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.

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 fuiture 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–N\(^{3}\) 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 essencial 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,\(^6\) 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 Mn\(_{100-x-y-z}\)Sn\(_x\)Co\(_z\) (y = 5–20 at%; z = 0–15 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 Mn\(_{90}\)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 Mn\(_{90}\)Sn\(_{10}\) samples before and after nitriding at 1000°C. The XRD pattern before nitriding contained \(\beta\)-Mn peaks, whereas after nitriding it contained Mn\(_3\)N and Mn\(_3\)SnN peaks. Because Mn\(_3\)N is ferromagnetic\(^5\) and Mn\(_3\)SnN is antiferromagnetic\(^6\) at room temperature, Mn\(_3\)N 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

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

### 3.2 Mn–Co–Sn–N system

Co was substituted for Mn in the Mn\textsubscript{90–x}Sn\textsubscript{x}Co\textsubscript{z} nitride alloys and their magnetic properties were investigated. Figure 4 shows the values of $J_s$ and $H_c$ as a function of the nitriding temperature for the Mn\textsubscript{80}Sn\textsubscript{10}Co\textsubscript{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, $H_c$ reached a maximum value of 458 kA/m at 900°C. Compared with the Mn\textsubscript{100–x}Sn\textsubscript{x} nitrided alloys, $J_s$ was similar although $H_c$ was increased by the addition of Co.

Figure 7 shows the XRD patterns of the Mn\textsubscript{80}Sn\textsubscript{10}Co\textsubscript{10} alloys before and after nitriding. The XRD patterns shown in Fig. 5(a) reveal that the sample before nitriding consists of $\beta$-Mn with a small amount of an unknown phase. The sample after nitriding consists of Mn\textsubscript{4}N, $\beta$-Mn, and a small amount of an unknown phase (Fig. 5(b)).

The microstructure was determined in order to investigate the cause of the high coercivities in the nitrided Mn\textsubscript{90}Sn\textsubscript{10}Co\textsubscript{10} alloys. Figure 6 shows the backscatter electron images (BEI) of the Mn\textsubscript{90}Sn\textsubscript{10}Co\textsubscript{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 0.5–2 µm 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 at% Mn, 9.97 at% Sn, 14.10 at% Co, 2.95 at% N, and that of the dark phase was 71.64 at% Mn, 10.25 at% Sn, 3.58 at% Co, 14.53 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 $\beta$-Mn and the dark phase was Mn\textsubscript{4}N,
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$_4$N and $\beta$-Mn.

We investigated the dependence of the magnetic properties on the composition of the Mn$_{100-x-y}$Sn$_x$Co$_y$ (x, y = 7.5–15) alloys nitrided at 850–1000°C. Figure 7 shows the variation of $H_c$ 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 Mn$_{82.5}$Sn$_{10}$Co$_{7.5}$ sample nitrided at 950°C exhibited the highest coercivity. The hysteresis loop of the corresponding Mn$_{82.5}$Sn$_{10}$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.

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$_4$N and $\beta$-Mn. The formation of this two-phase microstructure has possibilities to reduce the grain size of magnetic phase (Mn$_4$N) and to lead to isolation of the magnetic phase by non-magnetic phase ($\beta$-Mn), which results in high coercivity. K. M. Ching et al. also reported that the inducement of stress increase the anisotropy of Mn$_4$N phase from research in Mn$_4$N films. Therefore, there is a possibility that the phase separation and the formation of two-phase microstructure induce stress in Mn$_4$N 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.
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REFERENCES