Materials Transactions, Vol. 50, No. 3 (2009) pp. 679 to 682

EXPRESS REGULAR ARTICLE

Formation and Mechanical Properties of New Cu-Rich Cu-Zr-Al-Ag Glassy Alloys with High Glass-Forming Ability

Wei Zhang[1,*], Qingsheng Zhang[2] and Akihisa Inoue[2]

[1]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[2]*WPI, Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

We have discovered new Cu-rich Cu-Zr-Al-Ag bulk glassy alloys with high glass-forming ability and excellent mechanical properties. As the composition shifted to Cu-rich range in the $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ alloy series, the supercooled liquid region, reduced glass transition temperature and γ value increased, leading to the improvement of the GFA. The full glassy samples with a diameter of 10 mm could be fabricated by copper mold casting for the $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–3) alloys. In addition to high GFA, the BGAs exhibit good mechanical properties under a compressive deformation mode, i.e., large Young's modulus of 104–109 GPa, high fracture strength of 1905–1932 MPa and distinct plastic strain of 0.2–0.4%. [doi:10.2320/matertrans.MER2008384]

(Received October 16, 2008; Accepted December 17, 2008; Published February 25, 2009)

Keywords: *bulk glassy alloy, glass-forming ability, copper-rich copper-zirconium-aluminum-silver alloy, mechanical property*

1. Introduction

Bulk glassy alloys (BGAs) have been expected to be used in wide application fields, because they exhibit unique properties such as high strength, large elastic strain limit, high hardness, good soft magnetic properties, and viscous flow workability in the supercooled liquid region and excellent corrosion resistance.[1)] However, for practical applications, BGA are requested to simultaneously have high glass-forming ability (GFA), high strength, decent ductility, good corrosion resistance and low cost.

Recently, we have reported that Zr-rich Zr-Cu-Al-Ag alloys exhibit high reduced glass transition temperature (T_g/T_l, T_g: glass transition temperature; T_l: liquidus temperature)[1,2)] and γ value ($\gamma = T_x/(T_g + T_l)$, T_x: crystallization temperature)[3)] as well as a large supercooled liquid region ($\Delta T_x = T_x - T_g$),[1,4)] enabling the formation of BGA rods with diameters of over 10 mm by copper mold casting in a wide composition range.[5)] A eutectic $Zr_{48}Cu_{36}Ag_8Al_8$ alloy exhibits the best GFA and its the critical sample diameter (d_c) for glass formation reaches 25 mm.[6,7)] In addition, the BGAs also exhibit high compressive fracture strength above 1800 MPa with distinct plastic strains and excellent corrosion resistance in 1 N H_2SO_4 solution.[5)] If a new Cu-rich Zr-Cu-Al-Ag BGA with lower Ag concentrations and high GFA (e.g., d_c over of 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.[8–10)]

We have reported that the high GFA of the Zr-Cu-Al-Ag alloys is attributed to the eutectic composition, at which solidification occurs via homogeneous nucleation and limited growth rate of the nuclei.[7)] It is also known that the multi-component alloy systems have several deep eutectic points. Therefore, a Cu-rich alloy with high GFA may be obtained in the other composition region in the quaternary alloy system. It has been also demonstrated that the Zr-Cu-Al alloys possess high GFA in the Cu-rich[9)] and Zr-rich[11)] compositions which are closed to each eutectic point. This article aims to examine the thermal stability, melting behavior and GFA of Cu-rich Cu-Zr-Al-Ag glassy alloys with lower Ag concentrations, to develop new BGAs with high GFA and lower cost. The mechanical properties of the resulting BGAs were also investigated.

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

2. Experimental Procedure

The ingots were prepared by arc melting the mixtures of pure Cu, Zr, Ag and Al metals with purity of over 99.5 mass% in an argon atmosphere. The alloy ingots were re-melted four times to ensure chemical homogeneity. The mass losses were measured for each ingot after melting and were less than 0.1 mass%. The glassy alloy was produced by copper mold casting for bulk cylindrical rods with diameters of 2 to 12 mm. The glassy phase was identified by X-ray diffraction (XRD) and optical microscopy (OM). The OM observation was made for the samples which were etched for 2–5 s at 298 K in a 0.5% fluoride acid aqueous solution. The thermal stability of the glassy alloy was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature and melting behavior were examined with a differential thermal analyzer (DTA) at a heating rate of 0.33 K/s. Mechanical properties were measured with an Instron testing machine. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height for compressive test and the strain rate was $5 \times 10^{-4}\,s^{-1}$. The fracture surface was examined by SEM.

3. Results and Discussion

We first examined the thermal stability and melting behavior of Cu-rich Cu-Zr-Al-Ag glassy alloys containing 6 at%Ag. Figure 1 shows DSC and DTA curves of $Cu_{44+x}Zr_{44-x}Ag_6Al_6$ ($x = 0$–6) glassy alloys. It is seen that the T_g increases gradually with increasing Cu content (*see* Fig. 1(a)), while the ΔT_x increases from 92 to 98 K with increasing x from 0 to 2, and then remarkably decreases to

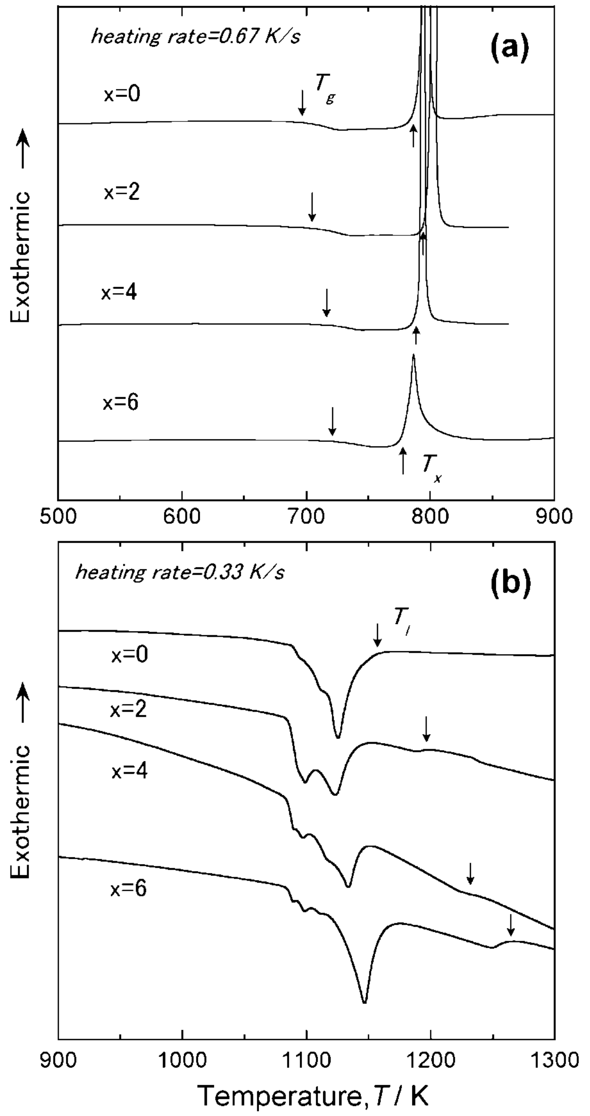

Fig. 1 DSC (a) and DTA (b) curves of $Cu_{44-x}Zr_{44-x}Ag_6Al_6$ ($x = 0$–6) glassy alloys.

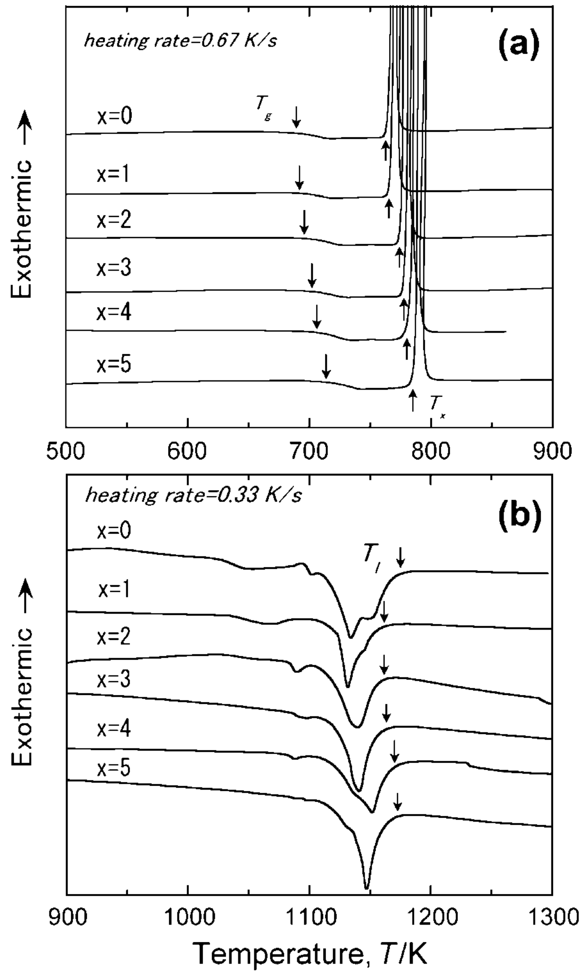

Fig. 2 DSC (a) and DTA (b) curves of $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 0$–5) glassy alloys.

62 K with further increasing x to 6. The T_l and melting behavior of the alloys are affected significantly as the composition shifts to the Cu-rich range (*see* Fig. 1(b)). With increasing x from 0 to 6, T_l increases from 1144 to 1263 K. In addition, the endothermic peaks during melting increase, indicating that the alloy series go far from the eutectic composition with increasing Cu content. As a result, the T_g/T_l and γ values gradually decrease from 0.610 and 0.439 at $x = 0$, to 0.567 and 0.392 at $x = 6$, respectively, indicate the reduction of GFA.[1–4)]

On the other hand, the composition shift to the Cu-rich range in the $Cu_{46}Zr_{46}Ag_4Al_4$ alloy was found to improve the stabilization of supercooled liquid as well as the GFA. Figure 2 shows DSC and DTA curves of $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 0$–5) glassy alloys. The T_g and T_x gradually increase with increasing Cu content (*see* Fig. 2(a)), while the ΔT_x increases from 81 to 87 K with increasing x to 2, and then decreases to 78 K with further increasing x to 5. From DTA scans (Fig. 2(b)), it can be seen that the multiple events are observed during melting of the alloy with $x = 0$, indicating that this alloy is far from the eutectic composition. The T_l decreases with increasing x from 0 to 2, and the alloy with $x = 2$ exhibits the lowest T_l, and only a distinct endothermic peak. When the Cu content is further increased, the T_l and the endothermic peaks increase. These results indicate that the $Cu_{48}Zr_{44}Ag_4Al_4$ alloy is located near a deep eutectic in the quaternary alloys. Figure 3 shows the changes in the ΔT_x, T_g/T_l and γ values as a function of x for the $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–5) glassy alloys. The T_g/T_l gradually increases from 0.587 to 0.604 with increasing x from 0 to 5. In addition, the ΔT_x and γ values increase from 81 and 0.414 to 87 K and 0.422 with increasing x to 2, respectively, and then both of them decrease with further increasing Cu content. It is noticed that the alloys with $x =$ 1–4 show the larger ΔT_x, T_g/T_l and γ values simultaneously, indicating the higher GFA.[1–4)]

We examined the GFA of the Cu-rich alloys by copper mold casting. Figure 4 shows the XRD patterns of the as-cast $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–4) alloy rods with diameters of 10–12 mm. The sample with $x = 4$ shows some crystalline peaks with a broad background, indicating a mixed structure with glassy and crystalline phases. However, the XRD patterns consist only of broad peaks for $x = 1$–3 alloy samples with a diameter of 10 mm, indicating a full glassy structure. The samples exhibit very smooth surface and shiny luster (Fig. 5). Neither ruggedness nor concave is observed

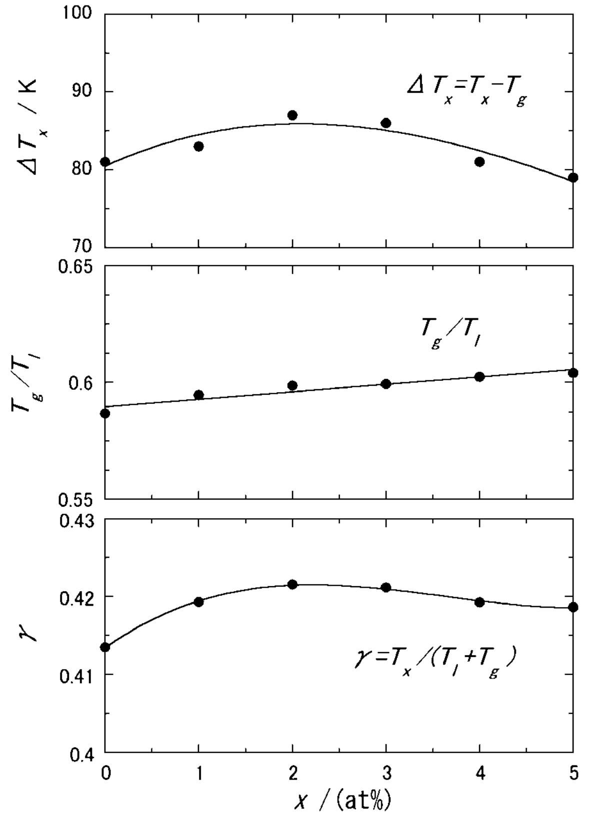

Fig. 3 The changes in the ΔT_x, T_g/T_l and γ values as a function of x for the $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 0$–5) glassy alloys.

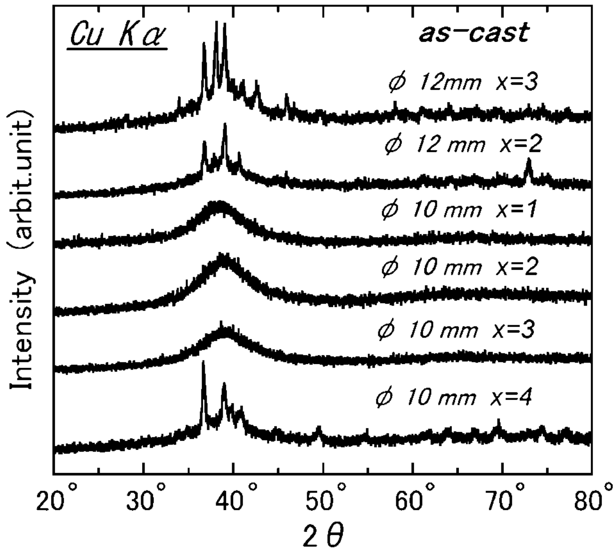

Fig. 4 The cross-sectional XRD patterns of as-cast $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–4) rods with diameters of 10–12 mm.

over the whole outer surface, which are also typical features of BGAs. The further increase in the sample diameter to 12 mm results in the precipitation of crystalline phases. It is therefore concluded that the critical sample diameter for formation of the glassy phase lies between 10 and 12 mm.

It has been reported that the d_c of the $Cu_{46}Zr_{46}Ag_4Al_4$ glassy alloy is below 7 mm.[5] By changing Cu and Zr contents of only 1–3 at%, the GFA of the alloys significantly increases. It can be noticed that the best GFA and highest stabilization of supercooled liquid in this alloy series are obtained around $Cu_{48}Zr_{44}Ag_4Al_4$, which is almost located at a deep eutectic composition. This 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 quaternary 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 the glass formation[12] and the increase of ΔT_x.[1,4]

Figure 6 shows compressive stress-strain curves of $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–3) BGAs. It is seen that the glassy alloys exhibit high fracture strength with a distinct plastic strain. The compressive fracture strength, Young's

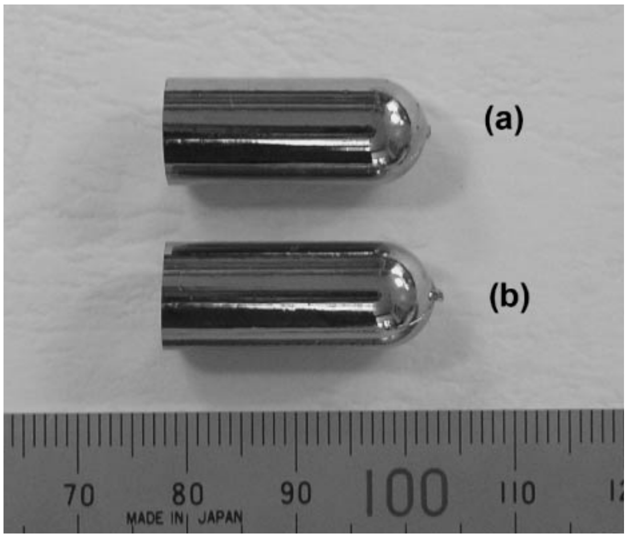

Fig. 5 Image of as-cast $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 2$ (a) and 3 (b)) rods with a diameter of 10 mm.

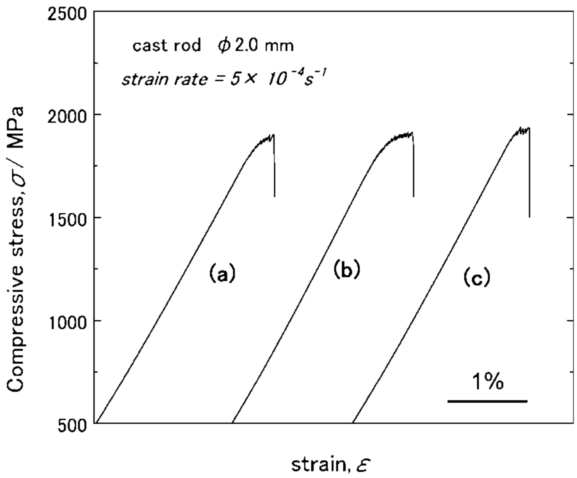

Fig. 6 Compressive stress-strain curves of $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$ (a), 2 (b) and 3 (c)) BGA rods with a diameter of 2 mm.

modulus, and plastic strain are 1905 MPa, 104 GPa and 0.2%, respectively, for $x = 1$ alloy, 1915 MPa, 105 GPa and 0.4%, respectively, for $x = 2$ alloy, and 1932 MPa, 109 GPa and 0.2%, respectively, for $x = 2$ alloy. It has been confirmed by SEM that the deformation and final fracture of all the alloys occurred along the maximum shear stress plane which was declined by about 45 degrees to the direction of applied load. In addition, the fracture surfaces consist mainly of a well-developed vein pattern, which is typical to other BGAs with good toughness.[8,13)]

4. Summary

With the aim of developing a new Cu-Zr-Al-Ag BGA with high GFA, good mechanical properties and low cost, we examined the thermal stability, melting behavior and GFA of Cu-rich Cu-Zr-Al-Ag glassy alloys with lower Ag concentrations. The mechanical properties of the BGAs with high GFA were also investigated. The results obtained are summarized as follows:

(1) The ΔT_x of $Cu_{44+x}Zr_{44-x}Ag_6Al_6$ glassy alloys increased from 92 to 98 K with increasing x from 0 to 2, and then gradually decreased to 62 K at $x = 6$. The T_l remarkably increased with increasing Cu content, leading to the decrease of T_g/T_l and γ values from 0.610 and 0.439 at $x = 0$, to 0.567 and 0.392 at $x = 6$, respectively.

(2) The T_g and T_x of $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ glassy alloys gradually increase with increasing Cu content, while the ΔT_x increases with increasing x from 0 to 2, and then decreases. The $x = 2$ and 3 alloys exhibit high stabilization of supercooled liquid, and their ΔT_x values are 87 and 86 K, respectively. In addition, the T_l decreases with increasing x from 0 to 2, and then increases. The T_g/T_l gradually increases with increasing Cu content. The largest γ value of 0.422 is obtained for the $x = 2$ alloy.

(3) The $Cu_{46+x}Zr_{46-x}Ag_4Al_4$ ($x = 1$–3) alloys exhibited high GFA. The BGA rods with a diameter of 10 mm were formed by copper mold casting method.

(4) The BGAs with high GFA exhibit good mechanical properties, i.e., compressive fracture strength of 1905–1932 MPa, Young's modulus of 104–109 GPa, and plastic strain of 0.2–0.4%. The success of forming the larger scale BGAs with excellent mechanical properties for the Cu-rich Cu-Zr-Al-Ag alloys with low Ag concentrations is useful for further extension of application fields of BGAs.

Acknowledgements

This work was financially supported by Research and Development Project on Advanced Metallic Glasses, Inorganic Materials and Joining Technology from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

1) A. Inoue: Acta Mater. **48** (2000) 279–306.
2) D. Turnbull: Contempt Phys. **10** (1969) 473–488.
3) Z. P. Lu and C. T. Liu: Acta Mater. **50** (2002) 3501–3512.
4) A. Inoue: Mater. Trans. JIM **36** (1995) 866–875.
5) W. Zhang, Q. Zhang, C. Qin and A. Inoue: Mater. Sci. Eng. B **148** (2008) 92–96.
6) Q. S. Zhang, W. Zhang and A. Inoue: Mater. Trans. **48** (2007) 629–631.
7) W. Zhang, Q. Zhang and A. Inoue: J. Mater. Res. **23** (2008) 1452–1456.
8) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: Acta Mater. **49** (2001) 2645–2652.
9) A. Inoue and W. Zhang: Mater. Trans. **43** (2002) 2921–2925.
10) K. Okazaki, W. Zhang and A. Inoue: Mater. Trans. **47** (2006) 2571–2575.
11) Y. Yokoyama, H. Inoue, K. Fukaura and A. Inoue: Mater. Trans. **43** (2002) 575–579.
12) D. H. Xu, G. Duan and W. L. Johnson: Phys. Rev. Lett. **92** (2004) 245504-1–245504-4.
13) W. Zhang and A. Inoue: Scripta Mater. **48** (2003) 641–645.