ELSEVIER

Journal of Alloys and Compounds 434–435 (2007) 160–163

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Volume change in $Zr_{50}Cu_{40}Al_{10}$ glassy alloys

Y. Yokoyama [a,*], T. Yamasaki [b], P.K. Liaw [c],
R.A. Buchanan [c], A. Inoue [a]

[a] Advanced Research Center of Metallic Glasses, Institute for Materials Research, Tohoku University, Katahira, Aobaku, Sendai 980-8577, Japan
[b] Material Science and Engineering, Graduate School of Engineering, University of Hyogo, Shosha 2167, Himeji City 671-2201, Japan
[c] Department of Materials Science and Engineering, College of Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Abstract

Quaternary $Zr_{47}Cu_{40}Al_{10}M_3$ (M: IVA ∼ VIA), $Zr_{50}Cu_{37}Al_{10}M_3$ (M: VIIA ∼ IB), and $Zr_{50}Cu_{40}Al_7M_3$ (M: IIB∼) bulk glass alloys (BGAs) were examined to clarify the glassy structure of $Zr_{50}Cu_{40}Al_{10}$ BGA. The glass structural difference was evaluated by the volume change due to structural relaxation at the glass-transition temperature (T_g); the volume shrinkage was estimated using density measurement. The results indicated that Pd, Ag, Pt, and Au, which are characterized by a filled d-shell electron structure, are effective for enhancing volume expansion in a glass structure. Furthermore, the volume changes in quaternary Zr–Cu–Al–M BGAs could be classified into two groups. This implies a difference in glass structure between the $Zr_{50}Cu_{37}Al_{10}M_3$ (M = Pd, Ag, Pt, and Au) BGA and others examined in this study.

Keywords: $Zr_{50}Cu_{40}Al_{10}$; Bulk glassy alloy; Glass structural change; Young's modulus; Small addition elements

1. Introduction

Glassy alloys exhibit ductile metallic bonding and have a non-periodic structure. Some crystalline metals or alloys can exhibit superior plasticity due to systematic dislocation movement. The deformation mechanism of glassy alloys is by adiabatic shear band movement [1,2]. Microscopic fracture-surface images reveal a vein pattern caused by a pseudo-melting state [3] in the shear band. Once a shear band begins moving, it can result in final fracture with minimal uniform plastic deformation. The lack of uniform plastic deformability of glassy alloys has been considered to limit the toughness [4].

Some glassy alloys have recently been found to exhibit very good glass-forming ability [5]. We can fabricate bulk samples using a conventional metallic mold-casting process. Bulk glassy alloys have new application potential as structural material [6,7]. However, casting defects [8–10] in these structural BGAs must be considered. Crystalline inclusions, which act as crack-initiation sites and enhance crack propagation, must be reduced to examine the intrinsic features of BGAs [11]. we must control the glass structure to obtain consistent quality [12]. We estimate the volume change in this study by the volume-shrinkage ratio via structural relaxation at T_g, to evaluate the quantity of excessive free volume in a glass structure.

Ductile glassy alloys require sufficient elastic deformability to avoid localized stress or strain. Novikov and Sokolov [13] recently described the relationship between the Poisson ratio and the fragility of glass-forming liquids. The Poisson ratio for BGAs, which is influenced by the isotropy of the atomic-bonding configuration, is usually 0.35–0.4. This large Poisson ratio value is caused by the volume effect [14], which is closely related to the localized glass structure. Jan Schroers and Johnson [15] reported a ductile Pt-based BGA with a substantial Poisson ratio of 0.42. Volume change, which is assumed to be the degree of volume expansion from the fully relaxed state, is also an important factor in the ductility of BGAs since it influences the modulus (i.e. Young's modulus) and Poisson ratio [16,17].

The objective of this paper is to use small additional elements to clarify the relationship between the glass structure and mechanical features in $Zr_{50}Cu_{40}Al_{10}$ BGAs.

2. Experimental procedure

Master-alloy ingots of ternary Zr–Cu–Al and quaternary Zr–Cu–Al–M alloys were prepared by arc-melting mixtures of pure Zr, Cu, Al, and other metals in an argon atmosphere. We used a special Zr crystal rod with an oxygen

---

* Corresponding author.
E-mail addresses: yy@imr.tohoku.ac.jp (Y. Yokoyama), yamasaki@eng.u-hyogo.ac.jp (T. Yamasaki), pliaw@utk.edu (P.K. Liaw), rab1@utk.edu (R.A. Buchanan), ainoue@imr.tohoku.ac.jp (A. Inoue).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.320

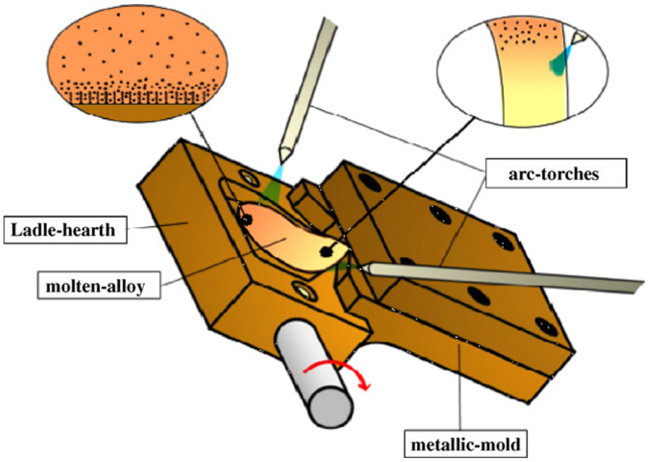

Fig. 1. Schematic illustration of the tilt-casting process in an arc furnace.

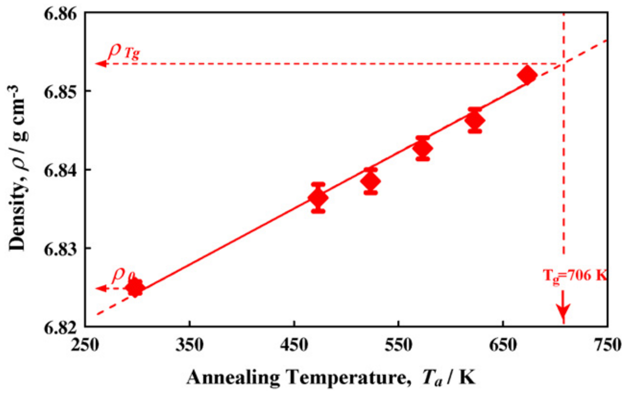

Fig. 2. Relationship between the annealing temperature and density of $Zr_{50}Cu_{40}Al_{10}$ BGAs.

concentration of less than 0.05 atomic percent (at.%) to maintain a low oxygen concentration in the alloys. Zr–Cu–Al BGAs were cast into rod-shaped specimens 8 mm in diameter and 60 mm long using a tilt-casting technique [11], as illustrated in Fig. 1. This casting method has the advantage of restricting the formation of cold shuts, which act as crack-initiation sites and enhance crack propagation. We determined the standard density of a $Zr_{50}Cu_{40}Al_{10}$ BGA to be 6.825 ± 0.005 g cm^{-3} in this study, which we used to control the quality of the cast glassy rods. Densities were measured by the Archimedes method using the same shaped samples (Ø8 × 20 mm). The fluid for the Archimedes method was purified water. We also verified the cast structure using optical microscopy (OM) and scanning-electron microscopy (SEM) to confirm the quality of the glassy structure. The phase was characterized by X-ray diffractometry. Tensile tests were performed using an Instron 5582 testing machine to estimate the Young's modulus. A Charpy impact test was also performed in air using a special sample that was 55 mm long, 10 mm wide, and 5 mm thick, U-notched to a 2 mm depth.

3. Results and discussion

Glass is solidified at a glass-transition temperature; however, the free volume in a glassy alloy may change with the cooling rate. The quantity of free volume may also be changed by the alloy composition. It is difficult to determine the absolute value of the free volume, and therefore we used the volume change via structural relaxation at T_g to evaluate the free volume difference in the glass structure. We used the following equation to determine the volume change value.

$$\text{volume change} = \frac{\rho_0^{-1} - \rho_{T_g}^{-1}}{\rho_0^{-1}}$$

where ρ_0 is the density of the as-cast state and ρT_g is the density after annealing at T_g for 90 min [17]. The volume change is considered to be the volume change ratio from the as-cast state to the annealed state at T_g. The relation between the density and annealing temperature of a $Zr_{50}Cu_{40}Al_{10}$ BGA is depicted in Fig. 2. This figure indicates that the density and annealing temperature are linearly related. We can estimate the density ρT_g after full relaxation by extrapolating the relation at T_g as indicated in Fig. 2.

We also examined the compositional dependence of the volume change using a U-notched Charpy impact test in Zr–Cu–Al glassy alloys. Fig. 3 depicts the relationship between the U-notched Charpy impact energy and volume change in Zr–Cu–Al glassy alloys. The correlation factor was 0.8 with a linear relationship. This test is sensitive to stress accommodation since a Charpy impact fracture requires the immediate release of the applied impact stress. A large volume change indicates the existence of more voids in the glass structure if we assume that the glass structure is simply composed of clusters and voids. However, the change in volume is roughly related to the excess free volume Where atoms are probably easy to move. This atom-movement flexibility most likely leads to superior stress accommodation. Consequently, the volume change is a significant structural parameter for the toughness of glassy alloys.

We examined the addition of a fourth element to enhance the volume change. The volume change consisted of thermally unstable voids in a glass structure; we speculated that there could be an additional element effect that would change the short-range atomic configuration. Alteration of the volume change with the addition of a fourth metal to a $Zr_{50}Cu_{40}Al_{10}$ BGA is illustrated in Fig. 4. The open mark indicates a crystallized region created by a small additional element. The dotted lines in the figure denote the volume change (0.41%) of a standard $Zr_{50}Cu_{40}Al_{10}$ BGA. The quantity of the additional element (M) is normally 3 at.%, and the alloy compositions are $Zr_{47}Cu_{40}Al_{10}M_3$ (M: IVA ∼ VIA), $Zr_{50}Cu_{37}Al_{10}M_3$ (M:

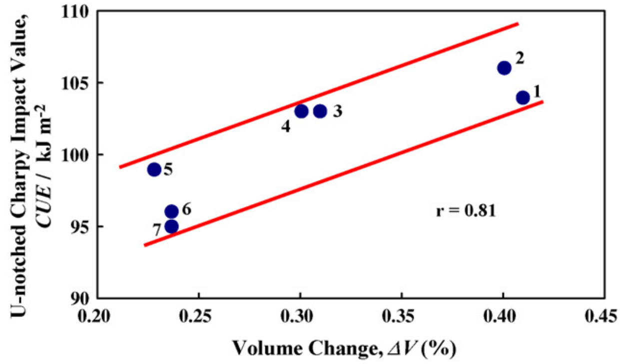

Fig. 3. Relationship between the tensile strength and glass-transition temperature in a Zr–Cu–Al alloy system. Alloy compositions are (1) $Zr_{50}Cu_{40}Al_{10}$, (2) $Zr_{52.5}Cu_{37}Al_{10}$, (3) $Zr_{50}Cu_{37.5}Al_{12.5}$, (4) $Zr_{50}Cu_{42.5}Al_{7.5}$, (5) $Zr_{55}Cu_{35}Al_{10}$, (6) $Zr_{60}Cu_{30}Al_{10}$, and (7) $Zr_{47.5}Cu_{42.5}Al_{10}$, r: correlation number.

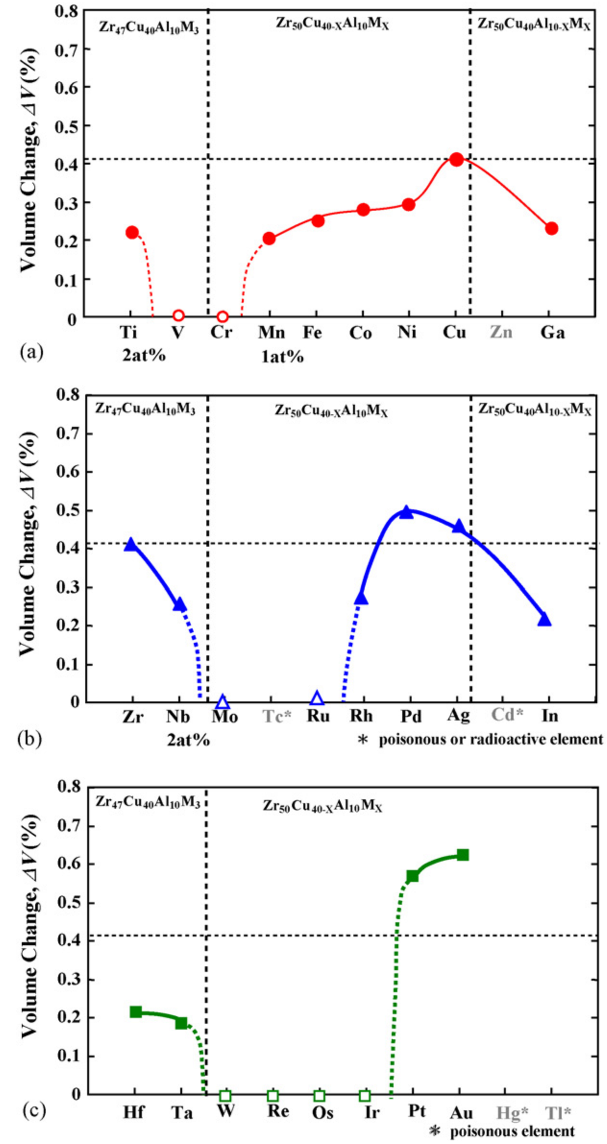

Fig. 4. Volume change in $Zr_{47}Cu_{40}Al_{10}M_3$ (M: IVA ∼ VIA), $Zr_{50}Cu_{37}Al_{10}M_3$ (M: VIIA ∼ IB), and $Zr_{50}Cu_{40}Al_7M_3$ (M: IIB∼) BGAs with additional M elements. The chained line indicates the volume change in a standard $Zr_{50}Cu_{40}Al_{10}$ BGA.

VIIA ∼ IB), and $Zr_{50}Cu_{40}Al_7M_3$ (M: IIB∼). No effective elements to enhance the volume change of the $Zr_{50}Cu_{40}Al_{10}$ BGA existed in the fourth period, as indicated in Fig. 4(a). The volume change with additional elements from the fifth period is presented in Fig. 4(b). This figure indicates that Pd and Ag effectively increase the volume change of a $Zr_{50}Cu_{40}Al_{10}$ BGA. The response of the volume change with supplementary sixth-period metals added to a $Zr_{50}Cu_{40}Al_{10}$ BGA is illustrated in Fig. 4(c). This figure also indicates that Pt and Au effectively increase the volume change of a $Zr_{50}Cu_{40}Al_{10}$ BGA. We also studied the relationship between the volume change and Young's modulus to clarify the effect of the small additional element in the $Zr_{50}Cu_{40}Al_{10}$ BGA. The relationship between the Young's modulus and volume change revealed two groups, as indicated in Fig. 5. One group, with the addition of Ag, Pd, Pt, or Au, the elements of which are characterized by a filled d-shell electron structure, exhibited a low volume change dependence on Young's modulus. The glass structure of this group was imaged as flexible metallic bonding and an expanded glass structure. The other group, which consists of the fourth additional element, exhibited a high volume change dependence on Young's modulus. The star symbol in Fig. 5 indicates the Young's modulus (89 GPa) and volume change (0.41%) of a standard $Zr_{50}Cu_{40}Al_{10}$ BGA. The volume change and Young's modulus varied along the broken line by annealing below T_g, as indicated in Fig. 5. This variation of Young's modulus with volume change was similar to that of the former group with additional noble metals. The similar gradient between the structurally relaxed $Zr_{50}Cu_{40}Al_{10}$ BGA and as-cast $Zr_{50}Cu_{37}Al_{10}M_3$ (M = Pd, Ag, Pt and Au) BGAs is probably attributable to their similar glass structural changes.

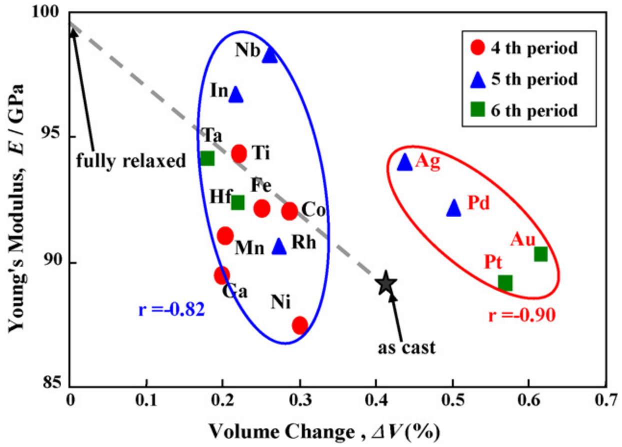

Fig. 5. Relationship between the volume change and Young's modulus in $Zr_{47}Cu_{40}Al_{10}M_3$ (M: IVA ∼ VIA), $Zr_{50}Cu_{37}Al_{10}M_3$ (M: VIIA ∼ IB), and $Zr_{50}Cu_{40}Al_7M_3$ (M: IIB∼) BGAs. A star indicates the ternary $Zr_{50}Cu_{40}Al_{10}$ glassy alloy with structural change indicated by the broken line.

We can thus conclude that a change in Young's modulus caused by a glass structural change is a very important factor in evaluating a glass structure. For example, nickel has stronger bonding force to Zr and Al compared with Cu, but while it resembles Pd in terms of affinity force, it belongs to another group. The mixing enthalpy is not sufficient to explain the glass structural change with a small additional element. The addition of Ni to a $Zr_{50}Cu_{40}Al_{10}$ BGA would be very effective, however, for obtaining the lowest Young's modulus. Nonetheless, the glass structure must be classified into more precise states to define the relationship between the glass structure and mechanical properties in detail.

4. Conclusions

We attempted to control the volume change in $Zr_{50}Cu_{40}Al_{10}$ glassy alloys by adding small amounts of additional elements to reveal the relationship between the glass structure and mechanical properties. Quaternary $Zr_{47}Cu_{40}Al_{10}M_3$ (M: IVA ∼ VIA), $Zr_{50}Cu_{37}Al_{10}M_3$ (M: VIIA ∼ IB), and $Zr_{50}Cu_{40}Al_7M_3$ (M: IIB∼) BGAs were examined in terms of the Young's modulus during a tensile test. The change in the glass structure was evaluated by the volume change due to structural relaxation at T_g. The results obtained can be summarized as follows.

(1) Pd, Ag, Pt, and Au, elements characterized by a filled d-shell, effectively enhance the volume change in the glass structure of a $Zr_{50}Cu_{40}Al_{10}$ BGA.
(2) Young's modulus decreases with an increase in the volume change. The relationship between the Young's modulus and volume change implies that the glassy structure differs between a $Zr_{50}Cu_{37}Al_{10}M_3$ (M = Pd, Ag, Pt and Au) BGA and other BGAs.

Acknowledgements

We wish to thank Prof. T. Egami from the University of Tennessee for his valuable advice. This research was supported by New Energy and Industrial Technology Development Organization (NEDO). The authors are grateful to the Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, for technical support of this research. We appreciate the financial support provided by the U.S. National Science Foundation, the Integrative Graduate Education and Research Training (IGERT) program (DGE-9980948), the combined Research and Curriculum Department (CRCD) program (EEC-0203415), and the International Materials Institutes (IMI) program.

References

[1] H.S. Chen, T.T. Wang, J. Appl. Phys. 41 (1970) 5338–5339.
[2] B. Yang, M.L. Morrison, P.K. Liaw, R.A. Buchanan, G.Y. Wang, C.T. Liu, M. Denda, Appl. Phys. Lett. 86 (2005), pp. 141904-1–141904-3.
[3] H.J. Leamy, H.S. Chen, T.T. Wang, Met. Trans. 3 (1972) 699–708.
[4] C.C. Hays, C.P. Kim, W.L. Johnson, Phys. Rev. Lett. 84 (2000) 2901–2904.
[5] A. Inoue, Bulk Amorphous Alloys, Trans Tech Publication, Zurich, 1998.
[6] H. Kakiuchi, A. Inoue, M. Onuki, Y. Takano, T. Yamaguchi, Mater. Trans. 42 (2001) 678–681.
[7] W.L. Johnson, JOM 3 (2002) 40–43.
[8] Y. Yokoyama, T. Shinohara, K. Fukaura, A. Inoue, Mater. Trans. 45 (2004) 1823–1891.
[9] Y. Yokoyama, A. Kobayashi, K. Fukaura, A. Inoue, Mater. Trans. 43 (2002) 571–574.
[10] G.Y. Wang, P.K. Liaw, A. Peker, B. Yang, M.L. Benson, W. Yuan, W.H. Peter, L. Huang, M. Freels, R.A. Buchanan, C.T. Liu, C.R. Brooks, Intermetallics 13 (2005) 429–435.
[11] Y. Yokoyama, K. Inoue, K. Fukaura, Mater. Trans. 43 (2002) 2316–2319.
[12] Y. Waseda, T. Masumoto, Phys. States Solid 31 (1975) 477–483.
[13] V.N. Novikov, A.P. Sokolov, Nature 431 (2004) 961–963.
[14] T. Egami, V. Vitek, J. Non-Cryst. Solids 61/62 (1984) 499–510.
[15] Jan Schroers, W.L. Johnson, Phys. Rev. Lett. 93 (2004) 255503–255510.
[16] A.L. Greer, J. Non-Cryst. Solids 61/62 (1984) 737–748.
[17] Y. Yokoyama, Y. Akeno, T. Yamasaki, P.K. Liaw, R.A. Buchanan, A. Inoue, Mater. Trans. 46 (2006) 2755–2761.