Fabrication and Mechanical Properties of Zr46.9Cu45.5Al5.6Y2.0 Metallic Glass In-situ Composite Containing B2-CuZr Phase Postprint

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Abstract

By increasing the diameter of the casting rod to adjust the cooling rate of the melt, in-situ composites with relatively large dimensions can be obtained in Zr46.9Cu45.5Al5.6Y2.0 bulk metallic glass (BMG), wherein spherical B2-CuZr phases with variable volume fractions are uniformly distributed in the metallic glass matrix. For the composite containing 25% B2-CuZr phase (volume fraction), the plastic strain under compressive loading increases from 1.6% for the monolithic metallic glass to 6.5%; however, no obvious ductile strain was observed in the sample under uniaxial tension. Analysis suggests that the intrinsic reason for brittle fracture of the composite under tensile loading is that the grain size and spacing of the CuZr phase do not satisfy the size matching relationship with the plastic zone size of the metallic glass matrix. Adding 2% Y (atomic fraction) to the ZrCuAl alloy severely degrades the fracture toughness and plastic zone size of the metallic glass matrix. Compared with Zr46.9Cu45.5Al5.6Y2.0 BMG, Y-free Zr48Cu45Al7 BMG samples can be pre-cracked with fatigue cracks, and the fracture toughness measured by three-point bending tests is (62$\pm$3) MPa · m1/2, with the plastic zone size at the crack tip reaching up to 150 mm under plane strain conditions.

Full Text

Preamble

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Title

Preparation and Mechanical Properties of Zr46.9Cu45.5Al5.6Y2.0 In Situ BMG Composites with B2-CuZr Phase

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Abstract

Bulk metallic glass (BMG) composites containing B2-CuZr phase are of interest due to their large plastic strain and apparent work hardening in tension. Nevertheless, most BMG composites containing B2-CuZr phase reported to date are based on Cu47.5Zr47.5Al5 or Zr48Cu47.5Al4Co0.5 BMG, which have limited glass forming ability (GFA). The prepared sample sizes are small, restricting their potential engineering structural applications. In this work, the Zr-Cu-Al-Y quaternary system was selected due to its high GFA. By tuning the composition close to CuZr alloy in the Zr-Cu-Al-Y quaternary system, Zr46.9Cu45.5Al5.6Y2.0 BMG was chosen because it has proper GFA (critical diameter Dc=5 mm) and relatively large fracture toughness (K_Q=(49$±3)$MPa\cdot m^{\{1\}/}$\{2\}$). By decreasing the cooling rates of the melt via increasing the diameter of casting rods, large-sized in situ Zr46.9Cu45.5Al5.6Y2.0 BMG composites containing 13% and 25% volume fractions of spherical B2-CuZr phase were prepared in casting rods with 6 mm and 7 mm diameters, respectively. In compression testing, the in situ BMG composites containing 25% B2-CuZr phase promote multiple shear bands within the glass matrix and exhibit remarkable global plastic deformation, accompanied by a large compressive plastic strain of 6.5%. Nevertheless, in tension testing, no obvious global ductility was achieved, which attributes to the low mode I fracture toughness and small plastic zone size (R_P=88 mm, $R_P = (1/3\pi)(K_Q/\sigma_y)^2$) of the glass matrix.

Three-point bending test results show that Y has an adverse effect on the fracture toughness and plastic zone size of Zr-Cu-Al BMGs. In contrast to Zr46.9Cu45.5Al5.6Y2.0 BMG, fatigue pre-cracked Zr48Cu45Al7 BMG plate samples can be prepared and exhibit a high fracture toughness (K_Q=(62$±3)$MPa\cdot m^{\{1\}/}$\{2\}$) and a large plastic zone size (R_P=150 mm) in a plane strain state. Our results show that GFA and fracture toughness of the glass matrix should be balanced when designing new BMG composites containing B2-CuZr phase.

KEY WORDS bulk metallic glass, composite, B2-CuZr, fracture toughness

Introduction

Unlike conventional crystalline metallic materials, bulk metallic glass (BMG) has attracted attention as a new class of structural material due to its high strength, high elastic limit, and excellent corrosion resistance. However, one bottleneck limiting BMG applications is strain localization, which leads to catastrophic fracture under tensile loading due to the instability of a single shear band. One approach to improve the plastic deformation capability of monolithic BMG is to introduce a second phase to form BMG composites, which can obtain plastic strain through the delocalization of shear bands and promotion of multiple shear band formation. Therefore, in situ BMG composites with good interfacial bonding between the matrix and second phase are more favorable for plastic deformation.

Hays et al., Szuecs et al., and Hofmann et al. first developed in situ BMG composites with large tensile ductility in Zr-based and Ti-based systems, but these alloys contained toxic Be element, and the plastic deformation was limited to inhomogeneous plastic deformation (necking) without overall work hardening capability. In addition to β-phase solid solution as the second phase, composites containing CuZr phase can also be formed in ZrCu-based BMGs. Sun et al. found that BMG composites containing B2-CuZr phase can exhibit large compressive plastic deformation under compressive loading. Notably, compared with other structurally complex intermetallic compounds, B2-type compounds are more prone to plastic deformation and can serve as a soft phase in BMG composites, inducing shear band initiation at low stress and hindering shear band propagation at high stress, thereby promoting the formation of multiple shear bands in the metallic glass matrix. For example, Mg-based BMG composites with in situ B2-AgMg phase show superior plasticity and toughness compared to monolithic Mg-based BMG.

The B2-structured CuZr is stable in the temperature range between its melting point and 988 K. When slowly cooled to 988 K, it undergoes a eutectoid transformation of CuZr → Cu10Zr7 + Zr2Cu, while rapid cooling to 440 K induces a martensitic transformation of B2-CuZr → B19' -CuZr. Wu et al. first reported obtaining composites with 25% B2-CuZr phase (volume fraction) uniformly distributed in a BMG matrix using Zr48Cu47.5Al4Co0.5 BMG. By utilizing stress-induced martensitic transformation of the B2-CuZr phase, the composites exhibited obvious work hardening and macroscopic plastic deformation capability under tensile loading. Subsequently, Wu et al. calculated that adding trace Co helps reduce the stacking fault energy of the B2-CuZr phase, promoting deformation twinning and martensitic transformation, which gives the composites apparent work hardening behavior. Additionally, since the primary B2-CuZr phase has a fast growth rate and tends to coarsen and interconnect, controlling the nucleation and growth of B2-CuZr phase to adjust its size, distribution, and volume fraction is crucial for further improving the tensile plasticity of these composites.

Most reported BMG composites with tensile plasticity containing B2-CuZr phase are based on Cu47.5Zr47.5Al5 or Zr48Cu47.5Al4Co0.5 BMG, which have limited glass forming ability. The prepared composites are restricted to small sample sizes, and developing large-sized BMG composites containing B2-CuZr phase with good plastic deformation capability is urgently needed for structural applications. Xu et al. and our previous work have shown that adding the rare earth element Y to Zr-Cu-Al ternary alloys can significantly enhance the glass forming ability, and the B2-CuZr phase is one of the competing crystalline phases for BMG formation in Zr-Cu-Al-Y alloys. In this work, by adjusting the cooling rate of the melt, we obtained in situ composites with variable volume fractions of B2-CuZr phase uniformly distributed in the glass matrix in Zr46.9Cu45.5Al5.6Y2.0 BMG (optimized composition in Zr-Cu-Al-Y quaternary alloys), with relatively large sizes (6 mm and 7 mm in diameter), enabling comparison of mechanical properties under uniaxial tension and compression.

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1. Experimental Methods

Starting materials of elemental Zr, Cu, Al with purity higher than 99.9% (mass fraction) and Y blocks with purity higher than 99.5% (mass fraction) were used to prepare master alloys with nominal compositions (atomic fraction) by arc melting. Before melting the master alloys, Ti pellets were melted first to absorb O2 and other impurities in the protective atmosphere for further purification. The alloy ingots were remelted at least five times with electromagnetic stirring to ensure compositional homogeneity. Appropriate amounts of master alloy were remelted in an arc melting furnace equipped with a tiltable water-cooled Cu crucible and cast into rods with diameters ranging from 4 to 14 mm. For rods with diameters of 6, 7, and 8 mm, the Cu mold casting yielded rod lengths of 100 mm. Sections were cut from 20 mm and 70 mm positions from the rod bottom to obtain 50 mm long middle sections.

Samples for microstructural observation and compositional analysis were taken from the middle position of these 50 mm sections. The alloy samples were ground with 400–1000 grit SiC water-resistant abrasive paper until no obvious scratches remained, then mechanically polished with diamond paste of 3.5 m and 1.5 m particle sizes. Low-magnification microstructural observation was performed using a Leica MPS 30 optical microscope with analysis software. Phase analysis was conducted using a D/max 2400 X-ray diffractometer (XRD) with CuKα radiation (incident wavelength 0.1542 nm). Glass transition and crystallization behavior of BMG samples were characterized using a Perkin-Elmer DSC-diamond differential scanning calorimeter (DSC). Samples weighing approximately 10 mg were sealed in Al2O3 crucibles and measured at a continuous heating rate of 40 K/min. High-purity Ar gas was flowed during measurement. After the first measurement, samples were rapidly cooled to room temperature and a second measurement was immediately performed under identical conditions as a baseline. At least three specimens were tested for each alloy to ensure reproducibility.

Uniaxial compression tests were conducted at room temperature on a Shimadzu AG-1/500 KN testing machine at a strain rate of 1\$×10ˆ{-4}\$ s^{-1}. Compression specimens were prepared by cutting sections from 20 mm and 70 mm positions from the rod bottom. The middle 50 mm section from a 7 mm diameter rod was centerless ground to 3 mm diameter, then mechanically ground and polished. Cylindrical compression specimens with a height-to-diameter ratio of 2:1 were cut from the middle position. Both ends of compression specimens were ground flat with parallelism error within 10 m. Uniaxial tensile tests were performed at room temperature on a Zwick Z050 testing machine at a strain rate of 1\$×10ˆ{-4}\$ s^{-1}. Tensile specimens were machined from the middle 50 mm section of 7 mm diameter rods according to ASTM standard E 8M-04 into dog-bone shape with a gauge diameter of 3 mm, gauge length of 20 mm, and threaded grip ends. The gauge section was ground and polished to a bright surface. A strain gauge with 15 mm gauge length was used to measure strain in real-time during tensile testing. At least three samples were tested to ensure reproducibility. Fracture surfaces and side surfaces of tested specimens were observed using a Quanta 600 scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS).

Fracture toughness of amorphous samples was measured using plate specimens. As-cast BMG plate samples with dimensions of 3.2 mm × 9 mm × 30 mm were mechanically ground and polished to obtain fracture toughness specimens with thickness B=3 mm, width W=6 mm, and span S=24 mm (B:W:S ratio of 1:2:8). A straight notch with length 0.25W and root radius of 150 m was cut at one end using a diamond wire saw. The specimens were then pre-cracked by fatigue on a 2.5 kN MTS fatigue testing machine at 30 Hz frequency. Following ASTM standard E1820-08, the ratio of maximum to minimum load was maintained at 0.1 during fatigue, with corresponding stress intensity factor ΔK of 30–45 MPa• $\mathrm{m}^1/^2$. After approximately 1\$×10$^{\{5\}-4\times10}${5}\$ cycles, when the fatigue crack length reached (0.5–0.7)W, the specimens were unloaded. Three-point bending (3PB) fracture toughness tests were conducted on a 5 kN Instron 8871 testing machine at a displacement rate of 0.3 mm/min. Crack opening displacement (COD) was measured using a clip gauge mounted at the knife edges. According to ASTM E399, the stress intensity factor K was calculated by:

$$K = \frac{P \cdot S}{B \cdot W^{3/2}} \cdot f\left(\frac{a}{W}\right)$$

where $f(a/W)$ is a geometry factor. In this work, $f(a/W)$ was taken as:

$$f\left(\frac{a}{W}\right) = 2.7 + 4.5\left(\frac{a}{W}\right) - 4.8\left(\frac{a}{W}\right)^2 + 2.0\left(\frac{a}{W}\right)^3$$

where a is the sum of notch length and pre-crack length, and P is the load. If the material exhibits completely linear elastic deformation before fracture, showing linear behavior on the load-displacement curve, P takes the maximum load at fracture P_{max}. If the material shows deviation from linear elasticity, a straight line with 0.95 times the slope of the linear segment is drawn, and the load at the intersection with the load-displacement curve is P_Q. If P_{max}/P_Q is less than 1.1, the small-scale yielding condition is satisfied and P_Q is used for fracture toughness calculation.

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2. Results and Discussion

2.1 Preparation of BMG Composites Containing B2-CuZr Phase

Our previous work has shown that Zr44.4Cu42Al10Y3.6 (hereinafter referred to as Y1 alloy) has a critical diameter Dc of 16 mm for BMG rod formation by Cu mold casting, with B2-CuZr and t3 phases being the competing crystalline phases for BMG formation in Y1 alloy. Therefore, Y1 alloy can be prepared as BMG in situ composites containing CuZr phase. However, Y1 BMG tends to fracture into many small fragments under compressive loading, showing brittle fracture characteristics, making it unsuitable as a glass matrix for composite design.

It should be emphasized that designing BMG composites containing B2-CuZr phase should aim to retain only the B2-CuZr phase while eliminating other crystalline phases, and simultaneously optimize a toughened metallic glass matrix. Figure 1 [Figure 1: see original paper] illustrates the three-dimensional composition space of the Zr-Cu-Al-Y quaternary alloy system, showing our strategy for evolving in situ B2-CuZr phase composites in composition space. As shown in Figure 1, alloy compositions along the tie-line between Y1 alloy (marked with a star) and the CuZr compound can be expressed as $(\mathrm{Cu}_{0\cdot5}\mathrm{Zr}_{0\cdot5})\ \mathrm{M}_{100}$ $(\mathrm{M} = \mathrm{Zr}_{0\cdot15}\mathrm{Y}_{0\cdot225}\mathrm{Al}_{0\cdot625})$. It can be predicted that as the alloy composition is adjusted from Y1 toward the CuZr compound, the crystalline phases competing with glass formation will evolve to the CuZr phase. Furthermore, in materials processing, by appropriately increasing the diameter of as-cast alloy rods (i.e., decreasing the cooling rate), the CuZr phase can be expected to form as the primary crystalline phase in the glass matrix, yielding metallic glass matrix composites with CuZr phase as the primary phase.

On the other hand, our previous work has shown that approaching the B2-structured CuZr compound in composition space leads to a gradual decrease in the shear modulus of $(\mathrm{Cu}_{0\cdot5}\mathrm{Zr}_{0\cdot5})\ \mathrm{M}_{100}$ series BMGs, indicating a progressive reduction in the barrier for shear flow in the BMG, which helps improve the toughness of the metallic glass matrix. Figure 2 [Figure 2: see original paper] shows a schematic diagram of the phase composition in the core of as-cast rods with different diameters for the $(\mathrm{Cu}_{0\cdot5}\mathrm{Zr}_{0\cdot5})\ \mathrm{M}_{100}$ series alloys. It can be seen that increasing the rod diameter leads to an evolution in phase selection at the rod core from fully amorphous to composite structures with an amorphous matrix plus B2-CuZr crystalline phase, and finally to fully crystalline structures.

The resulting in situ composites containing CuZr phase can be obtained in BMG rods with diameters ranging from 4 mm (x=93) to 12 mm (x=88). Notably, Zr46.9Cu45.5Al5.6Y2.0 (x=91, hereinafter referred to as YC alloy) has moderate glass forming ability (Dc=5 mm). Its as-cast rods with 6 mm and 7 mm diameters form in situ CuZr phase composites at the core, while increasing the diameter to 8 mm yields fully crystalline structures.

2.2 Structural Characterization

Figure 3 [Figure 3: see original paper] shows optical microscopy (OM) images of the central portion of cross-sections from as-cast YC alloy rods with 6 mm and 7 mm diameters. Spherical crystalline particles are observed to be uniformly distributed in the amorphous matrix. XRD analysis (Figure 4 [Figure 4: see original paper]) indicates that the spherical crystalline phase is B2-structured CuZr. EDS analysis shows that the composition of the B2-CuZr phase is essentially the same as that of the glass matrix, with no obvious difference. Figure 3 also reveals that in the core of the 6 mm rod, spherical B2-CuZr particles have diameters of 5–100 m, while in the 7 mm rod core, particle diameters range from 10–180 m. Compared with the 6 mm rod, the 7 mm rod shows larger B2-CuZr particle sizes and greater volume fraction, consistent with the decreased cooling rate of the melt. Image J analysis indicates that the volume fractions of B2-CuZr phase in the cores of 6 mm and 7 mm rods are 12% and 24%, respectively. Additionally, the difference in B2-CuZr volume fraction between the top and bottom ends of the 50 mm long sections is less than 3.5% and 7% for the 6 mm and 7 mm rods, respectively.

Figure 4 [Figure 4: see original paper] presents XRD spectra from the core of cross-sections of YC alloy as-cast rods with diameters of 6, 7, and 8 mm. The 6 mm and 7 mm samples show typical composite characteristics, with B2-CuZr crystalline diffraction peaks superimposed on the broad diffraction peak of the amorphous phase. The diffraction intensity of B2-CuZr crystalline phase in the 7 mm sample is significantly stronger than that in the 6 mm sample, consistent with the larger volume fraction of crystals observed in Figure 3 for the 7 mm sample. The crystalline phases in the 8 mm as-cast rod consist mainly of B2-CuZr and a small amount of B19’ -CuZr, with negligible residual amorphous phase.

Figure 5 [Figure 5: see original paper] shows DSC curves for samples taken from the core of as-cast YC alloy rods with diameters of 5, 6, and 7 mm. All DSC curves exhibit a distinct endothermic step due to glass transition and an exothermic peak due to crystallization, with the glass transition temperature Tg indicated by arrows. Table 1 lists the Tg, crystallization enthalpy ΔH, and volume fractions of B2-CuZr phase for the 5, 6, and 7 mm YC alloy as-cast rods. The Tg of the amorphous matrix in the composites is the same as that of the monolithic amorphous phase. Assuming that the volume fraction of the amorphous phase is proportional to the heat of crystallization, the volume fractions of B2-CuZr phase in the YC alloy composites with 6 mm and 7 mm diameters are estimated from the crystallization enthalpy to be 13% and 25%, respectively, which basically matches the results from Image J analysis.

2.3 Compressive and Tensile Properties of YC BMG Composites

The YC BMG composite containing 25% B2-CuZr phase was selected for compressive and tensile property testing, with the second-phase volume fraction consistent with that developed by Wu et al. for Zr48Cu47.5Al4Co0.5 BMG composites. Figure 6 [Figure 6: see original paper] shows the compressive engineering stress-strain curve for this BMG composite. For comparison, the compressive stress-strain curve for monolithic Zr47.2Cu46Al5Y1.8 BMG (x=92, Figure 2) with 2 mm diameter is also included. The monolithic BMG shows a compressive yield strength of 1830 MPa and apparent plastic strain of 1.6%. In contrast, the YC BMG composite containing 25% B2-CuZr phase exhibits a compressive yield strength of 1350 MPa, maximum compressive strength of 2000 MPa, and apparent plastic strain of 6.5%, which is nearly four times that of the monolithic BMG. The large plastic strain indicates that the B2-CuZr phase significantly improves the plastic deformation capability of the monolithic BMG under compressive loading.

Figure 7a [Figure 7: see original paper] shows the tensile engineering stress-strain curve for the YC BMG composite containing 25% B2-CuZr phase. The specimen exhibits a yield strength of (1210$±80)*MPaandfracturestrengthof*(1340±$80) MPa, but the ductility measured by the strain gauge is only 0.3%. The specimen fractures shortly after yielding (defined as 0.2% plastic strain), indicating that the B2-CuZr phase does not significantly improve the plastic deformation capability of the BMG under tensile loading. It should be noted that monolithic YC BMG rods are too brittle to be machined into tensile specimens without fracturing, and only the composite rods could be successfully processed into tensile specimens meeting the dimensional requirements.

Figure 7b shows the stress-strain curve for the specimen marked with an arrow in Figure 7a. Although the specimen shows no obvious ductile strain, the stress-strain curve begins to deviate from linearity at relatively high stress, which differs from the linear elastic mechanical behavior of monolithic BMG. Our previous work has shown that even for BMGs with high fracture toughness, such as Zr55Ti2Co28Al15 BMG (K_Q=89 MPa·m^{1}/^{2}) and Zr61Ti2Cu25Al12 BMG (K_Q=130 MPa·m^{1}/^{2}), all tensile specimens fractured in the linear elastic stage with zero ductility when tested using the same specimen dimensions and testing conditions.

Figure 8a [Figure 8: see original paper] shows an SEM image of the side surface of a fractured tensile specimen of the YC BMG composite. The fracture surface is flat and oriented at approximately 90° to the tensile stress direction, characteristic of brittle fracture. Figure 8b is a magnified view of the boxed area in Figure 8a, showing only a few shear steps near the fracture surface. Figure 8c shows the fracture surface morphology of the composite tensile specimen. No obvious casting defects such as pores are observed, indicating that the brittle fracture is not caused by casting defects. Figures 8d and 8e show magnified images of local areas near the surface (boxes 1 and 2 in Figure 8c). Clear vein patterns around the CuZr phase crystals indicate that shear flow occurred near the CuZr phase crystals during tensile deformation, which contributes to plastic deformation and is consistent with the micro-yielding behavior observed in the tensile stress-strain curve. Figure 8f shows a magnified image of the central area (box 3 in Figure 8c). The crack propagation pattern points toward some smooth spherical crystals, which are identified as grain boundaries of spherical CuZr phase particles oriented perpendicular to the tensile stress axis. The absence of dimple patterns on the crystal particle fracture surfaces indicates weak bonding between particles. The fracture morphology analysis suggests that under tensile loading, these CuZr phase particles with grain boundaries perpendicular to the stress axis first crack along the grain boundaries, initiating mode I cracks that serve as crack sources for brittle fracture of the composite tensile specimens. Under compressive stress, however, these CuZr phase particle boundaries can effectively transfer compressive stress without initiating cracks, allowing the metallic glass matrix to generate high-density shear bands and achieve plastic deformation.

2.4 Plastic Zone Size at Crack Tip in Zr48Cu45Al7 BMG

Compared with the Zr48Cu47.5Al4Co0.5 BMG composite developed by Wu et al., our YC BMG composite has similar B2-CuZr phase volume fraction and uniform distribution morphology, but only exhibits trace ductile strain under tensile loading before brittle fracture occurs. The size matching between precipitate dimensions/spacing and the plastic zone size of the metallic glass matrix is an important factor determining whether in situ BMG composites can achieve tensile plasticity. Using the fracture toughness K_Q of (49\$±3)$MPa\cdot m^{\{1\}/}$\{2\}\$ and tensile yield strength σy of 1700 MPa, the plastic zone size of YC BMG under plane strain conditions (R_P=(1/3π)(K_Q/σy)^2) is calculated to be only about 88 m, which is smaller than some B2-CuZr phase particle diameters (10-180 m) and spacings (10–300 m) in the composite structure. Due to this size mismatch, when B2-CuZr phase grains crack along brittle grain boundaries perpendicular to the stress axis under tensile loading (mode I), the low toughness of the metallic glass matrix causes this to be equivalent to initiating a mode I crack in the matrix, leading to unstable crack propagation and brittle fracture.

This work demonstrates that adding element Y to Zr-Cu-Al ternary alloys, while greatly enhancing glass forming ability and enabling uniform precipitation of CuZr phase, severely degrades the fracture toughness and plastic zone size of the BMG. He et al. measured the fracture toughness K_Q of ternary Zr48Cu45Al7 BMG to be (101\$±9)$MPa\cdot m^{\{1\}/}$\{2\}\$. We further found that Zr48Cu45Al7 BMG can be pre-cracked under fatigue loading. Table 2 lists the three-point bending fracture toughness test results for three Zr48Cu45Al7 BMG samples. Although all test samples have Pmax/PQ less than 1.1, satisfying the linear elastic fracture requirement according to ASTM E399, none of the sample thicknesses meet the requirement of B $\geq$ 2.5(K_Q/σy)^2, so they do not represent valid KIC values. The average fracture toughness K_Q is (62\$±3)$MPa \cdot m^{\{1\}/}\{2\}.WithK_Q = 62MPa \cdot m^{\{1\}/}\{2\}$\$ and σy=1650 MPa, the plastic zone size R_P for Zr48Cu45Al7 BMG under plane strain conditions is 150 m, which is significantly larger than that of YC BMG (R_P=88 m).

3. Discussion

3.1 Preparation of BMG Composites Containing B2-CuZr Phase

The preparation of ZrCu-based BMG composites containing B2-CuZr phase involves controlling the nucleation, growth rate, and stability of the primary B2-CuZr phase. However, the B2 structure of CuZr is only stable in the high-temperature region (>988 K). When cooled to 440 K (the martensitic transformation start temperature Ms), CuZr undergoes a martensitic transformation from B2 structure to B19' structure. The strength and hardness of B19' -CuZr are comparable to those of Cu50Zr50 BMG, but BMG composites with a hard phase as the primary phase do not satisfy the conditions for obtaining ductile strain under tensile loading. Therefore, obtaining a single B2-CuZr phase in BMG composites at room temperature requires lowering the Ms temperature. Pauly et al. have shown that adding 5% Al (atomic fraction) to equiatomic binary CuZr alloy can effectively reduce Ms from 440 K to 323 K, a decrease of 117 K. The presence of 5.6% Al in our YC BMG composites should similarly be attributed to the stabilization of single B2-CuZr phase. In addition to Al, adding Ti can also significantly reduce the Ms temperature of CuZr alloys.

Lowering Ms stabilizes the primary B2-CuZr phase to room temperature. However, the B2-CuZr phase has a fast growth rate and tends to interconnect, making it difficult to adjust the volume fraction and prevent it from dividing the amorphous matrix and adjusting the length scale. In our YC BMG composites, the primary B2-CuZr phase exhibits uniform distribution morphology and tunable volume fraction, mainly attributed to the addition of Y. First, Y significantly improves the glass forming ability of Cu-Zr-Al alloys, providing sufficient adjustment space in the temperature-time-transformation relationship to control the size and volume fraction of primary CuZr particles by adjusting the melt cooling rate. Second, adding a small amount of Y, which has positive mixing enthalpy with Zr (Y-Zr: +35 kJ/mol), to Cu-Zr-Al alloys helps promote uniform precipitation of CuZr phase from the melt. Park and Kim applied HRTEM to study the structure of Cu-Zr-Al-Y BMG and found that adding (2-5)% Y promotes local chemical composition heterogeneity in the glass matrix. Similarly, adding other elements with positive mixing enthalpy with major constituent elements, such as Co, Nb, and Gd, to Zr-Cu-Al alloys has been observed to result in relatively uniform precipitation of B2-CuZr phase in the metallic glass matrix.

3.2 Tension-Compression Asymmetry of In-Situ Composites

This work demonstrates that YC BMG composites containing 25% B2-CuZr phase can achieve a plastic strain of 6.5% under uniaxial compressive loading, but do not exhibit obvious plastic deformation capability under uniaxial tensile loading, fracturing shortly after yielding. The intrinsic reason for the lack of size matching between the metallic glass matrix plastic zone size and the B2-CuZr phase particle size/spacing is the fundamental cause of brittle fracture in YC BMG composites under tensile loading. Although YC BMG was obtained through composition optimization, its fracture toughness remains insufficient, resulting in a plastic zone size smaller than the B2-CuZr phase particle size and spacing. This work shows that adding a small amount of Y to ZrCuAl ternary alloys can greatly enhance the glass forming ability but severely damages the mode I fracture toughness and plastic zone size of the BMG. Compared with YC BMG, Y-free Zr48Cu45Al7 BMG plate samples can be pre-cracked by fatigue, exhibiting a fracture toughness of (62\$$\pm 3)MPa \cdot m^{\{1\}/}\{2\}$\$ and a plastic zone size of 150 m at the crack tip under plane strain conditions. Therefore, BMG composites containing B2-CuZr phase based on tough ZrCuAl BMG can more easily satisfy the size matching relationship under tensile loading. For instance, literature reports have shown that small samples of Zr48Cu48Al4 BMG composites containing B2-CuZr phase exhibit obvious ductile strain under tensile loading. This work demonstrates that developing large-sized BMG composites containing B2-CuZr phase with good plastic deformation capability requires balancing both the glass forming ability and fracture toughness of the amorphous matrix.

On the other hand, unlike the fracture mode under tensile loading, shear fracture of metallic glass under compressive loading approaches mode II (sliding mode). Previous studies have shown that the fracture toughness KII of metallic glasses is several times larger than KI, resulting in a larger plastic zone size at the crack tip. Flores and Dauskardt measured the mode II fracture toughness KII of Zr41.25Ti13.75Ni10Cu12.5Be22.5 (Vitreloy1) BMG to be (75\$$\pm 4)MPa \cdot m^{\{1\}/}\{2\}, approximately four times its mode I fracture toughness((15–20)MPa \cdot m^{\{1\}/}\{2\}). Madge et al. also found that even for brittle Mg-based BMG, the mode II fracture toughness KII can re$ $m^{\{1\}/}\{2\}$\$, about 3–4 times larger than mode I fracture toughness. Tandaiya et al. applied finite element simulations to show that under mode II stress state, shear bands at the crack tip extend approximately straight along the crack propagation direction, with an extension distance at least six times larger than the mode I plastic zone width, indicating a much larger plastic zone size. He et al. observed that when measuring fracture toughness of pre-cracked ZT1 BMG using three-point bending, introducing a mode II component through crack tip deflection can help consume system energy and increase resistance to crack propagation, thereby enhancing mode I fracture toughness. Therefore, the intrinsic reason for the tension-compression asymmetry in plastic strain of YC BMG composites lies in the insufficient plastic zone size of the metallic glass matrix under tensile loading, which is smaller than the spherical B2-CuZr particle size and spacing, failing to satisfy the size matching condition. Under compressive loading, however, the matching condition is satisfied. Consequently, the B2-CuZr phase in YC BMG composites can promote the formation of multiple shear bands in the metallic glass matrix under compressive loading, achieving large plastic strain, whereas under tensile loading, the B2-CuZr phase does not improve plastic deformation capability, and the material fails without obvious ductile strain.

Conclusions

1. By increasing the casting rod diameter to limit the cooling rate of the melt, in situ composites with 13% and 25% (volume fraction) of B2-CuZr phase uniformly distributed in the metallic glass matrix were obtained in Zr46.9Cu45.5Al5.6Y2.0 (YC) bulk metallic glass (BMG) with a critical diameter of 5 mm. The composite rods have diameters of 6 mm and 7 mm, respectively.
2. Under compressive loading, the apparent plastic strain of YC BMG composites containing 25% B2-CuZr phase increases from 1.6% for monolithic BMG to 6.5% for the composite. However, no obvious ductile strain was observed under uniaxial tension, and the B2-CuZr phase did not improve the plastic deformation capability. The intrinsic reason for this tension-compression asymmetry in plastic strain is that the plastic zone size of the metallic glass matrix does not satisfy the size matching relationship with the B2-CuZr phase particle size and spacing under tensile loading.
3. Adding a small amount of Y to ZrCuAl ternary alloys can greatly enhance the glass forming ability but severely damages the mode I fracture toughness and plastic zone size of the BMG. Compared with YC BMG, Y-free Zr48Cu45Al7 BMG can be pre-cracked by fatigue, exhibiting a fracture toughness of (62\$±3)$MPa \cdot m^{\{1\}/}${2}\$ and a plastic zone size of 150 m at the crack tip under plane strain conditions.

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Note: Figure translations are in progress. See original paper for figures.