Preparation and magnetic properties of anisotropic bulk MnBi/NdFeB hybrid magnets

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ABSTRACT: Anisotropic hybrid bulk magnets of MnBi/NdFeB with different composition ratio have been prepared with starting MnBi and Nd₂Fe₁₄B powders as well as epoxy resin as a binder in case it is needed to form bulk samples. It has been found that the ratio between the two phases in content has a remarkable influence on the magnetic properties, the thermal stability and the density of the bulk magnets. With increasing MnBi content the binder addition can be reduced. When the MnBi content is larger than 30 wt. %, no binder is needed. On the other hand, the coercivity and saturation magnetization were increased significantly with increasing NdFeB content. When the NdFeB content was increased from 0 to 50 %, the maximum energy product was enhanced from 4.7 to 10.0 MGOe, respectively. The energy product then decreased gradually with the NdFeB content due to the reduced density of the hybrid magnet. The thermal stability measurements showed that the temperature coefficient of coercivity grew with the MnBi content and became positive with MnBi = 80 wt. %.

Key Words: permanent magnets; hybrid magnets; magnetic anisotropy; sintering; thermal stability

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1. Introduction

In recent years, rare-earth-free hard magnetic materials have attracted considerable attention due to the concern over cost and supply of rare-earth raw materials [1-3]. MnBi alloys are one of the promising candidates for permanent magnet applications since the MnBi low-temperature phase (LTP) has high magnetocrystalline anisotropy and a remarkable positive temperature coefficient of coercivity below 300 °C [4, 5].

Though MnBi LTP has a high anisotropy, its saturation magnetization is only 80 emu/g that is about a half of the Nd₂Fe₁₄B phase. The low magnetization value leads to low energy product $(BH)_{\max}$ values that limits its applications as a permanent magnet. Moreover, it is also difficult to prepare MnBi alloy with high purity of LTP phase since that Mn can segregate from the Mn-Bi liquid below the peritectic temperature according to the Mn-Bi phase diagram. In order to obtain a high coercivity, MnBi alloys should be pulverized to particles with a single domain size. However, the LTP phase is easy to be decomposed during pulverization process. Furthermore, there are still some technical challenges to prepare bulk MnBi with high properties. First, the orientation degree of bulk MnBi should be as high as possible for getting a high coercivity, since that the magnetic reverse process is mainly controlled by coherent rotation of single domain grains [6]. Second, it is also difficult to inhibit the decomposition of LTP phase during the preparing bulk MnBi with high density.

In order to get MnBi alloy with good permanent magnetic properties, many efforts have been made to prepare high purity MnBi powders and bulk magnets with high density [2, 6-9]. N. V. Rama Rao obtained the MnBi powders and bulk magnet by applying the low energy ball milling and hot compaction technique, and their maximum energy products are 9 MGOe and 5.8 MGOe respectively [2]. J. B. Yang obtained the MnBi powders with high coercivity and high LTP phase content larger than 95% prepared by melt-spinning and subsequently annealing [6]. V. V. Nguyen prepared MnBi powders by the profiled heat treatment and low-energy ball milling, and obtained the bulk MnBi magnet with density of 8.2 g/cm³ and $(BH)_{\max}$ of 6.1

MGOe using warm compaction technique [7]. By improving the preparing process, the magnetic properties of MnBi alloy could be further enhanced. However, the best energy products for powders and bulks are only 11.9 MGOe and 7.8 MGOe, respectively [9], which are well below the theoretical value of ~ 18 MGOe [10].

It is well known that Nd-Fe-B permanent magnets have been widely used in a great variety of electromechanical applications because of their high performance at room temperature. However, the low thermal stability has limited their applications at elevated temperatures [11]. Hybrid magnets consisting of different hard magnetic phases may take respective advantages of the phases and therefore compensate their shortcomings. Recently, hybrid bulk magnets based on MnBi phase have been prepared by several research groups, and most of them are resin-bonded with low density. Yang et al. fabricated anisotropic MnBi/Sm₂Fe₁₇N_x powder with $(BH)_{\max}$ 18 MGOe at 300 K [12]. Zhang et al. have reported MnBi/Sm₂Fe₁₇N_x and MnBi/Nd₂Fe₁₄B bonded magnets with enhanced thermal stability [13, 14]. Rama Rao et al. obtained anisotropic hybrid MnBi/Sm₂Fe₁₇N_x magnets by applying hot compaction technique, but the best energy product obtained was only 7 MGOe [15]. In order to further study magnetic properties of hybrid MnBi-containing magnets, bulk anisotropic MnBi/Nd₂Fe₁₄B magnets with different Nd-Fe-B content were prepared via improved sintering and compaction process in present investigation.

2. Experiments

MnBi alloys were prepared by arc-melting in argon atmosphere. The ingots were annealed at 563 K for 20 h in the argon atmosphere and subsequently crushed into coarse powders. Then the coarse MnBi powders were milled for 3h in heptane by low-energy ball-milling. The MnBi powders had a particle size range of 0.5-5 μm . The NdFeB powders were MQ-A commercial magnetic powders from Magnequench International Inc. The as-prepared MnBi powders were mixed with NdFeB powders by ball milling (in the proportion of 0, 20, 30, 50, 70, and 100 wt. %). The powders

were then aligned in a field of 1.8 T and pressed under a pressure of 200 MPa. The compacts were sintered at 573 K for 30 minutes in the argon atmosphere to form bulk magnets. However, the NdFeB powders and MnBi/NdFeB (70 wt. %) mixed powders must be added with proper epoxy resin before alignment to form bonded magnets for magnetic measurements.

Density of the bulk magnets was determined by Archimede's method. The crystal structures of the magnets were measured using x-ray diffraction (XRD) with Cu-K α radiation. The microstructures of bulk samples were observed using a scanning electron microscope (SEM). Magnetic properties of the samples including demagnetization curves and coercivity at different temperature were measured using a Quantum Design SQUID and PPMS magnetometer with applied magnetic fields up to 3 T.

3. Results and discussion

The starting MnBi and NdFeB powders have their maximum energy products of 6.0 and 29.8 MGOe, respectively. XRD patterns of different magnets from the surface normal to the alignment were obtained after the field alignment and the compaction, as seen in Fig. 1. As it shows, the NdFeB magnet consists of only Nd₂Fe₁₄B phase and while the MnBi magnet has two constituent phases: LTP MnBi and Bi. Usually, MnBi alloys consist of LTP MnBi, Bi and Mn phases since a pure MnBi phase is very difficult to prepare and there are always unreacted Bi and Mn in the alloys. In the sample studies, the Mn phase has been reduced to the extent that XRD does not detect the diffraction peaks.

In XRD patterns of a MnBi or a NdFeB sample, enhanced (00 l) peaks usually indicate a better c-axis texture (alignment). It is thus a common practice to quantitatively describe the alignment degree using a ratio value γ of intensity of a (00 l) peak and another selected peak. In case of MnBi the γ value is determined by the intensity ratio

between the (002) and (101) peaks. As shown in Fig. 1, both the pure MnBi and NdFeB samples exhibit a strong anisotropy since their (00 l) peaks are high. However, the alignment degree of the hybrid samples is relatively low, as seen from the ratio. The γ value is less than 1 for all the hybrid magnets, indicating that the hybrid magnets have a lower c-axis texture for MnBi. This observation is interesting but not fully understood.

Fig. 2 shows the demagnetization curves of the hybrid MnBi/NdFeB magnets at room temperature with different compositions. The coercivity and remanence of the magnets increase gradually with increasing NdFeB content, owing to the high remanence magnetization (M_r) of 92 emu/g and coercivity (H_c) of 14.6 kOe for NdFeB phase. For the pure MnBi sample, M_r and H_c are only 42.4 emu/g and 6.3 kOe, respectively. Upon mixing with 50 % NdFeB, M_r and H_c of the magnet increased to 75.2 emu/g and 12.8 kOe, respectively. Moreover, all the M_r/M_s ratio values (measured at 30 KOe) are larger than 0.75 (shown in Fig. 2), indicating that all the magnets are anisotropic which shows that the processing method adopted in this study is effective for preparing bulk anisotropic hybrid MnBi/NdFeB magnets. On the other hand, it is seen that the M_r/M_s ratio value decreases gradually with increasing NdFeB content, from 0.93 at 0 % to 0.82 at 50 wt. % of NdFeB, and to 0.75 for the bonded NdFeB magnet. Clearly, this M_r/M_s ratio is consistent with the ratio γ measured from XRD patterns, because both are the measure of the grain alignment (texture).

Although M_r and H_c of the hybrid MnBi/NdFeB magnets increase with increasing NdFeB content monotonously, the maximum energy product $(BH)_{\max}$ has a different variation trend. Fig. 3 shows the remanent magnetic induction B_r , $(BH)_{\max}$ and density of the hybrid magnets with the NdFeB content. From Fig. 3, B_r and $(BH)_{\max}$ increase significantly with NdFeB content till 50 wt. %, then start to decrease with the content. The highest $(BH)_{\max}$ of 10 MGOe was obtained at 50 wt. % of NdFeB content, which is an increment of 112.8 % as compared to the pure MnBi magnet. Obviously, the increased $(BH)_{\max}$ can be attributed to the NdFeB phase that has higher remanence and coercivity at room temperature. However, when NdFeB content is larger than 50

wt. %, the $(BH)_{\max}$ starts to decline due to the remarkable reduce of the density of the hybrid magnets.

It is well known that the sintering temperature for preparing a bulk NdFeB is usually higher than 950 °C, and the hot-pressing temperature is higher than 650 °C (since the melting-point of Nd-rich phase is about 650 °C) [16]. However, the hybrid magnets we prepared here were treated at relatively low temperature (~ 300 °C) for the reason for protecting the LTP MnBi. Thus, the densification of NdFeB powder could not be realized at such low temperatures and the density of hybrid magnets becomes lower with increasing NdFeB content.

Fig.4 is the SEM images of the hybrid MnBi/NdFeB magnets with different MnBi content. Four kinds of phases can be identified: MnBi matrix (light grey), NdFeB matrix (dark grey), Bi (white) and Mn (black). This observation is also consistent with the XRD results. The free Bi phase, however, which has a low melting point (about 271 °C), was a liquid during the sintering that facilitated the solidification. Therefore, the higher the MnBi content, the higher the magnet density.

In the hybrid magnets, NdFeB particles have a large average size of about 50 μm, and are separated by the MnBi matrix. When the MnBi content is higher than 50 wt. %, NdFeB particles can be evenly distributed and separated by the MnBi matrix, as seen from Fig.4 (a). But when the MnBi content is less than 50 %, NdFeB particles have poor distribution uniformity as shown in Fig. 4 (c) and the particles may not be wetted well by MnBi during sintering, leading to a lower density of the bulk sample.

Figure 5 shows the demagnetization curves of anisotropic hybrid MnBi/NdFeB magnets with different MnBi content at 375 K. With increasing NdFeB content, the M_r and M_s have a similar trend of variation as observed at room temperature, but the coercivity variation is very different. The pure MnBi sample has the highest coercivity and the coercivity decreases gradually with increasing NdFeB content. The coercivity values were 13 kOe, 8.8 kOe and 7.8 kOe with the NdFeB content of 0, 50 and 100 wt. %, respectively, which were 106%, 31 % and 47 % of the values respectively,

compared with the values measured at room temperature. Therefore, the addition of MnBi greatly enhanced the coercivity of the hybrid magnets at elevated temperatures. This is due to the positive temperature coefficient of coercivity of the LTP MnBi, even though the NdFeB component has a negative coefficient. The maximal $(BH)_{\max}$ of 7.7 MGOe is obtained at 50 wt. % of NdFeB at 375 K which indicates that the hybrid MnBi/NdFeB magnets can also have good magnetic properties at high temperatures. It is noteworthy that all the demagnetization curves at room temperature and the high temperature are smooth with a single-phase-like demagnetization behavior. Obviously, this is not derived from the exchange coupling interaction between grains since the NdFeB and the MnBi particles which are larger than 1 μm and have uneven distribution. Further research should be conducted to investigate the mechanism.

In order to further understand the thermal stability of the hybrid magnets, temperature coefficients of coercivity of the hybrid samples with different MnBi content were examined. As shown in Fig. 6, the temperature coefficient of coercivity is positive for the pure MnBi sample and the hybrid MnBi/NdFeB samples with NdFeB content up to 20 wt. %. When the MnBi content is smaller than 80 %, the temperature coefficients of coercivity for the hybrid magnets remained negative while their absolute values decreases with increasing MnBi content. In other words, there is a remarkable improvement of the thermal stability for hybrid MnBi/NdFeB magnets with increasing MnBi content.

4. Conclusion

Anisotropic bulk hybrid MnBi/NdFeB magnets have been prepared via improved warm compaction and sintering techniques. It is found that a proper processing and suitable composition lead to high density bulk magnets that possess advantages of both the MnBi and NdFeB phases. An energy product $(BH)_{\max}$ of 10 MGOe has been obtained at NdFeB content of 50 wt. %, which is substantially higher than any reported values of the energy density for bulk MnBi-based magnets. Meanwhile, the

hybrid magnets also have a better thermal stability at elevated temperatures compared to the NdFeB magnets due to the positive temperature coefficient of coercivity of the MnBi phase. Further research is needed to understand the “compensation” mechanism in the hybrid system and the optimization of the processing methodology.

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Fig.1 XRD patterns of anisotropic hybrid MnBi/Nd-Fe-B magnets with different MnBi content (wt. %): (a) 100%; (b) 70%; (c) 50%; (d) 30%; (e) 0.

Fig.2 Demagnetization curves of anisotropic hybrid MnBi/Nd-Fe-B magnets with different MnBi content (wt. %) at room temperature

Fig. 3 The magnetic properties and density of hybrid MnBi/NdFeB magnets with different Nd-Fe-B content.

Fig.4 BSEM images of anisotropic hybrid MnBi/Nd-Fe-B magnets with different MnBi content (wt. %): (a) 70%; (b) 50%; (c) 30%.

Fig.5 Demagnetization curves of anisotropic hybrid MnBi/Nd-Fe-B magnets with different MnBi content (wt. %) at 375K.

Fig. 6 Temperature coefficients of Coercivity of bulk hybrid MnBi/Nd-Fe-B with MnBi content (wt. %).

Fig.1

Fig.2

Fig.3

Fig.4a

Fig.4b

Fig.4c

Fig.5

Fig.6