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ScienceDirect
Acta Materialia 59 (2011) 1037–1047
Acta MATERIALIA
www.elsevier.com/locate/actamat

A plastic Zr–Cu–Ag–Al bulk metallic glass

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Received 24 July 2010; received in revised form 13 October 2010; accepted 15 October 2010
Available online 9 November 2010

Abstract

An intrinsically plastic $Zr_{53.8}Cu_{31.6}Ag_{7.0}Al_{7.6}$ bulk metallic glass with large bending and compressive plastic strains was fabricated. Through transmission electron microscopy, three-dimensional atom probe and anomalous small-angle X-ray scattering techniques, the possibility of plasticity induced by microstructural and chemical inhomogeneity was ruled out in the as-cast alloy. The plasticity can change dramatically in a narrow composition range, even though all the other properties vary slightly or even do not change. In comparison with $Zr_{46}Cu_{37.6}Ag_{8.4}Al_8$, the increase in Zr content in $Zr_{53.8}Cu_{31.6}Ag_{7.0}Al_{7.6}$ results in an increased portion of the Zr–Zr atomic pair in the nearest shell of a pair distribution function. A steep peak profile on the right side of the pair distribution function in $Zr_{53.8}Cu_{31.6}Ag_{7.0}Al_{7.6}$ suggests that more atoms are involved upon yielding, and the opportunity of forming more shear bands increases. This finding may provide useful guidelines for the development of plastic metallic glasses from a structural aspect.

Keywords: Metallic glasses; Mechanical property; Free volume; Pair distribution function; Shear band

1. Introduction

Bulk metallic glasses (BMG) combine superior mechanical properties such as high strength and large elastic strain with excellent glass-forming ability (GFA), making them attractive for certain structural applications [1]. Great success in improving critical diameters of BMG above 20 mm has been achieved in Zr [2,3], Pd [4], Y [5], Mg [6] and La-based alloys [7]. However, their main drawback, catastrophic failure through unhindered shear banding, has not been conquered, significantly limiting their structural reliability. Great efforts have been made recently to enhance their plasticity. For instance, BMG/crystal composites were found to possess some tensile ductility, since the interaction of glass matrix and second-phase crystalline particles effectively inhibits the propagation of shear bands [8,9]. Pre-straining of BMG by cold-rolling, compression and surface shot-peening was also found to lead to improved plastic strain, owing to the introduction of shear bands and compressive residual stresses [10–12]. Interestingly, a number of monolithic BMG showing remarkable compressive plasticity emerged owing to: (a) high Poisson's ratio [13]; (b) chemical and microstructural inhomogeneity, including phase separation [14–18], soft and hard regions with the same composition [19]; (c) in situ nanocrystallization during deformation [20,21]; (d) more free volume by cooling faster or minor alloying [22,23]. These hypotheses have not been fully verified, but still provide instructive clues for enhancing the plasticity of monolithic BMG.

Recently, a series of Zr–(Cu, Ag)–Al BMG with diameters at least 20 mm were developed, and even 25-g ingots became full glass upon slow cooling in an arc-melting machine in a wide Zr–(Cu, Ag)–Al composition range [3]. These Zr–(Cu, Ag)–Al BMG still suffer from low plasticity.

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doi:10.1016/j.actamat.2010.10.034

Therefore, further development of Zr–(Cu, Ag)–Al alloys, simultaneously having good plasticity and relatively high GFA, is desirable. In the present work, systematic composition tuning in the Zr–(Cu, Ag)–Al alloy system was carried out. After testing more than 100 alloys with fine composition variations, one composition was successfully singled out which can form 1-mm-thick and 10-mm-wide BMG plates exhibiting distinct plasticity under both bending and compression. The thermal and mechanical properties and atomic structure for the newly developed Zr–Cu–Ag–Al BMG are presented. The intrinsic plastic deformability of the new BMG is discussed from the aspects of micro and atomic structure.

2. Experimental

The compositions of the alloys studied were chosen in the following way. First, a pseudo-ternary composition map was plotted by fixing the Cu–Ag atomic ratio at 4.5:1. Secondly, $Zr_{46}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_8$ (labeled Z0) was selected as the starting point of multiple lines owing to its excellent GFA [3], providing a wide composition space to tune for BMG with optimized structure and plasticity, and multiple lines according to certain chemical formula were drawn, as shown in Fig. 1. The formula can be expressed as $[Zr_{46}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_8]_{(100-x)}(M_{100-y}N_y)_x$ (M, N = Zr, Al, $Cu_{4.5/5.5}Ag_{1/5.5}$), M, N and y determine the position of end point of the line in the coordinate axis, and x indicates different points along the line. A family of master ingots was prepared by arc-melting 99.9% pure elemental Zr, Cu, Ag and Al several times under a Ti-gettered argon atmosphere. Plates with thickness 1 mm and width 10 mm and rods with diameter 2 mm were fabricated by suction-casting into a water-cooled copper mold. Bending samples with dimensions $14 \times 1.25 \times 0.95\ mm^3$ were cut from the as-cast plates, and polished by 1200-grit SiC paper. Cylindrical rods 2 mm in diameter and 4 mm long were prepared for compression tests, which were performed on a universal testing machine (CMT5205 SANS, China) at a strain rate of $4 \times 10^{-4}\ s^{-1}$ after calibration. Both ends of the compression samples were polished to be parallel, and at least five samples were measured for each composition. Transverse cross sections of the rod and surface of the plate were examined on a Rigaku X-ray diffractometer with Cu Kα radiation. Structural analyses of newly developed Zr–Cu–Ag–Al BMG were also conducted using synchrotron radiation X-ray diffraction (SR-XRD) at BW5 station of HASYLAB/DESY, Hamburg. The beam size was $1 \times 1\ mm^2$, and the wavelength used was 0.1132 Å. High-resolution XRD patterns were recorded on an MAR 345 image plate with pixel size $150 \times 150\ \mu m^2$. Scattering intensity $I(q)$ was extracted using the FIT2D software package [24]. Then, the structural factor $S(q)$, reduced pair distribution function (PDF) $G(r)$, and PDF $g(r)$ were obtained by PDFgetX2 [25] according to the following equations:

$$G(r) = 4\pi r[(\rho(r) - \rho_0)] = \frac{2}{\pi}\int_0^\infty q \cdot I(q) \cdot \sin(qr)dq \quad (1)$$

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{G(r)}{4\pi r \rho_0} \quad (2)$$

$$S(q) = 1 + \frac{4\pi\rho_0}{q}\int_0^\infty r[g(r) - 1]\sin(qr)dr \quad (3)$$

where $\rho(r)$ is the radial density function, ρ_0 the average atomic number density, q the scattering factor, and $q = 4\pi\sin(\theta)/\lambda$. Anomalous small-angle X-ray scattering (ASAXS) was measured with the B1 beamline at the DORIS storage ring at HASYLAB/DESY, Hamburg. The measurements were performed with three X-ray energies in the vicinity of the K-absorption edges of Zr, Cu and Ag, respectively.

Scanning electron microscopy (SEM) images were obtained on a Carl Zeiss CrossBeam 1540 EsB, and the element mapping was carried out with a beam voltage of 5 kV. Transmission electron microscopy (TEM) samples were prepared by a focused ion beam (FIB) machine (Hitachi FIB-2000) equipped with a micro-sampling system which allows for the preparation of site-specific micrometer-sized samples for TEM observation. Note that, in order to avoid damage from Ga ion, the beam current was

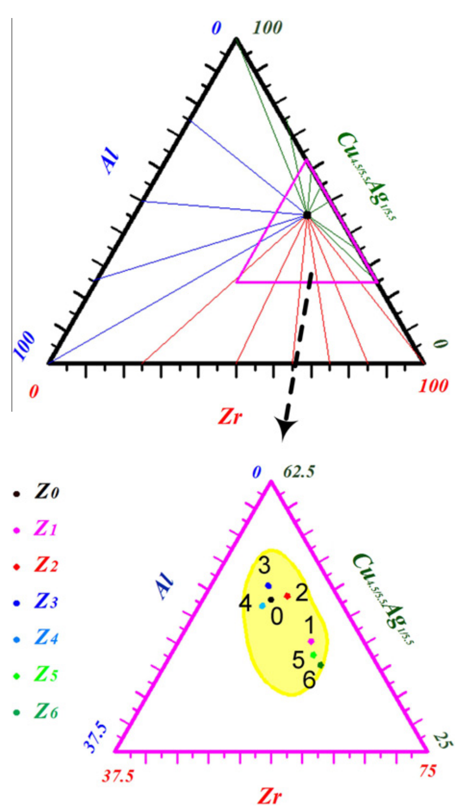

Fig. 1. Scanned pseudo-ternary composition map (yellow elliptic region) with a fixed Cu–Ag atomic ratio of 4.5. Z0–Z6 represent $Zr_{46}Cu_{37.6}Ag_{8.4}Al_8$, $Zr_{53.8}Cu_{31.6}Ag_{7.0}Al_{7.6}$, $Zr_{46.9}Cu_{38.4}Ag_{8.5}Al_{6.2}$, $Zr_{43.2}Cu_{39.1}Ag_{8.7}Al_9$, $Zr_{44.6}Cu_{36.5}Ag_{8.1}Al_{10.8}$, $Zr_{55.7}Cu_{30.9}Ag_{6.9}Al_{6.5}$ and $Zr_{56.8}Cu_{30.1}Ag_{6.7}Al_{6.4}$, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)