Synthesis and Mechanical Properties of New Cu-Based Cu-Zr-Al Glassy Alloys with Critical Diameters up to Centimeter Order

B. W. Zhou^{1,2}, X. G. Zhang³, W. Zhang^{3,4,*}, H. Kimura⁴, T. Zhang¹, A. Makino⁴ and A. Inoue⁵

¹Graduate school, School of Materials Science and Engineering, Dalian University of Technology, Dalian, 116024, P. R. China

²Graduate School, Tohoku University, Sendai 980-8577, Japan

³School of Materials Science and Engineering, Dalian University of Technology, Dalian, 116024, P. R. China

⁴IMR, Tohoku University, Sendai 980-8577, Japan

⁵WPI, Tohoku University, Sendai 980-8577, Japan

A new Cu-based Cu-Zr-Al glassy alloy has been found to exhibit very high glass-forming ability, wide supercooled liquid region and high fracture strength. The addition of Al to a binary eutectic Cu₅₅Zr₄₅ alloy significantly increases the stabilization of supercooled liquid as well as glass-forming ability in Cu_{55-x}Zr₄₅Al_x ($x = 0$ to 10) alloy series. The largest supercooled liquid region of 80 K, reduced glass transition temperature of 0.60 and γ value of 0.417 are simultaneously obtained for a ternary eutectic Cu₄₇Zr₄₅Al₈ alloy, which can fabricate fully glassy sample with critical diameters up to 15 mm by copper mold casting. The bulk glassy alloy also exhibits high compressive fracture strength of over 1900 MPa and the high Young's modulus above 100 GPa. [doi:10.2320/matertrans.MBW200928]

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1. Introduction

Bulk glassy alloys (BGAs) have been expected to be used in wide application fields, because they exhibit many unique properties such as high strength, large elastic strain limit, high hardness, good soft magnetic properties, excellent corrosion resistance and viscous flow workability in the supercooled liquid region.^{1,2)} However, for practical applications as the structural materials, BGAs are requested to simultaneously possess high glass-forming ability (GFA), high strength, good toughness, high corrosion resistance and low cost. The BGAs with high strength and good toughness can be obtained for the alloys consisting only of metallic elements, such as Zr-,^{2,3)} Ti-,⁴⁾ Ni-,⁵⁻⁷⁾ Cu-Ti-⁸⁾ and Cu-based⁹⁻¹¹⁾ systems, and the Zr-based alloys have higher GFA more than other alloys. Recently, much attention has been paid to Cu-based BGAs because they not only have lower cost, but also exhibit higher strength and higher thermal stability against crystallization as compared to Zr-based BGAs.¹²⁻¹⁴⁾

It is important to develop binary or ternary glassy alloys with high GFA because they are base of the multi-component BGAs, and the GFA can be improved by alloying more components into the base alloys. Actually, the Cu-based BGAs can be prepared in the binary Cu-Zr alloys by copper mold casting,¹⁵⁻¹⁷⁾ and the GFA is effectively enhanced by addition of a small amount of third elements, resulting in development of the ternary Cu-based BGAs with high GFA in Cu-Zr-Ti and Cu-Zr-Al, and Cu-Zr-Ag systems.⁹⁻¹¹⁾ However, their critical diameters (d_c) for glass formation were below 6 mm, and the d_c are only 3–4 mm for Cu-Zr-Ti and Cu-Zr-Al alloys, which have lower cost.^{9,10)}

It has been reported that Zr-rich Zr-Cu-Al alloys exhibit high reduced glass transition temperature ($T_{rg} = T_g/T_l$, T_g : glass transition temperature; T_l : liquidus temperature)¹⁸⁾ and

γ value ($\gamma = T_x/(T_g + T_l)$, T_x : crystallization temperature)¹⁹⁾ as well as a large supercooled liquid region ($\Delta T_x = T_x - T_g$),^{1,20)} enabling the formation of BGA rods with diameters of centimeter order by copper mold casting. An eutectic Zr₅₀Cu₄₀Al₁₀ alloy exhibits the best GFA and its d_c reaches 16 mm.²¹⁾ In addition, the Zr-based BGAs also exhibit high fracture strength above 1800 MPa with good toughness and excellent corrosion resistance in 1 N H₂SO₄ solution.^{22,23)} If a new Cu-rich Zr-Cu-Al BGA with high GFA (e.g., d_c of over 1 cm via copper mold casting) is developed, it will be important for scientific studies as well as practical applications. In addition, the Cu-rich BGAs can be expected to exhibit higher mechanical strength and higher thermal stability than those of the Zr-rich alloys. In this article, we report the finding of a new ternary Cu-based Cu-Zr-Al BGA, what can be produced with the d_c up to 15 mm, and exhibits large ΔT_x of 80 K, high T_x of 794 K and high compressive fracture strength of over 1900 MPa. The possible mechanism for the high GFA of the Cu-based alloys is also discussed.

2. Experimental Methods

The master ingots were prepared by arc melting the mixtures of pure metals with purities of 99.9 mass% for Zr, 99.99 mass% for Al and Cu in an argon atmosphere. The alloy compositions present nominal atomic percentages. The injection casting method was applied to prepare glassy alloy rods of 2–5 mm in diameter and 40–50 mm in length by using a rectangular Cu-mold of 40 mm in thickness, 50 mm in width and 120 mm in length. The tilt casting method²⁴⁾ was used to prepare alloy rods of 6–16 mm in diameter and 40–65 mm in length by using the rectangular Cu-molds of 60 mm in thickness, 70 mm in width and 100 mm in length. The surface of the cylindrical cavities was polished by 0.04 μ m Al₂O₃ powder to obtain a surface with roughness less than Ra 0.2. Ribbon samples with a cross section of 0.02 $\times$ 1.2 mm² were prepared by melt spinning. The glassy structure of the

*Corresponding author, E-mail: wzhang@imr.tohoku.ac.jp

cast alloy rods was identified by X-ray diffraction (XRD) and optical microscopy (OM). The etching for OM observation specimen was made in a 0.5% aqueous fluoride acid solution for 5 s at 298 K. The rods were sectioned transversely, etched and observed by optical microscopy. The thermal stability associated with glass transition, supercooled liquid region and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature and melting behavior was measured with a differential thermal analyzer (DTA) at a heating rate of 0.33 K/s. Mechanical properties under a compressive applied load were measured by using an Instron testing machine. The gauge dimensions for the mechanical test specimens were $\varnothing 2 \times 4 \text{ mm}^2$ and $2 \times 2 \times 4 \text{ mm}^3$ for the compressive test and the strain rate was fixed as $5 \times 10^{-4} \text{ s}^{-1}$. Young's modulus was measured by the strain gauge. Fracture morphology was examined by scanning electron microscopy (SEM).

3. Results and Discussion

We examined the effect of Al addition on the thermal stability and melting behavior of a binary $\text{Cu}_{55}\text{Zr}_{45}$ glassy alloy, what can form a bulk shape glassy sample with a d_c of 1.5 mm by a injection copper mold casting.¹⁶⁾ Figure 1 shows the DSC and DTA curves of melt-spun $\text{Cu}_{55-x}\text{Zr}_{45}\text{Al}_x$ ($x = 0-10$) glassy alloys. The T_g , T_x , melting temperature (T_m) and T_l are marked with arrows. All the samples exhibit a distinct endothermic heat event characteristic of the glass transition, followed by exothermic transformations from the under-cooled liquid due to crystallization (*see* Fig. 1(a)). The T_g and T_x increase from 695 to 714 and 752 to 794 K, respectively, with increasing Al content from $x = 0$ to 8, and then decrease with increasing Al content to $x = 10$. The largest ΔT_x of 80 K is obtained for the alloy with $x = 8$. From

Fig. 1 DSC and DTA curves of $\text{Cu}_{55-x}\text{Zr}_{45}\text{Al}_x$ ($x = 0-10 \text{ at}\%$) glassy alloys.

Fig. 2 ΔT_x , T_g and γ values of $\text{Cu}_{55-x}\text{Zr}_{45}\text{Al}_x$ ($x = 0-10 \text{ at}\%$) glassy alloys as a function of Al concentration.

DTA curves (*see* Fig. 1(b)), only one endothermic peak is observed during melting of the alloy with $x = 0$, because it is located near a deep binary eutectic.²⁵⁾ The T_l decreases with increasing Al content from $x = 0$ to 8, and the $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy exhibits the lowest T_l of 1190 K, the narrowest temperature interval between T_m and T_l and only a distinct endothermic peak. When the Al content is further increased to $x = 10$, the T_l rises. These results indicate that the $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy is located near a deep eutectic point in the ternary alloy system. Figure 2 shows the ΔT_x , T_g and γ values as a function of Al concentration. It is seen that the large ΔT_x exceeding 65 K, T_g above 0.585 and γ of over 0.40 are obtained in the Al content range of 4–10 at%. The $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy possesses simultaneously the largest ΔT_x of 80 K, T_g of 0.60 and γ value of 0.417, indicating the best glass former in the alloy series.^{1,18–20)}

We examined the GFA of $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy by copper mold casting. Figure 3(a) shows the outer shape of the as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ rods with diameters ranging from 10 to 15 mm. These alloy rods exhibit very smooth surface and shiny luster. Neither ruggedness nor concave is observed over the whole outer surface. Figure 3(b) shows the XRD patterns of the as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy rods with diameters from 10 to 15 mm. It can be seen that the patterns consist of only broad peaks, and no diffraction peak corresponding to a crystalline phase is seen, indicating that a single glassy phase is formed. A further increase in the sample diameter to 16 mm results in the precipitation of crystalline phases. Thus, it is concluded that the critical sample diameter for formation of the glassy phase lies between 15 and 16 mm in the case of copper mold casting process. This equals to the best GFA for all Cu-based BGAs. Based on a simple relationship between the maximum thickness of the glassy alloys and the critical cooling rate (R_c) suggested by Lin *et al.*,⁸⁾ the R_c of $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy for glass formation is estimated to be 18.9 K/s or less.

The $\text{Cu}_{55}\text{Zr}_{45}$ alloy showed a narrower ΔT_x of 57 K and lower GFA ($d_c = 1.5 \text{ mm}$). The stabilization of supercooled liquid and GFA greatly increase by the addition of Al in the $\text{Cu}_{55-x}\text{Zr}_{45}\text{Al}_x$ series, and the large ΔT_x of 80 K and the very high GFA with a d_c of 15 mm are obtained for the alloy with $x = 8$. The empirical rules^{1,20)} drawn from experimental

Fig. 3 (a) Outer shapes of as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ rods with the diameters of 10–15 mm; (b) The cross-sectional XRD patterns of as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ rods with the diameters of 10–15 mm. The data of the ribbon sample is also shown for comparison.

results have shown that certain atomic-size mismatch and strong chemical affinities may enhance the stabilization of supercooled liquid and GFA of a multi-component system. In the present system, the atomic radii of the component atoms are 0.162 nm for Zr, 0.143 nm for Al and 0.128 nm for Cu, respectively,²⁶⁾ and hence $R_{\text{Zr/Cu}} = 1.27$, $R_{\text{Al/Cu}} = 1.12$ and $R_{\text{Zr/Al}} = 1.13$. Therefore, the present combination of atomic sizes can produce an efficiently packed local structure, which is often associated with low energy and high viscosity of liquids. In addition, the addition of Al into the Cu–Zr alloy (heats of mixing for Cu–Zr pair is -23 kJ/mol) causes the generation of new chemical affinities of Al–Zr (-44 kJ/mol) and Al–Cu (-1 kJ/mol) pairs,²⁷⁾ which can improve the local packing efficiency and restrain long range diffusion of atoms. These factors lead to the high stability of the supercooled liquid and the high GFA.

It is noticed that $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy appears to be located near a deep eutectic composition. This also suggests that the GFA and stability of the glassy alloys are related to the eutectic composition. It is well known that alloys with compositions around the deep eutectic have high GFA and large ΔT_x in any given system. A deep eutectic means that the liquid has the highest stability against crystallization. Thus, the present high GFA is greatly favored thermodynamically. In addition, from the viewpoint of kinetics, the multi-component eutectic alloys consist of multiple ordered phases competing with each other, and crystallization of the liquid requires the simultaneous rearrangement of different species of atoms, which significantly suppresses the kinetics of crystallization process, leading to the enhancement of glass formation and the increase of ΔT_x .^{1,28)} Figure 4(a) shows a magnification picture of whole cross section of the

Fig. 4 (a) The optical micrographs of cross section of the as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy rod with a diameter of 16 mm; (b) The cross-sectional structure taken from center of the as-cast alloy rod; (c) The cross-sectional XRD pattern taken from center of the as-cast alloy rod.

as-cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy rod with a diameter of 16 mm. It can be seen that there is a crystalline region (dark contrast) in the center of the cross section. The uniform and fine eutectic structure consisting of $\text{Cu}_{10}\text{Zr}_7$, Al_2Zr and other unknown phases (see Fig. 4(b) and (c)) is observed in the crystalline region. These results also confirm that the solidification of the supercooled liquid occurs through an eutectic reaction.

Figure 5 shows compressive stress-strain curves of the cast $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy rod with the diameters of 2 and 12 mm. The test specimens were taken from the central and outer surface regions in the transverse cross section at the fixed site which is about 10 mm away from the bottom surface of the alloy rod with a diameter 12 mm (*see* Ref. 29)). The glassy rod sample with a diameter of 2 mm exhibits high fracture strength ($\sigma_{c,f}$) of 1923 MPa, and the Young's modulus (E) is estimated to be 108 GPa. Although the alloy does not show a distinct plastic strain, it is confirmed that the samples fracture along the maximum shear stress plane which is declined by about 45 degrees to the direction of applied load and the fracture surface consists of mainly a well developed vein pattern, suggesting that the fracture behavior is similar to

Fig. 5 Compressive stress-strain curves of $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ glassy rods with a diameter of 2 and 12 mm.

other BGAs with some plastic strain before fracture.^{9,11)} For the glassy rod sample with a diameter of 12 mm, the $\sigma_{c,f}$ and E values are 1900 MPa and 101 GPa respectively, at the central region, and 1915 MPa and 103 GPa, respectively, at the outer surface region. Thus, the mechanical properties appear to be independent of the sample size and the sample site in the transverse cross section.

4. Summary

With the aim of developing new Cu-based BGAs with a critical size of centimeters in a simple system, the thermal stability, melting behaviors and GFA of $\text{Cu}_{55-x}\text{Zr}_{45}\text{Al}_x$ ($x = 0-10$) alloys were investigated. The large ΔT_x exceeding 65 K, T_{rg} above 0.585 and γ of over 0.40 are obtained in the Al content range of 4–10 at%. The eutectic $\text{Cu}_{47}\text{Zr}_{45}\text{Al}_8$ alloy simultaneously exhibits the largest ΔT_x of 80 K, T_{rg} of 0.60 and γ of 0.417, leading to formation of full glassy samples with diameters up to 15 mm. This is comparable to the best GFA for all Cu-based BGAs. The Cu-based BGA exhibits high compressive fracture strength of over 1900 MPa and the high Young's modulus above 100 GPa. The combination of high GFA, high stabilization of supercooled liquid and good mechanical properties for a simple Cu-based alloy composition with low materials cost is providing the base alloy for further exploring the BGAs' formers with higher GFA, and giving them excellent promise for both scientific and engineering applications.

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