Preparation and magnetic properties of MnBi alloy and MnBi/Fe hybrid magnets

1 INTRODUCTION

Permanent magnets are important basic functional material and have been widely used in the fields of medical devices, motors, transportation, aerospace, communications and instrumentation [1]. The development of permanent magnets has experienced metal permanent magnets, ferrite permanent magnets and rare earth permanent magnets. MnBi alloy belongs to rare-earth-free permanent magnet, which has attracted much attention of researchers due to the resource crisis and high price of rare earth materials [2, 3]. Moreover, because of the large magnetocrystalline anisotropy and favourable positive temperature coefficient of coercivity, MnBi can be used as an attractive candidate material for compounding with other permanent magnets to prepare permanent magnet composites with low or even zero coercivity temperature coefficient and high magnetic properties. These kinds of magnet composites can be used as special permanent magnet materials applied in many fields, such as high temperature and strong magnetic field [4, 5]. It was found that the temperature stability of the magnetic properties of the NdFeB and Sm2Fe17Nx magnet could be improved by compounding MnBi [6, 7].

There are many phases in MnBi materials, but only low-temperature-phase MnBi shows ferromagnetism and its coercivity temperature coefficient is positive. The ferromagnetic low-temperature phase (LTP) MnBi exhibits a hexagonal structure and has uniaxial magnetocrystalline anisotropy at room temperature [8–10]. The magnetic properties of MnBi alloy are extremely sensitive to the content of low-temperature MnBi phase. Therefore, researchers hope to obtain more LTP content in the preparation of the material. The composition and preparation process affect the content of low-temperature phase in MnBi alloy, as Jun Cui [11] demonstrated. Therefore, it is necessary to systematically study the effect of composition and preparation process on the microstructure and magnetic properties of MnBi alloy. Moreover, the preparation of MnBi magnetic powder is the key to the preparation of composite magnets, and ball milling is the most common method for this preparation. However, it was found that the saturation magnetization of MnBi decreased during the preparation of MnBi magnetic powders by ball milling. It is critical to find a method that can increase the saturation magnetization of MnBi magnetic powder without obvious loss of coercivity. Soft magnetic materials have high saturation magnetization. Adding soft or semi-hard magnetic materials to MnBi alloy is an attractive path to improve the magnetic properties of MnBi magnetic materials. Yue et al. investigated MnBi/Co and MnBi/Fe65Co35 nanocomposite permanent magnets by micro-magnetic finite element method and found that the maximum magnetic energy product of MnBi/Co and MnBi/Fe65Co35 nanocomposite magnets increased significantly compared with MnBi magnet [12]. Hong et al. studied the magnetic properties of MnBi, MnBi-Co, and MnBi-Co-Fe alloys by First-principles calculation and discovered the saturation magnetization and effective anisotropy constant increased with the addition of Co [13]. However, most of this research is based on simulation. Research on adding soft or semi-hard magnetic materials to MnBi alloy needs to be strengthened with respect to experiments.

In this study, MnBi alloy was prepared by arc melting and heat treatment. The MnBi magnetic powder was prepared by ball milling of heat-treated MnBi alloy. MnBi/Fe composite magnets were prepared by ball milling after mixing MnBi magnetic powders derived from arc melting and heat treatment with Fe powders. The microstructure evolution, the content of low-temperature phase MnBi and the magnetic properties of MnBi alloys with different atomic ratios after arc melting and heat treatment were discussed in detail. The effects of different MnBi contents on the structure and properties of MnBi/Fe composite were studied. The purpose of this study is to clarify the factors affecting the magnetic properties of MnBi alloy and MnBi/Fe hybrid magnets, exploring the preparation methods of MnBi magnetic materials and MnBi/Fe hybrid magnets with excellent magnetic properties.

2 EXPERIMENTAL

Samples with different compositions of Mn1-xBix (x = 0.4, 0.5, 0.55, 0.6, and 0.7) were prepared by mixing uniformity and arc-melting of high-purity Mn chips (99.98 wt%) and Bi shot (99.99 wt%) in argon atmosphere. The ingots were re-melted three times to ensure composition homogeneity and annealed...
at 573 K for 30 h, respectively, using a tube furnace in vacuum. After annealing, the ingots were crushed into coarse powders. The coarse powders were milled in heptane for 2.5 h at room temperature. The weight ratio of ball to powder was about 10:1 and the milling speed was 300 rpm. The as-prepared MnBi powders (in proportions of 0, 25, 50, 70, 85, and 100 wt%) were mixed with Fe powders by ball milling for 40 min. Finally, the mixed powders were pressed under 500 MPa in a field of 1.8 T.

The morphologies of MnBi alloy and MnBi/Fe powders were observed under field emission scanning electron microscopy (FE-SEM) with a JEOL JSM-7800F instrument, equipped with an Oxford Instrument Aztec energy dispersive spectrometer (EDS). The MnBi alloy before and after heat treatment was prepared through conventional grinding and mechanical polishing before morphology observation. The crystal structure of MnBi alloy and MnBi/Fe bulk magnets were examined by X-ray diffraction (XRD) using a Rigaku SmartLab-9 instrument with Cu Kα radiation at 45 kV and 200 mA. The hysteresis loops of the ingots and powders were obtained using magnetic property measurement system (MPMS) by a Quantum Design MPMS3 instrument with a maximum field of 30 KOe.

## RESULTS AND DISCUSSION

### 3.1 Preparation and magnetic properties of MnBi magnetic material

Figures 1 and 2 show the microstructures of arc-melted ingots with different atomic proportions between Mn and Bi. The microstructures indicate that there are three areas with distinct colours for each specimen, which are black, dark gray and light gray, respectively. Figure 3(a) is the typical EDS mapping distributions of the ingot with 55 at% Mn. As shown in Figure 3(a), it can be observed that Mn and Bi are rich in dark gray area. Meanwhile, Mn is clustered in the black areas and Bi is clustered in the light gray areas. Figure 3(b) shows EDS line scan results corresponding to the indicated line. From EDS line analysis, it is found that the black areas contain only Mn element and the light gray areas contain Bi element. Meanwhile, dark gray areas contain both Mn and Bi elements and the ratio of relative peak values is about 1:4. Consequently, there are three types of phases in the arc-melted ingots, namely Mn-Bi phase, Mn phase and Bi phase, respectively. Combined with XRD patterns, which show that there are only MnBi, Mn and Bi phases in the alloy, it is inferred that light gray areas correspond to Bi phase, black areas correspond to Mn phase and dark gray areas correspond to MnBi phases, respectively. Moreover, SEM back scattered electron images are sensitive to the composites and related back to the average atomic number. The area with a high atomic number collects more scattered electrons and the corresponding position of the image is bright. Therefore, the areas of Mn show black, the areas of Bi show light gray and the areas of MnBi show dark gray. A noticeable amount of Mn and Bi phases can be found in all ingots before heat treatment. The black areas become larger with increasing Mn atomic proportion, indicating that the content of Mn phase increases. Meanwhile, the light gray areas become larger with the increase of Bi atomic proportion, indicating that the content of Bi phase increases. However, the change for the content of MnBi phase is not obvious as increasing the atomic proportion of Mn or Bi. The low-temperature phase MnBi is formed by peritectic reaction according to the Mn-Bi phase diagram [14]. Mn and Bi are easy to precipitate from the alloy during the solidification process [15, 16]. The reaction kinetics of the precipitated Mn and Bi is poor and synthesizing high purity LTP MnBi is difficult. Therefore, the content of low-temperature MnBi phase is less in the alloy after arc melting.

Figures 4 and 5 show the microstructures of MnBi alloy with different proportions of components after heat treatment. There are still three phases in all samples, namely Mn, Bi and MnBi respectively. The contents of Bi and Mn phases are reduced obviously after heat treatment. Meanwhile, the contents of LTP MnBi increase significantly after heat treatment, especially with 50 and 55 at% Mn, which indicates heat treatment is beneficial to the formation of a low-temperature phase. The time of the heat treatment is 30 h. Mn can diffuse and react with Bi to produce LTP MnBi fully by prolonging the heat treatment time. The alloy contains a large amount of Mn phase and the content of Bi phase is less when the content of Mn is 70 at% or 60 at%, as shown in Figures 4(a) and 4(b), respectively. However, the alloy contains a large amount of Bi phase and the

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**FIGURE 1** SEM back-scattered electron images of MnBi alloy with different atomic proportions of Mn and Bi after arc melting: (a) 7:3; (b) 6:4

**FIGURE 2** SEM back scattered electron images of MnBi alloy with different atomic proportions of Mn and Bi after arc melting: (a) 5.5:4.5; (b) 5:5; (c) 4:6
content of Mn phase is quite small when the atomic ratio of Mn is 40%, as shown in Figure 5(c). The areas of Mn become larger with the increase of Mn content, while the areas of Bi become smaller. Moreover, the areas of LTP MnBi increase firstly and then decrease with increasing Mn content, which is different from the MnBi alloy before heat treatment.

Figure 6 demonstrates the XRD spectra of MnBi alloy with different component proportions before and after heat treatment. XRD analysis reveals that there are only three phases in the alloys with different atomic ratios before and after heat treatment, which are Mn phase, Bi phase and LTP MnBi. Before heat treatment, the peak ratio of Mn phase to LTP MnBi increases with the increase of the atomic percentage between Mn and Bi, while the peak ratio of Bi phase to LTP MnBi decreases. The peak ratios of LTP MnBi to Bi phase and Mn phase increase greatly after heat treatment, which shows that LTP MnBi is formed by the reaction of Bi and Mn during the heat treatment. The peak values of Mn are very small when the atomic ratio of Mn to Bi is 4:6, indicating the content of residual Mn is less. The peak values of Bi are very low when the ratio of Mn to Bi is 6:4 or 7:3, indicating the content of residual Bi is less. The peak values corresponding to Mn phase and Bi phase are low as the ratio of Mn to Bi is 5.5:4.5 or 5:5, while the peak values corresponding to MnBi phase are large indicating the content of LTP MnBi is high, which agrees with the results of the SEM analysis.

Figure 7 shows the hysteresis loops of MnBi alloy with different atomic ratios before and after heat treatment. The maximum magnetic field is 30 KOe. Before heat treatment, the mag-
FIGURE 7 M-H curves of the MnBi alloy with different component proportions: (a) after melting; (b) after heat treatment

netization of the MnBi alloy is only 16.2 emu/g when the ratio of Mn to Bi is 7:3. With the increase of the ratio of Mn to Bi, the magnetization increases until it reaches a maximum value when the ratio of Mn to Bi atoms is 5.5:4.5, and then decreases. The range of the magnetization differences is small. After heat treatment, the magnetization of the alloy at 30 KOe is greatly increased compared with that before heat treatment. The magnetization at 30 KOe is 50.3 emu/g when the ratio of Mn to Bi is 7:3. It increases to 57.2 emu/g as the atomic ratio is 6:4. The magnetization reaches the maximum of 62.0 emu/g when the atomic ratio is 5:5. However, it decreases to 52.7 emu/g as the atomic ratio is changed to 4:5. Therefore, the magnetization of the alloy at 30 KOe after heat treatment increases firstly and then decreases with the increase of the atomic ratio of Mn to Bi. The variation range is larger than that before heat treatment. The saturation magnetization of MnBi alloy is determined by the low-temperature-phase MnBi. The saturation magnetization increases with increasing the content of LTP MnBi. According to SEM and XRD analysis, the LTP MnBi increases greatly after heat treatment, so the saturation magnetization increases obviously after heat treatment. After heat treatment, the low-temperature MnBi phase increases firstly and then decreases with the increase of the percentage of Mn atoms, so the saturation magnetization increases firstly and then decreases simultaneously.

3.2 Preparation and magnetic properties of MnBi/Fe hybrid magnets

The sample used for ball milling is MnBi alloy after heat treatment and the atomic ratio of Mn to Bi is 5:5. The corresponding SEM images for MnBi and Fe particles are shown in Figures 8(a) and 8(b), respectively. MnBi particles, with a size range from 1 to 10 μm, are magnetically hard. Fe particles, with an average size of 50 nm, are magnetically soft. Figure 9 shows the SEM images of the hybrid of MnBi/Fe powders with different MnBi contents. The nanoscale Fe particles distribute on the surface of MnBi particles uniformly when the MnBi content is higher than 50 wt%, as shown in Figure 9(a,b). Fe particles distribute on the surface of MnBi particles and among the MnBi particles uniformly as the MnBi content is less than 50 wt%, as shown in Figure 6(c,d).

Figure 10 shows the XRD pattern of the hybrid of MnBi/Fe magnets with different MnBi contents. Three kinds of phases, which include Bi phase, Mn phase and low temperature MnBi phase, still exist in the alloy after ball milling. However, the ball milling results in the decomposition of low temperature MnBi phase, which decreases the relative peak value of low temperature MnBi phase and increases the relative peak values of Bi phase and Mn phase. The XRD spectra reveal that there are no new phases in the MnBi/Fe magnets composites except MnBi, Bi, Mn and Fe, which indicates that there is no reaction between phases during the preparation of the composites.

The M-H loops of MnBi/Fe composites with different MnBi contents are shown in Figure 11. The loops are smooth with characteristics of a single hard magnetic phase, which indicates that there is exchange coupling between MnBi and Fe. The sat-
The saturation magnetization of MnBi particle is very low. The saturation magnetization of the alloy decreases after ball milling and this is attributed to the decomposition of low temperature MnBi phase, which is consistent with the XRD analysis shown in Figure 10. When the magnetic materials are magnetized and demagnetized, magnetic domains are pinned by defects, grain boundaries and weak magnetic and non-magnetic phases, which hinder the movement of magnetic domains, leading to the increase of coercivity [17]. The residual stress, dislocation and other defects present in the alloy during milling from plastic deformation. Besides, the grain size of the alloy decreases, which leads to the increase of grain boundary. Moreover, more contents of Mn and Bi phases appear due to the decomposition of LTP MnBi by ball milling. Therefore, the resistance to the movement of the magnetic domain increases after ball milling, resulting in the increase of coercivity. The composition ratio between the MnBi and Fe plays an important role in the magnetic performance of MnBi/Fe hybrid magnets. The coercivity of the composite magnet increases dramatically with increasing the content of MnBi. As the weight percentage of MnBi increase from 0% to 50%, the coercivity increases from 101 Oe to 296 Oe. The saturation magnetization increases significantly with increasing the content of Fe. As the weight percentage of Fe increase from 0% to 50%, the saturation magnetization increases from 34 emu/g to 128 emu/g.

4 | CONCLUSION

We prepared MnBi alloy and MnBi/Fe hybrid magnets with different compositions using arc melting, heat treatment and ball milling. The magnetic performance of the MnBi alloy is sensitive to the composition and preparation process. The magnetization increases significantly as the LTP MnBi phase increases following heat treatment. After heat treatment, the mass percentage of the LTP MnBi and the magnetization initially increases and then decreases with increasing the content of Mn. The MnBi alloy with 50 at% Mn exhibits maximum magnetization of 62.0 emu/g with 30 KOe applied field at 300 K. After ball milling, the magnetization of the MnBi alloy decreases obviously, but the coercivity increases greatly. The M-H loops of the MnBi/Fe hybrid magnets are smooth with characteristics of a single hard magnetic phase, indicating there is exchange coupling between MnBi and Fe. The composition ratio between the MnBi and Fe plays an important role in the magnetic performance of MnBi/Fe hybrid magnets. The coercivity of the composite
magnet increases dramatically with increasing the content of MnBi and the saturation magnetization increases with increasing the content of Fe. As the weight percentage of Fe increase from 0% to 50%, the saturation magnetization increases from 34 to 128 emu/g. It has been demonstrated that heat treatment, composition changes and adding Fe are effective methods to increase the saturation magnetization of MnBi alloy.

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