Relationship between composite structures and compressive properties in CuZr-based bulk metallic glass system

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Bulk metallic glass (BMG) composites with the austenite B2 phase as reinforcement macroscopically showed strain hardening behavior due to the plasticity induced by martensitic transformation during deformation. Relationship between characteristics of the B2-CuZr reinforcing phase and uniaxial compressive properties of CuZr-based BMG composites was studied. Mechanical properties of these BMG composites were found to depend on not only the reinforced phases but also the amorphous matrix, and the yield and fracture strength can be roughly estimated by the rule of mixture principle. Distribution of the reinforced B2-CuZr phase has an important impact on the compressive plasticity even for the composites with a similar volume fraction of the crystal-line phase.

bulk metallic glass composites, transformation-induced plasticity, compressive mechanical properties

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To overcome the Achilles's heel of bulk metallic glasses (BMGs), i.e., room temperature brittleness and strain-softening, many approaches have been attempted [1–3]. Among which, formation of BMG composite structures has been proved to be an effective way in enhancing the room-temperature plasticity, and large tensile ductility has been achieved by proper introduction of the dendritic reinforcing phases into Zr- or Ti-based BMGs [4–10]. However, these types of BMG composites still show the strain-softening behavior [9,10]. Recently, the concept of transformation-induced plasticity (TRIP) was applied into the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ ($x = 1, 2, \dots, 10$ at%) BMG system and both tensile ductility and work-hardening capability were obtained [11–15]. The martensitic transformation of the B2-CuZr phase was found to be responsible for the enhanced tensile properties [14,15].

However, the super-cooled austenitic B2-CuZr phase is

metastable which only exists above 988 K [16,17], and it has already been found that formation of the B2-CuZr phase is extremely sensitive to the composition and fabrication process [15]. On the other hand, it was also suggested that the volume fraction and distribution of the B2-CuZr phase both could affect the mechanical properties of the TRIP-BMG composites [13,15]. However, the relationship between the characteristics of the B2 phase and macroscopic properties of these special BMG composites, and the contribution from the B2 phase to the work hardening are still needed further investigation. In this paper, we will focus on dependence of compressive deformation behavior on the characteristics of the B2-CuZr phase in the CuZr-based TRIP-BMG system.

1 Experimental

Alloy ingots with nominal compositions of $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$

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($x=3, 4, \dots, 10$ at%) were prepared by arc-melting a mixture of constituent elements with a purity of above 99.9% in a Ti-gettered atmosphere. The alloy ingots were melted six times to ensure compositional homogeneity. Cylinder composite samples with different diameters were fabricated by suction casting using copper molds. Thermal properties were analyzed by differential scanning calorimetry (DSC) (Netzsch STA449C) at a rate of 10 K/min. Longitudinal and cross-section surfaces of the as-cast and strained samples were examined in a ZEISS SUPRA 55 scanning electron microscope (SEM). Volume fractions of crystalline phases were estimated from the SEM images with an Imagetool software. Compression samples with a diameter of 2 mm and a height of 4 mm were cut from the center of the as-cast rods. Uniaxial compression tests were conducted between two tungsten carbide platens at an engineering strain rate of $2 \times 10^{-4} \text{ s}^{-1}$ in a SANS testing machine with a maximum load of 300 kN.

2 Results

2.1 Effects of alloy compositions

To study effects of the amorphous matrix which is closely associated with the alloy composition, samples of $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ ($x=3, \dots, 10$, at%) with a diameter of 2 mm were fabricated, and X-ray diffraction results (not shown here) suggested that all these samples are fully amorphous. Compressive stress-strain curves of these amorphous samples with different Al contents are shown in Figure 1. As shown, alloys with a low Al content (i.e., $\leq 6\%$) show considerable plasticity, whilst alloys with a large Al content (8%) display a quasi-brittle fracture without any appreciable plasticity, strongly implying a dramatic change in the local atomic structure of these amorphous alloys. As the Al content increases, another distinct feature observed in Figure 1 is the notable increment in the yield strength. The $\text{Cu}_{48.5}\text{Zr}_{48.5}\text{Al}_3$ alloy shows a yield strength of about 1700 MPa while that of the $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ alloy increases to about 1950 MPa.

It has been proposed that yield strength of metallic glasses has a close correlation with their glass transition temperature (T_g) [18,19]. Thermal analysis of the

Figure 1 Compressive stress-strain curves of the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ amorphous samples with different Al contents.

$(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ ($10 \geq x \geq 3$) alloys with different casting diameters were also conducted. DSC traces of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ and $\text{Cu}_{47}\text{Zr}_{47}\text{Al}_6$ alloys are shown in Figure 2 as examples, and the measured thermal parameters are listed in Table 1. A distinct glass transition event was detected for all the specimens, even for those partially amorphous ones. The glass transition temperature (T_g) and the crystallization temperature (T_x) are almost unchanged for alloys with the same composition in spite of different casting diameters. These observations suggest that atomic structure of the glassy phase for the same alloy composition is not sensitive to the cooling rates studied. In contrast, the enthalpy of crystallization of the same alloy varies with different casting diameters, and a larger casting diameter (i.e., a lower cooling rate) gives rise to a smaller crystallization enthalpy, indicating a higher volume fraction of crystalline phases. It can also be easily seen that T_g and T_x of the $\text{Cu}_{47}\text{Zr}_{47}\text{Al}_6$ alloy are higher than those of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy, showing an increase trend of T_g and T_x with the increase of Al. By taking the mean molar volume (V_m) of the current BMG alloy system as about $10.43 \text{ cm}^3/\text{mol}$ [20], the correlation between T_g and the yield strength of the current alloy system can be expressed as $\sigma_y = 50.05 \Delta T_g / V_m$, as shown in Figure 3, which is consistent with the empirical equation previously proposed by Yang et al. [18]. Additions of Al in the CuZr-based BMG can promote formation of dense localized packing clusters (e.g., icosahedrals) [21], which have a strong atomic bonding and large resistance to deformation, and

Figure 2 DSC curves of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ and $\text{Cu}_{47}\text{Zr}_{47}\text{Al}_6$ alloys with different casting diameters.

Table 1 Thermal parameters of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ and $\text{Cu}_{47}\text{Zr}_{47}\text{Al}_6$ alloys with different casting diameters

Alloys	Casting diameter (mm)	T_g (K)	T_x (K)	ΔT_x (K)	Crystallization enthalpy (J g^{-1})
Al=4%	2	682.1	737.4	55.3	7.33
	3	682.7	736.6	53.9	6.90
	4	681.6	736.0	54.4	3.82
Al=6%	2	690.4	751.9	61.5	9.76
	4	690.4	752.5	62.1	7.12
	6	689.6	751.2	61.6	5.90

therefore increase the glass transition temperature and yield strength of the amorphous phase. Thus, it is reasonable to speculate that the composite with a higher Al content would possess a higher ultimate strength. Next, effects of the amorphous phase and crystalline phase on the macroscopic deformation behavior of the current BMG composites will be discussed in detail.

2.2 Effects of phase selection

It was known that the strength of BMG composites has a close correlation with type of the crystalline phases presented in the glassy matrix. In the present $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ alloy system, it was found that characteristic of the precipitated crystallites were extremely sensitive to the composition and cooling rates applied during fabrication. For the as-cast samples with a Al content not more than 8%, microstructure of the composites varies as follows: fully amorphous $\rightarrow$ amorphous+B2-CuZr $\rightarrow$ amorphous+B2-CuZr+ Al_2Zr as the cooling rate decreases (i.e., the casting diameter increases) [15]. Figure 4 demonstrates the microstructure change of the cross-section of the as-cast $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy as a function of the casting diameter. When being cast in 3 or 4 mm rods, the alloy exhibited a composite structure with crystalline precipitates identified as bcc B2-CuZr phase with a volume fraction of about 15% and 45%, respectively. Nevertheless, the B2-CuZr phase in the 4 mm as-cast rods combined with each other to form patch-like morphology across the amorphous matrix. With the further decrease of the cooling rate, in addition to the spherical B2 phase, another phase, the intermetallic compound Al_2Zr was formed, which are shown in Figure 4(e) and (f).

Along with the variation in the microstructure, the compressive behavior changed accordingly. Figure 5(a) shows the compressive stress-strain curves of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloys with different casting diameters. To avoid the so-called "size effect" [22,23], all the testing samples were cut from the center part of the as-cast rods and had a diameter of 2 mm. For the fully amorphous sample, a typical stress-strain

Figure 3 Dependence of yield strength on the glass transition temperature of the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}\text{Al}_x$ BMG alloys.

Figure 4 SEM images of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy cut from rods with different casting diameters. (a) $d=3$ mm, (c) $d=4$ mm, (e) $d=5$ mm. Images (b), (d) and (f) are the enlargements of (a), (c) and (e), respectively.

curve with serration flows is observed. For the sample cut from the 3 mm rods, the compressive plasticity and the ultimate fracture strength are remarkably increased. It is interesting to note that at the early stage of the plastic deformation, no distinct serration flow was seen, indicating a change in deformation mode. For the sample cut from the 4 mm rods, the stress-strain curve exhibits a much lower yield strength and smaller plasticity but a more pronounced work-hardening behavior. For the sample cut from 5 mm rods, the compressive stress-strain curve displays a very low yield strength of about 300 MPa, a fracture strain of no more than 5% and fracture strength of no more than 1500 MPa. The specimen broke into several pieces after fracture, exhibiting a brittle deformation mode. It can be seen that compressive plasticity of the sample cut from the 3 mm as-casts (around 15% B2-CuZr phase) was remarkably increased without deteriorating the strength. With more B2-CuZr phase present, the composites possess a low yield strength but a similar fracture strength. However, if any brittle phases like Al_2Zr precipitates, the composites became extremely brittle without any plasticity.

True stress-strain curves of several other alloys with different Al additions are illustrated in Figure 5(b), and a similar dependence of deformation behavior on the cooling rates was also observed. In general, compressive deformation behavior of the current composite system can be categorized into three types. For the BMG composites containing Al_2Zr phase, appreciably low strength and plasticity can be seen. For the specimens with a volume fraction of 10%–30% B2 crystals homogeneously distributed in the amorphous matrix, high yield strength and distinct work-hardening can be

Figure 5 Uniaxial compressive true stress-strain curves of (a) the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy with different casting diameters, and (b) the other BMG composites.

observed. As the B2 crystals are increased to more than 40%, however, the specimens initially yielded at a much lower stress but underwent a more pronounced work-hardening behavior and subsequently the second yielding. The double yielding phenomenon could be linked to a change in the deformation mechanism from being borne by a martensitic transformation to a process mediated by dislocation movement [24].

2.3 Effects of volume fractions of the B2 phase

Volume fractions of the crystal phase were found to severely affect mechanical properties in the dendrites reinforced composite [9,10,25]. Crystalline volume fractions can be varied by changing the applied cooling rates (i.e., the casting diameter) during fabrication of the composites and the longitudinal position of the as-cast rods. By properly adjusting the fabrication process, composite specimens of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy with different crystalline volume fractions were fabricated and tested under uniaxial compression, and the corresponding values of the yield strength, fracture strength and fracture strain are listed in Table 2. Variation of the yield strength and fracture strength with volume fractions of the B2-CuZr phase was shown in Figure 6. As the volume fraction of B2-CuZr increases, the yield strength gradually decreases. It was known that yield strength of composite materials can usually be estimated from properties of the constituent phases by the rule of mixtures (ROM) principle. With the yield strength of the amorphous matrix and pure B2-CuZr phase [24], the estimated values of these BMG composites are also shown as the dashed line in Figure 6. It can be seen that the variation trend of the experimental data roughly agrees with the predication by the ROM principle. It is worthy to be noted that the above trend observed in the present experiment is not consistent with previous report [13], which may arise from different distribution of the B2-CuZr phase. Unlike the yield strength, the fracture strength hovers around 2100 MPa. Full B2-CuZr materials have a relatively low yield strength of about 470 MPa but a high fracture strength of about 2100 MPa which is close to that of the amorphous matrix [24]. Therefore, different volume fractions of the B2 phase have dramatic

Table 2 Yield strength, fracture strength and fracture strain of $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ BMG composites with different crystalline volume fractions

Crystalline volume fraction (%)	Yield strength (MPa)	Fracture strength (MPa)	Fracture strain (%)
0.3	1598	2038	6.1
2.5	1653	2087	11.6
2.5	1656	1963	16.2
4.7	1770	2077	10.3
5.2	1651	2010	15.6
7.0	1563	2067	7.1
8.8	1669	2040	7.9
8.9	1751	2205	10.0
9.8	1619	1994	5.1
9.9	1626	2238	21.7
19.6	1592	2210	14.5
20.2	1567	2075	10.3
24.0	1538	2109	7.8
26.2	1348	2084	10.3

Figure 6 Variation of the yield and fractured strength with volume fraction of reinforced B2 phase in $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ BMG composites.

effects on the yield strength but not the fracture strength.

2.4 Effects of distribution of the B2 phase

Even for the BMG composites with a similar crystalline volume fraction, the fracture strain may vary tremendously due to different distribution of the reinforcing phase. As an example, Figure 7 shows the stress-strain curves of three BMG composites with ~10% B2 phase for the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy. Surprisingly, the fracture strain changes dramatically from 6% to 22%. SEM images in Figure 7 indicate that all

Figure 7 Compressive true stress-strain curves of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4$ alloy with about 10% B2 phase, and SEM images of the three samples with a similar crystal volume fraction of B2 phase but different distribution pattern.

the three samples contain one large spherical crystal and some small spherical crystals. Specimen A has only four small crystals, whilst B and C have more tiny crystals which are distributed more homogeneously in specimen C. As can be seen, homogeneous distribution of the B2 phase gives rise to a large fracture strain, manifesting that distribution of the reinforced crystals also play important roles in obtaining macroscopic plasticity of the current BMG composites.

3 Conclusions

Mechanical properties of the current CuZr-based TRIP BMG composite were found to have a close relationship with characteristics of the B2-CuZr phase. Strength of the amorphous phase increases with additions of Al, which has large influences on the fracture strength of the BMG composites. BMG composites with single B2-CuZr phase as reinforcement possess better mechanical properties as compared with those containing Al_2Zr . With the increase of B2-CuZr phase, the yield strength of the present composites decreases but the fracture strength is almost unchanged, which can be roughly explained by the role of mixture principle. Besides the volume fraction, distribution of the reinforcing B2 phase also strongly affects the fracture strain and homogeneous distribution favors a large fracture strain.

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