Cu₄₅Zr₄₅Al₅Ag₅ Bulk Glassy Alloy with Enhanced Compressive Strength and Plasticity at Cryogenic Temperature

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Compressive tests were made for the as-cast Cu₄₅Zr₄₅Al₅Ag₅ bulk glassy alloy rods with a diameter of 3 mm at 298 and 77 K, at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. It was found that at 77 K, the compressive yield strength, maximum strength and plastic strain to fracture of the glassy alloy rod are higher than those at 298 K. The maximum strength measured at 77 K is about 13% larger than that measured at 298 K. In particular, its plasticity at 77 K is significantly enhanced. SEM observations reveal that more shear bands appear near the fracture plane at 77 K. The higher strength and ductility at a cryogenic temperature (77 K) are probably due to the lower mobility of the squeezed free volume.

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1. Introduction

Since the first success of synthesizing bulk glassy alloys in Ln⁻¹ based alloys in 1989, they have attracted great attention as a novel bulk metallic material in science and engineering fields. In recent years, several families of multicomponent alloys exhibiting excellent glass-forming ability have been developed. They include Mg-,²⁾ Zr-,^{3,4)} Ti-,⁵⁾ Fe-,⁶⁾ Pd-,⁷⁾ Ni-,⁸⁾ Co-⁹⁾ and Cu-¹⁰⁾ based alloys. They possess many unique properties, such as good corrosion resistance, extremely high strength, relatively high fracture toughness¹¹⁾ at ambient temperature and high strain rate formability and workability at elevated temperature, applicable to industrial materials.¹²⁾

Although it is important to evaluate the mechanical properties of the bulk metallic glasses at cryogenic temperatures for wider applications, such as in the field of space exploration and liquefied gas storage,¹³⁾ few data associated with Zr-based metallic glasses have been reported. Tabachnikova and Bengus *et al.*^{14,15)} investigated the compressive fracture behavior of a Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni₁₀Be_{22.5} alloy at temperatures of 300 and 77 K and a strain rate of $2.8 \times 10^{-4} \text{ s}^{-1}$. The fracture stresses (σ_{cf}) of the alloy under compression at temperatures of 300 and 77 K were $1.75 \pm 0.25 \text{ GPa}$ and $1.35 \pm 0.35 \text{ GPa}$, respectively. On the other hand, Li *et al.*^{13,16)} reported that both σ_{cf} and plastic strain (ε_{cp}) of a Zr_{57.4}Cu_{17.9}Ni_{13.4}Al_{10.3}Nb₁ glassy alloy increased at 77 K and a strain rate of $2 \times 10^{-4} \text{ s}^{-1}$. Accordingly, the mechanical properties at cryogenic temperature of the glassy alloys are different depending on the alloy system. In comparison with Zr-based glassy alloys, no information is available about the mechanical properties at the cryogenic temperature of a Cu-Zr-based glassy alloy¹⁷⁾ containing 45 at% Cu.

The objective of this work is to investigate the mechanical properties at 77 K of a Cu₄₅Zr₄₅Al₅Ag₅ glassy alloy.

2. Experimental Procedure

The alloy composition of the sample was Cu₄₅Zr₄₅Al₅Ag₅ (at%). An alloy ingot was prepared by arc melting the mixtures of pure Cu, Zr, Al and Ag metals with purity of over 99.5 mass% in a purified argon atmosphere. The alloy ingot was re-melted four times to ensure chemical homogeneity. The bulk glassy alloy of cylindrical rods with a diameter of 3 mm was prepared by a high pressure die casting method²⁾ in an argon atmosphere. The copper mold was cooled with flowing water. The ribbons with a cross section of $0.013 \times 1.0 \text{ mm}^2$ were also prepared for comparison by a single roller melt spinning method in an argon atmosphere. The amorphicity of the cylindrical and ribbon samples was investigated by the diffractometer X-ray method (XRD) using Cu K α radiation and thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The compressive tests were conducted at 298 and 77 K using a servo-hydraulic testing machine (Shimadzu Servopulser of 50-kN shear type load cell) at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The sample dimension for the compressive test was 3 mm in diameter and 6 mm in length. In order to reduce the frictional stress, both ends of the specimens were lubricated with lubricating grease. The fracture and side surfaces were examined by scanning electron microscopy (SEM).

3. Results and Discussion

Figure 1 shows an example of x-ray diffraction pattern of an as-cast cylindrical Cu₄₅Zr₄₅Al₅Ag₅ alloy specimen with a diameter of 3 mm, together with that of the melt-spun ribbon of the alloy about 13 μm in thickness. It is clear that the XRD pattern of the cylindrical sample exhibits a halo and no diffraction peaks corresponding to the crystalline phase are seen, indicating the formation of a glassy structure. Figure 2 shows the DSC curve of the as-cast cylindrical Cu₄₅Zr₄₅Al₅Ag₅ alloy specimen with the diameter of 3 mm,

Fig. 1 XRD patterns of as-cast and ribbon shaped $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ alloy.

Fig. 2 DSC curves of as-cast and ribbon shaped $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ alloy at a heating rate of 0.67 K/s.

along with that of the melt-spun ribbon. The cylindrical sample exhibits typical glassy characteristics, i.e., an apparent endothermic reaction due to glass transition, followed by a sharp exothermic peak due to crystallization. The glass transition temperature (T_g) and the onset of crystallization temperature (T_x) for the as-cast specimen are 700 and 781 K, respectively, being nearly the same as those for the melt-spun ribbon (698 and 782 K). These results indicate that there is no distinct difference in the amorphous structure between the as-cast cylindrical alloy specimen and the melt-spun ribbon.

Figure 3 shows the compressive stress-strain curves of the as-cast cylindrical $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ alloy specimen with the diameter of 3 mm and length of 6 mm at the strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ tested at 298 and 77 K. Both the glassy alloy specimens show an initial elastic strain, then begin to yield, followed by an appreciable amount of plastic strain. It should be noted that the yield strength (σ_{cy}), maximum strength (σ_{cf}) and plastic strain (ϵ_{cp}) at 77 K are distinctly higher than those at 298 K; i.e., σ_{cy} , σ_{cf} and ϵ_{cp} at 77 K were $2098 \pm 25 \text{ MPa}$, $2112 \pm 35 \text{ MPa}$ and $0.93 \pm 0.29\%$ respectively, whereas those at 298 K were $1873 \pm 43 \text{ MPa}$, $1873 \pm 25 \text{ MPa}$ and $0.14 \pm 0.06\%$, respectively. σ_{cf} measured at 77 K is about

Fig. 3 Compressive stress-strain curves of as-cast $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy rods with 3 mm in diameter and 6 mm in length tested at 298 and 77 K, at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

13% higher than that at 298 K. In particular, the plasticity at 77 K is significantly enhanced, which is not observed for the conventional crystalline alloys. Similar enhancement in strength and plasticity at 77 K was obtained for a $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ ¹⁸⁾ and a $\text{Zr}_{57.4}\text{Cu}_{17.9}\text{Ni}_{13.4}\text{Al}_{10.3}\text{Nb}_1$ ¹⁶⁾ glassy alloys. On the other hand, as mentioned above, Tabachnikova *et al.*^{14,15)} reported that the fracture stress of the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy decreased at 77 K. They also reported that at 77 K chevron pattern typical of brittle failure was present on some areas of the fracture surface. They prepared the specimens from the ingot with a diameter of 40 mm, suggesting increasing effects of inhomogeneity in microstructures and resulting in decrease in fracture stress at 77 K.

It is well known that large homogenous plastic deformation of glassy alloys by viscous flow takes place under the condition of the super-cooled liquid region, while at temperatures lower than T_g , plastic deformation becomes inhomogeneous with highly localized shear bands.¹⁹⁾ Glassy materials start yielding at the onset of formation of shear bands. It is not certain whether or not glassy alloys become stiff at cryogenic temperatures. Accordingly, we examined the temperature dependence of elastic parameters for the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy using an ultrasonic pulse method.²⁰⁾ Longitudinal and transverse wave velocities and eight kinds of the elastic parameters were measured simultaneously as a function of temperature in the range of 77 and 373 K. The results showed that the Young's and shear moduli and the elastic Debye temperature gradually increased with decreasing temperature from room to cryogenic temperatures. This means that the glassy alloy becomes stiff and the effective atomic distance of the alloy decreases at cryogenic temperatures. Furthermore, Poisson's ratio decreased at cryogenic temperatures, indicating that the rigidity of the alloy increased. At cryogenic temperature, therefore, the glassy alloy becomes stiff and rigid, accompanied by the decrease in the effective atomic distance, which results in squeezing the free volumes. It is currently accepted that shear band initiation in glassy alloys is related to free volume coalescence.^{19,21)} At cryogenic temperatures, increased stiffness of the atomic bond makes the squeezed free volume

Fig. 4 SEM micrographs showing the compressive fracture feature of as-cast Cu₄₅Zr₄₅Al₅Ag₅ bulk glassy alloy rods with a diameter of 3 mm at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$; (a)–(d) tested at 298 K, (e)–(h) tested at 77 K. (a), (b), (e) and (f) are compressive fracture surfaces at different magnifications; (c) and (g) are shear fracture geometries of the compressive specimens; (d) and (h) are shear band morphologies near the fracture surfaces.

coalescence more difficult, since the mobility of the free volume at 77 K would be much lower than that at 298 K. The coalescence of the free volume requires a higher applied load, resulting in the increase of the yield strength at 77 K.

Figure 4 shows SEM micrographs exhibiting the compressive fracture feature of the as-cast Cu₄₅Zr₄₅Al₅Ag₅ bulk glassy alloy rods tested at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ at 298 and 77 K. SEM observations show that compressive fracture always occurs in the shear mode, as shown in Fig. 4(c) and (g). In both cases, the compressive fracture surfaces have an angle of about 40° with respect to the loading axis, which indicates that the alloy does not follow the von Mises criterion²²⁾ and consist only of a vein-like pattern typical for an amorphous structure, shown in Fig. 4(b) and (f). A large difference is observed in the shear bands near the fracture plane. As shown in Fig. 4(d) and (h), at 77 K, the shear bands have a relatively higher density than those at 298 K. The ductility of glassy alloys is governed by the cumulative behavior of shear-band development and the dynamic propagation of the shear band is associated with the mobility of the free volume.^{16,23)} As mentioned above, the mobility of squeezed free volume at cryogenic temperatures would be much lower than that at room temperature. This is responsible for the enhancement of the formation of more shear bands. Therefore, the higher is the shear band density, the larger is the value of compressive plastic strain, as shown in Fig. 3.

4. Conclusions

The compressive tests were carried out for as-cast Cu₄₅Zr₄₅Al₅Ag₅ bulk glassy alloy rods with a diameter of 3 mm and a length of 6 mm at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$ and 298 and 77 K. The main results obtained are as follows.

- (1) The compressive yield strength, maximum strength and plastic strain to fracture of the glassy alloy rod measured at 77 K are higher than those at 298 K. The maximum strength at 77 K is about 13% larger than that measured at 298 K. The plastic strain at 77 K is about 0.9%, while that at 298 K is 0.14%.
- (2) At 77 K, more shear bands are observed near the fracture plane.
- (3) In both cases, the compressive fracture surfaces have an angle of about 40° with respect to the loading axis and consist only of a vein-like pattern.

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REFERENCES

- 1) A. Inoue, K. Kita, T. Zhang and T. Masumoto: *Mater. Trans. JIM*. **30** (1989) 722–725.
- 2) A. Inoue, T. Nakamura, N. Nishiyama and T. Masumoto: *Mater. Trans. JIM*. **33** (1992) 937–945.
- 3) A. Inoue, T. Zhang and T. Masumoto: *Mater. Trans. JIM*. **36** (1995) 391–398.
- 4) A. Pecker and W. L. Johnson: *Appl. Phys. Lett.* **63** (1993) 2342–2344.
- 5) A. Inoue, N. Nishiyama K. Amiya T. Zhang and T. Masumoto: *Mater. Lett.* **19** (1994) 131–135.
- 6) A. Inoue and J. S. Gook: *Mater. Trans. JIM*. **36** (1995) 1180–1183.
- 7) A. Inoue, N. Nishiyama and T. Matsuda: *Mater. Trans. JIM*. **37** (1996) 181–184.
- 8) X. M. Wang, I. Yoshii and A. Inoue: *Mater. Trans. JIM*. **41** (2000) 539–542.
- 9) T. Itoi and A. Inoue: *Mater. Trans. JIM*. **41** (2000) 1256–1262.
- 10) A. Inoue W. Zhang, T. Zhang and K. Kurosaka: *Mater. Trans.* **42** (2001) 1149–1151.
- 11) A. Kawashima, H. Kurishita, H. Kimura, T. Zhang and A. Inoue: *Mater. Trans.* **46** (2005) 1725–1732.
- 12) H. Kakiuchi, A. Inoue, M. Onuki, Y. Takano and T. Yamaguchi: *Mater. Trans.* **42** (2001) 678–681.
- 13) H. Li, K. Tao, C. Fan, P. K. Liaw and H. Choo: *Appl. Phys. Lett.* **89** (2006) 041921.
- 14) E. Tabachnikova, V. Bengus, J. Miskuf, K. Csach, V. Ocelik, W. Johnson and V. Molokanov: *Mater. Sci. Forum* **343–346** (2000) 197–202.
- 15) V. Bengus, E. Tabachnikova, J. Miskuf, K. Csach, V. Ocelik, W. Johnson and V. Molokanov: *J Mater. Sci.* **35** (2000) 4449–4457.
- 16) H. Li, C. Fan, K. Tao, H. Choo and P. K. Liaw: *Adv. Mater.* **18** (2006) 752–754.
- 17) W. Zhang, F. Jia, Q. S. Zhang and A. Inoue: *Mater. Sci. Eng. A* **459** (2007) 330–336.
- 18) T. Okuno, A. Kawashima, H. Kurishita, W. Zhang, H. Kimura and A. Inoue: *Collected Abstract of the 2007 Spring Meeting of the Japan Inst. Metals* (2007) p. 405.
- 19) A. S. Argon: *Acta Metall.* **27** (1979) 47–58.
- 20) M. Fukuhara, A. Kawashima, W. Zhang, A. Inoue and F. Yin: *J. Appl. Phys.* submitted.
- 21) K. M. Flores and R. H. Dauskardt: *Acta Mater.* **49** (2001) 2527–2537.
- 22) P. E. Donovan: *Acta Mater.* **37** (1989) 445–456.
- 23) B. Yang, M. L. Morrison, P. K. Liaw, R. A. Buchanan, G. Wang, C. T. Liu and M. Denda: *Appl. Phys. Lett.* **86** (2005) 141904.