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Enhanced plasticity of Fe-based bulk metallic glass by tailoring microstructure

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Abstract: The room temperature compressive plasticity of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ bulk metallic glass (BMG) was improved from 0.5% to 1.8% by increasing the sample diameter from 1.5 mm to 2.0 mm. With increasing the sample diameter to 2.0 mm, a heterogeneous microstructure with in-situ formed α-Fe dendrite sparsely distributed in the amorphous matrix can be attained. This heterogeneous microstructure is conceived to be highly responsible for the enhanced global plasticity in this marginal Fe-based BMG.
Key words: bulk metallic glass; composite; rapid-solidification; mechanical property

1 Introduction

Fe-based bulk metallic glasses (BMGs), which possess ultrahigh strength, relatively low cost and excellent magnetic softness, can be exploited for future engineering materials [1,2]. However, the most disappointing shortcoming of these materials is the severe brittleness at room temperature, which has restricted their structural and functional applications. In order to overcome this critical problem, great efforts have been devoted to improve the plasticity by compositional and structural design: 1) intrinsic self-toughening by tailoring the elastic properties with a higher Poisson ratio or a lower shear to bulk modulus ratio [3−5]; and 2) extrinsic toughening by geometric confinement [6] or introducing a composite structure with different length scale heterogeneities, such as medium range ordering [7], liquid phase separation[8], nano- or micro-crystalline phase [9].

More recently, we have successfully fabricated an in situ formed α-Fe dendrite/Fe-based BMG composite via carefully adjusting the alloy composition [10]. The crystalline phase uniformly dispersed within the glass matrix turns out to behave as an obstacle to the rapid propagation of the shear bands, giving rise to a pronounced compressive plasticity above 30% (for specimens with 1 mm rod in diameter). It has been appreciated that a larger sized BMG prepared under a lower cooling rate is usually more susceptible to catastrophic failure [11]. From the standpoint of structural applications, however, it is worthwhile to develop larger sized Fe-based BMGs coupled with higher room-temperature plasticity. In the present study, we investigate the influence of cooling conditions by controlling the sample size on the structure evolution and mechanical properties of an $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy [10], which was selected primarily due to the easy precipitation of heterogeneities during solidification. The underlying mechanism of the improved plasticity achieved in the larger sized Fe-based BMG is discussed in terms of microstructure observation.

2 Experimental

Alloy ingots with a nominal composition of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ were prepared by arc melting of raw materials under a titanium metal gettered argon

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atmosphere. Sample rods with diameters of 1.5 and 2.0 mm were produced by suck casting the molten alloy into water-cooling copper moulds. The structure of the as-cast alloys was identified by X-ray diffraction (XRD, Philips X'Pert PRO) and transmission electron microscopy (TEM, JEOL 2010F). The glass transition and crystallization behaviors were investigated in a differential scanning calorimeter (PE, DSC−7) under flowing purified argon at a heating rate of 20 K/min. The uniaxial compressed BMG samples with 1.5 and 2.0 mm in diameter were prepared with a length-to-diameter ratio of 2:1. Room-temperature compression tests were performed on a MTS810 testing machine at a strain rate of 10^{-4} s^{-1}. At least five specimens were tested for each sample to ensure the reproducibility of the results. The fracture morphologies were examined on a scanning electron microscope (SEM).

3 Results

Figure 1(a) shows the XRD patterns of the as-cast $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ samples with two different diameters (1.5 and 2.0 mm). It can be observed that all the alloys can be cast into fully amorphous phase except for a typical broad halo diffraction peak, confirming the absence of crystalline phase in this alloy at the sensitivity of XRD techniques. Figure 1(b) displays the DSC traces of the BMGs, from which a distinct glass transition was detected, followed by a wide supercooled liquid region before multi-crystallization. Both the glass transition temperature (T_g) and the onset crystallization temperature (T_x), which are summarized in Table 1, rise gradually with the increase of sample size, reflecting a higher thermal barrier for the nucleation of crystalline phase [12].

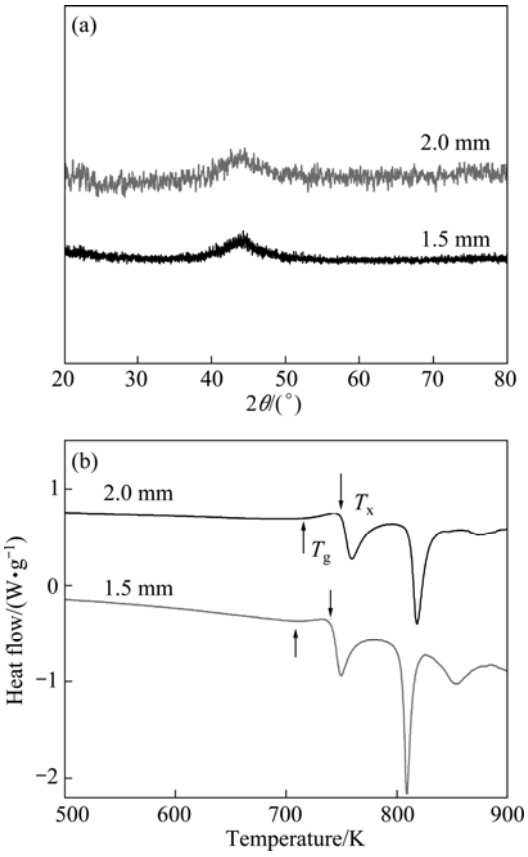

Fig. 1 XRD patterns of as-cast $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ (a) and DSC curves of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy rods (b) with diameters of 1.5 mm and 2.0 mm, respectively

Table 1 Thermal and mechanical properties of as-cast $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy rods with diameters of 1.5 mm and 2.0 mm, respectively

d/mm	T_g/K	T_x/K	ΔT_x/K	σ_c/GPa	ε_p/%
1.5	708	740	32	3.2	0.5
2.0	716	749	33	3.1	1.8

Figure 2 shows the room temperature engineering stress — strain curves of the two different scaled $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ specimens under uniaxial compression. The curves have been shifted apart from each other so as to avoid overlapping for a clearer observation. The compressive strength, σ_c, and plastic strain, ε_p, of the $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloys with different sizes are listed in Table 1. It is interesting to notice that the plastic strain of this alloy increases from 0.5% for 1.5 mm to 1.8% for 2.0 mm. The plasticity of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy with a diameter of 2.0 mm is one of the largest plasticity among all the 2.0 mm Fe-based glassy rods reported up to now. Previous studies have reported that the Fe-based BMGs with enhanced plasticity usually have a small size of 1.5 mm or less in diameter [13,14]. If the sample size increased, a ductile-to-brittle transition would occur significantly. However, the present results clearly indicate that the larger sample permits an increase in certain plasticity.

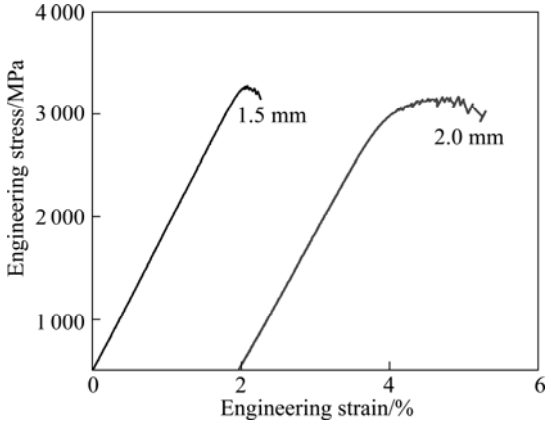

Fig. 2 Engineering stress—strain curves of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy rods with diameters of 1.5 and 2.0 mm under room-temperature compression

The possible reason of this unusual phenomenon will be discussed in detail later.

Figure 3 displays the SEM images of the fracture surfaces of the $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloys with different diameters. The 1.5 mm-diameter sample exhibited a lot of fragments shown in Fig. 3(a) after fracture, manifesting a "fragmentation mode" which was previously reported in other brittle Fe-based BMGs [15]. By carefully observing the fragments after failure, numerous vein-like patterns were formed to arrange in long narrow ridges, as shown in Fig. 3(b), akin to those happened in brittle Fe-based BMGs with less than 1% plasticity reported previously [3,16]. In general, fragmentation deformation feature is more easily to be discovered in BMG samples with larger sizes. Strikingly, in the present study, the larger sample displayed a visible shear banding deformation fashion shown in Fig. 3(c), namely, the plastic deformation is highly localized into shear bands, which propagated rapidly until a sudden final fracture. The exposed shear-off surface reveals robust plastic flow patterns, as shown in Fig. 3(d), which has always been observed in those reported for ductile metallic glasses.

In this work, the plasticity of the Fe-based BMG can be raised by increasing the sample size. Commonly, the mechanism of improved plasticity of BMG is mostly attributable to the heterogeneous structure [7−9], which is beneficial to the shear formation and impeding its propagation effectively. This simulates us to re-examine the microstructure of the present $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy. The rod with a diameter of 1.5 mm exhibits the featureless SEM appearance, demonstrating a fully amorphous microstructure [10]. However, from the SEM image for the alloy rod with 2.0 mm in diameter, it can be seen that a tiny amount of dendrites were embedded in the glassy matrix, as shown in Fig. 4(a). Due to the system with very small crystals embedded in an amorphous matrix, the XRD measurement may not be able to clearly verify the microstructure [17]. The dendritic crystalline phase accounts for approximately 3% in volume fraction of the entire sample, according to the area analysis from the SEM micrographs. To further elucidate the microstructure of this alloy, TEM technique was employed. Figure 4(b) shows the selected area electron diffraction (SAED) pattern of the dendritic phase taken along [111] zone axis. It was found to consist of a BCC phase with a lattice constant of 2.87 Å, which is thought to correspond to BCC α-Fe. Figure 4(c) shows the SAED pattern obtained using TEM recorded from the matrix region, indicating the typical characteristics of a glassy phase.

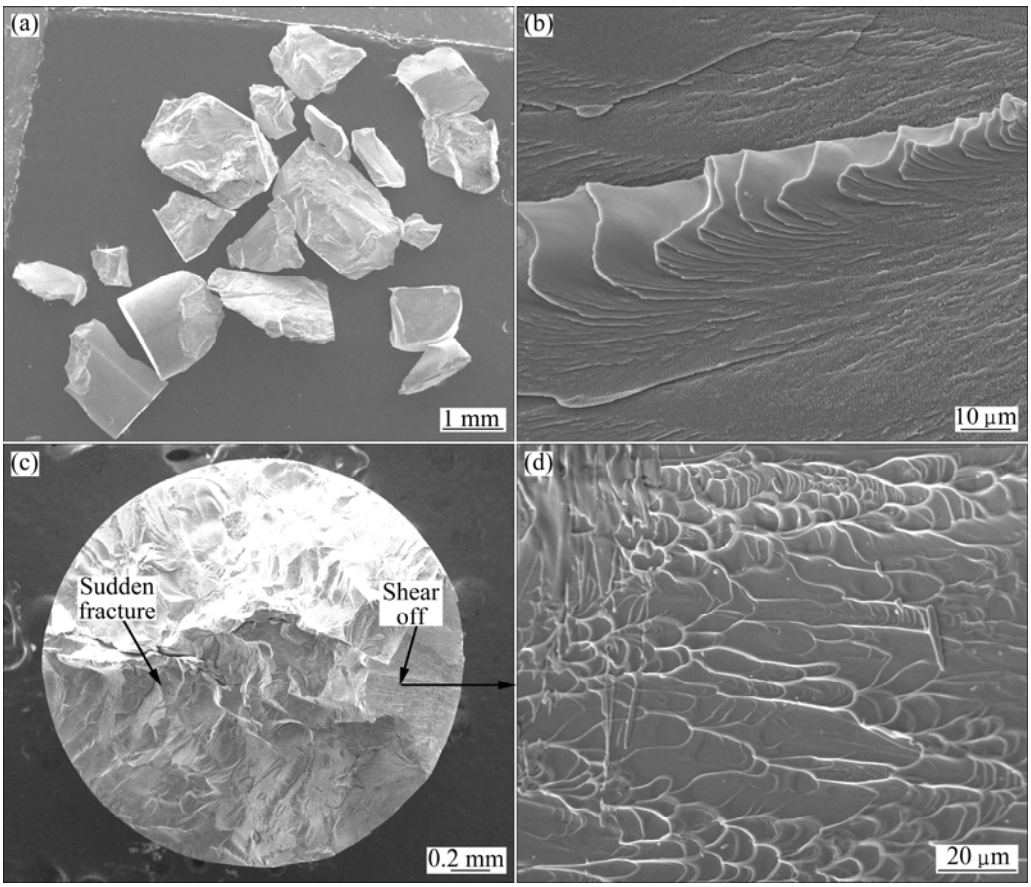

Fig. 3 SEM images of fracture surfaces of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy rods with 1.5 mm (a, b) and 2.0 mm (c, d) in diameter

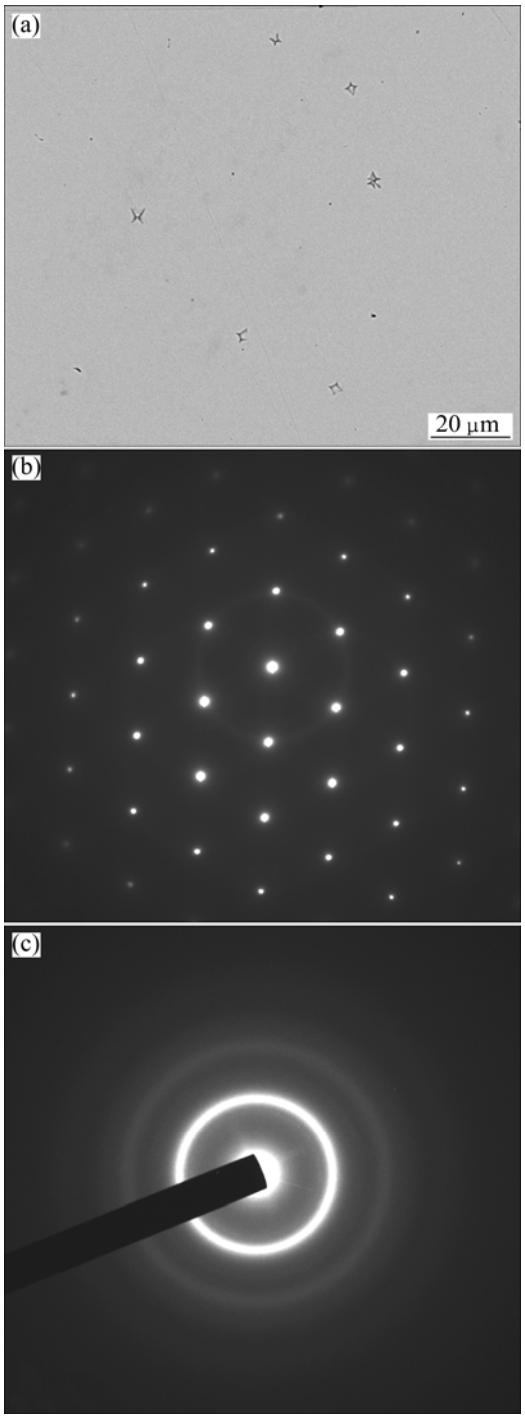

Fig. 4 High-magnification SEM image of $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy with 2.0 mm in diameter (a) and SAED pattern of dendrite phase taken along [111] zone axis (b) and SAED pattern from matrix region (c)

4 Discussion

Through carefully adjusting the alloy composition, we have obtained an in situ α-Fe reinforced Fe-based BMG matrix composite previously [10]. In this work, the microstructure of a fixed $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ alloy was variously tailored by means of tuning the cooling rate during solidification, which was accomplished via increasing the sample size. Faster cooling yields a fully amorphous structure at 1.5 mm scale. A slow cooling rate with the increment of the sample size is able to alter the as-cast amorphous sample into an in situ tiny α-Fe dendrite/BMG composite, which can be named Fe-based marginal BMG, in the case of a specimen with 2.0 mm in diameter.

It is known that the elastic modulus of the inclusion is very important for the BMG toughening, especially for the BMG matrix composite under tensile conditions. HOFMANN et al [18] proposed that the shear modulus of the reinforced phase in an as-cast composite is smaller than that of the amorphous matrix, which enables attraction and/or arrest of shear bands by the crystalline phases and hence results in tensile ductility. Moreover, WU et al [19] suggested that the hardness disparity between the crystalline phase and the amorphous matrix is also a significant reason for the enhanced plastic deformability of a BMG composite. Due to the ferromagnetic signature interference, it is difficult to accurately measure the elastic modulus of the second phase and the glassy phase by resonant ultrasound spectroscopy as explained by GU et al [4]. Herein, the nanoindention testing was carried out to clarify the hardness of the dendrites and amorphous phase. We selected the $Fe_{77}Mo_5P_9C_{7.5}B_{1.5}$ BMG matrix composite with a diameter of 1.5 mm to compare the hardness disparity [10], due to the fact that the α-Fe dendrites were too tiny to measure, as seen in Fig. 4(a). Figure 5 illustrates the typical load—depth curves of $Fe_{77}Mo_5P_9C_{7.5}B_{1.5}$ alloy under a load of 330 mN. It is noted that the nanoindentation hardness of the dendrite phase (6.4 GPa) is substantially lower than that of the amorphous phase (8.2 GPa) loading, once the soft phase yields, slip systems existing in dendrites are activated and readily accommodate the plastic strain,

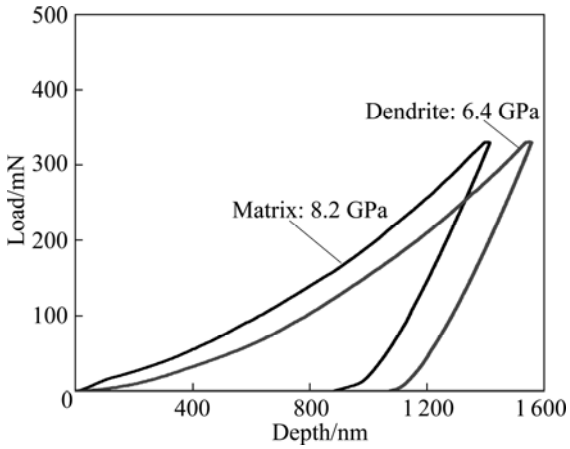

Fig. 5 Load—depth curves of nanoindentation under 330 mN for $Fe_{77}Mo_5P_9C_{7.5}B_{1.5}$ BMG composite with diameter of 1.5 mm [10]

evidenced by the steps which are usually formed at the interface between the soft dendrites and the glass matrix to harmonize the strain, and consequently lead to the enhancement of the compressive plasticity [20].

Recently, CHENG et al [21] have demonstrated that the mechanical properties of the composites are closely related to the length scales of the precipitated phase. With the increase in the characteristic size scale, the plasticity of the BMG matrix composites can be significantly enhanced. HOFMANN et al [18] argued to stabilize the shear banding behavior through introducing inhomogeneity as a special microstructural length scale L. Stabilization requires that $L \approx R_p$, where R_p is correlated with $(K_c/\sigma_y)^2$ for different metallic glasses; K_c and σ_y denote the notch fracture toughness and the yielding strength, respectively. For the current studied Fe-based BMG, the value of R_p is estimated to be 6 μm [22] and the fitting length scale L of the precipitated α-Fe dendrite phase is about 5 μm derived from the high-magnification SEM image. Accordingly, the shear bands are believed to interact with the ductile α-Fe dendrite phase during the propagation and their propagation direction is deflected, thus delaying the shear banding instability and enhancing the global plasticity.

As discussed above, the marginal Fe-based bulk metallic glass (2.0 mm in diameter) with superior plasticity (~2%) has been achieved by controlling the microstructure evolution. This finding in the present work is suggestive for a promising method to exploit large sized Fe-based marginal BMGs with increased plasticity [23].

The present BMG is an FeP-based one, where it has been proven that both of ductile secondary crystalline phases and impurties may precipitate [22]. Thereby, if one continues to further increase the sample size, in all probability, the precipitated impurities can predominantly pose a threat to the mechanical properties of the amorphous matrix/crystaline phase interfaces and this role overweighs the ameliorative effect of the ductile secondary phases on the ductility enhancement during the plastic deformation of the BMG composite. As a result, a further increase of the sample size might only deteriorate or even devastate the plastic deformability of the entire BMG sample. Giving a certain volume fraction, the morphology and the size of the precipitated crystalline phase play important roles in the mechanical properties of BMG matrix composites. There is no doubt that further work is required to further understand the micro-mechanisms of plastic deformation in the current marginal BMG.

5 Conclusions

1) Bulk metallic glass $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ rods with diameter of 1.5 and 2.0 mm were, respectively, synthesized by copper mold casting method. With increasing the sample diameter to 2.0 mm, a heterogeneous microstructure with a little bit of in-situ formed α-Fe dendrite can be obtained.

2) The marginal Fe-based bulk metallic glass (2.0 mm in diameter) with good plasticity (1.8%) has been achieved by controlling the microstructure evolution. These findings will open the way for the enhanced plasticity of marginal BMG at large size.

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References

[1] INOUE A, SHEN B L, YAVARI A R, GREER A L. Mechanical properties of Fe-based bulk glassy alloys in Fe–B–Si–Nb and Fe–Ga–P–C–B–Si systems [J]. J Mater Res, 2003, 18: 1487−1492.

[2] GUO S F, LIU L, LIN X. Formation of magnetic Fe-based bulk metallic glass under low vacuum [J]. J Alloys Compd, 2009, 478: 226−228.

[3] GU X J, MCDERMOTT A G, POON S J, SHIFLET G J. Critical Poisson's ratio for plasticity in Fe–Mo–C–B–Ln bulk amorphous steel [J]. Appl Phys Lett, 2006, 88: 211905.

[4] GU X J, POON S J, SHIFLET G J, WIDOM M. Ductility improvement of amorphous steels: Roles of shear modulus and electronic structure [J]. Acta Mater, 2008, 56: 88−94.

[5] YAO J H, WANG J Q, LI Y. Ductile Fe–Nb–B bulk metallic glass with ultrahigh strength [J]. Appl Phys Lett, 2008, 92: 251906−251908.

[6] CHEN W, CHAN K C, GUO S F, YU P. Plasticity improvement of an Fe-based bulk metallic glass by geometric confinement [J]. Mater Lett, 2011, 65: 1172−1175.

[7] PARK J M, NA J H, KIM D H, KIM K B, MATTERN N, KUHN U, ECKERT J. Medium range ordering and its effect on plasticity of FeMnBYNb bulk metallic glass [J]. Philosophical Magazine, 2010, 90: 2619−2633.

[8] YAO K F, ZHANG Q S. Fe-based bulk metallic glass with high plasticity [J]. Appl Phys Lett, 2007, 90: 061901−061903.

[9] MAKINO A, LI X, YUBUTA K, CHANG C T, KUBOTA T, INOUE A. The effect of Cu on the plasticity of Fe–Si–B–P-based bulk metallic glass [J]. Scr Mater, 2009, 60: 277−280.

[10] GUO S F, LIU L, LI N, LI Y. Fe-based bulk metallic glass matrix composite with large plasticity [J]. Scr Mater, 2010, 62: 329−332.

[11] WU Y, LI H X, JIAO Z B, GAO J E, LU Z P. Size effects on the compressive deformation behaviour of a brittle Fe-based bulk metallic glass [J]. Phil Mag Lett, 2010, 90: 403−412.

[12] KUMAR G, OHKUBO T, HONO K. Effect of melt temperature on the mechanical properties of bulk metallic glasses [J]. J Mater Res, 2009, 24: 2353−2360.

[13] ZHANG T, LIU F J, PANG S J, LI R. Ductile Fe-based bulk metallic glass with good soft-magnetic properties [J]. Mater Trans, 2007, 48: 1157−1160.

[14] GUO S F, LI N, ZHANG C, LIU L. Enhancement of plasticity of Fe-based bulk metallic glass by Ni substitution for Fe [J]. J Alloys

Compd, 2010, 504: s78−s81.
[15] WU F F, ZHANG Z F, SHEN B L, MAO S X, ECKERT J. Size effect on shear fracture and fagmentation of a $Fe_{57.6}Co_{14.4}B_{19.2}Si_{4.8}Nb_4$ bulk metallic glass [J]. Adv Eng Mater, 2008, 10: 727−730.
[16] QIU K Q, PANG S J, REN Y L, ZHANG H B, MA C L, ZHANG T. Fe-based bulk metallic glasses with a larger supercooled liquid region and high ductility [J]. Mater Sci Eng A, 2008, 498: 464−467.
[17] JIANG J Z, SAIDA J, KATO H, OHSUNA T, INOUE A. Is $Cu_{60}Ti_{10}Zr_{30}$ a bulk glass-forming alloy? [J]. Appl Phys Lett, 2003, 82: 4041−4043.
[18] HOFMANN D C, SUH J Y, WIEST A, DUAN G, LIND M L, DEMETRIOU M D, JOHNSON W L. Designing metallic glass matrix composites with high toughness and tensile ductility [J]. Nature, 2008, 451: 1085−1089.
[19] WU Y, XIAO Y H, CHEN G L, LIU C T, LU Z P. Bulk metallic glass composites with transformation-mediated work-hardening and ductility [J]. Adv Mater, 2010, 22: 2770−2773.
[20] QIAO J W, ZHANG Y, LIAW P K, CHEN G L. Micromechanisms of plastic deformation of a dendrite/Zr-based bulk-metallic-glass composite [J]. Scr Mater, 2009, 61: 1087−1090.
[21] CHENG J L, CHEN G, XU F, DU Y L, LI Y S, LIU C T. Correlation of the microstructure and mechanical properties of Zr-based in-situ bulk metallic glass [J]. Intermetallics, 2010, 18: 2425−2430.
[22] GUO S F, CHAN K C, LIU L. Notch toughness of Fe-based bulk metallic glass and composites [J]. J Alloys Compd, 2011, 509: 9441−9446.
[23] ZHANG L C, JIANG F, ZHAO Y L, ZHANG J F, HE L, SUN J. Stable shear of $Cu_{46}Zr_{47}Al_7$ bulk metallic glass alloy by controlling temperature rise [J]. Mater Sci Eng A, 2010, 527: 4122−4127.

合金微结构的调整对铁基块体金属玻璃室温塑性的影响

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摘 要：报道一种新奇的现象，即随着 $Fe_{75}Mo_5P_{10}C_{8.3}B_{1.7}$ 块体金属玻璃的直径从 1.5 mm 增加到 2.0 mm，其室温压缩塑性反而从 0.5%增加到 1.8%。这主要归因于随着铁基块体金属玻璃样品直径的增加，原位形成了零星的 α-Fe 枝晶相，这种在边缘化的块体金属玻璃中出现的异质结构是提高当前铁基块体金属玻璃室温塑性的主要原因。

关键词：块体金属玻璃；复合材料；快速凝固；力学性能

(Edited by YANG Hua)