Microstructure and Magnetic Properties of Mn–Sn–N and Mn–Sn–Co–N Alloys

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The microstructure and magnetic properties of Mn–Sn–N and Mn–Sn–Co–N alloys were investigated. All the samples showed low remanences, although high coercivity of 876 kA/m was observed in the Mn–Sn–Co–N alloys. The substitution of Co for Mn increased coercivity. The sample with high coercivity consisted of a fine two-phase microstructure of 0.5–2 μm in size.

[doi:10.2320/matertrans.M2013113]

(Received March 22, 2013; Accepted May 8, 2013; Published June 25, 2013)

Keywords: coercivity, magnetization, magnet, nitride, remanence

1. Introduction

Permanent magnets such as Nd–Fe–B magnets^{1,2)} are widely used and have played an important role in modern technology. Therefore, their industrial production has been increasing year by year. However, high coercivity and high heat resistance are required in Nd–Fe–B magnets and currently shipped Nd–Fe–B magnets contain Dy. Dy addition has a crucial disadvantage because of short supply of Dy owing to its low natural abundance and limitation of producing countries. In order to secure a stable future supply of these high-performance Nd–Fe–B magnets, the realization of high coercivity in Nd–Fe–B magnets without Dy or with a much-reduced Dy content is strongly demanded. In addition, new types of magnets have not been developed since the discovery of Nd–Fe–B and Sm–Fe–N³⁾ magnets. So, the interest in the development of new magnets that are free of critical elements as Dy is growing. Many researchers including us have tried to develop new magnets. However, the prospective new compound and alloys have not been discovered yet. The difficulty for developing new magnets is to achieve a balance between high saturation magnetization and coercivity (or high anisotropy). Therefore, at first, we have focused on coercivity and anisotropy of the materials, which are essential properties for becoming permanent magnets.

Mn based alloys such as MnBi, Mn–Al–C or Mn–Ga,⁴⁾ show relatively high coercivity and unique magnetic properties. Furthermore, Mn is naturally abundant and nitriding changes its magnetic properties from antiferromagnetic to ferromagnetic.⁵⁾ We reported that Mn–Ni–N alloys show high coercivity,^{6,7)} and we have continued to investigate the magnetic properties of Mn–X–N (X = Fe, Sn, Ti, Zr, B, or Nb). This paper describes that Mn–Sn–Co–N alloys exhibit high coercivity more than 800 kA/m.

2. Experimental Procedure

The composition of the alloys was $\text{Mn}_{100-y-z}\text{Sn}_y\text{Co}_z$ ($y = 5\text{--}20\text{ at\%}$; $z = 0\text{--}15\text{ at\%}$). The alloys were prepared by arc melting. The alloys were annealed at 950–1050°C for

20 h in an argon atmosphere, and crushed into 0.5–3 mm pieces. The pieces were nitrided at 850–1050°C for 5 h and then slow-cooled (furnace cooling) to room temperature in a nitrogen atmosphere. The magnetic properties of the samples were measured by using a vibrating sample magnetometer (VSM). The microstructure was observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The composition of the phases was analyzed by electron probe micro analyzer (EPMA).

3. Results and Discussion

3.1 Mn–Sn–N system

Figure 1 shows the hysteresis loops of the $\text{Mn}_{90}\text{Sn}_{10}$ alloys before and after nitriding at 1000°C for 5 h in a nitrogen atmosphere. This figure shows that the magnetic properties were drastically altered by nitriding. The coercivity (H_c) and saturation magnetization (J_s) changed from 15.9 to 245 kA/m and from 13.1 to 77.9 mT, respectively.

The change in the phases caused by nitriding was investigated by XRD. Figure 2 shows the XRD patterns of the $\text{Mn}_{90}\text{Sn}_{10}$ samples before and after nitriding at 1000°C. The XRD pattern before nitriding contained $\beta\text{-Mn}$ peaks, whereas after nitriding it contained Mn_4N and Mn_3SnN peaks. Because Mn_4N is ferromagnetic⁵⁾ and Mn_3SnN is antiferromagnetic⁸⁾ at room temperature, Mn_4N contributed to the increase in magnetization after nitriding.

We also investigated the effect of Sn content on the magnetic properties. Figure 3 shows the variation of the

Fig. 1 The hysteresis loops of $\text{Mn}_{90}\text{Sn}_{10}$ alloys before and after nitriding.

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Fig. 2 XRD patterns of $\text{Mn}_{90}\text{Sn}_{10}$ (a) before and (b) after nitriding.

Fig. 3 J_s and H_{cJ} of $\text{Mn}_{100-x}\text{Sn}_x$ as a function of Sn content.

magnetic properties of the $\text{Mn}_{100-x}\text{Sn}_x$ ($x = 5\text{--}20$) alloys after nitriding at 1000°C for 5 h in a nitrogen atmosphere. The addition of Sn affected the magnetic properties, and the nitrided $\text{Mn}_{90}\text{Sn}_{10}$ sample showed the best magnetic properties: $H_{cJ} = 245 \text{ kA/m}$ and $J_s = 77.9 \text{ mT}$.

3.2 Mn–Co–Sn–N system

Co was substituted for Mn in the $\text{Mn}_{90-z}\text{Sn}_{10}\text{Co}_z$ nitride alloys and their magnetic properties were investigated. Figure 4 shows the values of J_s and H_{cJ} as a function of the nitriding temperature for the $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ nitride alloys. The value of J_s increased with the nitriding temperature and a maximum value of 60 mT was obtained for the sample nitrided at 1000°C . However, H_{cJ} reached a maximum value of 458 kA/m at 900°C . Compared with the $\text{Mn}_{100-x}\text{Sn}_x$ nitrided alloys, J_s was similar although H_{cJ} was increased by the addition of Co.

Figure 7 shows the XRD patterns of the $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys before and after nitriding. The XRD patterns shown in Fig. 5(a) reveal that the sample before nitriding consists of $\beta\text{-Mn}$ with a small amount of an unknown phase. The sample after nitriding consists of Mn_4N , $\beta\text{-Mn}$, and a small amount of an unknown phase (Fig. 5(b)).

Fig. 4 (a) J_s and (b) H_{cJ} as a function of nitriding temperature for the nitrided $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys.

The microstructure was determined in order to investigate the cause of the high coercivities in the nitrided $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys. Figure 6 shows the backscatter electron images (BEI) of the $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys without nitriding, and after nitriding at 900 and 1000°C in a nitrogen atmosphere. The sample without nitriding consisted of a single phase, although the samples nitrided at 900 and 1000°C were composed of two phases of $0.5\text{--}2 \mu\text{m}$ in size. The two-phase microstructure of the sample nitrided at 900°C , which shows a high coercivity, was finer than that nitrided at 1000°C .

The EPMA analysis of the two-phase microstructure of the sample nitrided at 900°C showed that the composition of the bright phase was $72.99 \text{ at\% Mn}$, $9.97 \text{ at\% Sn}$, $14.10 \text{ at\% Co}$, $2.95 \text{ at\% N}$, and that of the dark phase was $71.64 \text{ at\% Mn}$, $10.25 \text{ at\% Sn}$, $3.58 \text{ at\% Co}$, $14.53 \text{ at\% N}$ (Fig. 6(b)). The nitrogen content in the dark phase was larger than that in the bright phase. Therefore, the EPMA analysis suggested that the bright phase was $\beta\text{-Mn}$ and the dark phase was Mn_4N ,

Fig. 5 XRD patterns of $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys (a) before and (b) after nitriding.

Fig. 6 BEI of the $\text{Mn}_{80}\text{Sn}_{10}\text{Co}_{10}$ alloys (a) without nitriding, and nitrided at (b) 900°C and (c) 1000°C in a nitrogen atmosphere.

Fig. 7 H_c of Mn-Sn-Co-N as a function of the Co and Sn content at various nitriding temperatures.

judging with the results of XRD analysis. In addition, the high coercivity of the sample nitrided at 900°C was probably related to this fine two-phase microstructure composed of Mn_4N and $\beta\text{-Mn}$.

We investigated the dependence of the magnetic properties on the composition of the $\text{Mn}_{100-y-z}\text{Sn}_y\text{Co}_z$ ($y, z = 7.5-15$) alloys nitrided at 850–1000°C. Figure 7 shows the variation of H_{cJ} as a function of the Co and Sn content at various nitriding temperatures. The composition and nitriding temperatures strongly affected the magnetic properties, and the $\text{Mn}_{82.5}\text{Sn}_{10}\text{Co}_{7.5}$ sample nitrided at 950°C exhibited the highest coercivity. The hysteresis loop of the corresponding $\text{Mn}_{82.5}\text{Sn}_{10}\text{Co}_{7.5}$ alloy is shown in Fig. 8. The sample showed a low J_s of 26 mT but high H_{cJ} of 876 kA/m.

Fig. 8 Hysteresis loop of $\text{Mn}_{82.5}\text{Sn}_{10}\text{Co}_{7.5}$ alloy nitrided at 950°C.

From the results described above, it is considered that the fine two-phase microstructure is closely related to the high coercivities in these Mn-Sn-N and Mn-Sn-Co-N alloys. Figure 6(b) indicates that the sample with high coercivities shows a phase separation and a fine two-phase microstructure consisting of Mn_4N and $\beta\text{-Mn}$. The formation of this two-phase microstructure has possibilities to reduce the grain size of magnetic phase (Mn_4N) and to lead to isolation of the magnetic phase by non-magnetic phase ($\beta\text{-Mn}$), which results in high coercivity. K. M. Ching *et al.* also reported that the inducement of stress increase the anisotropy of Mn_4N phase from research in Mn_4N films.^{9,10} Therefore, there is a possibility that the phase separation and the formation of two-phase microstructure induce stress in Mn_4N phase resulting in the increase of coercivity.

Further investigation is required to determine the origin of the high coercivity. It is expected that the clarification of the origin and the application to the alloys with high magnetization such as Fe or Co alloy lead to the fabrication of new type permanent magnets.

Acknowledgements

This research was supported by Japan Science and Technology Agency (JST), Core Research for Evolutionary Science and Technology (CREST).

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