Bulk metallic glass composite with good tensile ductility, high strength and large elastic strain limit

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Bulk metallic glasses exhibit high strength and large elastic strain limit but have no tensile ductility. However, bulk metallic glass composites reinforced by in-situ dendrites possess significantly improved toughness but at the expense of high strength and large elastic strain limit. Here, we report a bulk metallic glass composite with strong strain-hardening capability and large elastic strain limit. It was found that, by plastic predeformation, the bulk metallic glass composite can exhibit both a large elastic strain limit and high strength under tension. These unique elastic mechanical properties are attributed to the reversible B2→B19' phase transformation and the plastic-predeformation-induced complicated stress state in the metallic glass matrix and the second phase. These findings are significant for the design and application of bulk metallic glass composites with excellent mechanical properties.

Though their toughness or ductility is significantly increased, the yield strength and the elastic strain limit of BMGCs are decreased dramatically in contrast to monolithic BMGs15,18,19. Usually, the second phases have a relatively small elastic strain limit (not larger than 1%), which results in the premature yield of the BMGCs. Furthermore, the volume fraction of the soft second phase should be higher than 50% to toughen the MG matrix, which severely decreases the elastic strain limit and the strength of BMGCs14–18. Therefore, second phases are in-situ or ex-situ introduced to reinforce the MG matrices22–11, such as dendrite-reinforced Zr- or Ti-based bulk metallic glass composites (BMGCs)14–18.

In this work, we report a metastable B2 reinforced BMGC (B2-BMGC) with excellent plastic deformation capability under tension. We demonstrate that the B2 phase effectively improves the plastic deformation capability of the B2-BMGC under tension, and the plastic predeformation endows this B2-BMGC with high strength and a large elastic strain limit by reversible B2→B19' phase transformation.
Results

Microstructure of as-cast B2-BMG. Figure 1a shows an optical metallograph of the microstructure of the as-cast B2-BMG. The round and dark particles are B2 crystals, which are homogeneously distributed in the amorphous MG matrix. The average chemical compositions for the B2 phase and the amorphous MG matrix are detected by energy-dispersive spectroscopy (EDS) to be $Zr_{52.1}Cu_{41.7}Al_{3.9}Nb_{2.3}$ and $Zr_{50.7}Cu_{42.2}Al_{4.1}Nb_{3.0}$, respectively. It is clear that the difference between the chemical compositions of the B2 phase and the amorphous MG matrix is very small, which indicates the precipitation of B2 phase from the melt during solidification does not involve strong element diffusion, like that usually occurring in in-situ dendrite-reinforced BMGCs. The volume fraction of the B2 phase is about 32.2% and the average grain size of the B2 particles is $67 \pm 5 \text{ mm}$ in diameter. Figure 1b shows the high-resolution transmission electron microscope (HRTEM) image of the interface between the B2 phase and the amorphous matrix. The electron diffraction patterns show that the disorder region is fully amorphous (see lower left inset in Fig. 1b) and the adjacent region is of long-range order (see upper

Figure 1 | (a) OM metallograph showing the microstructure of the as-cast B2-BMG. The round particles are the B2 phase, and the matrix is amorphous MG. (b) HRTEM image of the interface between the B2 phase and the amorphous matrix. Inset at the lower left corner shows the selected area diffraction pattern of the amorphous structure; the inset at the upper right corner shows the selected area diffraction pattern of the crystalline structure, and the inset at the middle right shows the X-ray diffraction pattern of the B2-BMG.

Figure 2 | (a) Engineering tensile stress-strain curve of the as-cast B2-BMG showing large homogeneous plastic deformation capability. The inset in (a) is the true stress-strain curve of the as-cast B2-BMG showing significant strain-hardening. The error bars were based on standard deviation. (b) cyclic loading stress-strain curves showing large elastic strain limit and nonlinear elasticity for the (I) 10.2%, (II) 12.6%, and (III) 15.0% plastically predeformed B2-BMGs. (c) and (d) Deformation feature of the as-cast B2-BMG after tensile fracture.
right inset in Fig. 1b). The crystalline phase is further confirmed to be B2 phase with a body-centered cubic structure by the use of X-ray diffraction (see middle right inset in Fig. 1b).

**Tensile deformation of as-cast B2-BMGC.** Figure 2a shows the engineering stress-strain curve of the as-cast B2-reinforced BMGC subjected to tensile loading. It is seen that the sample underwent a large homogeneous plastic deformation with a total engineering strain of 22.3% on average (the maximum engineering plastic strain before fracture was 19.3%). Close examination indicates that the stress-strain curve can be divided into four stages. Firstly, the sample undergoes an initial linear elastic stage under relatively low stress. In this region, both the B2 phase and the MG matrix synchronously deform elastically. Secondly, the sample slightly yields at 387 MPa with recoverable elastic strain of about 0.2%. In this region, the MG matrix is still in elastic state, but the B2 phase reaches its yield point and begins to plastically deform. Thirdly, the sample yields apparently at a stress of 1100 MPa and is strain-hardened to more than 1400 MPa at an engineering strain of 17.8%. Fourthly, a small stress decrease starts and is a prelude to the beginning of tensile instability and final fracture. The inset in Fig. 2a is the true stress-strain curve corresponding to the engineering stress-strain curve for the as-cast B2-BMGC. It demonstrates that the as-cast B2-BMGC possesses a strong strain-hardening capability under tension: beginning from the apparent yield stress of \( \sigma_y = 1100 \) MPa, the true stress continues increasing to the fracture strength of 1765 MPa, as seen in the inset of Fig. 2a. The average strain-hardening rate (\( \theta = \frac{d\sigma}{d\epsilon} \)) in the smooth region (true strain between 0.05 and 0.15) is 3366 MPa, and the normalized strain-hardening rate (\( \theta_0 = \theta/\epsilon_0 \)) is 3.1, which is higher than most previously reported BMGCs.

**Elastic response of plastically predeformed B2-BMGC.** Figure 2b shows the true tensile stress-strain curves of the B2-BMGC after plastic predeformation with a total engineering tensile strain of 10.2%, 12.6%, and 15.0%, as marked with cycles I, II, and III, respectively. In this region, the MG matrix is still in elastic state, but the B2 phase yields at 387 MPa with recoverable elastic strain of about 0.2%. In this region, the MG matrix is still in elastic state, but the B2 phase reaches its yield point and begins to plastically deform. Thirdly, the sample yields apparently at a stress of 1100 MPa and is strain-hardened to more than 1400 MPa at an engineering strain of 17.8%. Fourthly, a small stress decrease starts and is a prelude to the beginning of tensile instability and final fracture. The inset in Fig. 2a is the true stress-strain curve corresponding to the engineering stress-strain curve for the as-cast B2-BMGC. It demonstrates that the as-cast B2-BMGC possesses a strong strain-hardening capability under tension: beginning from the apparent yield stress of \( \sigma_y = 1100 \) MPa, the true stress continues increasing to the fracture strength of 1765 MPa, as seen in the inset of Fig. 2a. The average strain-hardening rate (\( \theta = \frac{d\sigma}{d\epsilon} \)) in the smooth region (true strain between 0.05 and 0.15) is 3366 MPa, and the normalized strain-hardening rate (\( \theta_0 = \theta/\epsilon_0 \)) is 3.1, which is higher than most previously reported BMGCs.

**Structural evolution of B2-BMGC during plastic predeformation and elastically reloading.** Figure 3a shows the X-ray diffraction (XRD) patterns of the B2-BMGC during plastic predeformation. For the as-cast B2-BMGC, it shows that a strong diffraction peak (20 = 39.1°) of the B2 phase superimposed in the scattering diffraction peak of the amorphous MG matrix, as seen in Fig. 3a. When plastically predeformed with a total engineering tensile strain of 10.2%, a sharp diffraction peak appears at 20 = 43.8°, which is confirmed to be the B2→B19' phase transformation. After removing the load, the diffraction peak at 20 = 43.8° decreased in intensity, but still existed, implying that the B19' remained although some B19' transformed backwards to B2, as shown in Fig. 3a and 3c. Figure 3b shows the XRD patterns of the plastically predeformed B2-BMGC during elastically reloading. It shows that, with the load increasing, the diffraction peak at 20 = 43.8° was strengthened, which means more of the B2 phase was transformed to the B19' phase. Once the load decreased, the diffraction peak of the B19' phase weakened again, as in its original profile (Fig. 3b). This structural evolution revealed by XRD is consistent with the nonlinear elastic stress-strain behavior of the plastically predeformed B2-BMGC (see Fig. 2b).

**Discussion**

**Large plastic stability of as-cast B2-BMG under tension.** The above results indicate that the as-cast B2-BMGC can undergo large tensile plastic deformation. The plastic strain before fracture is about 19.3%, and the normalized strain-hardening rate (\( \theta_0 = \theta/\epsilon_0 \)) is about 3.1. The prominent tensile plastic deformation capability of the as-cast B2-BMGC can be attributed to the high strain-hardening capability of the B2 phase and its effectiveness in activating multiple shear bands in the MG matrix. It was previously reported that the normalized strain-hardening rate of CuZr-based B2 phase was about 17.4, which is far larger than that of \( \beta \) dendrite in-situ formed in Ti- or Zr-based BMGCs. For instance, the normalized strain-hardening rate of the \( \beta \) dendrite \( \text{Zr}_{72.4}\text{Ti}_{16.3}\text{Nb}_{9.2} \) is 1.7, which is only one tenth of the present B2 phase. From the viewpoint of the microstructure, the B2→B19 phase transformation can produce hierarchical deformation structures with macrotwins, microtwins, stacking fault and dislocation, which yields dense
stress-concentration sites at the interface and can trigger profuse tiny multiple shear bands in the MG matrix.\textsuperscript{24,29,35} Even shear bands excited from one B2 crystal can have different propagation directions and can intersect with each other, as shown in Fig. 2d. Furthermore, these shear bands will propagate forwards and intersects with those excited from the neighbouring B2/MG interfaces. Therefore, the B2 phase is a very effective exciter for the initiation of multiple shear bands in the MG matrix. However, small β dendrites can only excite a few shear bands and can easily cut off by the propagating shear bands. The shear bands around one dendrite almost have the same propagation direction, and their interaction among them is very limited.\textsuperscript{29,36,37}

Large elastic strain limit of plastically predeformed B2-BMGC.Usually, the elastic strain limit of monolithic BMGs is about 2.0%\textsuperscript{38,39}, while the elastic strain limit of classical BMGCs is much smaller than 2.0%.\textsuperscript{17} However, the present plastically predeformed B2-BMGC has a large elastic strain limit of 2.7%. This unique deformation behavior of the B2-BMGC can be explained as follows. Figure 4a schematically shows the loading history of the B2-BMGC during plastic predeformation: lines ON, NG, and GB are the stress-strain curves for the elastic deformation, plastic deformation, and elastic recovery of the MG matrix; lines OM, MH, HD are the stress-strain curves for the elastic deformation, plastic deformation, and elastic recovery of the B2 phase; point C is the final stress balance point after unloading. Both the MG matrix and the B2 phase can be regarded as a parallel connection of two rigid-plastic bodies series-connected with ideal-elastic bodies, as shown in Fig. 4b–I. For the as-cast B2-BMGC, it is assumed that the MG matrix and the B2 phase have the same length. When plastically predeformed to a certain strain, due to the B2 « B19' reverse phase transformation, the B2 phase has a larger elastic strain limit than the MG matrix, while the MG matrix has a larger plastic strain than the B2 phase, due to the plastic strain of the B2 phase, and \( \varepsilon_p^B \) the plastic strain of the B2 phase, as shown in Fig. 4b–II. After plastic predeformation, the external force is removed, and the elastic strain will tend to recover. In an ideal free-standing situation, both MG matrix and B2 phase will recover to the zero stress state, as shown in the red spring in Fig. 4b–III. However, due to the elastic strain mismatch and the mutual constraint, the recovery of the B2 phase will be inhibited by the MG matrix, while the recovery of the MG matrix will be promoted by the recovery of the B2 phase. Therefore, the MG matrix will be in a compressive stress state and the B2 phase will be in a tensile stress state, as shown in the blue spring in Fig. 4b–III. Thus, we have

\[
\varepsilon_c^M + \varepsilon_p^M = \varepsilon_c^B + \varepsilon_p^B. \tag{2}
\]

Here \( \varepsilon_c^M \) and \( \varepsilon_c^B \) are the residual elastic strains in the MG matrix and the B2 phase, respectively. According to the static balance between the MG matrix and the B2 phase, one gets

\[
E_M \varepsilon_c^M + E_B \varepsilon_c^B = 0. \tag{3}
\]

\( E_M \) and \( E_B \) are the elastic modulus of the MG matrix and the B2 phase after plastic predeformation. Substituting Equations (1) and (2) to Equation (3), we get the residual elastic strain in the MG matrix as

\[
\varepsilon_c^M = -\frac{E_B (\varepsilon_c^B - \varepsilon_c^M)}{E_M + E_B}, \tag{4}
\]

and the residual elastic strain in the B2 phase is

\[
\varepsilon_c^B = \frac{E_M (\varepsilon_c^B - \varepsilon_c^M)}{E_M + E_B}. \tag{5}
\]

Obviously, Equations (4) and (5) demonstrate that the residual elastic strain in the MG matrix is compressive, while the residual elastic strain in the B2 phase is tensile. Due to the elastic strain limit of the MG matrix being smaller than that of B2 phase, the elastic strain limit of the B2-BMGC will be decided by the MG matrix. Therefore, when subject to tensile loading, the apparent elastic strain limit of the plastically predeformed B2-BMGC is

\[
\varepsilon_e = \frac{EM (\varepsilon_e^B - \varepsilon_c^M)}{E_M + E_B}.
\]
MG matrix could elastically recover to the zero stress state from the originally compressive stress state. Further loading caused the MG matrix to be in a tensile stress state. Meanwhile, the former B2 phase recovering from B19' in the plastically predeformed B2-BMGC would transform to B19' again. Theoretically, the apparent elastic strain limit of the plastically predeformed B2-BMGC is $\varepsilon_{\text{BC}} + \varepsilon_{\text{BA}} = 0 - 2\% + 2\% = 0 - 4\%$ ($\varepsilon_{\text{BC}} = 2\%$ is an ideal value that cannot be reached unless the B2 phase possesses a high enough strength and superelasticity), as shown in Fig. 4a. Obviously, a large elastic strain limit of about 2.7% for the plastically predeformed B2-BMGC is reasonable.

Figure 5 shows the tensile yield strength-elastic strain limit data from previous reported Cu-, Zr-, and Ti-based BMGCs and the present B2-BMGC. The line $\varepsilon = 2.0\%$ is a typical elastic strain limit for monolithic BMGs. For the previous reported BMGCs$^{15-19,22,42,43}$, they are located on the left of the line $\varepsilon = 2.0\%$. Their elastic strain limit approximately ranges from 1.4\% to 1.9\%, with yield strength ranging from 900 MPa to 1560 MPa. As to the plastically predeformed B2-BMGC, they are shown on the upper right corner of the diagram, and are obviously away from the line $\varepsilon = 2.0\%$, exhibiting a good combination of large elastic strain limit and high strength, as shown in Fig. 5a.

In summary, this study demonstrates that the metastable B2 phase can effectively promote multiple shear bands and thus significantly improve the plastic deformation capability of B2-BMGCs, and plastically predeformed B2-BMGCs can exhibit a large elastic strain limit. These unique mechanical properties are attributed to the reversible B2$\rightarrow$B19' phase transformation and the complicated stress states of the MG matrix and the second phase. This finding implies that the elastic properties of BMGCs can be tailored by carefully choosing the reinforcement, with suitable treatment, and can be potentially used as elastic devices or special elastic structure components in engineering fields.

**Methods**

**MGC alloy production.** The B2-BMGCs with nominal chemical compositions of Zr$_{63}$Cu$_{27}$Al$_{10}$Nb$_{3}$ were prepared by arc melting the elements with purity better than 99.9\%, and by casting into a copper mold. Ingotcs of diameter 3 mm and length 85 mm were produced.

**Microstructure characterization.** The phases of the BMGC ingots were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer (SmartLab) with Cu K$_{\alpha}$ radiation and an in-situ loading unit. The structure of the B2/MG interface was observed under a JEM-2100F high-resolution transmission electron microscope (HRTEM). The microstructure was also examined by using a JEM 6490.
scanning electronic microscope (SEM) and a Carl Zeiss optical microscope (OM). The volume fraction was determined from the OM images.

**Tensile test.** The tensile samples are in a dog-bone shape. Its gauge length is 10 mm and the dimension of the cross-section is 1 x 1 mm². The tensile samples were prepared by the electric spark method. The lateral surfaces of all tensile samples were ground and finely polished using a 1.0 µm diamond paste. Tensile tests were conducted in an Instron testing machine at room temperature, using a constant strain rate of 1 x 10⁻⁴ s⁻¹. In determining the tensile properties of the composite, five tensile samples were tested. Their average values and standard deviations were calculated. The deformed samples were investigated by SEM to reveal the deformation and fracture features.

**Finite element modeling.** Finite element modeling was utilized to undertake stress analysis for the plastic predeformation of the B₂-BMGC. The constitutive equations were directly acquired from the true stress-strain curves of the B₂ and MG matrix. The shear stress, von Mises stress and elastic strain of the B₂ and MG matrix were measured and compared.

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**Author contributions**
F.W. and K.C. designed the study. F.W., S.I., and S.C. conducted the experiments. F.W., K.C., and G.W. analysed the results and wrote the manuscript.

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