Magnetic Properties of MnBi Fine Particles Fabricated Using Hydrogen Plasma Metal Reaction

Keita Isogai*, Masashi Matsuura, Nobuki Tezuka and Satoshi Sugimoto

Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Fine particles of MnBi were prepared by the hydrogen plasma metal reaction method and their magnetic properties were investigated. The particle size of the as-prepared MnBi particles was 70–950 nm with a median diameter of 269 nm. Heat treatment and ball milling with a dispersant improved the magnetic properties of the particles. The sample annealed at 330°C for 5 h in Ar then ball-milled for 10 min with a dispersant showed the largest energy product of $105 \text{ kJ}\cdot\text{m}^{-3}$ and a saturation magnetization of $71.0 \text{ Am}^2\cdot\text{kg}^{-1}$. High coercivity of $1380 \text{ kA}\cdot\text{m}^{-1}$ was also obtained for the sample that was ball-milled for 2 h. [doi:10.2320/matertrans.MAW201306]

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1. Introduction

Fine particles or nanoparticles of hard magnetic materials are attractive materials for potential use in microactuators, microdevices and nanocomposite magnets.^{1–4)} Several preparation methods have been reported, and they can be classified into three main categories: gas phase methods,^{5,6)} such as chemical vapor deposition and evaporation; liquid phase methods,^{7,8)} such as liquid-phase reduction and the polyol process; and solid phase methods,⁹⁾ such as mechanical pulverizing and milling.

Hydrogen plasma reaction methods have been used to produce fine particles of metal alloys and intermetallic compounds.^{10–15)} In this method, the dissociated hydrogen in arc plasmas dissolves in the molten metal and enhances the vaporization of the metal when the hydrogen is emitted. The method has the advantages such simple equipment, low levels of contamination and high productivity. For example, the productivities of Fe and Mn are $5.86\text{--}7.86 \times 10^{-5} \text{ mol}\cdot\text{s}^{-1}$ and $2.81\text{--}6.00 \times 10^{-3} \text{ mol}\cdot\text{s}^{-1}$, respectively.¹⁰⁾ Moreover, the composition and size of fine particles can be easily controlled by parameters such as the composition of the mother ingot, H_2 concentration and reaction time.¹⁶⁾ Although all types of alloys can be obtained by the hydrogen plasma metal reaction method, the only hard magnetic materials reported have been Mn–Al–C magnets.¹⁷⁾ However, because Mn–Al–C magnets must be annealed at temperatures greater than 500°C to achieve the transformation from the ε -phase to the τ -phase, grain growth can occur during annealing.

The low temperature phase (LTP) of MnBi is a ferromagnetic intermetallic phase with a NiAs-type hexagonal crystal structure. Additionally, the LTP of MnBi exhibits a large magnetocrystalline anisotropy ($K \approx 10^6 \text{ J}\cdot\text{m}^{-3}$) and a positive temperature coefficient of coercivity.^{18,19)} MnBi is formed by a peritectic reaction between the liquid phase and the Mn phase at temperatures of less than 446°C. The LTP of MnBi is transformed from the high temperature phase (HTP) at temperatures of less than 355°C.^{20,21)} Because grain growth is suppressed at these low temperatures, the material

is suitable for forming hard magnetic ultrafine particles or nanoparticles. However, a long low-temperature annealing process is required to obtain a single LTP with superior magnetic properties. On the other hand, the hydrogen plasma metal reaction method has advantages of direct fabrication of fine particles, low contamination and high productivity. Therefore, in this study we used the hydrogen plasma metal reaction method to prepare fine MnBi particles.

2. Experimental Procedure

Figure 1 shows the experimental procedure. MnBi ingots with a composition of $\text{Mn}_{100-x}\text{Bi}_x$ ($x = 50, 70$) were fabricated from metallic Mn (99.9 mass%) and Bi (99.9 mass%) by arc melting under an Ar atmosphere. Particles of MnBi were prepared using these ingots by the hydrogen plasma metal reaction method. The equipment for the hydrogen plasma metal reaction method consisted of an arc-melting chamber and a metal filter for the collection of particles (Fig. 2). The arc-melting chamber was supplied with Ar/H_2 (7 : 3) at a pressure of 0.1 MPa. The $\text{Mn}_x\text{Bi}_{100-x}$

Fig. 1 Flow chart for the experimental procedure.

*Corresponding author, E-mail: k-isogai@material.tohoku.ac.jp

Fig. 2 Equipment for the hydrogen plasma metal reaction.

Fig. 3 SEI of the as-prepared MnBi particles.

ingots were melted by the arc plasma and formed fine particles. The arc current for the hydrogen plasma metal reaction was 100 A. The fine particles were carried by the gas flow and collected on the metal filter.

The MnBi particles were annealed at 330°C in Ar to form the LTP and crushed by ball milling at a speed of 150 rpm for 30–120 min to isolate the particles. The solvent for ball milling was heptane, and oleic acid was added as dispersant. After ball milling, the samples were washed with heptane 5 times to remove the dispersant. The washed samples were dried in a glove box to suppress oxidation and the dried powders were used for the measurements.

The magnetic properties were measured by using a vibrating sample magnetometer (VSM) after applying a magnetic pulsed field of $6.4 \text{ MA} \cdot \text{m}^{-1}$. The saturation magnetization (σ_s) was evaluated using the magnetization at an applied magnetic field of $1.6 \text{ MA} \cdot \text{m}^{-1}$. The energy product ($(BH)_{\text{max}}$) of the MnBi particles was calculated by using the theoretical density of the LTP of MnBi ($8.9 \text{ Mg} \cdot \text{m}^{-3}$).

The phases present in the particles were characterized by X-ray diffraction (XRD). The size distribution and shape of the particles were observed by scanning electron microscopy (SEM). The chemical compositions of the particles were determined by energy dispersive X-ray spectrometry (EDX).

3. Results and Discussion

Initially, we prepared a MnBi ingot with a composition of $\text{Mn}_{50}\text{Bi}_{50}$ by arc melting and the fine particles were fabricated by the hydrogen plasma metal reaction method. However, EDX analysis revealed that the composition of particles was 30.4 at% Mn–69.6 at% Bi and the composition was influenced by the evaporation rate of the metals. To fabricate $\text{Mn}_{50}\text{Bi}_{50}$ compositional particles, the composition of the MnBi ingots used in the hydrogen plasma metal reaction method was altered because of the difference between the nominal composition of the ingot and the EDX composition of the MnBi particles. The $\text{Mn}_{70}\text{Bi}_{30}$ alloy was found to produce MnBi particles with the desired composition.

Figure 3 shows secondary electron images (SEIs) of the as-prepared MnBi particles. The particle size distribution of the as-prepared MnBi particles was also evaluated using 200 particles chosen from the SEI (Fig. 4). The size of the particles was 70–950 nm with a median diameter (d_{50}) of 269 nm. EDX analyses also showed that the composition of

Fig. 4 Particle size distribution of the as-prepared MnBi particles.

Fig. 5 Hysteresis loops of the as-prepared MnBi particles and the particles annealed at 330°C for 5 h in Ar.

as the prepared MnBi particles was 49.9–50.3 at% Mn–49.7–50.1 at% Bi, which is close to the stoichiometric composition of the MnBi phase.

Figure 5 shows the hysteresis loops of the as-prepared MnBi particles and the particles heat-treated at 330°C for 5 h in Ar. The magnetization of the as-prepared particles was very low; however, the magnetic properties were dramatically enhanced by annealing. Coercivity (H_{cJ}) increased from 111 to $255 \text{ kA} \cdot \text{m}^{-1}$, and saturation magnetization (σ_s) increased from 0.132 to $53.4 \text{ Am}^2 \cdot \text{kg}^{-1}$.

Therefore, the phase transformation was caused by annealing and the particles were examined by using XRD. Figure 6 shows the XRD patterns of the as-prepared sample

Fig. 6 XRD patterns of (a) the as-prepared MnBi particles and (b) the particles annealed at 330°C for 5 h in Ar.

Fig. 7 SEI of the MnBi particles annealed at 330°C for 5 h in Ar.

and the sample annealed at 330°C for 5 h in Ar. The XRD pattern of the as-prepared sample contained only Bi and β -Mn peaks. However, MnBi (LTP) and Bi XRD peaks were observed after annealing. Therefore, the formation of the MnBi LTP improved the magnetic properties.

Although the magnetization was improved by annealing, H_{cJ} was small for MnBi. The microstructure of the particles was observed by SEM. Figure 7 shows the SEI of the MnBi particles annealed at 330°C for 5 h in Ar. The particles agglomerated and joined together, which probably caused the low H_{cJ} .

The annealed particles were crushed by ball milling in order to increase H_{cJ} . After ball milling, the MnBi particles were aligned by applying a magnetic field of $1600 \text{ kA} \cdot \text{m}^{-1}$. Figure 8 shows the hysteresis loops of the particles annealed at 330°C for 5 h in Ar and ball-milled at 150 rpm for 30 min, measured parallel or perpendicular to the magnetic field. H_{cJ} was $1040 \text{ kA} \cdot \text{m}^{-1}$, which was higher than that of the sample shown in Fig. 5 ($H_{cJ} = 255 \text{ kA} \cdot \text{m}^{-1}$). Therefore, H_{cJ} was increased by ball milling. However, the hysteresis loops measured parallel and perpendicular to the magnetic field were similar. Figure 9 shows the SEI of the ball-milled MnBi particles, and the corresponding particle size distribution is shown in Fig. 10. Many agglomerated particles are visible in Fig. 9 and the particle size distribution shown in Fig. 10 is

Fig. 8 Hysteresis loops of the aligned MnBi particles annealed at 330°C for 5 h in Ar and ball-milled at 150 rpm for 30 min. Measurements were parallel (//) or perpendicular (⊥) to the magnetic field.

Fig. 9 SEI of the MnBi particles annealed at 330°C for 5 h in Ar and ball-milled at 150 rpm for 30 min.

Fig. 10 Particle size distribution of the MnBi particles annealed at 330°C for 5 h in Ar and ball-milled at 150 rpm for 30 min.

broad, because the agglomerated particles formed larger single particles, resulting in a large d_{50} of 766 nm. The large agglomerated particles probably prevented the powder from being aligned by the magnetic field.

A dispersant was used during ball milling to inhibit the agglomeration and to improve the alignment of particles. The hysteresis loops of the particles aligned in a magnetic field of $1600 \text{ kA} \cdot \text{m}^{-1}$ are shown in Fig. 11. The sample measured parallel to the magnetic field showed a high H_{cJ} of $1380 \text{ kA} \cdot \text{m}^{-1}$, which was higher than that of the sample shown in Fig. 8 ($H_{cJ} = 1040 \text{ kA} \cdot \text{m}^{-1}$). In addition, there was

Fig. 11 Hysteresis loops of the aligned MnBi particles annealed at 330°C for 5 h in Ar and ball-milled with a dispersant. Measurements were parallel (//) or perpendicular (⊥) to the magnetic field.

Fig. 12 SEI of the MnBi particles ball-milled with a dispersant.

Fig. 13 Particle size distribution of the MnBi particles ball-milled with a dispersant.

a marked difference in the parallel and perpendicular hysteresis loops. Figures 12 and 13 show the SEI and particle size distribution of the MnBi particles milled with a dispersant. There were many agglomerated particles (Fig. 12) which meant the particle size distribution was broad (Fig. 13). However, the microstructure of the sample milled with dispersant had smaller, more dispersed particles with a d_{50} of 671 nm, compared with the sample milled without dispersant (Figs. 9 and 10). Therefore, the particles could be aligned with a magnetic field and the magnetic properties were improved.

Fig. 14 Dependence of the magnetic properties of MnBi particles on milling time. (a) σ_s and H_{cJ} and (b) σ_r/σ_s and $(BH)_{\max}$.

Fig. 15 Hysteresis loop of MnBi particles annealed at 330°C for 5 h in Ar and ball-milled for 10 min with a dispersant.

Figure 14 shows the dependence of the magnetic properties of the MnBi particles on the milling time for ball milling carried out at 150 rpm for 30–120 min with dispersant. Figure 14(a) summarizes σ_s and H_{cJ} , and Fig. 14(b) shows the squareness (σ_r/σ_s) and energy product $(BH)_{\max}$. From 0 to 10 min, σ_s and σ_r/σ_s increased sharply and then decreased slightly as the milling time increased. Similarly, H_{cJ} increased rapidly from 0 to 10 min and then increased slightly with the milling time. The XRD patterns taken from the samples ball-milled for 30 min, 1 h and 2 h, only XRD peaks from MnBi were observed and their half widths were similar. This indicates that the samples consisted of the MnBi phase and their crystal structure was not damaged by ball milling. Thus, the sample that was ball-milled for 10 min exhibited the highest $(BH)_{\max}$ of 105 kJ·m⁻³, a σ_s of 71.0 Am²·kg⁻¹ and an H_{cJ} of 1090 kA·m⁻¹. The hysteresis loop for this sample is shown in Fig. 15. The magnetic properties were higher or

comparable to previously reported values.^{22–25)} The magnetic properties of the MnBi particles prepared in this study demonstrate that the combination of the hydrogen plasma metal reaction method and ball milling with a dispersant is suitable for preparing fine particles of the MnBi LTP. In addition, further refinement of the preparation conditions to decrease the particle size is required in order to expand the potential applications of the MnBi particles.

4. Conclusion

MnBi particles 70–950 nm in size with an average particle diameter of 269 nm were prepared by the hydrogen plasma metal reaction method. The magnetic properties of the particles were improved by heat treatment and subsequent ball milling with a dispersant. A relatively high $(BH)_{\max}$ of $105 \text{ kJ} \cdot \text{m}^{-3}$ and σ_s of $71.0 \text{ Am}^2 \cdot \text{kg}^{-1}$ were obtained for the sample annealed at 330°C for 5 h in Ar and then ball-milled for 10 min with a dispersant. A high H_{cJ} of $1380 \text{ kA} \cdot \text{m}^{-1}$ was also obtained for the sample ball-milled for 2 h.

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