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## Formation of magnetic Fe-based bulk metallic glass under low vacuum

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### Abstract

Bulk metallic glass (BMG)  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  can be cast into glassy rod with a diameter of at least 2 mm by copper mold casting technique under a low vacuum of 1.5 Pa. The alloy exhibits a large supercooled liquid region of 57 K and high glass transition temperature of 855 K, demonstrating a good thermal stability. Moreover, the as-cast BMG also shows good soft magnetic properties with a high saturation magnetization of 95 emu/g and low coercivity around 1.4 Oe at room temperature.

*Keywords:* A: Metallic Glasses; B: Rapid-solidification; D: Magnetic Measurements

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## 1. Introduction

Bulk metallic glasses (BMGs) have attracted increasing attention during the last decade because of their fundamental scientific interest and promising potential for industrial applications [1, 2]. Among the large number of BMGs, Fe-based glassy alloys are of high interest due to their excellent soft magnetic properties, which are potential candidate for soft magnetic applications. Since the first synthesis of Fe-based BMG in Fe–(Al, Ga)–(P, C, B) [3], a series of Fe-based BMGs have been developed with an enhanced glass forming ability (GFA) and good soft magnetic properties [4-8]. However, most of the Fe-based BMGs were prepared using high purity raw materials and under high vacuum condition (at least in a vacuum of  $10^{-3}$  Pa), because a scantling of oxygen or other impurities would drastically deteriorate the GFA [9, 10]. Therefore, some special methods, such as flux melting and ultra-high vacuum casting were adopted when preparing the BMG materials [11, 12]. However, the high purity of raw materials and strict environmental requirements lead to the increase of the unit cost and the cycle time for the production of BMGs, thus limit their industrial applications.

In recent years, great efforts have been made to improve the manufacturability of BMGs by alloying with rare earth elements. For example, some Zr-based and Mg-based BMGs can be successfully prepared under a low vacuum by rare earth doping [13-15]. Afterward, the doping strategy has been applied to the preparation of non-ferromagnetic Fe-based BMGs [16]. It has been reported that a few amorphous steels can be fabricated in low vacuum or even in air by the microalloying of a trace amount of Y or Er [17, 18]. However, to the best of our knowledge, little work has been done to prepare magnetic

Fe-based BMGs under low vacuum environment, as any oxygen contamination can considerably deteriorate not only GFA but also magnetic properties. In this paper, an attempt has been made to prepare a new magnetic Fe-based BMG with the composition of  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  in a low vacuum condition with doping of a small amount of Y. It is shown that the Fe-based BMG exhibit a high glass forming ability and pretty good soft magnetic properties.

## 2. Experimental

A multi-component master alloy with the composition of  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  (at. %) were prepared by arc melting of commercial-grade raw materials [19] at a vacuum of 1.5 Pa, which was realized by only using a conventional mechanical pump. From the master alloy, sample rods with a diameter of 2 mm and 3.3 mm were then produced by a water-cooled copper mould casting method at the same vacuum condition. The structure of the as-cast alloys was identified by X-ray diffraction (XRD, Philips X'Pert PRO) using  $\text{Cu K}_\alpha$  radiation. The thermal stability associated with glass transition, crystallization and melting events of amorphous alloy was characterized by differential thermal analyzer (Perkin-Elmer, DTA-7) under argon atmosphere at a heating rate of 20 K/min. Magnetic measurement was carried out with a vibrating sample magnetometer (VSM, Lake Shore-7410) under an applied magnetic field of 20 kOe at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  samples with a size of 2 and 3.3 mm in diameter prepared at an air pressure of 1.5 Pa. It can be observed that the

specimen with a diameter of 2 mm is fully amorphous alloy as no any Bragg peaks, except for a broad diffraction hump, can be detected in the x-ray diffraction pattern. However, a mixed structure of amorphous matrix together with a little amount of Fe crystalline phase was formed in the rod of 3.3 mm in diameter, indicating that this alloy is amorphous matrix composite.

Fig. 2 shows the DTA curve of as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  alloy with 2 mm in diameter. The alloy exhibits a distinct glass transition and a multi-stage crystallization with a wide supercooled liquid region. From the DTA curve, the glass transition temperature ( $T_g$ ), the onset of the crystallization temperature ( $T_x$ ) and liquidus temperature ( $T_l$ ) can be determined to be 855 K, 912 K and 1440 K, respectively. This yields a supercooled liquid region  $\Delta T_x = T_x - T_g = 57$  K, reduced glass transition temperature  $T_{rg} = T_g / T_l = 0.59$  and parameter  $\gamma = T_x / T_g + T_l = 0.40$ , respectively. The large value of  $T_{rg}$  and  $\gamma$  indicates that the present alloy possesses a very good GFA even though it was prepared in the low vacuum condition. The nearly single melting event demonstrates that the alloy is closer to the eutectic composition. This is believed to be beneficial to the GFA according to the Turnbull's criterion [20].

Fig. 3 shows the M–H hysteresis loop of the as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  alloy with 2 mm in diameter. The hysteresis loop exhibits a typical ferromagnetic feature, i.e., magnetization rises sharply with increasing applied field at low field side and approaches rapidly the saturation at higher field. The saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) of the alloy derived from the M–H loop are 95 emu/g and 1.4 Oe, respectively,

indicating that the as-cast BMG has fairly good soft magnetic properties.

The above results demonstrate that  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  alloy can be cast into a fully amorphous structure with dimension of at least 2 mm diameter using industrial raw materials under a very low vacuum condition (1.5 Pa). The good glass forming ability and the excellent resistance to oxidation of the present alloy system are considered to be significant to reduce the complexity and expenses for the fabrication of Fe-based bulk metallic glasses, which are usually prepared under highly restricted conditions. The good GFA and excellent oxidation resistance are probably due to the involvement of a small amount of the rare earth element Y in the alloy system. It has been reported previously that Y can increase considerably the anti-oxidation capability of an alloy by forming a compact oxide layer outside, which prevents the oxygen contamination of the alloy inside [17, 21]. The preferential formation of Y-oxides is, in fact, thermodynamically favored because the heat of formation for  $\text{Y}_2\text{O}_3$  (1905 KJ/mol) is much higher than that for other oxides in alloy system ( $\text{Fe}_2\text{O}_3$ , 823.4 kJ/mol;  $\text{MoO}_3$ , 745 kJ/mol;  $\text{HfO}_2$ , 1117.5 kJ/mol;  $\text{B}_2\text{O}_3$ ,  $1271.9 \pm 2.1$  kJ/mol) [22]. Thus, Y can preferentially react with oxygen during melting and formed an oxide layer on the surface, which in turn prevents the further oxidation of other elements inside. The similar result was also found in  $\text{Fe}_{43.7}\text{Co}_{7.3}\text{Cr}_{14.7}\text{Mo}_{12.6}\text{C}_{15.5}\text{B}_{4.3}\text{Y}_{1.9}$  alloy system, for which the oxygen content was found to keep a very low level (less than 100 ppm) inside even the ingot was melt in air. The purified effect of Y is believed to account for the good GFA of the present alloy in the low vacuum condition.

Furthermore, the as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  BMG was also found to have good soft magnetic properties with relatively high saturation magnetization (95 emu/g) and low

coercivity (1.4 Oe). The large  $M_s$  should mainly result from the high content of ferromagnetic element Fe (75 at. %). The low value of coercivity indicates a very high degree of magnetic uniformity due to the amorphous structure of the BMG [23]. The excellent soft magnetic properties of the Fe-based BMG prepared in this work may suggest a promising application in the magnetic industry.

#### 4. Conclusions

A novel Fe-based bulk metallic glass with composition of  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  and a diameter of at least 2 mm was successfully prepared by copper mould casting method at the low vacuum condition (1.5 Pa). The Fe-based BMG exhibits a high thermal stability characterized by a high glass transition temperature and large supercooled liquid region. In addition, the as-cast BMG also shows good magnetic properties with high saturation magnetization of 95 emu/g and a very low coercivity of around 1.4 Oe, demonstrating promising applications in magnetic industry.

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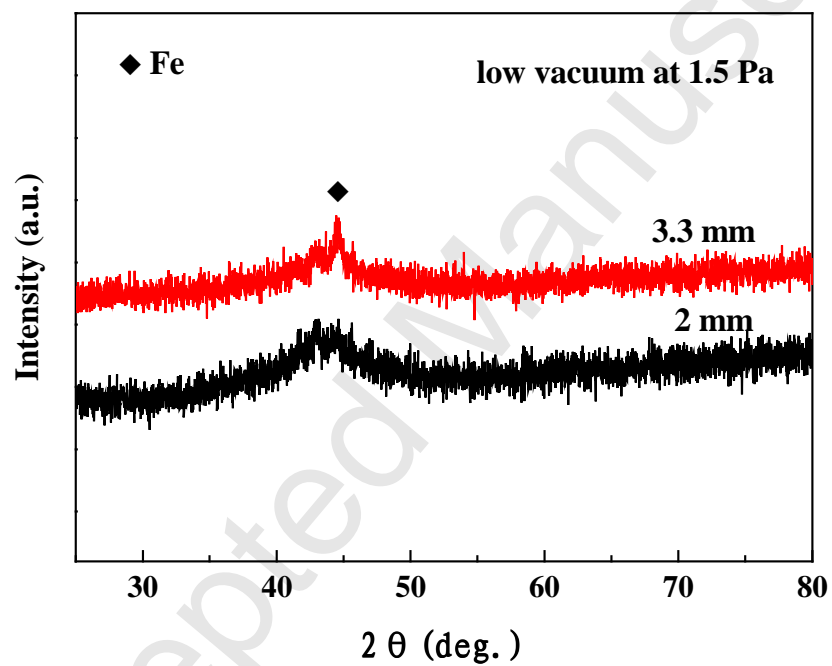
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## Figure Captions

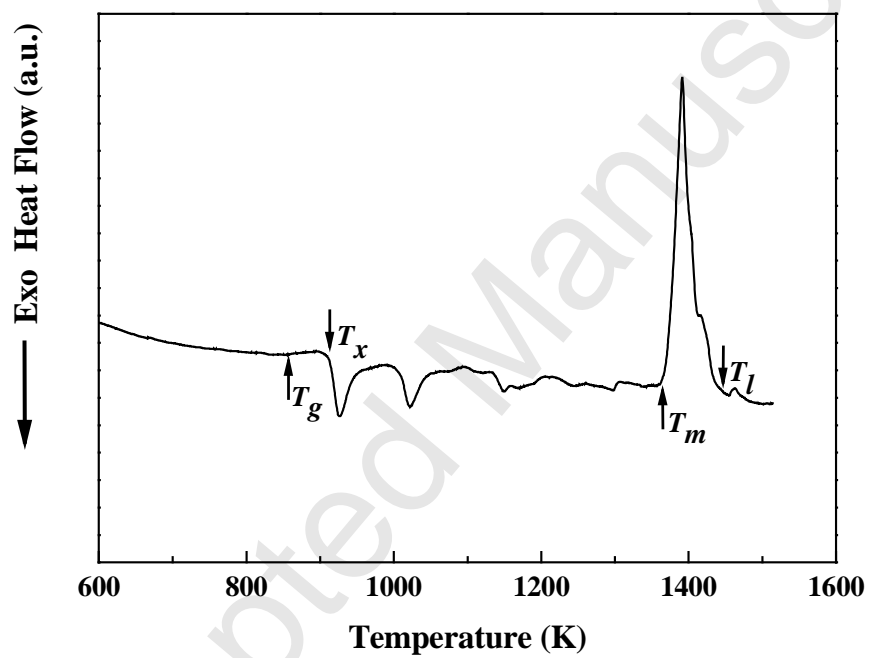
**Fig. 1 X-ray diffraction patterns of the as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  alloy rods with a diameter of 2 and 3.3 mm prepared under low vacuum.**

**Fig. 2 DTA curve of the as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  glassy rod of 2 mm in diameter at a heating rate of 20 K/min.**

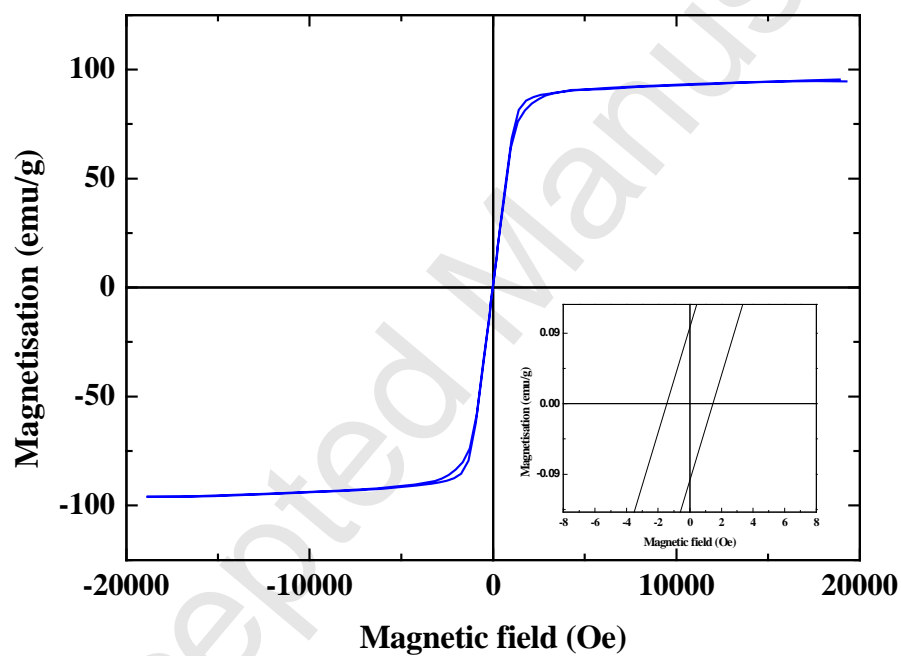
**Fig. 3 Magnetization curve (M-H loop) of as-cast  $\text{Fe}_{75}\text{Hf}_3\text{Mo}_3\text{B}_{15}\text{Y}_4$  glassy rod of 2 mm in diameter measured at room temperature.**



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