Transition from Plasticity to Brittleness in Cu-Zr-Based Bulk Metallic Glasses

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The effects of addition of Al and Ag on the mechanical properties of the $\text{Cu}_{50}\text{Zr}_{50}$ alloy are investigated. It is found that the plasticity of the Cu-Zr-based BMGs decreases as the content of the alloying elements of Al and Ag increases. A clear transition from plasticity to brittleness occurs for the Cu-Zr-based BMGs with increasing the content of Al and Ag. Combining with previous work on the plasticity or brittleness of the Cu-Zr-based BMGs, the role of the atomic binding force between the solute and solvent atoms is suggested to understand the transition from plasticity to brittleness for the Cu-Zr-based BMGs. [doi:10.2320/matertrans.MF200620]

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1. Introduction

Bulk metallic glasses (BMGs) have been developed in a number of alloy systems in the last decade.¹⁾ Because of their unique physical and mechanical properties, BMGs have been considered as the promising structural materials. As compared with the conventional crystalline metals, the deformation of BMGs is concentrated into the localized shear bands. As a result, BMGs typically display limited plastic flow in compression (0%–2%) and none in tension at room temperature. BMGs can be divided into two types: tough BMGs and brittle BMGs.^{2,3)} The tough BMGs exhibit high fracture toughness ($K_{\text{IC}} > 20 \text{ MPa m}^{1/2}$) and a vein pattern of fracture surface with high local plasticity arising from instabilities in the band of lowered viscosity.^{4–7)} The Zr-based, Pd-based, Cu-based and Ti-based BMGs belong to the tough BMGs. The brittle BMGs are both globally and locally brittle. Typical characteristics of the brittle BMGs are the low fracture toughness ($K_{\text{IC}} < 5 \text{ MPa m}^{1/2}$) and a flat mirror fracture surface.⁸⁾ BMGs based on magnesium and iron are the brittle BMGs. In addition, the precipitation of the crystalline phase always results in low ductility of BMGs.⁹⁾ Recently, several correlations were established in order to understand the brittleness or plasticity of the BMGs. It was reported that there existed a correlation between the fracture toughness and plastic process zone size for various glasses.⁸⁾ Lewandowski *et al.*²⁾ found another clear correlation between the energy of fracture G and elastic modulus ratio μ/B for metallic glasses, which showed that a brittle-to-tough transition occurs at a critical value of $\mu/B > 0.41$ – 0.43 (or, equivalently, with Poisson's ratio $\nu > 0.31$ – 0.32). Gu *et al.*¹⁰⁾ reported that the elastic moduli of Fe-Mo-C-B bulk amorphous steel changed with adding different content of lanthanides, and an onset of plasticity was observed as ν approached 0.32 from below. They also suggested that the brittleness of metallic glasses could be alleviated by alloying elements with high ν as constituents, or introducing the elements with strong interatomic interaction.^{2,10)}

It is well known that Cu-Zr-based BMGs exhibit high strength and high ductility under compression tests, which is a kind of typical tough BMGs. Recently, we found that

addition of Al and Ag significantly improved the glass-forming ability of $\text{Cu}_{50}\text{Zr}_{50}$ binary alloys.¹¹⁾ Interestingly, the Cu-Zr-based BMGs were found to make a transition from plasticity to brittleness with increasing the content of Al and Ag. It is a useful work to investigate the effects of the alloying elements on the plasticity or brittleness of the BMGs, which will help us to understand the nature of the plasticity or brittleness of the BMGs and develop the ductile BMGs. In this work, the compressive properties of the Cu-Zr-based BMGs with different contents of Al and Ag were examined, and the effect of the content of alloying elements on the plasticity or brittleness of the Cu-Zr-based BMGs was also discussed.

2. Experimental Methods

Multicomponent alloy ingots with nominal composition $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}(\text{Al}_{0.5}\text{Ag}_{0.5})_x$ ($x = 4, 8, 12, 16, 20$) were prepared by arc melting mixtures of Cu, Zr, Al and Ag with a purity of 99.99%, 99.5%, 99.99% and 99.99%, respectively, in a high purity argon atmosphere. Bulk cylindrical rods were prepared by copper mold casting in an argon atmosphere. The structure of the as-cast samples was examined by X-ray diffraction (XRD). Room temperature compression tests were carried out using an Instron testing machine and the strain rate was $5 \times 10^{-4} \text{ s}^{-1}$. The strain gages were used to measure the elastic modulus. The test specimen had a cylindrical form of 2 mm in diameter and 4 mm in height. Fracture surface was examined by scanning electron microscopy (SEM).

3. Results

Before compression tests, all the samples were examined for amorphicity by XRD. Figure 1 shows the nominal compressive stress-strain curves of the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}(\text{Al}_{0.5}\text{Ag}_{0.5})_x$ as-cast rods with a diameter of 2 mm. The elastic moduli had been calibrated using the strain gages glued on the samples. For the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ BMG, the compressive fracture strength (σ_f), yield strength (σ_y) and plastic strain (ϵ_f) are 1834 MPa, 1790 MPa and 2.37%, respectively. As the contents of Al and Ag increase, the strength increases, but the plastic strain decreases. The σ_f , σ_y

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Fig. 1 Compressive stress-strain curves of the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}-(\text{Al}_{0.5}\text{Ag}_{0.5})_x$ (A: $x = 4$; B: $x = 8$; C: $x = 12$; D: $x = 16$; E: $x = 20$) glassy rods with a diameter of 2 mm.

Fig. 2 SEM micrographs of the out surface of the as-cast rods with a diameter of 2 mm after compressive test for the Cu-Zr-based BMGs (a) $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$; (b) $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$; (c) $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$.

and ε_f are 1864 MPa, 1810 MPa and 0.33%, respectively, for the $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_4\text{Ag}_4$ BMG, and 1906 MPa, 1868 MPa and 0.29%, respectively, for $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$ BMG. The $\text{Cu}_{42}\text{Zr}_{42}\text{Al}_8\text{Ag}_8$ BMG exhibits high yield strength of 1953 MPa and low plastic strain of 0.14%. For the $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ BMG, neither any yielding nor plastic strain was observed on the stress-strain curves. It is obvious that the $(\text{Cu}_{0.5}\text{Zr}_{0.5})_{100-x}-(\text{Al}_{0.5}\text{Ag}_{0.5})_x$ BMGs become brittle with increasing the content of Al and Ag.

In order to simplify the analysis, we selected the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$, $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$ and $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ BMGs as the following research targets. Figure 2 shows the outer surface of the Cu-Zr-Al-Ag alloy rods after compressive fracture. The fracture of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ alloy rod occurred in a shear mode. The angle between the fracture surface and compression axis is close to 45° . The sample broke into two parts after compression test. As shown in Fig. 2(a), a large number of shear bands, indicated with arrows, appear on the outer surface of the fracture sample. Similar to the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ alloy, the $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$ alloy rod also broke into two parts with an angle of 45° between the fracture surface and the compression axis. However, only one shear band was observed on the outer surface. For the $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ alloy, the angle between the fracture surface and the compression axis is about 90° . Except for the part shown in Fig. 2(c), the other had broken

Fig. 3 SEM micrographs of the compressive fracture surface of the Cu-Zr-Al-Ag BMGs (a) $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$; (b) $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$; (c) $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$.

into pieces. No evidence for a shear band was observed on the outer surface of the $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ sample. Figure 3 shows the SEM images of the fracture surface of the Cu-Zr-Al-Ag alloy rods. The fracture surface of the $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ alloy rod exhibits a vein-like pattern. In addition, a lot of melted liquid balls appear on the surface for the Cu_{48} -

Fig. 4 Compressive stress-strain curves (a) and SEM images (b), (c) of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ (A) and $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ (B) BMGs.

$\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ alloy rod, suggesting that a larger amount of strain along the shear band led to localized melting before fracture. For the $\text{Cu}_{44}\text{Zr}_{44}\text{Al}_6\text{Ag}_6$ alloy, the fracture surface exhibits a typical vein-like pattern of glassy alloys. In the case of $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ alloy, the fracture surface exhibits a cleavage feature without any vein-like pattern, which is a characteristic of brittle fracture. These results clearly indicate that the glassy alloys make a transition from plasticity to brittleness as compositions change from $\text{Cu}_{48}\text{Zr}_{48}\text{Al}_2\text{Ag}_2$ to $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$. For comparison, we also examined the compressive properties of the ternary $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ and $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ BMGs. Figure 4 shows the compressive stress-strain curve and the fracture morphologies of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ and $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ glassy rods with a diameter of 2 mm. The $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ and $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ BMGs exhibit high yield strengths of about 1900 MPa and plastic strains of about 0.2~0.3%. As shown in Fig. 4, the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ and $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ BMGs failed in the same shear mode with a vein-like pattern on the fracture surface.

4. Discussion

The stress-strain curves and the appearance of fracture surfaces reveal a typical transition from plasticity to brittle-

Fig. 5 Plastic strain as a function of the content x of the alloying elements in Cu-Zr-based BMGs. The data of Cu-Zr-Al-Y BMGs comes from ref. 14), the data of Cu-Ag-Zr-Ti and Cu-Ni-Zr-Ti comes from ref. 13).

ness in fracture mode for the Cu-Zr-Al-Ag BMGs with increasing the contents of Al and Ag. It is noted that Ag has a high Poisson ratio of 0.37 as compared with Zr (0.34), Cu (0.34) and Al (0.35). Actually, high content of Ag decreased the plastic strain of the Cu-Zr-based BMGs,¹²⁾ inconsistent with Lewandowski's suggestion.²⁾ It seems that the brittleness of the $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ BMG results from the addition of Ag. However, the corresponding $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ glassy rod exhibited the same typical ductile fracture mode as the ternary $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ BMG. It has been reported that enhanced plasticity can be obtained for the BMGs with an alloying element having a positive heat of mixing with some of the constituent elements,^{13,14)} such as Cu-Zr-Ti-Ag, Cu-Zr-Ni-Ti and Cu-Zr-Al-Y BMGs, in which Cu has a positive heat of mixing with Ag, Ni and Y. Figure 5 summarizes the fluctuations of the plastic strain of the Cu-Zr-based BMGs as the content of the alloying elements increase. It is seen that the plasticity is only obtained in a limited composition range. Beyond the limited composition range, the Cu-Zr-based BMGs exhibit a brittle fracture mode. Park *et al.*¹³⁾ suggested that the addition of an alloying element having a positive heat of mixing might influence local chemical inhomogeneity, which affected the formation and propagation of the shear bands during deformation. However, they did not give an explanation for that higher content of alloying elements resulted in extreme brittleness for the Cu-Zr-based BMGs. The plasticity or brittleness of the Cu-Zr-based BMGs is sensitive to not only the alloying elements but also the concentrations of the alloying elements.

Up to now, the detailed atomic structure of the glassy alloys has not been quantitatively established, especially for the multicomponent glassy alloys. Recently, Miracle^{15,16)} presented an efficient cluster packing model for metallic glasses, which combined random positioning of solvent atoms with atomic order of solutes. Good agreement between experiment and predication has been achieved for this model. For the Cu-Zr-based BMGs, let it be supposed that the Cu and Zr atoms are the solvent atoms and the other atoms such as Al, Ag, Y, Ni and Ti are the solute atoms. It is noted that the heats of mixing for the Cu/Ag or Ni and Zr/Y atomic pairs

are positive and the heat of mixing between Al and Cu is only -1 kJ/mol, which means a low atomic binding force for the Cu/Ag (Ni or Al), and Zr/Y atomic pairs.¹⁰⁾ On the contrary, Ag, Al and Ni have strong negative heats of mixing with Zr, suggesting that strongly-bound atomic pairs may form among these atomic pairs. Consequently, the Cu/Ag (Ni or Al), and Zr/Y pairs might be the “weak” pairs in the efficient atomic dense packing of the Cu-Zr-Al-Ag(Y) glassy alloys, which results in formation of the “weak point” in glassy structure. When the glassy alloys deforms under compressive loading, the “weak” atomic pairs might be easy to be broken as compared with the strongly-bound atomic pairs. As the content of the alloying elements increases, the number of the “weak” point will increase. When the number of “weak” points reaches a critical value, the glassy alloys might change to brittle. As shown in Fig. 3(c), the fracture surface of the brittle $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ BMG exhibits a cleavage pattern, not the typical vein-like pattern of the glassy alloys. This indicates that the failure of the $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ BMG might result from the catastrophic split of the “weak” atomic pairs, not the viscous flow of the localized shear bands. Moreover, different from the shear mode of the ductile BMGs, the brittle $\text{Cu}_{40}\text{Zr}_{40}\text{Al}_{10}\text{Ag}_{10}$ glassy sample finally failed into a lot of pieces under compressive loading, which also shows that the catastrophic split of the “weak” atomic pairs leads to the failure of the glassy alloys. As consistent with our results, Zhang’s work¹⁷⁾ also demonstrated that the fracture mode of the BMGs was related with the surface energy or bonding strength of the atomic pairs.

As cited in the above, the addition of Y, Ag or Ni to Cu-Zr-based BMGs increases the “weak” atomic pairs and leads to brittleness. Nevertheless, the total brittleness of the BMGs requires enough content of these alloying elements. As shown in Figs. 1 and 5, the Cu-Zr-based BMGs with low contents of alloying elements exhibit a small amount of plastic deformation under compressive loading. This result indicates a small amount of “weak” atomic pairs cannot evidently degrade the intrinsic toughening of metallic glass. It exist a critical content of the alloying elements for the brittleness of BMGs. In addition, the Cu-Zr-based alloys with low contents of alloying elements usually always have a low glass-forming ability, and then the nanocrystalline phases easily precipitate from the glassy matrix. It has been reported that a positive heat of mixing also contributes to formation of nanocrystalline particles or chemical inhomogeneity.^{14,18,19)} Therefore, the nanocrystalline particles in the ductile glassy matrix can stop the propagation of the shear bands and improve the plasticity of the BMGs with low content of alloying elements.^{18,19)} However, if the content of the alloying elements or the amount of the “weak” atomic pairs reaches the critical value, the metallic glasses will lose their intrinsic toughening. Under this condition, the metallic glasses will not exhibit any plasticity, even though the nanocrystalline phases precipitate from the glassy matrix.

Perhaps, a new correlation between the plasticity or brittleness and the content of alloying elements should be established to help us to design the ductile BMGs.

5. Conclusions

The present works show that the plasticity of the Cu-Zr-based BMGs decreases as the content of the alloying elements of Al and Ag increases. The plasticity of the Cu-Zr-based BMGs is only obtained by adding a limited content of the alloying elements. Beyond the limited composition range, the Cu-Zr-based BMGs exhibit a brittle fracture mode. A clear transition from plasticity to brittleness occurs for the Cu-Zr-based BMGs with increasing the content of Al and Ag. The plasticity or brittleness of the Cu-Zr-based BMGs is sensitive to the concentrations of the alloying elements.

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