Glass-Forming Ability and Mechanical Properties of the Ternary Cu-Zr-Al and Quaternary Cu-Zr-Al-Ag Bulk Metallic Glasses

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The effects of addition of Al and equivalent atomic ratio of Ag and Al on the glass-forming ability (GFA) of the Cu$_{50}$Zr$_{50}$ alloy are investigated. It is found that the alloy with the highest GFA is the Cu$_{46}$Zr$_{42}$Al$_{8}$ alloy in ternary (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ alloys, and the critical diameter is at least 8 mm. The simultaneous addition of Ag and Al is more effective to increase the glass-forming ability of the binary Cu$_{50}$Zr$_{50}$ alloy. The critical diameter of a glassy rod is 12 mm for the Cu$_{50}$Zr$_{50}$Al$_{8}$ alloy. High stabilization of the supercooled liquid is the reason for high GFA of the Cu$_{50}$Zr$_{50}$Al$_{8}$ and Cu$_{50}$Zr$_{50}$Ag$_{8}$ alloys. Both glassy alloys exhibited high fracture strength above 1960 MPa, but no distinct plastic strain is seen. There is no evident difference in the mechanical properties of the as-cast Cu$_{50}$Zr$_{50}$Al$_{8}$ and Cu$_{50}$Zr$_{50}$Ag$_{8}$ glassy rods with different diameters.

1. Introduction

In the last decade, bulk metallic glasses (BMGs) have been developed in many multicomponent alloy systems. BMGs have been considered as the promising structural materials because of their unique physical and mechanical properties. Recently, much attention has been paid to Cu-based BMGs, which exhibit higher strength and lower material price as compared with Zr-base BMGs. Development of the Cu-based BMGs with large size will contribute to their industrial application as engineering materials. The Cu-rich BMGs were first reported in Cu-Zr-Ti and Cu-Zr-Al ternary alloy systems by Inoue group. Since then, a number of studies have been subsequently performed to improve the GFA by adding the fourth elements to the Cu-Zr-Ti and Cu-Zr-Al ternary alloys. Recently, it was found that addition of Y or Ag element can remarkably enhance the GFA of Cu-based alloys. The critical diameter of Cu-based BMGs has been raised from 4 mm to 10 mm.

It has been found that binary Cu-Zr alloys can form BMGs including nanocrystalline particles in a wide range of compositions, among which Cu$_{50}$Zr$_{50}$ has a small critical casting thickness below 2 mm. Considering that very high GFA is obtained in Zr-Cu-Al system, it is possible to increase GFA of the Cu$_{50}$Zr$_{50}$ alloy by addition of Al. Moreover, we also found that addition of Ag can improve the GFA of the Cu$_{50}$Zr$_{50}$ alloy. According to the multicomponent rules for alloy design of BMGs, it is expected that simultaneous addition of Al and Ag elements to Cu$_{50}$Zr$_{50}$ alloy can develop Cu-based BMGs with higher GFA. In this paper, the effect of addition of Ag and/or Al on the GFA and mechanical property of Cu$_{50}$Zr$_{50}$ alloy was systemically investigated, and the reason for high GFA of quaternary Cu-Zr-Al-Ag alloys was discussed.

2. Experimental Methods

Multicomponent alloy ingots with nominal compositions of (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ ($x = 0, 2, 4, 6, 8, 10$) and (Cu$_{50}$Zr$_{50}$)$_{100-x}$Ag$_{x}$ ($x = 0, 4, 8, 12, 16, 20$) 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. In addition, ternary (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ alloys were prepared by arc melting under the same condition. Bulk cylindrical rods were prepared by copper mold casting in an argon atmosphere. Ribbon samples were prepared by melt spinning. The structure of the as-cast samples was examined by X-ray diffraction (XRD) with Cu-K$_\alpha$ source. The glass transition and the crystallization were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The melting points were measured by differential thermal analysis (DTA) at a heating rate of 0.33 K/s. Transmission electron microscopy (TEM) investigation and energy dispersive X-ray analysis were performed using a JEOL 2010 microscope. Room temperature compressive tests were carried out using an Instron testing machine and the strain rate was $5 \times 10^{-4}$ s$^{-1}$. The test specimen had a cylindrical form of 2 mm in diameter and 4 mm in height.

3. Results

3.1 GFA of the ternary (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ alloys

In order to evaluate the GFA of the (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ alloys, we examined the effect of Al addition on the thermal stability of supercooled liquid. Figure 1 shows the DSC curves of the melt-spun (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ ($x = 0$ to 10) glassy alloys. All the samples exhibit a clear endothermic heat event characteristic of the glass transition, followed by characteristic exothermic transformations from the undercooled liquid to the equilibrium crystalline phases. The glass transition temperature $T_g$ and the onset temperature of the first crystallization event $T_i$ are marked with arrows in Fig. 1 and summarized in Table 1. The $T_g$ increases monotonously from 675 to 710 K with increasing Al content from 0 to 10 at%, while the $T_i$ increases from 724 to 789 K as the content of Al increases from 0 to 8 at%, and then decreases to 77 K for the Cu$_{50}$Zr$_{50}$Al$_{10}$ alloy. Figure 2 shows the DTA curves of the (Cu$_{50}$Zr$_{50}$)$_{100-x}$Al$_{x}$ alloys, where the liquidus temperature $T_l$ is marked with arrows (also in Table 1). As

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the Al content increases from 0 to 8 at%, the $T_l$ decreases from 1246 to 1172 K. Then the $T_1$ increases to 1230 K for the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy. Here, it is noticed that the melting process of the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy exhibits only one major exothermic event characteristic of a ternary eutectic reaction. Based on the thermal data of DSC and DTA, the temperature interval of the supercooled liquid region $\Delta T_g$ ($\Delta T_g = T_l - T_e$), the reduced glass transition temperature $T_{rg} (T_{rg} = T_l / T_1)$ and the new criterion for GFA $\gamma (\gamma = T_l / (T_g + T_1))^{15}$ are listed in Table 1. As the Al content changes from 0 to 8 at%, the $\Delta T_g$ increases significantly from 47 K to 93 K, indicating that stabilization of supercooled liquid against crystallization is distinctly enhanced. For a further increase of Al content, the $\Delta T_g$ begins to decrease. Similar as the result of $\Delta T_g$, the $T_{rg}$ and $\gamma$ increase with increasing Al content from 0 to 8 and then decrease with further increasing Al content. It is clear that the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy exhibits the largest values of $\Delta T_g$, $T_{rg}$ and $\gamma$ among the (Cu$_{0.5}$Zr$_{0.5}$)$_{100-x}$Al$_x$ alloys. Therefore, the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy is expected to have the best GFA.

We examined the GFA of the (Cu$_{0.5}$Zr$_{0.5}$)$_{100-x}$Al$_x$ alloys by copper mold casting. Consistent with the desired results, the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy exhibits the highest GFA among the (Cu$_{0.5}$Zr$_{0.5}$)$_{100-x}$Al$_x$ alloys. Figure 3 shows the XRD patterns of the Cu$_{46}$Zr$_{50}$Al$_{10}$ alloy rods with diameters of 8 and 10 mm, together with the result of the melt-spun glassy alloy ribbon. It can be seen that the pattern of the 8-mm rod consists of only broad diffraction maxima without any sharp Bragg peaks, indicating that this 8-mm rod is a glassy structure. Moreover, the 10-mm rod, even though one sharp peak appears on the XRD pattern, still possesses very large glassy fraction judging from the broad diffraction background on its XRD pattern. This result indicates that the critical diameter of the Cu$_{46}$Zr$_{50}$Al$_{10}$ fully glassy alloy is at least 8 mm.

### 3.2 GFA of the quaternary (Cu$_{0.5}$Zr$_{0.5}$)$_{100-x}$Ag$_{0.5}$Al$_x$ alloys

Figure 4 shows the DSC curves of the melt-spun (Cu$_{0.5}$-
Zr$_{0.5}$ alloys. As the composition changes from Cu$_{0.5}$Zr$_{0.5}$ to Cu$_{0.4}$Zr$_{0.6}$Al$_{0.5}$Ag$_{0.5}$, the $T_g$ increases from 675 to 716 K, whereas the $T_f$ increases from 724 to 790 K and then decreases to 765 K. As a result, the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy exhibits the largest $T_g$ decrease among this alloy system (as shown in Table 1). Figure 5 shows the DTA curves of the Cu$_{0.5}$Zr$_{0.5}$ (100−$x$)(Ag$_{0.5}$Al$_{0.5}$)$_x$ alloys, where the liquidus temperature $T_l$ is marked with arrows. It is seen that the alloy compositions significantly affect $T_l$ and the melting behavior. As the content of Al and Ag increases from 0 to 12, the $T_l$ decreases. The Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy exhibits the lowest melting point. With further increasing the content of Al and Ag, the $T_l$ begins to increase. As shown in Table 1, the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy also exhibits the largest $T_l$ and $T_g$ values among the (Cu$_{0.5}$Zr$_{0.5}$)$_{100-}$ (Ag$_{0.5}$Al$_{0.5}$)$_x$ alloys.

In order to examine the GFA of the (Cu$_{0.5}$Zr$_{0.5}$)$_{100-}$ (Ag$_{0.5}$Al$_{0.5}$)$_x$ alloy, the bulk as-cast rods with different diameters were prepared by copper mold casting. It was found that a bulk glassy rod with a diameter of up to 12 mm was obtained for the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy. However, the critical diameter for the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy is less than 10 mm. This result deviates from the evaluation based on the thermal data. Figure 6(a) shows XRD patterns of the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy rods with diameters ranging from 8 to 12 mm, together with the result of the melt-spun glassy alloy ribbon. The XRD patterns of all the samples consist only of a broad peak, and no diffraction peak corresponding to a crystalline phase is seen, indicating that a glassy single phase was formed. Figure 6(b) shows the TEM micrograph and electron diffraction pattern of the central part of the as-cast Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy rod with a diameter of 12 mm. Neither obvious crystals nor splitting of the halo peak is observed in the bright-field TEM image and selected-area diffraction pattern, in agreement with the XRD result. It has been reported that the critical diameter of the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ BMG is 8 mm. Therefore, a slight deviation of the composition from the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy results in higher GFA of the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloy.

### 3.3 Mechanical properties of ternary Cu-Zr-Al and quaternary Cu-Zr-Al-Ag BMGs

Figure 7 shows the compressive stress-strain curves of the as-cast glassy Cu$_{44}$Zr$_{44}$Al$_6$ and Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ alloys. Both glassy alloys exhibited high fracture strength above 1960 MPa, but no distinct plastic strain is seen. Sung et al. has reported that the Cu$_{44}$Zr$_{44}$Al$_6$Ag$_8$ BMG exhibits a
The effectiveness of the three component rules for which satisfy the three empirical component rules, into the effective way is to add special multicomponent elements, about considerable discrepancy in the glassy structure. 

In order to develop the alloys with high GFA, a simple and effective way is to add special multicomponent elements, which satisfy the three empirical component rules, into the alloys. The effectiveness of the three component rules for stabilization of supercooled liquid has been proved on the basis of a number of successful finding of new bulk glassy alloy systems.\(^1\) We found that addition of Al can significantly improve the GFA for the (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)Al\(_x\) alloys. As shown in Fig. 3, the critical diameter increases from 5 mm to 8 mm with increasing the Al content from 4 to 8 at\%. It has been suggested that addition of Al to Cu-Zr alloys contributed to formation of a unique glassy structure with highly dense random packing owing to negative mixing heat and large atomic size mismatch among the constituents.\(^4\) It is found that the liquidus temperature decreases with increasing the Al content from 0 to 8 at\%. The Cu\(_{46}\)Zr\(_{46}\)Al\(_8\) alloy lies near a ternary eutectic (Fig. 2). Therefore, high GFA of the Cu\(_{46}\)Zr\(_{46}\)Al\(_8\) alloy is associated with deep eutectic and high stabilization of supercooled liquid, which suppress nucleation and growth reactions of a crystalline phase from liquid.

Addition of Ag to Cu-Zr-Al does not satisfy the three component rules, since the Cu-Ag pair has a slightly positive heat of mixing. However, Zhang et al. found that addition of Ag can evidently improve the GFA of binary Cu-Zr alloys.\(^{14}\) The critical diameter of the Cu\(_{44}\)Zr\(_{45}\)Al\(_{10}\) BMG is up to 6 mm. Moreover, the addition of Ag was reported to increase the GFA of the ternary Cu-Zr-Ti alloys.\(^9\) High GFA of these Cu-Zr-based alloys was found to be related to the high stabilization of liquid. It was found that addition of Ag remarkably decreases the melt points of these Cu-Zr-based alloys. For the ternary Cu-Zr-Ag alloys, the addition of Ag to Cu-Zr binary alloys lowers the liquidus temperature and brings the ternary alloy closer to a eutectic at 10 at\% Ag. For the Cu-Zr-Ti-Ag alloys, addition of Ag lowers the melt point by 70 K, and the critical diameter of the Cu\(_{44}\)Zr\(_{45}\)-Al\(_{10}\) BMG is 10 mm.\(^{39}\) The Cu-Zr-Ag-Al alloys were also found to obtain a deep quaternary eutectic at the Cu\(_{36}\)Zr\(_{48}\)Al\(_8\)Ag\(_8\) alloy, the critical diameter of which exceeds 15 mm.\(^{18}\) For the current (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)(Ag\(_{0.5}\)Al\(_{0.5}\))\(_x\) alloy system, the melting point decreases as the content of Al and Ag increases, similar as the ternary Cu-Zr-Ag and quaternary Cu-Zr-Ti-Ag alloys. Thus, addition of Ag appears to contribute to formation of high stabilization of supercooled liquid, which leads to high GFA of (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)(Ag\(_{0.5}\)Al\(_{0.5}\))\(_x\) alloy. Although the Cu\(_{46}\)Zr\(_{46}\)Al\(_8\)Ag\(_8\) alloy is located near the eutectic point, the GFA of the Cu\(_{46}\)Zr\(_{44}\)Al\(_8\)Ag\(_8\) alloy is lower than the Cu\(_{46}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) alloy. The displacement of the best glass-forming compositions from eutectic compositions may be attributable to asymmetry in the eutectic coupled zone. A skewed eutectic-coupled zone, normally associated with irregular eutectic growth, is always skewed towards the faceted phase owing to its persistence of growth difficulty even at high undercooling.\(^{19,20}\) As a result, much higher critical cooling rates are required for the formation of a fully glassy phase for the eutectic alloys (see ref. 19 for the detailed discussion). In many systems, the better glass formers are found at off-eutectic compositions, e.g. La-Al-Cu-Ni alloy system,\(^{19}\) Cu-Zr binary alloys\(^{20}\) and (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)(Al\(_{0.5}\)Ti\(_{0.5}\))\(_x\) alloys.\(^{21}\) Therefore, the alloy with the best GFA locates at the Cu\(_{42}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) alloy, not the eutectic Cu\(_{44}\)Zr\(_{44}\)Al\(_8\)Ag\(_6\) alloy in the current alloy system. In addition, we found that high casting temperature was beneficial to the formation of bulk glassy samples with larger sizes for the Cu\(_{44}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) alloy. Such a condition is probably related to total melting of the primary phases in the off-eutectic Cu\(_{44}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) alloy, which promotes the constituent homogenization of the melt and contributes to the formation of Cu\(_{42}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) BMG with large size.

5. Conclusions

We examined the GFA of ternary (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)Al\(_x\) alloys and quaternary (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)(Ag\(_{0.5}\)Al\(_{0.5}\))\(_x\) alloys. The results obtained were summarized as follows:

1. Among the ternary (Cu\(_{0.5}\)Zr\(_{0.5}\))\(_{100-x}\)Al\(_x\) alloys, the Cu\(_{46}\)Zr\(_{46}\)Al\(_8\) alloy exhibits the largest values of \(T_g\) and \(\gamma\). Actually, the Cu\(_{46}\)Zr\(_{46}\)Al\(_8\) alloy exhibits the best GFA in this alloy system, and the critical diameter of glassy alloy is at least 8 mm.

2. The addition of Ag and Al is more effective to increase the glass-forming ability of the binary Cu\(_{46}\)Zr\(_{50}\) alloy. The critical diameter of a glassy rod is 12 mm for the Cu\(_{42}\)Zr\(_{42}\)Al\(_8\)Ag\(_8\) alloy, which exhibits the best GFA in this alloy system.
(3) The Cu_{46}Zr_{46}Al_{8} and Cu_{42}Zr_{42}Al_{8}Ag_{8} glassy alloys exhibited high fracture strength above 1960 MPa, but no distinct plastic strain is seen. There is no evident difference in the mechanical properties for the glassy Cu_{42}Zr_{42}Al_{8}Ag_{8} as-cast rods with different diameters.

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