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EFFECT OF PRE-ALLOY COMPOSITION ON THE CONTENT OF FERROMAGNETIC PHASE OF MnBi MELT SPUN RIBBONS[#]

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Abstract. The rare-earth-free hard magnetic material MnBi is potential for permanent magnet high-temperature applications with the ferromagnetic phase formed at low temperature (noted as a Low Temperature Phase – LTP). Up to now, the MnBi powders with high LTP content and coercivity have usually been prepared using the melt-spinning technique. However, the large difference in the melting temperature T_m of the two constituents, Mn and Bi, and the strong reactivity of Bi with the copper-based wheel make the preparation of high-performance MnBi ribbons to be difficult. By using a novel approach which creates buffer layers on the inner wall of quartz tube and the cooper wheel surface, we overcame these difficulties and prepared the MnBi ribbons on the conventional commercial melt-spinning furnace ZGK-1. We prepared the melt-spinning Mn_xBi_{100-x} ribbons with x = 45, 50, 55 and 60. The highest performance of milled ribbons is featured by H_c = 4.52 kOe and M_s = 55 emu/g for x = 55. The influences of pre-alloy compositions on the magnetic properties of MnBi melt - spun ribbons will be discussed in detail.

Keywords: MnBi hard magnetic material, MnBi LTP, spontaneous magnetization, as – spun ribbons.

Classification numbers: 2.2.1, 2.8.2, 5.1.1.

1. INTRODUCTION

MnBi-based hard magnetic materials have been investigated since the early 1950s [1], however over past 60 years the quality of MnBi bulk magnets is restricted by the value of 8.4 MGOe that is far below the theoretical limit of 17.6 MGOe [2]. The MnBi material shows the spontaneous magnetization M_s of ~ 8.2 kG, the high magneto-crystalline energy K_a of 0.9

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MJ/m^3, the elevated Curie temperature T_c of 360 ^oC, and in particular, the positive temperature coefficient of coercivity $d({}_iH_c)/dT > 0$. These features make MnBi-based magnets promising for high-temperature applications [3].

For MnBi alloys, the Bi-decomposition effect caused by the peritectic nature of solidification is unavoidable, so the preparation of high-performance single-phase MnBi alloys becomes a great challenge during the last years [4-21]. Up to now, the MnBi powders with high LTP content and coercivity are usually prepared using the melt-spinning technique [19, 22-28]. However, the large difference in the melting temperature T_m of the two constituents, Mn and Bi, and the strong reactivity of Bi with the copper-based wheel make the preparation of high-performance MnBi ribbons difficultly. We developed a technique to overcome the mentioned restrictions and prepared the MnBi ribbons by using the conventional commercial melt-spinning furnace ZGK-1. The MnBi LTP formation and the magnetic properties of prepared ribbons will be discussed in detail.

2. MATERIALS AND METHODS

The alloys with nominal compositions of Mn_xBi_{100-x} (x = 45-60) were arc-melted from the starting high-purity 99.9 % metals Mn and Bi under argon atmosphere. The ingots were melted three times to ensure their homogeneity. These pre-alloys were melted in the high-quality quartz tube with buffer layers on the inner wall and rejected onto a rotating cooper wheel with modified surface in 0.05 MPa argon atmosphere. The batch amount of pre-alloys was kept around 10 g. The wheel speed was chosen at 20 m/s, the quartz tube orifice diameter was fixed at 1.0 mm, the distance between the nozzle and the wheel surface was kept constant by 3 mm. The melt-spun ribbons were annealed at 280 ± 5 ^oC in argon for 8 h. The composition phases of as-spun ribbons and annealed ones were carried out by using D8 advance Bruker X-ray diffractometer (XRD) with Cu-Kα radiation with the scattering 2θ angle scan in the range from 20 to 80 degrees by the scanning step of 0.05° for 3 s. The LTP contents of ribbons were estimated quickly using the instant method described in Ref. [29]. The morphology of ribbon was studied by using scanning electron microscopy (SEM). The hysteresis loops of prepared MnBi ribbons were measured by the homemade pulse magnetic field magnetometer (PFM) with the magnetizing field magnetized of 90 kOe .

3. RESULTS AND DISCUSSION

Figure 1 plots the powder XRD patterns of the Mn_xBi_{100-x} (x = 45, 50, 55 and 60) as – spun ribbons prepared with the wheel speed of 20 m/s. All the peaks belong to the phases of Mn, Bi and MnBi. The main peaks of Bi and MnBi LTP are located at 27.16 and 28.14 degrees, respectively. According to the instant method of determining the LTP content [29], the intensity ratio $\gamma = (I_{MnBi(101)}/I_{Bi(012)})$ reflects the LTP content δ of the alloy taken under XRD measurement by the formula $\delta(wt\%) = 44.6 + 51.3\log\gamma$. The MnBi LTP contents are 29.8, 29.25, 23.85 and 18.34 wt% for the as-melt-spun ribbons with x = 45, 50, 55 and 60, respectively. This monotonous dependence of δ versus x reflects the nature of rapid quenching process, where the solidification of ribbons is proceeded under a high cooling rate so the Mn-rich starting alloys lead to the less content of LTP and more content of Mn-inclusions precipitated during the quenching melted alloys to the ribbons. The fractions of the said Mn-inclusions are obviously observed for ribbons by watching the peak of Mn at 2θ = 43.02^o. This peak is increased by increasing x values.

The cooling rate, the most important parameter of the melt-spinning process, also depends on the x value. The larger x value is, the greater cooling rate and subsequently, the thinner thickness of ribbons is observed as seen on the Fig. 2. The graph of cross sections of ribbons reveal that the ribbons are fairly uniform with the thickness in range 28 – 34 µm. The highly uniform ribbons presented in Fig. 2 show the success of applied approach in using the buffer layers on the inner wall of the quartz tube and on the wheel surface to cancel the cling effect of melted Bi. Moreover the Mn-rich composition of starting alloys reduces also the viscosity of melt batch caused by the melting Bi. Both these evidences effect on the cooling rate and the composition conservation for melt-spun ribbons.

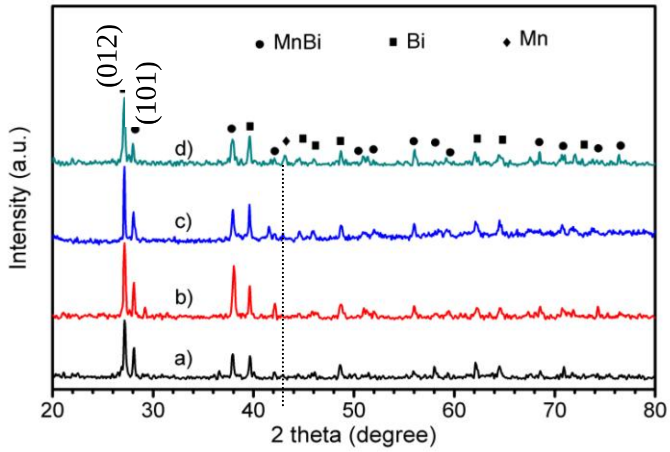

Figure 1. XRD patterns of Mn_xBi_{100-x} as spun ribbons at v = 20 m/s: a) x = 45; b) x = 50; c) x = 55; d) x = 60. The dotted vertical line denotes the position of the strongest peak of Mn.

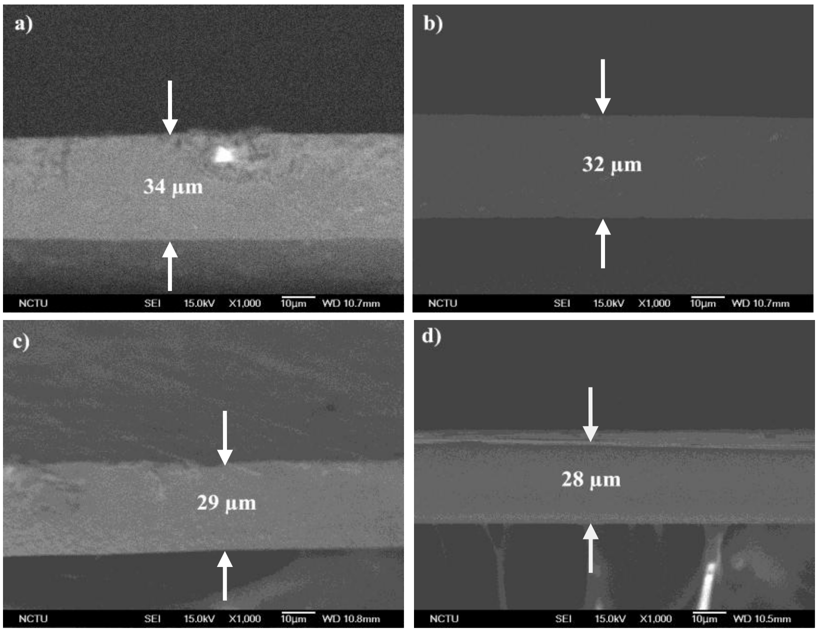

Figure 2. The cross section of as-spun Mn_xBi_{100-x} ribbons: a) x = 45; b) x = 50; c) x = 55; d) x = 60.

Figure 3 show the hysteresis loops of the as-spun (Fig. 3A) and annealed MnBi ribbons (Fig. 3B). One notes that despite the annealing process occurred at relatively low temperature of

280 °C for a short time of 8 h (in comparison with 300 °C and 20 h used for massive alloys [29]), the LTP formation has been well performed. The reason of this phenomenon is explained in [30] and based on the fact that inside the ribbons the size of Mn inclusions is very small, in the range of few micrometers in comparison with tens and hundreds micrometers inside the arc-melted alloys. Once Mn grains small in size, the reaction between them and the surrounding Bi matrix is accelerated and thus enhances the LTP content enhancement.

The highest value of the saturation magnetization M_s of MnBi ribbons at x = 55 is 63 emu/g reveal the good crystallization process occurred during the short time anneal of ribbons. After annealing, the M_s values of annealed ribbons are in the range from 56 to 63 emu/g, but the H_c values stay low in the range of 2.07 ÷ 2.36 kOe. It is noted that the optimal composition $Mn_{55}Bi_{45}$ helps to obtain high performance magnetic of MnBi ribbons which can be compared with previous results reported in Ref. [27]. The M_s and H_c values of ribbons were summarized in Table 1.

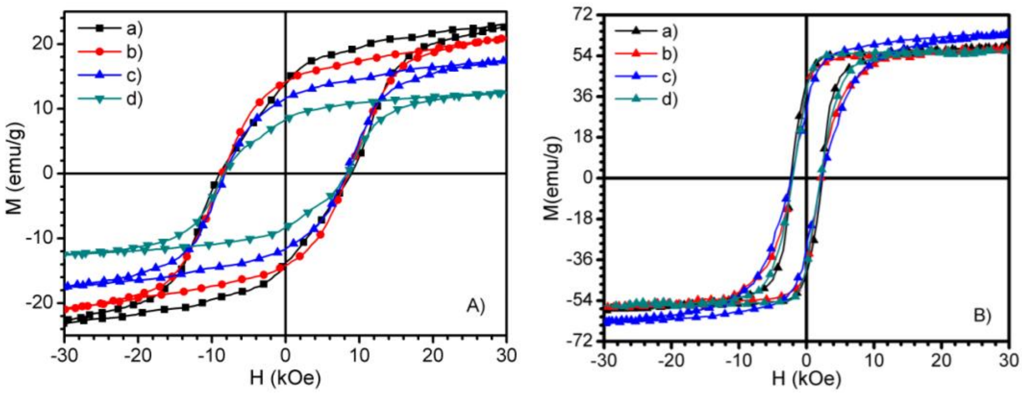

Figure 3. The M(H) curves of the as-spun (A) and annealed (B) Mn_xBi_{100-x} ribbons at 280 °C, 8 h: a) x = 45; b) x = 50; c) x = 55; d) x = 60.

Table 1 shows that by increasing the x values, the coercivity and the saturation magnetization of the as-spun ribbons are decreased weakly from 8.92 to 8.34 kOe and significantly from 22 to 13 emu/g, respectively. One remarks here the obvious decrease of coercivity of the annealed ribbons, for example from about 8.56 to 2.25 kOe for x = 50, this change of coercivity is involved by the crystalline growth during the annealing process.

Table 1. The summary magnetic properties of as – spun MnBi ribbons and as-annealed MnBi ribbons.

Mn_xBi_{100-x}	As-spun ribbons		As-annealed ribbons	
	H_c (kOe)	M_s (emu/g)	H_c (kOe)	M_s (emu/g)
x = 45	8.92	22	2.36	58
x = 50	8.56	21	2.25	57
x = 55	8.25	18	2.15	63
x = 60	8.34	13	2.07	56

Figure 4 presents plots of the PFM-measured loops and the M_s as well H_c of the powder samples ball-milled from the annealed ribbons. After 120 min of milling, the coercivity H_c of all samples are increased (Example: we see Fig. 4B, for x = 55, H_c increase from about 2.15 kOe to around 4.52 kOe) due to the refinement of the particle size from 5 µm to below 1 µm. However, this coercivity enhancement is paid by the reduction of the magnetization M_s. Due to brittleness of ribbons, the value M_s of MnBi ball-milled ribbon powders is reduced a little about 12.6 % (from 63 emu/g to 55 emu/g) in comparison with reported results (MnBi powders ground from the arc-melted and annealed bulk sample) in Ref. [9]. The moderate reduction of M_s and the large increase of H_c of ball-milled ribbon powders make MnBi melt-spun ribbons to become preferred for preparing MnBi high performance magnets.

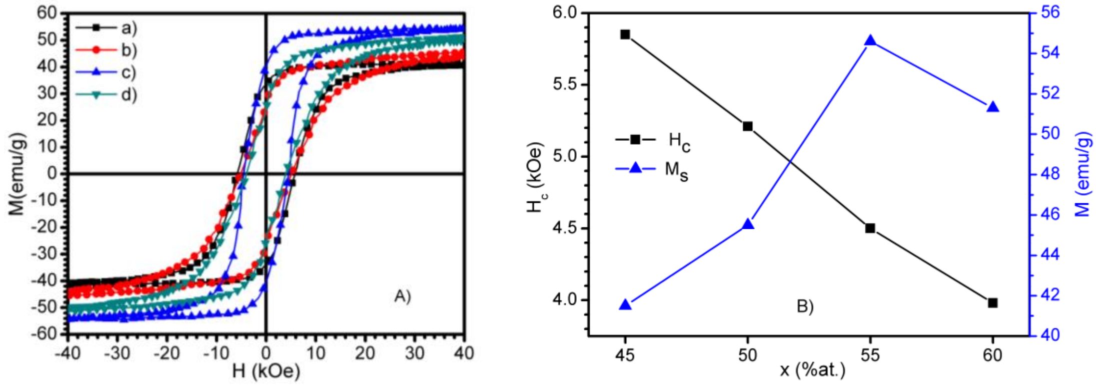

Figure 4: A) M(H) loops of MnBi powders milled in silicon oil for 120 min. B) The summary of M_s and H_c dependence on composition Mn_xBi_{100-x} (x = 45 – 60).

4. CONCLUSIONS

The paper presents the results concerning the MnBi LTP melt-spun ribbons. The technique solving the effect of melted batches in cling the inner walls of quartz tube and the copper wheel surface were applied. Hence, the uniform ribbons are fabricated well. The influences of the starting compositions of the melt-spinning batches Mn_xBi_{100-x} with x = 45, 50, 55 and 60 were investigated. In the range of x-values used, the as-spun (at 20 m/s of wheel speed) ribbons own the high coercivity H_c of around 8.34 – 8.92 kOe, but low magnetization M_s of about 13 - 22 emu/g. The short time (8 h) and low temperature (280 ^{o}C) anneal increases M_s up to 56 - 63 emu/g but paid by decreasing H_c down to 2.07 - 2.36 kOe. The Mn rich starting alloys helped to form uniform ribbons with thinner thickness. The highest performance of ribbons was obtained with x = 55, for this composition and for the melt-spinning parameters used the milled ribbons of grain sizes of micrometers and H_c = 4.52 kOe and M_s = 55 emu/g. This result can be competitive with the values of M_s of massive arc-melted and milling powders [8, 19]. By further improvement of the magnetic performance of MnBi ribbons, our novel approach will be promising for the massive production of high performance MnBi ribbons with the optimized intrinsic magnetization and coercivity for preparing high performance bulk magnets.

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