Metal frame reinforced bulk metallic glass composites

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ABSTRACT

Inspired by the aseismic structure of skyscrapers, Ti6Al4V frames with tubular structure were designed, 3D printed and thermoplastic formed with Zr35Ti30Be26.75Cu8.25 bulk metallic glass matrix under ultrasonic vibration, forming sandwich-structured bulk metallic glass composites. The interface characterization between matrix and frame reveals a typical metallurgical bonding. By tuning the geometry of Ti6Al4V frame, the composites manifest an enhanced fracture toughness of 213 MPa m\(^{1/2}\), 2.3 times higher than that of the monolithic bulk metallic glass. Our findings provide a promising route for the development of metallic composites.

Highlights

- Our findings providing a promising route for the fabrication of strong-and-tough BMG composites.
- Metallurgical bonding was achieved at the interface between BMG matrix and the Ti6Al4V frame.
- By tuning the geometry of Ti6Al4V frame, the BMG composites exhibited high fracture toughness of about 213 MPa m\(^{1/2}\) and a bending strength of about 1 GPa.

IMPACT STATEMENT

A promising route for the design and fabrication of bulk metallic glass composites with tailored mechanical properties was developed by combing ultrasonic vibration-assisted thermoplastic forming and 3D printing.

1. Introduction

Bulk metallic glasses (BMGs) display a plethora of desirable mechanical, chemical and physical properties [1,2]. However, the plastic deformation of BMG always localizes in very narrow shear bands of \(\sim 10\) nm in thickness [3], which tends to evolve into open cracks and catastrophic broken at ambient temperature [4,5], severely hampering their industrial applications. To impede the catastrophic failure, ductile phases were generally introduced into BMGs to form BMG matrix composites, hindering the extension while encouraging the proliferation of shear bands.

In general, there are two pathways to synthesize BMG composites. (i) ‘In situ’ precipitation of crystalline phases. Hays et al. [6] for the first time prepared an in-situ Zr-based BMG composite consisting of ductile \(\beta\)-(Ti–Zr–Nb) phase dendrites, which exhibited an extended plasticity \(\sim 7\)%. By controlling the dendrite size and inter-dendrite spacings, Hofmann et al. [7] fabricated a series of dendrites reinforced Zr-based BMG...
composites that exhibit a pronounced tensile ductility > 10% and a fracture toughness as high as 170 MPa m^{1/2}. Utilizing the transformation of metastable B2-CuZr phase to martensite B19′ phase during the loading process, Wu et al. [8] fabricated a B2-CuZr phase reinforced CuZr-based BMG composites, which even exhibits work-hardening under tensile loading. Qiao et al. established a quantitative tensile model [9] to elucidate the respective contribution of dendrites and BMG matrix in the ductility of in-situ dendrites reinforced BMG composites, and derived an universal Hall-Petch-like relationship [10] which reveals the strengthening effect of dendrites on the composites. Although a series of in-situ BMG composites with high-performance have been developed, the spatial distribution of crystalline phases remains tough to control [11,12], which limits the reliability and stability of BMG composites.

(ii) ‘Ex-situ’ addition of crystalline phases. With the melt infiltration casting method, particulates (WC and Ta) [13] and fibers (ceramic and metallic fibers) reinforced BMG composites [14] have been prepared with varying mechanical properties depending on the reinforcement. For example, the Mo particulate reinforced Mg-based BMG composites [15] exhibited a fracture toughness of ~ 50 MPa m^{1/2}; compared with the W fiber reinforced Zr-based BMG composite (~ 65 MPa m^{1/2}) [16], the Ta fiber with better plasticity led to a more excellent fracture toughness ~ 109 MPa m^{1/2}. In addition to discrete reinforcements, BMG composites containing continuous reinforcements, i.e. interpenetrating phase composites, such as porous tungsten [17], porous SiC [18], and porous Ti [19] reinforced BMG composites, have also been developed and exhibit exciting mechanical properties, e.g. high strength and high plasticity. The ex-situ pathway demands an excellent combination between BMG matrix and secondary crystalline phase; otherwise, the existence of impurities, oxides, and voids, on the interface of BMG matrix/crystalline phase will profoundly deteriorate the mechanical properties of BMG composites [11].

To the above situation, we report a series of Ti6Al4V frame reinforced Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25} BMG composites. Here, the structure of Ti6Al4V frame with tunable structure was designed in accord with the aseismic structure of skyscrapers [20] that exhibits excellent resistance to fracture. An ultrasonic vibration-assisted thermoplastic forming technique [21] was introduced to extrude the Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25} BMG into the internal space of Ti6Al4V frame, which enables metallurgical bonding at the interface between two phases through ultrasonic welding [22]. The fracture toughness of the BMG composite was measured as 213 MPa m^{1/2}, i.e. 2.3 times higher than that of monolithic BMG (80 MPa m^{1/2}).

2. Materials and methods

A Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25} (at.%) BMG [23] with excellent anti-oxidation capability, thermal stability, and thermoplastic formability was chosen as the matrix. BMG plates of 15 mm in length, 8 mm in width, and 1.5 mm in thickness were used for thermoplastic forming.

As illustrated in Figure 1(a), compared to rigid frames and interacting systems, tubular systems, i.e. frame 1# and 2 # exhibit superior seismic resistance in high-rise buildings [24]. We chosen this geometry and selected Ti6Al4V alloy to fabricate frame, because (i) Ti and Zr are infinitely miscible without the formation of brittle intermetallics; (ii) Ti6Al4V alloy exhibits excellent corrosion resistance, low density (4.5 g/cm³), high specific strength (1 GPa), and a tensile fracture stain ε > 20% [25]. For the superiority of 3D-printing in manufacturing complex structures, Ti6Al4V frames with a length of 15 mm, a width of 8 mm and a thickness of 10 mm were prepared by selective laser melting on a BLT S200 equipment (from Xi’an Bright Laser Technologies Co., Ltd, BLT). The frame was built from the commercial Ti6Al4V powders of a diameter of 15–53 μm. For thermoplastic forming, the frames were wire-cut into two kinds of slices of 0.5 and 1.5 mm in thickness, respectively.

In the thermoplastic forming process, the frame and BMG plates are positioned as BMG-(Ti6Al4V frame)-BMG, as illustrated in Figure 1(b). After ultrasonic vibration-assisted thermoplastic forming, the BMG was extruded into the internal space of the frame. A homemade ultrasonic vibration generator with a frequency of 20 kHz was adopted for thermoplastic forming. As illustrated in Figure 1(c), two YP5020-4D ultrasonic transducers, two ultrasonic step horns and a special TJS-3000 porous sonotrode (From Hangzhou Success Ultrasonic Equipment Co., Ltd., Hangzhou, China) were used. A cylindrical ultrasonic horn was connected to the porous sonotrode, which converts the horizontal vibrations generated by the ultrasonic transducers into vertical vibrations. The forming temperature was 643 K (an incubation time of 300 min for crystallization). The temperature fluctuation was less than ±1 K. The prepared BMG composite is of 15 mm in length, 8 mm in width, and 2 mm in thickness.

The samples for 3-point notched-beam bending test were of 15 mm in length, 3.2 mm in width, and 1.6 mm in thickness. The notch is of a ‘U’-shape of 300 μm in root diameter and 1.6 mm in depth. To capture both elastic and plastic contribution from deformation and crack
Figure 1. Schematic on the fabrication of frame reinforced BMG composites. (a) Geometries of the frame, (b) assembly of BMG plates and the frame for thermoplastic forming, the inset is the magnification of Area ‘A’ and (c) ultrasonic vibration-assisted thermoplastic forming.

growth, for the small sample size, the fracture toughness of BMG composites $K_J$ using the standard mode I $J-K$ equivalence relationship [26],

$$K_J = \sqrt{JE'} = \sqrt{1.9A_{tot}E/(1 - \nu^2)Bb},$$

where $E' = E/(1 - \nu^2)$, $E = 90$ GPa is Young's modulus, and $\nu = 0.37$ is the Poisson ratio of the Zr$_{35}$Ti$_{30}$Be$_{26.75}$Cu$_{8.25}$ BMG [27]. $J$ is the $J$-integral and a function of the crack propagation distance ($\Delta a$). $A_{tot}$ is the total area under the load-displacement curve, including both the elastic and plastic contributions to the loading work, $B$ is the thickness of the specimen, and $b$ is the uncracked height of the specimen.

3. Results and discussion

Figure 2(a) represents a sketch of the Ti6Al4V frame reinforced BMG composite. Figure 2(b) shows the fabricated BMG composite. As a whole, the BMG matrix combined with Ti6Al4V frame without an obvious gap. To examine the bonding between BMG matrix and Ti6Al4V frame, a section of the interfaces (‘S1’ in Figure 2(b)) were magnified, as seen in Figure 2(c). The BMG and frame integrate
Figure 2. The fabricated frame reinforced BMG composites. (a) Schematic illustration, (b) interface of BMG composites, (c) close-up on S1 in (b) and (d) elements distribution along ‘L1’ in (c).

tightly on the interface after ultrasonic vibration-assisted thermoplastic forming, which is clearly different from the case observed after merely thermal co-pressing without the application of ultrasonic vibration which shows obvious gaps [28]. Elements distribution across the interface along Line L1 in Figure 2(c) reveals a clear transition zone of 1 μm in width, as shown in Figure 2(d), indicating the atomic interdiffusion and suggesting the metallurgical bonding between BMG matrix and the frame.

To verify the metallurgical bonding, the area S2 in Figure 2(c) was selected for TEM observation as provided in Figure 3. Figure 3(a) shows a tight connection between BMG matrix and the Ti6Al4V frame on the bright-field image. The diffraction pattern from area C1 represents a typical single crystal with a zone axis along [0001] indicating the side of Ti6Al4V. On the other side, no crystalline diffraction pattern from area C2 was observed, indicating the BMG matrix. By magnifying the area in Square S3 in Figure 3(a), as displayed in Figure 3(b), an interlayer at the interface between the BMG matrix and the Ti6Al4V frame can be observed. The element distributions along Line L2 are shown in the inset, indicating a transition zone of 60 nm in thickness.

Region C3 was further characterized by HRTEM, as shown in Figure 3(c). The boundaries of an interlayer of about 60 nm in thickness can be clearly detected, as marked with the dashed lines. The areas marked with 1, 2, 3 were also magnified. Area 1 shows crystalline grains. Area 3 is purely amorphous. Area 2 comprises lattice stripes and labyrinth pattern, confirming the coexistence of amorphous phase and crystalline phase in the interlayer. The diffraction pattern taken from the interlayer (area C3) is shown in Figure 3(c) inset. A halo ring can be observed, indicating that the interlayer contains amorphous phase. Debye rings corresponding to the crystalline lattice of hcp-Ti (d1 = 0.25 nm, d2 = 0.18 nm, d3 = 0.153 nm, d4 = 0.125 nm) were also observed. Besides, some spots are located inside the halo ring (indicated by the arrows). The diffraction pattern from C3 suggests the existence of much finer nanocrystals of intermetallic compound dispersed in the interlayer. Inverse Fast Fourier Transform (IFFT) was performed in region S4, as shown in the insert. Clear lattice fringes with spacings of 0.215 and 0.189 nm suggest that the nanocrystals are the AlTi2Zr phase. These results demonstrate the metallurgical bonding between BMG and Ti6Al4V frame.

Figure 4 describes the fracture toughness $K_I$ and bending strength of the BMG composites, and the inset shows the fixture of 3-point bending. The monolithic BMG (without adding Ti6Al4V frame) exhibits a fracture toughness of approximately 80 MPa m$^{1/2}$ and a bending
strength of about 780 MPa, consistent with previous works [27]. However, by adding 1-layer Ti6Al4V frame (frame #1 with a thickness of 0.5 mm, representing the rigid frame in Figure 1), the fracture toughness of BMG composite increases to \( \sim 110 \text{ MPa m}^{1/2} \), and the bending strength increases to \( \sim 930 \text{ MPa} \). For the BMG composite reinforced with 2-layers Ti6Al4V frame (frame #1 with a thickness of 1.5 mm), the fracture toughness markedly increases to 185 MPa m\(^{1/2}\), and the bending strength increases to 980 MPa. Moreover, with the Ti6Al4V frame changing from frame #1 into frame #2 (honeycomb), the fracture toughness further increases to 213 MPa m\(^{1/2}\), which indicates an increment of 170% compared with monolithic BMG (85 MPa m\(^{1/2}\) [27]), and the bending strength also increases to \( \sim 1030 \text{ MPa} \).

The cracking paths were provided in Figure 5(a–c). For monolithic BMG, it can be clearly seen that a main crack initiates from the root of the notch and propagates without conspicuous deflection. The specimen surface is smooth and no shear band generates during the fracture, which demonstrates a catastrophic fracture and a low fracture toughness. In Figure 5(b), for the BMG composite that contains 1-layer Ti6Al4V frame #1 which represents the rigid frame in Figure 1(a), along the main crack, crack deflections can be clearly detected, as marked by the red arrows. A number of shear bands can also be observed on the two sides of the main crack, indicating the plastic deformation around the crack tip during fracture. These phenomena suggest the enhanced resistance of BMG composite to fracture, i.e. an increased fracture toughness. Figure 5(c) shows the surface of the BMG composites containing 2-layers Ti6Al4V frame #2 which is of the tubular structure. As a whole, more crack deflections can be observed along the main crack. Increased number of shear bands along the two sides of the crack are displayed, suggesting the advantages of the tubular structure in resisting fracture, compared to Figure 5(b).
As indicated by the arrows in the inset C4, the shear bands intersect with each other and tend to branch and deviate during their propagation, indicating more conspicuous plastic deformation around the crack tip during fracture. More importantly, as shown in C5, dimples and slip bands are observed on the Ti6Al4V frame, suggesting that the Ti6Al4V frame also affords considerable plastic deformation during the crack propagation process and enhances the fracture toughness [10]. The deflection of cracks and the deformation of the frame explain the significantly increased fracture toughness of the BMG composite reinforced with 2-layers frame #2.

The fractographies of monolithic BMG and BMG composite were displayed in Figure 5(d,e). As shown in Figure 5(d), for monolithic BMG, the fracture surface contains three regions [29]: (i) a shear offset region where shear bands-mediated plastic flow originates from the notch root; (ii) a craggy region where a crack initiates and grows inside a dominant shear band with Taylor’s fluid meniscus instability criterion being satisfied,
producing ‘vein-like’ patterns (S5) that run perpendicular to the notch; and (iii) a smooth region generated by the catastrophic crack propagation with the formation of numerous tiny dimple patterns. As to the BMG composite, the fracture surfaces of the composite containing 1-layer Ti6Al4V frame #1 were characterized. This is because the frame is totally wrapped by BMG in this composite, wherein the fracture surfaces would provide more information on the effect of the frame on the fracture of BMG. As displayed in Figure 5(e), the fracture surface first shows a shear-off region near the notch root followed by a propagation region which displays vein-like patterns similar to what was observed in monolithic BMG, indicating that the fracture of this area is still caused by the shear banding of BMG. Then, the crack propagates near and encounters the Ti6Al4V frame. Interestingly, compared to monolithic BMG in Figure 5(d), Figure 5(e) shows that the propagation region of BMG composites is separated by smooth regions. This is because of the impeding effect of the Ti6Al4V frame on shear banding mediated crack propagation [9]. When the main crack broke through the frame as shown in the inset S6, it propagated gradually fast, leading to the formation of the smooth regions, as can be observed in the areas behind the frame. When the crack propagated near the frame and was blunted, the propagation of crack was slowed down, leading to the formation of propagation region. The fracture surface of Ti6Al4V frame with dimples and pulling-out characteristic (see the inset C6) which suggests a typical ductile fracture, also indicates that the Ti6Al4V frame played a tremendous role in hindering crack extension during the fracture.

4. Conclusions

In summary, assisted by ultrasonic vibration-assisted thermoplastic forming, Ti6Al4V frame reinforced BMG composites with metallurgical bonding at the interface were successfully prepared. The fabricated Zr-BMG composites exhibited conspicuously enhanced fracture toughness, for the existence of Ti6Al4V frame which proliferates multiple shear bands and deflects the propagation of cracks. Combining ultrasonic vibration-assisted thermoplastic forming with 3D printing provides a promising route for the fabrication of BMG composites.

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Disclosure statement

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