

## Magnetic and Structural Properties of $\text{MnBi}_{1-x}\text{Ti}_x$ Alloys

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(Received 25 December 2013, Received in final form 29 May 2014, Accepted 11 June 2014)

$\text{MnBi}_{1-x}\text{Ti}_x$  ( $x = 0, 0.4, 0.7, 1$ ) alloys were prepared by arc-melting, followed by heat treatment. X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) were used to measure and investigate the phase structure and magnetic properties. The temperature dependent magnetization curves indicate that the phase transitions between LTP and HTP MnBi occur with heating or cooling in  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x \leq 0.7$ ) samples. However, MnTi samples are in  $\text{Mn}_2\text{Ti}$  single-phase, with very low magnetic properties. Furthermore, the coercivity exhibits a positive temperature coefficient. The results show that the optimal content of Ti for the coercivity of  $\text{MnBi}_{1-x}\text{Ti}_x$  alloy is  $x = 0.4$ . For MnBi sample, the coercivity reaches a maximum value of 1.13 T at 550 K. However, the remanence and energy product show apparent decrease with the addition of Ti in  $\text{MnBi}_{1-x}\text{Ti}_x$  alloys.

**Keywords :** MnBi, phase transition, magnetic properties

### 1. Introduction

MnBi is a ferromagnetic intermetallic compound with NiAs-type hexagonal crystal structure. It has attracted research interest, mainly due to its unusually large magnetic anisotropy of the low-temperature phase (LTP) [1, 2], and the excellent magneto-optical properties of the quenched high-temperature phase (QHTP) [3]. It is remarkable that the coercivity of the LTP exhibits a positive temperature coefficient, and is much larger than that of Nd-Fe-B magnets at high temperature [4-6]. Therefore, MnBi has good potential to be used in high temperature circumstances [7]. However, the segregation of Mn during peritectic reaction makes it difficult to obtain single-phase MnBi by conventional techniques, such as high temperature sintering and induction melting, which also makes it difficult to study the magnetic properties of MnBi. Many efforts have been made to produce single-phase MnBi. Yoshida *et al.* [8] prepared the MnBi magnet with about 90 wt.% LTP by zone-arc-melting under He atmosphere, followed by heat treatment. The Curie temperature was measured at 633 K. Furthermore, fine powders obtained by grinding the strongly orientated bulk possess a large coercivity of 0.7 T, and this large coercivity is considered to be due to the large crystalline

anisotropy of the particles in the single domain state. It is verified that doping with transitional elements, such as Ti, Zr, Cu etc, evidently promotes crystallization and refines grain sizes in the metastable disordered structure, and hence results in a significant remanence enhancement and high performance [9, 10]. The intrinsic coercivity  $iH_c$  of 9797 Oe has been obtained for the  $\text{SmCo}_{7.1}\text{Ti}_{0.4}$  as-spun ribbons [11]. Hono *et al.* [12] reported that the addition of 4 at.% Ti significantly modified the solidification path, by suppressing the formation of  $\text{Nd}_2\text{Fe}_{23}\text{B}_3$  phase and promoting the formation of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase, subsequently resulting in a improvement in the coercivity and energy product. Also, Harrison *et al.* [13] reported that the co-addition of Ti and C in nanocomposite alloys could refine the nanocomposite microstructure, and finally enhanced coercivity. Up to now the addition of Ti in the intermetallic compound MnBi has not been reported.

In this article, titanium substitutes for bismuth, with the chemical formula  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x = 0, 0.4, 0.7, \text{ and } 1$ ) in the intermetallic structure. The temperature dependent magnetization (350-700 K) and demagnetization (100-600 K) curves are measured by vibrating sample magnetometer (VSM). The purpose of this investigation is to detect the effect on the phase formation structure and magnetic properties in MnBi alloy, by the substitution of Ti for Bi. This is helpful for further investigations into  $\text{MnBi}_{1-x}\text{Ti}_x$  systems.

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## 2. Experimental

MnBi<sub>1-x</sub>Ti<sub>x</sub> ingots were prepared by arc-melting with high purity manganese, bismuth and titanium (both of 99.99% purity) in atomic ratios. Heat treatment was performed in a vacuum for 30 minutes, at a fixed temperature ranging from 380 to 600 K, and the sample was finally transformed into the LTP. X-ray diffraction (XRD) measurements were made at room temperature to characterize the samples phase structure, using Rigaku diffractometer with CuK $\alpha$  radiation. Temperature dependent magnetization measurements were made using a Lakeshore 7407 vibrating sample magnetometer with high temperature oven, which were used to measure the magnetization hysteresis loops of the magnet at different temperature (100 K-600 K).

## 3. Results and Discussion

The X-ray diffraction (XRD) patterns of MnBi<sub>1-x</sub>Ti<sub>x</sub> ( $x = 0, 0.4, 0.7$  and  $1$ ) samples are shown in Figure 1. Comparison reveals that the positions and intensities of the peaks are different. This indicates that MnBi<sub>1-x</sub>Ti<sub>x</sub> ( $x = 0, 0.4, 0.7$ , and  $1$ ) samples have different structures. So the substitution of Ti has greatly affected the phase structure of MnBi<sub>1-x</sub>Ti<sub>x</sub> alloy. Figure 1 shows the characteristic intensity peaks of the LTP along with strong Bi peaks due to unreacted Bi, for  $x = 0$ , and  $0.4$ . Characteristic intensity peaks of Mn<sub>2</sub>Ti begin to emerge for  $x = 0.7$  sample, and the sample is completely single Mn<sub>2</sub>Ti phase when the value of  $x$  is  $1$ ; meanwhile, both LTP and Bi peaks disappear in Fig. 1(d). Detailed analysis of the XRD pattern in Fig. 1(c) shows that the  $x = 0.7$  sample

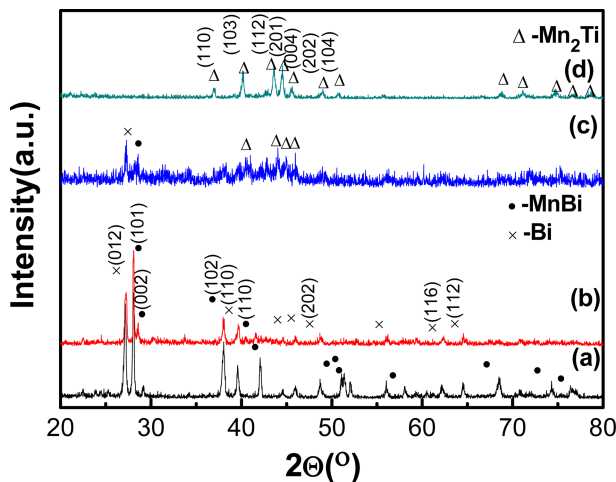


Fig. 1. (Color online) XRD pattern of the MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys, with (a)  $x = 0$ , (b)  $x = 0.4$ , (c)  $x = 0.7$ , and (d)  $x = 1$ .

mainly contains four phases: low-temperature phase of MnBi, Bi phase, Mn<sub>2</sub>Ti phase, and a small amount of an amorphous phase. The intensity of the diffraction peaks for the  $x = 0.7$  sample was lower than that of the MnBi sample. A higher background was found in the pattern of the  $x = 0.7$  sample. This suggests that the grain size was refined, as a consequence of the Ti substitution.

Figure 2 shows the temperature dependent magnetization for MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys for (a)  $x = 0$ , (b)  $x = 0.4$ , (c)  $x = 0.7$ , and (d)  $x = 1$  samples, in an applied field of 500 Oe. As shown in Fig. 2(a), with the increase of temperature, magnetization of MnBi alloy decreases slightly, reaches minimum value at around 497 K, and then increases gradually up to 590 K. Increase of magnetization with temperature is considered to be due to increasing the volume fraction of LTP MnBi, which possesses a higher magnetization value [8]. The increase of magnetization above 500 K is due to the formation of the LTP of MnBi [14]. At 620 K, the value of magnetization drops dramatically to nearly zero, which is due to the magnetic phase transition of MnBi from LTP to paramagnetic high-temperature phase (HTP) [15]. When the temperature decreases again after heating up beyond 670 K, the magnetization retains a very small value down to 610 K, then increases sharply with further decrease of temperature. This means that a large amount of LTP MnBi compound is again formed during the cooling down process. Temperature dependent magnetization measurements have been performed on other samples. Both Fig. 2(b) for  $x = 0.4$  and 2(c) for  $x = 0.7$  have similar phase transition, compared to

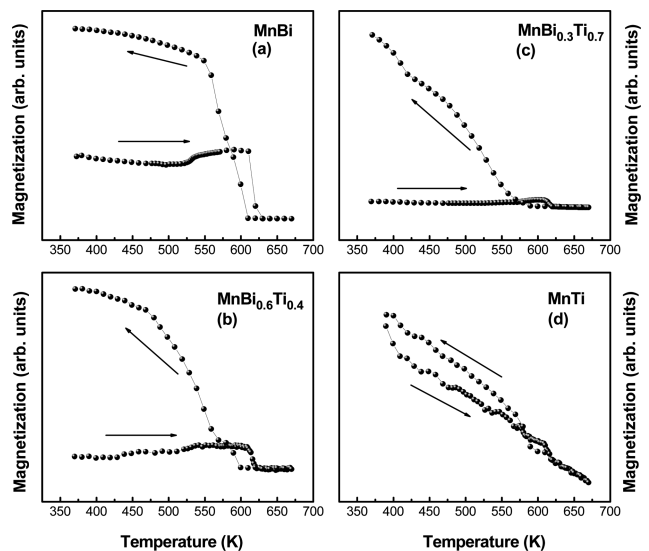
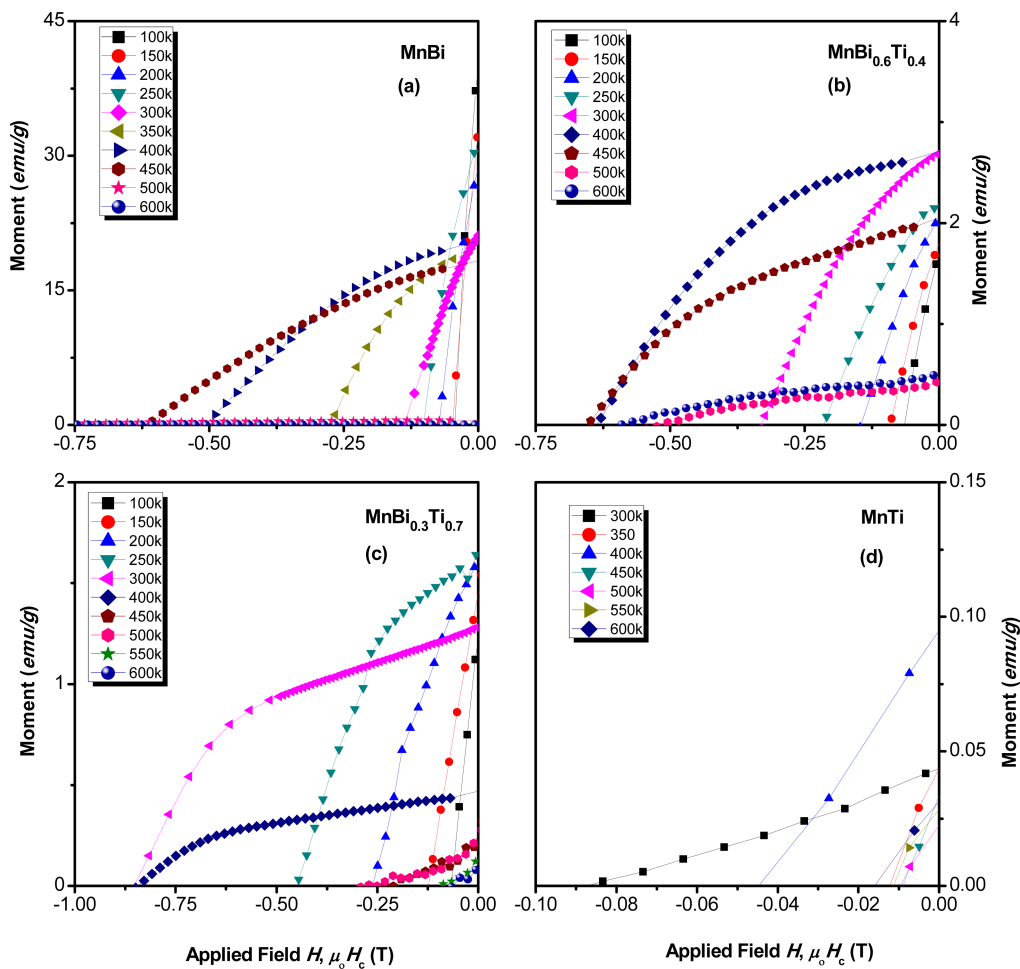


Fig. 2. Magnetization as a function of temperature in an applied field of 500 Oe for MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys, with (a)  $x = 0$ , (b)  $x = 0.4$ , (c)  $x = 0.7$ , and (d)  $x = 1$ .



**Fig. 3.** (Color online) Demagnetization curve of  $\text{MnBi}_{1-x}\text{Ti}_x$  alloys measured at different temperature, with (a)  $x = 0$ , (b)  $x = 0.4$ , (c)  $x = 0.7$ , and (d)  $x = 1$ .

Ti free doped MnBi sample. In  $\text{MnBi}_{0.6}\text{Ti}_{0.4}$  sample, the LTP-HTP and the HTP-LTP transition temperatures are 614 K and 599 K, respectively. In  $\text{MnBi}_{0.3}\text{Ti}_{0.7}$  sample, the LTP-HTP transition temperature is 612 K, and the HTP-LTP transition temperature decreases to 589 K. So the different phase transition temperatures are related to the content of Ti in  $\text{MnBi}_{1-x}\text{Ti}_x$  alloys. In Fig. 2, the increase of magnetization with cooling, compared with that with heating, is most likely due to the formation of more LTP, as the sample passes through the heat treatment [16]. In MnTi sample, as shown in Fig. 2(d), magnetization decreases linearly as temperature increases, and *vice versa*. This coincides with structural transformation, and indicates that MnTi sample is a single  $\text{Mn}_2\text{Ti}$  phase, and no phase transform has taken place while heating or cooling.

Figure 3 presents the demagnetization curves of the  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x = 0-1$ ) samples measured at different temperature. The coercivity of  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x \leq 0.7$ ) alloys shows

large temperature dependence, and exhibits a positive temperature coefficient. For each sample (except MnTi sample), the coercivity increases with temperature at first, and then decreases, as the temperature increases further. Both the coercivity and remanence value of MnTi sample are very small. That is due to no LTP being formed in the MnTi sample. This is in agreement with the former XRD results in Fig. 1(d).

Figure 4 shows the magnetic properties of the  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x = 0-1$ ) samples. For Ti-free sample, with increasing temperature, its coercivity increases from 0.04 T at 100 K, to a maximum value of 1.13 T at 550 K; and then decreases to 0.95 T, when the temperature gets to 600 K in Fig. 4(a). This coincides with what Ref. [17] reported. Variation of the coercivity with temperature is supposed to be controlled by the change of magnetocrystalline anisotropy. Therefore, the coercivity exhibits a positive temperature coefficient. The coercivity value of  $\text{MnBi}_{1-x}\text{Ti}_x$  ( $x \leq 0.7$ ) is higher than that of MnBi below 400 K,

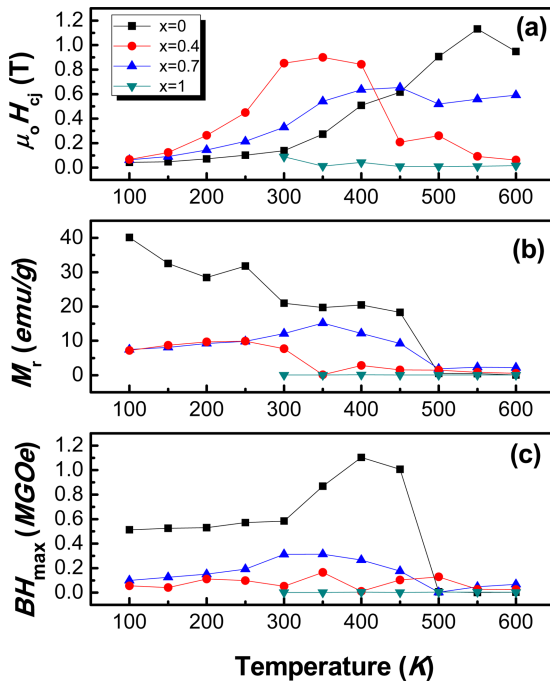


Fig. 4. (Color online) Temperature dependence of magnetic properties of MnBi<sub>1-x</sub>Ti<sub>x</sub> sample.

according to the magnetic properties of different temperature. The results show that the optimal content of Ti for the coercivity of MnBi<sub>1-x</sub>Ti<sub>x</sub> alloy is x = 0.4. As shown in Fig. 4(b), the remanence decreases gradually as the temperature increases, from 40.11 emu/g at 100 K, to 18.30 emu/g at 450 K; then decreases sharply to 0.51 emu/g, while the temperature increases to 550 K. The value of remanence drops to nearly zero, when the temperature gets to 600 K. This coincides with the LTP-HTP transition at around 610 K. For the MnTi sample, both coercivity and remanence remain at a very small value, in the temperature range from 300 K to 600 K. When the temperature goes below 300 K, its magnetic properties are out of the range that the Lakeshore 7407 can detect. This clearly demonstrates that no ferromagnetic phase is formed in the MnTi sample. Fig. 4 shows that substitution of Ti for Bi causes the coercivity rise below 400 K. In part, this may be due to the refinement of grain size, and may partly be attributed to the strong pinning of the walls of the ‘interaction domains’ by the network of grain boundaries between the nanocrystalline grains [18]. Ti substitution has also changed the temperature dependence of coercivity. Guo *et al.* [19] presented a theory that relates the temperature dependence of the anisotropy field and coercivity. According to their theory, the anisotropy field is modified by Ti substitution for Bi. But the remanence and energy product show apparent

decrease, with the addition of Ti in MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys; this may be caused by an increase in the amount of Mn<sub>2</sub>Ti phase. However, in doping samples, Ti substitutions in this lattice could be complicated. Therefore, investigation of the theory mechanism of Ti possibly occupying sites in MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys is in progress.

#### 4. Conclusion

In conclusion, the microstructure and magnetic properties of MnBi<sub>1-x</sub>Ti<sub>x</sub> (x = 0~1) arc-melting alloys have been measured and investigated, using X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). The phase transitions between LTP and HTP MnBi have been analysed with heating or cooling, by measuring the temperature-dependent magnetization in MnBi<sub>1-x</sub>Ti<sub>x</sub> (x ≤ 0.7) samples. The results indicate that the different phase transition temperatures are related to the content of Ti in MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys. MnTi samples are in Mn<sub>2</sub>Ti single-phase, with very low magnetic properties. Furthermore, below 400 K, the coercivity increases, while the remanence and energy product decrease, with the substitution of Ti for Bi in MnBi<sub>1-x</sub>Ti<sub>x</sub> alloys. The coercivity exhibits a positive temperature coefficient. The results show that the optimal content of Ti for the coercivity of MnBi<sub>1-x</sub>Ti<sub>x</sub> alloy is x = 0.4. For MnBi sample, the coercivity reaches a maximum value of 1.13 T at 550 K.

#### Acknowledgments

This work was supported by the National Science Foundation (no. 51371163, 51301158), Zhejiang Province Innovative Research Team (2010R50016), Provincial Major Science and Technology Project of Zhejiang (2012C01031-5), Education Department Scientific Research Project of Zhejiang Province (Y201329502), and National Public Research Project Special for Quality Testing (201210107).

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