Delta K \) [5,7]. It suggests that the ZT1 possesses an appreciable crack growth resistance even under rather severe fatigue loading conditions.
In this low and values, linear elastic fracture mechanics (1) are given by

\[ K = \frac{\sqrt{2\pi} \sigma_y}{C_0} \]

where \( K \) is the Mode I stress intensity factor for the crack. The local stress intensity factors at the tip of the crack, no shear banding took place. The fracture surface is featureless in low-magnification SEM images, as shown in Fig. 6(b). At high magnifications, elongated ridges with a width of about 400 nm are visible, and they extend along the crack growth direction, as shown in Fig. 6(c). Furthermore, fatigue striations perpendicular to the crack growth direction are present, as shown in Fig. 6(d). The striation spacing is \( \sim 20 \) nm, which is nearly one order of magnitude larger than the crack advancement distance per cycle (see Fig. 5). As the applied \( K \) decreases down to \( K_{th} \), the elongated ridges and fatigue striations disappeared gradually, and the fracture surface appeared mirror-like at \( K_{th} \).

The elongated ridges on fracture surface were quantitatively characterized using the LOM, as displayed in Fig. 7(a) and (b). Fig. 7(c) shows a plot of the wave length (\( \lambda \)) and the height of the ridges against the maximum stress intensity factor, \( K_{max} \). Both increase with rising \( K_{max} \) and the magnitude is in a range of 400–650 nm and 25–110 nm, respectively.

### 3.2.2. Fractography and crack trajectory observation

#### 3.2.2.1. Region I: Near-threshold regime (\( \Delta K < 4 \) MPa\( \sqrt{m} \)).

In this low \( \Delta K \) regime, the crack trajectory on specimen-side surface is very straight, as shown in Fig. 6(a). In the vicinity of the advancing crack, no shear banding took place. The fracture surface is featureless in low-magnification SEM images, as shown in Fig. 6(b). At high magnifications, elongated ridges with a width of about 400 nm are visible, and they extend along the crack growth direction, as shown in Fig. 6(c). Furthermore, fatigue striations perpendicular to the crack growth direction are present, as shown in Fig. 6(d). The striation spacing is \( \sim 20 \) nm, which is nearly one order of magnitude larger than the crack advancement distance per cycle (see Fig. 5). As the applied \( \Delta K \) decreases down to \( K_{th} \), the elongated ridges and fatigue striations disappeared gradually, and the fracture surface appeared mirror-like at \( K_{th} \).

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#### 3.2.2.2. Region II: The Paris regime (4 MPa\( \sqrt{m} < \Delta K < 17 \) MPa\( \sqrt{m} \)).

In this steady-state growth regime with relatively low and well-controlled \( \Delta K \), very few shear bands appear ahead of the crack tip during crack propagation, as shown in Fig. 8(a). Regular striations were found to accompany the crack growth, as shown in Fig. 8(b). The average spacing of the striations is at the level of 70–200 nm, which is nearly one order of magnitude larger than the crack growth distance per cycle (in the range of \( 2 \times 10^{-5} \sim 3 \times 10^{-8} \) m/cycle, see Fig. 5). It indicates that dozens of loading cycles were required for the crack front to march forward by one striation spacing.

#### 3.2.2.3. Region III: High-growth rate region (\( \Delta K > 17 \) MPa\( \sqrt{m} \)).

Fig. 8(c) displays a SEM image taken from an area around the crack tip on the specimen side surface. In this regime, the crack propagates in a wavy (zigzag) pattern, and the formation of many shear bands (see their offsets on the surface) becomes prominent. The plastic zone in this \( \Delta K \) range is several tens of micrometers in size. The apparent acceleration in \( da/dN \) in Fig. 5 is then partly because at the high \( K_{max} \) values, linear elastic fracture mechanics is no longer valid [34], and fatigue-sensitive shear bands become the pathway for crack growth. The crack-growth characteristics become similar to the case of the uncracked beam under four-point bending, as shown in Fig. 4 in Section 3.1.

Fig. 8(d) reveals that very fine striations and coarser striations coexist, at the level of \( \sim 0.25 \) \( \mu \)m and \( \sim 1 \) \( \mu \)m, respectively. For comparison, the fine striation spacing as a function of \( \Delta K \) is also included in Fig. 5. The fine-striation spacing matches that expected from the \( da/dN \), whereas the coarse-striation spacing is much larger than the corresponding \( da/dN \). This suggests that the fine striation is the result of a single step of crack advancement, i.e., the forward distance in a single loading cycle. On the other hand, the coarse striations are generated by the periodic action of the main crack, i.e., the zigzag turns made during its propagation.

### 4. Discussion

#### 4.1. Sources responsible for fatigue crack growth resistance

As shown in Fig. 4(b), under fatigue loading, the initiated macroscopic crack can maintain a steady propagation before catastrophic failure. As is well understood [19,35], such subcritical extension of a crack is controlled by the competition between two major events, the intrinsic damage mechanisms ahead of the crack tip that promote cracking, and the extrinsic shielding mechanisms, mainly behind the tip, that impede cracking. In the current ZT1 case, the intrinsic toughening is mainly contributed by the crack-tip plastic shielding, which is associated with the numerous shear bands and their interactions, as shown in Figs. 4(c) and 8(c). Shear banding plays a key role for crack-tip blunting and release of local high stresses.

Another toughening mechanism arises from the crack deflection seen in Fig. 4(d). As the segment size \( \sim 0.20 \) \( \mu \)m of the zigzag crack is much smaller than the length of the macroscopic main crack \( \sim 1.9 \) \( \mu \)m, one can treat each segment as a small crack deviating at an angle \( \alpha \) from the plane of the main Mode I cracking. As such, the local Mode I and Mode II stress intensity factors at the tip can be expressed as [36]:

\[
K_1 (x) = C_{11} K_1 \\
K_II (x) = C_{22} K_1
\]

where \( K_1 \) and \( K_II \) are the local stress intensity factors at the tip of the small crack (segment), \( K_1 \) is the Mode I stress intensity factor for the main crack, and the coefficients \( C_{11} \) and \( C_{22} \) are given by

\[
C_{11} = \frac{3}{4} \cos\left(\frac{3\alpha}{2}\right) + \frac{1}{4} \cos\left(\frac{3\alpha}{2}\right)
\]

\[
C_{22} = \frac{1}{4} \left[\sin\left(\frac{3\alpha}{2}\right) + \sin\left(\frac{3\alpha}{2}\right)\right]
\]

The energy release rate for the zigzag crack is given by

\[
G(x) = \frac{K_1^2(x) + K_II^2(x)}{E}
\]

where \( E \) is equal to \( E \) (in plane stress) or \( E/(1 - \nu^2) \) (in plane strain). As observed in Fig. 4(d), \( \alpha \) is about 41°, such that the effective energy release rate \( G_{eff} \) can be calculated using Eqs. (3)–(7) to be \( \sim 77% \) of the nominal energy release rate. This proves that local crack deflection has a significant effect on reducing the crack driving force.

As seen in Fig. 4(c) and (d), the crack deflection leaves staircase-like crack behind the crack tip, which brings about more contacts of mating crack surface under cyclic loading. Such roughness-induced crack closure has an effect to reduce the driving force for crack propagation. As a matter of fact, such extrinsic
toughening mechanism is in accord with the finding previously reported for the damage-tolerant Pd-based BMG [28]. An important message here is that these high-toughness BMGs characterized by an extensive crack-growth resistance (R-curve behavior) all exhibit a consistent behavior that their fatigue endurance is enhanced through a “staircase-like fracture mechanism”.

For comparison purposes, the S–N curves of several typical BMG materials tested under a condition identical to ours are summarized in Fig. 9. It is seen that the current ZT1 BMG exhibits the highest fatigue endurance strength, $/C24$, among all monolithic BMGs. It is even comparable to that of the Zr$_{39.6}$Ti$_{33.9}$Nb$_{7.6}$Cu$_{6.4}$Be$_{12.5}$ BMG-matrix composite (DH3) containing second-phase dendrites [12], in which the higher fatigue limit is provided by microstructural barriers that suppress the propagation of damage to below a critical size.

4.2. Crack growth micromechanisms under different $\Delta K$

Different micromechanisms are at play, for different $\Delta K$ ranges. As noted earlier, shear bands are absent in low $\Delta K$ regimes, but resurface at high $\Delta K$.

4.2.1. The near-threshold regime

As shown in Section 3.2.2, it is noticed in Fig. 6(c) that elongated ridges parallel to the direction of crack growth appear on the fracture surface. Such ridge patterns were first observed by Alpas et al. [38] in Ni$_{72}$Si$_{10}$B$_{12}$ metallic glass ribbons at room temperature. For BMGs, Hess et al. [39] also found similar ridges in Vitreloy 1 tested at elevated temperature: it was suggested that positive $T$-stress surrounding the crack tip led to the instability of the Mode I crack front and induced the ridge formation. In the current three-point bending tests, the $T$-stress would be positive when the $a/W$, the ratio of crack length to sample width, exceeds 0.36 [34]. When the applied $\Delta K$ decreased into the near-threshold regime, the crack size is in a range of 0.5–0.6$W$, indeed larger than 0.36 already. As a result, it is likely that the ridges seen in Fig. 6(c) are caused by the presence of a positive $T$-stress. If it is the case, the wavelength of the ridges, $\lambda$, is expected to scale with the crack tip opening displacement, $\delta$, and $K_{\text{max}}^2$ [39],

$$\lambda \propto \frac{K_{\text{max}}^2}{\delta E}.$$  

The data as shown in Fig. 7(c) appear to prove out such a scaling relationship between $\lambda$ and $K_{\text{max}}^2$.

4.2.2. The Paris regime

In this regime, typical fatigue striations form on the fracture surface, as shown in Fig. 8(b). As proposed by Laird [40], the striation formation in crystalline metals is associated with alternating crack-tip blunting and resharpening. This model was also applied to BMGs [5,39]. It should be emphasized that based on this model, each striation should be generated by a single loading cycle. As shown in Fig. 5, however, the striations spacing is significantly larger than that expected from $da/dN$. It means that a number of loading cycles are required to produce a unit increment of crack growth. As a result, our finding does not support the direct application of the Laird’s model to every BMG.

In fact, such an observation was first made by Davis in melt-spun ribbons of Ni$_{39}$Fe$_{38}$P$_{14}$B$_{6}$Al$_{3}$ [41]: the striation spacing was about 6 times larger than $da/dN$; the authors only mentioned in passing that this may be caused by oscillation in the local crack growth direction. For Vitreloy 1 BMGs, Gilbert et al. [5] observed
As noticed, for crystalline metals, crack blunting is usually accommodated through dislocations sliding on two slip-systems roughly at ±45° from the crack plane at the crack tip [19]. In contrast, for the dislocations-free BMGs, crack-tip blunting may be accomplished by shear band sliding [25,42]. Considering this, we propose in the following a simple rationale to explain the inconsistency between striation spacing and \( da/dN \).

As shown in Fig. 8(a), very few shear bands are generated at the crack tip at the \( \Delta K \) level in this regime. Thus, one may assume that there exists an upper-limit situation that only a pair of shear band is generated, at an angle of 45° away from the crack-growth direction. These two shear bands independently slide along the two directions of \( X \) and \( Y \), but only the shear-induced sliding along the \( X \) direction is effective for crack blunting. Fig. 10 displays a schematic of such a scenario.

Then, the crack-tip-opening displacement (CTOD) in plane strain can be expressed as [34]

\[
\delta = \frac{4K^2}{\sqrt{3}\pi \sigma_y E}
\]

where \( \sigma_y \) is the yield strength. As indicated in Fig. 10(b), the shear offset, \( u \), of a shear band along the \( X \) direction can be estimated to be

\[
u = \frac{\delta}{\sqrt{2}} = \frac{4K^2}{\sqrt{6}\pi \sigma_y E}
\]

Under the situation of \( \Delta K = 10 \text{ MPa}\sqrt{m} \) as shown in Fig. 8(a), the maximum shear offset within one cyclic loading, \( u_{\text{max}} \), is approximately 0.42 \( \mu \text{m} \), according to Eq. (10).

Before opening into a crack under bending, the shear offset of a shear band must exceed a critical value, \( u^* \), as suggested by Conner et al. [43]. In fact, the magnitude of the \( u^* \) is a measure of the shear-flowing capability before the shear band evolves into a crack via cavitation. In this regard, a dimensionless parameter, \( f \), was proposed by Demetriou et al. [25] to describe the number of net activated shear-transformation events before a cavitation event occurs in the core of an operating shear band,

\[
\log(f) = \frac{T \frac{T}{G} \langle B \rangle - 1}{T + G}
\]

where \( B \) and \( G \) are the bulk modulus and shear modulus of the BMG, respectively. Using the available data for the current ZT1 BMG (Table 1), the right-hand side of Eq. (11) is calculated to be \(-5.34\). This value sits in between those of two typical Zr-based BMGs, 4.83 [25] for Vitreloy 1 and 6.36 for Vitreloy 106 [44,45]. Since it is reasonable to believe that \( u^* \) scales with \( f \), or \( \log(f) \), the \( u^* \) of ZT1 should be between those of Vitreloy 1 (\( u^* \sim 10 \mu \text{m} \)) [43] and Vitreloy 106 (\( u^* \sim 20 \mu \text{m} \)) [46]. The shear offset of \(-0.42 \mu \text{m} \) calculated above is clearly much less than the required \( u^* \) value (10–20 \( \mu \text{m} \)). As a result, the sliding induced by shear bands, a couple of them at the maximum, is obviously insufficient to immediately produce new crack opening under short-term loading.

In addition, during the unloading half period of a loading cycle, elastic push-back takes place from the matrix around the shear bands. It pushes the shear band to slide in the opposite direction. Concurrently, the crack tip opening displacement is mitigated. Since the viscosity within the shear band is much lower than that in the undeformed matrix, the reversal shearing would operate within the existing shear bands during the subsequent loading–unloading cycles. Such a cyclic shear reversal process is expected to generate free volume within the shear bands [7,21]. Subjected to a number of loading cycles, voids and cavities can then be nucleated and accumulated in the shear bands. Eventually, the crack tip links to these voids or cavities, leading to one increment of crack advancement along the shear band. Based on this picture,
it can be understood why multiple loading cycles are necessary to drive the crack forward by one step.

4.2.3. The high growth rate regime

In this region, the staircase-like crack path, as shown in Fig. 8(c), formed due to the competition between two factors. On the one hand, due to the softening within the shear bands, which become operative in this regime, the crack is prone to propagating along them. It tends to induce crack deflection away from the original Mode I crack plane, as the shear band is inclined at an angle. On the other hand, the crack is driven to propagate along the direction of maximum mechanical driving force (defined by the maximum strain energy release rate \( G_{\text{max}} \)) [34]. From the calculation in Section 4.1, any deflection from the global Mode I crack plane is accompanied by a decrease in \( G \). Thus, the crack has a tendency to return to the Mode I crack plane during propagation. These two processes alternate to dominate the crack growth, and as a result, generate the zigzag crack trajectory. This is similar to the mechanism in the \( S/N \) test (Fig. 4). In other words, the zigzag manner of crack propagation under the \( S/N \) test is associated with the case that the loading state at crack tip actually reached a high \( D_K \) level.

4.3. Correlation of fatigue cracking threshold with fracture toughness

It is noticed in the present work that the crack-closure load, \( K_{cl} \), is at about 13–15% of the \( K_{\text{max}} \) at the fatigue threshold. This was determined from the initial deviation from linearity of the unloading load versus crack mouth-opening displacement (CMOD) data. Thus, the effective fatigue threshold \( \Delta K_{\text{eff}} = (K_{\text{max}} - K_{cl}) \) of ZT1 was determined to be \( 2.7 \pm 0.15 \text{ MPa}\cdot\text{m} \). Apparently, the relatively high fatigue threshold value of ZT1 cannot be attributed to the effect of fatigue crack closure.

Fig. 9. Comparison of stress–life (S–N) fatigue data for several representative BMGs, in terms of the number of loading cycles, \( N_f \), versus the applied stress amplitude, \( \sigma_a \), normalized by the ultimate tensile strength, \( \sigma_u \). These data were all obtained in four-point bending tests [5,12,14,16,28,37].

To make a comparison among BMGs, Fig. 11 shows a plot of fatigue threshold \( \Delta K_{\text{fr}} \) (at \( R = 0.1 \)) versus fracture toughness \( K_{\text{IC}} \), using the literature data of monolithic BMGs. In the plot, the \( K_{\text{IC}} \) of the
Pd-BMG is taken to be 150 MPa \( p \) [25], if we follow ASTM E813-87 which defines \( J_{IC} \) at 0.2 mm crack extension (this is when the crack advance distance remains short with respect to the ligament length). To avoid misunderstanding, it should be noted here that the \( D_K \) is not a true material constant since it usually depends on the \( R \) ratio used in the tests [34]. Nevertheless, as a general trend, the fracture toughness of the BMGs scales with their \( D_K \). The tougher the BMG, the higher its \( D_K \) tends to be.

As revealed in previous work [27], the high fracture toughness of the ZT1 BMG results from a sizable plastic zone ahead of the crack tip, with proliferated shear bands. However, under a loading of near-threshold \( D_K \), this mechanism is not at play, as seen from the lack of shear-banding events ahead of the crack tip shown in Fig. 6(a). The cyclic plastic zone size (\( L \)) at the threshold \( \Delta K_{th} \) is only 76 nm, estimated for plane strain [50] using

\[
L = \frac{1}{3\pi} \left( \frac{\Delta K_{th}}{2\sigma_f} \right)^2
\]

(12)

This length scale is too small to nucleate many shear bands [51]. In fact, the absence of mature shear bands has also been reported for MG samples that have sizes of the order of 100 nm [52,53].

As is well known, the fatigue threshold, similar to the fatigue endurance limit, characterizes a critical loading state below which no fatigue-induced damage accumulates ahead of the crack tip [54]. For crystalline metals, the \( \Delta K_{th} \) is highly affected by the microstructure, particularly the grain size and slip characteristics [50]. For BMGs, it would also be useful to consider the influence of the glass structure. Under monotonic loading, a high fracture toughness is known for ZT1; the structural reason for that is rooted in the internal structure, in terms of easy proliferation of shear bands. More specifically, MD simulation results [55] suggest that compared with other BMGs, the Zr-rich ZT1 appears to contain a wider variety of local motifs that easily turn into geometrically unfavored motifs (GUMs) under applied stresses, leading to a higher population of fertile sites for shear transformation [56], such that a high density of shear bands get to form in the plastic zone. The GUMs are the undesirable and hence more flexible coordination polyhedra that have a higher propensity to become fertile sites for shear transformations. Under cyclic loading at the fatigue threshold, shear bands do not form, but the spread-out GUM-rich local regions and shear transformations throughout the BMG would also help to relieve free volume localization [21] and decrease the likelihood of cavity formation ahead of the crack tip.

An interesting question is whether softening indeed takes place at the crack tip of BMG under cyclic loading. With nanoindentation testing, Schuh et al. [57–60] found hardening of BMG, rather than softening, via cyclic loading in the elastic range. Sun et al. [61] also presented a Bauschinger-type effect when BMGs were loaded under pure shear stress reversal in the elastic range. These results indicate that one possible consequence of cyclic sub-yield loading is to lead to structural changes in the direction of higher density, lower free volume, and higher structural order. However, it should be emphasized that such an ordering and hardening process is unlikely in our case due to completely different stress condition.

Fig. 10. Schematic diagram illustrating the crack blunting through shear bands under opening stresses. (a) Cracked samples prior to applied external loading and (b) crack blunts through shear bands at an angle of 45° from the crack plane. Note that shearing can take place along two directions, \( X \) and \( Y \), but only shearing along the \( X \) direction plays a role of crack blunting with the crack tip opening displacement CTOD = \( \delta \), and corresponding shear offset \( u = (\sqrt{2}/2)\delta \).

Fig. 11. Correlation of fracture toughness with fatigue threshold for monolithic BMGs. The data are taken from Refs. [7,8,13–16,18,25,28,39,47–49].
Firstly, the stress level in the cyclic plastic zone ahead of the crack tip is necessarily larger than the yield strength of the material [62], rather than loading in the elastic regime as performed by Sun et al. [61] (24% \(r_f\) and Schuh et al. (35–60% yield load) [57–60]. Secondly, the triaxial stress state ahead of the crack tip is completely different from that under the indenter [57–60] and torsional loading [61]: tensile mean stresses dominate ahead of the crack tip, while compressive mean stresses surround the indent. As indicated by Flores et al. [63,64], the former stress state increases, while the latter decreases, the free volume in BMGs. This was in fact confirmed with the experimental finding of Kruzic et al. [7,22,65], who detected a fatigue transformation zone with increased free volume ahead of the crack tip at the near-threshold regime via the positron annihilation spectroscopy technique. In other words, there are prior data demonstrating that cyclic Mode I loading does cause softening at the crack tip in a BMG.

Finally, as suggested by Fleck et al. [54], the ratio of \(\Delta K_{th}\) to \(K_{IC}\) is an important parameter for engineering materials. The \(\Delta K_{th}/K_{IC}\) of the ZT1 is found to be 0.02. This suggests that high-toughness monolithic BMGs with pre-existing flaws remain sensitive to fatigue damage induced by cyclic loading. The plastic deformation mode of BMGs is responsible for this difference in damage tolerance between monotonic loading and fatigue loading. Under monotonic loading, it is the shear bands ahead of the crack tip that are effective to shield the crack, but they are vulnerable to fatigue loading because cyclic shear facilitates cavitation in these bands. Near the \(\Delta K_{th}\), or below certain stress intensity, the cyclic plastic zone size ahead of the crack tip is small enough to exclude the shear band formation. Usually, the space required for shear band nucleation is at the length scale of \(-100\) nm for BMGs [66,67], thus the fatigue threshold of Zr-based BMGs, \(\sigma_{f}^\prime\) of 1.6–1.9 GPa) would be 1600 MPa), which is comparable to that of many BMGs approximately scales with its fracture toughness. To encourage spread-out shear transformation events and hence more shear bands, ZT1 was made at a Zr-rich composition [26,56] where the BMG internal structure is composed of a variety of local environments that were found to more easily turn into geometrically unfavored motifs (GUMs) [59] under applied stresses.

The GUMs are and hence more flexible coordination polyhedra that have a higher propensity to become fertile sites for shear transformations.

In terms of fatigue resistance, this study shows that ZT1, with the characteristics discussed in the preceding paragraph, also fares better than other BMGs and is on par with another BMG with an extensive crack-resistance curve (R-curve), \(Pd_{79}Ag_{1}P_{5}Si_{39}Ge_{2}\). Specifically, ZT1 exhibits a record fatigue endurance strength among BMGs in stress/life tests, with a normalized fatigue limit of \(\sigma_{f}^\prime = 440\) MPa (in four-point bending at \(R = 0.1\) and \(-0.27\) of tensile strength \(\sigma_{f} = 1600\) MPa), which is comparable to that of many polycrystalline metals. The fatigue life of ZT1 is dominated by macroscopic crack initiation. In the phase of crack propagation, the resistance to crack growth is contributed by two sources, crack-tip plasticity via shear-banding and crack-deflection in a “zigzag” manner. This mechanism seems to be common to high-toughness BMGs, as it was also recently reported for the Pd-based BMG [28]. A higher propensity for multiple shear banding, similar to the case for high fracture toughness, improves the fatigue resistance in the high \(\Delta K\) regime.

The relation between the stress intensity factor range \(\Delta K\) and crack-growth rates \((da/dN)\) was determined for ZT1. The fatigue threshold, \(\Delta K_{th}\), and the crack-growth exponent in the Paris regime, \(m\), are found to be 2.8 MPa\(_{\Delta}\)m and 2.3, respectively. This \(\Delta K_{th}\) comparable to aluminum alloys, can be attributed to the more spread-out shear transformations in ZT1, and therefore the reduced tendency for free volume localization and void formation in the cyclic plastic zone (or fatigue transformation zone). As a general trend, the \(\Delta K_{th}\) of BMGs approximately scales with its fracture toughness. We propose that the fatigue threshold and steady crack growth can be influenced by a critical length scale in the cyclic plastic zone ahead of the crack tip under cyclic loading. Above this length scale (and correspondingly at sufficiently high \(\Delta K\)), shear bands get to nucleate, which are susceptible to fatigue damage. In other words, in this near-threshold \(\Delta K\) case, the onset of shear banding plays the role of escalating the crack growth rate.

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References
