Original Article

Thermoplastic deformation behavior of a Fe-based bulk metallic glass within the supercooled liquid region

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Fe₄Cr₁₂Co₂Mo₁₄C₁₂B₈Y₂ (Fe–B9) bulk metallic glass (BMG) rods with high glass forming ability and large supercooled liquid (SCL) region were fabricated by arc melting and suction casting. The amorphous state of these Fe–B9 BMG rods was ascertained by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The thermoplastic deformation behavior of these BMG rods was studied by using the hot compression test at different temperatures (873 K, 883 K, 893 K, and 903 K in the SCL region) and strain rates (1 × 10⁻³–5 × 10⁻² s⁻¹). The results of the hot compression test reveal that the flow stress of Fe–B9 BMG reduces systematically with increasing temperature and decreasing strain rate. Strain sensitivity exponent (m) values of the Fe–B9 BMG were calculated to be about 0.36–0.59 in the SCL region, indicating that Fe–B9 BMG possesses superplasticity. Overall, the optimum working conditions of thermoplastic forming for Fe–B9 BMG can be achieved by compressively deforming the sample with a constant strain rate of 2.5 × 10⁻³ s⁻¹ at a temperature from 873 to 883 K.

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1. Introduction

Fe-based bulk metallic glasses (BMGs), also called bulk amorphous steels, have attracted the attention of many scientists due to their unique properties, such as the ultrahigh hardness and fracture strength, superior wear resistance, excellent corrosion resistance, good magnetic properties, and higher thermal stability for engineering applications [1–10]. In addition, Fe-based BMG can be fabricated by using industrial raw materials (pig-iron and boron ferrous alloy), leading to a reduced production cost. Recently, some researchers have used Fe-based BMG to make surgical blades and apply a metallic glass thin film (MGTF) coating on the surgical blades.

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The edge-tip of both BMG-made and MGTF-coated blades is extremely flat. The surface roughness of the blade edge can decrease down to nanoscale due to the amorphous nature with no crystal defects. As a result, the cutting sharpness was enhanced significantly in comparison with commercial surgical blades [11–14]. In addition, the Fe-based BMG/MGTF blades exhibit much better cutting durability than the Zr-based BMG/MGTF blades [11] due to their ultrahigh hardness and superior wear resistance. Therefore, workers of amorphous alloys suggest that the Fe-based BMG can be a priority choice for surgical tools and other biomedical related parts.

One of the most regarded features of metallic glasses is thermoplastic forming (TPF). This is typically carried out in the supercooled liquid region (SCL) between the glass transition temperature (Tg) and the crystallization temperature (Tc), where the metallic glass exhibits very low viscosity (~10⁻⁸ Pa s) [15,16]. This TPF ability has been used for a wide range of applications, such as writing-erasing, blow molding, and surface embossing, particularly for complex-shaped micro-components of near-net-shape fabrication [16–25]. Fe-based BMGs do not easily form complex structures by traditional machine processing due to their ultrahigh hardness and relative brittleness compared with Zr-based BMGs. Therefore, the TPF process may be a good way to make the Fe-based BMG miniature parts for engineering and medical applications. Several Fe-based BMG TPF systems, such as Co₁₅Fe₁₅Nb₁₂B₃₀ [26], Fe₇₈B₁₃Si₁₉ [27], Fe₄₀Co₂₀Ni₁₅P₁₀C₁₀B₃ [28], have been developed. However, these alloys exhibit too low a glass-forming ability (GFA) to perform a TPF process for feasible engineering applications.

In the literature, Fe₂₁Co₁₀Cr₁₅Mo₁₄C₁₂B₈Y₂ BMG [29] was the first reported to have high GFA (critical size 16 mm), high fracture strength (3500 MPa), and ultrahigh hardness (1250 HV). However, this Fe-based BMG exhibits a small SCL (ΔTₓ = 38 K), and is not easily used with TPF technology. Furthermore, by modifying the carbon/boron ratio from the previous Fe-based BMG, another Fe-based BMG, Fe₄₁Cr₁₅Co₉Mo₁₄C₁₂B₈Y₂ (Fe-B9) with wide SCL (ΔTₓ = 81 K) has been explored [11]. This Fe-B9 BMG presents superior corrosion resistance in simulated body fluids, compared with 316 stainless steel. In this study, we investigate the thermoplastic deformation behavior of Fe₄₁Cr₁₅Co₉Mo₁₄C₁₂B₈Y₂ BMG with industrial raw materials and characterize the process window of thermoplastic forming for further engineering applications.

1.1. Experimental procedure

The alloy ingots based on the compositions of Fe₄₁Cr₁₅Co₉Mo₁₄C₁₂B₈Y₂ (Fe-B9) in atomic percentage were first prepared by arc melting of the appropriate mixture of ferrous alloys and pure elements, such as pig iron (94.2 wt. % Fe, 4.6 wt. % C, 1 wt. % Si, 0.2 wt. % P), ferro-boron (77.45 wt. % Fe, 21 wt. % B, 0.55 wt. % C), Cr₁₅C₁₂, Cr, Co, Mo, Fe, and Y (purity > 99%) under a Ti-gettered argon atmosphere. The ingots were re-melted at four times in the arc-melting furnace under purified argon atmosphere to ensure their homogeneity. Sample rods with a diameter of 2–4 mm were produced by suction-cast into the water-cooling Cu mold under a high purity Ar atmosphere. Amorphous state of the BMG rods was ascertained by X-ray diffraction analysis (XRD, Bruker D8A X-ray diffractometer) with monochromatic Cu-Kα radiation. The XRD patterns were obtained from the central area of the BMG rods. Thermal analyses of the as-cast samples were carried out by differential scanning calorimeter (DSC, METTLER TOLEDO DSC 1) and high temperature differential scanning calorimeter (HTDSC, Netzsch STA449F3), respectively. The hardness of the specimens was measured by using a Vickers hardness tester (Mitutoyo, HM-220 Series 810) under a load of 2 kgf for 10 s.

Fig. 1 – (a) DSC scans of Fe-B9 BMG sample with different scanning rates, (b) Plots of Tg, Tc and ΔTₓ as a function of scanning rates of Fe-B9 BMG. Real Tg, Tc and ΔTₓ were extrapolated to the value at the heating rates of 0 K/s. (c) XRD patterns of Fe-B9 BMG alloy with diameters of 4 mm.
For investigating the thermoplastic deformation behavior of Fe-B9 BMG sample, several work temperatures within the SCL region (namely 873 K, 883 K, 893 K, 903 K) were selected for high temperature compression tests by a Hon-Ta mechanical test system with different strain rates (1 × 10⁻³ and 5 × 10⁻² s⁻¹). The compression testing was conducted on the as-cast specimens with a diameter and a height of 2 and 4 mm, respectively. For the accuracy, the both ends of samples were polished carefully to ensure parallelism and flatness. Finally, the hot-compressed samples were examined by X-ray diffraction (XRD, Bruker D8A X-ray diffractometer) with monochromatic Cu-Ka radiation and transmission electron microscopy (TEM, JOEL FX2000) operated at 200 kV. TEM samples were sliced from the as-cast and the hot-compressed samples by using the focused ion beam system (FEI Versa 3D Dual Beam FIB, operated at 30 kV) with special care to minimize the ion damage to samples. The appearance of as-cast and hot-compressed sample was examined by using scanning electron microscopy (SEM, FEI Inspect F50, operated at 25 kV).

2. Results and discussion

Before studying the thermoplastic deformation behavior of a Fe-B9 BMG rod, the amorphous state of the as-cast Fe-B9 alloy rod was examined by DSC and XRD analyses. The DSC scans of a Fe-B9 alloy sample with different heating rates exhibit the typical phase transformation behavior of a metallic glass. There is a clear glass transition, followed by a supercooled liquid region, and then an exothermic reaction due to crystallization, as shown in Fig. 1(a). According to the results of DSC and HTDSC analyses, the thermal properties of the Fe-B9 sample, including the real glass transition temperature ($T_g$), real crystallization temperature ($T_x$), supercooled liquid region ($\Delta T_x$), liquidus temperature ($T_l$), and GFA index ($\gamma$ and $\gamma_m$), where $\gamma = T_g/(T_g + T_l)$ [30] and $\gamma_m = (2T_x - T_g)/T_l$ [31], are summarized and listed in Table 1 and Fig. 1(b). This Fe-B9 BMG has a good GFA ($\gamma$ and $\gamma_m$ are 0.405 and 0.699, respectively) as well as a large supercooled region ($\Delta T_x = 74$ K). The XRDP pattern of the Fe-B9 alloy rod with a diameter of 4 mm is amorphous with only broadened and diffused humps in the 2θ range of 35°–55°, as shown in Fig. 1(c). The results of both XRD and DSC analyses are evidence that the Fe-B9 alloy rods possess an amorphous structure with high GFA. However, in the as-cast sample, there is a small amount of micro-sized flower-like precipitates co-existing in the amorphous matrix (as shown in Fig. 2) by SEM, suggesting that there is a Y-rich compound via EDS analysis. The Y content in the precipitate (15.3 at. %) is much higher than that in the matrix (1.2 at. %). The selected area diffraction (SAD) patterns confirm that these precipitates are a Ca₃C₂-structured YC₂ compound (by TEM examination), as illustrated in Fig. 3. Because the Y element has a strong affinity with non-metallic elements (C, O, P and N), the impurity can form stable compounds, leaving the remaining material as amorphous. Consequently, an enhanced glass formability of the alloy is achieved [32]. In this study, the Fe-based BMG used industrial ferrous-alloys. Therefore, the credited Y-rich compound in the matrix can be predicted. Since the Y-rich compound only occupies 0.77 vol.% of the matrix from statistical estimates of the volume fraction (the remaining 99.23 vol.% is amorphous), this crystalline phase could not be resolved by our XRD analysis.

The thermoplastic deformation behavior of Fe-B9 BMG was investigated by the hot compression test at different temperatures (873 K, 883 K, 893 K, 903 K) with different strain rates (1 × 10⁻³–5 × 10⁻² s⁻¹) in the SLC region. The true stress–strain curves of the BMG samples, deformed at different conditions, are summarized in Fig. 4 and Table 2 the stress–strain curves (especially for lower temperatures and higher strain rates) show a stress overshoot at the beginning of compression, and then reduce to a steady-state flow with increasing plastic strain. The stress overshoot and steady-state flow reduce systematically with a decreasing compressive strain rate and increasing compression temperature, as shown in Fig. 4. This can be explained by free volume theory [33]. The production rate of the free volume is proportional to the deformation amount and strain rate. In contrast, the degradation rate of the free volume is proportional to the environmental temperature and time. Due to the competition between the deformation-induced production of the free volume and the thermal annihilation, the stress overshoot shows non-Newtonian flow at the beginning of high-temperature compression in the SCL. Once a free volume has a large enough amount to influence strain softening, the stress value is reduced until the degradation rate of the free volume equals the production rate (equilibrium state). The lowest flow stress, 510 MPa, is obtained at 873–883 K with an initial strain rate of 2.5 × 10⁻³ s⁻¹ for all hot compression conditions. During the compression test, more than 60% plastic strain is attained at the SCL region with strain rates of 2.5 × 10⁻³–2.5 × 10⁻² s⁻¹, as shown in Fig. 5.

**Table 1 – Thermal properties of Fe-B9 BMG sample.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$T_l$ (K)</th>
<th>$\gamma$</th>
<th>$\gamma_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-B9</td>
<td>832</td>
<td>906</td>
<td>74</td>
<td>1374</td>
<td>1419</td>
<td>0.405</td>
</tr>
</tbody>
</table>

![Fig. 2 - Cross sectional SEM images of as-cast Fe-B9 BMG sample; insert is the enlarged image.](image-url)
Fig. 3 – (a) TEM image from Fig. 2 of flower-like precipitate phase, and (b) B[013] of the micro-beam diffraction pattern (MBDP) of YC₂ precipitate from (a).

The XRD results of the hot compressed samples reveal that the thermoplastic deformed samples remain in the amorphous state. The XRD patterns exhibit broadened and diffused humps in the 2θ range of 30°–50°, and no apparent crystalline peaks can be detected, as shown in Fig. 6. A TEM analysis of the hot compressed sample at a higher temperature with a lower strain rate (at 903 K and 2.5 × 10⁻³ s⁻¹, respectively) shows a few submicron particles. They seem to form a new precipitate (marked II) on the surface of the sharp-edged Y-rich precipitate (marked I), as two kinds of crystalline precipitates embedded in the glass matrix, as shown in Fig. 7. Precipitate I and Precipitate II were identified to be the CaC₂-structured YC₂ and hexagonal-structured (Cr, Mo)B₂ compounds by nanobeam electron diffraction patterns, as illustrated in Fig. 7(c) and (d). Precipitate II is presumed to be formed during the hot compression test. Following the previous arguments in [34],

Fig. 4 – True stress–strain curves of hot compression test for the Fe-B9 BMG samples at different temperatures with different strain rates.
Yan et al. show that the mechanically induced crystallization behavior is related to the stress. It is possible for Fe-based BMG to induce a (Cr, Mo)B₂ phase during the hot compression test. In addition, the YC₂ precipitate provides a multitude of heterogeneous nucleation sites for precipitating the (Cr, Mo)B₂ with a lower energy barrier of nucleation, as shown in Fig. 7. Overall, the XRD analyses and TEM characterization confirm that the Fe-B9 BMG has good thermal stability during the hot compression test, except with a higher temperature and lower strain rate.

For the viscous flow behavior of the Fe-B9 BMG, the Backofen equation is used [35]:

$$\sigma_{\text{flow}} = K \dot{\varepsilon}^m$$

where $\sigma_{\text{flow}}$ is the flow stress, $K$ is a constant, is the strain rate, and $m$ is the strain rate sensitivity. Fig. 8 shows the plots of the flow stress (ln$\sigma$) as a function of strain rate (ln$\dot{\varepsilon}$) at different temperatures. The calculated $m$-values of strain rate sensitivity for Fe-B9 BMG are from 0.36 to 0.59. At a higher working temperature, the $m$-value is about 0.59, which is close to that for Newtonian flow, but gradually changes to non-Newtonian at a lower working temperature. This transition between non-Newtonian and Newtonian flow was also observed in several other BMG systems [15,16,36–38]. Following the previous definition [39,40], the 0.3–0.8 $m$-value is usually found in superplastic crystalline alloys, and an $m$-value of 0.5 is commonly associated with excellent plasticity. The $m$-values of Fe-B9 BMG are similar to the $m$-values of the Cu-based (0.4–0.6) [41] and Zr-based (0.4–0.56) [15] BMGs. Although the minimum stress overshoot at a temperature from 873 to 883 K is 510 MPa, this is much higher than that of the Cu-based and Zr-based BMGs. The current Fe-B9 BMGs possess high $m$-values that are above 0.36–0.59 and have good superplasticity within the SCL region. Therefore, Fe-B9 BMG is believed to be a promising material for fabricating miniature industrial parts.

![Fig. 5 – A representative photograph of the Fe-B9 BMG rods deformed at 873 K with a strain rate $5 \times 10^{-2}$ s⁻¹; (a) top view and (b) side view. In each picture, left side is the original specimen and right side is deformed specimen.](image)

![Fig. 6 – XRD patterns of the as-cast and hot compressed Fe-B9 BMG samples at higher temperature conditions.](image)

| Table 2 – Flow stress (MPa) of Fe-B9 BMG samples under different hot compression test conditions. |
|---------------------------------------------|-------------|-------------|-------------|-------------|
| Temperature | 873 K | 883 K | 893 K | 903 K |
| Fractured  | Fractured | Fractured | Fractured | Fractured |
| 1296  | 984 | 914 | 864 |  
| 1144  | 982 | 803 | 766 |  
| 754  | 725 | 709 | 603 |  
| 511  | 509 | 693 | Crystallized |  
| 560  | Crystallized | Crystallized | Crystallized |  

![Fig. 7 – Dislocation contrast TEM micrograph showing a typical deformation microstructure.](image)
Fig. 7 – (a) TEM image of the thermoplastic deformed Fe-B9 sample after hot compression test at 903 K and $5 \times 10^{-2} \text{s}^{-1}$; (b) SADP of amorphous matrix, (c) B MBDP of YC$_2$ precipitate (I), and (d) MBDP of crystallized (Cr, Mo) B$_2$ phase (II).

Fig. 8 – Plots of the flow stress as a function of strain rate at different temperatures; insert is the $m$-value.

3. Conclusion

Based on the results of the DSC and XRD analyses, hot compression test, and TEM examination, the deformation behavior of Fe-B9 BMG within the SCL region can be summarized as follows.

(1) The results of XRD and DSC analyses reveal that the Fe-B9 alloy rods possess an amorphous structure with good GFA ($\gamma$ and $\gamma_m$ are 0.405 and 0.699, respectively) and a large supercooled region ($\Delta T_x = 74 \text{K}$). However, SEM and TEM observations found a little amount of YC$_2$ crystals co-existing with the amorphous matrix. The estimated amount is about 0.8 vol.\% and is less than the resolution of a regular X-ray diffractometer.

(2) The stress overshoot and steady-state flow reduce systematically with decreasing compressive strain rate and increasing compression temperature. The lowest flow
stress of 510 MPa is obtained at the test conditions of 873–883 K and 2.5 × 10⁻³ s⁻¹.

(3) The thermoplastic deformed samples remain in their amorphous state (by XRD analysis). However, TEM characterization detected a few submicron hexagonal-structured (Cr, Mo)B₂ particles at the surface of the pre-existing YC₂ precipitate. This partial crystallization is attributed to the mechanically induced crystallization behavior during the hot compression test.

(4) A strain rate sensitivity exponent (m) of 0.36–0.59 value can be obtained for the Fe–B9 BMG, deformed at a temperature of 873–903 K. This implies that Fe–B9 BMG behaves like a superplastic metal. Therefore, thermoplastic forming is a feasible method to fabricate complex-shaped miniature parts.

Conflicts of interest
The authors declare no conflicts of interest.

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