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RESEARCH PAPER

Effects of Annealing Temperature and Composition on Magnetic Properties of Manganese-Bismuth Homogenized in Tube Furnace

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Abstract: *Repeated heat treatment on manganese-bismuth (MnBi) in a tube furnace increased the homogeneity of rare-earth-free magnets. Ferromagnetic low temperature phase (LTP) MnBi, was formed after heating Mn and Bi in a 2:1 ratio at 1000℃ for 1 h and then at 400℃ for 1 h. Areas with comparable amounts of Mn and Bi were detected, but some Mn and Bi elements remained segregated after using the above heat treatment schedule for 3 times. The subsequent annealing at 340℃ gave rise to higher magnetizations and coercivity compared to using 410℃ as an annealing temperature. Increasing the starting Mn:Bi ratio to 4:1 reduced the coercivity and remanent magnetization as a result of an increase in the Mn oxidation.*

Keywords: *MnBi, Rare-earth-free magnet, Coercivity, Remanent magnetization, Tube furnace.*

1. INTRODUCTION

Manganese-bismuth (MnBi) has attracted great interest for its hard ferromagnetic properties at room temperature and a recently reported magnetoresistance at low temperature [1]. As a rare-earth-free magnet, the coercivity of MnBi is increased with increasing temperatures up to 327°C. Such a higher performance at elevated temperatures is an opposite trend to those exhibited by other ferromagnetic materials. To utilize this unique magnetic characteristic, MnBi must be in low temperature phase (LTP) with the NiAs-type hexagonal crystal structure [2-4]. From the induction or arc melting, this phase is derived by a cooling of the high temperature phase (HTP) MnBi through the peritectic reaction at 355°C.

The segregation between Mn and Bi rich liquids with a large difference in the melting points of Mn and Bi lead to a mixture of the LTP-MnBi with other nonmagnetic phases [2, 5]. To enhance the LTP-MnBi formation and the phase homogeneity, the MnBi powders from the melting are subsequently annealed at 250°C-355°C [2-9]. The annealing in high magnetic field was further explored to improve the magnetic properties of MnBi [10]. In addition to the post treatment, the repeated steps of arc melting for a few times also increase homogeneity of MnBi phase and texture [2, 7, 8, 11-14]. Fang et al. repeated heating cycle to orient MnBi crystals via the self-flux [15].

Tube furnaces are commonly deployed in the annealing [5, 8, 10]. Interestingly, Nguyen and Nguyen described the temperature-gradient-driven annealing process by the tube furnace to promote the LTP-MnBi [14]. In another work, Saetang and co-workers studied the LTP-MnBi from the repeated heating in a tube furnace [16]. In this work, Mn flakes and Bi ingots were heated in a standard tube furnace up to 3 times. Homogenization by each heating cycle was monitored by Differential Thermal Analysis (DTA), which was used to study other Mn alloys [17]. For MnBi, thermal analysis has been employed to investigate the phase transformation related to the magnetic properties [15, 18-21]. Bulk magnets were then consolidated by simultaneous pressing and annealing MnBi powders. The influences of the annealing temperature and composition on magnetic properties were studied.

2. EXPERIMENTAL PROCEDURES

Mn flakes (99.9% min) and Bi ingots (99.99% min) were used as starting materials in atomic ratios of 2:1 and 4:1. A higher content of Mn over Bi has been recommended to compensate the Mn segregation and oxidation [2, 5, 13, 15]. They were placed in alumina crucibles and heated in a tube furnace (Carbolite GHA12/300). Under argon atmosphere, the temperatures were kept at 1000°C for 1 h and then 400°C for 1 h. The samples produced in atomic ratios of 2:1 and 4:1 are referred to as A1 and B1, respectively. This stepped heating was repeated on each sample twice, giving rise to samples A2, A3, B2, B3. After each heating, the products were coarsely ground and measured by DTA (Perkin Elmer DTA7) with the rate of 5°C/min to investigate the heat transfer during this stepped heating cycle. The morphology of samples after the third heating, i.e., A3 and B3, was examined by a Field-Emission Scanning Electron Microscope (FESEM, Zeiss Merlin Compact). The distribution of elemental composition was also measured by an Energy Dispersive X-ray Spectroscopy (EDX, Oxford Aztec) probe attached to the FESEM.

The MnBi powders were consolidated for 12 h in the annealing-pressing system developed and detailed in the published work [22]. The applied pressure was 50-60 psi and the temperature was varied as 340°C and 410°C. Magnetic properties of MnBi magnets after annealing at 2 different temperatures were compared by an in-house developed vibrating sample magnetometer (VSM) in sweeping fields between -16 and 16 kOe. A Ni sphere of 3 mm in diameter was used for calibration with a standard VSM (Lakeshore 730908).

3. RESULTS AND DISCUSSION

Fig. 1 reveals sharp endothermic peaks of the Bi melting in the DTA curves of all samples. The temperature is increased from 273°C in sample A1 to 275°C in sample A3, contrasting with the reduction from 272°C in sample B1 to 270°C in sample B3. This slight peak shift after each heating is consistent with the literature that the transition temperatures are highly influenced by the phase composition [19, 20]. Different heating rates also give rise to the peak shift in thermogram [19]. According to thermograms in the literature [18, 20, 21], the eutectic Bi melting is followed by other endothermic peaks signifying the LTP to HTP transition around 355°C and the peritectic decomposition of HTP into Mn and Bi rich liquid above 446°C. However, these peaks are not clearly observed for all samples in Fig. 1. The absence of the MnBi transformation peak, previously reported by Janotova et al. [21], is due to the oxidation of Mn in ambient atmosphere. It is also related to a lower percentage of LTP-MnBi in the mixed phase than those obtained from the literature using the induction and arc melting [19, 20].

In addition to the Bi melting peak, Fig. 1 also show small broad endothermic peaks preceding the Bi melting at varying temperatures. At higher temperatures, a broad exothermic peak present around 980°C after each heating with the Mn:Bi composition of 2:1 in Fig. 1a is attributed to the crystallization. By increasing the Mn:Bi composition to 4:1, these exothermic peaks are replaced by the smaller endothermic peaks occur at lower temperatures of 730-747°C in Fig. 1b. The different peaks at varying temperatures suggest the influence by different phase compositions, which is further supported by the following structural and magnetic characterizations.

The LTP-MnBi phase in the samples prepared using the starting Mn:Bi of 2:1 and 4:1 after each heating was previously confirmed by X-ray diffractometry (XRD) [16]. XRD patterns also revealed the presence of Mn and Bi peaks with different intensity after each heating. The MnBi crystallite size, determined from the Scherrer formula, was maximized after the third heating at 23.8 nm for sample A3, and 23.1 nm for sample B3 [16].

Fig. 2 shows agglomerations of the mixed phase into microstructures that could be related to the ratio of starting materials. With the Mn:Bi ratio of 2:1, sample A3 has predominantly plate-like morphology with some smooth surfaces exemplified in Fig. 2a. The particles tend to agglomerate into globular and irregular aggregates, when the Mn:Bi is increased to 4:1 for sample B3 in Fig. 2b.

Figs. 2a and 2b also indicate ten areas in each sample for measuring the elemental composition.

The EDX spectra (not shown here) were grouped in Table 1 into the Bi rich areas and those with a more balanced composition.

Eight spectra indicate comparable atomic percent of Mn and Bi in sample A3, giving rise to the average Mn:Bi ratio of 1.21 ± 0.20. The two other spectra correspond to the Mn and Bi segregations. Spectrum 31 indicates an area with 12 times Bi over Mn, whereas spectrum 40 (not listed in Table 2) exhibits the Mn:Bi ratio of 11.03. Approximately 20% oxygen was detected in all areas because Mn is susceptible to the oxidization in ambient atmosphere after the process [2, 21]. The EDX was further used to inspect the area with a balanced composition of Mn and Bi. In a highly magnified image in the inset of Fig. 2a, five EDX spectra obtained from the same particle yield the average Mn:Bi ratio of 1.11 with a reduction in standard deviation to 0.13. A particle nearby in the inset contains a lower Mn, having the average Mn:Bi ratios of 0.7468 and 0.9861. Sample B3, prepared using the starting Mn:Bi ratio of 4:1 has a larger distribution in the elemental composition. The number of spectra classified as Bi rich in Table 1 increases to four.

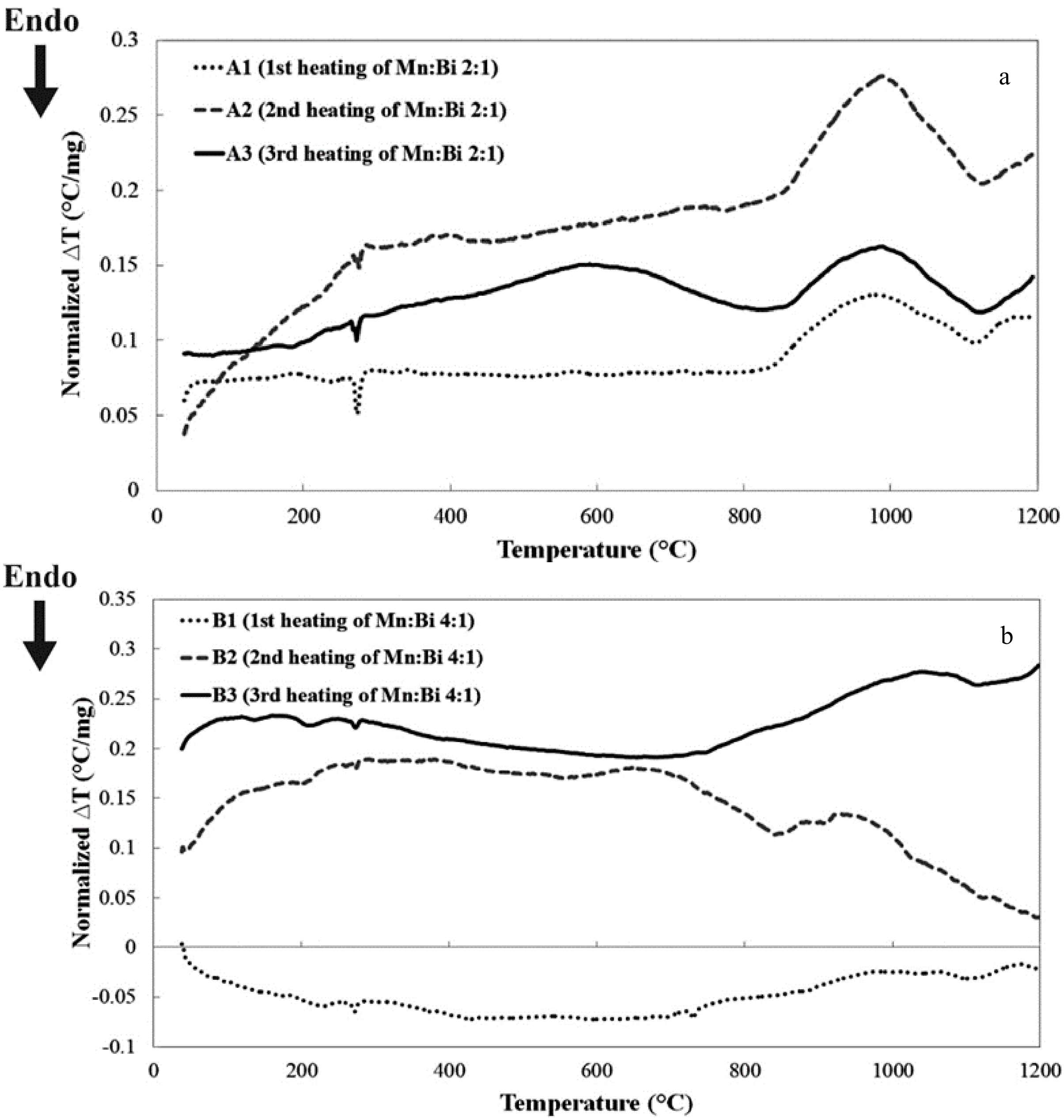

Fig. 1. DTA curves of the samples prepared with Mn:Bi of (a) 2:1 and (b) 4:1 after each step heating

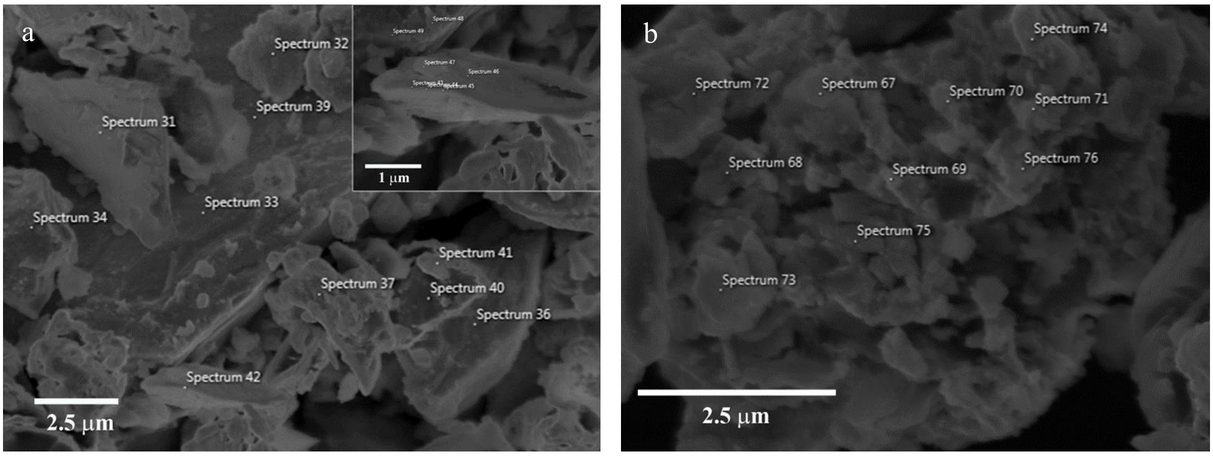

Fig. 2. FESEM images of the samples prepared with Mn:Bi of (a) 2:1 and (b) 4:1 after the third step heating.

Table 1. Elemental composition of MnBi samples after the third heating in the tube furnace.

Sample	Balanced areas			Bi rich areas		
	Spectrum	Mn:Bi	O	Spectrum	Mn:Bi	O
A3 (Fig 1a)	32, 33, 34, 36, 37, 39, 41, 42	1.21	23.39%	31	0.079	18.20%
B3 (Fig 1b)	68, 70, 71, 73, 74, 76	1.01	29.45%	67, 69, 72, 75	0.210	31.23%

In areas of a balanced composition, the resulting Mn:Bi composition averaged from six spectra is close to 1 but the standard deviation is increased. Furthermore, the percentage of oxygen is approximately 30% more than those in sample A3 for both balanced and Bi rich areas. This result suggests that the additional Mn does not promote the LTP-MnBi but is partly oxidized.

Ferromagnetic characteristics in Fig. 3 correspond to the LTP-MnBi. The magnetizations in all cases are increased with increasing magnetic field exceeding 10 emu/g without saturation in 16 kOe field. These maximum values, listed as M_{max} in Table 2, are much lower than the theoretical limit of 80 emu/g [2]. The difference in hysteresis loops show the effects of annealing and composition on magnetic properties. The largest coercivity (H_c) (1474 Oe) and remanent magnetization (M_r) (5.16 emu/g) occur in the case of Mn:Bi composition of 2:1 and annealing temperature of 340°C. The magnetic squareness, approximated from the ratio of M_r to M_{max}, is slightly below the typical values of 0.5 in the review literature [2]. For a higher Mn:Bi composition of 4:1, the coercivity and remanent magnetization are respectively decreased to 999 Oe and 3.65 emu/g after the annealing at 340°C. Such drops are consistent with the increase in oxygen shown in Table 2, signifying the reduction in the ferromagnetic LTP MnBi phase. These values are comparable to those of MnBi powders homogenized in the tube furnace [16], but somewhat lower than those obtained by heating Mn and Bi powders in a crucible under low pressure of 2×10^{-7} mbar to minimize the oxidation [23].

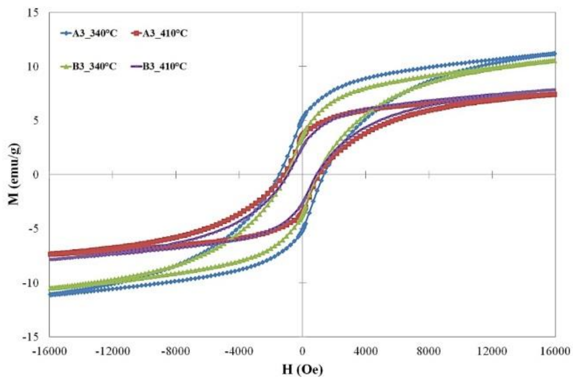

Fig. 3. Comparison of hysteresis loops after annealing the magnets prepared with Mn:Bi composition of 2:1 (A3) and 4:1 (B3) at 340°C and 410°C.

The increase in the annealing temperature to 410°C aimed to promote the ferromagnetic LTP-MnBi by increasing the diffusion rate. However, the coercivity is substantially reduced to 923-1175 Oe whereas the remanent magnetization is decreased to 7.39-7.85 emu/g. The reduction in hard magnetic characteristics can be explained by the LTP to HTP transition around 355°C. The annealing at 340°C is therefore favorable, consistent with the suggestion in the literature [12].

Table 2. Magnetizations and coercivity of the magnets prepared with Mn:Bi composition of 2:1 and 4:1 and annealed at 340°C and 410°C.

Sample	**M_{max} (emu/g)**	**M_r (emu/g)**	**H_c (Oe)**	**Magnetic squareness**
A3_340°C	11.13	5.16	1,474	0.46
A3_410°C	7.39	3.58	1,175	0.48
B3_340°C	10.53	3.65	999	0.35
B3_410°C	7.85	2.61	923	0.33

4. CONCLUSIONS

Elemental composition and thermal properties of MnBi after each heating cycle at 1000°C for 1 h and then 400°C for 1 h were correlated with the magnetic properties. With the starting Mn:Bi ratio of 2:1, the resulting composition around 1 corresponds to the MnBi phase but the LTP to HTP transition was not observed in the DTA curve. The subsequent annealing at 340°C promoted the formation of ferromagnetic phase. However, the magnetization and coercivity were decreased when the annealing temperature was raised to 410°C. A higher starting Mn:Bi ratio of 4:1, reduced the amount of ferromagnetic phase, resulting in coercivity values of less than 1000 Oe.

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