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The structural relaxation effect on the nanomechanical properties of a Ti-based bulk metallic glass

Yongjiang Huang [a,b,c,*], Binjun Zhou [b], YuLung Chiu [d,*], Hongbo Fan [b], Dongjun Wang [b,c], Jianfei Sun [b], Jun Shen [b]

[a] State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[c] Key Laboratory of Micro-Systems and Micro-Structures Manufacturing, Harbin Institute of Technology, Ministry of Education, Harbin 150001, China
[d] School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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ABSTRACT

Indentation experiments were performed on the as-cast and the annealed Ti-based bulk metallic glass samples to investigate the effect of structural relaxation on the nanomechanical behaviors of the material. The onset of pop-in event, Young's modulus, and hardness were found to be sensitive to the structural relaxation of the testing material. The difference in nanomechanical properties between the as-cast and annealed BMG samples is interpreted in terms of free volume theory.

1. Introduction

Bulk metallic glasses (BMGs) have triggered considerable interest due to the basic science and great potential for widespread applications as structural and functional materials [1,2]. Lacking dislocations and grain boundaries inherent in crystalline materials, BMGs usually exhibit unique properties, including extremely high strength and hardness, large elastic strain limit of up to 2% combined with relatively high fracture toughness, as well as excellent wear and corrosion resistance [3]. Despite of these advantages, monolithic BMGs have not been utilized much so far as structural materials due to their severely limited global plasticity when deformed at room temperature, as they tend to fail catastrophically along one dominant shear band of few tens of nanometers thickness [4,5]. Clearly, an improved understanding of plastic deformation mechanism of BMGs can benefit the development and design of strong and tough BMGs.

Compared with their thermodynamically stable crystalline counterparts, BMGs are in a considerably higher energy state. As such, their thermophysical properties are metastable [6]. A sufficiently long time exposure of BMGs to high temperatures close to the glass transition temperature, T_g, may result in a considerable change in their properties, even if there is no structural change from amorphous to crystalline state [7]. Such structural relaxation usually causes degradation of mechanical properties such as loss of plasticity [8]. Meanwhile, structural relaxation by annealing has been used to study the role of free volume in mechanical behaviors of BMGs [8]. Nowadays, nanoindentation has been considered to be an effective method with high spatio-temporal and force resolution in studying the fundamental deformation mechanisms of BMGs, thereby providing important information that may lead to tougher materials [6,8,9–12]. Wright et al. [13] observed that the onset of plasticity during nanoindentation of a Zr-based BMG occurred at a discrete displacement burst (a "pop-in"). This result has an analog in nanoindentation studies of crystalline materials, which have such bursts when dislocations are nucleated [14]. Golovin et al. [15] and Greer et al. [16] have successfully correlated the number of "pop-in" events during the indentation of Pd- and Ni-based glasses to the number of surface shear bands as determined by microscopy. However, few studies have been devoted to the effect of structural relaxation on the nanomechanical behaviors of BMGs until now.

In this work, nanoindentation tests have been conducted on a TiZrNiCuBe BMG, in as-cast state and annealed state, aiming at understanding the relationship between the free volume and the nanomechanical behaviors in BMGs.

* Corresponding authors. Address: State Key Laboratory of Advanced Welding Production Technology, Harbin Institute of Technology, Harbin 150001, China (Y. Huang). Tel./fax: +86 451 86403196.

E-mail addresses: yjhuang@hit.edu.cn (Y. Huang), y.chiu@bham.ac.uk (Y. Chiu).

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2. Experimental details

The master ingots of $Ti_{40}Zr_{25}Ni_3Cu_{12}Be_{20}$ (at.%) BMG were produced by arc melting pure metals of Ti, Zr, Ni, Cu, and Be with purity of 99.9% or higher on a water-cooled copper hearth in a Ti-gettered argon atmosphere. To achieve compositional homogeneity, the master alloys were remelted at least four times, followed by drop casting into a copper mold. The obtained as-cast cylindrical alloy samples have a dimension of $\Phi 5$ mm × 60 mm. Thermal properties of the as-cast alloys were examined by differential scanning calorimetry (DSC) at a continuous heating rate of 0.33 K/s. The glass transition temperature (T_g) for this alloy is 603 K, as measured from DSC at a heating rate of 0.33 K/s. The as-cast samples were sealed in evacuated quartz capsules and annealed for 3, 6, 12, 24, and 48 h at 553 K (below T_g), respectively. The amorphous structure of the as-cast samples and the annealed samples was confirmed by X-ray diffraction (XRD) with Cu Kα radiation.

Nanoindentation tests were performed on the polished cross-section of the alloy samples at room temperature at a constant loading rate of 0.025 mN/s with a maximum applied load of 10 mN using an MTS Nano indenter® XP system with a Berkovich diamond indenter. All the tests were conducted in a load-controlled mode, and the loading and unloading rates were kept the same, and a holding time of 5 s was used at the maximum load. Fused silica was used as the standard sample for the initial indenter tip calibration. At least 10 indents at each condition were performed and the results presented in this paper have the standard deviation of less than 10%. After 90% unloading, a dwell period of 100 s was imposed to correct for the thermal drift, which was found to be less than 0.1 nm/s. The hardness and elastic modulus were calculated using Oliver–Pharr method [17].

The microstructure of the as-cast and the annealed samples was characterized by using a high resolution transmission electron microscope (HRTEM, Philips Tecnai TF30ST) operated at 200 kV. In order to measure the amount and extent of local ordering in electron microscope images, which can be subsequently used as a basis for the quantitative comparison of the degree of local ordering between related samples, an autocorrelation function (ACF) was applied on the obtained HRTEM images. The ACF treatment has been considered as a statistical interpretation of the HRTEM images [18], and is often applied to the quantitative estimation of the degree of local ordering in non-periodic objects [19,20], showing the reliability of the data obtained.

3. Results and discussion

Fig. 1 shows the XRD spectra obtained from the as-cast sample and the 553 K annealed Ti-based BMG samples. All of the spectra exhibit the broadened diffuse peak without any detectable Bragg crystalline peaks, indicating the mostly amorphous states before and after the annealing process.

HRTEM observations were performed to reveal the details of the atomic level structure. Fig. 2a shows the HRTEM image and the corresponding selected area electron diffraction (SAED) patterns (inset) obtained from the as-cast sample and the sample annealed for 48 h. The HRTEM images obtained from both the as-cast and annealed samples exhibits a featureless and homogeneous contrast without any noticeable long-range atomic order or chemical inhomogeneity, typical of a fully amorphous alloy. The solely amorphous phase was also confirmed by one strong inner diffraction ring with a rather faint, diffuse outer ring in the corresponding SAED pattern.

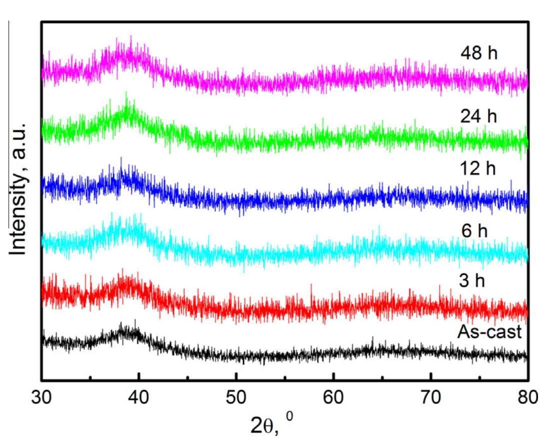

Fig. 1. XRD patterns of the as-cast and annealed $Ti_{40}Zr_{25}Ni_3Cu_{12}Be_{20}$ BMG samples with 5 mm diameter.

The ACF analysis was adopted in order to statistically determine the local ordering in the as-cast and annealed BMG samples. To perform the local ordering analysis, an area of 17.8 × 17.8 nm^2 was randomly selected from Fig. 2a and b, and divided into 49 sub-images with 2.54 × 2.54 nm^2 dimension, a size similar to the medium-range order (MRO). In the present work, one sub-image, which had some crystal-like diffraction spots in the fast Fourier transformation pattern, was selected as a reference pattern to describe the local ordering, as indicated by the red[1] rectangles in Fig. 2c and d. Thus all the sub-images with clearer atomic fringe arrangements than the reference pattern were considered to be more ordered. Statistical analysis of all the sub-images in Fig. 2c and d revealed that the local ordering content on the MRO scale in the as-cast Ti-based BMG sample was about 8 ± 1%. Similarly, the local ordering content in BMG samples annealed for 3 h, 6 h, 12 h, 24 h, and 48 h were estimated to be about 10 ± 1%, 12 ± 1%, 16 ± 1%, 19 ± 1%, and 21 ± 1%, respectively. The above results strongly suggest that the level of local ordering increases with annealing time.

Fig. 3 displays the DSC curves obtained from the as-cast and the annealed samples. All samples exhibit very similar thermal behavior with a distinct glass transition and a wide supercooled liquid region before crystallization. However, the exothermic signals before glass transition in DSC curves are very different among these samples, as indicated in the inset of Fig. 3. It is well known that prior to T_g, the exothermic event (i.e., the heat release during relaxation) is related to the free volume in BMGs [21]. For instance, Slipenyuk and Eckert [22] experimentally showed that the change in free volume in a metallic glass is linearly correlated with the enthalpy released during structural relaxation below the glass transition temperature, that is:

$$(\Delta H)_{fv} = \beta \Delta v_f \quad (1)$$

where $(\Delta H)_{fv}$ is the change in enthalpy, Δv_f the change of free volume per atomic BMG volume, and β is a constant. The exothermic heat due to the structural relaxation below T_g of the studied BMG can be calculated by integration of the heat flow in the nearby range below T_g (as shown in Fig. 3 inset). Fig. 3 shows that the as-cast BMG sample has the largest exothermic enthalpy, suggesting the existence of a fairly large amount of free volume. For the annealed samples, their exothermic enthalpy values decrease with the increase in the annealing time.

Fig. 4a shows the load–displacement (P–h) curves recorded from nanoindentation tests of the as-cast and the annealed Ti-based BMG samples. It should be noted that, for the same maximum load of 10 mN, the penetration depth is the largest for the as-cast sample, meaning that the as-cast sample exhibits the lowest nano-hardness value among the samples studied, as summarized in Table 1. Fig. 4b illustrates the enlarged views of the typical P–h curves below 2 mN. Beyond a critical load, rapid depth excursions can be seen in the P–h curves, corresponding to the shear banding events, as commonly seen in nanoindentation experiments of glassy metals [10,23–25]. The occurrence of the first pop-in is normally attributed to the onset of plastic flow, thus the completion of the shear band nucleation; indentations beyond this point always exhibit measurable residual displacements after unloading [23]. Prior to the first pop-in, the P–h curve can be usually fitted with the Hertzian elastic contact analysis [26]:

$$P = \frac{4}{3} E_r R^{1/2} h^{3/2} \quad (2)$$

[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.