Journal of Alloys and Compounds 434–435 (2007) 6–9

Journal of ALLOYS AND COMPOUNDS

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Ductilization of BMGs by optimization of nanoparticle dispersion

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Abstract

In situ optimized heat treatment in high-energy monochromatic beam of synchrotron light was conduced to generate fine nanoparticle dispersions in Zr-based alloys. Effect of embedded nanocrystals on the mechanical properties of our BMG-composites was investigated by compressive testing at room temperature. We found that the newly created nanostructured composites show good strength at high ductility with no work hardening. Based on TEM observations, a new mechanism was proposed which compensates for shear softening. The nanocrystals initially smaller than the elementary shear band were expected to growth in active shear band during deformation.

Keywords: Metallic glasses; Synchrotron radiation; Nanocrystals; Shear bands; Semi-solid slurry

1. Introduction

Bulk metallic glasses (BMG) reveal interesting mechanical properties, such as a high strength up to 5 GPa [1], high elastic strain up to 2% and many others additional desirable properties [2,3]. However, BMGs loaded under constrained geometry fail catastrophically on one dominant shear band and show little global plasticity in an apparently brittle manner [4]. This behaviour so-colled 'strain softening' remains the biggest obstacle to wider exploitation of bulk metallic glasses in structural applications.

Attempts to improve ductility have concentrated on making composite materials consisting of mixing a metallic glass matrix with a dispersed crystalline phase. Methods for doing so include producing a dispersion of nanocrystals through partial devitrification of bulk metallic glasses [5–7], adding crystalline particles to the melt prior to casting [8], casting a glass forming alloy around particles or fibers of a second phase [9], or precipitating a dendritic intermetallic phase from the melt [10]. While such composites show improved plastic deformation, the mechanism by which these particles interact with shear bands and their propagation is still not clear and subject of further extensive work.

Furthermore, there have been recently several reports of significant macroscopic plastic deformation in Cu-based metallic glasses [11–13] containing nanocrystals as well as in Pt-based glass [14]. The binary CuZr glass was repeatedly found to undergo plastic deformation of more than 50% in uniaxial compression [15]. CuZr metallic glass is a marginal bulk metallic glass which appears "X-ray amorphous" (no detectable Bragg peaks) when cast to up to 1 mm thickness but microscopic examination shows presence of a fine dispersion of nanocrystals with dimensions of the order of 5 nm. TEM examination after heavy deformation found these nanoparticles to be larger than prior to deformation and often interconnected. The nanoparticle dispersion in the CuZr glass reported by Inoue et al. in Ref. [15] was formed during casting under somewhat unique conditions in the sense that the 1 mm thick specimen is cooled at or near the minimum critical cooling rate for vitrification, a process that is difficult to control.

The purpose of this paper is to present a new method by which we can control crystallization and arrest their process when crystallites are only few nanometer sizes. The resulting nanocrystalline composites materials lead to an increase of both ductility and strength. This behavior was interpreted to be due to the growth of fine nanocrystal in active shear bands during deformation. The shear zones then behave as a semi-solid slurry with the glassy component behaving liquid-like and the nanocrystals behaving like a growing solid phase.

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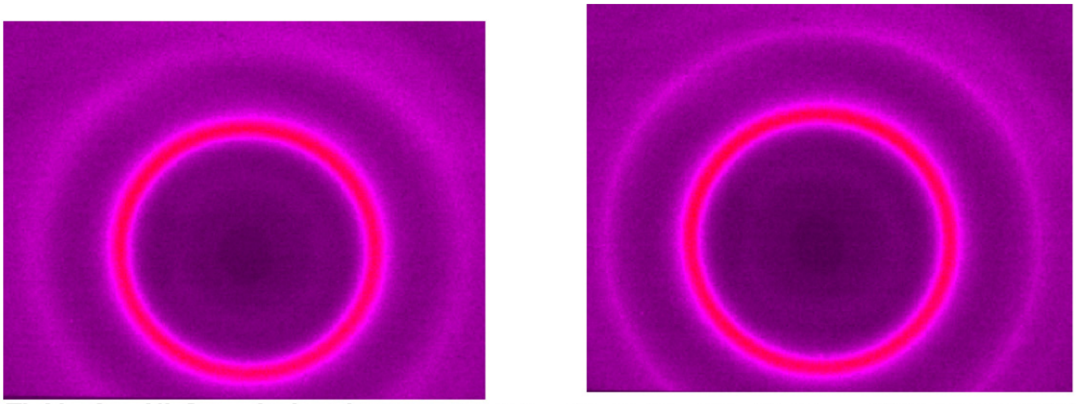
doi:10.1016/j.jallcom.2006.08.290



$Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$- before heat treatment

$Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$- After heat treatment

Fig. 1. Diffraction patterns of BMGs from synchrotron light in transmission detecting very fine rings due to real-time nanometer-scale crystallite formation during heating.

2. Experimental techniques

Bulk metallic glass of compositions $Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$ was prepared by arc melting the pure elements under Ti-gettered Ar atmosphere followed by casting into a water-cooled copper mould. The resulted ingots were bars with dimensions 2 mm × 4 mm × 75 mm. The amorphous structure of these samples was checked by standard X-ray diffraction (XRD) using a Siemens Kritalloflex D500 diffractometer and Cu Kα radiation.

The bulk samples were cut into 10 mm long pieces and placed on a computer-controlled Linkam hot stage under vacuum for heat treatment in a synchrotron beam in transmission through the sample thickness. The synchrotron source was the high-energy, high flux ID-11 beamline of the European Synchrotron Radiation Facilities (ESRF). The radiation of this beamline is monochromatized using a nitrogen-cooled double crystal silicon monochromator. The photon energy was 90 keV corresponding to an X-ray wave-length of about 0.0137 nm. The heat treatment consists of heating the sample at 100 K/min under argon gas until initial detection of very fine diffraction rings signalling the formation of nanocrystals in the glassy matrix. The specimen is then rapidly cooled (≈100 K/min). A diffraction spectrum is acquired every 3 s.

Compression test specimens with dimensions of 2 mm × 2 mm × 4 mm (aspect ratio 2:1) were cut from the BMGs before and after this heat treatment. The outer surfaces of the specimens, especially the ends in contact with the cross-head, were mechanically polished to ensure flat and parallel surfaces. Compression tests were conducted at constant strain rate of $8 \times 10^{-4}\ s^{-1}$ using a Schenck hydraulic testing machine at room temperature. After fracture, all the specimens were investigated by a JEOL 6400 scanning electron microscope (SEM) to reveal the fracture features and morphology of outer lateral surfaces. Transmission electron microscopy (TEM) investigation was performed on a JEOL 3010 microscope operating at 300 kV, on cross-section samples thinned using dimpling and ion-milling.

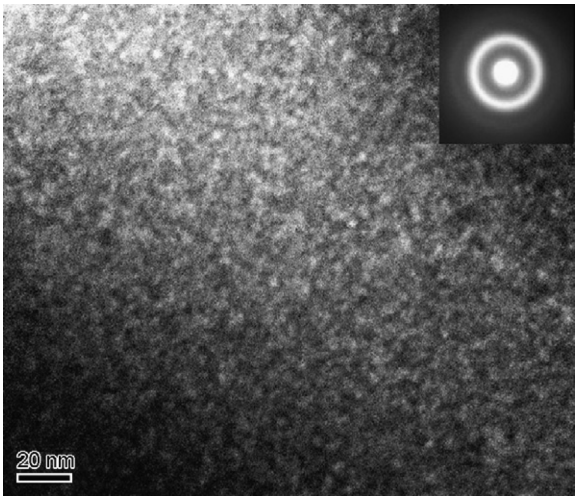


Fig. 2. Dark field TEM micrographs of $Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$ BMG samples after heat treatment of Fig. 1 showing dense network of very fine nanocrystals.

3. Experimental results

Fig. 1 shows diffraction patterns obtained in transmission before and after heat treatment in the synchrotron beam for $Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$ BMGs. The samples were cooled down upon the first detection of diffraction rings due to nanocrystal formation. The heat treated samples were cut, thinned and examined by transmission electron microscopy. Fig. 2 shows typical TEM images of the heat treated samples to compare to the synchrotron diffraction in transmission patterns of Fig. 1. Clearly nanocrystals of an average size of about 2–5 nm have formed after heat treatment that resulted in the observed plasticity in compression.

Fig. 3 shows stress versus strain curves for the BMGs obtained in compression before and after the heat treatment resulting in the weak changes in the diffraction patterns. While the as-cast BMGs all break at or below the limit of the elastic deformation range near 2%, the heat treated samples all show extensive plastic strain to fracture occurring at near 10% strain. The external surfaces of the deformed samples show a maze of slip bands and steps at near 45° angle to the compression axis with nearly perpendicular slip systems crossing and

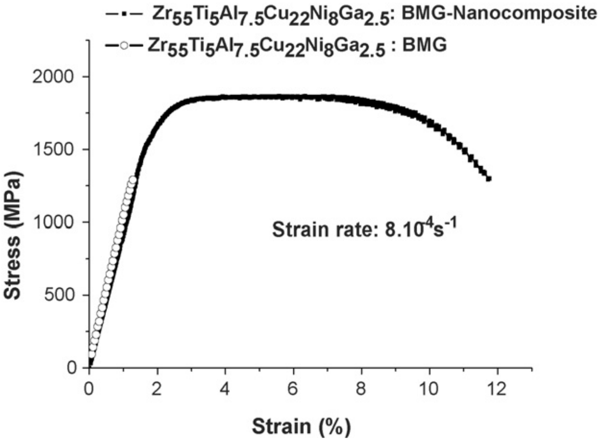


Fig. 3. Stress vs. strain curves in compression for $Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$ BMGs after heat treatment. Significant plastic deformation is observed resulting in the diffraction pattern changes of Fig. 1.

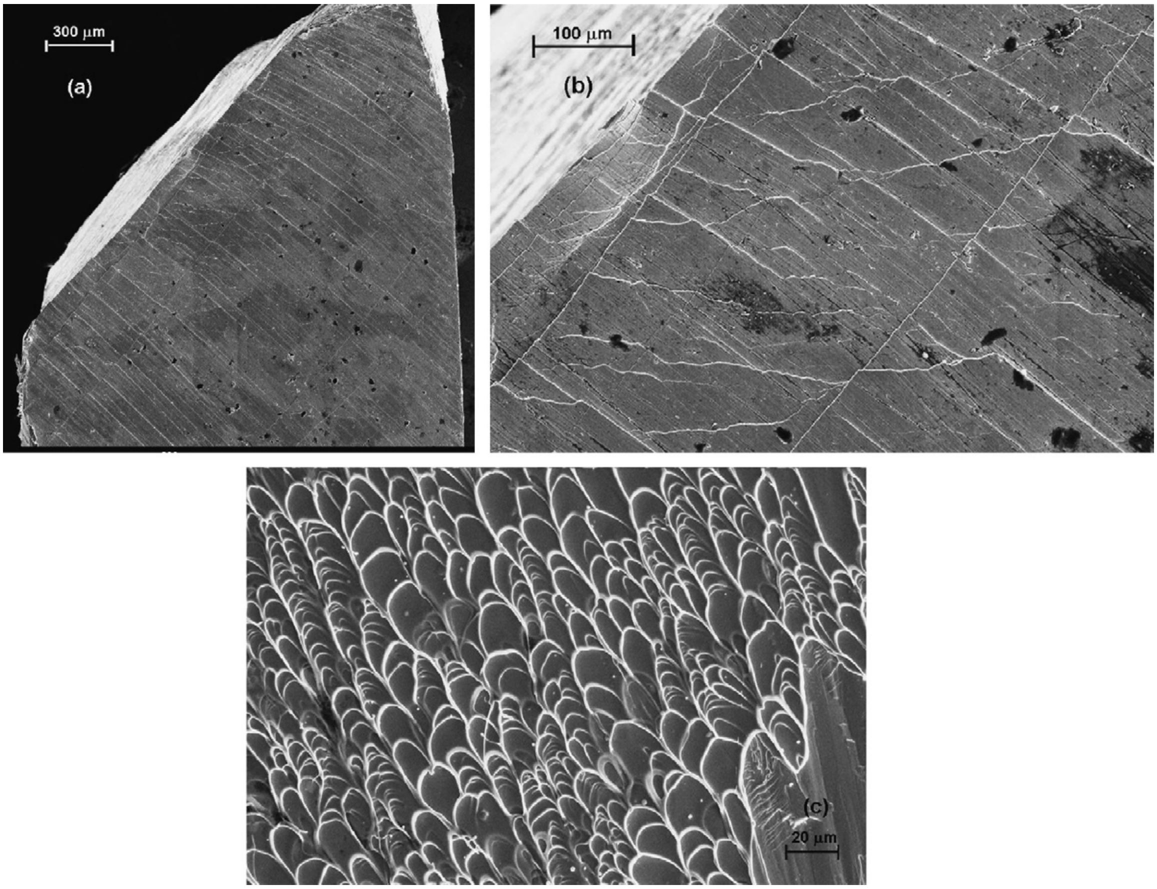


Fig. 4. SEM micrographs of the heat treated then deformed BMG sample of Fig. 3 ($Zr_{55}Ti_5Al_{7.5}Cu_{22}Ni_8Ga_{2.5}$-BMG nanocomposite) showing dense network of shear steps of crossing (multiple) shear systems at near 45° to the applied stress axis. (b) Micrograph of the failure surface shows typical void morphologies and dispersed molten droplets.

jogging each other's surface steps as shown in typical scanning electron microscope images of Fig. 4a and b. Voids and evidence of local melting are visible in micrograph of the failure surface as seen in Fig. 4c.

4. Discussion

Local plastic deformation in a monolithic metallic glass will depend on the natural ductility of the metallic glass [14,16] which requires Poisson ratios $\nu > 0.36$ (this for example, is not the case of the Fe-based metallic glass matrix of magnetic FINEMET tapes [17]) but will in any case be heterogeneous in nature with shear softening leading to failure at negligible macroscopic plastic strain. A macroscopic dispersion of crystals (μm size or larger) in the form of dendrites or added second phase particles can generate some plasticity in compression [10,18–20].

While presence of nanocrystals has previously been associated with the appearance of ductility in some metallic glasses, the underlying mechanism has not been determined. Having demonstrated the contribution of the presence of nanocrystal dispersions to ductility in several BMGs and in order to examine the mechanism by which the nanocrystal dispersions contribute to the ductile behaviour shown in the stress–strain curves as compared to the monolithic glassy states, we refer to recently observation of Yavari et al. [21] during in situ tensile deformation in the TEM undergo in CuZr-nanoparticles prepared by the same method. They show that the nanoparticles with initial size of 2–5 nm grow in the vicinity of shear bands during deformation and reach more than 15–20 nm. This observation was reported also by Inoue et al [15] for the as-cast CuZr BMG containing a dispersion of very fine nanocristals introduced by partial devitrification during casting.

Moreover, it is well established that shear in metallic glasses generates free volume which reduces viscosity and leads to liquid-like behaviour in the shear bands with significant rise in temperature [22–26]. Under these conditions, any nanocrystals present in the shear zone before deformation can grow rapidly as the zone becomes liquid-like. Active shear band regions are then constituted of two phases: the glassy phase with reduced viscosity and increased temperature behaves liquid-like and the nanocrystals that are a growing solid phase component: the deformation behaviour is like that of a semi-solid slurry. It is well known [27] that at a given high shear rate, the mechanical properties of semi-solid slurries of a variety of materials including metals depend exponentially on the varying fraction of the solid component as for example reproduced in Fig. 5 [28] for PbSn semi-solid slurries. It is generally accepted that the viscosity of such semi-solid slurries diverges with increasing solid

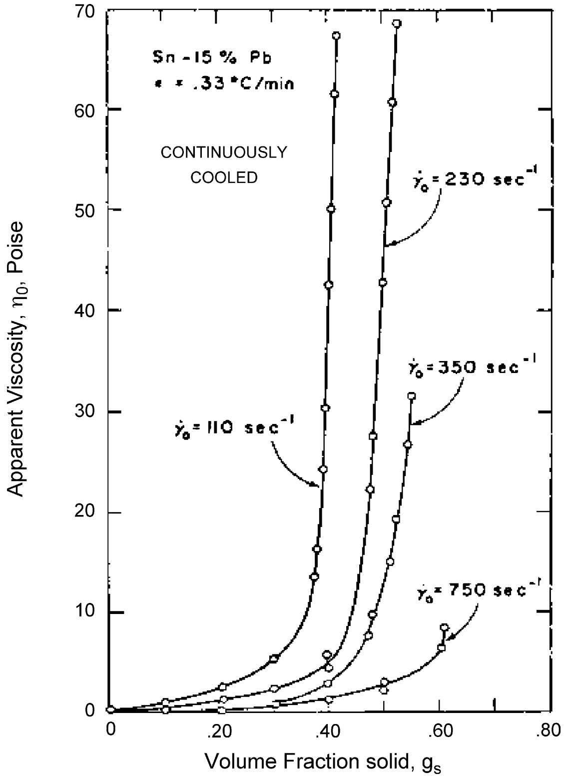


Fig. 5. Typical viscosity vs. solid-component at various deformation rates for a semi-solid slurry [28] showing divergence of viscosity with increasing solid component.

fraction according to [27]:

$$\frac{\eta}{\eta_0} = \left(\frac{1-\Phi_s}{\Phi_c}\right)^{-2.5\Phi_c} \qquad (1)$$

where η_0 is the viscosity of the liquid phase, Φ_s is the solid fraction of the suspension and Φ_c its maximum value (at about 60% solid component when the remaining liquid component is fully trapped).

Thus, as nanoparticles grow during shear, the solid fraction increases and the viscosity in the bands is expected to increase sharply. Therefore, contrary to the case of deformation of a monolithic metallic glass, in the case of these metallic glass-based nanocomposites, nanocrystal growth leads to hardening of the shearing zone forcing the deformation to delocalize into neighbouring undeformed regions (with lower solid-like fractions). Thus, the deformation became more homogenous and more shear bands appears in the total volume of samples as seen in Fig. 4c and d.

5. Conclusion

Generation of a very fine dispersion of nanocrystals in a bulk metallic glass leads to significant plastic deformation at room temperature. The nanocrystals are found to grow during shear. The behaviour of the material in shear bands active in metallic glasses containing nanocrystal dispersions is compared to that of semi-solid slurries where the metallic glass behaves liquid-like under shear and the nanocrystalline phase acts as a solid component whose volume fraction grows during shear. The increase in the solid component of the slurry under shear then leads to sharp increase in viscosity and shear delocalization to neighbouring undeformed regions with smaller crystalline volume fraction. Shear delocalization mechanisms of the kind observed here are expected to enhance ductility without loss of hardness in various metallic glass-based nanocomposites.

Acknowledgements

This work was funded by the EU under MCRTN contract “Ductile BMG Composites” coordinated by ARY. K.H. is grateful for a European Union Ph.D fellowship.

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