Preparation of Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ Bulk Metallic Glass with a Diameter of 25 mm by Copper Mold Casting

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The Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ alloy exhibits very high glass-forming ability. We have succeeded in synthesizing a Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ bulk glassy alloy with a diameter of 25 mm using the conventional copper mold injection casting. The absence of a crystalline phase was confirmed by X-ray diffraction and differential scanning calorimetry examinations. The critical cooling rate for formation of a glassy phase for the Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ alloy was estimated to be less than 6.4 K/s. High glass-forming ability and high strength might contribute to its commercial application for the Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ bulk metallic glass. [doi:10.2320/matertrans.48.629]

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1. Introduction

Bulk metallic glasses (BMGs) have been developed in a number of alloy systems in the last decade.1) BMGs have been considered as the promising structural and functional materials because of their unique physical and mechanical properties. However, dimension of the BMGs for commercial applications as structural materials is not always large enough to be used. Up to now, several BMGs (Zr-based: Zr$_{55}$Al$_{10}$Ni$_{33}$Cu$_{30}$,2) Zr$_{41.2}$Ti$_{13.3}$Cu$_{31.2}$Ni$_{10.0}$Be$_{22.5}$,3) Pd-based: Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$,4) Pt-based: Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$,5) Y-based: Y$_{30}$Sc$_{20}$Al$_{25}$Co$_{10}$,6) and Mg-based: Mg$_{50}$Cu$_{26.5}$Ag$_{8.5}$Gd$_{11.5}$7) were reported to have critical diameters more than 20 mm. This indicates that the development of a new BMG with high glass-forming ability (GFA) in a transition metal base system enables the appearance of a new type of engineering structural materials. Consequently, much effort has been devoted to develop a transition metal base BMG with high GFA.

In the Cu-Zr-based alloy system, high GFA was firstly found in Cu-Zr-$\alpha$-Ti8) and Cu-Zr-Al$\beta$9) ternary alloy systems, the maximum diameter of which was only about 4 mm. Later, it was found that fully glassy alloys with a diameter of 6 mm were formed in the ternary Cu-Zr-Ag alloys10) and Cu-Zr-based BMGs with a diameter of 10 mm were synthesized in Cu$_{46}$Zr$_{42}$Al$_{8}$Y$_{5}$11) and Cu$_{44.25}$Zr$_{55.75}$Ti$_{3}$Ag$_{14.75}$12) alloys. Recently, we found a series of quaternary Cu-Zr-based BMGs with high GFA in Cu$_{32}$-$\alpha$Zr$_{2}$-$\alpha$Ag$_{8}$Al$_{8}$ ($x = 0, 2, 4, 6, 8$) alloys.13) The bulk glassy alloys with a diameter of 15 mm were obtained in Cu$_{40}$Zr$_{24}$Ag$_{8}$Al$_{8}$, Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ and Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloys. It is worth noted that the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy is located at a quaternary eutectic point (liquidus temperature $T_L = 1143$ K) and has a large supercooled liquid region $\Delta T_L$ of 101 K.13) Therefore, it is expected that a larger bulk glassy alloy can be obtained for the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy. In this paper, we present the formation of the BMG with a diameter of 25 mm in Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy by copper mold injection casting. Moreover, the reason for the excellent GFA for the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy will be discussed.

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2. Experimental Procedure

A multicomponent alloy ingot with nominal composition Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ was 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. The ingots were then remelted in a quartz tube using an induction heating coil and injected through a nozzle into copper molds with diameters from 10 to 25 mm in an argon atmosphere. Ribbon sample was 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).

3. Results and Discussion

In order to evaluate the critical diameter of the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy, bulk cylindrical rods with diameters from 10 to 25 mm were prepared by copper mold injection casting. Figure 1(a) shows the XRD patterns of the bulk rods with diameters of 10, 20 and 25 mm, together with the result of the melt-spun glassy ribbon. For the bulk rods with diameters of 20 and 25 mm, the detected regions are the centre of the cross-section of the samples. It can be seen that the patterns of all the samples consist of only one broad diffraction maxima, indicating that these samples had a glassy structure. This result also indicates that the critical diameter of BMG is at least 25 mm for the Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ alloy. Based on a simple relationship between the maximum thickness of the glassy alloy and the critical cooling rate suggested by Lin et al.,14) the critical cooling rate for formation of a glassy phase is estimated to be less than 6.4 K/s. Figure 1(b) shows the pictures of two as-cast cylindrical samples with diameters of 20 and 25 mm. Both samples exhibit good metallic luster and no distinct concave can be recognized on their surface, which indicates that no crystalization occurred during the formation of these samples.

Figure 2 shows the DSC curves of the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ rod with a diameter of 25 mm in comparison with that of the melt-spun glassy ribbon. For the 25-mm rod, the samples for DSC examination were taken from the center and the place...
near the outer surface, respectively. As shown in Fig. 2, the three curves are nearly identical, with the same glass transition temperature $T_g$, except the onset temperature of the first crystallization event $T_x$ of the bulk sample decrease 2 K as compared with the ribbon. The total heats of crystallization for the ribbon and bulk samples are 55.2, 54.6 and 54.3 J/g, respectively, further confirming that the 25-mm as-cast rod is fully glassy.

Usually, the critical diameters of as-cast BMGs vary depending on casting conditions. The Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ alloy was reported to form 30-mm as-cast glassy rod using a copper mold suction method, in which the ingot was melted by arc melting. However, it cannot form 20-mm glassy rod using the current copper mold injection method. As compared with the Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ alloy, the Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ alloy exhibits higher GFA. The Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ alloy reaches number 3 in GFA order, following the Pd$_{40}$Cu$_{30}$-Ni$_{10}$-P$_{20}$ and Zr$_{41}$Ti$_{13}$Cu$_{12}$Ni$_{10}$Be$_{22}$ alloys.

It has been reported that high GFA of the Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ alloy was related with the high stabilization of supercooled liquid, which was represented by a large value of $\Delta T_x$ of about 101 K (as shown in Fig. 2) and a low melting temperature of 1143 K. In order to further understand the reason for high GFA of the Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ alloy, the supercooled liquid behavior of the Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ glassy alloy was investigated in terms of fragility concept. The glass-forming materials have been classified as three categories: strong, intermediate and fragile liquid. The stronger the liquid becomes, generally the higher is the GFA. In order to quantify the fragility, a fragility parameter $m$ has been introduced, which can be expressed by the following relationship:

$$m = \frac{D^* T_g^0}{(T_g - T_x)^2 \ln 10},$$

where $T_g$ is the VF temperature, and $D^*$ is the strength parameter. For many glass-forming liquids, the temperature dependence of heating rate can be described by a Vogel-Fulche (VF) type equation:

$$\phi(T_g) = B \exp[D^* T_g^0/(T_g - T_x)],$$

where $B$ is a constant, $T_g^0$ is the VF temperature, and $D^*$ is the strength parameter. Therefore, $T_g^0$ and $D^*$ in Eq. (1) can be obtained from the plot of $\phi$ versus $T_g$. Figure 3 shows the DSC curves of the Cu$_{36}$Zr$_{48}$Al$_{8}$Ag$_{8}$ glassy ribbon at different heating rates from 5 to 120 K/min. As the heating rate increased from 5 K/min to 120 K/min, $T_g$ increases monotonically from 673 to 700 K. The variation of $\ln \phi$ as a function of $T_g$ is showed in Fig. 4. The fitting shown in Fig. 4
demonstrates that the relationship of $\ln \phi$ versus $T_g$ fits the VFT equation well. The fit to data yields $D^* = 9.6$ and $T_0 = 480$. By using eq. (1), the calculated $m$ value of the Cu$_{36}$Zr$_{48}$Al$_8$Ag$_8$ alloy at a heating rate of 20 K/min is 33. According to Angell’s classification, $m$ is lower than 30 with a lower limit of 16 for strong liquid. Fragile liquids, on the other hand, are associated with $m/\phi < 100$. It has been reported that the BMGs with excellent GFA display relatively small fragility parameters in the range 30–40. Therefore, the Cu$_{36}$Zr$_{48}$Al$_8$Ag$_8$ alloy is also a fairly strong liquid. Strong liquid implies sluggish kinetics in the entire range of the supercooled liquid, which hinders the nucleation and growth of the crystalline phases and thus leads to high GFA of Cu$_{36}$Zr$_{48}$Al$_8$Ag$_8$ alloy.

4. Conclusions

We have succeeded in synthesizing Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ bulk glassy alloy with a diameter of 25 mm by copper mold injection casting, which was verified by XRD and DSC results. The critical cooling rate for formation of a glassy phase for the Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ alloy is estimated to be 6.4 K/s. The Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ alloy is a strong liquid with a fragility parameter $m$ of 33, resulting in high GFA of Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ BMG. The Cu$_{36}$Zr$_{48}$Al$_8$Ag$_8$ BMG exhibits high fracture strength of 1850 MPa with a distinct plastic strain. It is expected that high GFA and high strength of the Cu$_{36}$Zr$_{48}$Al$_8$Ag$_8$ BMG might contribute to its useful application in the future.

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