Phase formation, glass forming ability, mechanical and thermal properties of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) glass forming alloys

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Phase formation, glass forming ability, mechanical and thermal properties of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) glass forming alloys were systematically investigated. The results show that $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy has the best glass forming ability (GFA), lowest fragility index (m) and highest fracture strength. There are B2 CuZr and B19' CuZr phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 5.0$) alloys. B2 CuZr phase disappears and two new phases ($\text{Cu}_{10}\text{Zr}_7$ and CuZr_2) appear when $5.0 < \text{Al} < 8.0$. Another new AlCu_2Zr phase can be clearly observed when $\text{Al} > 8.0$. The glass transition temperature (T_g), the sensitivity of the T_g to the heating rate (B), the activation energy for T_g (E_g) and the m value all increase with increasing Al content. The supercooled liquid region (ΔT_x) is larger for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \leq 5.0$) than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x > 5.0$). $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 4.0$) alloys are off-eutectic compositions while near-eutectic compositions for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($5.0 \leq x \leq 11.0$) alloys. The E_g , E_x and E_p decrease with increasing sensitive factor (β) for the studied Cu-based alloys characterized in the room-temperature brittleness. The dependence of the phase formation and GFA on the Al content is discussed.

INTRODUCTION

Cu-based bulk metallic glasses (BMGs) have been extensively investigated due to their interesting properties including work hardening [1], martensitic transformation [2–5], magnetism [6], catalytic activity [7,8], cryogenic temperature plasticity [9] and room-temperature plasticity [10–14], which enable their applications as structural and functional materials.

Cu-Zr binary alloy system is characterized by good glass forming ability (GFA) and wide composition region for the formation of glass alloys [15]. Among Cu-Zr binary glass alloys, $\text{Cu}_{50}\text{Zr}_{50}$ alloy is a good glass forming precursor. Although $\Phi 1\text{mm}$ $\text{Cu}_{50}\text{Zr}_{50}$ BMG possesses room-temperature plasticity up to $\sim 7.0\%$ [16], its critical dimension for the

formation of glassy state is only $\Phi 2\text{mm}$ by suction casting method [16–18]. Small critical dimension of $\text{Cu}_{50}\text{Zr}_{50}$ BMG limits its engineering application.

Element minor addition/substitution is a well-known method for improving the GFA and other properties of glass forming alloys [6,12–14,19,20]. For example, Mattern *et al.* [6] found that a ferromagnetic Gd-enriched nanocluster could form in $\text{Cu}_{50}\text{Zr}_{50-x}\text{Gd}_x$ ($x=5$) metallic glasses due to the phase separation by Gd minor addition. Xi *et al.* [20] found that Gd minor addition improved the combination of the GFA and the room-temperature plasticity of $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ BMG. Ma *et al.* [12] investigated the effect of substituting Al by Ti on the GFA and the mechanical properties of brittle $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ BMG and found that the Ti addition significantly increased the plasticity although the characteristic temperatures including the glass transition temperature (T_g), onset crystallisation temperature (T_x) and supercooled liquid region (ΔT_x) decreased with increasing Ti content. Kuo *et al.* [13] investigated the effect of V on the phase formation and plasticity in $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glassy alloy and found that V minor addition improved the plasticity by doubling the fracture strain to 9.4% in $(\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5)_{99}\text{V}_1$ due to the formation of B2-CuZr precipitates. Recently, Cai *et al.* [14] found that the substitution of Ti by Ni significantly influences the GFA, mechanical, electrical and thermal properties of $\text{Cu}_{50}\text{Zr}_{40}\text{Ti}_{10}$ glassy alloy.

Many researches have clarified that Al addition can improve the GFA and other properties of $\text{Cu}_{50}\text{Zr}_{50}$ BMG [1,18,21–26]. For example, the critical dimension of $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x=0-12$) can be increased up to $\Phi 5\text{mm}$ by Al addition [18,22]. The T_g , T_x , ΔT_x , hardness, and elastic modulus (E) all increase with increasing Al content for $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x=0-8$) [23]. Under the same size

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($\Phi 2$ mm), the room-temperature plasticity is 4 times larger for $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ BMG (~16% [1,22]) than for $\text{Cu}_{50}\text{Zr}_{50}$ BMG (~4% [22]). The T_g , yield strength (σ_y) and fracture strength (σ_f) of the micron-sized $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x=0, 2, 4, 6$) metallic glassy wires increase with increasing Al content [24]. However, there are few reports for the effect of the substitution of Zr by Al on $\text{Cu}_{50}\text{Zr}_{50}$ glass forming alloy [26]. It was found that the T_g , σ_p and hardness of $\text{Cu}_{50}\text{Zr}_{50}$ BMG were decreased by the substitution of Zr by Al, and inversely for the E , Debye temperature (θ_D), and shear modulus (G) [26].

In the present work, we systematically investigate the effect of the substitution of Zr by Al on the phase formation, GFA, thermal and mechanical properties of $\text{Cu}_{50}\text{Zr}_{50}$ glass forming alloy.

EXPERIMENTAL

Master ingots of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys with normal compositions, as shown in Table 1, were prepared by arc melting the mixture of ultrasonically cleaned high purity Cu (99.99%), Zr (99.99%), and Al (99.99%) in a Ti-gettered argon atmosphere. Then $\Phi 2$ mm samples were prepared by suction casting into a water-cooled Cu mold. Ribbon samples were prepared by melt spinning at a wheel speed of 30 m s^{-1} . The glassy natures of the as-cast samples were characterized by X-ray diffraction (XRD) using an XD-3A diffractometer with Cu-K α . The thermal analyses for the fully amorphous ribbons were investigated by DSC-404C differential scanning calorimeter (DSC) at heating rates of 10, 20, 25, 35 K min^{-1} , respectively. Room-temperature uniaxial compression tests were performed on $\Phi 2 \times 4$ mm samples with a gauge aspect ratio of 2:1 using an Instron 3369 testing machine at a primary strain rate of $1 \times 10^{-5} \text{ s}^{-1}$. Two polished end surfaces of the samples for the compression tests were parallel each other and vertical to the symmetry axis. Polished cross sections for $\Phi 2$ mm samples were etched by 10 wt.% FeCl_3 solution for 10 s to expose the microstructures. Microstructures and fracture morphologies of $\Phi 2$ mm samples were observed by scanning electron microscopy (SEM). Compositions of the phases were analyzed by electron dispersive spectroscopy (EDS). Amorphous structure of $\Phi 2$ mm $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ was examined by selected area electron diffraction (SAED).

RESULTS

Fig. 1 presents the XRD patterns for the as-cast $\Phi 2$ mm $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys, indicating that the substitution of Zr by Al significantly affects the phase formation and GFA of these Cu-based alloys. As shown in Fig. 1, $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy has the best GFA among $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$

($0 \leq x \leq 11.0$) alloys because there are only two broad diffuse diffraction peaks, while sharp Bragg peaks corresponding to crystals for the other studied Cu-based alloys. $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 < x < 3.0$ and $x > 8.0$) alloys are almost in crystalline state, while amorphous composites for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 < x \leq 8.0$) alloys. It is found from Fig. 1a that there are only two crystalline phases, i.e., B2 CuZr and B19' CuZr for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 5.0$) alloys, the content of the two phases varies with Al content. As shown in Fig. 1b, when $5.0 < \text{Al} < 8.0$, B2 CuZr disappears and there are two new phases, i.e., $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 . Another new AlCu₂Zr phase can be clearly observed when $\text{Al} \geq 8.0$.

Polished cross-sections of the as-cast $\Phi 2$ mm samples were etched by 10 wt.% FeCl_3 solution in order to investigate the microstructures. SEM images for these Cu-based alloys are presented in Fig. 2. It is clearly seen from Fig. 2 that the microstructures were significantly changed by Al addition. There are white dot-like and cross-like phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 2$) alloys (see Figs 2a and b), dot-like and needle-like phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($4 \leq x \leq 8$) alloys (see Figs 2d and e), and bulk, dot-like and dendritic phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($9 \leq x \leq 11$) alloys (see Fig. 2f), respectively. Interestingly, although the morphologies of the phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x=0-2, 4, 5$) alloys are different from each other, their compositions are almost the same. These phases are all CuZr phase containing different Al content, but the grey phase contains more Al content than the white phase. As for $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy (see Fig. 2c), although there are many pits uniformly distributed in the matrix, no crystals can be observed. The ring halo of the SAED result (see the inset of Fig. 2c) indicates that $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy is fully amorphous state. The pits would be due to pitting corrosion resulted from the different Al content between the pits and the matrix which was examined by the EDS (not shown here). As for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($6 \leq x \leq 8$) alloys (see Fig. 2e), one can observe three phases including needle-like phase (CuZr_2), dot-like phase ($\text{Cu}_{10}\text{Zr}_7$), and the matrix (CuZr). As shown in Fig. 2f, $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($9 \leq x \leq 11$) alloys contain CuZr phase (the matrix), $\text{Cu}_{10}\text{Zr}_7$ phase (dot-like), CuZr_2 phase (dendrite), and AlCu₂Zr phase (bulk), respectively. It should be noted that all Cu-Zr phases for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($1 \leq x \leq 2$ and $4 \leq x \leq 11$) contain different Al content. The black dots in all studied Cu-based alloys belong to the corrosion pits whose composition is almost the same as the matrix.

Fig. 3 presents DSC curves of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 8.0$) fully amorphous ribbon alloys at heating rates of 10, 20, 25, 35 K min^{-1} , respectively. It is found that there is only an exothermal peak corresponding to crystallization procedure for these alloys in the studied temperature region.

Table 1 Glass transition temperature T_g , onset crystallization temperature T_s , crystallization peak temperature T_p , solidus temperature T_m , liquidus temperature T_L , supercooled liquid region ΔT_s , reduced glass transition temperature T_{rg} , $\gamma = T_s/(T_g + T_L)$, $K = (T_s - T_g)/(T_L - T_s)$, $\delta = T_s/(T_L - T_g)$, $\beta = T_s T_g/(T_L - T_s)^2$, $T_L - T_m$ at a heating rate of 10 K min⁻¹, crystallization enthalpy ΔH_s , activation energies for T_g (E_g), T_s (E_s), and T_p (E_p), sensitivity of T_g , T_s , and T_p to heating rate (β_g , β_s , β_p), fragility index m , fracture strength σ_t , and fracture strain ϵ_t , respectively

Al content (at.%)	0	1	2	3	4	5	6	7	8	9	11
T_g (K)	/	/	/	669.2	673.9	677.5	692.4	709.3	719.0	/	/
T_s (K)	/	/	/	743.1	749.1	743.3	755.6	766.0	770.2	/	/
T_p (K)	/	/	/	744.6	750.5	748.4	760.0	772.3	777.0	/	/
ΔT_s (K)	/	/	/	73.9	75.2	65.8	63.2	56.7	51.2	/	/
T_m (K)	1158.7	1146.6	1139.5	1127.5	1125.0	1136.7	1132.4	1127.5	1129.9	1134.6	1134.6
T_L (K)	1229.1	1212.0	1204.9	1192.8	1182.9	1162.3	1170.8	1170.8	1170.8	1170.8	1168.7
$T_{rg} = T_g/T_m$	/	/	/	0.5935	0.5990	0.5960	0.6114	0.6291	0.6363	/	/
$T_{rg} = T_g/T_L$	/	/	/	0.5610	0.5697	0.5829	0.5914	0.6058	0.6141	/	/
γ	/	/	/	0.3991	0.4034	0.4040	0.4055	0.4074	0.4076	/	/
K	/	/	/	0.1643	0.1734	0.1570	0.1522	0.1401	0.1278	/	/
δ	/	/	/	1.4192	1.4717	1.5332	1.5794	1.6598	1.7047	/	/
β	/	/	/	2.4590	2.6826	2.8684	3.0348	3.3157	3.4507	/	/
$T_L - T_m$ (K)	70.4	65.4	65.4	65.3	57.9	25.6	38.4	43.3	40.9	36.2	34.1
ΔH_s (J g ⁻¹)	/	/	/	46.5	48.8	45.6	44.2	46.2	48.2	/	/
E_g (kJ mol ⁻¹)	/	/	/	186.5	225.3	263.1	274.0	395.0	455.5	/	/
E_s (kJ mol ⁻¹)	/	/	/	408.6	410.7	337.8	490.1	359.6	326.8	/	/
E_p (kJ mol ⁻¹)	/	/	/	399.9	406.1	401.4	468.9	275.6	252.4	/	/
β_g	/	/	/	19.4	16.2	14.0	13.7	10.4	9.0	/	/
β_s	/	/	/	10.9	10.5	13.2	9.6	13.3	14.6	/	/
β_p	/	/	/	11.2	11.3	11.2	10.1	17.5	19.2	/	/
m	46.1 [1]	/	/	28.7	30.5	32.8	33.9	35.4	39.0	/	/
σ_t (MPa)	1500.4	1899.7	1588.8	2051.2	2042.4	1412.1	1273.7	1227.3	1281.7	1059.2	1265.0
ϵ_t (%)	9.3	10.7	8.1	8.9	7.7	5.8	5.3	7.6	6.0	5.3	8.1

Figure 1 XRD patterns for $\Phi 2$ mm $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) samples.

Figure 2 SEM microstructures for $\Phi 2$ mm $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ alloys. (a) $x = 0$ at.%, (b) $x = 1$ and 2 at.%, (c) $x = 3$ at.% (the inset is SAED pattern), (d) $x = 4$ and 5 at.%, (e) $x = 6-8$ at.%, and (f) $x = 9-11$ at.%.

The characteristic temperatures including T_g , T_x , ΔT_x , and crystallization peak temperature (T_p) were carefully determined. The relationships between the characteristic temperature and the B are shown in Figs 4a–d, respectively. These characteristic temperatures increase all with increasing B except for the ΔT_x . As shown in Fig. 4a, the T_g increases with increasing Al content for all studied heating rates, which is similar with the results for the effect of Al addition on Cu–Zr–Al amorphous alloys [18,23,25,27]. As shown in Fig. 4b, the T_x increases with increasing Al

content for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 4.0$ and $5.0 \leq x \leq 8.0$), but the T_x of $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ are higher than those of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ for all studied B . Although the dependence of the ΔT_x on the B and the Al content is more complex than that of the T_x (see Fig. 4c), the ΔT_x is larger for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \leq 5.0$) than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x > 5.0$). It indicates that the thermal stability is higher for the former than for the latter. However, researches indicate that the T_x and the ΔT_x increase with increasing Al content for $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($3.0 \leq x \leq 8.0$) amorphous alloys [18,23]. In addition, the T_p

Figure 3 DSC curves for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x = 3.0\text{--}8.0$) fully amorphous ribbons. (a) $x = 3.0$ at.%, (b) $x = 4.0$ at.%, (c) $x = 5.0$ at.%, (d) $x = 6.0$ at.%, (e) $x = 7.0$ at.%, and (f) $x = 8.0$ at.%.

increases with increasing Al content at the heating rates of 10 and 25 K min^{-1} (see Fig. 4d). As for the heating rates of 20 and 35 K min^{-1} , the T_p increases with increasing Al content when $\text{Al} \leq 4.0$ and $\text{Al} > 5.0$, while inversely for $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (see Fig. 4d). Table 1 lists the average crystallization enthalpy (ΔH_x) for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 8.0$) alloys at heating rates of 10, 20, 25, 35 K min^{-1} , respectively. As shown in Table 1, the ΔH_x increases with increasing Al content when $\text{Al} \leq 4.0$ and $6.0 \leq \text{Al} \leq 8.0$, while inversely

for $4.0 \leq \text{Al} \leq 6.0$. On the other hand, the melting curves at a heating rate of 10 K min^{-1} are shown in Fig. 5a. The values of the solidus temperature T_m , liquidus temperature T_L and $T_L - T_m$ are listed in Table 1. As shown in Fig. 5a and Table 1, one can clearly observe two melting procedures for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 4.0$) alloys but one for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($5.0 \leq x \leq 11.0$) alloys. The distance between two melting peaks decreases with increasing Al content. It indicates that $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($5.0 \leq x \leq 11.0$) alloys have the characteristic of

Figure 4 Dependence of characteristic temperatures on heating rates, (a) T_g , (b) T_x , (c) ΔT_x , and (d) T_p .

Figure 5 DTA curves for $\Phi 2\text{mm Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) samples at a heating rate of 10 K min^{-1} (a) and dependence of T_m , T_L , and $T_L - T_m$ on Al content (b).

near-eutectic compositions as compared with off-eutectic compositions for the other studied Cu-based alloys. Fig. 5b presents the dependence of T_m , T_L and $T_L - T_m$ on the Al content, respectively. It is obviously seen from Fig. 5b and Table 1 that there are complex correlations of the T_m , T_L and $T_L - T_m$ on the Al content but the T_m , T_L and $T_L - T_m$ are

all decreased by Al addition. $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ alloy characterizes in smallest T_m and $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloy in smallest T_L and $T_L - T_m$ among the studied Cu-based alloys.

The activation energies for T_g , T_x and T_p (E_g , E_x and E_p) are calculated by Kissinger equation [28] and listed in Table 1. The dependence of E_g , E_x , and E_p on Al content is shown

in Fig. 6. The E_g increases with increasing Al content, while both E_x and E_p appear a complex correlation with the Al content and have the biggest values for $\text{Cu}_{50}\text{Zr}_{44}\text{Al}_6$ alloy. In addition, the liquid behaviors of the alloys were studied by the fragility index m . The m values of the alloys were estimated by $m = DT_g/[(T_g - T_0)^2 \ln 10]$ [25] (D is the strength parameter, T_0 is the Vogel-Fulcher (VF) temperature, and T_g is glass transition temperature at a heating rate of 10 K min^{-1}). The D and T_0 are obtained through the best fitting of the tested T_g values at different heating rates according to the VF relation [25]: $B(T_g) = A \exp[DT_0/(T_0 - T_g)]$ (A is a constant). The estimated m values for these Cu-based metallic glasses are listed in Table 1. It can be found that the m values of the studied Cu-based alloys increase with increasing Al content, indicating that these Cu-based metallic glasses are more and more fragile according to Angell's point [29]. In addition, the dependence of the characteristic temperature (T_g , T_x and T_p) on the $\ln B$ was investigated and it was found that the characteristic temperature (T_g , T_x and T_p) and the $\ln B$ can be well fitted by the Lasocka's equation [30]: $T = \alpha + \beta \ln B$ (T is the characteristic temperature, α and β are constants). Obviously, β can reflect the sensitivity of the characteristic temperature to the B . The higher the β , the more is the sensitivity of the characteristic temperature to the B . The β values for T_g , T_x and T_p are listed in Table 1 and the relationships between the β and the Al content are shown in Fig. 7a. As shown in Fig. 7a and Table 1, the β_g decreases with increasing Al content, indicating that the sensitivity of the T_g to the heating rate decreases with increasing Al content. The β_p almost maintains the same when $\text{Al} \leq 6.0 \text{ at.}\%$ and sharply increases when $\text{Al} \geq 6.0 \text{ at.}\%$, indicating that the sensitivity of the T_p to the heating rate is stronger for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \geq 6.0$) alloys than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 6.0$) alloys. However, the dependence of β_x on the Al content is more complex than that of the β_g and β_p .

Figure 6 Relationships between activation energy and Al content.

Figure 7 Dependence of sensitive factors on Al content (a) and activation energy on sensitive factor (b).

Nevertheless, the β_x is larger for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \geq 6.0$) alloys than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 6.0$) alloys, indicating that the sensitivity of the T_x to the heating rate is stronger for the former than for the latter. More interestingly, both β_x and β_p have the smallest values for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x = 6.0$) alloy, indicating that the sensitivity of the T_x and T_p to the heating rate is the lowest for $\text{Cu}_{50}\text{Zr}_{44}\text{Al}_6$ alloy among all studied Cu-based alloys. The relationships between the activation energy and the β were also investigated (see Fig. 7b). Obviously, the activation energy decreases with increasing β for all studied Cu-based alloys, which is similar to Cai's results for Zr-Al-Ni-Cu BMGs [31].

Mechanical properties of the studied Cu-based alloys were investigated by room-temperature uniaxial compression tests at a primary strain rate of $1 \times 10^{-5} \text{ s}^{-1}$. Stress-strain curves are shown in Fig. 8 and the corresponding mechanical properties are listed in Table 1. It is found from Fig. 8 that all studied Cu-based alloys display room-temperature brittleness. As shown in Table 1 and Fig. 8, the fracture strength (σ_f) is higher for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x = 1.0, 3.0$,

Figure 8 Room-temperature uniaxial compression stress-strain curves for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys.

and 4.0) alloys than for the other Cu-based alloys. The σ_f is 1.8–2.1 GPa for the former and 1.0–1.6 GPa for the latter. The fracture strain (ε_f) varies in the range of 5.0–11.0 %. In addition, fracture images of the samples were observed by SEM and are shown in Fig. 9. Figs 9a–d all show typical cleavage fracture characteristics, indicating that the studied Cu-based alloys are all brittle. However, it can be clearly

seen from Figs 9b and c that there are vein-like patterns, indicating that $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 8.0$) alloys are in amorphous states [12,23,24,26,32]. The magnitude of the vein-like patterns is more for $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy (see Fig. 9b) than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($4.0 \leq x \leq 8.0$) alloys (see Fig. 9c), indicating that the amorphization is higher for the former than for the latter.

DISCUSSION

As shown in Fig. 1, the substitution of Zr by Al significantly influences the GFA and phase formation of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys. It is well-known that the GFA of the glass forming alloy is related with the atomic size, type and electronegativity, and interaction among the atoms. The atomic radius is 0.128 nm for Cu, 0.162 nm for Zr, and 0.143 nm for Al, respectively. The electronegativity is 1.9 for Cu, 1.4 for Zr, and 1.5 for Al, respectively. The mixing enthalpy is -23 kJ mol^{-1} for Cu-Zr, -44 kJ mol^{-1} for Al-Zr, and -1 kJ mol^{-1} for Al-Cu, respectively [33]. According to Inoue's empirical rules [33], the magnitude of the alloy elements in the present Cu-based alloys increases from two to three by Al addition, leading to the increase of mixing entropy. Al addition results in the increase of the size difference and negative mixing enthalpy among the atoms.

Figure 9 SEM images for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys, (a) $x = 0$ at.%, (b) $x = 3.0$ at.%, (c) $4.0 \leq x \leq 8.0$ at.%, (d) $x = 1.0, 2.0, 9.0 \leq x \leq 11.0$ at. %.

In addition, negative mixing enthalpy is larger for Al-Zr than for Cu-Zr, resulting in the increase of the category and the magnitude of short range order (see Fig. 1). These results are advantageous of the improvement in the GFA of the glass forming alloy. However, researches show that there is optimal composition regions for glass formation in any alloy system [10,14,15,18,19,25]. Thus the composition with best GFA locates at $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ among $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys. On the other hand, B19' CuZr phase is more stable than B2 CuZr phase [5,34]. The mixing enthalpy is larger for Al-Zr than for Cu-Zr, indicating that the bonding is stronger for the former than for the latter. It results in partial even full collapse of B2 CuZr phase by Al addition. In addition, there exists a transformation: $\text{CuZr} \rightarrow \text{Cu}_{10}\text{Zr}_7 + \text{CuZr}_2$ [5]. Thus $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 phases can simultaneously form when $\text{Al} \geq 6.0$, as shown in Fig. 1b. In fact, the phenomenon was found by Lin *et al.* [35] in as-cast ($\text{Cu}_{50}\text{Zr}_{50}$)₉₇ Al_3 and by Pauly *et al.* [21] in heat-treated $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$. When the Al content increases up to 8.0, AlCu_2Zr can easily form due to enough Al content (see Fig. 1b).

In addition, the GFA of the studied Cu-based alloys were evaluated by the GFA indicators, such as $T_g = T_g/T_m$ or T_g/T_L , $\gamma = T_x/(T_g + T_L)$, $K = (T_x - T_g)/(T_L - T_x)$, $\delta = T_x/(T_L - T_g)$, and $\beta = T_x T_g / (T_L - T_x)^2$ [36–39]. Fig. 10 presents the relationships between these GFA indicators and the Al content. Generally, the larger these GFA indicators, the better is the GFA for glass forming alloy. It can be observed from Fig. 10 that the GFA indicators except for K increase with increasing Al content, indicating that the GFA for the studied Cu-based alloys increases with increasing Al content. Wang *et al.* [27] found that the T_g of series of Cu-Zr-Al BMGs increase by Al addition. However, the K increases up to a

maximum at $\text{Al} = 4$ at.%, then decreases with increasing Al content, indicating that $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ is the optimal glass forming composition among $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys. As shown in Fig. 1, $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ is the optimal glass forming composition among $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) alloys. It indicates that the K is better than the other GFA indicators for the evaluation of the GFA of glass forming alloy, which is similar with our previous work [39]. In addition, previous researches [14,25,40,41] have found that the m can be considered as an indicator for the GFA of the glass forming alloy. Generally, the smaller is the m , the better is the GFA of the alloy [14,41]. If the $m = 46.1$ [1] of $\text{Cu}_{50}\text{Zr}_{50}$ amorphous alloy was considered, the m decreases when $0 \leq \text{Al} \leq 3.0$ at.%, then increases with increasing Al content, as shown in Table 1. It indicates that $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy has the smallest m (the best GFA) among $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 8.0$) alloys, which is coherent with the XRD results in Fig. 1. It is well-known that the decrease of the T_m or T_L is advantageous of the stability of the alloy liquid, resulting in the increase of the GFA [36–39,42–44]. Fig. 5b and Table 1 show the decrease of the T_m and T_L by Al addition, the lowest T_m of $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ alloy and the lowest T_L of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ alloy. Nevertheless, previous researches [42–44] have clarified that the best GFA composition for the alloy is close to deep eutectic point. It is obviously from Fig. 5b that the dependence of T_L on the Al content is significantly larger in the range of $0 \leq x \leq 5.0$ than in the range of $5.0 \leq x \leq 11.0$. Comprehensively, the GFA of $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy is the best among the studied Cu-based alloys.

CONCLUSIONS

Phase formation, glass forming ability, mechanical and thermal properties of $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$) glass forming alloys were systematically investigated. The following conclusions can be drawn.

Among the studied Cu-based alloys, $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ alloy has best GFA and can be cast into $\Phi 2$ mm BMG. $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($4.0 \leq x \leq 8.0$) alloys can be cast into $\Phi 2$ mm BMG composites, while fully crystalline for the other studied Cu-based alloys. There are two crystalline phases, i.e., B2 CuZr and B19' CuZr for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 5.0$) alloys. When $5.0 < \text{Al} < 8.0$, B2 CuZr disappears and two new phases, i.e., $\text{Cu}_{10}\text{Zr}_7$ and CuZr_2 can be formed. When $\text{Al} \geq 8.0$ at.%, another new AlCu_2Zr phase can be clearly observed.

The T_g increases with increasing Al content for all studied heating rates (B). The T_x increases with increasing Al content for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($3.0 \leq x \leq 4.0$ and $5.0 \leq x \leq 8.0$), but the T_x of $\text{Cu}_{50}\text{Zr}_{46}\text{Al}_4$ are higher than those of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ for all studied B. The ΔT_x is larger for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \leq 5.0$) than for $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x > 5.0$). The T_p increases with increasing

Figure 10 Relationships between GFA indicators and Al content.

Al content at the heating rates of 10 and 25 K min⁻¹. As for the heating rates of 20 and 35 K min⁻¹, the T_p increases with increasing Al content when Al ≤ 4.0 at.% and Al > 5.0 at.%, while the T_p of Cu₅₀Zr₄₆Al₄ are larger than those of Cu₅₀Zr₄₅Al₅. There are two melting procedures for Cu₅₀Zr_{50-x}Al_x (0 ≤ x ≤ 4.0) alloys but one for Cu₅₀Zr_{50-x}Al_x (5.0 ≤ x ≤ 11.0) alloys. The distance of two melting peaks decreases with increasing Al content. The T_m , T_L and $T_L - T_m$ are all decreased by Al addition and there are complex correlations of the T_m , T_L and $T_L - T_m$ on the Al content. Cu₅₀Zr₄₆Al₄ alloy characterizes in the smallest T_m and the smallest T_L and $T_L - T_m$ for Cu₅₀Zr₄₅Al₅ alloy among the studied Cu-based alloys.

The E_g increases with increasing Al content, while both E_x and E_p appear a complex correlation with the Al content and reach the maximum for Cu₅₀Zr₄₄Al₆ alloy. The m values of the studied Cu-based alloys increase with increasing Al content. The β_g increases with increasing Al content. Both β_x and β_p are smaller for Cu₅₀Zr_{50-x}Al_x (3.0 ≤ x ≤ 6.0) alloys than for Cu₅₀Zr_{50-x}Al_x (x ≥ 6.0) alloys. Cu₅₀Zr₄₄Al₆ alloy has the smallest β_x and β_p among all studied Cu-based alloys. The activation energy all decreases with increasing β for all studied Cu-based alloys.

All studied Cu-based alloys show the room-temperature brittleness. The fracture strength (σ_f) is higher for Cu₅₀Zr_{50-x}Al_x (x = 1.0, 3.0, and 4.0) alloys than for the other Cu-based alloys. The σ_f is 1.8–2.1 GPa for the former and 1.0–1.6 GPa for the latter.

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 本文系统地研究了 $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 11.0$)合金的相形成、玻璃形成能力、热学和机械性能。结果表明, $\text{Cu}_{50}\text{Zr}_{47}\text{Al}_3$ 合金具有最好的玻璃形成能力、最小的脆性参数和最高的断裂强度。 $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 5.0$)合金由B2 CuZr和B19' CuZr两相组成, 当 $5.0 < \text{Al} < 8.0$ at.%时, B2 CuZr相消失而 $\text{Cu}_{10}\text{Zr}_7$ 和 CuZr_2 两个新相形成, 当 $\text{Al} \geq 8.0$ at.%时, 可以明显观察到另一 AlCu_2Zr 新相。玻璃转变温度、玻璃转变温度对升温速度的敏感性、玻璃转变激活能和脆性参数随Al含量的增加而增加。 $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x \leq 5.0$)合金的过冷液相区比 $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($x > 5.0$)合金的大, $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($0 \leq x \leq 4.0$)合金的成分偏离共晶成分, 而 $\text{Cu}_{50}\text{Zr}_{50-x}\text{Al}_x$ ($5.0 \leq x \leq 11.0$)合金为近共晶成分。玻璃转变激活能、晶化激活能和晶化峰激活能随其敏感性因素的增加而降低。所述的铜基合金都表现为室温压缩脆性。另外, 对其相的形成和玻璃形成能力与Al含量的关系也进行了探讨。