Journal of Non-Crystalline Solids 459 (2017) 130–141

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Serrated flow of CuZr-based bulk metallic glasses probed by nanoindentation: Role of the activation barrier, size and distribution of shear transformation zones

R. Limbach [a], K. Kosiba [b], S. Pauly [b], U. Kühn [b], L. Wondraczek [a,*]

[a] Otto Schott Institute of Materials Research, University of Jena, Fraunhoferstraße 6, 07743 Jena, Germany
[b] Institute for Complex Materials, IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form 3 January 2017
Accepted 4 January 2017
Available online 18 January 2017

Keywords:
Metallic glass
Nanoindentation
Strain-rate sensitivity
Shear transformation zone

ABSTRACT

We report on the effect of Al and Co alloying in vitreous $Cu_{50}Zr_{50}$ on local deformation and serrated flow as a model for relating the size and localization of shear transformation zones (STZ) to Poisson ratio and strain-rate sensitivity of metallic glasses. Alloying with Al results in significant variations in mechanical performance, in particular, in Young's modulus, hardness and strain-rate sensitivity. Increasing strain-rate sensitivity with increasing degree of alloying indicates a reduced tendency for shear localization. In parallel, a gradual transition from inhomogeneous to homogeneous plastic flow is observed. Using a statistical analysis of the shear stress associated with the initiation of the first pop-in in the load-displacement curve during spherical indentation, the activation volume for plastic flow at the onset of yielding is reported. This analysis is employed for experimental evaluation of the compositional dependence of activation barrier, size and distribution of STZs. It is demonstrated that the STZ size does not change significantly upon Al alloying and encompasses a local volume of around 22–24 atoms. However, the barrier energy density for the initiation of a single STZ progressively increases. The broader distribution of STZs impedes their accumulation into larger-size flow units, leading to a lower number and reduced size of serrations in the load-displacement curve. On the contrary, lower barrier energy densities enable a larger quantity of STZs to be activated simultaneously. These STZs can easily percolate into large flow units, promoting plastic flow through their interaction. We employ Poisson's ratio as an indicator for plasticity to shown that this interpretation can be transferred to other types of metallic glasses. That is, larger flow units were found for metallic glasses with higher Poisson ratio and more pronounced plasticity, while the flow units in alloys with very low Poisson ratio and high brittleness are significantly reduced in size and more homogeneously distributed throughout the material.

1. Introduction

Since their first discovery, metallic glasses have received considerable attention. This has been due to their assumed potential for application as structural material [1]. Compared to their polycrystalline counterparts, metallic glasses exhibit a disordered structure of densely packed atomic clusters with predominantly metallic bonding character [2–4]. This atomic configuration and, in particular, the absence of long-range order result in an interesting set of mechanical properties, i.e., typically high elastic limit, exceptional strength and hardness or strong abrasion wear resistance [1]. However, actual use of metallic glasses is still restricted to niche applications, a fact that originates mainly from limitations in their processing as well as the lack of ductility [5]. To address these issues, research has been focusing on the technical exploitation of new alloys with improved glass-forming ability [6,7], and on the understanding of fundamental deformation processes and their consequences for macroscopic mechanical behavior [4,8–11].

In the present understanding, the deformation of metallic glasses is generally thought to be determined by a cooperative rearrangement of a group of atoms [12], termed *shear transformation zone* (STZ) [13]. A STZ typically comprises a volume of up to about 100 atoms, and is preferentially formed around regions of high free volume [8]. However, as opposed to structural defects in crystalline materials (such as dislocations), a STZ is a transient state induced through externally applied stress and, hence, the operation of a STZ can effectively be identified only from differences in the atomic configuration before or after deformation [4]. Experimental evaluation of the shape, size or activation energy of a STZ is difficult, and most of the present understanding is obtained from computational simulation. However, over the past years, various protocols have been proposed also for the experimental observation of STZs. For example, Choi et al. [14] estimated the

* Corresponding author.
E-mail address: lothar.wondraczek@uni-jena.de (L. Wondraczek).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.01.015

activation volume of a single STZ from a statistical analysis of the maximum shear stress associated with the initiation of the first discontinuity, or "pop-in", in the load-displacement curve of a nanoindentation experiment. Pan et al. [15] utilized a nanoindentation set-up with strain-rate jumps and derived the STZ volume from the strain-rate sensitivity. In both approaches, the STZ volume was calculated following the cooperative shear model of Johnson and Samwer [16]. Results obtained in these preliminary investigations were found to be in good agreement with those from other reports. Subsequent studies tried to establish fundamental correlations between the STZ size and other physical properties, such as the glass-transition temperature [17–19], elastic modulus [20] or toughness [15,21]. It was found that the STZ size seems to be strongly related to the atomic configuration in the metallic glass, i.e., order on short and intermediate length scale, as well as on the amount and local distribution of free volume [18,22–26]. On the other hand, most studies performed so far did focus on the comparison of very different alloy systems, ranging from Pt-, Pd-, Co- and W-based metallic glasses and metalloid-free alloys with Cu, Ni or Zr as the host element to compositions based on La [15,17,19,21,27]. Information on the influence of minor compositional variations on the STZ size in a specific alloy system are relatively sparse [20,24,28]. In particular, although the initiation of a STZ is supposed to be the fundamental process in the strong localization of plastic flow in metallic glasses via the operation of individual shear bands, to our knowledge, no studies have investigated the relationship between the STZ size and the shear band formation upon indentation in a systematic series of interrelated glass-forming alloys.

For that reason, we studied the indentation response of metallic glasses in the well-known ternary Cu-Zr-Al. With the addition of Al to binary $Cu_{50}Zr_{50}$ alloys, not only the glass-forming ability significantly increases [29–34], but also the mechanical properties are known to change notably (for example, room-temperature plasticity [33–36] or elastic modulus [33,35,36]). We now relate these changes to changes in strain-rate sensitivity and serrated flow behavior. In addition to Al, we further consider the impact of alloying with Co. The activation volume of STZs is then determined using a statistical analysis of the maximum shear stress at the initiation of the first pop-in [14], as well as through the nanoindentation strain-rate jump test [37]. Finally, correlations are drawn between the STZ size and the plastic flow of ternary $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$ and quaternary $Cu_{46-y}Zr_{46}Al_8Co_y$ (y = 1 and 2 at.%) alloys.

2. Materials and methods

Precursor alloys with nominal compositions of $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$ (x = 4, 5, 6, 7 and 8 at.%), $Cu_{46-y}Zr_{46}Al_8Co_y$ (y = 1 and 2 at.%) and $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ (as a reference material) were obtained by mixing high-purity elements (≥99.99%) in a Ti-gettered Ar atmosphere using an arc melter (Edmund Bühler GmbH). The ingots were remelted three times in order to ensure chemical homogeneity. From the ingots, cylindrical rods with a length of 35 mm and a diameter of 2 mm were prepared by suction casting inside the arc melter. The structure of the specimen was investigated by means of X-ray diffraction in a STOE STADI P diffractometer (STOE & Cie GmbH) using $MoK_{\alpha 1}$ radiation and operating in transmission mode. A Perkin-Elmer differential scanning calorimeter (Diamond DSC, PerkinElmer Inc.) was employed to determine the glass-transition temperature, T_g, and the onset of crystallization, T_x, at a heating rate of 40 K/min.

The mechanical properties were investigated by instrumented indentation testing, using a nanoindenter (G200, Agilent Inc.). For this purpose, samples of about 1.5 mm in height were taken from the bottom end of the cylindrical rods and polished in both ends. Depth profiles of the modulus, E, and hardness, H, were obtained through constant strain-rate indentations conducted in the continuous stiffness measurement mode [37]. In this setup, a weak oscillation ($\Delta h = 2$ nm, $f = 45$ Hz) is applied to the three-sided Berkovich diamond tip used for indentation (Synton-MDP Inc.), which enables the simultaneous determination of E and H as a function of the indenter displacement. On every sample, at least 15 indents with a maximum depth of 2 μm were created at a strain-rate of 0.05 s^{-1}.

Additionally, a nanoindentation strain-rate jump test [37], was performed to study the indentation creep behavior. In this test, the Berkovich indenter tip initially penetrates the sample surface to a depth of 800 nm at a constant strain-rate of 0.05 s^{-1}. Subsequently, the strain-rate was changed across intervals of 200 nm. The resulting variation of the hardness was determined using the continuous stiffness measurement mode ($\Delta h = 5$ nm, $f = 45$ Hz). Ten strain-rate jump tests with strain-rates of 0.014, 0.004 and 0.001 s^{-1} (in a descending order) were performed on each sample.

The rate-dependence of the indentation deformation was further studied using a conical diamond indenter tip (SURFACE Systems & Technology GmbH & Co. KG) with a tip-angle of 60° and an effective radius of 4.53 μm. Indents with a peak load of 50 mN were created at varying loading rates, ranging from around 0.033 up to 10 mN/s, and the resulting load-displacement curves were recorded with data acquisition rates of up to 500 Hz. The dwell-time at maximum load was kept constant at 5 s.

The tip area function of both the Berkovich and conical diamond tips as well as the instrument's frame compliance were calibrated prior to the measurements on a fused silica reference glass sample (Corning code 7980, Corning Inc.), according to the method introduced by Oliver and Pharr [38]. To avoid the influence of residual stress fields, consecutive indents were conducted at distances of 30 μm (conical tip) and 50 μm (Berkovich tip), respectively [39]. All experiments were performed in laboratory air under ambient conditions at temperatures of around (30 ± 2) °C and with thermal drift rates of <0.05 nm/s.

3. Results and discussion

3.1. Glass formation and thermal stability

The X-ray diffraction patterns of the ternary $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$ (x = 4, 5, 6, 7 and 8 at.%) and the quaternary $Cu_{46-y}Zr_{46}Al_8Co_y$ (y = 1 and 2 at.%) alloys are presented in Fig. 1. All samples exhibit a characteristic broad diffraction maximum with no evidence of crystallinity. This finding is also supported by the results from the thermal analysis shown in Fig. 2 and summarized in Table 1. With increasing temperature, a weak endothermic event corresponding to the glass-transition is seen in all samples. This is followed by a supercooled liquid region, and a single sharp exothermic peak, indicating crystallization. Regarding the ternary $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$, the values of T_g and T_x increase with increasing Al content, i.e., from $T_g = 691 \pm 2$ K and $T_x = 754 \pm 2$ K ($Cu_{48}Zr_{48}Al_4$) up to $T_g = 711 \pm 2$ K and $T_x = 794 \pm 2$ K ($Cu_{46}Zr_{46}Al_8$), respectively. Furthermore, the incorporation of additional Al results in an expansion of the supercooled liquid region, $\Delta T = T_x - T_g$, by about 19 K ($Cu_{48}Zr_{48}Al_4$: $\Delta T = 63 \pm 2$ K and $Cu_{46}Zr_{46}Al_8$: $\Delta T = 82 \pm 2$ K), indicating an increased stability of the supercooled liquid against crystallization and an associated increase of glass-forming ability [6]. Both these compositional trends as well as the absolute values of T_g, T_x and ΔT of these glasses agree very well with previous investigations [29–34]. The enhanced thermal stability of Al-containing $Cu_{50}Zr_{50}$ alloys has been assigned to the significant size mismatch among the densely packed Cu (0.135 nm), Zr (0.155 nm) and Al (0.125 nm) atoms on the one hand [6,40,41]. On the other hand, the larger negative enthalpy of mixing between Al and Zr (−44 kJ/mol) compared to Al and Cu (−1 kJ/mol) or Cu and Zr (−23 kJ/mol) is supposed to counteract the crystallization of ternary Cu-Zr-Al alloys during cooling [29,42]. In contrast to the effect of Al, the addition of small amounts of Co seems to have only negligible impact on the glass-forming ability of the $Cu_{46}Zr_{46}Al_8$ alloy, as the values of T_g, T_x as well as ΔT remain almost unchanged within the limits of experimental error.