Formation and Mechanical Strength of Bulk Glassy Alloys in Zr–Al–Co–Cu System

Tao Zhang and Akihisa Inoue

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

By choosing a new alloy composition of $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$, we succeeded in forming bulk glassy alloys in rod and sheet forms by copper mold casting. The maximum diameter and sheet thickness were 5 mm and 3 mm, respectively. The T_g , ΔT_x and T_g/T_l are 750 K, 80 K and 0.60, respectively, being independent of sample thickness. The bulk alloy sheet exhibits Young's modulus of 92 GPa, elastic elongation limit of 2.1% and high tensile strength of 1960 MPa. These strength values are considerably higher than those for the other Zr-based bulk glassy alloys reported up to date. The synthesis of the new Zr-based bulk glassy alloy with high glass-forming ability and high tensile strength approaching 2000 MPa is expected to result in a future extension of application fields as a high strength material.

(Received February 28, 2002; Accepted April 5, 2002)

Keywords: bulk glassy alloy, new zirconium base system, glass-forming ability, glass transition temperature, mechanical strength

1. Introduction

Since Zr-based glassy alloys with a large supercooled liquid region before crystallization were found in Zr–Al–Ni,¹⁾ Zr–Al–Ni–Cu²⁾ and Zr–(Ti, Nb)–Al–Ni–Cu³⁾ systems and the high thermal stability of the supercooled liquid caused the formation of bulk glassy Zr-based alloys with good mechanical properties, much attention has been paid to bulk glassy alloys. It has subsequently been reported that bulk glassy alloys with good mechanical properties are formed in the other Zr-based alloy systems such as Zr–Ti–Be–Ni–Cu,⁴⁾ Zr–(Pd, Ta)–Al–Ni–Cu⁵⁾ and Zr–Al–Be–Ni–Cu⁶⁾ systems. These Zr-based bulk glassy alloys exhibit high tensile fracture strength of 1500 to 1700 MPa and have been used as sporting goods materials and connecting tubes for optical communication fibers.^{7–10)} As is the case for the Zr-based bulk glassy alloys, Ln–Al–(Co, Ni, Cu)¹¹⁾ and Pd–Cu–Ni–P¹²⁾ bulk glassy alloys possess good mechanical properties as is evidenced from much higher tensile fracture strength as compared with those for the corresponding crystalline alloys. However, there have been no data on bulk glassy alloys in Zr-, Ln- and Pd-based systems exhibiting high tensile fracture strength of about 2000 MPa. Very recently, we have found new Cu-^{13–15)} and Ni-¹⁶⁾ based bulk glassy alloys with high tensile fracture strength exceeding 2500 MPa. Simultaneously, we have investigated a dominant factor for achievement of high tensile fracture strength. It has been pointed out that the tensile fracture strength has a strong correlation with glass transition temperature (T_g) and liquidus temperature (T_l) and there is a clear tendency for tensile strength to increase with increasing T_g and T_l .^{13–16)} Based on the strong correlation, we have searched for a new Zr-based bulk glassy alloy with much higher tensile fracture strength. As a result, it was found that high tensile fracture strength of approximately 2000 MPa is obtained for a number of bulk glassy alloys in Zr–Al–Co base systems such as Zr–Al–(Co, Fe), Zr–Al–(Co, Cu), Zr–M–Al–(Co, Fe), Zr–Al–(Co, Fe, Ni), Zr–M–Al–(Co, Fe, Cu), Zr–Al–(Co, Ni, Cu) and Zr–M–Al–(Co, Ni, Cu) (M = Ti, Nb, Ta) systems. This paper presents the glass transition temperature (T_g), crystallization temperature (T_x), supercooled liquid re-

gion ($\Delta T_x = T_x - T_g$) and reduced glass transition temperature (T_g/T_l) of a $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ glassy alloy and the formation tendency and mechanical properties of the bulk glassy Zr-based alloy.

2. Experimental Procedure

A multi-component $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ alloy was examined because its alloy had the largest ΔT_x in $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{25-x}\text{Cu}_x$ ($x = 0, 5, 10, 15, 20$ and 25 at%) alloy series. The alloy composition represents the nominal composition of the mixture. The alloy ingot was prepared by arc melting the mixture of pure metals in an argon atmosphere. Bulk glassy alloys in rod and sheet forms were produced by copper mold casting and melt-clamp die forging, respectively. The sample dimension was 70 mm in length and 2 to 5 mm in diameter for the cast rods and 2 mm in thickness, 50 mm in width and 70 mm in length for the forged sheets. A glassy alloy ribbon with a cross section of $0.02 \times 1.2 \text{ mm}^2$ was also produced by melt spinning. The glassy phase was identified by X-ray diffraction and optical and transmission electron microscopies (OM and TEM). Thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The melting and liquidus temperatures (T_m and T_l) were measured with a differential thermal analyzer (DTA) at a cooling rate of 0.33 K/s. Mechanical properties were measured in tensile and compressive deformation modes with an Instron testing machine. The gauge dimensions were 1 mm in thickness, 5 mm in width and 15 mm in length for the tensile specimen and 2 mm in diameter and 4 mm in length for the compressive specimen, respectively. The strain rate was $5.0 \times 10^{-4} \text{ s}^{-1}$ for the tensile deformation and $2.5 \times 10^{-3} \text{ s}^{-1}$ for the compressive deformation. Fracture surface was examined by scanning electron microscopy (SEM).

3. Results

Figure 1 shows X-ray diffraction patterns of the cast $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ samples in a rod form of 3 and 5 mm in diameter and in a sheet form of 2 mm in thickness. The patterns

Fig. 1 X-ray diffraction patterns of a $Zr_{55}Al_{20}Co_{20}Cu_5$ alloy in a rod form of 3 and 5 mm in diameter and a sheet form of 2 mm in thickness.

Fig. 2 DSC curves of the glassy $Zr_{55}Al_{20}Co_{20}Cu_5$ alloy in the rod and sheet forms.

consist only of a broad peak with a wave vector of 25.9 nm^{-1} for all the samples and no appreciable crystalline peak is observed. We have also confirmed the absence of appreciable crystalline phases in the optical micrographs and TEM images of the transverse cross section of the rod and sheet samples. Figure 2 shows DSC curves of the bulk glassy samples in the rod and sheet forms, together with the data for the corresponding melt-spun glassy ribbon. All of the DSC curves show nearly the same endothermic and exothermic reactions, *i.e.*, the glass transition, followed by a large supercooled liquid region and then main exothermic peak due to crystallization. The feature of the DSC curves is almost independent of sample thickness. The T_g and T_x are 750 and 830 K, respectively, and the ΔT_x is as large as 80 K which is comparable to those (70 to 127 K)²⁾ for Zr–Al–Ni–Cu glassy alloys. With the aim of determining the reduced glass transition temperature (T_g/T_l), we measured the T_l value by DTA. As shown for the DTA curve in Fig. 3, the alloy solidifies through slightly divided two-stage exothermic reactions and the T_l is determined as 1260 K. The resulting T_g/T_l is evaluated to be 0.60 which is high enough to form a bulk glassy alloy by copper

Fig. 3 DTA curve of a $Zr_{55}Al_{20}Co_{20}Cu_5$ alloy prepared by arc melting.

Fig. 4 Stress-elongation curves in tensile (a) and compressive (b) deformation modes for the glassy $Zr_{55}Al_{20}Co_{20}Cu_5$ alloy in a rod form of 2 mm in diameter and a sheet form of 1 mm in thickness.

mold casting, being consistent with the present results. The DTA data also imply that the elimination of the low intensity exothermic peak causes a significant decrease in T_l , leading to an increase of T_g/T_l .

Figure 4 shows stress-elongation curves of the bulk glassy $Zr_{55}Al_{20}Co_{20}Cu_5$ samples in rod and sheet forms under tensile and compressive deformation modes. No distinct plastic elongation is seen in the tensile stress-elongation curve, but the compressive stress-elongation curve shows a distinct plastic elongation of about 0.6% before final fracture. The Young's modulus (E), elastic elongation limit (ϵ_E), tensile fracture strength ($\sigma_{t,f}$), compressive fracture strength ($\sigma_{c,f}$) and total compressive fracture elongation including elastic elongation (ϵ_f) are 92 GPa, 2.1%, 1960 MPa, 2200 MPa and 2.7%, respectively. It is noticed that the tensile fracture strength reaches 1960 MPa which is considerably higher than those (1500 to 1700 MPa)⁷⁻¹⁰⁾ for the previously reported Zr-based bulk glassy alloys in Zr–Al–Ni–Cu, Zr–(Ti, Nb, Pd)–Al–Ni–Cu and Zr–Ti–Ni–Cu–Be systems. The fracture under the tensile or compressive deformation mode occurs along a maximum shear stress plane which is declined by about 45 de-

Fig. 5 Fracture surface of the glassy $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ alloy sheet subjected to fracture in a uniaxial tensile deformation mode.

agrees to the direction of applied load and the fracture surface consists mainly of a well-developed vein pattern, as exemplified for the tensile fracture sheet in Fig. 5. The feature of the fracture mode agrees well with those for the other Zr-based bulk glassy alloys.

4. Discussion

4.1 High glass-forming ability

As described in Section 1, a number of bulk glassy alloys have been synthesized in Zr-based alloy systems. The alloy systems can be classified into two groups of Zr–Al–Ni–Cu type including Ti, Nb, Ta and Pd as additional elements and Zr–Ti–Ni–Cu–Be type.^{7–10} There have been no data on the formation of bulk glassy alloys in Zr–Al–Co base system and the Al content in the previously reported Zr–Al–Ni–Cu bulk glassy alloys is usually in the range from 5 to 15 at%. The higher Al content of 20 at% is another feature of alloy composition for the present Zr-based alloy. Considering that the maximum sample diameter of the $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ glassy alloy is above 5 mm in the case of the copper mold casting method, the glass-forming ability is concluded to be comparable to those for the Zr–Al–Ni–Cu and Zr–(Ti, Nb, Pd)–Ni–Cu systems. We consider the reason for the high glass-forming ability of the new Zr–Al–Co base alloy. It is thought that the base components in the present alloy are the three elements of Zr, Al and Co, though a small amount of Cu (5 at%) is included. It is known that all bulk glassy alloys in metal-metal type system have the following empirical component rules, *i.e.*, (1) multi-component consisting of more than three elements, (2) significant difference in atomic size ratios above 12% among the main three constituent elements, and (3) suitable negative heats of mixing among the main elements.^{7–10} The atomic size ratio is 1.12 for Zr/Al, 1.14 for Al/Co and 1.28 for Zr/Co,¹⁸ and the heat of mixing is -44 kJ/mol for Zr–Al pair, -19 kJ/mol for Al–Co pair and -41 kJ/mol for Zr–Co pair.¹⁹ These data clearly indicate that the Zr–Al–Co

base alloy satisfies the above-described empirical component rules for formation of bulk glassy alloys as well as for stabilization of supercooled liquid. It has previously been reported that the bulk glassy alloys with the component rules can have a unique glassy structure with three features of (1) a higher degree of dense random packing state, (2) new local atomic configurations, and (3) long-range homogeneity with attractive interaction.⁹ It is reasonably interpreted that the glassy alloy with such structural features can have a highly stable supercooled liquid state through high resistance against crystallization. The detailed mechanism for the stabilization of supercooled liquid has been described previously.⁹

4.2 High tensile strength

It is shown in Fig. 4 that the tensile and compressive fracture strength values of the $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ alloy are 1960 MPa and 2200 MPa, respectively. It is noticed that these strength values are much higher than those (1500 to 1800 MPa) for the previously reported Zr-based bulk glassy alloys in Zr–Al–Ni–Cu, Zr–(Ti, Nb, Pd)–Al–Ni–Cu and Zr–Ti–Ni–Cu–Be systems.^{7–10} We discuss the reason for the higher tensile and compressive strength values of the present Zr–Al–Co–Cu bulk glassy alloy. It has been pointed out that the tensile strength has a good linear relation with Young's modulus, T_g and liquidus temperature (T_l) for bulk glassy alloys.^{14,19} The Young's modulus, T_g and T_l of the present Zr-based alloy are 92 GPa, 750 K and 1260 K, respectively, being considerably higher than those (89 to 90 GPa, 690 K and 1113 K) for the other Zr-based bulk glassy alloys. It is therefore concluded that the bonding force among the constituent elements in the Zr–Al–Co–Cu glassy alloy is stronger than that for the other Zr-based glassy alloys. Considering the difference in the alloy components in these Zr-based glassy alloys, the stronger bonding force for the present alloy seems to be mainly attributed to the following two reasons, *i.e.*, (1) the increase in the bonding numbers of Zr–Al, Co–Al and Cu–Al pairs resulting from the higher Al content (20 at%) and (2) the

larger average negative heats of mixing (–19 to –41 kJ/mol) for Zr–Co and Al–Co pairs than those (–1 to –49 kJ/mol) for Zr–Ni, Zr–Cu, Al–Ni and Al–Cu pairs.¹⁸⁾

5. Summary

A new Zr-based bulk glassy alloy with a diameter up to 5 mm was formed for the alloy component of $\text{Zr}_{55}\text{Al}_{20}\text{Co}_{20}\text{Cu}_5$ by copper mold casting. The T_g , ΔT_x and T_g/T_l of the bulk glassy alloy are 750 K, 80 K and 0.60, respectively. The Young's modulus, elastic elongation limit, tensile fracture strength, compressive fracture strength and compressive plastic elongation are 92 GPa, 2.1%, 1960 MPa, 2200 MPa and 0.6%, respectively. It is noticed that the tensile fracture strength is considerably higher than those (1500 to 1700 MPa) for the other Zr-based bulk glassy alloys. The higher strength combined with high glass-forming ability is promising as a new type of high-strength bulk glassy alloy.

REFERENCES

- 1) A. Inoue, T. Zhang and T. Masumoto: Mater. Trans., JIM **30** (1989) 965–972.
- 2) T. Zhang, A. Inoue and T. Masumoto: Mater. Trans., JIM **32** (1991) 1005–1010.
- 3) A. Inoue, T. Shibata and T. Zhang: Mater. Trans., JIM **36** (1995) 1420–1426.
- 4) A. Peker and W. L. Johnson: Appl. Phys. Lett. **63** (1993) 2342–2344.
- 5) A. Inoue, Y. Yokoyama, Y. Shinohara and T. Masumoto: Mater. Trans., JIM **35** (1994) 923–926.
- 6) A. Inoue, T. Zhang, N. Nishiyama, K. Ohba and T. Masumoto: Mater. Trans., JIM **34** (1993) 1234–1237.
- 7) A. Inoue: Mater. Trans., JIM **36** (1995) 866–875.
- 8) A. Inoue: Acta Mater. **48** (2000) 279–306.
- 9) A. Inoue: Mater. Sci. Eng. **A304–306** (2001) 1–11.
- 10) *Supercooled Liquid Bulk Glassy and Nanocrystalline States of Alloys*, ed. by A. Inoue, A. R. Yavari, W. L. Johnson and R. H. Dauskardt (MRS, Warrendale, 2001) pp. L12.13.1–L12.13.6.
- 11) A. Inoue, T. Nakamura, T. Sugita, T. Zhang and T. Masumoto: Mater. Trans., JIM **34** (1993) 351–358.
- 12) A. Inoue, N. Nishiyama and T. Matsuda: Mater. Trans., JIM **37** (1996) 181–184.
- 13) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: Acta Mater. **49** (2001) 2645–2652.
- 14) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: Mater. Trans. **42** (2001) 1142–1145.
- 15) A. Inoue, W. Zhang, T. Zhang and K. Kurosaka: Mater. Trans. **42** (2001) 1149–1151.
- 16) A. Inoue, T. Zhang, K. Kurosaka and W. Zhang: Mater. Trans. **42** (2001) 1800–1804.
- 17) *Metals Databook*, ed. by Japan Inst. Metals, Maruzen, Tokyo (1983) p. 8.
- 18) F. R. Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen: *Cohesion in Metals*, (North-Holland, Amsterdam, 1988) pp. 103–637.
- 19) H. S. Chen: Rep. Prog. Phys. **43** (1980) 353–432.