Influences of Temperature and Strain Rate on Mechanical Behavior of a $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ Bulk Glassy Alloy

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Since the invention of bulk glassy alloys, a number of studies have been performed at ambient temperatures or above. However, little is known about mechanical properties of bulk glassy alloys at cryogenic temperatures. In this study, we investigated the effects of temperature and strain rate on the mechanical properties of a $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy fabricated by high pressure die casting methods. Compression tests were performed for the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy rods with a diameter of 3 mm at temperatures of 298, 223, 173 and 77 K and at strain rates from 5×10^{-5} to $5 \times 10^{-3} \text{ s}^{-1}$. It is found that the maximum compressive stress and plastic strain to failure increase monotonically with decreasing testing temperature. Multiple shear bands are observed on the side surface of the specimen deformed plastically at cryogenic temperatures. The maximum compressive stress and plastic strain are almost independent of strain rate. The reason for the changes in the maximum compressive stress and plastic strain with temperature and strain rate is discussed. [doi:10.2320/matertrans.MBW200734]

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1. Introduction

Kui and Turnbull¹⁾ succeeded in producing Pd-Ni-P bulk glassy alloys by water quenching of flux melted liquid in 1985, but nobody paid special attention on the result. However, since Inoue *et al.* created various bulk glassy alloys in Mg-Ln-M (Ln = Lanthanoid Metal, M = Ni, Cu, Zn), Ln-Al-TM (TM = Fe, Co, Ni, Cu) and Zr-Al-TM by copper mold casting from 1988 to 1990,²⁻⁴⁾ bulk glassy alloys have drawn great attention as novel materials in scientific and engineering aspects. For the last dozen years or so, a wide variety of bulk glassy alloys such as Ti-,⁵⁾ Fe-,⁶⁾ Co-,⁷⁾ Pd-,⁸⁾ Ni-,⁹⁾ Cu-,¹⁰⁾ Pt-¹¹⁾ and Au-¹²⁾ based systems have been synthesized. They possess many unique properties, such as extremely high fracture strength and large elastic strain, relatively high fracture toughness¹³⁾ at ambient temperatures, high corrosion resistance and high strain rate formability and workability at elevated temperatures, which are applicable to industrial materials.¹⁴⁾

It is important to study the mechanical properties of bulk glassy alloys at cryogenic temperatures from viewpoints of wider ranges of applications, such as space exploration, liquefied gas storage¹⁵⁾ and cooling pipe of experimental thermonuclear reactor. However, the literature associated with the mechanical behavior of the glassy alloys at low temperatures is available only for Zr-based glassy alloys and the number of literature is few.¹⁵⁻¹⁷⁾ Therefore, for $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods,¹⁸⁾ we¹⁹⁾ performed compression tests at 298 and 77 K and at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. It was found that the compressive maximum strength and plastic strain to fracture of the rods are higher at 77 K than at 298 K. Li *et al.*¹⁶⁾ reported similar results for a $\text{Zr}_{57.4}\text{Cu}_{17.9}\text{Ni}_{13.4}\text{Al}_{10.3}\text{Nb}_1$ glassy alloy. They also presented

that the maximum strength and plastic strain at 77 K increased with increasing strain rate. Although mechanical properties of the Cu-Zr-based bulk glassy alloy at cryogenic temperature were reported only for maximum strength and plastic strain at 77 K, little is known about the influence of strain rate on the mechanical properties of the bulk glassy alloy at cryogenic temperatures. This work aims to investigate the influences of temperature and strain rate on the mechanical properties of a $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy.

2. Experimental Procedure

The alloy composition of the sample was $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ (at%), and $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ (at%) was also used for comparison. Alloy ingots were prepared by arc melting the mixtures of pure Cu, Zr, Al, Ag and Ni metals with purity of over 99.5 mass% in a purified argon atmosphere. The alloy ingots were re-melted over five times to ensure chemical homogeneity. Cylindrical rods of bulk glassy alloys with a diameter of 4 mm were prepared by a high pressure die casting method²⁰⁾ in a purified argon atmosphere, where the copper mold was water-cooled. The cylindrical rods were machined into 3 mm in diameter and then mechanically polished with SiC paper up to No. 1000. The glassy structure of the as-received materials was confirmed by X-ray diffraction (XRD) using Cu K α radiation and differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s.

In order to investigate the temperature dependence of mechanical properties, compression tests were conducted at 298, 223, 173 and 77 K using a servo-hydraulic testing machine (Shimadzu Servopulser of 50-kN shear type load cell) at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. To examine strain rate dependence, compression tests were conducted at 298, 223, 173 and 77 K at various strain rates of 5×10^{-3} ,

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Fig. 1 Compressive stress-strain curves of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods at room temperature (298 K) and cryogenic temperatures (223, 173 and 77 K), at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

5×10^{-4} and $5 \times 10^{-5} \text{ s}^{-1}$. The sample size for compression tests was 3 mm in diameter and 6 mm in height. The deformation and fracture behavior was examined by scanning electron microscopy (SEM).

3. Results and Discussion

Figure 1 shows compressive stress-strain curves of the cylindrical $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods tested at 298, 223, 173 and 77 K and at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The slopes of the stress-strain curves were calibrated by the Young's modulus obtained by an ultrasonic pulse method.²¹⁾ The values of the Young's modulus measured at 298, 223, 173 and 77 K were 108, 110, 111 and 114 GPa, respectively. Because the difference in those at 298 and 77 K is 6 GPa ($\sim 5\%$), it is difficult to see the difference of the slopes of the stress-strain curves, as shown in Fig. 1. At 298 K, the specimen shows initial elastic strain, followed by final fracture immediately after the onset of yielding. On the other hand, below 223 K, the specimens show initial elastic strain, and then they begin to yield, followed by an appreciable amount of plastic strain. The maximum compressive stress ($\sigma_{\text{m.c.}}$) and plastic strain (ϵ_{p}) increase with decreasing testing temperature; i.e. $\sigma_{\text{m.c.}}$ and ϵ_{p} are $1873 \pm 25 \text{ MPa}$ and $0.14 \pm 0.06\%$, respectively at 298 K, $1920 \pm 38 \text{ MPa}$ and $0.69 \pm 0.15\%$, respectively at 223 K, $1930 \pm 20 \text{ MPa}$ and $0.96 \pm 0.21\%$, respectively at 173 K, $2112 \pm 35 \text{ MPa}$ and $0.93 \pm 0.29\%$, respectively at 77 K. In particular, the enhancement of plastic strain is significant.

Figure 2 shows the temperature dependence of the maximum compressive stress and plastic strain of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rod at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The data of the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ glassy alloy rod are also shown for comparison. It is clear that the maximum compressive stress and plastic strain for both the glassy alloys increase monotonically with decreasing testing temperature. The maximum compressive stress of the glassy alloys at 77 K is about 13% higher than that at 298 K. Furthermore, the plastic strain of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy at 77 K is about 7 times higher than that at 298 K. A similar result was obtained for a $\text{Zr}_{57.4}\text{Cu}_{17.9}\text{Ni}_{13.4}\text{Al}_{10.3}\text{Nb}_1$

Fig. 2 Temperature dependence of the maximum compressive stress and plastic strain of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ and $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ glassy alloy rods at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

glassy alloy.¹⁶⁾ It is thus concluded that glassy alloys become stiff and rigid at cryogenic temperatures.¹⁹⁾ This means that the effective atomic distance of the alloys decreases with decreasing testing temperature, resulting in squeezing the free volumes. It has currently been accepted that shear band initiation in glassy alloys is related to free volume coalescence.^{22,23)} Since the mobility of free volumes decreases with decreasing temperature, stiffness of atomic bond increases through the increase in the difficulty of free volume coalescence. The coalescence of free volume requires a higher applied load at cryogenic temperatures, resulting in an increase of the maximum compressive stress.

Figure 3 shows SEM images of the fracture and peripheral surfaces of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods at various temperatures and at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The fracture surfaces at each temperature consist of only a vein-like pattern typical for a glassy structure, as shown in Fig. 3(a), (c), (e) and (g). A significant difference is observed in the shear band structure on the peripheral surface near the fracture surface. As shown in Fig. 3(b), (d), (f) and (h), the relative density of shear bands increases with decreasing testing temperature.

Figure 4 shows SEM images of the peripheral surface of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rod subjected to the compressive plastic deformation at 77 K and at the initial strain rate of $5 \times 10^{-5} \text{ s}^{-1}$. A number of multiple shear bands are observed on the peripheral outer surface. It is well known that plastic deformation of bulk glassy alloys occurs inhomogeneous by accompanying the generation of highly localized shear bands at temperatures much lower than the glass transition temperature.²²⁾ The ductility of glassy alloys is governed by the generation, propagation and accumulation behaviors of shear bands and the dynamic propagation of shear bands is associated with the mobility of free volumes. The mobility of squeezed free volumes at cryogenic temperatures is much lower than that at ambient temperatures. This is the reason why a number of shear bands can generate at different sites. Similarly, the increase of the strain rate causes the increase in the density of shear bands.

Li *et al.*¹⁶⁾ have reported that when the glassy alloy starts yielding, the localized plastic deformation makes the temperature in front of the shear band tip increase, and this is one of

Fig. 3 SEM images of compressive fracture and peripheral surfaces of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods at various temperatures and at an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$.

Fig. 4 SEM images of peripheral outer surface of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rod deformed plastically at 77 K and at an initial strain rate of $5 \times 10^{-5} \text{ s}^{-1}$.

the reasons for early catastrophic fracture at ambient temperatures. They also described that the cryogenic environment can partially relieve the local heating ahead of the shear band tip; that is, the relief of local temperature rise and the decreasing mobility of free volumes cause the glassy alloy to be highly ductile. However, according to the literature,²⁴⁾ temperature rise can be as high as a few thousand Kelvin within a few nanoseconds. Therefore, it is difficult to presume the relief of the temperature rise of the glassy alloy

at the cryogenic temperatures.

The multiple shear bands at cryogenic temperatures are attributed to reduction of the propagation rate of shear band and an increase in the sites of shear band nucleation. The nucleation of nanocrystallites in the glassy matrix may be one of the reasons for the generation of the multiple shear bands. Eckert *et al.*²⁵⁾ explained the source of ductility for a Cu-based glassy alloy by the atomic-scale heterogeneities that enable easy nucleation and continuous multiplication of

Fig. 5 Compressive stress-strain curves of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods at various strain rates at 77 K.

shear bands at ambient temperatures. Accordingly, further studies regarding the atomic scale inhomogeneity in microstructure using transmission electron microscopy (TEM) should be needed.

Figure 5 shows compressive stress-strain curves for the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy at 77 K at different strain rates of 5×10^{-3} , 5×10^{-4} and $5 \times 10^{-5} \text{ s}^{-1}$. The $\sigma_{\text{m.c.}}$ is $2119 \pm 25 \text{ MPa}$ at $5 \times 10^{-3} \text{ s}^{-1}$, $2112 \pm 35 \text{ MPa}$ at $5 \times 10^{-4} \text{ s}^{-1}$ and $2149 \pm 6 \text{ MPa}$ at $5 \times 10^{-5} \text{ s}^{-1}$ and the ϵ_{p} at the corresponding strain rates are $1.27 \pm 0.34\%$, $0.93 \pm 0.29\%$ and $1.56 \pm 0.63\%$, respectively.

Figure 6 shows strain rate dependence of the maximum compressive stress and plastic strain of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods measured at 298, 223, 173 and 77 K. It is seen that the maximum compressive stress is almost independent of strain rate and testing temperature, in accordance with the previous result that the maximum compressive stress of glassy alloy is independent of quasi-static strain rate at ambient temperatures.²⁶⁾ The present result demonstrates that the similar result is also obtained even at cryogenic temperatures. This is different from the literature data that the maximum strength increases with increasing strain rate.¹⁶⁾ The plastic strain at 298 K tends to increase with increasing strain rate. But at 77 K, the strain rate dependence of plastic strain is not clear. Thus, there is no distinct dependence of the plastic strain on strain rate. The above results indicate that the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ bulk glassy alloy possesses good mechanical properties in a cryogenic environment.

4. Conclusions

Compression tests were conducted for $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods with a diameter of 3 mm and a height of 6 mm at 298, 223, 173 and 77 K at a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. In addition, compression tests at different strain rates of 5×10^{-3} , 5×10^{-4} and $5 \times 10^{-5} \text{ s}^{-1}$ were carried out at various temperatures. The main results obtained are as follows.

- (1) The maximum compressive stress and plastic strain increase monotonically with decreasing temperature. A similar result is obtained for a $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ bulk

Fig. 6 Strain rate dependence of the maximum compressive stress and plastic strain of the $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_5\text{Ag}_5$ glassy alloy rods.

glassy alloy. The maximum compressive stress at 77 K is about 13% higher than that at 298 K. The plastic strain at 77 K is about 7 times as high as that at 298 K.

- (2) The compressive fracture surfaces consist of a vein-like pattern typical for a glassy structure at each testing temperature. The peripheral surfaces of the specimen deformed plastically at 77 K show multiple shear bands.
- (3) There is no distinct dependence of the maximum compressive stress and plastic strain on strain rate at each testing temperature.

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