

Improved tensile plasticity of bulk metallic glasses by heightening microstructural heterogeneity and energy state

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Abstract

Bulk metallic glasses (BMGs) generally fail in a brittle manner at room temperature upon uniaxial tensile loading. In the present work, we disclose that high microstructural heterogeneity fabricated in high energy glass could obviously enhance the macroscopic tensile plasticity of BMGs. Such a unique structure can promote the lower formation energy and the difficulty to propagate shear bands, resulting in detectable yielding and certain tensile plasticity. This work may widen the pathway to overcoming the brittleness and is believed to aid in structural application of BMGs greatly.

Key words: bulk metallic glasses, tensile plasticity, high energy, microstructural heterogeneity

1. Introduction

As an important high-performance material, bulk metallic glasses (BMGs) are always considered potential candidates for structural applications. However, catastrophic failure along one main shear band under uniaxial tensile loading at room temperature seriously limits potential engineering applications of BMGs [1–3].

In recent years, although some studies report excellent compressive ductility of monolithic BMGs, they still exhibit nearly zero in tension [4]. Compared with the compression, tensile properties always play a more significant parameter for structural materials [5]. The tensile plasticity is always used as the main indicator of the material structures design and the prediction of other mechanical properties [6]. Previously, extensive studies reported that fabricating high microstructural heterogeneity in BMGs could improve the tensile plasticity, such as the high-pressure torsion [7], the surface nanoindentations [8], and the introduction of the various microstructure of the crystalline phases [9]. However, there still exist not a few drawbacks.

On the one hand, it is complex and time-consuming

to process BMGs through traditional pre-deformation treatments due to the intrinsic high strength and hardness of BMGs; on the other hand, the increase in plasticity is at the cost of a large decrease in strength and the quasicrystal-BMG composites have already stretched beyond the monolithic BMGs. Furthermore, it is found that raising energy states could also be helpful in the plasticity of monolithic BMGs. For example, Ketov et al. reported that an increased energy state of BMGs induced by a cryogenic treatment could improve the plasticity [10].

In this paper, the high rheological rate forming method (HRRF) is proposed [11]. This method can make BMGs stay the amorphous microstructure and increase their microstructural heterogeneity and energy state within centesimal seconds [12, 13]. The result shows that this method can remarkably improve the tensile plasticity of BMGs.

2. Experimental procedure

Zr_{46.75}Cu_{45.75}Al_{6.5}Co₁ BMG was prepared by arc melting under an Ar atmosphere. Cylindrical rods

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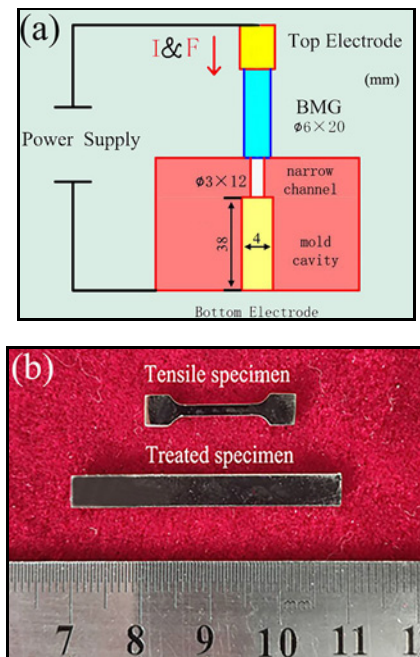


Fig. 1. Schematic illustration of the HRRF method for tension tests (a) and a treated BMG and a tensile specimen (b), respectively.

with 6 mm in diameter and 120 mm in length were synthesized by casting into a water-cooled copper mold and then cut into a length of 20 mm for HRRF. Tensile samples with gauge dimensions of $1 \times 1 \times 10 \text{ mm}^3$ (Fig. 1b) were tested in a Shimadzu AG-X with an initial strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. All test samples were carefully ground and polished. The structures of samples were examined by X-ray diffraction to make sure without crystallization. The surface of tension deformed samples was observed using the field emission scanning electron microscope (FESEM, SU8020). The thermal property was measured using different scanning calorimetry (DSC; NETZSCH 449F3) at a heating rate of 10 K min^{-1} . The nanoindentation test was conducted with an Agilent G200 Nano-indenter. Thirty-six indentations were loaded in a 6×6 matrix with the same penetration depth (300 nm) at a constant strain rate of 0.05 s^{-1} . The spacing between adjacent indents was set at $12 \mu\text{m}$ to avoid disturbance of neighboring strained zones. Before the experiment, the surfaces of all these samples were carefully polished to a mirror finish.

According to our early exploration that HRRF could both enhance the microstructural heterogeneity and the energy state of $\text{Zr}_{46.75}\text{Cu}_{45.75}\text{Al}_{6.5}\text{Co}_1$ BMGs [12]. Thus, we adopt this technique to treat the as-cast samples. During this process, the as-cast BMG (6 mm in diameter \times 20 mm high) was heated to a supercooled liquid region ($\sim 745 \text{ K}$, measured by a nano voltmeter) through the fast Joule heating [14] method squeezing the supercooled liquid

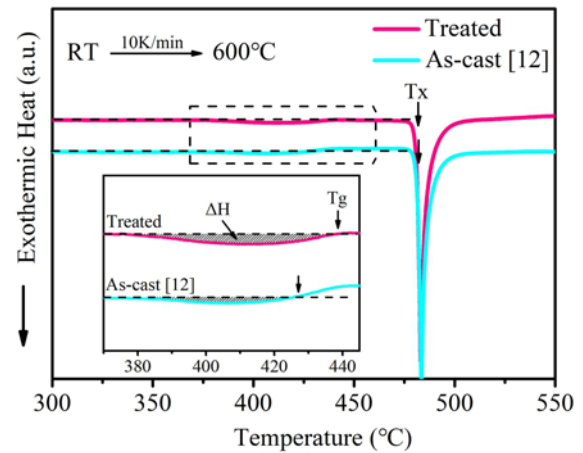


Fig. 2. DSC curves of the as-cast and treated BMGs. The enlarged view before T_g is shown in the inset.

into a small copper mold cavity under a preset load (seen in Fig. 1a). The more detailed information on the application of this method is described in earlier work [12, 13].

3. Results

The indicator of energy state in BMGs can be represented by relaxation enthalpy ΔH , which is an exothermic peak below T_g in the subsequent DSC measurements [15]. Therefore, as shown in Fig. 2, the treated BMG by HRRF has a higher released heat ΔH than that in the as-cast sample significantly (the black shaded areas in the inset of Fig. 2). By calculating, a relaxation enthalpy of 5.326 J g^{-1} is obtained for the treated sample, which is more than twice that of the as-cast samples [12]. This phenomenon reconfirms that HRRF is attributed to achieving the high stored energy in BMGs.

Additionally, the HRRF creates a more heterogeneous microstructure, as demonstrated by the spatial nano-hardness of the samples (Figs. 3a,b). The as-cast sample is rather homogeneous with different locations, with nano-hardness values ranging between 7.7 and 8.13 GPa (Fig. 3a). However, as shown in Fig. 3b, the treated sample shows a wider range of nano-hardness values (from 7.52 to 8.4 GPa), displaying much more heterogeneous. This indicates that the higher can be heterogeneous microstructure preserved in BMGs after HRRF.

To evaluate effectiveness in the tension by this method, the as-cast and treated BMGs were tested. Figure 4 shows the representative stress-strain curves for the BMG at different states. As expected, the as-cast sample exhibits typical brittle fracture without distinct yielding. While by raising energy state and microstructural heterogeneity, the treated sample

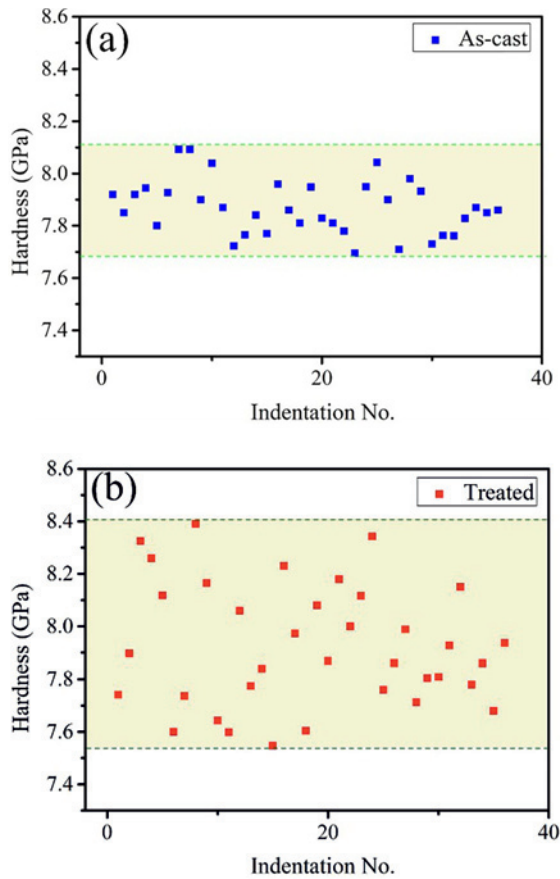


Fig. 3. (a) and (b) the distribution of the nanoindentation hardness of the as-cast and treated BMGs, respectively.

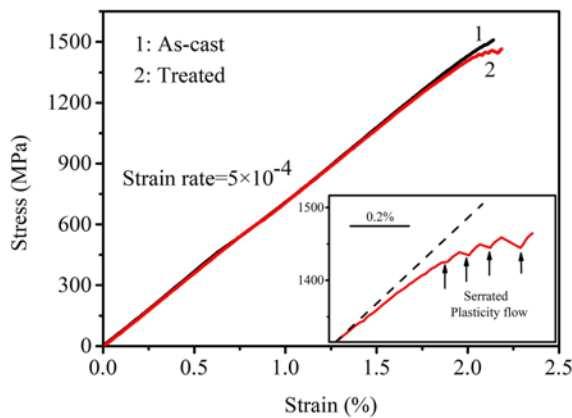


Fig. 4. Tensile stress-strain curves of $Zr_{46.75}Cu_{45.75}Al_{6.5}Co_1$ BMG for as-cast and treated samples, respectively.

displays clear yielding with considerable macroscopic plasticity, the tensile plasticity, surprisingly, can be enhanced to $\sim 0.5\%$ (The calculated yielding strength σ_y , ultimate strength σ_f , and the plastic strain ε_p are summarized in Table 1). Moreover, the enlarged por-

Table 1. Summary of the tensile properties of the $Zr_{46.75}Cu_{45.75}Al_{6.5}Co_1$ BMG as-cast and treated, respectively

Sample	ε_p (%)	σ_y (MPa)	σ_f (MPa)
as-cast	0	1510 ± 10	1516 ± 10
treated	0.4 ± 0.05	1300 ± 10	1464 ± 10

tion of the stress-strain curve at high stresses is shown in the inset of Fig. 4. Large serrations can be recorded for the curve of the treated sample. Such serrated flow for BMGs often implies that more stable shear bands can be formed during the deformation [16]. This gives evidence for the inference that the HRRF method has a prominent effect on improving the tensile plasticity of the metallic glass.

The global view of the lateral surface fractured samples as-cast and treated are given in Fig. 5. For the as-cast sample, a fracture angle (δ) is equal to 45° with respect to the loading axis (Fig. 5a). However, as shown in Fig. 5b, the treated sample exhibits an obviously larger fracture angle (83°). As we all know, the plastic deformation of bulk metallic glass is mainly dominated by shear bands. Thus, Figs. 5c,d exhibit the high-magnification detailed micrographs of Figs. 5a,b. It is found that the as-cast BMG fails by a single main shear fracture without any other shear bands on the lateral surface, indicating that the plastic deformation occurred along the main shear bands, which caused it without any plasticity (Fig. 5c). In turn, a successive rise of shear band population with more branching, interlacing multiple and intersecting shear bands can be observed in the gauge section of the treated sample (Fig. 5d). These results further unambiguously confirmed that introducing high microstructural heterogeneity in high energy BMGs can remarkably improve the tensile plasticity.

The fractography for as-cast and treated samples is presented in Fig. 6. As depicted in Fig. 6a, the as-cast sample shows a radial-like pattern consistent with the previous studies [17, 18]. Moreover, a closer inspection of this surface clearly displays that the radial-like pattern consists of cores and ridges (Fig. 6c). In contrast to the as-cast material, it is notable that a continuous river-like pattern with smooth regions appears on the fracture surface of the treated sample (Fig. 6b). This river-like pattern always can be used as a sign to evaluate the better plasticity of BMGs [19, 20].

4. Discussion

Combining with above results, we can conclude that the tensile plasticity of BMG is closely related

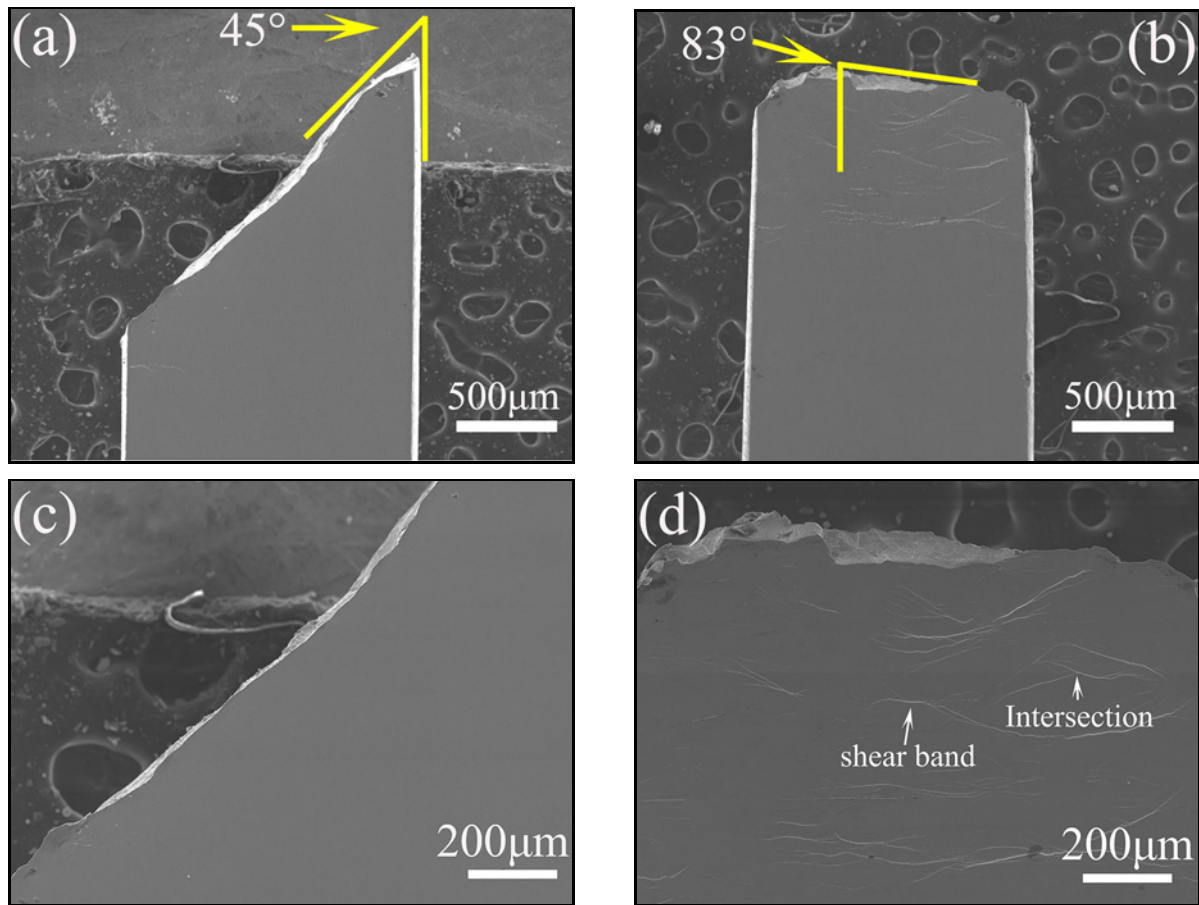


Fig. 5. (a) and (b) are the global view of the side surface fractured samples of the as-cast and treated, respectively; (c) and (d) are high-magnification detailed micrographs of the side surface fractured samples as-cast and treated, respectively.

to the energy state and microstructural heterogeneity. Thus, the question that naturally arises is how they affect tensile plasticity.

Essentially, tensile deformation is typical unconstrained behavior. This makes it more difficult to initiate shear bands than compression or bending. When the stress is applied to as-cast BMGs, the motion of atoms began along the tensile direction. A few shear transformation zones (STZs) could be activated with increasing strain, serving as the nucleation sites for shear bands [21]. The presence of these STZs significantly disturbed the original strain field, making it displace preferentially on the plane with the maximum shear stress [22]. Thus, the following STZs along the plane with maximum shear stress would be activated more easily than other regions. Subsequently, STZs gradually grew and converged into a domain shear band [23]. As the deformation continues, microporous structural defects appeared in the main shear band and evolved into microcracks. When a critical condition for fracture was coming, these microcracks would turn into cores, and the glass around microcracks would form ridges due to the thermal softening [24]. Eventually, a single shear band goes through the

entire specimen along the maximum shear plane, resulting in catastrophic fracture, as shown in Fig. 5a.

Based on our previous studies, the introduction of high energy into $Zr_{46.75}Cu_{45.75}Al_{6.5}Co_1$ BMG by HRRF can effectively enhance inhomogeneity at the microscale, displaying softening of soft regions and hardening the hard regions [12]. However, why the HRRF method can cause the rejuvenation of the BMGs. Due to the existence of the small 3 mm-diameter cavity in the HRRF device, the supercooled liquid would undergo a much pronounced rheological flow deformation during the HRRF treatment and alter the connection types of the clusters in BMGs. Such a rejuvenation process can retard the evolution of structural ordering and relaxation caused by the heating stage of the HRRF [25]. Consequently, for treated BMGs, the lower potential energy barrier of atomic moving due to the much energy content for the looser atomic arrangement in the soft regions makes STZs' activation and operation easier than the as-cast glass [13, 26]. In this scenario, many STZs are progressively activated, stimulating new strain fields to generate accordingly. These new strain fields do not induce the deflection of the atoms around the STZs migrating

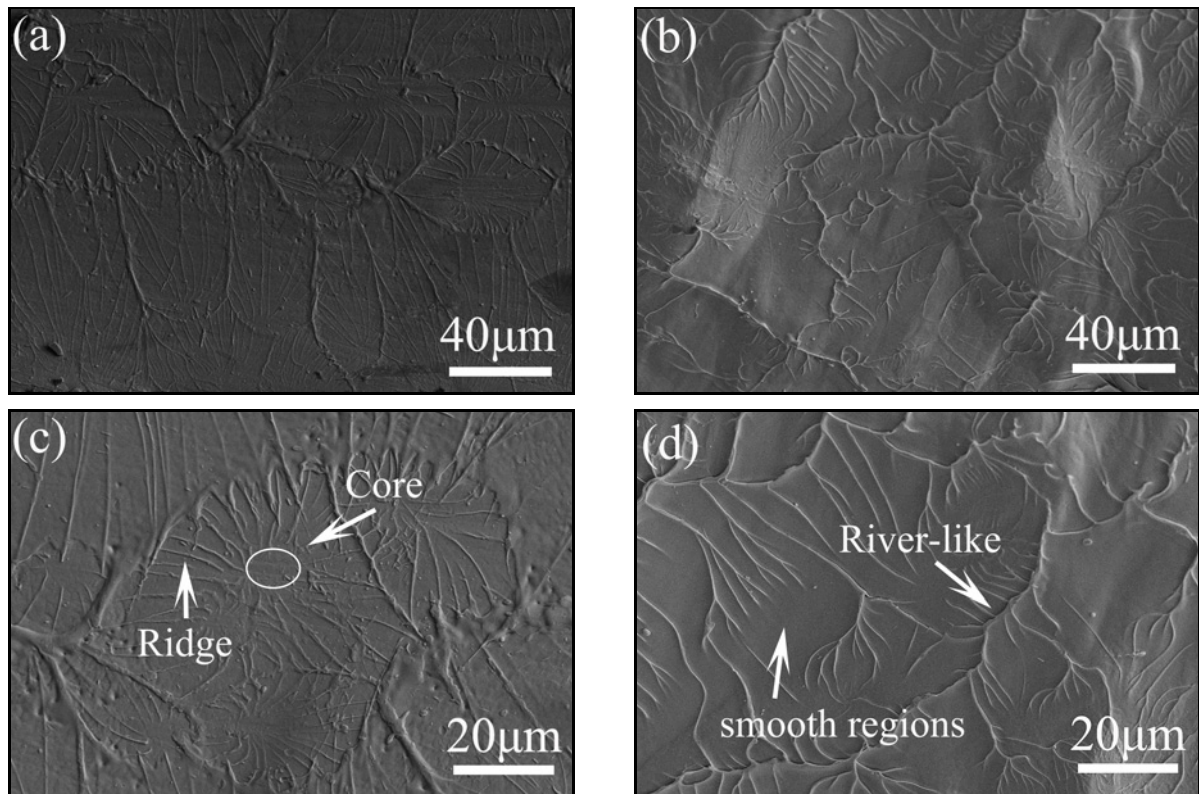


Fig. 6. (a) and (b) are global SEM images of the fracture surfaces for as-cast and treated samples, respectively; (c) and (d) are the high-magnification detailed micrographs in as-cast and treated samples, respectively.

along the maximum shear stress but prefer to move along the different shear planes [22].

Moreover, in the hard regions, a further densification of atomic packing would further alter the propagation directions and facilitates shear bands multiplication, exhibiting a typical pattern of formation of multiple shear bands (Fig. 5d) [14]. Additionally, with the increase of the tensile stress, microcracks are preferentially initiated from intersection points between these shear bands, where are peculiarly prone to occurring stress concentrations. When the specimen is about to break, these microcracks undergo plastic rheology together with the surrounding glass and then evolve into a river-shaped pattern instead of forming the radial-like pattern (Fig. 6) [15]. So, the treated BMGs can display macroscopic tensile plasticity avoiding the occurrence of failure with a single shear band as observed for the as-cast BMGs. Additionally, it is interesting that the tensile stress-strain curve of the treated BMG exhibits serrated plastic flow after yielding in Fig. 4. According to the recent research on the tensile serrated manner [27], only when the propagation length of shear bands is quite large, the materials can show serrated flow with stress drops and reloading stages. As seen in Fig. 6b, it is noteworthy that the nanoindentation data were measured at a distance of 12 μm which implies large-scaled soft and hard regions. Moreover, such struc-

tural heterogeneity on a large scale for BMGs requires a much higher critical stress for driving the propagation of shear bands in the soft and hard regions. Thus, more cooperative shear events will be activated during deformation, leading to apparent serrations on the stress-strain curves.

5. Conclusions

In summary, monolithic BMGs always show brittle fracture behavior upon tension. However, in this work, we found that macroscopic tensile plasticity for monolithic BMGs was achieved by enhancing their energy state and microstructural heterogeneity. Through this method, the lower shear band formation energy in soft regions and the complicated propagation of shear bands in hard regions contribute to generating multiple shear bands and obtaining the visible tensile plasticity. This present strategy provides a convenient and effective way to overcome the poor tensile plasticity of BMGs and greatly facilitates the industrial value of BMGs.

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