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Effect of ball milling and heat treatment process on MnBi powders magnetic properties

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Abstract

The metallic compound MnBi has high intrinsic coercivity with large positive temperature coefficient. The coercivity of MnBi exceeds 12 kOe and 26 kOe at 300 K and 523 K, respectively. Hence MnBi is a good candidate for the hard phase in exchange coupled nanocomposite magnets. In order to maximize the loading of the soft phase, the size of the MnBi particle has to be close to 500 nm, the size of single magnetic domain. Low energy milling is the common method to reduce MnBi particle size. However, only 3 – 7 micron size particle can be achieved without significant decomposition. Here, we report our effort on preparing submicron MnBi powders using traditional powder metallurgy methods. Mn₅₅Bi₄₅ magnetic powders were prepared using arc melting method, followed by a series of thermal-mechanical treatment to

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improve purity, and finished with low energy ball milling at cryogenic temperature to achieve submicron particle size. The $\text{Mn}_{55}\text{Bi}_{45}$ powders were decomposed during ball milling process and recovered during 24 hours 290 °C annealing process. With increasing ball-milling time, the saturation magnetization of MnBi decreases, while the coercivity increases. Annealing after ball milling recovers some of the magnetization, indicating the decomposition occurred during the ball-milling process can be reversed. The coercivity of $\text{Mn}_{55}\text{Bi}_{45}$ powders are also improved as a result of the heat treatment at 290 °C for 24 hours. The world record magnetization 71.2 emu/g measured applying a field of 23 kOe has been achieved via low energy ball mill at room temperature.

Key words: low energy ball milling, low temperature phase, MnBi powders, rare earth free permanent magnet

1. Introduction

Rare-earth-free permanent magnets have attracted great attention due to the criticality of rare earth elements such as Nd and Dy. MnBi permanent magnet as an alternative to rare-earth based permanent magnets has drawn attention due to its unique magnetic properties, especially the unusual positive temperature coefficient of coercivity [1.45%/K] in the temperature range 300 – 530 K [1]. Its coercivity increases with increasing temperature, reaching 25 kOe at 540 K [2-5] and up to 28.3 kOe at 530 K as recently reported by Rao [6]. This relatively large coercivity of the MnBi in its low-temperature phase (LTP) is attributed to its high uniaxial magnetocrystalline anisotropy ($1.6 \times 10^7 \text{ erg cm}^{-3}$ at 300 K and $2.3 \times 10^7 \text{ erg cm}^{-3}$ at 420 K) [1]. However, MnBi has relatively low room temperature saturation magnetization (75 emu/g measured with 23 kOe applied field [7] or 81 emu/g measured applying a field of 90 kOe [8]). Despite the large intrinsic

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coercivity, the theoretical maximum energy product of MnBi at room temperature is about 17 MGOe, much lower than that of NdFeB or SmCo.

One possible approach to improve MnBi's energy product is to exchange-couple it with a soft phase such as Co or FeCo [9-11]. This approach requires the size of the MnBi particles to be comparable to the size of its single magnetic domain (~ 500 nm) [12, 13]. Obtaining submicron MnBi powder with small size distribution and high purity is critical for a successful implementation of this approach. The most popular method to prepare MnBi powder is low energy ball milling because high mechanical energy input may lead to decomposition. Ball-milling at low temperature can mitigate the decomposition issue, but not completely. MnBi particles with size in the range of 400 – 500 nm can be prepared using cryo-milling method, but the decomposition is still significant. The resulted powders had a magnetization ~35 emu/g measured under 30 kOe applied field at room temperature, indicating nearly half of the LTP phase has decomposed [14]. Yin [15] attributed the decomposition to the strains accumulated in the crystals of MnBi during ball milling process. MnBi/Bi composite nanoparticles with size in the range 100–300 nm exhibiting anisotropic magnetic properties and high coercivity 16.3 kOe were fabricated using the mechanochemical synthesis method [16], however, the powder magnetization only reached 22 emu/g measured with 30 kOe applied field indicating large amount of impurity. Direct chemical synthesis of MnBi particles were carried out, but similar to the mechanochemical method, the resulted powder has low magnetization (~20 emu/g) [17]. It appears that a new method is needed to fabricate MnBi powder with high purity (magnetization >60 emu/g measured applying a field of 20 kOe) and with the desired 500 nm particle size. Here,

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we report our effort on fabrication of submicron MnBi particles using a combination of low temperature low energy ball milling and annealing.

2. Experiment

Mn₅₅Bi₄₅ powder was prepared using arc melting followed by grinding, annealing and low energy ball milling (LEBM). Mn₅₅Bi₄₅ alloys were prepared from high purity (> 99.95 %) elements (Aldrich and Alfa Aesar) by arc melting evacuated to 1×10^{-5} Torr. The mixture of raw elements was pressed into a pellet using a uniaxial press before arc melting. The alloy was annealed in pure hydrogen atmosphere to obtain high-purity low temperature phase (LTP) MnBi. The obtained ingot was pulverized into powder using mortar and pestle. The powders were sieved using #325 and #400 mesh screens. The particles size range is 37 – 44 μm . The powders were heat treated under vacuum at 290 °C for 48 h to increase LTP MnBi phase volume fraction. The MnBi powders were ball milled with LEBM either at room temperature or cryogenic environment (liquid nitrogen, – 70 °C) respectively. 5 grams of Mn₅₅Bi₄₅ powders were loaded in the glove box in a hardened stainless steel vial with toluene at room temperature and hexane at – 70 °C. The milling media were chrome steel balls from 4 – 12 mm in diameter. The ball to powders weight ratio was 20:1. The powders were milled for 3, 8, 24 hours respectively with a milling speed of 60 rpm and heat treated for at 290 °C for 24 hours, then ball milled for half an hour with the same milling speed.

Powder diffraction data were collected with a Panalytical MPD Bragg-Brentano diffractometer using Cu K α radiation ($\lambda = 1.5416 \text{ \AA}$), a graphite post-diffraction monochromator, and variable divergence and anti-scatter slits (illuminated length - 10 mm). The x-ray tube was operated at 50 kV and 40 mA and patterns were collected between 20 and 100° 2 θ , counting for 2 s at 0.04°

intervals. Phase proportions, cell parameters, and crystallite sizes were determined by whole-pattern Rietveld fitting using the fundamental parameters approach implemented in Topas (v4.2, Bruker AXS) and crystal structures from the Inorganic Crystal Structure Database. For MnO where the diffraction peaks were weak and relatively broad, the lattice parameter was not refined and the crystallite size was also fixed at 50 nm.

The magnetic properties were obtained using a vibrating sample magnetometer (VSM Model EZ9, Microsense) at room temperature with a maximum field of 23 kOe. Particle morphology and composition were investigated by scanning electron microscope (JSM-7001F, JEOL USA, Inc. Peabody, MA) with EDS capability (EDAX Li-drifted Si detector, AMETEK, Berwyn, PA). The focused ion beam technique was used to prepare samples for transmission electron microscopy (TEM), which was used to observe the microstructure of MnBi powders.

3. Result and discussion

Representative SEM morphologies of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ for varied milling times are demonstrated in Fig. 1. The Figure shows that the particle size decreases with increased milling time. With an initial powder size before LEBM being 37 — 44 μm , the particle size is reduced to 1 — 4 μm , 400 nm — 2 μm , 50 nm — 1 μm by 3, 8, and 24 hours of ball milling, respectively.

TEM microscopy and the corresponding selected area diffraction (SAD) patterns of the $\text{Mn}_{55}\text{Bi}_{45}$ powders ball milled for 3 hours and 24 hours are shown in Fig. 2. The SAD patterns of the $\text{Mn}_{55}\text{Bi}_{45}$ powders show presence of an amorphous phase in the ball-milled powders.

The X-Ray diffraction patterns of $\text{Mn}_{55}\text{Bi}_{45}$ powders ball milled for 8 hours, then heat-treated, and then ball milled for half hour are shown in Fig. 3. The peaks become broadened after ball

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milling indicating a reduction in grain size. The peaks get narrowed after heat treatment demonstrating a growth in grain size.

Table 1 shows X-Ray phase composition analysis of MnBi powders prepared by 8 hours of ball milling, followed by heat-treatment for 24 hours and then ball milling for half hour. The fractions of the magnetic MnBi phase are 77, 85.9, 81, 86.1 wt. % for ball milled, milled and annealed, milled plus annealed and milled, and the feedstock (before ball milling) MnBi powders respectively. The fractions of Bi are 13.7, 5.2, 10.2, and 5.0 wt. % for ball milled, milled and annealed, milled plus annealed and milled, and feedstock MnBi powders respectively. The fraction of MnBi decreases and that of Bi increases after ball-milling indicating there is decomposition. Ball milling was followed by annealing which resulted in partial recovery of the MnBi phase. This observation is in agreement with previously published results [18]. The phase fractions of Mn and MnO remain fairly constant (the sum is 8.7 to 9.3 wt. %). The average crystallite sizes calculated from XRD patterns are 52, 115, 85 and 215 nm for ball milled, milled and annealed, milled plus annealed and milled, original MnBi powders respectively. The crystallite sizes were obtained from the peak widths (Scherrer broadening) in excess of that calculated from instrumental factors during the whole-pattern fitting. Note that the crystallite size is a different measurement than particle size; the former estimates the domain size which contains a more or less perfect crystal lattice while the latter is the physical dimension of individually separable grains of material. The crystallite size of MnBi and Mn decreases as a result of ball milling. The Bi fraction was small to begin with and decreases much less noticeably. The lattice parameters increase slightly indicating that the strain of MnBi phase goes up as well during ball milling process. The strains caused by ball milling process are difficult to

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accumulate in the crystals of MnBi and lead to the decomposition. Yin [15] also reported that after ball milling over 2 hours, Bi is precipitated from the LTP MnBi phase.

Magnetization curves of $\text{Mn}_{55}\text{Bi}_{45}$ powders prepared by three, eight and twenty four hours of ball milling are shown in Fig. 4. The saturation magnetization M_s is reduced with increasing milling time, which indicates decomposition during ball milling. On the other hand, the coercivity H_c is increased with increasing ball-milling time, in accordance with the MnBi particle size reduction. Coercivity reaches its maximum at eight hours of ball milling. There are kinks on the magnetization curves of $\text{Mn}_{55}\text{Bi}_{45}$ powders prepared by eight and twenty four hours ball milling (see Fig. 4).

The comparison of magnetization curves of $\text{Mn}_{55}\text{Bi}_{45}$ powders prepared for eight hours ball milling, then heat-treated, and then ball milled again for half hour is demonstrated in Fig. 5. There is a kink in magnetization curves of $\text{Mn}_{55}\text{Bi}_{45}$ powders after eight hours ball milling, possibly due to the presence of amorphous phase. After the 24 hours heat treatment at 290 °C, the coercivity H_c is significantly improved. This indicates that the amorphous phase has been crystalized to recover some of the magnetic MnBi phase. However the magnetization M_s of $\text{Mn}_{55}\text{Bi}_{45}$ powders measured at 23 kOe applied field is slightly decreased. This is attributed to the unsaturated magnetization of MnBi powder. Measurements at higher fields should help achieve saturation. The coercivity H_c of $\text{Mn}_{55}\text{Bi}_{45}$ is reduced for only half hour ball milling after 290 °C for 48 h heat treatment. The record of magnetization 71.2 emu/g is achieved via milling for eight hours, heat treated, and ball milled for extra half an hour process.

The comparison of morphology of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders either at room temperature and cryogenic environment are demonstrated in Fig.6. Cryo ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders have less

agglomeration. Magnetization curves of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders at room temperature and cryogenic environment for 8 hours and 24 hours are shown in Fig.7 and Fig. 8 respectively. The magnetization of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders for 8 hours are 65.4 emu/g and 63.2 emu/g at cryogenic environment and room temperature respectively. The magnetization of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders for 24 hours 55.5 emu/g 47.8 emu/g at cryogenic environment and room temperature respectively. The magnetization of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders at cryogenic environment is higher than that at room temperature for both 8 hours and 24 hours ball milling. This indicates that the cryo ball milling retards decomposition. However this function is reduced after the ball milling time is above 8 hours. Both coercivity of ball milled $\text{Mn}_{55}\text{Bi}_{45}$ powders for 8 hours and 24 hours at cryogenic environment are lower than that at room temperature.

4. Conclusion

The $\text{Mn}_{55}\text{Bi}_{45}$ powders size is reduced dramatically from 44 μm to 1 — 4 μm , 400 nm — 2 μm , 50 nm — 1 μm by 3, 8, 24 hours ball milling respectively. The MnBi powders with grain size close to magnetic domain, i.e. 500 μm , can be produced via ball milling process and used as hard phase for exchange coupled nanocomposite magnets. An amorphous phase was found in 24 hours ball milled powders through TEM analysis. The XRD analysis demonstrates that the $\text{Mn}_{55}\text{Bi}_{45}$ powders were decomposed during ball milling process and recovered during 24 hours 290 °C annealing process. The saturation magnetization M_s is reduced with increasing ball milling time, which indicates that the decomposition is increased with increasing ball milling time. The coercivity of $\text{Mn}_{55}\text{Bi}_{45}$ powders are improved as a result of the heat treatment at 290 °C for 24 hours, indicating that the magnetic MnBi phase has been partially recovered. The

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world record magnetization 71.2 emu/g has been achieved via low energy ball mill at room temperature.

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Fig. 1 SEM morphology of ball milled powders for (a) 3 h, (b) 8 h and (c) 24 h

Fig. 2 TEM microscopy of the Mn₅₅Bi₄₅ powders ball milled for (a) 3 hours, (b) 24 hours

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Fig. 3 X-Ray diffraction patterns of Mn₅₅Bi₄₅ powders ball milled for eight hours; milled for eight hours and then heat-treated; and milled for eight hours, heat treated, and ball milled for extra half an hour

Fig. 4 M-H curves for Mn₅₅Bi₄₅ for varied ball milling durations

Fig. 5 M-H curves of $\text{Mn}_{55}\text{Bi}_{45}$ powders ball milled for eight hours; milled for eight hours and then heat-treated; and milled for eight hours, heat treated, and ball milled for extra half an hour

Fig. 6. The comparison of morphology of ball milled MnBi powders at (a) room temperature for 8 h, (b) cryogenic environment for 8 h, (c) room temperature for 24 h, (d) cryogenic environment for 24 h

Fig. 7. M-H curves for 8 hours ball milled $\text{Mn}_{55}\text{Bi}_{45}$ at room temperature and cryogenic environment

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Fig. 8. M-H curves for 24 hours ball milled $\text{Mn}_{55}\text{Bi}_{45}$ at room temperature and cryogenic environment

Table 1 X-Ray phase composition analysis of MnBi powders ball milled at room temperature for eight hours; milled for eight hours and then heat-treated for twenty-four hours; and milled for eight hours, heat treated, and ball milled for extra half an hour. Uncertainties in the last significant figures are shown in parentheses.

Sample	MnBi				Bi		Mn		MnO
	Wt %	a (Å)	c (Å)	Crystallite size (nm)	Wt %	Crystallite size (nm)	Wt %	Crystallite size (nm)	Wt %
Feedstock	86.1(6)%	4.2867(1)	6.1181(1)	215(20)	5.3(3)%		2.4(3)%		6.3(4)%
Milled	77.0(5)%	4.2876(1)	6.1178(2)	52(1)	13.7(2)%	39(1)	5.0(4)%	49(9)	4.3(4)%
Milled +annealed	85.9(4)%	4.2866(1)	6.1176(1)	115(3)	5.2(2)%	43(3)	5.5(3)%	103(20)	3.4(3)%
Milled +annealed +milled	81.0(4)%	4.2867(1)	6.1177(1)	85(2)	10.2(2)%	39(1)	4.5(3)%	89(18)	4.3(3)%