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Homogeneous plastic deformation in a Cu-based bulk amorphous alloy

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Abstract

The compressive deformation behavior of a cast $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass in the supercooled liquid region was investigated at strain rates ranging from 1×10^{-3} to $10^{-2}\ s^{-1}$. Glass transition and crystallization temperatures were determined by differential scanning calorimetry to be 721 and 766 K, respectively. Both strain rate and temperature were found to significantly affect deformation behavior in the supercooled liquid region. A strain rate change method was employed to obtain the strain rate sensitivity (m) and the maximum value of m was determined to be 0.61 at 750 K. A large compressive strain of 0.78 was achieved at a strain rate of $3 \times 10^{-3}\ s^{-1}$ at 740 K. Structures of the amorphous material, both before and after deformation, were studied using X-ray diffraction and high-resolution transmission electron microscopy. The compressive properties are presented and discussed in light of the structural change.

Keywords: B. Glasses, metallic; B. Plastic deformation mechanisms; B. Superplastic behaviour

1. Introduction

Recent advances in bulk metallic glasses (BMG, also known as bulk amorphous alloys) with high glass-forming ability and high thermal stability have given rise to a number of studies on fundamental science and practical applications. Inoue et al. [1,2] and other investigators [3,4] have reported the bulk Cu-based glassy alloys exhibit good mechanical properties at room temperature, i.e. compressive/tensile yield strengths exceeding 2000 MPa. The combination of high glass forming ability and good mechanical properties for the Cu-based alloys indicate the possibility of developing a new type of bulk structural materials. In contrast to Zr-based alloys, the Cu-based bulk metallic glass has major advantages of having a high strength and low cost. For structural applications, in particular, metallic glasses are often limited by their brittleness and lack of workability and machinability [5]. It is thus interesting to study the deformation behavior of the Cu-based bulk metallic glass with efforts to investigate whether this alloy exhibits good compressibility at high temperatures. In the present paper, the compressive deformation behavior of bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ metallic glass in the supercooled liquid region has been examined.

Kawamura et al. [6,7] investigated the superplastic deformation of a $Pd_{40}Ni_{40}P_{20}$ metallic glass in ribbon form having a wide supercooled liquid region of 72 K. The supercooled liquid above the glass transition temperature exhibited superplastic-like behavior at strain rates in the range from 10^{-4} to $10^{0}\ s^{-1}$. The maximum elongation to failure was more than 1260% at a strain rate of $1.7 \times 10^{-1}\ s^{-1}$ and at 620 K with a low flow stress of about 70 MPa. True Newtonian behavior, accompanied by good compressibility, was observed in the low strain rate region [8]. At high strain rates, the plastic flow became non-Newtonian, i.e. $m \neq 1$, in the equation $\sigma = K\dot{\varepsilon}^m$, where m is the strain rate sensitivity exponent, $\dot{\varepsilon}$ the strain rate, σ the flow stress and K a constant [9]. In previous studies, we found excellent plasticity in a bulk $Pd_{40}Ni_{40}P_{20}$ in compression [8] and $Zr_{55}Al_{10}Cu_{30}Ni_5$ in tension [10] when deformed in the supercooled region. The observation of non-Newtonian flow has also been reported in a Zr-based BMG [1]. In this case, the non-Newtonian behavior was suggested to be associated with a concurrent structural change in the glass during deformation.

2. Experimental procedure

The material investigated in this study, Cu-based BMG, prepared by cooper mold casting, had a dimension of 3 mm

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in diameter and 85 mm in length. Using an electron probe microanalyzer, the actual composition of the cast was determined to be 59.2%Cu–22.1%Zr–8.5%Hf–10.3%Ti (at.%), which is close to the nominal composition of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$. Compressive specimens with an aspect ratio of 1.5 were sliced directly from the cast rod. Both the top and bottom surfaces of a test specimen were polished before testing to ensure the specimen was parallel and smooth. To minimize friction between the test specimen and compression platform, BN powder was used as a lubricant.

Compressive tests were conducted in an argon atmosphere in the temperature range of 720–750 K at strain rates ranging from 1×10^{-3} to $2 \times 10^{-2}\ s^{-1}$ using Shimadzu AG250KN Autograph system, equipped with a heating furnace. To minimize possible crystallization during temperature transient, the holding time was 60 s before compressive test. Immediately after the completion of a test, the furnace was removed and the specimen was air cooled to room temperature. A strain-rate change method was used to determine the strain-rate sensitivity value, m. Thermal properties of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ were evaluated using a differential scanning calorimeter (DSC) at a heating rate of 40 K/min under argon atmosphere. X-rays diffractometry (XRD) with Cu Kα monochromatic radiation was used for the crystal structure characterization.

TEM samples were prepared by mechanical grinding, followed by ion milling to electron transparency in a liquid nitrogen cooled stage. High-resolution electron microscopy was carried out using a 200 kV JEOL 2010F field-emission TEM, which was equipped with an annular dark field detector, a post-column electron energy loss image (Gatan Enfina) and an Oxford energy-dispersive X-ray (EDX) detector. The duration of the EDX spectrum was 100 s and the spot size of the EDX spectrum is about 10 nm.

3. Results

A typical DSC scan of the bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ alloy sample at a heating rate of 40 K/min is shown in Fig. 1. The glass transition temperature (T_g) and crystallization temperature (T_x) are determined to be 721 and 766 K, respectively. The supercooled liquid region, ΔT, conventionally defined as the difference between T_x and T_g, is 45 K. This value is close to ~47 K for a similar alloy reported by Inoue et al. [2], but is much smaller than ~98 K usually observed in Zr-based metallic glass [10]. Apparently, Cu-based BMG has a less glass stability than Zr-Based BMG.

It is noted that Cu-base BMG readily oxidizes supercooled liquid region, i.e. above T_g [11]. However, it is not expected to have a significant effect on the mechanical properties. XRD patterns from the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG tested at 720, 740 and 750 K, along with that from the as-cast are shown in Fig. 2. (A 50 μm thick oxidized layer, formed during cooling after removing from furnace, was polished off before taking X-ray.) As can be observed in

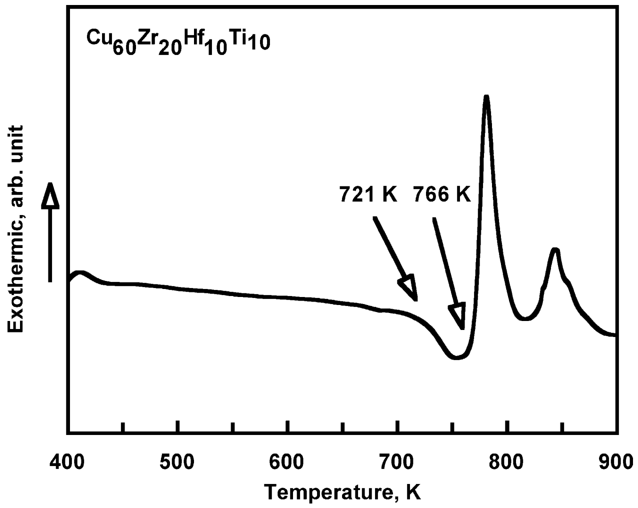

Fig. 1. DSC scan from bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass at a heating rate of 40 K/min. T_g and T_x are 721 and 766 K, respectively.

the figure, the broad Bragg peaks with no detectable crystalline phases are observed, suggestive of the amorphous structure being the major phase in the tested alloys. Thus, samples still have an amorphous structure after testing in the supercooled liquid region.

An edge view of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ samples before and after testing in compression is shown in Fig. 3. It is apparent in the figure that the Cu-based BMG is highly compressible at 740 K. Specifically, it shows a compressive strain of 0.77

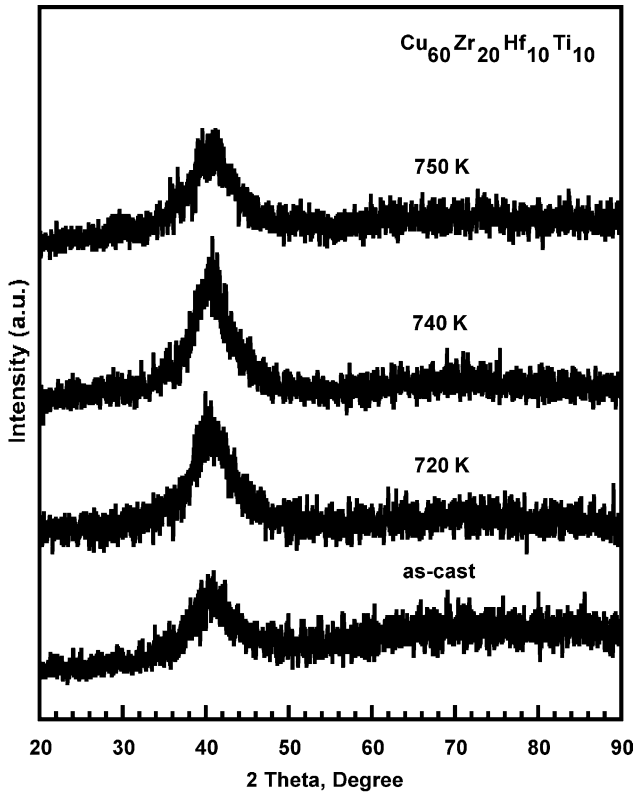

Fig. 2. XRD patterns from the bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glasses tested at 720, 740, 750 K, and in the as-cast condition.

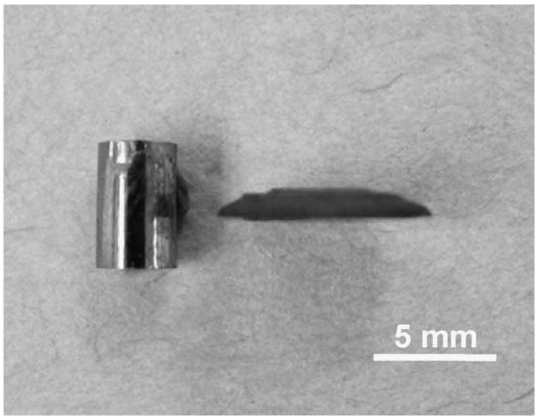

Fig. 3. An edge view of bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glasses before and after testing in compression at 740 K.

at 740 K and a strain rate of $3\times10^{-3}\ s^{-1}$. This value is lower than 0.94 in a Pd-based alloy [8] and is attributed to a narrow ΔT and high flow stresses, as will be discussed below. The relationship between compressive flow stress and strain rate at various temperatures for the $Cu_{60}Zr_{20}$-$Hf_{10}Ti_{10}$ glass is shown in Fig. 4. Compressive behavior of the bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass was evidently very sensitive to the test temperature and the applied strain rate. The flow stress is observed to increase with increasing the strain rate, and the maximum flow stress is 263 MPa at 720 K and a strain rate of $5\times10^{-3}\ s^{-1}$. For a direct comparison, results from a Pd-based alloy deformed in compression are also included [8]. It is noted that flow stresses of the Cu-based glass is about five times higher than those of the Pd-based glass in the supercooled liquid region. The high flow stress in the Cu-based glass appears to be intrinsic since the tensile strength of the Pd-based glass is also lower than that of the Cu-based glass at room temperature.

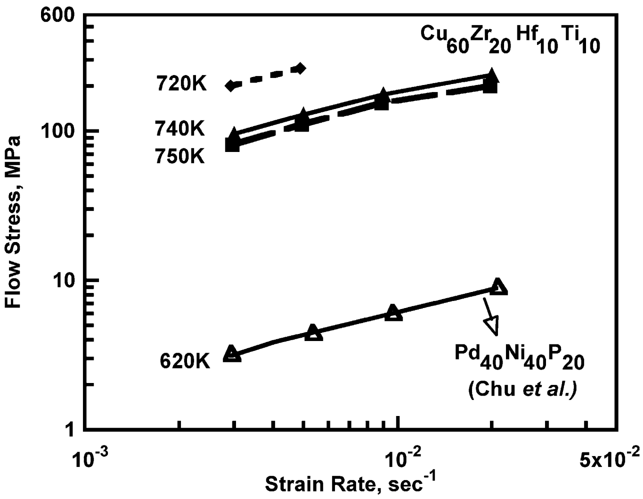

Fig. 4. Relationship between compressive flow stress and strain rate at various temperatures in bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass. Data obtained from a bulk $Pd_{40}Ni_{40}P_{20}$ alloy at 620 K in the supercooled liquid region are also included for comparison [8].

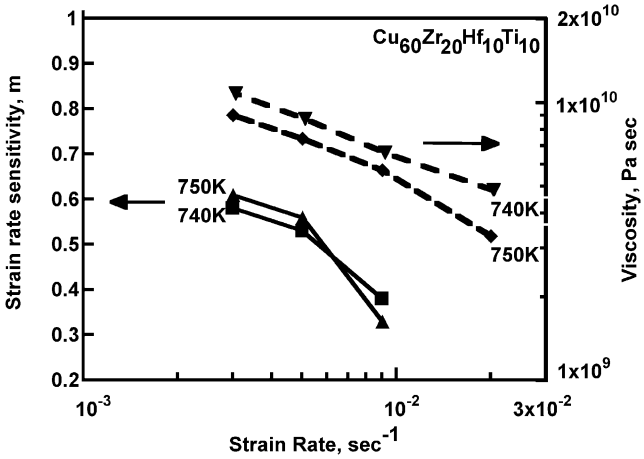

Fig. 5. Variation of strain rate sensitivity (m) and viscosity with strain-rate for bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass deformed at 740 and 750 K.

Strain rate sensitivity, m, where $m=\Delta\log\sigma/\Delta\log\dot{\varepsilon}$, was measured using a strain rate change method. Variation of strain rate sensitivity (m) and viscosity with strain-rate for the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass deformed at 740 and 750 K are shown in Fig. 5. It is readily observed that the m value of the supercooled liquid has a strong strain-rate dependence; it approaches 0.6 in low strain rates, but decreases rapidly with increasing strain rate in the high strain-rate region. The m value is always higher than 0.3 within the strain rate range examined in the present study. Viscosity is calculated using the conventional equation $\eta=\sigma_{flow}/3\dot{\varepsilon}$. In the strain rate region examined, an increase in strain rate leads to a decrease in viscosity. The viscosity varies with the strain rate, indicating deformation is non-Newtonian. In contrast to a Pd-based BMG, which shows a distinct transition from Newtonian to non-Newtonian flow [8], the present Cu-based BMG exhibits a non-Newtonian behavior in the strain-rate range examined. Newtonian flow was not observed.

To further investigate the deformation of the Cu-based glass, microstructural analyses were performed using electron microscopes. SEM images of the sample deformed to a strain of 0.65 at 720 K and $2\times10^{-2}\ s^{-1}$ are shown in Fig. 6. Fracture took place along a plane sharply declined about 44° from the loading axis. This sharp fracture appearance indicates shear localization and thus brittleness of the alloy under the test conditions. Well-developed vain-like patterns, typically observed in BMG deformed inhomogeneously, are also revealed. This result suggests that 720 K, which is close the glass transition temperature (721 K), is relatively low for the forming and shaping of the present Cu BMG.

A high-resolution TEM image together with a selected area diffraction pattern from a sample deformed to a strain of 0.68 at 750 K (i.e. 16 °C below the crystallization temperature) is presented in Fig. 7. Many ordered domains are readily observed; in fact, even some regulated lattice images can be seen. They are medium range ordered (MRO) clusters not nanocrystals, as revealed by the selected area

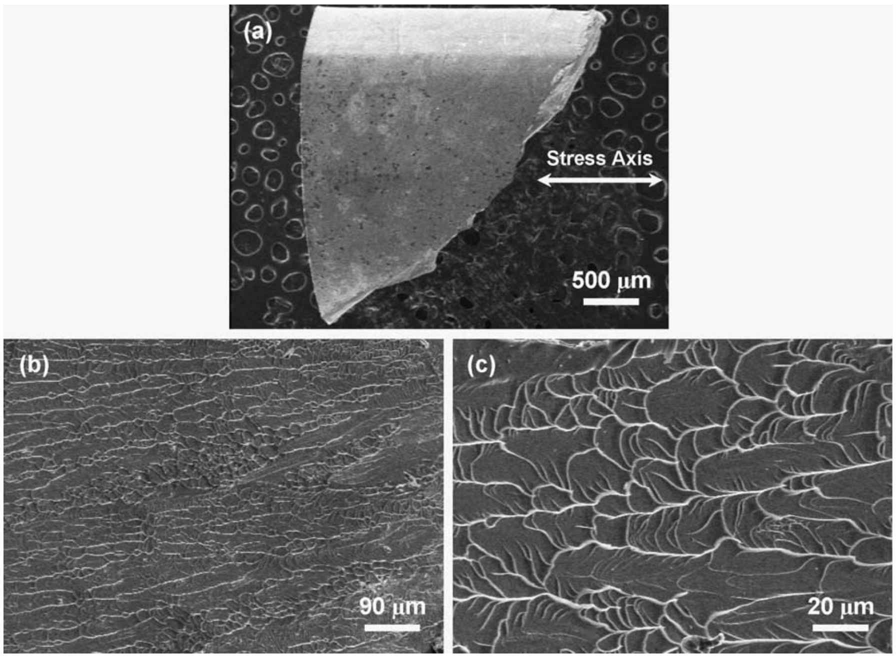

Fig. 6. SEM images revealing fracture feature of bulk $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass deformed in compression at 720 K and $2 \times 10^{-2}\ s^{-1}$: (a) longitudinal view, (b) and (c) fracture surface views.

diffraction pattern. The average size of these clusters is about 5 nm and the density is quite high, and they are uniformly distributed. It is especially noted that MRO domains were also observed in the starting (i.e. as-cast) material, but the population was much lower. The structure in the sample deformed at 720 K is quite similar to that in the sample tested at 750 K, except the size and density of MRO domains are both less. Specifically, the domain sizes are 1–2 and 3–5 nm at 720 and 750 K, respectively.

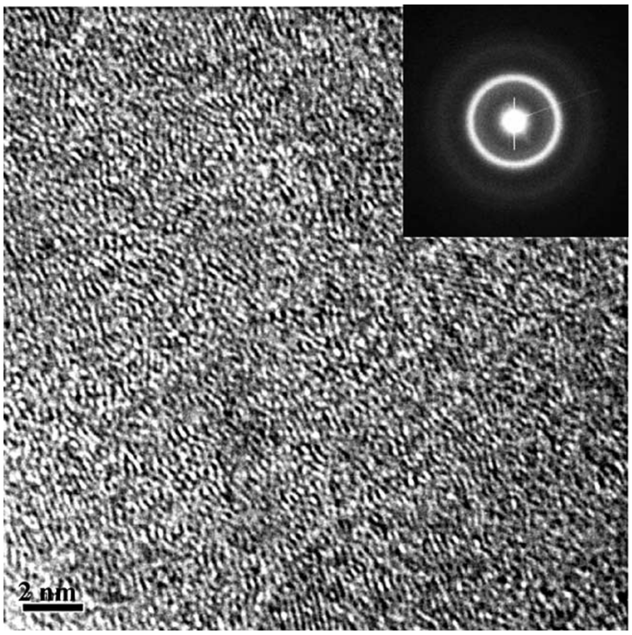

Fig. 7. High-resolution TEM image and a selected area diffraction pattern from the sample deformed to a strain of 0.68 at 750 K.

Apparently, MRO domains grow at increasing temperature. Detailed analyses of the structure and chemical composition of these MRO domains are currently underway.

4. Discussion

As discussed in Section 3, the TEM results showed that volume fraction of MRO domains was quite high after the amorphous $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ being tested in the supercooled liquid region. In fact, at the temperature of 750 K the majority of structure was composed of MRO domains. To further investigate the effect of MRO domains, DSC experiments were performed with the $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ samples to measure the exothermic peak and enthalpy of crystallization. The enthalpy of crystallization was directly compared with that of as-cast sample and yielded the crystalline volume fraction in the sample. The volume fractions of crystallized phase in samples deformed at 720 and 750 K are estimated to be 6 and 58%, respectively. This confirms that the amount of amorphous in the 750 K sample becoming low, which is in agreement with the TEM observation.

The MRO domains, even though their chemical compositions may vary from domain to domain, have well-defined crystalline characteristics. They are, therefore, expected to behave like ordinary fine crystalline grains during mechanical deformation. Since these domains are of nanometer in size, domain boundary sliding is expected to occur. This would be similar to the case of conventional superplastic deformation occurring in fine-grained materials.

The plastic flow of an amorphous alloy can be described by $\gamma_{am} = A\tau$, and for a nanocrystalline alloy it can be described by $\gamma_{cry} = B\tau^2$, where τ is the flow stress, and A and B are material constants. In the present Cu-BMG, when homogeneous deformation took place, the total plastic deformation, using the simple rule-of-mixture, can be expressed as [5]

$$\dot{\gamma}_{total} = (1 - f_v)A\tau + f_v B\tau^2 \quad (1)$$

where f_v stands for the volume fraction of nanocrystalline phase. The resultant strain rate sensitivity value, obviously depending upon the volume fraction of the nanocrystalline phase, must fall between 0.5, the value for domain/grain boundary sliding mechanism in a nanocrystalline material, and unity, the value for Newtonian viscous flow in a glassy medium. As shown in Fig. 5, the strain rate sensitivity is calculated to be approximately 0.6 at the maximum and decreases to about 0.4 at very high strain rates in the Cu-BMG. The strain rate sensitivity is closer to 0.5 for boundary sliding than unity for viscous flow in a pure amorphous alloy. This result further indicates that the volume fraction of nanocrystalline phase is high, which is consistent with the structural observation in Fig. 7.

5. Conclusion

The plastic deformation behavior of a $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glassy alloy in the supercooled liquid region was presented. A large compressive strain of 0.78 was achieved at 740 K and a strain rate of $3 \times 10^{-3}\ s^{-1}$. The flow stress of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ is generally much higher than that of Pd-based BMG in their respective supercooled liquid region. Also, the flow stress was observed to increase with increasing strain rate and decreasing temperature. The measured strain rate sensitivity value was approximately 0.6 at the maximum and decreased to about 0.4 at very high strain rates. Structural examinations indicated extensive formation of MRO domains in deformed samples. We thus proposed that, as a result of extensive MRO formation, domain sliding played a major role during homogeneous deformation of the Cu glassy alloy.

Acknowledgements

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