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Preliminary assessment of flow, notch toughness, and high temperature behavior of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass

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Abstract

Microhardness, hot hardness, uniaxial compression, and notched bending experiments were conducted on $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass (BMG). This Cu-based BMG possesses near theoretical strength but essentially zero compressive ductility at room temperature. Notch toughness values in excess of 65 MPa $\sqrt{m}$ were obtained, while significant softening was obtained near T_g.

Keywords: Copper alloys; Metallic glasses; Mechanical properties; Toughness

1. Introduction

Bulk metallic glasses exhibit a range of properties not available in other material systems. There have been considerable efforts devoted to the processing and characterization of glasses based on the Zr- [1], Al- [2,3], and Fe-based systems [4,5]. Much less work has investigated the balance of properties in Cu-based BMGs. Recent work by Nieh [6] has illustrated the interesting pop-in phenomenon in Cu-based glasses under nanoindentation conditions, although little information exists on properties such as toughness, compressive strength, and effects of changes in test temperature on properties. The purpose of this work is to provide some initial investigation into the balance of properties possible in Cu-based BMGs, while providing some comparison of the behavior of this system to other BMGs where significantly more information is available.

2. Experimental procedures

The $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ bulk metallic glass tested presently was produced in the manner described by Wang et al. [7]. Rods, 3 mm in diameter and 40 mm in length were received in the fully amorphous condition, as revealed by XRD, consistent with previous reports [7]. Initial testing determined the microhardness at room temperature on transverse cross sections of the rod. A Buehler Micromet 3 microhardness tester fitted with a diamond Vickers indenter was used with a load of 50 g and a loading time of 15 s. Microhardness testing was also performed at temperatures up to the glass transition temperature (i.e. 754 K [7]) using a Nikon QM Hot Hardness testing machine with a diamond Vickers indenter with a load of 50 g and a loading time of 15 s, in the manner described elsewhere [8]. Four indents were made at each test temperature prior to changing the temperature for the next set of indentations. The temperature variation monitored during the indentation was ±3 K and the specimens were held at temperature for 5 min prior to indentation. The indents were each measured four times after cooling to room temperature.

Compression tests were performed on an MTS servohydraulic system under displacement control with an initial strain rate of 10^{-3} s^{-1}. Tests were performed on specimens with $L/D = 2$ using a special highly aligned

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fixture to ensure uniform strain throughout the specimen during the test [9]. Load versus displacement traces were obtained from these tests, while the global fracture angle was recorded on fractured specimens using an optical comparator.

Notch toughness tests were performed on an MTS servohydraulic testing machine under a constant displacement rate of 0.1 mm/min. The tests were performed on cylindrical rods with a notch depth of one half of the diameter (i.e. 1.5 mm) and a span of 20.0 mm. The notch was placed using a slow speed diamond impregnated wire saw in the manner used elsewhere [10], with a root radius of 110 μm. Load versus load point displacement was monitored and the results were analyzed using available K-calibrations [11]. Fractured specimens were analyzed in a Philips XL 30 Environmental SEM operated at 15 keV.

3. Results

Microhardness values obtained at room temperature and elevated temperatures are provided in Fig. 1. The room temperature hardness of 7.0 GPa reduces slightly on going from room temperature to 577 K and, then, drops rapidly at higher temperatures. Specifically, the hardness is 5.1 GPa at 625 K and reduces to only 850 MPa at 729 K. It is noted that significant softening in the alloy occurs at temperatures between 0.7 and 0.8 $T_g (T_g = 754$ K). This result is consistent with recent reports on a Zr-based BMG tested in a similar manner [8]. Homogeneous deformation of metallic glasses is expected to occur usually at $T > 0.6T_g$ [12].

To further investigate the softening process, the logarithmic of hardness as a function of the inverse of temperature is plotted in Fig. 2. The activation energies for high-temperature flow of the Cu-based BMG can be deduced from the slopes of the curves in the high-temperature region in Fig. 2 in the following way. In general, plastic flow of a metal at high temperatures can be described by an equation [13] of the form

$$\dot{\varepsilon} = A\sigma^n \exp(-Q/RT) \quad (1)$$

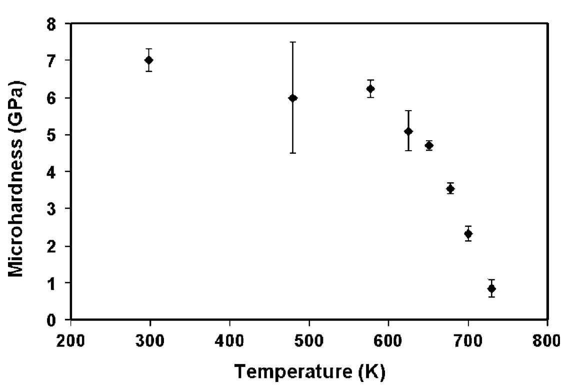

Fig. 1. Microhardness versus temperature for $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ BMG.

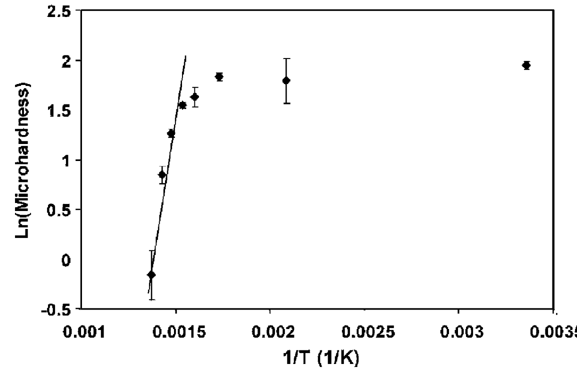

Fig. 2. Plot of the natural logarithm of the microhardness versus the inverse temperature. Linear regression of the high temperature region was used to determine the activation energy.

$\dot{\varepsilon}$ is the strain rate, σ is the flow stress, Q is the activation energy for deformation, T is the absolute temperature, and A and n (the stress exponent) are material constants. Furthermore, it is reasonable to assume that the hardness, H, is directly proportional to the flow stress, σ, in Eq. (1). Under the condition of a fixed strain rate, an approximation, Eq. (1) can then be converted to

$$H^n \propto \exp(Q/RT) \quad (2)$$

from which a value for activation energy can be derived as

$$Q = n \cdot R \cdot \{\mathrm{d}\ln(H)/\mathrm{d}\ln(1/T)\} = nS \quad (3)$$

where S is the slope of the curve in the high-temperature region (left) in Fig. 2. From the measurement of the slope the activation energy is computed to be 98 kJ/mol. Since homogeneous plastic flow in metallic glasses is usually Newtonian, i.e. $n = 1$ [14,15], the activation energy is thus also 98 kJ/mol. It is of interest to note that the activation energy for the crystallization of the present alloy has been reported to be 96 kJ/mol [7], which is remarkably close to the present Q value. Although mechanical softening and crystallization processes both involve atomic diffusion and rearrangement, the driving forces and specific diffusing species for the two processes are notably different.

The load versus displacement traces were linear to failure in compression at $L/D = 2$. The yield/fracture stresses were 1951 MPa, while the change in area was 0%, consistent with the lack of measurable compressive ductility. The fracture angle in compression was 40.5 degrees, consistent with much previous work on other bulk metallic glasses [16–18].

The notched toughness (K_q) was calculated using the maximum load at fracture, resulting in a notch fracture toughness (K_q) of 67.6 MPa$\sqrt{\text{m}}$. Fracture surfaces exhibited characteristic vein patterns and a relatively rough fracture surface with significant crack branching and bifurcation, similar to other reported work on notched Zr-based BMG [10]. The fracture surface near the notch is shown in Fig. 3.

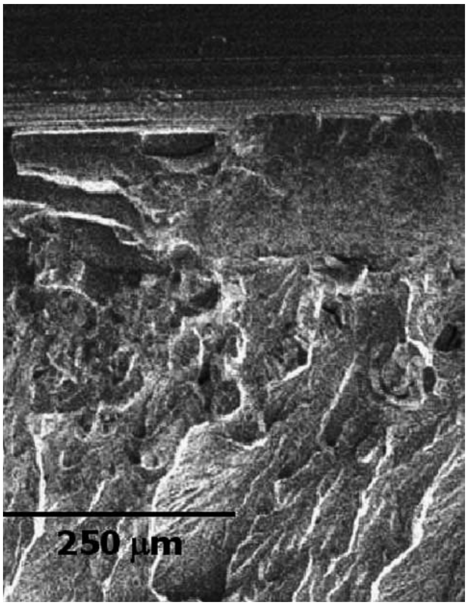

Fig. 3. Fracture surface near the notch for the notched toughness test.

4. Discussion

The trend of decreasing microhardness with increases in test temperature, particularly near T_g, is consistent with early compression results on Pd-based systems [19] and more recent results presented by Wesseling et al. [8] on a Zr-based system. Similar observations were reported for tensile tests on Pd-based systems conducted by Megusar et al. [20] and compression tests on Pd based systems conducted by Pampillo and Chen [21]. Le Bourhis and Rouxel [22] also conducted microhardness experiments at elevated temperature on a Zr-based BMG. Their results do not show such a significant drop in microhardness at, or above T_g. This apparently results from their experimental technique which heats the sample too close to T_x, the crystallization temperature of the material, before testing. This pre-exposure to high temperatures prior to microhardness testing likely changes the structure of the material and thus the properties. The present work involved much more rapid heating to $T < T_g$, thereby limiting the thermal exposure and any resulting changes in structure/properties.

The measured compressive strength, 1.95 GPa, is somewhat lower than expected from the microhardness values of 7.0 GPa, obtained at room temperature. Typical correlations relating hardness to yield strength are H/Y ≈3.1 [23], where H is the hardness and Y is the yield or fracture strength. The present results for compressive strength (i.e. 1.95 GPa) are about 15% lower than that predicted (i.e. 2.25 GPa) by this simple relationship. This somewhat lower value obtained for compressive strength may be affected by the presence of voids entrapped during processing of the glass rods. Isolated voids, as large as 500 μm, were observed on the fracture surface of the compression test specimens. The local stress concentration near such voids could produce early flow/fracture initiation, thereby reducing the strength from that predicted from the hardness measurements. Additional discussion on differences in hardness/strength correlations in metallic glasses are provided elsewhere [24]. Regardless, using the elastic modulus of 101.1 GPa produces a ratio of E/σ of 52, close to the theoretical strength of the material. This further emphasizes the importance that the presence of any defect can lead to premature flow/fracture in such materials.

The fracture angle of the compression specimens was 40.5°, not at the maximum shear angle of 45°. Similar observations of fracture at a non-45° shear angle in compression have been reported by others on Zr-based BMGs [16–18,25,26], and Pd-based BMGs [27,28]. This is the first report of such behavior in the Cu-based BMGs. While these previous works [16–18,27] have proposed a variety of different yield criteria (e.g., Coulomb-Mohr or Tresca) that invoke normal and/or pressure dependent flow, more work is needed on the present system over a wider range of stress states in order to address the appropriate flow/fracture law.

The high value for the notched (i.e. 110 μm notch root radius) toughness for the Cu BMG material (i.e. 67.6 MPa $\sqrt{m}$) is in the range of notch toughnesses reported for a Zr-based metallic glass (i.e. 95.3 ± 8.3 MPa $\sqrt{m}$) [10,29], and somewhat higher than toughnesses reported on fatigue precracked samples [10,29–33] of similar Zr-based metallic glasses. Both systems exhibited essentially zero compressive ductility with a strength level approaching theoretical levels, although toughness levels are well in excess of the surface energy. Part of the toughness increase appears to arise from the highly bifurcated nature of flow/fracture which propagates from the notch, producing highly non-planar fracture surfaces, as shown in detail elsewhere [10,31,33]. The source(s) of such high notch toughness in these ultra-high strength materials which fail via locally intense flow that produces essentially zero macroscopic tensile/compressive ductility is under investigation.

A plane strain plastic zone size can be estimated at 63.7 μm according to established procedures [34]:

$$r_p \approx \frac{1}{6\pi}\frac{K^2}{\sigma_0^2} \tag{4}$$

and is found to be on the same order of magnitude as that reported for a Zr-based BMG, i.e. 132 μm [8]. This calculated plastic zone size is small compared to the specimen dimensions (i.e. 3 mm diameter) and therefore the plane strain condition can be assumed to exist over the bulk of the specimen thickness.

5. Conclusions

Preliminary experiments have been conducted on a Cu-based BMG. Initial microhardness tests indicate that strength levels approaching theoretical values are possible in this material. Compression tests revealed strength levels close to that predicted by the hardness values, although somewhat reduced, possibly due to the presence of processing-induced voids in the specimen. Hot hardness testing at temperatures up to T_g revealed significant softening, consistent with recent work on other BMGs. Finally, notch toughness values in excess of 65 MPa $\sqrt{m}$ were obtained under nominally plane strain conditions. This level of notch toughness is remarkable given the high strength and limited compressive ductility exhibited by this material.

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