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Formation of Zr–Co–Al bulk metallic glasses with high strength and large plasticity

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ABSTRACT

A series of $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) bulk metallic glasses (BMGs) are obtained using water-cooled copper mold casting technique. With increasing Al/Co ratio, the BMGs exhibit a better thermal stability of the supercooled liquid, higher strength and larger plasticity. The origin of the high specific fracture strength lies in the increased strength and reduced mass density (more Al). Among them, $Zr_{56}Co_{26}Al_{18}$ BMG has a high fracture strength (~2477 MPa), small density (~6.31 g/cm^3) and very high specific fracture strength (~3.92×10^5 Nm kg^{-1}) exceeding the values of commercial stainless steel, light alloys as well as some popular BMGs. It seems to be a promising structural material owning to its excellent GFA, large plasticity and high specific strength.

1. Introduction

Bulk metallic glasses (BMGs) have attracted considerable attention in the past decade particularly motivated by their potential application as new structural materials [1–4]. However, many BMGs face the challenging problem that they deform by the formation of highly localized shear bands, making them susceptible to catastrophic failure without much macroscopic plasticity [5–8].

Our previous results showed that ductile $Zr_{56}Co_{28}Al_{16}$ BMGs have good glass forming ability (GFA) and excellent mechanical properties, e.g. a high fracture strength around 2.1 GPa and a pronounced compressive plasticity of about 10% [9]. Furthermore, minor addition of Fe or Ag can significantly improve the GFA of Zr–Co–Al system [10,11]. Moreover, it was also shown that the increase of the Ni-to-Fe concentration ratio effectively improves the compressive plasticity in Fe–Ni–Nb–B bulk glassy alloys [12]. Song and Wu et al. reported that the Al content affects the formation and the mechanical properties in Zr–Cu–Al BMGs [13,14], and it has been demonstrated that the mechanical properties of BMGs are very sensitive to their internal states [15–17]. It is therefore tempting to tune the internal states via composition optimization, e.g. by controlling the Al-to-Co concentration ratio, in order to achieve larger plasticity and better GFA in Zr–Co–Al BMGs.

In this work, a series of $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) rods were cast and the structural, thermal and mechanical properties were investigated systematically.

2. Experimental procedures

In this study, The alloy ingots with a nominal composition (at.%, shown in Fig. 1) of $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) were prepared by alloying pure elements of Zr, Co and Al (purity ≥ 99.99%) in a Ti-gettered high purity argon atmosphere (99.9999%) using the arc-melting technique. All the ingots were remelted five or six times to achieve chemical homogeneity. The ingots were cut into small pieces with a mass of around 5–6 g, and then they were melted and casted into cylindrical rods with a diameter of 2 mm and a length of about 50 mm using copper mold suction casting technique.

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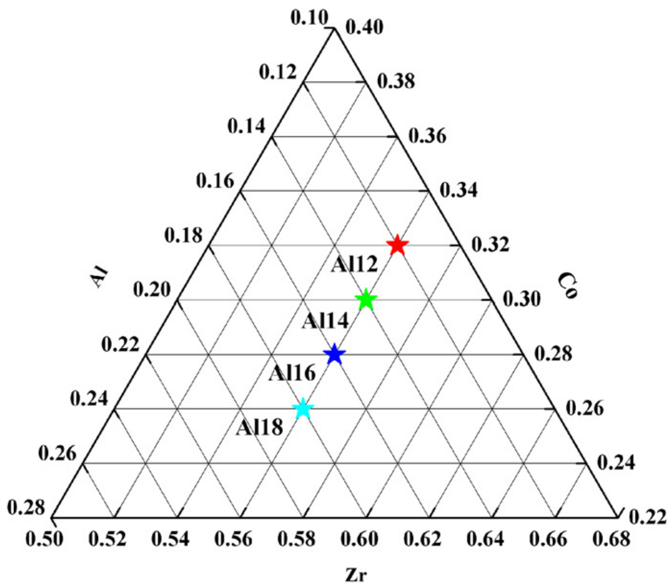

Fig. 1. Schematic phase diagram displaying the investigated $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, labeled as Al_{12}, Al_{14}, Al_{16} and Al_{18}, respectively) glassy alloys.

The amorphous nature of all samples was checked by X-ray diffraction (XRD, PANalytical X'Pert PRO Diffractometer, Co radiation, reflection geometry) and differential scanning calorimetry (DSC: Perkin Elmer DSC7) under argon atmosphere at a heating rate of 20 K/min. The DSC instrument was carefully calibrated using high purity In and Zn as reference materials before the measurement was conducted.

Utilizing a Metter Toledo UMT2 electrical balance with a sensitivity of 0.1 μg, the densities of the samples were measured with the help of an in-house designed apparatus using the Archimedean principle. The effective resolution was 0.0005 g/cm^3. The elastic properties were determined with an Olympus Panametrics-NDT 5900PR ultrasonic testing device.

Compression tests were performed with an Instron 5869 testing machine equipped with a laser extensometer (Fiedler) at a constant strain rate of 2.5×10^{-4} s^{-1} at room temperature. For this, carefully polished samples with a height-to-diameter ratio of 2:1 and good parallelism between the top and bottom ends were prepared. Compression tests were performed at least five to six times using the samples cut from similar positions of different as-cast rods, and the results turned out to be rather reproducible. The samples were ultrasonically cleaned in ethanol after compression tests. The morphologies of shear bands and deformation surfaces were investigated using high-resolution scanning electron microscopy (SEM, Carl Zeiss Gemini 1530).

3. Results and discussion

Fig. 2 shows X-ray diffraction patterns of the as-cast $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) samples in a rod form of 2 mm in diameter. The patterns of all the samples, taken from the cross-sectional surfaces of the as-cast rods, exhibit typical broad diffraction maxima without any detectable crystalline Bragg peaks, indicating that all samples are amorphous and there are no obvious differences within the resolution limits of XRD.

However, the DSC scans at a heating rate of 20 K/min of the monolithic glasses display remarkable changes as shown in Fig. 3. During the heating process, the samples exhibit a distinct glass transition followed by a supercooled liquid region prior to crystallization followed by two exothermic peaks due to the specific

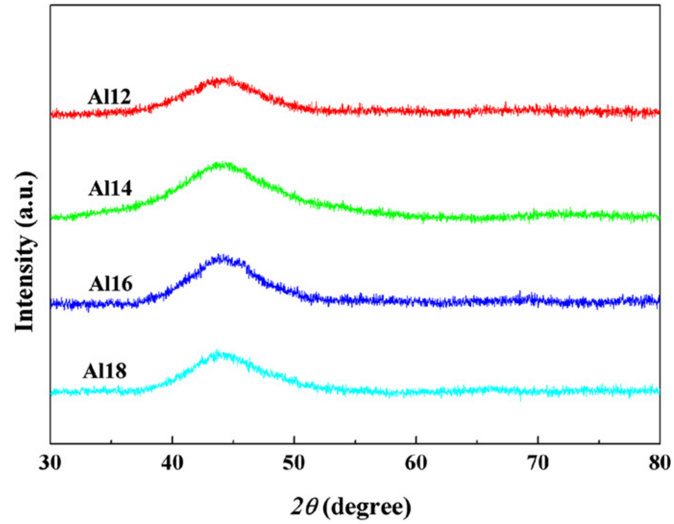

Fig. 2. XRD patterns of as-cast $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) alloys showing typical broad diffraction maxima without any detectable crystalline peaks, indicating fully amorphous nature.

crystallization events. The thermal properties for the $Zr_{56}Co_{44-x}Al_x$ BMGs are summarized in Table 1 and Fig. 4. With the increasing Al content, the glass transition temperature (T_g), the onset temperature of crystallization (T_x) and the first crystallization peaks all have a tendency toward higher temperatures, whereas the peaks corresponding to the second crystallization step decrease significantly. It is noticed that the width of the supercooled liquid region ΔT_x ($=T_x - T_g$) increases notably from 38 K (x = 12) to 59 K (x = 18), indicating a better thermal stability of the supercooled liquid [18], which is comparable to those for the Zr–Ni–Al and Zr–Cu–Al alloys developed previously [19,20].

Fig. 5 shows typical room temperature compressive stress–strain curves of the $Zr_{56}Co_{44-x}Al_x$ alloys with a diameter of 2 mm at a strain rate of 2.5×10^{-4} s^{-1}. All curves of the glassy rods

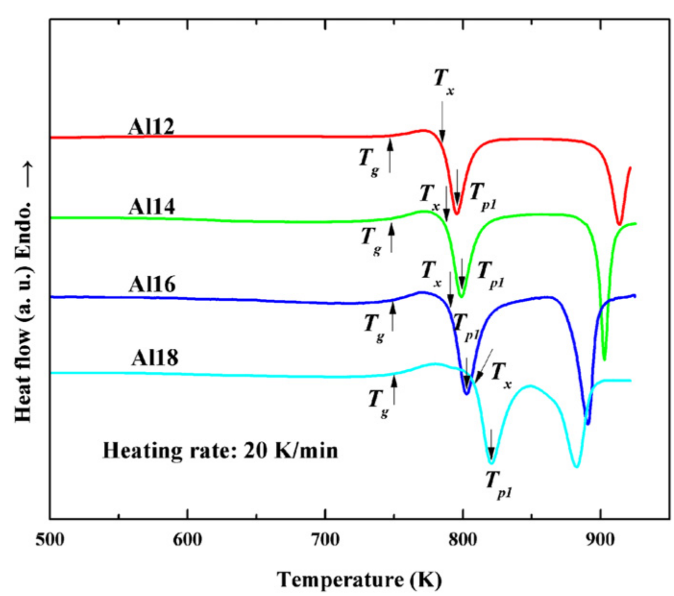

Fig. 3. DSC curves of $Zr_{56}Co_{44-x}Al_x$ (x = 12, 14, 16 and 18, respectively) glassy alloys at a heating rate of 20 K/min. The glass transition temperature (T_g), the onset temperature of crystallization (T_x), and the temperature of the first crystallization peak (T_{p1}) are marked with arrows.