



Mechanical properties of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass with different geometric confinements



Changqin Zhang^{a,*}, Haifeng Zhang^b, Qilei Sun^a, Kegao Liu^a

^a School of Materials Science and Engineering, Shandong Jianzhu University, Jinan 250101, China

^b Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 20 June 2017

Received in revised form 1 August 2017

Accepted 30 September 2017

Available online 5 October 2017

Keywords:

Bulk metallic glass

Geometric confinements

Mechanical properties

ABSTRACT

$Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ (Vit 1) bulk metallic glass with Cu sleeves at different positions was prepared by the Cu mold casting method, and the effects of different geometric confinements offered by Cu sleeves on the mechanical properties of Vit 1 were investigated. It was found that the mechanical properties were prominently influenced by different geometric confinements and the plasticity could be modified by optimizing the positions of Cu sleeves. The results revealed that shear band initiation and propagation could be efficiently intervened by changing the radial boundary restraints, which led to quite different mechanical behaviors.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Introduction

Compared with their crystalline counterparts, metallic glasses usually exhibit high-strength and large elastic strain [1–4], but their applications as structural materials are tightly restricted until the successful preparation of bulk metallic glasses (BMGs) of centimeter-scale thickness using relatively inexpensive materials and simple processing techniques [1,5]. The plastic deformation of BMGs at room temperature is strongly influenced by their compositions [6,7], elastic properties [7], internal microstructure [8–11] and processing parameters [12,13], and it ranges between brittle behavior and limited macroscopic plasticity [1–4] to superplastic deformation [7].

Generally, the plastic deformation of BMGs upon yielding at room temperature is highly localized into shear bands [14]. These shear bands can rapidly propagate across the sample after their initiation and lead to macroscopic catastrophic fracture. Over the past decades, numerous studies have focused on enhancing the plasticity of BMGs, and it has been observed that the increased plasticity of BMGs is accompanied by the proliferation of shear bands [14–20,6]. Strategies to achieve enhanced plasticity can be categorized into internal microstructure modification and surface modification. The former is usually realized through compositional modification of the matrix and/or incorporation of second phases, which facilitates the formation of multiple shear bands during deformation [16]. The latter commonly contributes to the large plasticity by

virtue of residual stress control [15] or geometric barrier formation [14,19]. The manipulation and/or control of shear band propagation in the surface/subsurface region has quite recently attracted the interest of some scholars [14,15,19].

Geometric confinement has been successfully employed to improve the room temperature plasticity of several BMGs. For example, Yu et al. [14] and Choi et al. [21] both found an enhanced plasticity of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass (Vit 1) through changing boundary conditions by geometric confinement and soft metal plating respectively. Recently, Scudino et al. [22] evaluated the effects of boundary conditions during uniaxial compression on the mechanical behaviors of Vit 1 by using a pure Cu foil as a lubricant material between loading platens and specimens. Their results revealed that the soft metal was very effective for reducing the contact friction at the platen–specimen interface, thus leading to a remarkable increase in plastic deformation with respect to more conventional semi-fluid lubricants [23,24]. Besides, plasticity improvement of an Fe-based bulk metallic glass by geometric confinement was also reported [25], and the authors attributed the increased compressive plastic strain to the nucleation, intersection and bifurcation of multiple shear bands due to the exterior impedance of the surrounding coating.

To sum up, the introduction of geometric confinement for enhancing plasticity can be applicable to many currently available BMGs without requiring internal microstructure modification, and may be a more cost-effective method than developing new BMG alloys and/or composites with modified micro/nanostructure. To the best of our knowledge, there is little work focusing on the effects of different geometric confinements on the plasticity

* Corresponding author.

E-mail address: zhangcq@alum.imr.ac.cn (C. Zhang).

enhancement. In this work, Vit 1 with Cu sleeves at different positions was prepared by the Cu mold casting method, and the effects of different radial boundary restraints by geometric confinement on the shear band formation and the plasticity of Vit 1 were investigated. The results revealed that the mechanical properties of Vit 1 were prominently influenced by different radial boundary restraints, and the plasticity could be modified by optimizing the positions of geometric confinement.

Experimental

The material used in this work had the composition of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ (at. %). Cu sleeves in different lengths of 12.0 mm, 6.0 mm and 4.0 mm with blank diameter of 6.0 mm and bore diameter of 4.5 mm were cut from Cu pipe by electric spark cutting machine. The sleeves were soaked by light petroleum and dilute HCl aqueous solution of 5% (wt. %) respectively for two hours at room temperature, and then rinsed twice by distilled water and ethanol of 99.9% (wt. %) orderly. After that, the sleeves were fixed in the cavity of the Cu mold. The melt of the alloy was cast into the mold and rod with Cu sleeves at different positions was obtained. As for contrast, rod without Cu sleeves was also prepared by this method. The structure of the cylindrical alloys (cross-sectional surface with and without Cu sleeve) was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2500

diffractometer with Cu $K\alpha$ radiation. Netzsch DSC 404 was used to conduct thermal analysis for the Vit 1 round strips from Cu-wrapped Vit 1 specimen. The cylindrical specimens of 6.0 mm in diameter and 11.0–13.0 mm in length were cut from the as-cast rods and tested under a uniaxial compressive deformation mode at room temperature using MTS 810 material testing system with a loading strain rate of 5×10^{-4} /s. The specimen and fracture surfaces after failure were investigated by a Cambridge S360 conventional scanning electron microscopy (SEM).

Results and discussion

The composition $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ (at. %) has an excellent glass-forming ability [26], which facilitates easy manufacture

Table 1

Compression test results for Vit 1 and four types of Cu-sleeve-wrapped Vit 1 specimens.

Specimen	σ_y (MPa)	σ_{max} (MPa)	ϵ_p (%)
Vit 1	1650–1800	1900–1970	0.1–0.3
A	1460–1530	1495–1620	0.2–0.5
B	1440–1550	1470–1620	2–3
C	1470–1540	1400–1500	0.2–0.4
D	1470–1550	1500–1650	3–8

σ_y , yield stress; σ_{max} , maximum compression stress; ϵ_p , plastic strain.

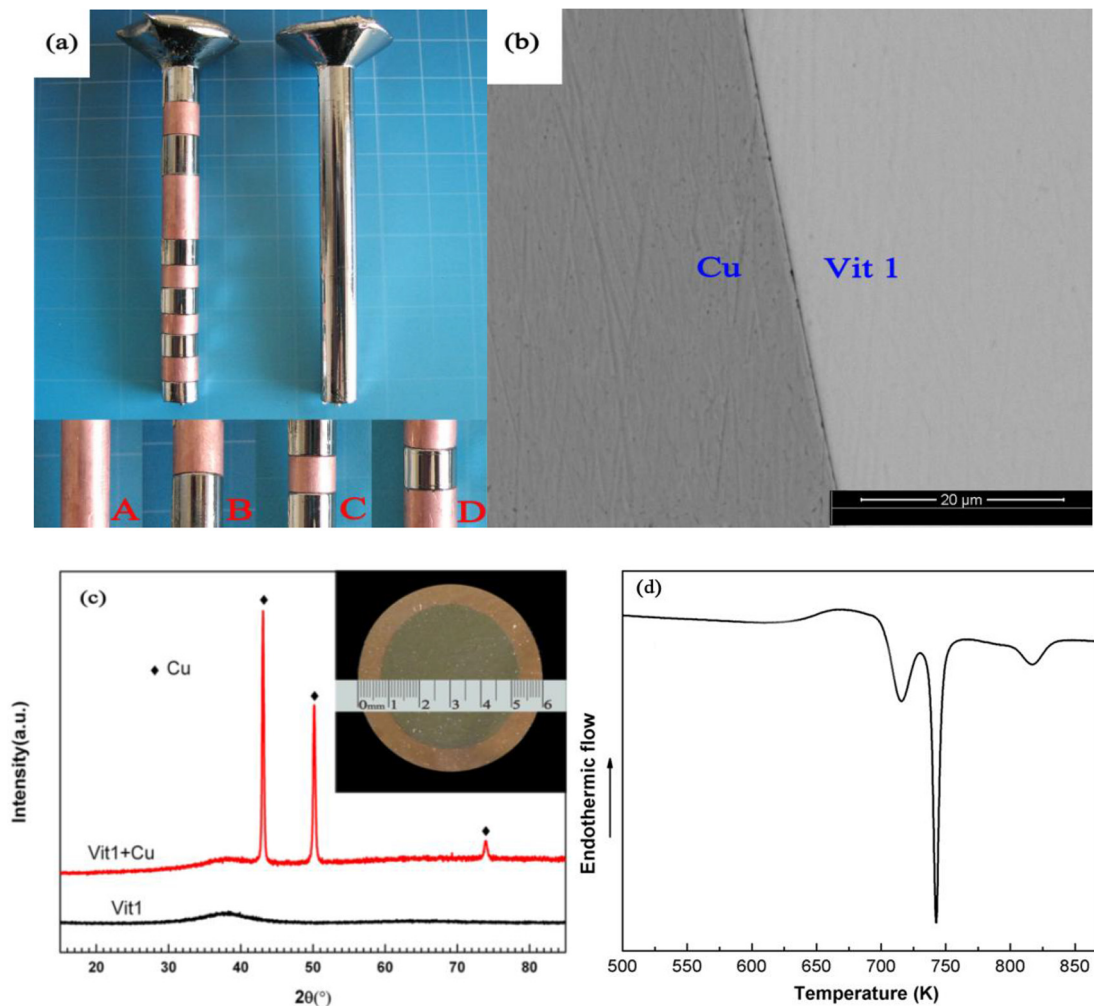


Fig. 1. (a) Digital photos of Vit 1 and Vit 1 with Cu sleeves; (b) SEM image of the interface of Cu sleeve and Vit 1; (c) XRD patterns of Vit 1 and Cu-wrapped Vit 1; (d) DSC curve of Vit 1 from Cu-wrapped Vit 1 specimen at a heating rate of 20 K/min.

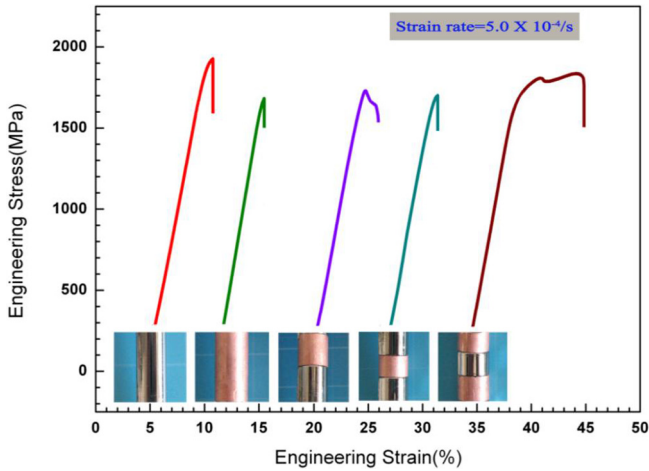


Fig. 2. Compression engineering stress-strain curves of Vit 1 and four specimens with Cu sleeve at different positions with a strain rate of 5.0×10^{-4} /s at room temperature.

of a glassy rod with shrink-fit sleeves (the sleeve can be Cu, steel and Al) by casting the melt into the mold with the fixed sleeves. Copper has a much larger coefficient of thermal expansion (CTE) 2.1×10^{-5} /K compared with that of Vit 1 (8.5×10^{-6} /K) [27]. Dur-

ing the casting process, the melt cools from processing temperature to room temperature in the mold with fixed sleeves, so the smaller CTE of Vit 1 is predicted to lead to less contraction compared with that of the Cu sleeve, which is helpful to make the sleeves wrap Vit 1 tightly. Fig. 1(a) shows the digital photos of as-cast Vit 1 rods with and without Cu sleeves. Compressive specimens with Cu sleeves at different positions, marked as A, B, C and D, were cut from the as-cast rods, and the images are also present in Fig. 1(a). The SEM image in Fig. 1(b) and the inset of Fig. 1(c) both demonstrate that the Cu sleeve wraps Vit 1 well, and no obvious gaps at their interface are observed. To examine the structure of the sample, cross-sectional surface of Vit 1 with and without Cu sleeve were scanned by XRD, and the patterns are shown in Fig. 1(c). Compared with the typical dispersive halo pattern of Vit 1, the pattern of the Vit 1 with Cu sleeve is just superposed by the diffraction peaks of Cu, and no other crystalline peaks are observed. Fig. 1(d) shows the DSC curve of Vit 1 from Cu-wrapped Vit 1 specimen at a heating rate of 20 K/min. In the curve, it can be seen that the glass transition begins at 628 K with a heat capacity maximum at slightly higher temperature. At higher temperatures, two crystallization events are seen. The onset of the first occurs at 702 K while the onset of the second is at 736 K. These thermal characteristics are basically identical to those in the DSC curve of Vit 1 reported by Peker and Johnson [26]. The XRD results together with the DSC thermal analysis confirm the fully glassy structure of the sample.

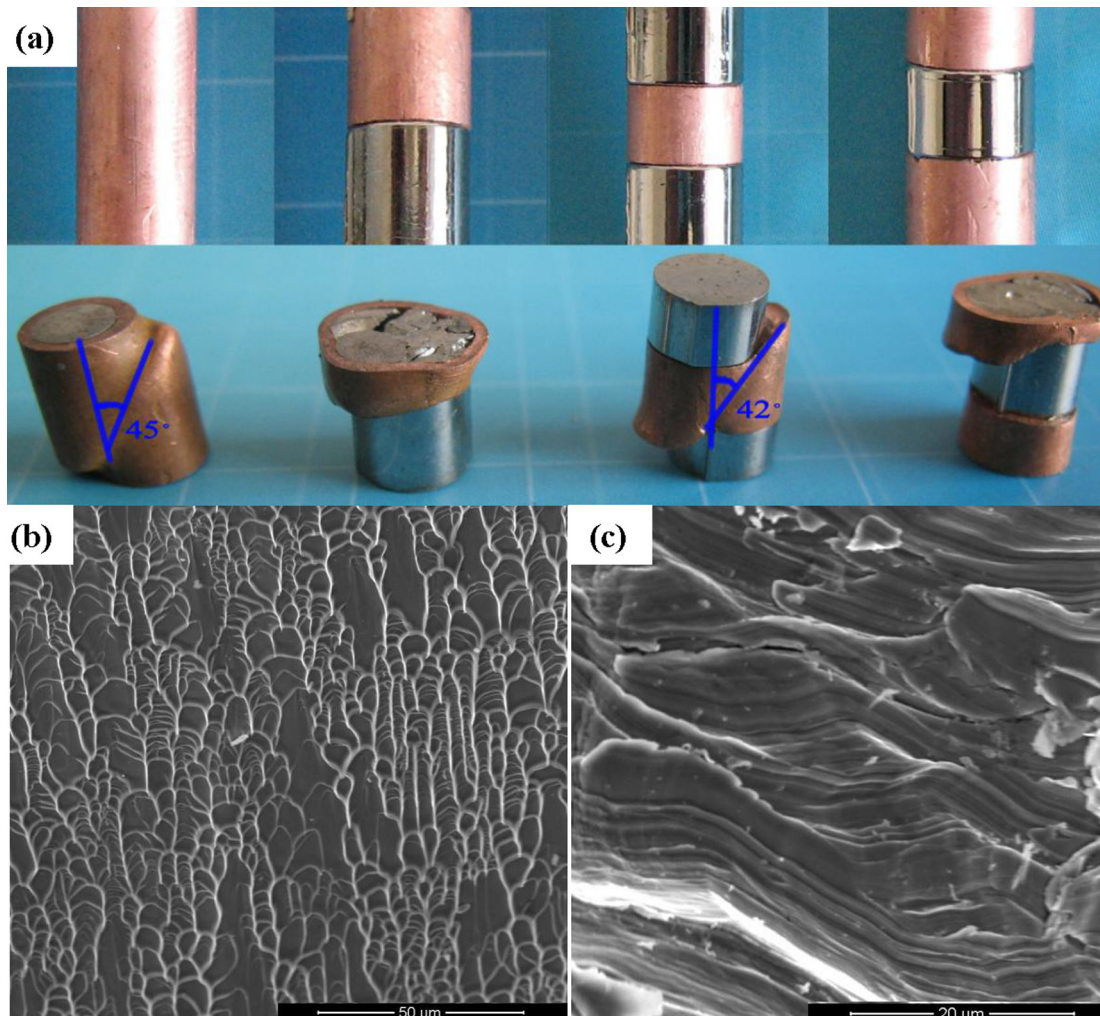


Fig. 3. (a) Digital images of the fractured sample; SEM images of (b) veinlike pattern on the fracture surface and (c) shear bands near the fracture surface of Specimen D after shear fracture.

The mechanical behaviors of at least three as-cast specimens of each type of sample were investigated under uniaxial compression tests at a strain rate of $5 \times 10^{-4}/s$ at room temperature, and the data are summarized in Table 1, combined with the stress-strain curves exemplified in Fig. 2. The specimens with Cu sleeves exhibit elastic modulus similar to those of Vit 1 within allowable error, which is verified by the parallelity of their stress-strain curves. However, the elastic strain limits and yield stress values of the specimens with Cu sleeves are all slightly smaller than those of Vit 1, just as Table 1 and Fig. 2 shows. Moreover, Vit 1 also presents prominently larger maximum compression stress values than

other specimens. These results may be closely related with the specimen diameter settings in the compression test. For Vit 1 with and without Cu sleeves, we all simply set the specimen diameter as 6 mm. Actually, however, the specimens with Cu sleeves have smaller Vit 1 diameter than those without Cu sleeves. As is well known, there are significant mechanical differences between Cu and Vit 1, and Cu generally shows much lower yield stress and maximum compression stress than Vit 1. Hence, the mechanical results of the specimens with Cu sleeves can be considered as the compromise between the mechanical properties of Cu and Vit 1. Besides, the mechanical properties of bulk metallic glasses

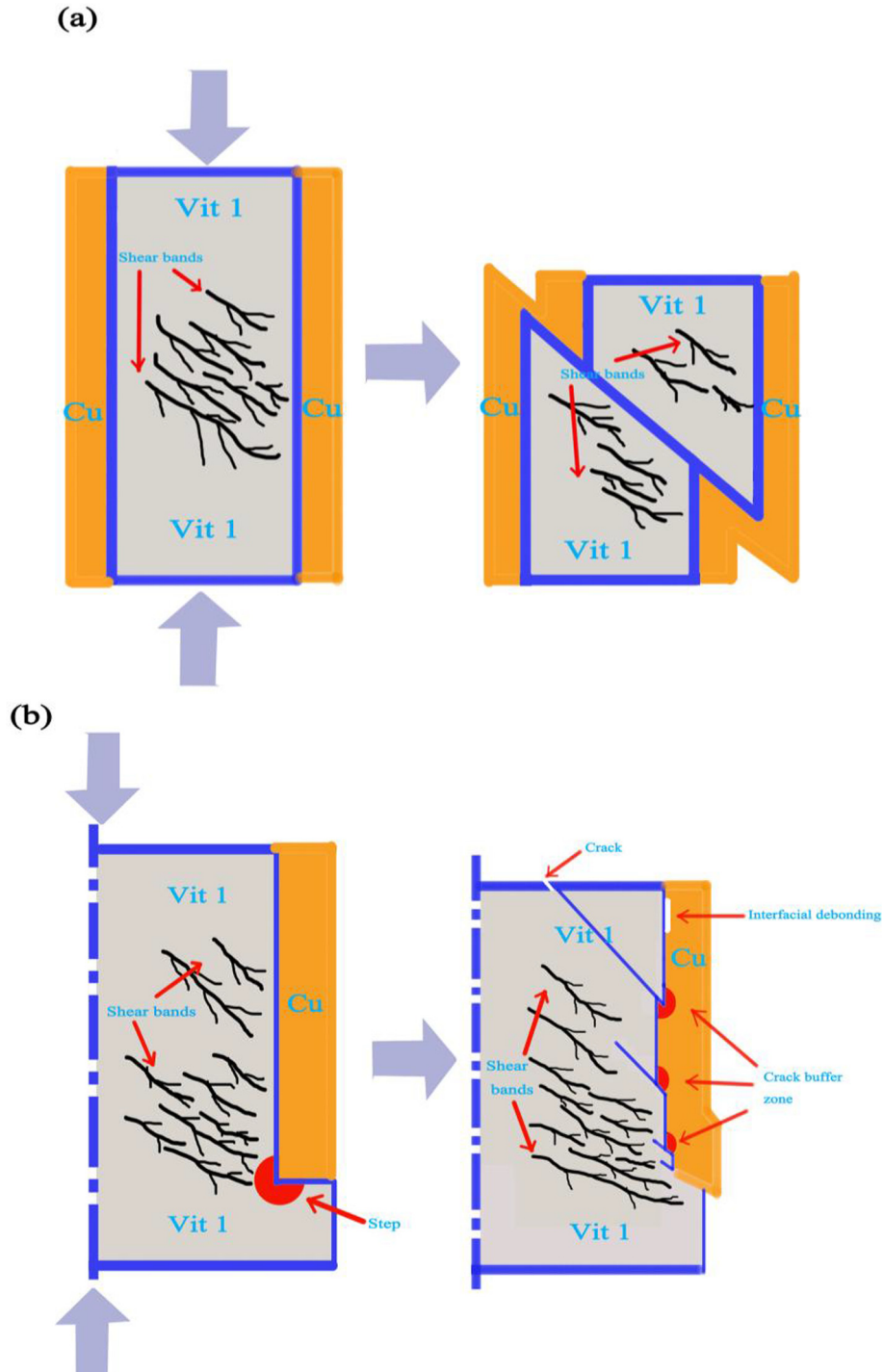


Fig. 4. Schematic drawing showing the failure mechanism for (a) Specimens A and C and (b) Specimens B and D.

are usually very sensitive to the surface state of the specimens [15]; hence, more casting flaws brought by the Cu sleeves during sample preparation may be partially responsible for these results.

Further study on the compressive data indicated that specimens with Cu sleeves at different positions possess different features. For the type of Cu sleeve wrapping the whole Vit 1 (Specimen A), Yu et al. [14] reported a 1851–2080 MPa maximum compression stress and a 2.0–8.3% plastic strain for Vit 1 specimens with a diameter of 3 mm wrapped with Cu sleeve of 0.5 mm in thickness. However, in our work, no noticeable plastic strain was observed during three tests, and the maximum compression stress was also not as large as that Yu et al. reported. The lower maximum compression stress is probably attributed to the specimen diameter settings in the compression test as mentioned above, whereas the absence of plastic strain may originate from the specimen size effect [28,29]. Specimen size has significant influences on the observed plasticity, and smaller size usually produces larger plastic deformation under the same testing conditions. In Yu's work, the real specimen size of Vit 1 was 3 mm; while in our work the specimen size can be considered to be in the range of 4.5–6 mm. According to Han's work [29], when the specimen size was large enough, no observable plastic strain can be detected; by contrast, smaller size is beneficial to the prevention of shear band propagation and the proliferation of new shear bands, which contribute a lot to the increased plasticity. Hence, it is more reasonable to ascribe the increased plasticity in Yu's work to the specimen size effect and the confinement of Cu sleeves. However, in our work, the specimen size is relatively large, and the size effect is impaired; meanwhile, only Cu-sleeve wrapping effect is not enough to prevent the rapid propagation of shear bands. As a result, Specimen A in our work exhibits no observable plastic strain. For the type of Cu sleeve wrapping the middle of Vit 1 (Specimen C), the yield stress and maximum compression stress were both decreased a lot, while the plasticity was enhanced little. Remarkable plastic strain was observed in Specimens B and D, combined with yield stress and maximum compression stress comparable to those of Vit 1. Especially for Specimen D, plastic strain could even reach to about 8%. As the compression test data show, the mechanical performance of specimens with Cu sleeves fluctuates in a wider scope than that of Vit 1 did. This phenomenon is partially attributed to the tightness of Cu sleeves wrapping Vit 1 as the results of Yu et al. implied [14], since the tightness of Cu sleeves wrapping Vit 1 may be different for the same type of specimen due to the differences in solidification conditions. On the other hand, Cu sleeves at different positions of Vit rods may lead to different solidification process of Vit 1 melt and thus make some slight differences in the microstructure, which can also cause the fluctuation of the mechanical performance of specimens.

Interestingly, specimens with Cu sleeves at different positions present completely different fracture behaviors. Fig. 3 shows the digital images of the specimens after compression. For Specimens A and C, the samples are all fractured along a single plane (shown in Fig. 3(a)) at the middle region along axial direction due to the symmetry of sample and load, revealing that a major shear band dominates the final fracture. By contrast, for Specimens B and D, there is no certain plane or direction along which the samples are fractured, and the samples are broken into several pieces. The Cu sleeves are seriously deformed and even torn, whereas the part of Vit 1 rod without Cu sleeves keeps undestroyed to the naked eyes. The typical veinlike patterns are well-developed and cracks extending from shear bands can also be observed on the surface of all the fractured samples, as Fig. 3(b) and (c) show.

Fig. 4 illustrates schematically the failure mechanism of the four radial boundary restraints. For Specimens A and C, the failure mechanism can be described as Fig. 4(a). Under compressive loading, a number of multiple shear bands initiate along the primary

shear band, which dissipates the loading energy and delays the fracture. However, boundary restraints of Cu sleeve are not enough to efficiently block the propagation of primary shear band, and the sample fails soon after a slight plastic strain. By contrast, for Specimens B and D, the catastrophic fracture is suppressed by the formation of plastic deformation region at the interface of Cu sleeves and Vit 1 in the axial direction, and the plastic deformation region can be called the “step”. As Fig. 4(b) shows, under compressive loading, a number of multiple shear bands initiate along the primary shear band, which dissipate the loading energy just as the case of Specimens A and C. The difference is that the confinement of Cu sleeve produces the step, and the step plays an important role in blocking the shear bands, which promotes the multiplication of shear bands and generates many crack buffer zones [21] near the steps. These zones can absorb the energy release during the compressive process and delays the fracture. Thus, Specimen B and D both have a high plasticity compared with Vit 1 and Specimen A and C. Especially for Specimen D, the plasticity can even reach to about 8% because of more crack buffer zones due to the blocking effect of two steps.

Conclusions

In summary, the present study demonstrates that shear band initiation and propagation can be efficiently intervened by changing radial boundary restraints, and the mechanical properties of Vit 1 can be prominently influenced by different radial boundary restraints. The results indicate the plasticity can be modified by optimizing the positions of radial boundary restraints. This work presents a simple approach of modifying the mechanical behaviors of BMGs, and is probably applicable to broad brittle metallic glassy alloys.

Acknowledgments

The authors gratefully acknowledge the financial support from the Doctor Fund of Shandong Jianzhu University (Grant No. XNBS1429), and A Project of Shandong Province Higher Educational Science and Technology Program (Grant No. J14LA54). Dr. Changqin Zhang would also like to appreciate the assistance of Dr. Na Liu for DSC measurement.

References

- [1] Johnson WL. *MRS Bull* 1999;24:42–56.
- [2] Inoue A. *Acta Mater* 2000;48:279–306.
- [3] Löffler JF. *Intermetallics* 2003;11:529–40.
- [4] Eckert J, Das J, Pauly S, Duhamel C. *J Mater Res* 2007;22:285–301.
- [5] Inoue A. *Bulk Amorphous Alloys: Preparation and Fundamental Characteristics*. (Trans Tech Publications, 1998).
- [6] Schroers J, Johnson WL. *Phys Rev Lett* 2004;93:255506.
- [7] Liu XF, Wang RJ, Zhao DQ, Pan MX, Wang WH. *Appl Phys Lett* 1903;91 (2007):041901–41904.
- [8] Kim HS, Hong SI. *Acta Mater* 1999;47:2059–66.
- [9] Eckert J, Reger-Leonhard A, Weiss B, Heilmaier M. *Mater Sci Eng A* 2001;301:1–11.
- [10] Szuets F, Kim CP, Johnson WL. *Acta Mater* 2001;49:1507–13.
- [11] Lee ML, Li Y, Schuh CA. *Acta Mater* 2004;52:4121–31.
- [12] Zhu ZW, Zheng SJ, Zhang HF, Ding BZ, Hu ZQ, Liaw PK, Wang YD, Ren Y. *J Mater Res* 2008;23:941–8.
- [13] Zhu ZW, Zhang HF, Wang H, Ding BZ, Hu ZQ, Huang H. *J Mater Res* 2009;24:3109–15.
- [14] Yu P, Liu YH, Wang G, Bai HY, Wang WH. *J Mater Res* 2007;22:2384–8.
- [15] Zhang Y, Wang WH, Greer AL. *Nat Mater* 2006;5:857.
- [16] Hofmann DC, Suh JY, Wiest A, Duan G, Lind ML, Demetriou MD, Johnson WL. *Nature* 2008;451:1085.
- [17] Liu YH, Wang G, Wang RJ, Zhao DQ, Pan MX, Wang WH. *Science* 2007;315:1385.
- [18] Fan C, Inoue A. *Appl Phys Lett* 2000;77:46.
- [19] Li HQ, Li L, Fan C, Choo H, Liaw PK. *J Mater Res* 2007;22:508.
- [20] Lewandowski JJ, Shazly M, Nouri AS. *Scripta Mater* 2006;54:337.
- [21] Choi YC, Hong SI. *Scripta Mater* 2009;61:481–4.

- [22] Scudino S, Surreddi KB, Wang G, Eckert J. *Scripta Mater* 2010;62:750–3.
- [23] Lewandowski JJ, Lowhaphandu P. *Phil Mag A* 2002;82:3427–41.
- [24] Wu WF, Li Y, Schuh CA. *Phil Mag* 2008;88:71.
- [25] Chen W, Chan KC, Guo SF, Yu P. *Mater Lett* 2011;65:1172–5.
- [26] Peker A, Johnson WL. *Appl Phys Lett* 1993;63:2342–4.
- [27] Conner RD, Dandliker RB, Johnson WL. *Acta Mater* 1998;46:6089–102.
- [28] Xie S, George EP. *Intermetallics* 2008;16:485–9.
- [29] Han ZH, He L, Zhong MB, Hou YL. *Mater Sci Eng A* 2009;513–514:344–51.