Toughening 3D-printed Zr-based bulk metallic glass via synergistic defects engineering

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ABSTRACT
3D printing provides a novel approach to fabricate bulk metallic glass components without limitations in size and geometry. However, defects (porosity and partial crystallization) are inevitable, which are detrimental to mechanical properties. The present work shows that by careful control of these defects in a 3D-printed BMG (Zr_{60.14}Cu_{22.31}Fe_{4.85}Al_{9.7}Ag_{3}), a promising combination of high strength (1.8 GPa), and fairly good plasticity (> 1%) and fracture toughness (∼ 45 MPa m^{1/2}) can be achieved via utilizing the strengthening effect (nanocrystalline precipitation) and toughening effect (micropores-induced shear banding). The results indicate that the mechanical properties of 3D-printed BMGs could be tailored by the defect engineering strategy.

IMPACT STATEMENT
A promising combination of high strength, and fairly good plasticity and fracture toughness is achieved in 3D-printed bulk metallic glasses via a novel strategy, namely synergistic defect engineering.

Introduction
Bulk metallic glasses (BMGs), a new type of metallic material, have attracted considerable interest due to their disordered atomic structure and unique properties [1–3]. However, the current preparation of BMGs mainly relies on the conventional casting methods [4], imposing the limitation of the size and geometries. In recent years, additive manufacturing (AM), especially selective laser melting (SLM), seems to break through the limitations and could fabricate BMG components with big size and complex geometries [5–8]. Unfortunately, almost all the 3D-printed BMGs prepared by SLM exhibit limited plasticity and fracture toughness, which are even worse than their cast counterparts, due to the introduction of various kinds of defects (e.g. pores, impurity, crystallization, and micro-cracks) during SLM process [9–13]. For example, Bordeenithikasem et al. [11] reported that the involvement of porosity of 0.04% in the printed Zr_{59.3}Cu_{28.8}Nb_{1.5}Al_{10.4} BMG leads to zero plasticity, while Best et al. [13,14] argued that the inclusion of a small number of oxide impurities could significantly reduce the fracture toughness. In addition, partial crystallization in the heat-affected zone (HAZs), which is another kind of defect, was also found to be harmful to both strength and plasticity in the SLMed Zr_{55}Cu_{45}Ni_{10} Al_{10} BMG [10]. Therefore, extensive efforts have been devoted to reducing or eliminating these defects to improve the mechanical properties of 3D-printed BMGs.

In fact, defects do not necessarily deteriorate the mechanical properties of BMGs. For example, by introducing micropores, tensile ductility can be achieved...
in a Zr$_{35}$Ti$_{30}$Cu$_{7.5}$Be$_{27.5}$ BMG due to the interaction between the micropores and shear bands [15]. Notably, it is reported that the yield strength of 3D-printed Zr$_{50}$Ti$_{35}$Cu$_{27}$Ni$_{10}$Al$_8$ BMGs could be enhanced by in situ precipitation of nanocrystals in HAZs [16]. These works indicate that manipulation of defects can be a potential route in tuning mechanical properties of 3D-printed BMGs. Therefore, in the present work, we proposed a new concept of synergistic defects engineering, i.e. by carefully and simultaneously controlling porosity and crystallinity, to achieve a good strength-plasticity/toughness combination in a 3D-printed Zr$_{60.14}$Cu$_{22.31}$Fe$_{4.85}$Al$_{9.7}$Ag$_3$ BMG. The underlying mechanism for the enhancement of plasticity and toughness by this synergistic effect of defects is discussed.

**Materials and methods**

Gas atomized powders (< 60 μm) of the pre-alloyed Zr$_{60.14}$Cu$_{22.31}$Fe$_{4.85}$Al$_{9.7}$Ag$_3$ (at%) were used as the feedstock. SLM experiments were conducted with a commercial machine (FORWEDO LM-120, Forwedo) equipped with a Nd: YAG fiber laser device. The laser has a wavelength of 1.06 μm, maximum power of 500 W, and a spot diameter of 80 μm. A strategy of scanning direction of 90° alternatively among layers was adopted to reduce residual stress. The chamber of the SLM machine was vacuumed firstly, then filled with high-purity argon gas to keep the oxygen content less than 100 ppm during SLM process. To investigate the effect of defects on mechanical properties, a set of experiments with various energy densities ($E = P_v h t$ [17], where $P$ is the laser power, $v$ is the scanning speed, $h$ is the hatch spacing and $t$ is the powder layer thickness) were conducted, as the two types of defects, i.e. porosity and crystallization fraction, can be adjusted by the applied energy density. The process parameters, such as layer thickness ($h = 60 \mu m$) and hatch distance ($t = 100 \mu m$), were kept to be constant, while scanning speed and laser power were varied (i.e., $v = 1000–1800 \text{ mm/s}$, $P = 120–260 \text{ W}$).

The microstructure of the 3D-printed samples under different energy densities was examined by X-ray diffraction (XRD, 7000SX, Shimadzu), scanning electron microscopy (SEM, FEI Sirion 200), and transmission electron microscopy (TEM, FEI Tecnai G20, 300 kV). The fraction of crystallinity of the printed samples was determined by differential scanning calorimetry (DSC, TA Q2000). The relative mass density of the 3D-printed samples was measured using the Archimedes principle. The density of the as-cast sample (i.e. $6.67 \pm 0.01 \text{ g/cm}^3$, also measured with Archimedes principle) was set as the reference. The crystallization fraction of 3D-printed samples was obtained by comparing the crystallization enthalpy of the 3D-printed samples with that of the reference amorphous powders [18]. The strength and plasticity of the 3D-printed BMGs were measured by uniaxial compression test at a strain rate of $10^{-4} \text{ s}^{-1}$ using a Zwick machine (Zwick/Roell 020). The strain rate was controlled by the displacement rate of the crosshead, referring to the elastic part. The true strain was calculated by the formula: $\varepsilon_{\text{true}} = -\ln(1-\varepsilon_{\text{engineering}})$.

The compression specimens have the dimension of $\varphi 2 \text{ mm} \times 4 \text{ mm}$. The fracture toughness was evaluated via a three-point bending test, and the samples have dimensions of $2 \times 4 \times 20 \text{ mm}^3$ with all surfaces being mechanically polished to a mirror finish. The span was set to be 16 mm, the roller diameter is 2 mm, and the notch depth was half of the sample height with a root radius of approximately 230 μm. The $K_q$ toughness was calculated using the equation [19]:

$$K_q = \frac{PS}{BW^{3/2}} F(a/W)$$

where $P$ is the fracture stress, $S$ is the span between the two support rollers, $B$ is the specimen thickness, $W$ is the specimen width, $a$ is the notch depth and $F(a/W)$ is a configuration correction factor. At least three tests were repeated for each sample to verify the accuracy of the data. Finite element modeling (FEM) simulation was conducted to study the stress/strain distribution in the samples containing various amounts of defects upon compression and three-point bending, and the details of the simulations are described in Figure S1 and Supplementary Note 1 in the Supplementary Materials.

**Results and discussion**

Figure 1(a) shows the XRD curves of a few SLMed BMG samples prepared using different energy densities. It can be seen that the structure of the printed samples is closely related to the energy densities applied. Nearly fully amorphous structure is obtained when energy density is below 36.67 J/mm$^3$, while partial crystallization occurs when energy density reaches 43.33 J/mm$^3$, as indicated by the appearance of a few weak diffraction peaks. Quantitatively, the proportion of the crystalline phase in 3D-printed samples was measured by DSC. Figure 1(b) shows the typical DSC curves of the amorphous powders and a few SLMed samples under different energy densities. The summary of the crystallization fraction under different energy densities is shown in Figure 1(c). The crystallization fraction is below 8.38% when the energy density is in the range of 14.29–26.67 J/mm$^3$, and increases to 18.12% when the energy density is higher.
Figure 1. (a, b) XRD and DSC results of the SLMed Zr_{60.14}Cu_{22.31}Fe_{4.85}Al_{9.7}Ag_{3} BMG samples fabricated using different energy densities, compared with the original powders; (c) Correlation between the crystallization/porosity fractions of as-printed samples and the energy density; (d) The bright field TEM image of the as-printed BMG with a crystalline fraction of 7.03%. Insets are the selected area electron diffraction (SAED) patterns from regions S1 and S2, respectively; (e) SEM images showing the samples with various porosities.

than 36.67 J/mm^3. A representative crystalline region (i.e. HAZ) in a printed BMG sample prepared under 19.05 J/mm^3 is shown in Figure 1(d), where spherical-like nanocrystals with diameter ranging from 50 to 200 nm are randomly distributed in the HAZ region (1.83 μm in width). The nanocrystals can be indexed as Al2Zr intermetallic compound based on the selected area electron diffraction (SAED) pattern (see insets of Figure 1(d)). The molten pools are fully amorphous as expected, due to the fast cooling rate achieved in SLM process.

The porosity of 3D-printed BMGs can be also adjusted by changing the energy density, as illustrated in Figure 1(c). The porosity decreases linearly from 17.4% at the lowest energy density of 14.29 J/mm^3 to 3.38% at a modest energy density of 16.67 J/mm^3. Further increase of energy density could lead to very low porosity (~0.67%). Figure 1(e) shows the typical cross-sectional SEM micrographs of three samples prepared under the energy density of 19.05, 16.67 and 14.29 J/mm^3, which have the porosity of 2.87%, 8.47% and 17.40%, respectively. In addition, the size and distribution of pores in the 3D-printed BMGs with low porosity were evaluated by X-ray tomography (XRT). It was found that the pores distribute randomly in the whole sample and most pores have a size of 10–30 μm, and both size and distribution of pores do not show significant difference in the samples with low porosity. These results demonstrate that both the porosity and crystalline fraction could be well adjusted by controlling the energy density, and the trend of the porosity and crystallization is opposite with the increase of energy density (Figure 1(c)).

Compressive stress–strain curves for the 3D-printed BMGs with varying porosity and crystalline fractions are shown in Figure 2(a). The results of yield strength (σ_y), fracture strength (σ_f) and plasticity (ε_f) are summarized in Table S1. In Figure 2(a), the change of mechanical properties in terms of fracture strength and plastic strain can be roughly divided into two regimes, i.e. the crystallization-controlled regime and porosity-controlled regime. In the former, the strength increases gradually with the decrease of crystallization fraction, and the plasticity in this regime is nearly zero. It is worthy of noting that, when the crystalline fraction is between 4% and 7%, the strength of the SLMed BMG samples is enhanced with the increase of crystalline phase, as shown
Figure 2. (a) Compressive stress-strain curves and (b) fracture toughness of the SLMed BMG samples with varying porosity and crystallization fractions.

In Table S1. In the porosity-controlled regime, the plasticity increases with increasing porosity. For example, the plastic strain increases from 1.05% to 6.6% as the porosity increases from 2.87% to 17.4%. Notably, even though the fracture strength starts to decrease when the porosity is higher than 5.36%, the 3D-printed BMG still has a strength of 1100 MPa when the porosity reaches 17.4%, this strength value exceeds that of most 3D-printed high-strength alloys reported so far [20].

The notch fracture toughness ($K_q$) of the as-printed BMG samples with different porosities and crystallization fractions were also measured by a three-point bending test, and the results are presented in Figure 2(b). Similar to the trend in Figure 2(a), the fracture toughness can be tailored by controlling the crystallization fraction and porosity, which also fall into two distinct regimes. In the left regime where the porosity is below 2.87%, increasing porosity leads to the enhancement of fracture toughness. For instance, when the porosity increases from 0.67 to 2.87%, and simultaneously the crystallization fraction decreases from 23.37% to 7.03%, the $K_q$ value increases from approximately 30 to 45 MPa m$^{1/2}$. In contrast, in the right regime where the porosity is above 2.87%, the toughness decreases with the increase of porosity even though the crystallization fraction is kept at a low level ($\sim$6.65%). The decrease of toughness in the right regime is attributed to the decreased strength of the high-porosity samples although the plasticity is increased with porosity in this regime. Notably, when the porosity is higher, e.g. at 8.5%, some irregular pores in addition to the round pores appear (as shown in Figure 1(e)), which cause more severe stress concentration near the notch, further deteriorate the fracture toughness.

The above results demonstrate that the mechanical properties of the 3D-printed BMGs can be adjusted by controlling porosity and crystallization fraction. The printed BMGs can be strong and tough if these two defects have a good collocation. For example, the sample with crystallization fraction below 4.1% and porosity around 17.4% exhibits the highest plasticity (a plastic strain of 6.5%) and pretty good strength (1.1 GPa) (see Figure 2(a)). To understand the mechanism of how porosity enhances plasticity, the sample with a porosity of 17.4% was carefully examined after deformation. To clarify how the pores affect shear banding during deformation, this sample was further subjected to compression test, in which a part of the side surfaces of the as-printed rod was first polished to a mirror finish (to help to see the interaction between pores and shear bands), then compressed to fracture. Figure 3(a,b) show that a large number of shear bands initiated around the pores. This likely results from the stress concentration around pores, which promotes the proliferation and propagation of shear bands. To correlate the porosity and shear band dynamics, we have made a statistical analysis of the serrations (i.e. stress drops, see the inset of Figure 3(c)) in the stress–strain curves. Generally, the stress drop magnitude reflects shear band stability, i.e. a smaller stress drop indicates a more homogeneous plastic flow, and vice versa [21]. Figure 3(c) shows the cumulative probability of stress drop as a function of porosity in the
Figure 3. (a, b) Cross-section SEM images showing the interactions between micro-pores and shear bands; (c) The cumulative probability of stress drops for samples with different porosities. Inset shows the enlarged serration region from stress-strain curves; (d, e) Strain field of two BMG samples with a porosity of 2.87% and 17.40% after being compressed to 4% strain in finite element simulation.

different 3D printed BMG samples. It is evident that the higher the porosity, the smaller the stress drop magnitude. Consequently, the high-porosity sample is capable of holding more homogeneous strain and thus better plasticity. This finding is further verified by finite element modeling (FEM) simulations, as displayed in Figure 3(d,e). As expected, the BMG with a higher porosity (e.g. 17.4% porosity) carried higher and more homogeneous plastic strains during compression than the one with a lower porosity (e.g. 2.87% porosity). It is seen that multiple shear bands along different directions are formed in the sample with higher porosity, while only a major shear band is formed in the sample with lower porosity. The simulations are in good agreement with our experimental observations.

As far as the fracture toughness is concerned, the maximum value of $K_q$ (45 MPa m$^{1/2}$) is obtained for the sample with a crystallization fraction of 7.03% and porosity of 2.87%. The high-plasticity sample (with a porosity of 17.4%) does not exhibit an optimized fracture toughness, which could be associated with its relatively low strength because fracture toughness is collectively determined by both strength and plasticity [22]. Therefore, differing from the correlation of plasticity and porosity (i.e. monotonous increase), the fracture toughness can only be optimized with an appropriate combination of porosity and crystalline fraction. As quantitatively illustrated in Figure 2(b) and Figure 4, with the increase of porosity or crystalline fraction, the toughness always increased first and decreased afterward. When the crystalline fraction is between 4% and 7%, and the porosity is between 0.67% and 2.87%, the toughness is enhanced with the increase of porosity and crystallization fraction due to the strengthening effect by crystalline phases and toughening effect by micro-pores. However, once the crystalline fraction is above 7%, the toughness is inversely deteriorated as compared with the optimized one (see Figure 4). Interestingly, this observation is in good consistency with a previous study, which revealed a similar critical crystallization of 7% for the embrittlement in BMGs [23]. The stress concentration between the Al$_2$Zr crystalline phase and the amorphous matrix in the HAZs would become more severe when crystallization fraction is high, leading to ease of crack initiation. Indeed, on the fractured surface, a typical smooth shear-off extension region is observed, which is a result of the discrete notch blunting at the line of intersection of the shear band with the notch root and is associated with the inherent capability of blunting a crack tip to a maximum radius during three-point bending [24]. The width of smooth shear-off extension region ($\Delta L$) reflects the ability against fracture initiation (shown in Figure S2). The trend of $\Delta L$ and crystalline fraction (Figure 4) fully agrees with the dependence of $K_q$ with crystalline fraction, verifying that a high crystalline fraction of above a critical value (e.g. 7%) leads to reduced initiation fracture toughness. Note that, previous works [25–28] demonstrate that the relaxation of amorphous phase may also play a role on the fracture toughness of BMG. Therefore, we also measured the relaxation enthalpy of the SLMed BMGs prepared with different energy densities from DSC curves, and the correlation between relaxation enthalpy and fracture toughness is summarized in Figure S3. This result reveals that, for 3D-printed BMGs, there is no
Figure 4. The relationship between the crystalline fraction and fracture toughness and width of shear-off region.

A correlated relationship between relaxation enthalpy and fracture toughness. For example, the 3D-printed sample with a higher value of relaxation enthalpy (∼7 J/g) exhibits inversely a lower fracture toughness than that with a lower relaxation enthalpy (∼2 J/g). This is different from the case of as-cast BMGs, which do not contain a high level of crystallinity and porosity. Therefore, the major effect on mechanical properties of the 3D-printed BMG is from porosity and crystallinity, rather than relaxation enthalpy (corresponding to free volume), which is possible because pores are mainly the triggers for shear banding, and crystals in HAZs can lead to ease of crack initiation in the 3D-printed BMG.

In the porosity control regime, it is noted that the fracture toughness decreased significantly with the increase of porosity. This is because that tensile stress, which is very sensitive to pores, exists in front of the notch during three-point bending. To confirm the effects of porosity and pore geometry on fracture toughness, we have carried out additional FEM simulations for samples with different pore geometries (e.g. round and rectangle pores) and porosities (2.87–17.4%) during three-point

Figure 5. Plot of fracture strength as a function of plasticity for 3D-printed BMGs and BMG composites. The overall mechanical performance of our optimized materials via defect engineering surpasses that of previously reported 3D-printed BMGs and BMG composites [7,9,10,14,29–41].
bending, and the results are shown in Figures S4 and S5. The simulation results show that the higher the porosity, the lower the load, and the lower fracture toughness, which is in good consistency with our experimental results. In addition, we found that when the porosity is lower than 9%, the pore geometry (e.g. the sharpness) does not affect the load. However, when the porosity is high (17.4%), the presence of rectangle pores could result in a smaller load, i.e. lower fracture toughness, as compared with round pores. Therefore, the presence of rectangle pores (as shown in Figure 1) in the 3D-printed BMG samples has an additional contribution to the reduction of fracture toughness in the high-porosity regime.

Finally, we compare the mechanical properties, in terms of fracture strength and plasticity, of the current 3D-printed BMGs with other reported 3D-printed BMGs and BMG composites [7,9,10,14,29–41], as illustrated in Figure 5. The conventional strategy via defect elimination is indeed able to effectively strengthen the 3D-printed BMGs, but is invalid to increase plasticity. The strategy via composite design, i.e. adding a secondary phase in BMG matrix, can toughen 3D-printed BMGs, but is always at a cost of strength. By contrast, our defect engineering strategy with a proper combination of porosity and crystallization fraction could achieve a good strength-plasticity combination, therefore, offers a different pathway to improve the mechanical properties of 3D-printed BMGs. Nevertheless, achieving a further combination of strength-plasticity-fracture toughness is still challenging, especially for intrinsically brittle BMG materials, which needs further improvement in future for practice applications.

Conclusions

In summary, we proposed a new strategy, namely synergistic defect engineering, to improve the mechanical properties of 3D-printed Zr$_{60.14}$Cu$_{22.31}$Fe$_{4.85}$Al$_{9.7}$Ag$_3$ BMGs. Two kinds of defects, porosity and crystallization, are precisely controlled via changing the energy density. The plasticity is improved significantly when the printed BMGs are with low crystallinity (typically less than 5%) and sufficient porosity (> 2.8%). The fracture toughness is enhanced when the sample contains a moderate porosity (< 2.8%) and crystallinity (< 7%). It is revealed that an appropriate amount of micropores can generate multiple shear bands and increase plasticity; while the synergistic effect of both micropores and partial crystallization can enhance the fracture toughness. Therefore, defect engineering is a promising strategy to achieve a good combination of strength-plasticity/toughness for 3D-printed BMGs.

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Disclosure statement

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