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Formation and Compression Behavior of Two-Phase Bulk Metallic Glasses with a Minor Addition of Aluminum *

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A remarkable enhancement in room-temperature compressive deformability is realized by the minor-addition of 1.5 at.% Al in ZrTi-based bulk metallic glass. Two amorphous phases are observed by transmission electron microscopy in the Al-containing alloys and this explains the improvement of compression deformability. The studies suggest that phase separation might occur in glass forming alloys with a negative enthalpy of mixing.

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Bulk metallic glasses (BMGs) have attracted wide attention due to the fact that BMGs possess remarkable physical, chemical and mechanical properties, as well as great potential for application in many areas.[1−4] However, their applicability has been limited by a lack of plasticity resulting from shear localization and work softening, even in some tougher zirconium-based BMGs.[5] Many approaches have been investigated to improve room-temperature plasticity, such as introducing a micrometer-size ductile crystalline phase[6] to form nano-size structural heterogeneity[7,8] and to enhance the Poisson ratio[9,10] of an alloy.

Recently, it has been reported that the formation of phase separation is an effective approach to enhance the plasticity of a BMG.[8−11] Microscopic heterogeneity has been found in (YTi)-, Ti-, (CuZr)- and Ni-based BMGs.[7,14−17] This kind of heterogeneity is generally ascribed to liquid phase separation because there are two distinguishable contrasts in the transmission electron microscopy (TEM) image, and the composition of the two phases are evidently different. It is suggested that liquid phase separation of a BMG could easily occur upon solidification, when the alloy system contains constituent elements with a positive heat of mixing.[18−23] It is reported that adding alloying elements with a lower positive enthalpy of mixing might lead to a relatively high GFA and phase separation.[24] This was demonstrated by a few glass-forming systems, such as Zr-Ni-Cu-Al (Ni-Cu: +4 kJ/mol[25]),[10,14,26] Cu-Zr-Al-Y (Zr-Y: +9 kJ/mol[25])[24] and Cu-Zr-Al-Fe (Cu-Fe: +13 kJ/mol[25])[23] alloy systems. However, until now, phase separation has never been found in an alloy system with a negative heat of mixing. The mixing enthalpy values of $\Delta H^{AB}_{\rm mix}$ between the elements in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ alloys are summarized in Table 1. Our recent publication studied the effect of a minor Al addition in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ ($x \leq 10$) alloys on the GFA,[27] and found that the change of the width of the supercooled liquid region ΔT_x and γ ($= T_x/(T_g + T_l)$) with GFA in the alloy scales proportionally with Possion's ratio, contrasting with the general tendency among various glass forming metallic systems. It is well known that elastic moduli are directly structurally associated and explain the rigidity of a structure. The unexpected change in Possion's ratio in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ ($x \leq 10$) glass forming alloys might imply structural evolution. Therefore, in this Letter, we study the effects of 1.5 at.% Al addition on the mechanical property of the $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ glass forming alloy.

Table 1. Mixing enthalpy values of ΔH^{AB}_{mix} between any two elements of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ BMGs (from Ref. [25]).

Elements	$\Delta H^{AB}_{\rm mix}$ (kJ/mol)	Elements	$\Delta H^{AB}_{\rm mix}$ (kJ/mol)
Zr-Ti	0	Zr-Cu	−23
Zr-Al	−44	Zr-Be	−43
Ti-Cu	−9	Ti-Al	−30
Ti-Be	−30	Cu-Be	0
Cu-Al	−1	Al-Be	0

Alloy ingots with nominal composition of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ ($x = 0$ and 1.5) were prepared by arc-melting the pure elements, with a purity of 99.99 wt%, under a Ti-gettered Ar atmosphere. From the master alloy, sample rods with different diameters (3, 15, 20 mm) were produced by copper mould casting for each composition. Glass structure and crystallization phases were examined by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. Glass transition, crystallization and melting behaviors of the as-cast BMG samples were characterized by dif-

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ferential scanning calorimetry (DSC, Netzsch STA 449C) under flowing purified argon with a heating rate of 20 K/min. The compression specimens with a diameter of 3 mm and a length of 6 mm were cut from the cast rods and the ends were polished to make them parallel to each other prior to the compression test. The rod specimens were tested in uniaxial compression under an initial strain rate of $1 \times 10^{-4}\,\mathrm{s}^{-1}$ at room temperature using an Instron 5582 universal testing machine. At least three samples were tested for each composition to obtain a statistically significant result. The detailed microstructure of the as-cast samples was further examined by a transmission electron microscope (TEM, Joel 2010) coupled with an x-ray energy dispersive spectrometer (EDS) operating at 200 kV. Thin foil specimens for TEM observation were cut from the the as-cast rod with 3 mm in diameter and prepared by standard twin-jet electrochemical polishing with a solution of 7% $HClO_4$ and 93% CH_3COOH at room temperature.

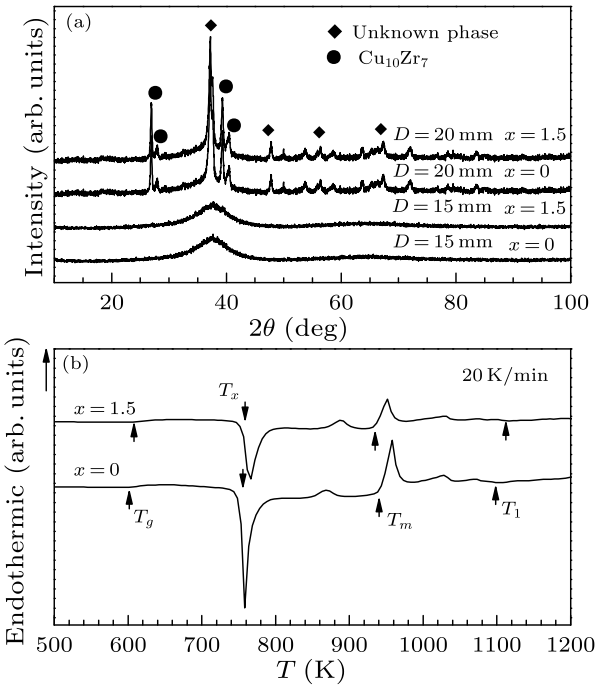

Fig. 1. XRD patterns (a) and DSC traces (b) of the as-cast $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ and $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ alloys.

Figure 1 shows the XRD patterns (a) and DSC traces (b) of the as-cast $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ and $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ alloys. XRD patterns from both samples with a diameter of 15 mm exhibited the broad diffraction maxima characteristic of amorphous structures. When the diameter was increased to 20 mm, both alloys showed some crystalline peaks, which mainly correspond to the $Cu_{10}Zr_7$ phase and some unknown crystal phases. Therefore, it is reasonable that addition of 1.5 at.% Al does not decrease the GFA of the base alloy. The DSC traces for both alloys are almost identical with a distinct glass transition and a wide supercooled liquid region around 155 K before crystallization. It can be clearly seen that 1.5 at.% Al does not change thermal behavior a great deal.

Figure 2 shows the room-temperature engineering stress-strain curves of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ and $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMGs under compression. The base alloy exhibits fracture strength and a relatively small compressive deformability of 2002 MPa and 0.78%, respectively. However, it is surprising that the 1.5 at.% Al addition results in a large improvement in compressive deformability. The maximum compressive deformability is about 15.1% for the $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMG, much larger than that for $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ BMGs. The inset in Fig. 2 shows the bending ductility of the as-cast $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ with a thickness of 1 mm (a) and 0.5 mm (b). The $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMG sheets could be bent into a "wave-like" pattern, illustrating its excellent deformability.

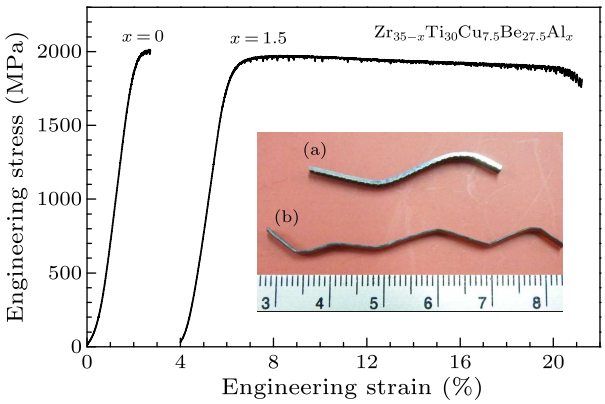

Fig. 2. Engineering stress-strain curves of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ and $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMGs under room-temperature compression. The inset shows the bending ductility of the as-cast $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ with thickness of 1 mm (a) and 0.5 mm (b).

In order to understand the different compression deformation behaviors of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Al_x$ BMGs, TEM observation was carried out to clarify the differences in their microstructures. The TEM bright-field image in Fig. 3(a), obtained from the as-cast $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ BMG, exhibits a uniform gray contrast. Additionally, the selected-area diffraction pattern (SADP) presents a halo diffraction intensity, i.e. the typical characteristic of an amorphous alloy. In contrast, the TEM bright-field image (as shown in Fig. 3(b)) of the as-cast $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMG shows the presence of two different phases with brighter and darker contrasts, indicating that phase separation might occur during solidification. The SADP for the $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ BMG does

not show any diffraction spots, confirming that the bright and dark contrast phases are all amorphous. The two amorphous phases are separated by a round interface, indicating that they are formed by separation in the liquid state during cooling.[15] It appears that the enhanced compressive deformability with 1.5 at.% substitution of Zr by Al is due to microstructure evolution.

Since Beryllium could not be detected due to the limitation of the TEM/EDS, the chemical compositions given by the EDS analysis denote the relative atomic percentage of the other four elements. The EDS analysis (see Table 2) for the as-cast $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ alloy reveals that the brighter phase was enriched with Zr and Ti, and the darker phase was enriched with Cu. The characteristic length scale for the glassy phase with a darker contrast was about 10 nm. Therefore, it is reasonable to suggest that phase separation occurred during solidification.

Table 2. Analytical compositions (at.%) over three measurements in the brighter phase and darker phase in the as-cast $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ glassy alloys.

	Zr	Ti	Cu	Al	O
Brighter phase	31.8	37	23.8	1.3	6.1
Darker phase	26.6	31.4	34.8	1.2	6

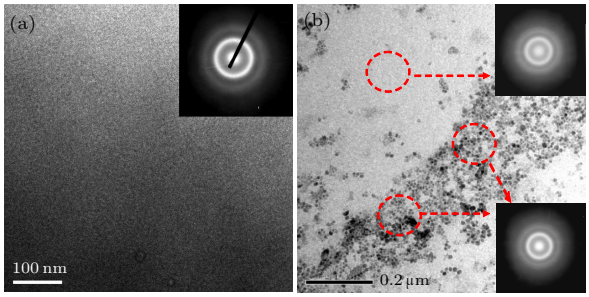

Fig. 3. TEM bright-field images with the inset of selected-area diffraction patterns for $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ (a) and $Zr_{33.5}Ti_{30}Cu_{7.5}Be_{27.5}Al_{1.5}$ (b) BMGs.

Generally, liquid phase separation can occur by two mechanisms, i.e., by spinodal decomposition or by nucleation and growth.[28] While spinodal decomposition results in two metastable liquid networks that interpenetrate each other, as reported in Pd-Si alloys,[8,29] liquid phase separation by nucleation and growth leads to a droplet-type structure.[30] As shown in Fig. 3(b), Cu-rich droplets with a darker contrast are embedded in the ZrTi-rich amorphous matrix, suggesting that the formation of the two glassy phases has most likely taken place in the nucleation and growth regime. According to the previous studies on liquid phase separation by Chang *et al.*,[30,31] the schematic pseudobinary phase diagram of the liquid phase is shown in Fig. 4. Under the condition of a high cooling rate, an alloy X will first nucleate a liquid rich in A as it enters the miscibility gap. However, the decomposition will not go to completion due to the reduced time available for mass transport due to the high cooling rate and the matrix will follow a path similar to that shown schematically by the dotted line in Fig. 4. The kinetics of phase separation will drastically slow down due to a large increase in viscosity when crossing T_g and thus the A rich droplets form by phase separation (nucleation and growth mechanism). This model can effectively explain the phase separation in the current ZrTiCuBeAl alloy. If the matrix composition reaches the spinodal above the glass transition temperature T_g, a spinodal phase decomposition will occur.

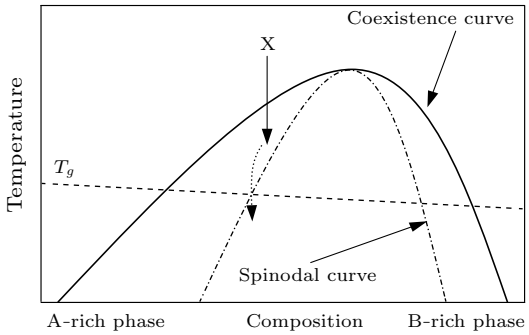

Fig. 4. Schematic drawing describing the phase separation during solidification in a pseudobinary system. The diagram includes the miscibility gap (coexist curve) and the spinodal boundary (dash-dotted line).

In summary, a significant enhancement of compressive deformability has been achieved for a Zr-based BMG by the substitution of Zr by 1.5 at% Al. The occurrence of phase separation with the formation of two glassy phases is responsible for the improvement of compressive deformability. The present study suggests that phase separation can occur in the alloy systems with a negative heat of mixing. It proves that the creation of nano-scaled two-glass phases through liquid phase separation is a promising route for enhancing the compressive deformability of BMGs.

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