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Magnetic properties of Mn–Bi melt-spun ribbons

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ABSTRACT

Mn–Bi melt-spun ribbons with the low temperature phase (LTP) of MnBi were produced by melt-spinning and subsequent annealing. The as-rapidly quenched Mn–Bi melt-spun ribbons contained some LTP MnBi phase and exhibited a high coercivity exceeding 8 kOe. Annealing of the melt-spun ribbons resulted in an increase in the amount of the LTP MnBi phase. A maximum remanence value of 42 emu/g was achieved in $Mn_{50}Bi_{50}$ melt-spun ribbon annealed at 673 K for 1 h. High-temperature measurements revealed that the coercivity of the annealed $Mn_{50}Bi_{50}$ melt-spun ribbon increased with increasing ambient temperature. Although the $Mn_{50}Bi_{50}$ melt-spun ribbons showed a much smaller coercivity than $Nd_{15}Fe_{77}B_8$ melt-spun ribbon at room temperature, it exhibited a higher coercivity at temperatures of 473 K and higher. Therefore, the magnetic properties of $Mn_{50}Bi_{50}$ melt-spun ribbon are comparable to those of Nd–Fe–B melt-spun ribbon at an ambient temperature of 473 K and become superior to those of Nd–Fe–B melt-spun ribbon at 573 K.

1. Introduction

Neodymium–iron–boron (Nd–Fe–B) magnets have been widely applied to many devices such as magnetic resonance imaging (MRI) devices and voice coil motors (VCMs) for hard disk drives [1]. In recent years, their application to motors for hybrid and electric vehicles has also been greatly expanding. However, the coercivity of Nd–Fe–B magnets is insufficient for use in motors in engine compartments where the ambient temperature becomes high. Therefore, the coercivity of these magnets is enhanced by the substitution of Dy for Nd in the proportion of about 30% for such high temperature applications [2]. There is growing interest in the development of new magnetic materials that are free of these rare-earth elements because of their high cost and limited availability. This is especially true for Dy. A trend towards the reduction of Dy content can therefore be seen in the research and development of rare-earth magnets [3], and demand has arisen for the development of a new permanent magnet that does not contain Dy.

The low temperature phase (LTP) of MnBi is one of the candidates for new permanent-magnetic materials for Dy-free magnets because of its large magnetocrystalline anisotropy [4–6]. Such a large magnetocrystalline anisotropy is essential to obtain the required coercivity in permanent-magnetic materials [7]. There have been several efforts to produce Mn–Bi magnets with the LTP MnBi phase [8–13]. It has been reported that the LTP MnBi phase is formed by a peritectic reaction from the liquid and the high temperature phase (HTP) of MnBi phase and that the HTP MnBi phase is itseld formed by a peritectic reaction from the liquid and the primary Mn phase [6]. When the HTP MnBi phase forms, it surrounds the primary Mn phase and prevents further peritectic reaction. As a result, the primary Mn phase always remains in alloy ingots. It is known that large undercooling is one of the most promising methods for forming peritectic compounds without the growth of the primary phase [14]. The most common techniques for obtaining large undercooling are rapid solidification processing techniques, such as melt-spinning or atomization [14,15]. Several efforts have been made to produce Mn–Bi magnets with the LTP MnBi phase using rapid solidification processing techniques [16–20]. Although Mn–Bi magnets with the LTP MnBi phase have been produced by melt-spinning, the reported coercivity of the Mn–Bi melt-spun ribbon is not yet satisfactory[17]. It has been reported that mechanical grinding of Mn–Bi melt-spun ribbon resulted in an increase in coercivity [19,20].

In the present study, Mn_xBi_{100-X} ($x=40$–60) alloys were produced by the melt-spinning technique and subsequenty annealed at various temperatures in order to obtain the LTP MnBi phase. The magnetic properties of the Mn–Bi melt-spun ribbons were then compared with those of Nd–Fe–B melt spun ribbon at elevated temperatures.

2. Experiment

Mn_xBi_{100-X} ($x=40$–60) alloy ingots were prepared by arc melting in an argon atmosphere. The starting alloy contained 5% excess of

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Bi compared with the normal composition of Mn_xBi_{100-X} (x=40–60) to compensate for losses of Bi such as by oxidation and vaporization during melting and melt-spinning. Small amounts of the alloy ingots were placed in a quartz crucible with an orifice of 0.6 mm at the bottom. The alloy ingots were induction melted in an argon atmosphere and then ejected through the orifice with argon onto a copper wheel rotating at a surface velocity of 50 ms^{-1}. The resultant melt-spun ribbons were obtained as fragmented pieces. The melt-spun ribbons were annealed in an argon atmosphere at temperatures between 373 K and 773 K for 1 h. For comparison, Nd–Fe–B melt-spun ribbons with the typical composition of $Nd_{15}Fe_{77}B_8$ were also produced.

The composition of the Mn–Bi melt-spun ribbon was identified by chemical analysis using inductively coupled plasma (ICP). The phases of the specimens were identified by X-ray diffraction (XRD) using Cu Kα radiation. The thermomagnetic curves of the specimens were examined by heating them at a rate of 0.16 K/s in a vacuum using a vibrating sample magnetometer (VSM) with an applied field of 500 Oe. The VSM was calibrated with a pure nickel sphere. The specimen used for VSM measurement had a rectangular shape with dimensions of 2 × 10 mm and a thickness of about 20 μm. The hysteresis loops were measured along the length direction of the specimen. No demagnetization correction was made in the hysteresis loop. The hysteresis loops of the specimens were measured at room temperature by VSM under a maximum applied field of 25 kOe. The specimens had been magnetized in a pulsed field of 50 kOe prior to the VSM measurements. Some of the specimens were further examined in a vacuum by VSM under a maximum applied field of 20 kOe at temperatures between 373 K and 573 K.

3. Results and discussion

It is difficult to obtain the single LTP MnBi phase in ordinary ingot making processes because the LTP MnBi phase is formed by a peritectic reaction from the liquid and the HTP MnBi phase, which is itself formed by a peritectic reaction from the liquid and the primary Mn phase. In order to obtain the LTP MnBi phase, Mn–Bi alloys with a composition of Mn_xBi_{100-X} (x=40–60) were produced by rapid solidification processing. The XRD patterns of the as-rapidly quenched Mn_xBi_{100-X} (x=40–60) melt-spun ribbons are shown in Fig. 1. Regardless of the Mn content, the Mn–Bi alloys consist of the LTP MnBi phase. However, clear diffraction peaks of Bi are noted in the XRD patterns. The diffraction peaks of the Bi phase become more pronounced as the Mn content of the Mn–Bi alloy increases. Due to the rapid solidification of melt-spinning, the peritectic reaction tends to be inhibited and thus the remaining liquid phase experiences significant undercooling before solidification occurs. During melt-spinning, the low-melting-point constituent Bi tends to nucleate from the undercooled melt before the formation of the peritectic phase of the LTP MnBi. In addition, a small diffraction peak of the Mn phase is also noted in the XRD pattern of the $Mn_{50}Bi_{50}$, $Mn_{55}Bi_{45}$, and $Mn_{60}Bi_{40}$ alloys.

Fig. 2 shows the dependence of the remanence and coercivity of the as-rapidly quenched Mn–Bi melt-spun ribbons on the Bi content. High coercivity values exceeding 8 kOe are seen regardless of the Bi content. This is due to the existence of the LTP MnBi phase in the Mn–Bi melt-spun ribbons. However, the remanence of the Mn–Bi melt-spun ribbons is very small. According to the XRD studies, these Mn–Bi alloys mainly consisted of the LTP MnBi and Bi phases. Thus, the small amount of the LTP MnBi phase in the Mn–Bi alloys is the reason for such a small remanence.

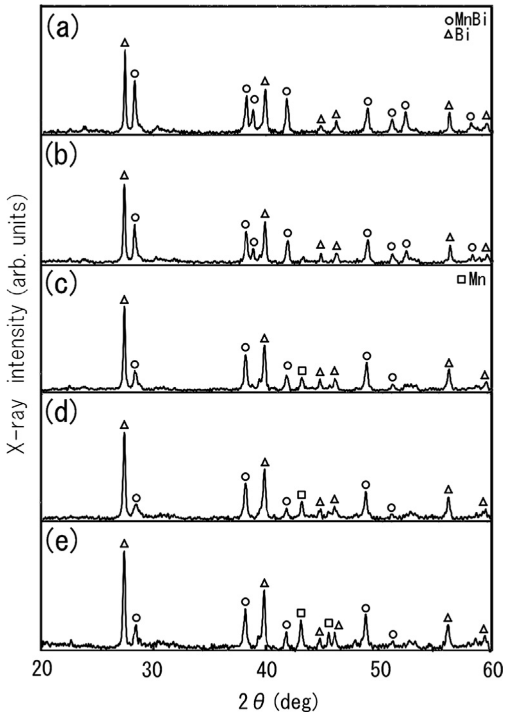

Fig. 1. XRD patterns of the as-rapidly quenched Mn–Bi melt-spun ribbons: (a) $Mn_{40}Bi_{60}$, (b) $Mn_{45}Bi_{55}$, (c) $Mn_{50}Bi_{50}$, (d) $Mn_{55}Bi_{45}$, and (e) $Mn_{60}Bi_{40}$ alloys.

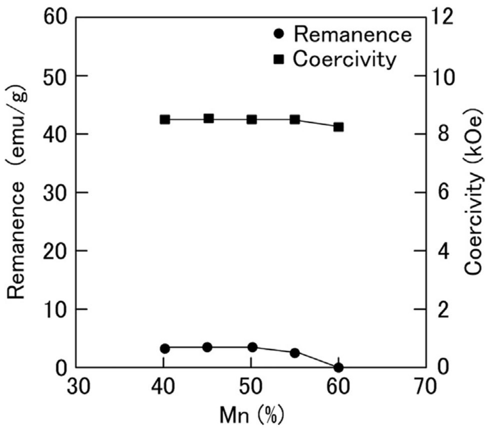

Fig. 2. Dependence of the remanence and coercivity of the as-rapidly quenched Mn–Bi melt-spun ribbons on the Mn content.

The thermomagnetic properties of the as-rapidly quenched Mn–Bi melt-spun ribbons were investigated by VSM. The results are shown in Fig. 3. The thermomagnetic curves of the Mn–Bi alloys show a large magnetic transition at around 630 K, which corresponds to the LTP MnBi phase. This confirms that the Mn–Bi alloys consisted of the LTP MnBi phase. The increase in magnetization as the temperature exceeds 400 K is believed to be due to the formation of the LTP MnBi phase at this temperature. Thus, annealing of the as-rapidly quenched Mn–Bi melt-spun ribbons can be expected to increase the amount of the LTP MnBi phase.

Heat treatment of the Mn–Bi melt-spun ribbons resulted in drastic changes in the remanence. Fig. 4 shows the dependence of the remanence of the Mn–Bi melt-spun ribbons on the annealing temperature. The remanence the Mn–Bi alloys increased with increasing annealing temperature. The $Mn_{50}Bi_{50}$ alloy showed the highest remanence value among the Mn–Bi alloys studied. As can be seen in the figure, the remanence of the $Mn_{50}Bi_{50}$ alloy gradually increases to a peak value of 42 emu/g at 673 K, then decreases to 11 emu/g as the annealing temperature rises further. This is due to the formation of the LTP MnBi phase formed during annealing of the as-rapidly quenched Mn–Bi melt-spun ribbons.