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Unusual plasticization for structural relaxed bulk metallic glass

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ABSTRACT

Unusual plasticization for structural relaxed CuZr-based bulk metallic glass (BMG) has been found. Even though thermal-annealing usually leads to unfavorable relaxation-induced embrittlement for most BMGs, this BMG exhibits an improved plasticity after annealing. This behavior is attributed to an evolution of nanolevel heterogeneity for this unstable or heterogeneous BMG. Less initiation of shear bands by structural relaxation and evolution of heterogeneity from thermal-annealing are considered to contribute cooperatively to the plasticity of relaxed glass. This study provides a new viewpoint to improve the mechanical properties of BMGs upon relaxation, in which a microstructural heterogeneity is distributed among a glassy matrix. This finding may also expand the applications of BMGs as promising structural materials because of unusual resistances to annealing-embrittlement.

1. Introduction

Bulk metallic glasses (BMGs) have attracted much attention in recent decades because of their superior mechanical properties, such as their high fracture strength and large elastic limit that result from their unique long-range disordered structures [1–3]. However, two main problems exist for the widespread applications of these materials: room-temperature brittleness and annealing-induced embrittlement [4–6]. Room-temperature brittleness results from highly concentrated plastic deformation in shear bands [7,8]; to overcome this disadvantage, small samples can be produced or BMG matrix composites can be developed [9,10]. BMGs are always treated as metastable materials because the required rapid cooling rate makes it inherit the disordered structure of liquids with intrinsic topological and geometric fluctuations as well as a large number of quench-in defects, thus they possess a higher configurational potential energy than their equilibrium crystalline counterparts [11]. They tend to change their structure progressively towards the crystalline state or to more stable glassy states when they are supplied with thermal energy, which is termed structural relaxation. Structural relaxation can affect the properties of BMGs, especially the mechanical properties, which induces their unfavorable embrittlement. The mechanism for this behavior is unclear and may result from a reduction in free volume [12] and local ordering [13]. Flow mechanisms in metallic glasses are understood in terms of free volume, which can be thought of as “defects” in amorphous alloys and similar to vacancies in crystalline materials [14–16]. During annealing, the excess free volume redistributes and is annihilated, which results in a loss of ductility.

Not all BMGs show room-temperature brittleness. Various BMGs have intrinsic plasticity at room temperature [17,18], which may be attributed to their unstable microstructures with nanolevel heterogeneity. These intrinsically plastic BMGs are more attractive for use in practical applications; however, the relaxation and its effect on mechanical properties has not been investigated.

We selected $Cu_{47.5}Zr_{47.5}Al_5$ (at%) as a typical plastic BMG with an unstable microstructure [17]. The microstructure and mechanical properties of the as-cast and as-relaxed state of this BMG have been investigated in detail.

2. Experimental

Master alloys were prepared by arc-melting high-purity Cu, Zr and Al metal pieces in a Ti-gettered argon atmosphere in a water-cooled copper hearth. The alloy was remelted four times to ensure chemical homogeneity. The BMG was fabricated by casting the master alloy into a copper mold to produce a 2-mm-diameter rod-shaped sample (as-cast sample). A ribbon sample with a 2.5 mm × 0.05 mm cross section was prepared by a single-roller melt-spinning method at 3000 rpm in argon. To produce a relaxed sample, the as-cast sample was heated to ~723 K (~$1.05T_g$) at 20 K/min, and kept for 120 s followed by cooling at 20 K/min. The structures of the as-cast and as-relaxed samples were examined by X-ray diffraction (XRD; Bruker D8 Advance) with Cu Kα radiation, and transmission electron microscopy (TEM, JEOL JEM-2100F) with an acceleration voltage of 200 kV. The glassy transition

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temperature (T_g) and the onset crystalline temperature (T_x) were measured by differential scanning calorimeter (DSC, Perkin Elmer DSC8000) in argon at 20 K/min. The specific heat capacities of both samples were measured by comparing them with a sapphire standard sample. The loss modulus was measured by dynamic mechanical analysis (DMA, Hitachi DMS6100) in tension mode at 5 K/min and at multiple frequencies (0.1, 0.2 0.5, 1, 2 and 5 Hz). Samples used in the hardness test (HM-102, Mitsutoyo Co. Ltd.) were cut into 2-mm-thick discs, which were polished mechanically to mirror faces. The density was measured by using a gas pycnometer (AccuPyc II 1340, Micromeritics Co. Ltd). Compression tests were performed at a strain rate of $5 \times 10^{-4}\,s^{-1}$ at room temperature using an Instron 5982 mechanical testing machine. Multiple compression tests using at least four samples each were conducted to confirm the reproducibility. Fractured samples were observed by XRD, TEM and scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX; Carl Zeiss Ultra 55 with Bruker AXS).

3. Results

3.1. Structural relaxation

XRD patterns for the as-cast and as-relaxed samples (Fig. 1(a)) exhibit a similar single broad peak of monolithic glassy phase for both samples, which indicates that no crystallization occurred during thermal-annealing. Fig. 1(b) shows the DSC curves for both samples. A clear endothermic heat behavior of the glass transition, followed by characteristic exothermic transformations from the supercooled liquid to the equilibrium crystalline states is visible [19]. The T_g and T_x for both samples appear to be similar, at 691 and 754 K for the as-cast and 690 and 754 K for the as-relaxed states, respectively.

The specific heat curves for the as-cast and as-relaxed samples (Fig. 2(a)) exhibit significant differences, which indicates that the as-cast state is more thermodynamically unstable than the as-relaxed state and relaxation occurred during thermal-annealing. To further confirm the occurrence of structural relaxation, the hardness and density for both samples were investigated as shown in Fig. 2(b), which indicates that a higher hardness and density are obtained in the as-relaxed sample. They are 656 ± 30 HV and 7.186 ± 0.006 g/cm^3 for the as-cast state, and 719 ± 33 HV and 7.201 ± 0.009 g/cm^3 for the as-relaxed state, respectively. These factors increase by 9.6% and 0.2% through the relaxation. The similar phenomenon can be found from our previous study, and the reason is considered to be the annihilation of free volume [20].

The normalized loss modulus plotted as function of temperature for both samples with a frequency fixed at 1 Hz is shown in Fig. 3. In the higher-temperature region (~650–720 K), the loss modulus for both samples does not show obvious differences or the peaks overlap each other; however, in the lower temperature region (~450–650 K), the hump-like behavior, which can be observed from as-cast sample, disappears for the as-relaxed state. Johari et al. found that glasses undergo two main relaxation processes: primary (α) and secondary (β) relaxations [21]. The α relaxation corresponds to the cooperative motion of atoms, or the escape from one megabasin and the jump into another from a potential-energy landscape point. The β relaxation, which is usually evident only below T_g, is related to more local dynamics, or hopping events across subbasins within an inherent megabasin [22]. Thus, from Fig. 3, it can be found that the structural relaxation behavior in the present study predominantly relates with β relaxation rather than α relaxation. The similar results can be found from our previous study [23]. It is considered that the low temperature annealing with less energy affects very local rearrangement of atoms (β relaxation) at weakly bonded or loose packed regions, causing hopping events across subbasins, while the α relaxation or jumping from one megabasin to another did not happen. However, the detailed investigations of this behavior should be our future work. From the above discussions, thermal-annealing-induced structural relaxation has been confirmed, as has been described previously [20].

3.2. Mechanical property

Fig. 4(a) shows compressive stress–strain curves for the as-cast and as-relaxed samples. Unusually, instead of relaxation-induced embrittlement, the as-relaxed sample shows a much larger plastic deformation than the as-cast counterpart. The fracture strain and strength for the as-relaxed sample are 6.6% and 2186 MPa, and these increase by 160% and 10% compared with the as-cast sample (~2.5% and 1980 MPa), respectively. The detailed data are summarized in Table 1. Fig. 4(b)-(e) show the SEM images of fracture surfaces for both as-cast and as-relaxed sample. A number of shear bands can be observed for the as-cast sample (Fig. 4(b)) and the fracture morphology contains mainly vein patters (Fig. 4(c)). In contrast, much developed multiple shear bands as well as more complicated fracture morphology can be found for as-relaxed sample (Fig. 4(d) and (e)), which is more like a composite materials rather than a monolithic BMG.

3.3. Deformation-induced crystallization for as-relaxed sample

To understand the mechanisms of this unusual plasticization, we firstly studied the XRD patterns from the fracture surfaces for both samples as shown in Fig. 5(a). The fracture surface for the as-cast sample still possesses a monolithic glassy phase, whereas deformation-induced crystallization occurred for the as-relaxed state because several crystalline peaks (B2-CuZr + B19′-CuZr) were detected. Furthermore,

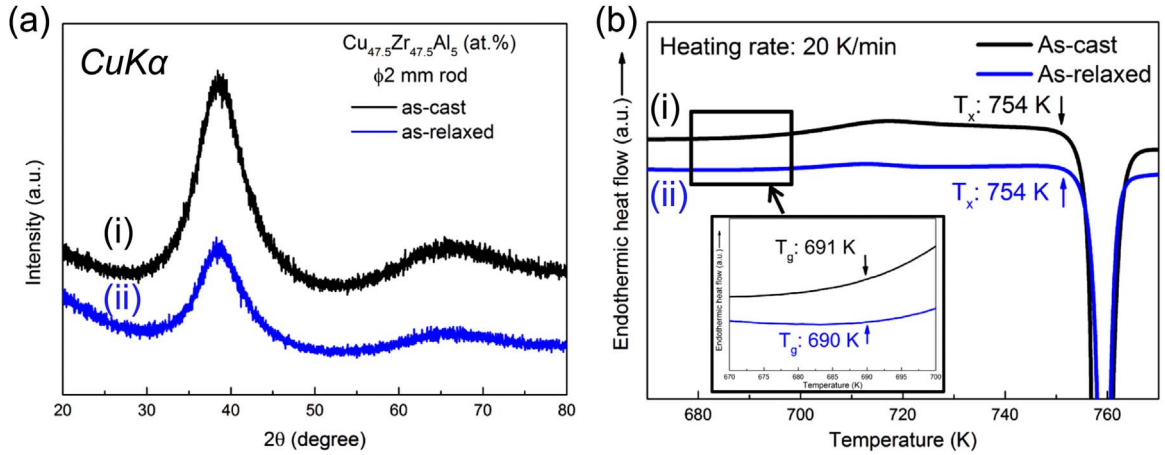

Fig. 1. (a) XRD patterns, (b) DSC curves, for (i) as-cast and (ii) as-relaxed samples (insert: enlarged parts for determining T_g).