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Research on deformation behavior of zirconium-based bulk metallic glasses containing hydrogen with different deformability

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ARTICLE INFO

Article history:

Received 6 March 2016
 Received in revised form
 14 April 2016
 Accepted 26 April 2016
 Available online 27 May 2016

Keywords:

Melt hydrogenation
 Metallic glasses
 Hydrogen
 Shear band
 Mechanical testing

ABSTRACT

Bulk metallic glasses (BMGs) have absorbed much attention for their potential applications as high-strength materials. However, they are notorious for being extremely brittle, failing in a catastrophic manner. A large number of researches indicated that, BMGs deform through the formation of highly localized shear bands under loading at room temperature, i.e., deformation of the BMGs take places just within very narrow shear bands. However, whether or not all the BMGs, including BMGs with high global deformability and poor plasticity, have the same deformation manner at room temperature is not very clear. In present paper, two Zr-based BMGs, marked by T1 and T2, were prepared via copper-mold vacuum suction casting under the gaseous mixture of hydrogen and argon, of which, T2 presents a large plasticity at room temperature, while T1 is prone to brittleness. The uniaxial compression experiments of T1 and T2 BMGs were carried out under a quasistatic condition to investigate the deformation manners of BMGs with different deformability at room temperature. The results showed that the differences of initiation and propagation of shear bands result in the different deformation behavior of T1 and T2 BMGs at room temperature.

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Introduction

Bulk metallic glasses (BMGs) are multicomponent alloys which have many excellent properties, such as great hardness, large elastic limits, good resistance to fatigue and corrosion [1]. In recent years, BMGs have acquired significant attention from the scientific and technological viewpoints [2,3]. Due to their unique structure, BMGs have a promising future in the field of hydrogen absorption and hydrogen storage. However, BMGs are also notorious for being extremely brittle, generally failing in a catastrophic manner [4]. A great number of studies showed that at room

temperature, BMGs usually display very limited plastic flow of about 2% under compression and none in tension [5,6]. Lack of plasticity makes BMGs prone to catastrophic failure in load-bearing conditions and restricts their wide spread applications, including the applications in hydrogen absorption and hydrogen storage, and also hinders precise study on some fundamental issues in BMGs, including conversion and release of hydrogen [4,6]. In 2007, Liu et al, firstly reported that super plastic BMGs at room temperature could be produced by selection of proper alloy compositions to control their Poisson's ratio [7]. Through optimizing technology and regulating the compositions, we prepared two ZrCuNiAl BMGs, marked by T1 and T2, by using copper-mold vacuum suction casting

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<http://dx.doi.org/10.1016/j.ijhydene.2016.04.234>

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under the gaseous mixture of hydrogen and argon, of which, T1 is prone to brittle fracturing, while T2 exhibits a large plasticity at room temperature. Successful preparations of BMGs with high plasticity at room temperature facilitate studying of many fundamental issues [8–11], such as deformation behavior, initiation and propagation of shear bands, etc. In general, BMGs deform through the formation of highly localized shear bands under loading at room temperature [12], i.e., deformation of the BMGs generally takes place within very narrow shear bands. However, whether or not all the BMGs, including BMGs with high global deformability and poor plasticity, deform in a same manner at room temperature is not very clear. In present paper, the uniaxial compression experiments of T1 and T2 BMGs containing hydrogen were carried out under a quasistatic condition to find out the differences between deformation behavior of BMGs with different deformability.

Materials and methods

Two amorphous alloy rods, $(Zr_{69.5}Cu_{19.5}Ni_{11.0})_{90}Al_{10}$ (marked T1) and $(Zr_{72.0}Cu_{16.5}Ni_{11.5})_{90}Al_{10}$ (marked T2), with a diameter of 2 mm were prepared by arc-melting mixtures of pure Zr (99.8%), Cu (99.9%), Ni (99.98%) and Al (99.9%) in a Ti-gettered gaseous mixture atmosphere of hydrogen and argon at least four times ($Ar+15\%H_2$), then casting into a copper mold with cool water surrounding it, respectively. The structure of the as-cast alloy samples was characterized by using a Rigaku D/MAX-Ultimal IV X-ray diffractometer (XRD) with a $Cu K\alpha$ radiation. The thermal analysis was examined by using an XDT2960 differential scanning calorimeter (DSC) at a heating rate of 20 K/min in a flow of purified nitrogen gas.

After the amorphous nature has been confirmed, the compression specimens with an aspect ratio of 2:1 were produced out of the as-cast 2 mm alloy rods for uniaxial compression tests by following steps. First, rods with a length of 4.5 mm were cut out using a linear cutting machine. Then, both ends of the specimens were ground and polished sequentially by using sandpapers with size of 1000#, 1200# and 1500#, respectively. The size of diamond particles ranges from 3 to 7 μm . Uniaxial compression experiments at room temperature were carried out on a WDW3100 Microcomputer Control Electronic Universal Testing Machine under a quasistatic loading strain rate of $4.2 \times 10^{-4} s^{-1}$. The displacement gauge of the platen of the testing machine was set to 3.42 mm, so the maximum engineering strain of the compression specimens were expected to be 85.5%, i.e., the maximum true strain of the compression specimens could exceed 193% during compression deformation processes. The initiation and propagation of shear bands and the fractured surface morphologies of the compressed specimens were observed with an S-3400N Scanning Electron Microscopy (SEM).

Results

A JRD-1010 micro-scale hydrogen analytic instrument was used to measure the hydrogen contents for the BMG specimens fabricated under gaseous mixture with argon and

hydrogen. The hydrogen contents in the as-cast specimens T1 and T2 fabricated in $Ar+15\%H_2$ were measured to be 318 and 345 ppm (w/w), respectively. Fig. 1 shows XRD patterns of the two as-cast bulk alloys. It can be seen that the XRD patterns of the two alloys both consist of only one broad diffraction peak without any sharp Bragg peaks, indicative of an amorphous structure in the two rod-like bulk alloys. In Fig. 2, the DSC curves of T1 and T2 reveal small endothermic peaks corresponding to the glass transitions followed by large super-cooled liquid regions and then exothermic peaks indicating the crystallization. As shown in the DSC curves, both T1 and T2 BMGs present single-stage crystallization. The glass transition temperatures (T_g), onset temperatures of exothermic reaction (T_x), super-cooled liquid regions ($\Delta T_x = T_x - T_g$) of the two BMGs were summarized in Table 1. From the DSC curves, the structural relaxation enthalpy of T1 and T2 was calculated to be about 8.56 and 9.43 cal/g, respectively, indicating that more free volume was induced in T2 compared with T1 by hydrogen.

The volume fraction of precipitated crystals during the crystallization event can be obtained from the DSC curve by using equation of $x = \Delta H_x / \Delta H_0$ or $x = S_x / S_0$ where x is the crystallization volume fraction, ΔH_0 the total exothermic enthalpy of the amorphous alloy, ΔH_x the total exothermic enthalpy at any temperature T ($T_x \leq T \leq T_{end}$), S_0 the total area under the crystallization curve, and S_x the area between T_x and T . Fig. 3 shows the crystallization volume fraction x as a function of temperature T for T1 and T2 under a heating rate of 20 K/min, respectively. It can be found that both relation curves between x and T present a sigmoid-like shape. Meanwhile, the two curves exhibit a similar characteristic, i.e., with the increasing of temperature, crystallization rate of x versus T rises slowly initially, then grows swiftly in the middle of crystallization process, becomes slowly again at the last stage. Outwardly, T1 and T2 seem to have a similar crystallization process and the consequent same crystallization precipitated phases. However, careful examination of the crystallization processes of the two BMGs shows that the crystallization rate of T2 is more retarded than that of T1. For example, when the crystallization rate x is 50%, the corresponding crystallization temperatures for T1 and T2 are 759.6 K and 762.2 K, respectively, in which the latter retards a 2.6 K compared to the former. At 759.6 K, the crystallization rate of T2 is 36.8%, smaller than that of T1 by 13.2%, while, at 762.2 K, the

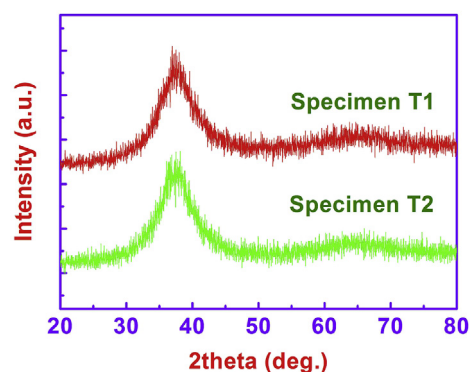


Fig. 1 – X-ray diffraction patterns of as cast T1 and T2 BMGs.

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