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Plastic deformability and precipitation of nanocrystallites during compression for a Cu–Zr–Ti–Sn bulk metallic glass

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Abstract

$(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ bulk metallic glass with a glass transition temperature of 683 K and a supercooled liquid region of 47 K was synthesized by copper mold casting. The bulk glassy alloy exhibits high strength of 1810 MPa and superior plasticity in uniaxial compression at ambient temperature. High resolution transmission electron microscopy for the bulk glassy sample subject to a plastic strain of 3% shows the formation of nanocrystallites in the glassy matrix. The plastic deformability of the $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ bulk metallic glass is attributed to the in situ precipitation of nanocrystallites during the compression.

Keywords: Amorphous materials; Copper-based alloy; Nanostructures; Mechanical properties

1. Introduction

Most bulk metallic glasses (BMGs) exhibit high strength and large elastic limit, but limited plasticity (0–2% plastic strain) prior to failure in an unconfined geometry at ambient temperature [1]. In this case, plastic deformation is highly localized into a single or few shear bands, and these bands are typically 20–30 nm thick. Shear bands can initiate cracks, which will cause the macroscopic fracture of the sample [2]. On the other hand, metallic glassy matrix composites can possess significantly enhanced ductility, in which a second crystalline phase can act both as initiation sites for shear bands and as barriers to shear band propagation and result in a dramatic increase in the number density of shear bands [3,4]. Recently, Schroers and Johnson [5] reported a monolithic $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ BMG showing a large plastic strain of 20%, and proposed that the plasticity is attributed to a high Poisson ratio and a low glass transition temperature close to ambient temperature.

This paper presents the pronounced plasticity of $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ BMG in a compression mode. Nanocrystallites were observed in the glassy matrix of the deformed sample subject to a plastic strain of 3%, and the in situ precipitation of nanocrystallites during the compression significantly improved the plasticity to failure.

2. Experimental procedures

Alloy ingot was prepared by arc melting the mixtures of pure Cu, Zr, Ti and Sn elements in a purified argon atmosphere. Cylindrical rods with diameters of 1–6 mm were prepared from the ingot by injection casting into a copper mold. Structure of the as-cast samples was examined by X-ray diffraction (XRD) with Cu Kα radiation and high resolution transmission electron microscopy (HRTEM). Thermal analysis was performed with a differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s. Cylindrical rods (Ø 2 mm × 4 mm) were used to measure compressive mechanical properties at a strain rate of $4 \times 10^{-4}\ s^{-1}$ on an Instron-type testing machine. The compression samples were sandwiched between two alumina platens, which were lubricated with lithium grease to minimize friction effects. Shear bands and fracture surface were investigated by scanning electron microscopy (SEM). Microstructure of the deformed samples was examined by HRTEM. For preparation of a TEM specimen, a disk of 0.5 mm thick was cut from the cylindrical rod, and then subject to mechanical thinning to 30 μm thick and finally ion-milled using a liquid-nitrogen specimen cooling stage.

3. Results and discussion

The XRD patterns of as-cast $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy rods with diameters of 2 and 6 mm are shown in Fig. 1. The XRD traces reveal only two broad diffuse halos, indicating that the samples of up to 6 mm in diameter are amorphous. A fully amorphous microstructure without any crystalline feature was confirmed for the as-cast 2 mm diameter rod according to the HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern with a diffused halo ring, as shown in Fig. 2. DSC curve of this glassy alloy (2 mm in diameter) is

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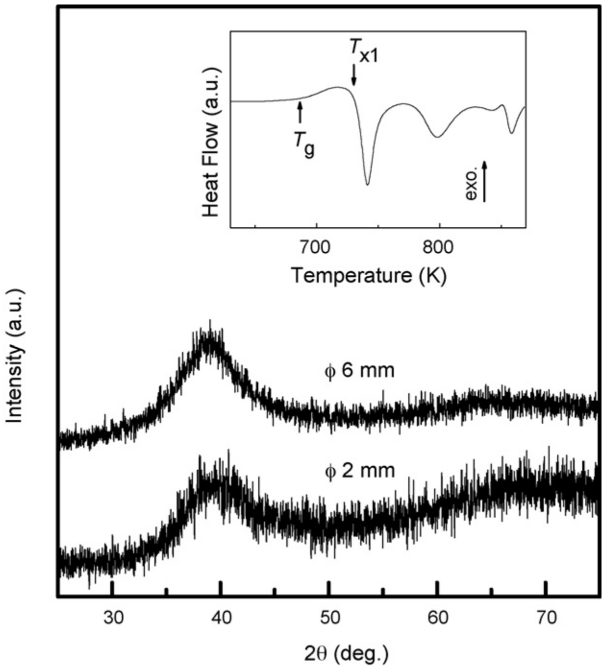

Fig. 1. XRD patterns of as-cast $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy rods with diameters of 2 and 6 mm. DSC curve measured at a heating rate of 0.67 K/s is also inset.

shown in inset in Fig. 1. A distinct glass transition and multiple exothermic events characteristic of crystallization can be seen. The glass transition temperature (T_g) and supercooled liquid region are about 683 and 47 K, respectively.

Fig. 3 shows the nominal stress–strain curve in uniaxial compression. It exhibits an elastic strain limit of about 2%, maximum strength of 1810 MPa and plastic strain to fracture of about 8% to failure. A large number of primary and secondary shear bands can be observed on the failed sample surface (Fig. 4a), and the fracture surface shows well-developed vein patterns (Fig. 4b).

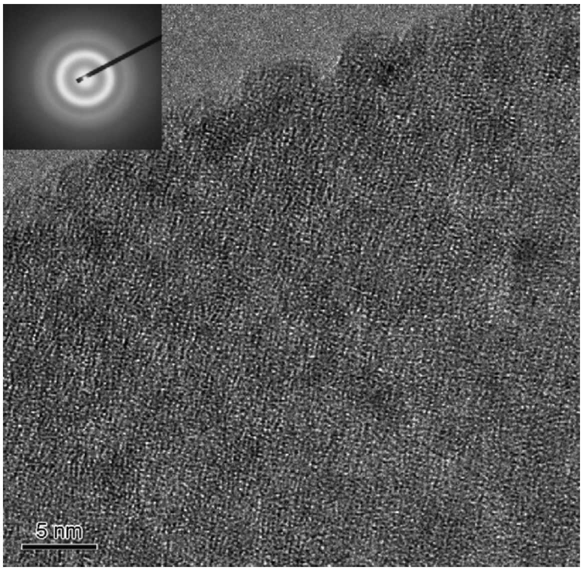

Fig. 2. HRTEM image and SAED pattern of as-cast $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy rod with a diameter of 2 mm.

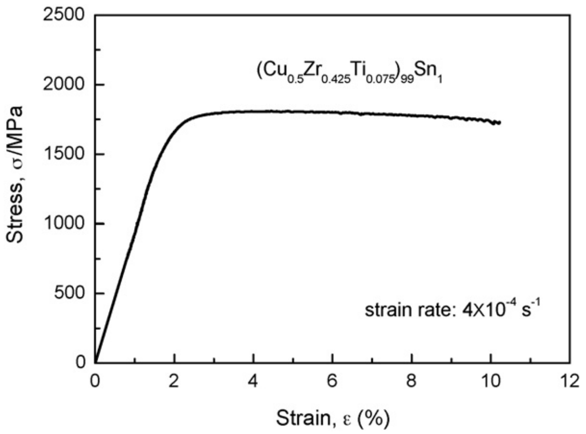

Fig. 3. Nominal stress–strain curve of bulk glassy $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy in a uniaxial compression mode.

To investigate the origin of the plastic deformability, a sample subject to the compression test was unloaded while the nominal plastic strain reaches about 3% and its microstructure was studied. It can be seen that the density of shear bands in this sample Fig. 4c is relatively lower than that of the failed sample. Fig. 5 shows HRTEM image for the sample subject to a plastic strain of about 3%. The HRTEM image shows that nanocrystallites with diameters of 2–5 nm are randomly distributed in the amorphous matrix. Jiang and Atzmon [6] reported that nanocrystallites formed only at shear bands in the compressive region but not in the undeformed region for the Al-based glassy ribbon bent 180°. It is implied that nanocrystallites possibly formed only within shear bands and the undeformed regions still remain glassy in this study.

Inhomogeneous deformation usually occurs when a metallic glass is deformed at ambient temperature in an unconfined geometry and is characterized by formation of the localized shear bands, followed by rapid propagation of these bands and catastrophic fracture. Despite limited macroscopic plasticity, local plastic strain within a single shear band can be quite significant. The Gibbs free energy of glassy state is higher than that of the corresponding crystalline state [7,8], and therefore glassy phases tend to transform into the more stable crystalline phases with the supply of thermal energy or the application of stress field [9,10]. On the other hand, there is higher free volume in the deformed sample, and as a result viscosity within shear bands is expected to decrease dramatically due to the highly localized deformation [11]. Consequently, atomic mobility in shear bands is substantially enhanced, and even the diffusion constant can approximate that of a metallic glass above glass transition temperature [12]. Therefore, it can enable nucleation and growth of the nanocrystallites in a severely deformed amorphous solid. It has been reported that precipitation of nanocrystallites are enabled in the deformed region of the samples subject to bending [6] or nanoindentation [12], or on the fracture surface of the sample subject to uniaxial compression [13]. Refs. [12,14,15] proposed that a large rise in local temperature, of up to several hundreds, may be likely during dynamic loading and/or fracture. On the other hand, it was estimated that the temperature

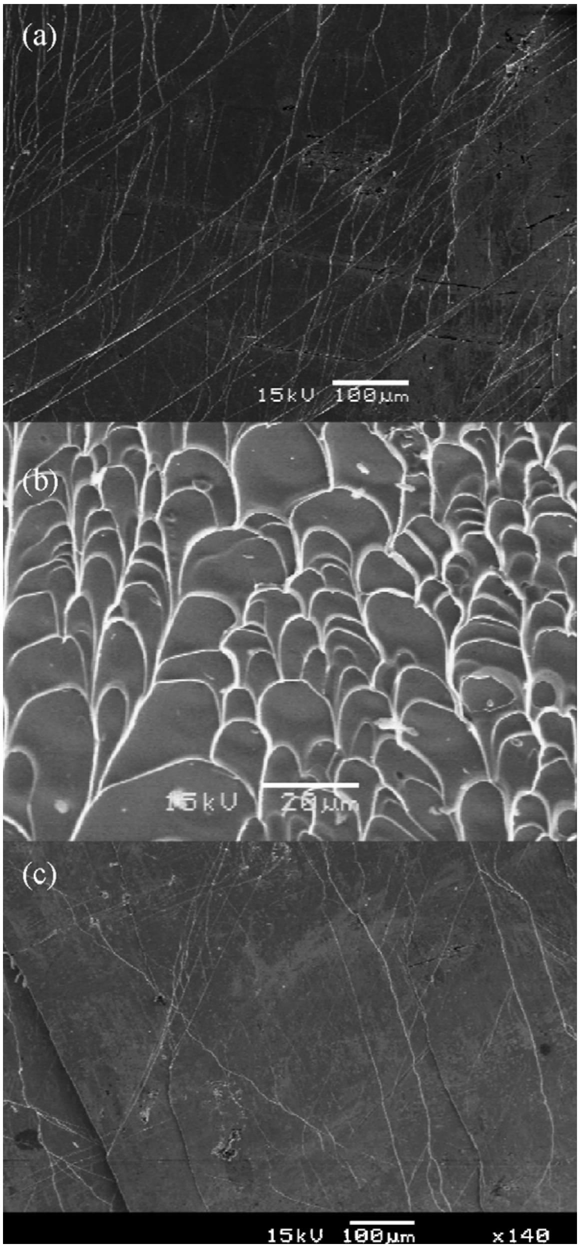

Fig. 4. SEM images of: (a) shear bands, (b) fracture surface of the failed sample and (c) shear bands of the bulk glassy $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy subject to a plastic strain of about 3%.

rise within shear bands is negligible, only several degrees or less, under quasi-static loading [12,14].

Therefore, nanocrystalization observed in this work may be not be due to the increase of temperature resulting from adiabatic heating. It is considered that the softening due to increase of free volume and the decrease of viscosity in shear band could be offset by the formation of nanocrystallites, and propagation of primary shear bands could be impeded by the in situ nanocrystalization. As a result, new shear bands would be initiated to accommodate the applied strain. As demonstrated by the evident increase of the number density of shear bands with increasing plastic strain (Fig. 4a and c). Macroscopic plasticity of the deformed sample sums the local strain from every shear band, and therefore the formation of a high density of shear bands led to the noticeable plasticity of this glassy alloy.

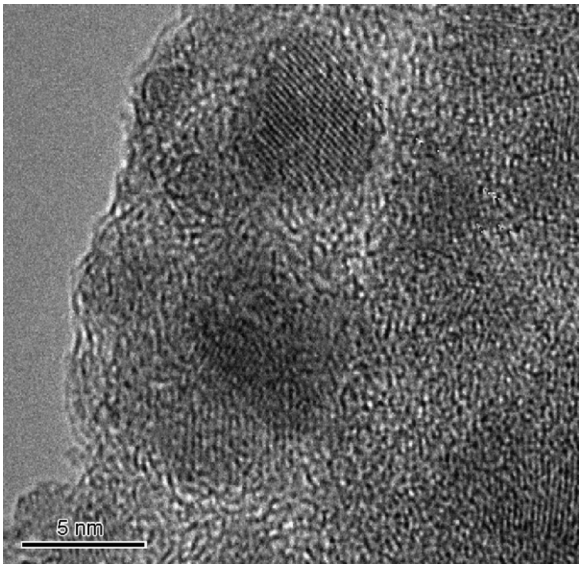

Fig. 5. HRTEM image of the bulk glassy $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ alloy subject to a plastic strain of about 3%.

4. Conclusions

In summary $(Cu_{0.5}Zr_{0.425}Ti_{0.075})_{99}Sn_1$ BMG exhibits a combination of high maximum strength of 1810 MPa and a plastic strain of about 8%. Nanocrystallites were observed in the sample subjected to a plastic strain of 3%. The superior plasticity of the BMG was attributed to in situ precipitation of the nanocrystallites during the deformation.

Acknowledgements

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