Effect of Composition and Heat Treatment on MnBi

Magnetic Materials

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Abstract: The metallic compound MnBi is a promising rare-earth-free permanent magnet material, unique among all candidates for its high intrinsic coercivity (H_{ci}) and its large positive temperature coefficient. The H_{ci} of MnBi in thin-film or in powder form can exceed 12 kOe and 26 kOe at 300 K and 523 K, respectively. Such a steep rise in H_{ci} with increasing temperature is unique to MnBi. Consequently, MnBi is a highly sought-after hard phase for exchange coupling nanocomposite magnets. However, the reaction between Mn and Bi is peritectic, so Mn tends to precipitate out of the MnBi liquid during the solidification process. As result, when the alloy is prepared using conventional induction or arc-melting casting methods, additional Mn is required to compensate the precipitation of Mn. In addition to composition, post-casting annealing plays

an important role in obtaining high content of MnBi low-temperature phase (LTP) because the annealing encourages the Mn precipitates and the unreacted Bi to react forming the desired LTP phase. Here we report a systematic study of the effect of composition and heat treatments on the phase content and magnetic properties of Mn-Bi alloys. In this study, 14 compositions were prepared using conventional metallurgical methods, and the resulting alloys were analyzed for compositions, crystal structures, phase content, and magnetic properties. The results show that the composition with 55 at.% Mn exhibits both the highest LTP content (93 wt.%) and magnetization (74 emu/g with 9T applied field at 300 K).

Keywords: MnBi, rare-earth free, permanent magnet

1. Introduction

MnBi compound is a promising permanent magnetic material because of its high coercivity with a large positive temperature coefficient. MnBi exhibits a first-order structural transition between temperatures of 613 K (340 °C) and 628 K (355 °C) [1]. The equilibrium phase below the transition point is commonly referred to as the low-temperature phase (LTP) and that above is the high-temperature phase (HTP). The composition, lattice structure, and parameters for the HTP phase are $\text{Mn}_{2.23}\text{Bi}_{1.88}$, *Pmma*, and $a = 0.5959$ nm, $b = 0.4334$ nm, $c = 0.7505$ nm, $\alpha = \beta = \gamma = 90^\circ$, respectively [2]. For the LTP phase, they are $\text{Mn}_{50}\text{Bi}_{50}$, *P63/mmc*, and $a = b = 0.4290$ nm, $c = 0.6126$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, respectively [3-5]. The LTP MnBi has a high magnetocrystalline anisotropy of $(1.6 \times 10^6 \text{ J/m}^3)$, and relatively low saturation magnetization (81 emu/g, ~9 kG) at 300 K [6]. Its theoretical maximum energy product is estimated to be 20 MGOe using the formula $(\text{BH})_{\text{max}} = M_s^2/4$, where M_s is the saturation magnetization. The first

bulk MnBi magnet was prepared by Adams in 1953 [7]; an energy product of 5.3 MGOe (42 kJ/m³) was achieved.

Part of the reason for such a low energy product compared to its theoretical maximum value was attributed to the difficulty of obtaining a high volume fraction of the desired LTP MnBi. The difficulty originates from the peritectic reaction between Mn and Bi, which causes Mn to solidify and segregate from the Mn-Bi liquid during the solidification process. The kinetics of the segregated Mn reacting with the excessive Bi to form LTP MnBi is slow [8]. Researchers tried to make MnBi alloy with high LTP content using various metallurgical methods, but all failed to exceed 90 wt.% [8-12].

In 1990, melt-spinning method was adopted for MnBi synthesis, and over 95 wt.% LTP MnBi was achieved [13-17]. This great achievement is attributed to the high cooling rate of the melt-spinning method, which is generally believed to be in excess of 10⁶ K/s. While it is common for a small (10-gram) capacity melt-spinning setup to reach the cooling rate necessary to obtain a MnBi ribbon free of Mn precipitates, it is rather difficult for a larger (kilogram or higher) capacity setup to achieve the same. A conventional metallurgical method, such as arc or induction melting casting followed by thermal-mechanical treatment, is much preferred for feasibility and cost effectiveness. We have been developing such a method for over two years, and reported the properties of the resulting high-purity powder with composition near 56 at.% Mn [18, 19]. The same method was used to prepare a series of Mn-Bi alloys to optimize composition for maximum magnetization. This paper presents details of this conventional metallurgical method and the result of composition optimization.

2. Experimental

2.1. Sample preparation

High purity Mn (manganese) chips (Alfa Aesar: 99.98 wt.%) and Bi (bismuth) shot (Aldrich: 99.999 wt.%) were weighed according to the designed atomic ratio, then mixed and pressed to form a pellet using a die with 19 mm inner diameter. The designed weight of each pellet is about 20 g; the actual weights of the as-obtained pellets vary, but are within ± 0.1 g error. In total, 14 pellets were prepared. The designed composition varied from 45 to 80 at.% Mn. These pellets were arc melted and cast into buttons.

2.2. Heat treatments

The LTP MnBi is sensitive to oxygen. According to the FactSage thermochemical database, the change in free energy for the MnBi oxidization reaction, $3\text{MnBi} + 4.25\text{O}_2(\text{g}) = \text{Mn}_3\text{O}_4 + 1.5\text{Bi}_2\text{O}_3$ is -156 kcal/mol at 300 K (27 °C). It appears that MnBi alloy is more oxygen sensitive than Cu (-130 kcal/mol). Hence, heat treatment of MnBi alloys must be carried out in an inert or reducing atmosphere.

The as-obtained buttons were heat-treated using a tube furnace under pure hydrogen gas atmosphere. The heat-treatment schedule had two steps: 1) ramp to 528 K (255 °C) at a rate of 10 K/min, hold for 8 hours; and 2) ramp to 625 K (352 °C) at a rate of 10 K/min, hold for 5 hours, then furnace cool to room temperature. The second step dwells at a temperature between the LTP and HTP MnBi formation temperatures of 613–628 K (340–355 °C). During this step, some LTP decomposes to liquid and HTP. However, the decomposition is expected to be small, and higher temperature is advantageous for the Mn and Bi precipitates to react.

Following the heat treatment, the buttons were crushed, ground and sieved to powders with three sizes ($>44\text{ }\mu\text{m}$, $37\text{--}44\text{ }\mu\text{m}$, and $<37\text{ }\mu\text{m}$). The $37\text{--}44\text{ }\mu\text{m}$ powder was further heat treated under vacuum ($\sim 100\text{ mTorr}$) at 563 K ($290\text{ }^{\circ}\text{C}$) for 24 hours.

2.3. Characterization

Compositions of the as-obtained samples were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray diffraction patterns of the powders were collected with a Panalytical X-Pert Bragg-Brentano diffractometer. A 0.05 mm receiving slit was used for increased resolution. Phase proportions and cell parameters 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*. Magnetic properties of the powders were characterized using vibrating sample magnetometer (VSM) and physical properties measurement system (PPMS). Microstructures of the ingots and morphology of the powders were analyzed using scanning electron microscope (SEM).

3. Experimental results

3.1. Microstructures of the MnBi ingots before and after the two-step heat treatment

Microstructures of the as-cast ingots with 45, 55, and 75 at.% Mn are shown in Fig. 1. The microstructures of these as-cast ingots show areas with three distinct colors: black, dark gray and light gray. Composition analysis shows that these colors correspond to Mn, MnBi, and Bi phases, respectively. Fig 1(a) shows that despite the ingot being 5 at.% Mn less than the stoichiometric point, noticeable amount of Mn phase can be still be found in the ingot. It is apparent that the cooling rate of the arc-melting casting process is not fast enough to prevent Mn from

precipitating. According to the Mn-Bi phase diagram shown in Fig. 2, the MnBi alloy with 45 at.% Mn remains liquid when the temperature is above ~1133 K (860 °C). If the liquid is quenched to below 535 K (262 °C), the ingot will have a small amount of Bi and a large amount of MnBi (~90 at.%). It will be free of Mn precipitate. In contrast, if the liquid is gradually cooled to below 535 K (262 °C), as much as 32 at.% of Mn may precipitate out and coexist with LTP and Bi phases in the ingot at room temperature. The phase diagram suggests the amount of Mn precipitates increases with increasing Mn content in the starting Mn-Bi mixture. This trend is evident by the increasing size of the Mn areas in the ingots with 55 and 75 at.% Mn, as shown in Fig. 1(b) and 1(c), respectively.

Microstructures of the heat-treated ingots are shown in Fig. 3. A significant increase of LTP MnBi phase (gray area) is observed for all three compositions. For the ingot with 45 at.% Mn, Fig. 3(a) shows that Mn metal still exists after the heat treatment, and the Mn metal is embedded in the LTP, suggesting it is the product of HTP to LTP transformation. For the ingot with 55 at.% Mn, Fig. 3(b) shows that the LTP is uniformly distributed and forms a matrix. The Bi phase is successfully minimized, but the amount of Mn metal appears to be significant and the formation of these Mn metal areas appears to be dendritic and embedded in the LTP. For the ingot with 75 at.% Mn, Fig. 3(c) shows significantly larger Mn areas. Interestingly, Bi areas are also observed despite the composition being far off the stoichiometric point. The hypothesis for Bi deposition is that forming large areas of Mn phase may cause nearby solution to be rich in Bi, which subsequently forms Bi phase. Fig. 3(c) shows most of the Bi areas (light gray in color) are near the Mn region (black in color).

3.2. Effect of grind-and-sieve and vacuum heat treatment on LTP content

After the two-step heat treatment, the ingots were ground into powders (37~44 μm), then heat treated under vacuum (~ 100 mTorr) at 563 K (290 $^{\circ}\text{C}$) for 24 hours to encourage the precipitated Mn and Bi to form more LTP MnBi. Fig. 4 shows the morphology of the powder before and after vacuum heat treatment. Similarity in size and shape of the particles before and after vacuum heat treatment implies little sintering occurred during the vacuum heat treatment.

To examine the effect of the vacuum heat-treatment on compositions and phase fractions of MnBi alloy, ICP-AES and XRD analysis were carried out for the powders. Fig. 5 shows the amount of excessive Mn before and after the vacuum heat treatment measured by ICP-AES. The compositions of the arc melted buttons and the heat-treated powders systematically deviate from the designed composition (i.e., the composition of the pellets before arc melting). Below the composition of 55 at.% Mn, the alloys tend to have more Mn than they are formulated to. For example, the pellet with 45 at.% Mn gained 2.2 at.% Mn (lost 2.2 at.% Bi) after the arc melting. Above the composition of 55 at.% Mn, the alloys tend to have less Mn than they are formulated to. For example, the pellet with 80 at.% Mn lost 3.4 at.% Mn after arc melting.

There are 4 steps to process a MnBi ingot to the powder containing high content of LTP MnBi. These steps are arc melting, two-step heat treatment in hydrogen, grind-&-seive, and vacuum heat-treatment. Figure 6 shows the XRD patterns of the powders after each processing step for the alloy with 55 at.% Mn. It shows that the intensity of the Bi peaks gradually decreases and eventually disappears as processing progresses. The phase fractions of each composition, before and after heat treatment, are summarized in Table 1 and plotted in Fig. 7. The plot in Fig. 7(a) shows that after the grind-and-sieve process, Bi decreases with increasing Mn content, almost linearly but with small fluctuation in the beginning ($\text{Mn} < 55$ at.%); Mn increases more linearly with increasing Mn content. More importantly, the amount of MnBi phase fluctuates around 65

mol.% before the Mn content exceeds 55 at.%, then linearly decreases with increasing Mn content. The overall trend of MnBi content is decreasing. Fig. 7(b) shows the phase fractions after the vacuum heat treatment. Clearly, the monotonic trends are broken and an optimum composition point emerges. First of all, most of the Mn phase is converted to MnO, and the percentage of MnO is relatively constant and independent of Mn content, indicating the kinetics of the Mn oxidization process is related to the heat treatment process. Second, Bi quickly decreases to less than 2 mol.% at 55 at.% Mn, then remains constant. More importantly, the amount of MnBi quickly increases to ~80 mol.% at ~55 at.% Mn, then decreases linearly with increasing Mn content.

3.3. Magnetic properties of the MnBi powders

The magnetizations of the MnBi powders versus compositions at 300 K (27 °C) are plotted in Fig. 8. The applied field was 2.3 T, which far exceeded the typical coercivity of these powders (< 3 kOe). Our experience for MnBi indicates that the particle size has to be less than 5 μm to show coercivity greater than 10 kOe. If the MnBi particle size is big (e.g., 25-40 μm), the highest coercivity it exhibits is about 3 kOe. Not surprisingly, Figure 8 shows the composition with 55 at.% Mn shows the highest magnetic moment given the fact that this is the composition possessing the highest LTP MnBi content, while the compositions away from this value show significantly reduced magnetic moments. Figure 9 shows the MH loop of the MnBi powder with 55 at.% Mn composition with 9 T field. It shows the saturation magnetization of the 55 at.% Mn powder is about 74 emu/g at 300 K. Recall that the LTP MnBi content in this powder is about 93 wt.%; a powder with 100% LTP MnBi would show a saturation magnetization of 80 emu/g.

4. Discussions

4.1. Deviation of the obtained compositions from the designed value

We think that the deviation of the as-obtained composition from the designed value is related to the *grind-and-sieve process* that removes Bi metal from the sample. The grinding process fractures particles to expose Bi, and then presses the exposed soft Bi onto the mortar wall, forming a dark metallic colored coating. The more Bi metal in the crushed MnBi powder the more Bi metal is removed by the grind-and-sieve process. In addition to Bi removal, the grinding process also removes Mn metal by first forming MnO, which is hard and easily broken into fine powder, then pressed the MnO powder into the soft Bi metal coating on the mortar. The residual on the mortar wall was analyzed for its composition using ICP-AES. It shows both Mn and Bi elements are present in the residual with Mn:Bi mole ratio close to 0.5. It appears that the grind-and-sieve process removes both Bi and Mn. It is a competing process during which Bi removal dominates below the 55 at.% Mn point while above that point Mn removal starts to take over.

4.2. Importance of HTP to LTP phase transformation

The HTP has about 54.3% at.% Mn. It transforms to LTP and Mn between 613 K (340 °C) and 628 K (355 °C). The 55 at.% Mn optimum point is thought to be closely related to this transformation. For the alloys with compositions < 55 at.% Mn during the solidification process, the alloy first forms the Mn phase, the HTP and a Bi-rich liquid phase. Then, the HTP transforms to the LTP and Mn. In the mean time, the Bi-rich liquid transforms to the LTP and a liquid phase containing even more Bi, of which eventually decomposes to the Bi and the LTP. For the alloys with compositions > 55 at.% Mn, the phase formation process is similar. The difference lies in

the phase ratios. Because the starting composition is on the right side of the HTP, the amount of the Bi-rich liquid is small and the resulting Bi phase is small. Apparently, the HTP is an intermediate phase that cannot be avoided during the cast-chill solidification process.

Fundamentally, the reason for preferential formation of HTP is that the energy barrier for Mn to diffuses in the quenched HTP (a partially-disordered structure with fractional occupancies) is lower than that in the LTP (a fully-ordered structure). Therefore, to maximize the LTP content, excessive 4.3% of Mn must be added to maximize the HTP content. A possible way to bypass formation of the HTP is to precipitate the LTP directly from the Bi-rich melt with <10 at.% Mn. In addition, the calculated energy barriers in the LTP for diffusion of Mn and Bi vacancies and interstitials at 0 K are all above 1 eV. Although these barriers become lower with increasing temperature, they are too high compared to $kT < 53$ meV at 613 K (340 °C). Consequently, diffusion of Mn and Bi to the LTP is not expected, explaining the sluggish kinetic of the reaction $\text{Mn} + \text{Bi} = \text{MnBi}$.

4.3. Weight changes of the phases during vacuum heat treatment

To understand the weight changes of these phases during the vacuum heat treatment, one can use the XRD phase fraction analysis in Table 1 and the mole ratios of the two reactions to derive approximate weight changes. For example, for the sample with 55 at.% Mn (designed composition), one gram of powder consists of 0.82 g of MnBi phase, 0.14 g of Bi phase, 0.05 g of Mn phase, and 0 g of MnO. Assume that during the vacuum heat treatment, the following occur: 1) Y g of Bi is vaporized and taken away by vacuum; 2) Z g of Bi reacts with Q g of Mn phase, forming X g of MnBi; 3) P g of Mn reacts with oxygen, forming N g of MnO phase. In addition, during each vacuum heat treatment run, the powder is weighed and the values before

and after the treatment are compared. It was found that for the sample with 55 at.% Mn (designed composition), the total weight change of the powder is negligible (<0.05 wt.%), therefore the sum of the weight changes for these phases can be set to zero, i.e.,

$$X - Y - Z - P - Q + N = 0 \quad (1)$$

Moreover, the loss of Bi to vacuum, Y, must be equal to the gain of oxygen; therefore,

$$N \times MW_O / MW_{MnO} = Y, \quad (2)$$

where MW_{MnO} and MW_O are the molecular weight of MnO and O, respectively. Furthermore, when the Bi and Mn react to form MnBi, their mole numbers must be equal; therefore,

$$Z / MW_{Bi} = Q / MW_{Mn} = X / MW_{MnBi}, \quad (3)$$

where MW_{Bi} , MW_{Mn} , and MW_{MnBi} are the molecular weights of the Bi, Mn and MnBi phases, respectively. Similarly, the mole number of the Mn phase reacting with oxygen to form MnO is equal to the mole number of the MnO phase:

$$P / MW_{Mn} = N / MW_{MnO}. \quad (4)$$

Lastly, according to Table 1, the weights of the MnBi and MnO phases before and after vacuum heat treatment are

$$0.82 + X = 0.93, \quad (5)$$

$$N = 0.04. \quad (6)$$

Based on the above equations, the six variables can be solved. The solution is $X = 0.11$ g, $Y = 0.01$ g, $Z = 0.09$ g, $P = 0.03$ g, $Q = 0.02$ g, $N = 0.04$ g. The interpretation of this solution is that during the vacuum heat treatment of 1 g of 55 at.% Mn powder, 0.09 g of Bi and 0.02 g of Mn reacted together, forming 0.11 g of MnBi; 0.01 g of Bi is lost to vacuum; and 0.03 g of Mn reacted with 0.01 g of oxygen, forming 0.04 g of MnO. The lost Bi has the same weight as the gained oxygen, resulting in zero overall weight change. The calculation further indicates that the

weight of the remaining Bi metal is about 0.04 g after heat treatment; this is reasonably close to the 0.02 g value observed by XRD, which has an error range of ± 0.01 g.

The main conclusion of this calculation is that the gain in LTP-MnBi phase fraction during the vacuum heat treatment is through the reaction of Mn and Bi. Vacuum helps but is not critical. If oxygen can be tightly controlled, it is possible to use unreacted Mn and Bi more effectively, and the optimum composition will be closer to the stoichiometric point. For example, with 52 at.% Mn composition, there is 4 wt.% MnO and 6 wt.% Bi in the heat-treated sample. These can form MnBi if oxygen is not present.

5. Conclusions

MnBi with LTP content is difficult to obtain because of the peritectic reaction between Mn and Bi, where Mn phase starts to separate during the solidification process. Due to the preferential formation of the HTP, which later transforms to LTP and Mn, excess Mn is required to compensate the Mn precipitation. A newly developed thermo-mechanical processing route is shown to be able to synthesize MnBi powder with > 90 wt.% LTP. The process takes advantage of the differences in physical properties of the phases coexisting in the cast MnBi alloys, such as hardness and vapor pressure, to remove the unreacted phases. The process also takes into account the excessive Mn required to compensate the Mn precipitation, therefore maximizing the amount of LTP MnBi. The process is easy to implement and compatible with the current industrial practice. In addition, for the developed process, 55 at.% Mn was identified as the optimum composition for the MnBi alloy with the highest LTP content and the highest magnetization.

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Figure 1. The microstructure of as-cast MnBi ingots obtained by arc melting.

(a) 45 at.% Mn, (b) 55 at.% Mn, and (c) 75 at.% Mn

Figure 2. The phase diagram of Bi-Mn [1].

Figure 3. The microstructure of two-step heat-treated samples.

(a) 45 at.% Mn, (b) 55 at.% Mn, and (c) 75 at.% Mn

(a)

(b)

Figure 4. Powder surface morphology (SEI) before and after vacuum heat treatment (55 at.% Mn); (a) as ground and sieved, (b) after vacuum heat treatment.

Figure 5. The chemical composition of samples before and after vacuum heat treatment. (Note: “Before HT” is as-ground and sieved sample and 37–44 μm size)

Figure 6. The normalized XRD patterns after each step (55 ± 1 at.% Mn).

(a)

(b)

Figure 7. Phase fractions analysis by XRD (a) before and (b) after vacuum heat treatment..

Figure 8. The composition effect on saturation magnetization of the MnBi powders. The magnetizations were measured with 2.3 T field at 300 K.

Figure 9. MH loop of the MnBi powders with 55 at.%Mn composition. The measurement was carried out at 300 K.

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Table 1. The chemical composition of samples before and after vacuum heat treatment (by XRD analysis).

Designed at.% Mn	Before vacuum heat treatment					After vacuum heat treatment				
	Actual at.% Mn	MnBi wt.%	Bi wt.%	α -Mn wt.%	MnO wt.%	Actual at.% Mn	MnBi wt.%	Bi wt.%	α -Mn wt.%	MnO wt.%
45	47	77	21	2	0	47	74	23	1	3
46	48	74	23	3	0	47	72	23	1	4
47	48	78	21	2	0	48	75	21	1	4
48	48	73	24	3	0	49	73	22	1	4
49	49	75	23	3	0	50	77	18	1	4
50	51	79	17	3	0	51	81	15	1	4
51	52	81	16	3	0	52	86	8	0	6
52	52	76	20	4	0	52	90	6	1	4
54	54	78	17	5	0	54	92	3	1	5
55	55	82	14	5	0	55	93	2	1	4
60	60	79	12	9	0	60	91	1	3	5
70	68	80	8	16	0	68	85	1	10	4
75	72	73	5	22	0	73	77	1	17	5
80	77	67	7	27	0	77	73	2	20	5