Compressive ductility and fracture resistance in CuZr-based shape-memory metallic-glass composites

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ABSTRACT
The uniaxial compression behavior of Cu51.5Zr48.5 shape-memory metallic-glass composites was systematically studied, from the perspective of discerning the salient micro-mechanisms controlling their deformation and fracture. Microstructurally, it was found that the particle size and volume fraction of CuZr precipitates formed in these glasses were highly sensitive to cooling rate and casting environment. Plastic flow was induced by a martensitic transformation of the CuZr particles in these materials, with additional contributions to their inelasticity arising from microcracking and crack deflection, which further served to promote ductility and resist fracture.

1. Introduction
Bulk-metallic glasses (BMGs) have many unique properties, such as an ease of processing, superior specific strength and hardness, and large elastic strain limits, high fatigue resistance, good corrosion resistance and ability to withstand irradiation damage (Brechtl et al., 2019; Hua et al., 2014; Huang et al., 2012; Lai et al., 2019; Naleway et al., 2013; Schuh et al., 2007). However, a major drawback of BMGs, which has limited their industrial application, is often their macroscopic brittleness, which can result in near-zero tensile ductility values due to local instability created by the propagation of single shear bands. One means to improve their macro-plasticity and hence ductility is by inducing multiple shear-banding. This has been achieved through the presence of a second phase, to arrest such shear bands before they become "fatal" cracks, in the form of both in situ and ex situ glass-matrix composites (Hofmann et al., 2008; Qiao et al., 2011). In this regard, shape-memory bulk-metallic glass composites have attracted particular interest of late because of their pronounced compressive (Gargarella et al., 2014; Sun et al., 2005) and tensile ductility (Liu et al., 2012; Pauly et al., 2010;...
One such class of glass-matrix composites are those based on the CuZr system, which interestingly display the additional property of shape memory. When the parent CuZr–B2 (cubic Pm-3m) parent (austenite) phase is cooled quickly to temperatures below 440 K, or under stress (Carvalho and Harris, 1980), a phase transformation can occur which involves the formation of a martensitic constituent reported to be integrally composed of two phases: a base structure (B19') with P21/m symmetry and a superstructure with Cm symmetry, similar to the well-known shape-memory NiTi system (Otsuka and Ren, 2005; Schryvers et al., 1997; Zhalko-Titarenko et al., 1994). It has been considered that the martensitic transformation (MT) could effectively lead to an enhanced fracture strain and pronounced work hardening, which has triggered interest in the development of CuZr-based metallic-glass matrix composites as potential structural materials (Hoffmann, 2010; Jiang et al., 2020; Pauly et al., 2009b, 2010; Song et al., 2016; Wu et al., 2011b, 2012, 2017).

In general, BMGs are prototypical brittle solids where even compression failure can be a complex process (Ashby and Hallam, 1986; Brace and Bombolakis, 1963; Horii and Nemat-Nasser, 1985; Suresh, 1983). Flaws, faults, discontinuities, inclusions, etc. in an elastic solid all can interact, leading to cracking, even under compressive loads, which can result in macroscopic failure. In certain brittle solids, such as ceramics, phase transformations can induce microcracking, the associated microcrack-induced strains being a potential contribution to the localized crack-tip plasticity. The micro-plasticity can also play an important role in compressive failure of ceramics (Lankford et al., 1998).

Furthermore, cracks may be deflected by the residual fields associated with the transformed particles; such crack deflection processes can also shield the crack path from the plane of maximum tensile stress, thus delaying the fracture process (Evans and Cannon, 1986). With such transformable brittle solids, such as zirconia-toughened alumina (ZTA), in situ phase transformations and microcracking can have a similar potency to improve localized plasticity (Hutchinson, 1987; Rühle et al., 1987), although too much microcracking can be detrimental to the effective strength and may cause catastrophic failure. In many brittle solids, microcracks create new surfaces and accordingly act to relieve the residual stress-producing strains which are manifest at the macroscopic scale as inelastic or transformation strains (Hutchinson, 1987). In ceramics and many natural materials, such as nacre (Wegst et al., 2014) and bone (Fratzl and Weinkamer, 2007; Peterlik et al., 2005), microcracking and crack deflection also can play a major role in promoting localized plasticity by dissipating more fracture energy or shielding a growing crack. However, these energy-absorbing mechanisms have seldom been reported for metallic materials, where the resistance to fracture is invariably intrinsic in nature [27]; further, there is little evidence to date of their role in affecting the mechanical properties of BMG composites.

The shear and volumetric dilatation associated with in situ martensitic transformations have been actively addressed in ceramics (Evans and Cannon, 1986; Green, 1982; Kelly and Rose, 2002) and in shape-memory metallic alloys, such as Nitinol (Plietsch and Ehrlich, 1997; Robertson and Ritchie, 2007). It is well known that the shear and dilatation effects could effectively improve the localized crack-tip plasticity of zirconia enhanced ceramics (Chen and Morel, 1986; Lambropoulos, 1986). However, a volume contraction in Nitinol caused by martensitic transformation (ΔV/V = −0.39%) makes a small negative contribution to the overall fracture resistance (Holtz et al., 1999; Otsuka and Ren, 2005; Yan et al., 2002). In geology, the dilatancy in rocks associated with microcracking is also known to have intriguing effects on inelasticity (Brace, 1978; Brace et al., 1966; Nemat-Nasser and Obata, 1988). Though the transformation-induced plasticity (TRIP) effect has been extensively discussed in shape-memory metallic-glass composites (Hofmann, 2010; Pauly et al., 2009b, 2010; Song et al., 2016; Wu et al., 2011b, 2012, 2017), the specific contributions to the ductility from the shear and volumetric effects associated with the phase transformation of the CuZr particles has seldom been addressed in these materials.

In this work, the uniaxial compression behavior of a Cu51.5Zr48.5 bulk-metallic glass composite, comprising CuZr particles embedded in an amorphous matrix, has been systematically studied. Specifically, the fracture kinetics of microcrack initiation and propagation within the CuZr particles are examined from the prospective of their role in creating positive contributions to the compressive ductility of the CuZr-based alloy. Multiple energy-absorbing mechanisms have been identified, namely martensitic transformation, microcracking, and microcrack deflection.

2 Fracture resistance can be considered as a mutual competition between two classes of toughening mechanisms: intrinsic mechanisms, which resist microstructural damage ahead of the crack tip and are motivated primarily by plasticity, and extrinsic mechanisms, which operate at, or in the wake of, the crack tip to inhibit fracture by ‘shielding’ the crack from the applied driving force. Whereas intrinsic toughening mechanisms are effective in inhibiting both the initiation and growth of cracks, extrinsic toughening mechanisms, such as crack bridging and crack deflection, are only effective in inhibiting crack growth (Launey and Ritchie, 2009).
Struers diamond cutter with a diamond blade thickness of ~0.5 mm; some small portion of the specimen thickness of these samples was lost due to the blade thickness. The distance of each specimen from the bottom to top of the casting are indicated along the x-axis in Fig. 1a, where the black- and white-colored areas are, respectively, the amorphous matrix and the crystalline second phase. Locations closer to the injection nozzle have progressively the slowest cooling rates; consequently, the percentage of the white phase here, representing the volume fraction of the crystalline phase, is increasing. Six samples were cut from each of the 30-mm long specimens at locations at varying distances from the injection nozzle, representing varying cooling rates and hence varying proportions of the amorphous and crystalline phase; these were used for compression and XRD testing. Each specimen used for uniaxial compressive testing was identified as L1S1, L1S2, L1S3, L1S4, L1S6, L1S7, etc., where the first two digits represent the sample location, and the second two digits the sample number. Samples for XRD characterization were numbered in the same manner, with the analysis performed using conventional X-ray diffractometry (Bruker Analytical X-Ray System, with Cu-Kα radiation, λ = 0.154056 nm) to identify the phases present. The volume fraction and size distribution of the crystalline phases were estimated using the Image-Pro plus 6.0 software (Wu et al., 2015) (Media Cybernetics, Inc., USA.) The microstructures of all samples were characterized using optical microscopy prior to testing.

Cylindrical samples with a 2:1 aspect ratio (2 mm in diameter, 4 mm in length) were prepared for the compression tests, with each sample ground parallel to an accuracy of better than 20 μm using SiC grinding papers, followed by polishing with 0.05-μm alumina powder; the lateral surfaces were also polished with a similar regimen. These samples were tested at room temperature under uniaxial compression between tungsten carbide platens at a strain rate of 10⁻⁴ s⁻¹, with a linear variable differential transformer (LVDT) used to monitor sample displacements.

After compression, the fracture morphology of the deformed samples was characterized in the scanning electron microscope (Philips XL30 FEG SEM) in the secondary electron mode at an accelerating voltage of 25 kV) before the samples were remounted in epoxy and examined metallographically to detect the nature of the deformation-induced microstructural changes. Appropriate locations on the as-cast and deformed specimens were selected for further examination using focused ion beam (FIB) machining in a FEI-600i FIB/SEM dual-beam system. An in situ lift-out technique was used to select specific locations for examination and transfer them to TEM grids; these samples were then examined with high-resolution transmission electron microscopy (HRTEM) using a JEM-2010F microscope operating at 200 kV.

Fig. 1. a) Scanned micrograph of the longitudinal section of a 2-mm rod of Cu₅₁.₅Zr₄₈.₅, showing the crystalline second phase non-uniformly distributed in the amorphous matrix. In general, the dark area is the amorphous phase; the white areas are the crystalline phases. The left side is from bottom of the mould, which located furthest from the crucible, indicating the highest cooling rate; the right side is from the top of the mould, which located nearest to the crucible, indicating the lowest cooling rate. The specimens for compression testing were cut from different locations of this sample. According to the position from bottom to top, the specimens were denoted L1, L2, L3, L4, L5 and L6. Specimen L1 is cut from the lowest position (with the fastest cooling rate), with L6 from the highest position (slowest cooling rate). Roughly, specimens L1 and L2 can be considered at a distance of 0–10 mm to the bottom of the copper mould; L3 and L4 can be considered as a distance of 10–20 mm to the bottom of the copper mould. Similarly, L5 and L6 located from the bottom of the copper mould at a distance of 20–30 mm. b) X-ray diffraction patterns of specimens from locations L1, L2, L3, L4, L5 and L6.
3. Results

3.1. Microstructure characterization of as-cast specimens

Because the distribution and volume fraction of CuZr in CuZr-based metallic-glass matrix composites, shown for the current as-cast Cu$_{51.5}$Zr$_{48.5}$ alloy in Fig. 1a, can be hard to control and predict as they are highly sensitive to temperature and cooling rate, measured strengths and ductility values can often show significant variation. Accordingly, to correlate the mechanical performance of this alloy with microstructure, the specimens were tracked according to their specific location and specimen ID.

The XRD characterization, shown in Fig. 1b, indicates that for the lower positioned samples, i.e., which experienced a higher cooling rate, there are only a few peaks superimposed on the continuous (amorphous) spectra, which is characteristic of the structure of glass-matrix composites. These peaks for the L1, L2 and L3 sample locations represent the metastable B2 (CuZr) and B19’ phases. As the sample location moves from bottom to top, concomitant with increasingly slower cooling rates, the fraction of B19’ increases while the fraction of B2 decreases, consistent with previous studies (Pauly et al., 2009a; Wu and Li, 2009). The properties of the material at these locations are listed in Table 1.

An enlarged view of framed region in Fig. 1a is shown in Fig. 2a. Irregular-shaped B2 particles are clearly evident; these particles are actually spherical, but as they grow and coalesce, they tend to form into a “Mickey Mouse” shape. To further verify the amorphous matrix and B2 type structure, samples were FIB machined from a location on the B2/amorphous matrix interface; the protective Pt strip is shown in Fig. 2b. TEM and HRTEM images of this interface are shown in Fig. 2c and d, respectively; corresponding selected-area electron diffraction (SAED) patterns for the amorphous matrix and B2 phase are shown as insets in Fig. 2d, respectively at the right-hand upper corner and the lower left-hand corners.

3.2. Uniaxial compression properties

Engineering stress-strain curves for samples taken at locations L1 through L6 are shown in Fig. 3a–f, respectively. Note that not all samples were tested due to excessive porosity, processing defects or testing misalignment, similar to previous studies on this material (Wang et al., 2008; Wu et al., 2008). The average value of the maximum strength, failure strain, yield strength and Young’s modulus for different locations are summarized respectively in Fig. 4a–d. From these figures, we can infer that samples which experienced the highest cooling rates, i.e., close to location 1 and location 2, displayed the higher strengths. In the middle region (location 3), where the volume fraction of crystalline phase becomes larger, the fracture strain tends to be higher, whereas at locations that are closer to the melting nozzle, where the cooling rate was progressively decreased, in general the strengths were reduced. Additionally, the Young’s modulus, $E$, dropped from 80 to 50 GPa at locations from L3 to L5, indicating that the composite structures with a higher proportion of amorphous matrix tended to exhibit a higher elastic stiffness as compared to those with a higher content of crystalline second phase, as identified by the XRD patterns in Fig. 1b. Indeed, the Young’s modulus of a Cu–Zr–Al composite material has been measured to be ~52–56 GPa when the CuZr crystalline volume fraction is between ~30 and 50% (Pauly et al., 2009a). These values of Young’s modulus are consistent with the values reported by Pauly et al. (2009b), where the Young’s modulus for a Cu–Zr–Al composite was found to be ~50 GPa when the crystalline volume fraction was ~50–80%, but as high as ~70–80 GPa for a crystalline volume fraction less than ~45%.

3.3. Microstructural analysis of deformed material

3.3.1. Crystalline volume fraction and particle size analysis

Even at the same location (which indicates a similar cooling rate), Fig. 3a–d shows that fracture strains can differ from 4% to 17%, as seen for example in specimens L1S6 and L1S12. This large variation in ductility was found to be associated with variations in the crystalline structure (Fig. 5). The volume percentage of B2 particles, denoted as $f$, in specimens a) L2S6, b) L2S10, c) L2S7, d) L4S9, e) L2S8, f) L3S9, g) L5S1 and h) L6S9, was found to be, respectively, 4%, 6%, 8%, 27%, 22%, 45%, 47% and 79%.

<table>
<thead>
<tr>
<th>Casting Condition (Distance from the bottom)</th>
<th>Cooling Rate Estimation (close to rod surface) (Kozieł, 2015)</th>
<th>Cooling Rate Estimation (Rod axis) (Srivastava et al. 2002; Kozieł, 2015)</th>
<th>Specimen ID</th>
<th>$d_{max}$ (μm)</th>
<th>f (%)</th>
<th>$E$ (GPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\sigma_{max}$ (MPa)</th>
<th>Fracture Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Same location (Bottom 0–10 mm)</td>
<td>~5000 K/s</td>
<td>~220 K/s</td>
<td>L2S6</td>
<td>48 μm</td>
<td>4%</td>
<td>85</td>
<td>1252</td>
<td>1840</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L2S10</td>
<td>30 μm</td>
<td>6%</td>
<td>93</td>
<td>1424</td>
<td>1935</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L2S7</td>
<td>19 μm</td>
<td>8%</td>
<td>94</td>
<td>1223</td>
<td>1847</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L2S8</td>
<td>87 μm</td>
<td>22%</td>
<td>78</td>
<td>1187</td>
<td>1521</td>
<td>4.9</td>
</tr>
<tr>
<td>Same Specimen (Middle 10–20 mm)</td>
<td>~5000 K/s</td>
<td>~175 K/s</td>
<td>L3S9</td>
<td>90 μm</td>
<td>45%</td>
<td>72</td>
<td>1116</td>
<td>1706</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L4S9</td>
<td>46 μm</td>
<td>27%</td>
<td>73</td>
<td>1142</td>
<td>1713</td>
<td>13.5</td>
</tr>
<tr>
<td>Top (20–30 mm)</td>
<td>~5000 K/s</td>
<td>~125 K/s</td>
<td>L5S1</td>
<td>77 μm</td>
<td>47%</td>
<td>47</td>
<td>1092</td>
<td>1452</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L6S9</td>
<td>103 μm</td>
<td>79%</td>
<td>54</td>
<td>898</td>
<td>1487</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 1

Summary of crystalline volume fraction $f$, maximum particle diameter $d_{max}$, and mechanical properties yield strength $\sigma_y$, maximum strength $\sigma_{max}$ and fracture strain for specimens at different cooling rates.
The maximum particle size, $d_{\text{max}}$, was measured as the maximum diameter of single CuZr particles before coalescence with adjacent particles (shown by light yellow circles in Fig. 5a–h). Such particle sizes were measured to be 48, 30, 19, 46, 87, 90, 77 and 103 μm, respectively, for specimens a) L2S6, b) L2S10, c) L2S7, d) L4S9, e) L2S8, f) L3S9, g) L5S1 and h) L6S9.

The enlarged view of the framed region in Fig. 5i-l shows the corresponding surface relief (SR) patterns, which are characteristic of the strain generated by the martensitic transformation. As noted in Fig. 5e, when the particle size exceeds a critical value, large cracks can be observed inside the crystalline particles, as shown in Fig. 5d, e, h. Such behavior of cracks initiating from inside CuZr particles has been previously reported for uniaxial compression (Jiang et al., 2007) and in situ tension testing (Sun et al., 2018) of CuZr glass composites.

3.3.2. Morphology of fractured specimens

Following testing, the fracture samples were examined in the SEM. The fracture surfaces for samples L2S7 ($f = 8\%$) with an 11.6% fracture strain, L2S10 ($f = 6\%$) with a 9.5% fracture strain, and L3S6 with a 9.6% fracture strain, are shown (in the direction perpendicular to the uniaxial loading direction) in Fig. 6, where $f$ is the volume fraction of the crystalline phase. The corresponding side and fracture surfaces of the deformed specimen L3S8, with an 8.1% fracture strain, are shown in Fig. 7. There are three main findings from these fractures. Firstly, typical vein-like fracture patterns are found on all samples. Secondly, all four fractured surfaces displayed evidence of surface relief and microcracking; the microcracks always initiated from the regions of surface relief, which were both perpendicular to the direction of uniaxial loading. Thirdly, the surface relief and microcracking were constrained by the vein patterns. All the microcracks can be seen to initiate from the martensite/parent interfaces. The associated surface relief represents a characteristic feature of martensitic transformation, and the surrounding vein patterns represent typical failure patterns for an amorphous alloy. The constraint of the tougher amorphous matrix is apparent as the microcracks were contained within the particles.

In Fig. 7a and b, the side surface (side view) and fracture surface (longitudinal frontal view) are compared. Fig. 7c and d shows the enlarged view of the framed region in Fig. 7a and b, respectively. Extensive microcracks can be seen on these fracture surfaces which display a one-to-one correspondence with the secondary/tertiary shear bands. The new surface area created by the microcracking may account for a significant proportion of the energy dissipated during shear fracture.

3.4. TEM verification of the martensitic transformation

Analysis of the fracture surfaces showed clear evidence of microcracking and surface relief which are characteristic features of a martensitic transformation. To confirm the occurrence of the in situ transformation, TEM specimens were carefully FIBed out from a location displaying surface relief that was adjacent to a region of microcracking (Fig. 8). The resulting TEM images in Fig. 9 clearly show the presence of martensitic plates and retained austenite, with the coexistence of $[\overline{1}11]_{\text{B2}}/\{100\}_{\text{B19}}$. Comparing this with the corresponding TEM image of the as-cast material (Fig. 2), the strained specimen shows a transition from the B2 to B19’ CuZr phase, consistent with previous reports on CuZr-based metallic glass-matrix composites (Pauly et al., 2007, 2009b; Wu et al., 2010, 2011b).
4. Discussion

4.1. Uniformity and distribution of CuZr crystals

The microstructural distribution of CuZr precipitates in CuZr-based shape-memory metallic-glass composites has been generally acknowledged to be non-uniform with agglomerations that are both difficult to predict and control (Liu et al., 2012; Pauly et al., 2009a, 2009b; Wu et al., 2011a, 2011b). However, no direct correlation between cooling rates and the B2 distribution has been made previously for these alloys.

To achieve this, the cooling rates generated from the bottom to the top of the copper mould during casting must be estimated, as the gradient in crystallization can be induced in a single cast rod (Hofmann et al., 2006). From the analysis of Lin and Johnson (1995), the critical cooling rate can be estimated by $T = \frac{dT}{dt} = \frac{10}{R^2}$, where $T$ is temperature (in K), $t$ is time (in seconds), and $R$ is the maximum thickness (in cm) of the formed amorphous alloy. To create a fully amorphous alloy with a 2-mm thickness, the critical cooling rate was estimated to be around 250 K/s. The maximum growth rate for Cu$_{50}$Zr$_{50}$ has been reported to be 23 mm/s (Orava and Greer, 2014; Wang et al., 2011), which is relatively high although comparable with many amorphous alloys (Greer, 1996). With the minimal
number of crystallites, we estimated the cooling rate at the bottom of the mould ($x = 0$ mm) to be less than 250 K/s. This is consistent with the results of Srivastava et al. (2002) who reported for a 40-mm long rod that the cooling rate along the axis near the bottom of a 3-mm thick rod ranges from ~50 to 220 K/s; near the top it decreases to ~40–125 K/s. Koziel (2015) estimated that for a 2-mm thick, 50-mm long rod, the cooling rate close to rod surface could exceed 5000 K/s along the whole rod; however, at the center along the rod axis, the effective cooling rate at the bottom of the rod would be ~200 K/s. Utilizing the above analyses (Koziel, 2015; Srivastava et al., 2002), we estimated that for our 2-mm thick, 30-mm long rod, the effective cooling rate close to the rod surface was generally higher than 5000 K/s along the entire rod, whereas at the central rod axial position, the cooling rate was ~220 K/s at $x = 0$, 165 K/s at $x = 10$ mm, 155 K/s at $x = 20$ mm, and 125 K (at $x = 30$ mm). Accordingly, the difference in cooling rate could be as large as 100 K/s at the top and bottom of the cast specimen. In Table 1, the estimated cooling rates close to the rod surface and near the rod axis are compared with the volume fraction of crystalline phase $f$, maximum particle diameter $d_{\text{max}}$ and their corresponding mechanical properties (yield strength $\sigma_y$, maximum strength $\sigma_{\text{max}}$ and fracture strain) for selected specimens. We now examine the relationships between mechanical performance, especially the fracture strain, in relation to the size and particle distribution characteristics of CuZr crystals, as shown in Fig. 5a–h.

For specimen L2S6 ($f \approx 4\%$, $d_{\text{max}} = 48 \mu m$), L2S7 ($f \approx 8\%$, $d_{\text{max}} = 19 \mu m$), L2S8 ($f \approx 22\%$, $d_{\text{max}} = 87 \mu m$), L2S10 ($f \approx 6\%$, $d_{\text{max}} = 30 \mu m$), the estimated effective cooling rates are quite similar both near the surface and axis of the rod as they represent similar locations within the cast specimen. But the volume percentage of CuZr particles ranges from 4% to 22%, and the maximum diameter of CuZr particles varies from 19 $\mu m$ to 87 $\mu m$. Although there was a large difference in cooling rates from the surface to the central rod axis (Srivastava et al., 2002), the microstructural images of the L2S10 and L2S8 samples in Fig. 5b, c clearly show CuZr particles near the surface of the cast rod, instead of at the center; similarly, for the L3S9 and L4S9 samples (Fig. 5d, e), large crystalline particles were observed over the rod surface area. Despite estimates of a difference in cooling rates, from above 5000 K/s near the rod surface (Koziel, 2015; Srivastava et al., 2002), there were no obvious differences in the distribution of the CuZr particles in our samples. A similar phenomenon has been reported previously for the transverse microstructure of this metallic glass composite (Pauly et al., 2009b; Wu et al., 2011b).

Samples L3S9 ($f \approx 45\%$, $d_{\text{max}} = 90 \mu m$) and L4S9 ($f \approx 27\%$, $d_{\text{max}} = 46 \mu m$) came from the same cast rod and share an adjacent location. Although the cooling rate of L3S9 was slightly lower than that of L4S9, the crystallinity of sample L3S9 is over 60% higher, with essentially twice the maximum particle size, than that of L4S9; correspondingly, their fracture strains were markedly different, i.e., 4.8% for L3S9 and 13.5% for L4S9. We can conclude from these results that the distribution and size of the CuZr particles can significantly affect the fracture strain of CuZr-based composites. The CuZr particles distribute quite randomly as their nucleation and impingement is difficult to control; this is apparent as cooling rate differences between 5000 and 200 K/s do not appear to affect their distribution in a prominent manner.
4.2. Effect of volume fraction and particle size

It is well known that the mechanical behavior of composites is a marked function of the volume fraction, size and distribution of the reinforcement phases (Fu et al., 2007b; Pauly et al., 2009b; Qiao et al., 2016; Wei et al., 2016). As shown in Fig. 10a, b, c, the yield strength, maximum strength and Young’s modulus can all be generally described by the rule-of-mixtures (Clyne and Withers, 1995):

$$E_c = fE_f + (1 - f)E_m;$$

(1)

where in this particular relationship for Young’s modulus, $E_c$, $E_f$ and $E_m$ are the moduli for the composite, reinforcement and glass matrix, respectively, and $f$ is the volume fraction of reinforcement. Similar expressions can be written for strength. However, as shown in Fig. 11, the fracture strain of the present CuZr-reinforced composite shows a distinctly nonlinear increase with reinforcement volume fraction at $f \sim 30\%$. Specifically, the fracture strain reaches a maximum value of $\sim 13.6\%$ at $f \sim 27\%$, whereas at $f \sim 45\%$, it decreases abruptly to $\sim 4.8\%$. A maximum in the ductility at a reinforcement volume fraction of $\sim 30\%$–$40\%$ is significant as once the proportion of the crystalline phase reaches this level, it exceeds the percolation threshold; at this point, the overall property of the composite reaches a topological transition in that the reinforcement phase is considered to dominate the properties (Fu et al., 2007a, b; Lee et al., 2004).

There is a similar transition when the particle size is smaller than a critical value; below this value, the composites exhibit relatively good ductility, whereas above it, cracks are apparent in the larger particles and the material fails with very limited plasticity. In sample L2S8 ($f \sim 22\%$, $d_{\text{max}} = 87\ \mu m$), for example, once the particle size exceeds $87\ \mu m$, with a volume fraction of $\sim 22\%$, obvious cracking was observed inside the large CuZr particles and failure occurred at a plastic strain of only $\sim 4.9\%$ (Fig. 5e).

The CuZr particle size and volume fraction accordingly have a marked effect on the compressive stress-strain curve and corresponding compressive fracture energy, which is depicted in the data shown in Fig. 12a–c. In Fig. 12a, when the CuZr particle volume fraction is below $30\%$ and the particle size is smaller than $87\ \mu m$, the CuZr$_{1.5}\text{Zr}_{48.5}$ glass composite shows a distinct failure strain which can be as high as $\sim 13.6\%$ at $f \sim 27\%$. The shaded green area displays a similarly distinctly large compressive fracture energy.
In sample L2S8 (f ~ 22%, $d_{max} = 87 \mu m$), failure was mainly associated with rapid crack propagation within the larger crystalline particles, which resulted in a lower compressive ductility and fracture strength, with the corresponding stress-strain curves exhibiting far less (~2%) plastic flow (Fig. 12b). Such limited ductility was characterized by all samples containing a high volume fraction of larger crystalline particles, such as L3S9 (f ~ 45%, $d_{max} = 90 \mu m$), L5S1 (f ~ 47%, $d_{max} = 77 \mu m$) and L6S9 (f ~ 79%, $d_{max} = 103 \mu m$); in composite samples with a low crystalline volume fraction, the ductility was slightly higher.

Sample L5S1 (f ~ 47%, $d_{max} = 77 \mu m$) had comparable ductility but a lower failure strength than sample L2S8 (f ~ 22%, $d_{max} = 87 \mu m$), as shown in Figs. 5g and 12b. Indeed, where the particulate fraction exceeded ~47%, failures were even more brittle, as shown in Fig. 12b and c. Sample L6S9 (f ~ 79%, $d_{max} = 103 \mu m$) represents a typical failure strength and strain from a high volume fraction of crystalline CuZr; the shaded purple area in Fig. 12c shows a distinctively lower compressive fracture energy than that of the shaded green area in Fig. 12a, which represents the composites with f ~30–40% with $d_{max} < 87 \mu m$.
4.3. Microfracture processes

To understand the non-linearity of the fracture strain and the underlying plasticity mechanisms in shape-memory glass-matrix composites, we first describe how the microfractures evolve during the failure process.

4.3.1. Microcrack initiation

As noted above and in Figs. 6, 7 and 9, the presence of a martensitic transformation is normally accompanied by surface relief and microcracking, the former signifying the martensite/parent (M/P) interface. The microcracking is presumed to result from two mechanisms associated with this transformation of the austenitic CuZr (B2) to martensitic CuZr (B19') structures, namely (i) the dilation, and (ii) the large shear force induced by the lattice distortion, which has been reported to concentrate along the M/P interfaces (Evans and Cannon, 1986).

A positive volume change of 0.187% has been measured for the B2 to B19' transformation of the CuZr particles (Zhalko-Titarenko et al., 1994). When the particles transform, they impose a compressive stress on the amorphous matrix; in return, their shape and volumetric change is constrained by the tougher amorphous matrix. This is apparent in Fig. 6c, i, q, r and is discussed in section 3.3.2.

The lattice parameters for the parent B2 and martensitic B19' structures are listed in Table 2. For the parent B2 phase, the lattice
parameter \(a_0 = 0.3263 \text{ nm}\); for the martensitic B19\(^\prime\) parameter, the corresponding lattice parameters are \(a = 0.3278 \text{ nm}\), \(b = 0.4161 \text{ nm}\), \(c = 0.5245 \text{ nm}\), and \(\beta = 103.88^\circ\). The atomic bond length along \([01\overline{1}]_{B2}\) and \([011]_{B2}\) vector can be calculated as 
\[
\sqrt{2} a_0 = \sqrt{2} \times 0.3263 \text{ nm} = 0.4615 \text{ nm}.
\]

Fig. 13 provides a schematic illustration of the crystallographic relationships between the parent and martensitic phases. Fig. 13a shows the B2 parent structure (four times in size), with a tetragonal cell delineated by red lines. In Fig. 13b, the cell delineated by red lines is the same one as that delineated in Fig. 13a. Upon transformation, the [T00]_{B2} vector remains virtually unchanged (axis \(a\)), the [01T]_{B2} vector shrinks to become the [001]_{B19}\(^\prime\) vector (axis \(b\)), [0TT]_{B2} expands to become the [001]_{B19} vector (axis \(c\)), before a shear is introduced to make the \(\beta\) angle change from 90\(^\circ\) to 103.88\(^\circ\) on the (011)_{B2} plane in the [100]_{B2} direction. Accordingly, the final monoclinic lattice is created, as shown by blue lines in Fig. 13b. In practice, the above process occurs in one step, but it is described here in two steps for mathematical clarity. The crystallographic relationships and lattice correspondence becomes [100]_{B2}//[100]_{B19}\(^\prime\), (011)_{B2}//(001)_{B19}, (01T)_{B2}//(010)_{B19}\(^\prime\) (Schryvers et al., 1997; Seo and Schryvers, 1998).

The martensitic transformation from austenite to a specific martensite variant can be decomposed into rotational, shear and distortional strains. As the similarity between the CuZr and NiTi unit cells is well known (Buhrer et al., 1983; Kudoh et al., 1985; Schryvers et al., 1997; Seo and Schryvers, 1998), it is of note that the stress-induced-martensite (SIM) transformational shape strain for different variants in the equiatomic NiTi alloy has been found to range from +9.7% (in tension) and −5.2% (in compression) (Plietsch and Ehrlich, 1997).

An approximate estimate for the current alloy of the strain caused by the transformation-induced shape change in the CuZr particles restrained within the tougher amorphous matrix can be deduced from the following argument. By shortening the [01T]_{B2} vector into axis \(b\), the atomic bond length changes from 0.46 nm to 0.41 nm, so that the axis will be strained by \((0.41-0.4615)/0.4615 = -0.11\). By elongating the [0TT]_{B2} vector into axis \(c\), the atomic bond length changes from 0.4615 nm to 0.527 nm, the lattice along \(c\) axis will be
We therefore conclude that the large rotational and shear stress due to the atomic shuffle and shear will lead to large internal stresses inside the CuZr particles while they are constrained by the amorphous matrix. These internal stresses will be mostly located at large shear stress concentration sites, specifically at the martensite/parent interfaces where the martensitic transformation occurs (Fig. 14a); as such, these interfaces become susceptible to microcracking. Although microcrack initiation along such interfaces has not been reported for CuZr shape-memory alloys previously, the phenomenon is not unusual for transformable materials, for example, as observed in TRIP steels (Lee et al., 2008), ZTA ceramics (Chen and Morel, 1986), and in in situ SEM imaging of tensile tests of CuAlNi shape memory alloys (Lu et al., 2002) and Z3CN20-09 M stainless steels (Lu and Zhu, 2014).

4.3.2. Microcrack propagation

Fracture in compression attracted significant interest in the 1960–1980s period, especially in the field of geology and mechanics (Ashby and Hallam, 1986; Brace and Bombolakis, 1963; Horii and Nemat-Nasser, 1985; Nikitin and Odintsev, 1999). For example,
Brace et al. (Brace and Bombolakis, 1963) first noted that cracking under far-field compression could still traverse in the tensile direction. This was confirmed by Horii et al. (Horii and Nemat-Nasser, 1985) who examined the micro-mechanisms of rock fracture under compression loading. These authors verified that cracks grow in tension following nucleation at the tips of pre-existing flaws or other geometric discontinuities; they further found that with increasing compression, crack paths tend to become parallel to the direction of the maximum far-field compression.

A frictional sliding shear crack model has been widely applied to explain the damage in brittle solids subjected to compression,
typically for rock mechanics (Ashby and Sammis, 1990; Kachanov, 1982a, b; Nikitin and Odintsev, 1999). Consider a pre-existing flaw in Fig. 14c, of length $2a$, which is subjected to principal stresses $\sigma_1$ and $\sigma_3$; the resulting stress concentrations at defects can translate the global compressive stress-state into a locally tensile one. Specifically, in Fig. 14c, the edge force $F_3$ generates tension to create the wing cracks PP$'$ and QQ$'$. The frictional sliding shear crack model has often been used to explain the inelasticity of natural rocks. Micromechanical events such as microcracking due to local stress concentration, frictional sliding on pre-existing microcracks accompanied by propagation of secondary (branched) tensile cracks have been proposed as the possible mechanisms responsible for inelastic behavior (Kachanov, 1982a, b). These tensile cracks match well with the microcracks displaying a zig-zag morphology that are observed in the present material (Fig. 6g, h, r).

We perceive that the fracture process in the CuZr-based metallic glass-matrix composites can be partitioned into three stages: (i) when the initial compressive stress is applied, the transformation-induced dilation and shear strain impose a compressive stress on the amorphous matrix, which in turn imparts a surrounding compressive stresses onto the CuZr particles (Fig. 15a); (ii) microcracks in these particles then initiate at martensite/parent interfaces due to the local concentration of shear stress there (Fig. 14a); (iii) these microcracks, which are constrained by the amorphous matrix, propagate in a zig-zag manner (Fig. 6g, h, r), with additional copious deflection between shear bands and propagating microcracks along the CuZr martensite/parent interfaces. The propagation of the microcracks, however, can be inhibited by the presence of the shear bands. They were often observed to form as a group of parallel microcracks, as they were initiated from parent/martensite interfaces. Such interactions between the microcracks and shear bands resulted in copious crack deflection which accordingly prolonged the fracture process and served to prohibit catastrophic failure.

Fig. 13. Schematic illustrations of the crystal structures of the CuZr phases showing a) four body cubic unit cells B2, b) one monoclinic basic structure B19'. Green and red spheres represent Cu and Zr atoms, respectively. $i$, $j$, and $k$ refer to parent lattice, and $i'$, $j'$ and $k'$ refer to the martensite lattice. The crystallographic relation and lattice correspondence $[100]_{B2}/[100]_{B19}$, $[011]_{B2}/[001]_{B19}$, $[01\overline{1}]_{B2}/[010]_{B19}$ are illustrated. When the B2 cubic CuZr transforms to monoclinic, CuZr phase, the volume expansion is around 0.187%. When the CuZr particles are constrained inside the tougher amorphous structure, both shape and volume change are restrained. Upon transformation, the $[100]_{B2}$ axis remains virtually unchanged. By shrinking $[01\overline{1}]_{B2}$ vector into $[010]_{B19}$, the atomic bond length changes from 0.4615 nm to 0.41 nm; therefore, the axis will be strained by $(0.41-0.4615)/0.4615 = -0.11$. By expanding $[01\overline{1}]_{B2}$ vector into $[001]_{B19}$, the axis length changes from 0.4615 nm to 0.527 nm; accordingly, the atomic bond length will be strained by $(0.527-0.4615)/0.4615 = 0.142$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
4.4. Micro-mechanisms of plasticity

Based on the microfracture processes, we now address the non-linearity in fracture strain and the significantly increased compressive plasticity in these shape-memory metallic-glass composites.

4.4.1. Microcracking-mediated plasticity by non-interacting microcracks

In situ stress-induced transformations result in large internal stresses, which can be relieved by plastic deformation or fracture (generally intergranular) (Miyazaki et al., 1982; Ueland and Schuh, 2013). Whereas a high strain is created due to a large dilation and/or shape change, microcracking can additionally act to relieve localized stresses, which is a common phenomenon in ceramics (Green, 1982) and rocks (Kachanov, 1982a, b). For non-transformable crystalline materials, such as granite (Moore and Lockner, 1995), the grain boundaries are obvious weak sites such that, rather than actual cracking, stress relief can also occur through debonding within the boundaries, between adjacent grains or between an aggregate and matrix, (Nirmalendran and Horii, 1992).

As demonstrated in Figs. 6, 7 and 9 and discussed in section 4.3.1, for transformable materials, the martensite/parent interfaces often serve as stress concentrators to cause microcrack nucleation and growth. Although the concept of microcracking has been studied extensively in transforming ceramics, such as zirconia-toughened alumina (Rühle et al., 1987), and other natural materials such as granite (Moore and Lockner, 1995), and bone (Launey et al., 2010), there have been few reports of microcracking-mediated plasticity in shape-memory glass-matrix composites.

For the present composite, microcracks were initiated within the nominally spherical CuZr particles mostly by debonding/delamination of the grain boundaries along martensite/parent interfaces (Fig. 6b, c, e, q). When these microcracks are constrained inside the amorphous matrix (Fig. 14b), the dilation δ, caused by the opening of each microcrack, contributes to an apparent dilatational strain in the normal direction, and thus will contribute to an enhanced plastic strain (Chen and Morel, 1986; Hutchinson, 1987). Therefore, their size, density and distribution serve as critical parameters in dictating the overall inelastic strain caused by the

![Diagram](image-url)
4.4.2. Microcrack deflection by interacting microcracks

Based on our experimental observations, and as noted above, copious deflection between shear bands and propagating microcracks is seen along CuZr martensite/parent interfaces, as shown in Fig. 6g, h, r. The zig-zag patterns reflect the local tensile stress field and display the phenomenon of crack deflection which acts to shield the crack tip and lower the probability of catastrophic failure.

We believe that the enhancement in the uniaxial compressive plasticity results from: i) the microcracked CuZr particles serving as microstructural barriers to deflect shear-band propagation, ii) the martensitic transformation itself which results in dilatation and shear, in the form of traditional transformation-induced plasticity (TRIP), iii) concomitant with the transformation, microcracking along the martensite/parent interfaces further can contribute to the dilation effects and to the relaxation of local stresses, which all thereby enhance the overall ductility, and iv) profuse deflections between microcracks, secondary tensile cracks and shear bands inhibit the fracture process, thus enhancing the overall fracture resistance.

Based on these micro-fracture mechanisms, we propose the micromechanical model schematically illustrated in Fig. 15. As the amorphous matrix is tougher than CuZr martensitic particles (Fig. 12), the CuZr particles transform while under volumetric and shear strain, leading to constraining compressive stresses around them (Fig. 15a). Surface relief and microcracking along the martensite/parent interfaces materialize as a result of stress concentrations induced by the martensitic transformation; such constrained microcracks do not enter the macroscopically brittle (amorphous) matrix, but rather contribute to the ductility by aiding the relief of local stress concentrations as a form of inelasticity (Fig. 15b). Further, the interactions between microcracking, secondary tensile cracks and shear bands create a series of micromechanical events which can serve to hinder the fracture process (Fig. 15c). Accordingly, if we revisit Fig. 12, the monolithic metallic glass matrix, which is intrinsically brittle, can be seen to display significant (compressive) ductility due to the inclusion of an appropriate volume fraction (close to the percolation threshold) of crystalline, yet brittle, CuZr particles; these particles further induce a significantly enhanced plasticity through the stress-induced martensitic transformation, as shown by the green area in Fig. 12a.

5. Implications and outlook

The current glassy particulate-reinforced composites may offer particularly sound resistance to thermal shock as microcrack-toughened materials are reportedly preferable under these conditions (Becker, 1981; Lu and Fleck, 1998; Swain, 1990), especially where high retained strength is important. Moreover, another source of fracture resistance in these materials is via interface delamination and the resulting zig-zag paths of the crack, with incumbent extrinsic toughening from crack deflection.

Although microcracking and microcrack deflection can be potent toughening mechanisms in shape-memory matrix composites, the crystallographic dependence of the kinetics of microcrack growth in these alloys certainly requires further investigation. The orientation and size distribution of the microcracks is strongly dependent on the crystallographic orientation of the CuZr crystallites. The ultimate objective here would be to tailor the microcrack size, density and distribution in a controlled manner to achieve optimal mechanical properties.

Finally, our experimental observations have shown that the salient role of microcracking and microcrack deflection in these materials evolves from micro-scale interactions between the microcracks and shear bands. Nanoscale structural heterogeneities in...
bulk-metallic glasses, such as liquid-like sites or soft-zone defects, are also known to have a profound effect on their mechanical behavior (Brechtl et al., 2020; Li et al., 2015). The interactions between such atomistic-scale heterogeneities within the tougher amorphous matrix and microcracking induced by martensitic transformation of constrained reinforcements presents an interesting area for future investigation.

6. Conclusions

Based on an experimental study of Cu\textsubscript{51.5}Zr\textsubscript{48.5} shape-memory metallic-glass composites subjected to uniaxial compression, the following salient conclusions can be made:

1. The size and distribution of the shape-memory CuZr particulate phase is quite random and hard to control. The compressive yield strength, maximum strength, Young’s modulus generally obey a rule-of-mixtures relationship, as found in many composites. The fracture strain, however, exhibits distinctly non-linear behavior. Nonetheless, this composite material, which comprises nominally brittle CuZr particles embedded in a brittle glassy matrix, can display considerable compressive ductility approaching ~10\% strain when the volume fraction of shape-memory phase reaches ~30\%.

2. Significant microcracking was observed during deformation; these microcracks generally initiated at the martensite/parent interface during the \textit{in situ} martensitic phase transformation of the CuZr particles. Such debonding of the martensite/parent interfaces serves to mediate the localized stress concentration, therefore contributing to the overall plastic strain.

3. As the microcracks formed at the martensite/parent interfaces occur within CuZr particles, which are constrained by the dilation associated with the martensitic transformation, these microcracks tend to not enter the amorphous matrix which would result in sudden catastrophic fracture. Moreover, the microcracks inside the CuZr particles appear to deflect the propagation of major and secondary shear bands.

4. The enhanced ductility of this composite can be described by a synergy of multiple plasticity mechanisms: transformation-induced plasticity, microcrack-mediated plasticity and microcrack deflection, or combinations thereof. The optimization of the above energy-absorbing mechanisms strongly depends on the crystallography of martensitic transformation, which requires further in-depth investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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Appendix A. Supplementary data

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