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High energy product in mechanically alloyed $ThMn_{12}$-type compound with exchange coupling effect

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Abstract

The phase formations and the magnetic properties of the mechanically milled $NdFe_{11-y}Co_yMo_1N_x$ ($y = 0$, 0.5, 1, 1.6, 2.2) compounds have been studied. A relatively high remanence to saturation magnetization ratio of 0.6–0.7 and a high coercivity up to 9.5 kOe were achieved for these nitrides. It is found that the substitution of Co for Fe plays a key role in the grain growth and the grain distribution of α-Fe. The remanences and the coercivities of these compounds increase with the Co content up to $y \leqslant 1.6$. These compounds show a significant remanence enhancement which can be attributed to the magnetic exchange coupling between $Nd(Fe, Mo)_{12}N_x$ and the α-Fe(Co) grains. The maximum energy product $(BH)_{max}$ of about 8.3 MG Oe is obtained for $NdFe_{10}Co_1Mo_1N_x$ with a H_c of ~9.5 kOe and a M_r of ~78 emu/g.

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Keywords: Nanostructure; Magnetically ordered materials; Exchange coupling

1. Introduction

It has been found that the Curie temperature, saturation magnetization and magnetocrystalline anisotropy of $ThMn_{12}$-type compounds can be drastically increased by the introduction of interstitial nitrogen atoms [1–3]. Many efforts have then been made to develop the high energy product magnets based on 1:12 nitrides. In order to obtain a high energy product, it is necessary to increase the remanence while keeping the coercivity sufficiently high. A significant remanence enhancement has been observed in nanostructured Fe-rich rare earth magnets, such as $Nd_2Fe_{14}B$/α-Fe or $Sm_2Fe_{17}C(N)$/α-Fe [4,5]. However, there are very few reports of the nanocomposite $Nd(Fe, Mo)_{12}N_x$ with an excess of α-Fe.

As an important preparation method, mechanically alloying (MA) is widely used to produce isotropic materials with a high coercivity. We had reported a maximum energy product of 7 MG Oe for the compound of $Nd_{10}Fe_{83}Mo_7$ prepared using MA method [6]. However, the coercivity dropped from 13 to 5.8 kOe with the decreasing of Mo content from $Nd_{10}Fe_{78}Mo_{12}$ to $Nd_{10}Fe_{83}Mo_7$. The low coercivity limits the practical use of 1:12 compounds as hard magnets. Previous studies showed that a certain amount of cobalt substitution for iron could increase the saturation magnetization M_s and Curie temperature T_c of the alloys. Furthermore, a small amount of Co addition does not decrease the anisotropy field H_a and may lead to a higher coercivity [7]. In this letter, we report the magnetic properties of exchange-coupling magnet based on $Nd(Fe, Mo)_{12}N_x$/α-Fe(Co). A record high energy product

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of 8.3 MG Oe has been obtained based on the exchange spring mechanism.

2. Experiment

Compounds with nominal compositions of $NdFe_{11-y}Co_yMo_1$ ($y = 0$, 0.5, 1, 1.6, 2.2) were prepared by arc melting under argon atmosphere with the constituent elements of purity $\geqslant$99.9% and a Fe–Mo pre-alloy. The ingots were annealed for 48 h at 1050 °C in a vacuumed silicon tube. The as-annealed alloys were crushed into particles with a size of less than 200 μm and sealed into a vial together with 10 mm diameter steel balls in the ratio of powder to ball 1:30 in a glove box containing argon atmosphere. The powders were then milled in a high energy ball mill for 3–10 h. Recrystallization was carried out for as-milled samples in a temperature range of 800−900 °C for 30–70 min under a vacuum of 4×10^{-3} Pa. The powders were further nitrided at 500−600 °C for 3–5 h in 1 bar of pure nitrogen gas. X-ray diffraction (XRD) analysis was performed using a Philip diffractometer with Cu-K_α radiation. An H-9000 transmission electron microscope (TEM) was used to observe the microstructure of the alloys. Magnetic properties were measured by a vibrating sample magnetometer (VSM) without demagnetization correction. A density of 8 g/cm^3 was used for the measurement of the nitrided samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-milled $NdFe_{11}Mo_1$, $NdFe_{9.4}Co_{1.6}Mo_1$, and the annealed $NdFe_{9.4}Co_{1.6}Mo_1$ and its nitride. Obviously, the Co-substituted samples exhibit a trend of less α-Fe nuclei shown as less intensive diffraction peaks around $2\theta = 44.1°$ (Fig. 1(a–d)). It is found that a small amount of Co substitution for Fe makes the high energy ball milling more efficient. The Co-substituted compounds are easier to become fully amorphous, which may result in a better grain size and a better distribution of α-Fe(Co) during the followed annealing process. After annealing at 825 °C for 70 min, $ThMn_{12}$ phase and some amount of α-Fe(Co) appear in the compounds (Fig. 1(e)). A Nd-rich phase is also detected in the as-annealed sample. The $ThMn_{12}$ and the α-Fe(Co) phases still exist, but the Nd-rich phase disappears after the nitrogenation at 550 °C for 3 h (Fig. 1(f)). The diffraction peaks of the $ThMn_{12}$ nitride shift to the lower angle region indicating that the nitrogen atoms enter the interstitial sites of $ThMn_{12}$ structure. The mean grain size of these compounds is under 30 nm according to Scherrer formula, and the grain size of the α-Fe remains almost the same before and after nitrogenation.

Since the diffraction peak of α-Fe and the (3 3 0) peak of 1:12 phase are almost at the same position in XRD patterns, micrographs obtained by TEM are used to verify the existence of α-Fe (Fig. 2(a)). 1:12 phase and α-Fe are distinguished by their characteristic interfacial distance of

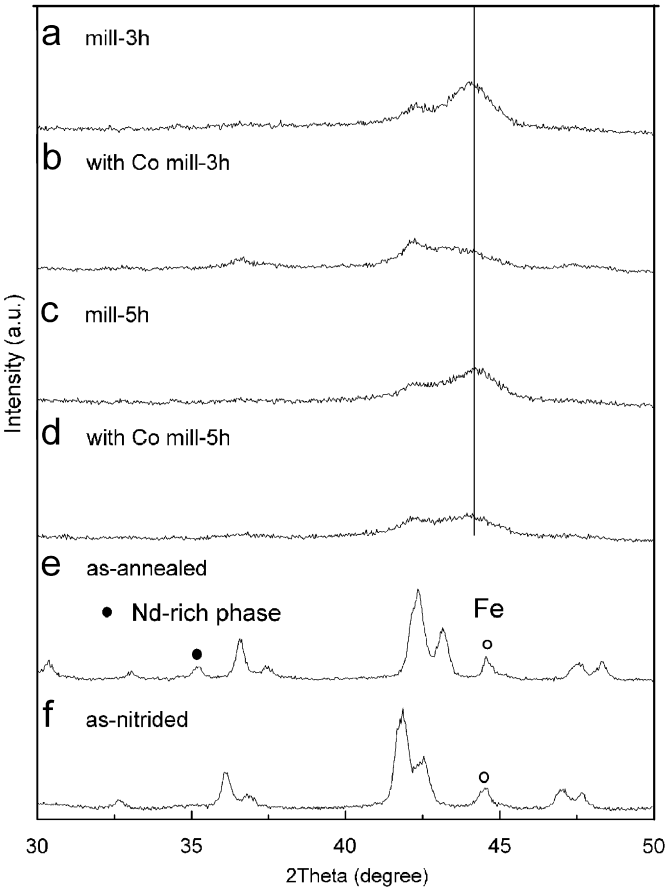

Fig. 1. The X-ray diffraction patterns of $NdFe_{11}Mo_1$, $NdFe_{9.4}Co_{1.6}Mo_1$ samples after milling for 3 and 5 h (a)–(d), and the annealed $NdFe_{9.4}Co_{1.6}Mo_1$ (e) and its nitride (f).

4.124 Å for (1 0 1) and 2.06 Å for (1 1 0). Their grains size shown in Fig. 2(b) is found to be well coincident with the results from XRD.

Normally, the presence of soft magnetic phase such as α-Fe would deteriorate the hard magnetic properties of the compound, unless the microstructure is controlled so that the magnetic soft phase is strongly exchange coupled with the hard one [5,8]. Table 1 listed the magnetic properties of $NdFe_{11-y}Co_yMo_1N_x$ compounds measured under an applied field of 20 kOe. The remanences and the coercivities of $NdFe_{11-y}Co_yMo_1N_x$ increase with Co content up to $y \leqslant 1.6$ resulting from the tuning effect of the Co to the microstructure.

Fig. 3 illustrates the hysteresis loop of the $NdFe_{10}Co_1Mo_1N_x$ sample. A coercivity of 9.5 kOe and a remanence of 78 emu/g were obtained for $NdFe_{10}Co_1Mo_1N_x$ at room temperature. The energy product is estimated to be 8.3 MG Oe. The ratio of the remanent magnetization M_r to the saturation magnetization M_s is about 0.63, which significantly exceeds the theoretical limit ($M_r \backslash M_s \leqslant 0.5$) for the isotropic materials [9]. This suggests that the exchange coupling occurs among the grains. Since the XRD patterns and the micrograph obtained by TEM have shown that certain amount of α-Fe(Co) exists in these

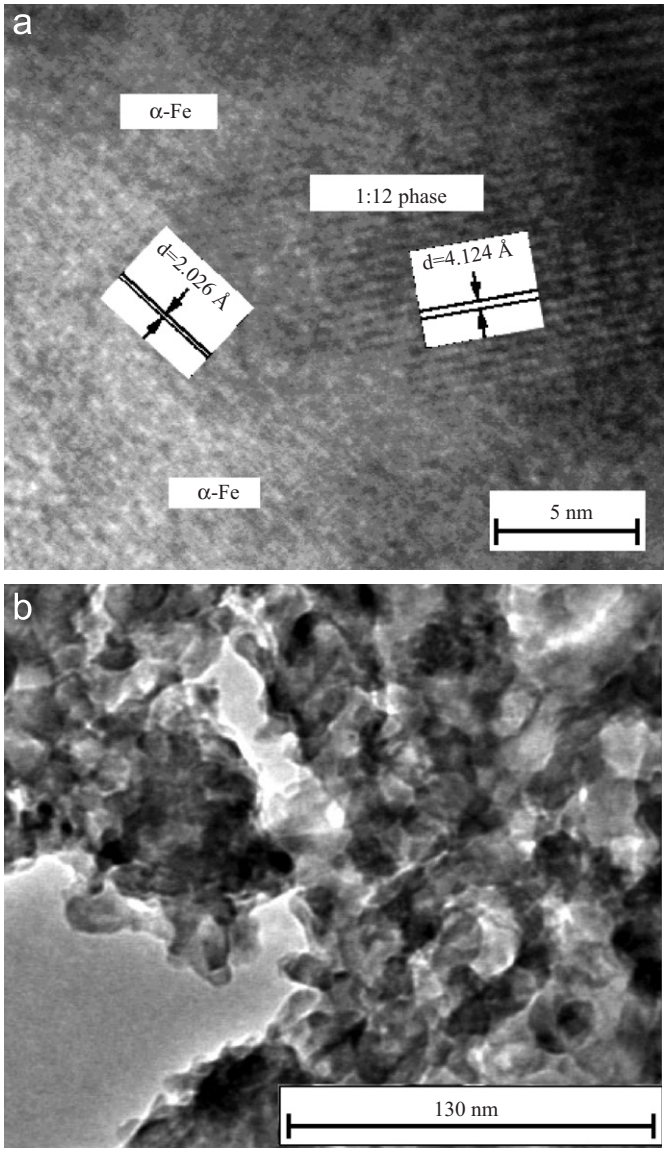

Fig. 2. (a) and (b). TEM observation for the as-annealed $NdFe_{9.4}Co_{1.6}Mo_1$ compound.

Table 1
Magnetic properties of $NdFe_{11-y}Co_yMo_1N_x$ measured in a maximum applied field of 20 kOe

Co content (y)	M_r (emu/g)	H_c (kOe)	$(BH)_{max}$ (MG Oe)
0	46	6.4	3.7
0.5	55	7.2	5.3
1	63	8.9	7.0
1.6	64	8.3	7.1
2.2	58	7.8	6.0

compounds, the exchange coupling effect is caused by a two-phase nanocomposite of $ThMn_{12}$/α-Fe, but not by the single-phase interaction between the hard grains [10]. It is noticed that a small concave was observed from the

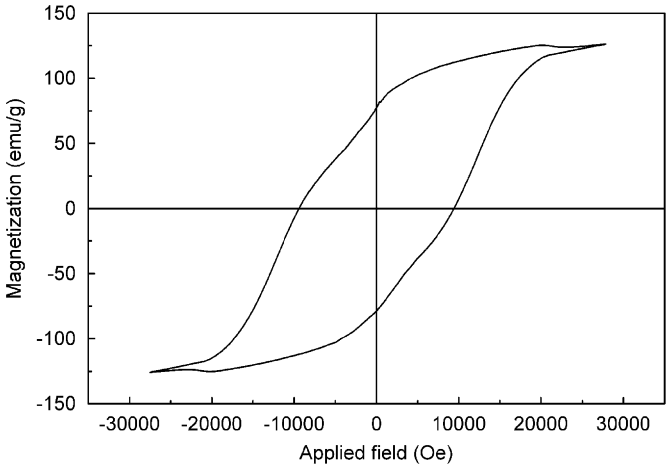

Fig. 3. Hysteresis loop of $NdFe_{10}Co_1Mo_1N_x$ at room temperature in an applied field of 28 kOe.

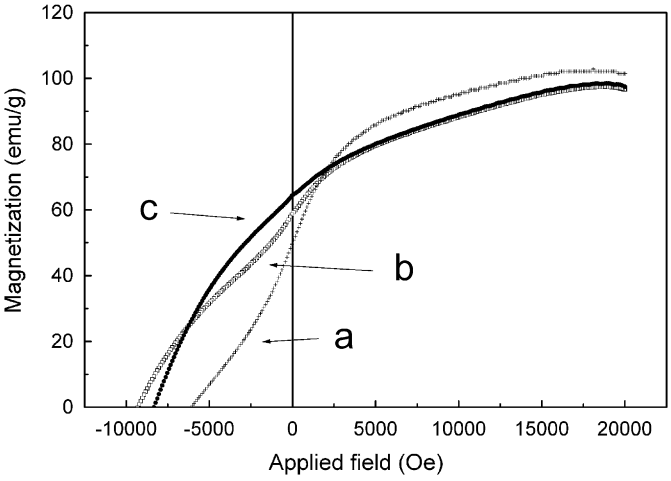

Fig. 4. Demagnetization curves of $NdFe_{11}Mo_1N_x$ (a), $NdFe_{10}Co_1Mo_1N_x$ (b) and $NdFe_{9.4}Co_{1.6}Mo_1N_x$ (c) samples prepared in the same conditions.

demagnetization curve of $NdFe_{10}Co_1Mo_1N_x$, a typical behavior for the nanocomposite of a magnetic hard/soft two-phase material which is attribute to that the average grain sizes of the hard and soft phases are much larger than the Bloch domain wall thickness of the magnetic hard phases. Based on the micromagnetic model of Kneller and Hawig [11], the optimum exchange spring microstructure should consist of homogeneously distributed hard/soft grains, with the lateral dimensions of both phases comparable to the double domain wall width (δ) of the hard phase. In the mechanically milled 1:12 compounds, it is critical to obtain intact and fine grains of the hard phase in order to realize the high coercivity. In the meantime, the growth of α-Fe grains should be rigorously suppressed to avoid the deterioration of the coercivity. Once the nuclei of α-Fe reach to certain amount in the as-milled sample, the α-Fe grains will grow more rapidly than that of 1:12 grains during the followed annealing process. During the ball-milling process, a proper amount of Co substitution for Fe

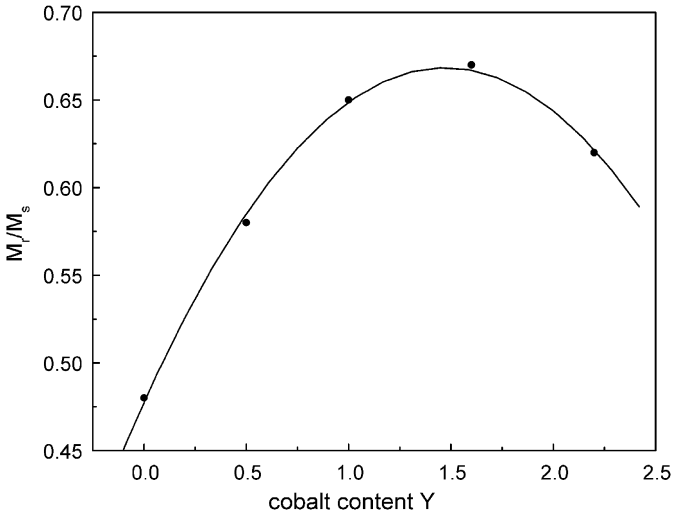

Fig. 5. The ratios of $M_r \backslash M_s$ vs. the cobalt content y for the compounds of $NdFe_{11-y}Co_yMo_1N_x (y = 0, 0.5, 1, 1.6, 2.2)$.

can suppress the presence of excessive α-Fe nuclei as indicated by XRD patterns, and thus leading to a homogenous distribution of α-Fe grains. Fig. 4 illustrates this effect by comparing the demagnetization curves of the samples $NdFe_{11}Mo_1N_x$, $NdFe_{10}Co_1Mo_1N_x$ and $NdFe_{9.4}Co_{1.6}Mo_1N_x$ prepared in the same conditions. A large concave and a relatively low coercivity are observed in the demagnetization curve of $NdFe_{11}Mo_1N_x$. The concave becomes smaller for $NdFe_{10}Co_1Mo_1N_x$ and disappears for $NdFe_{9.4}Co_{1.6}Mo_1N_x$ indicating that the magnetic hard and soft grains are in proper sizes and no significant α-Fe gathering in large scale. Fig. 5 plots the ratios of M_r/M_s for $NdFe_{11-x}Co_xMo_1N_x$ as a function of Co contents. $NdFe_{9.4}Co_{1.6}Mo_1N_x$ possesses the highest value of $M_r \backslash M_s \sim 0.67$ without the demagnetization modification. In fact, $NdFe_{9.4}Co_{1.6}Mo_1N_x$ has a higher $(BH)_{max}$ than $NdFe_{10}Co_1Mo_1N_x$ as shown in Table 1. Magnetic properties data are not yet obtained in 28 kOe field and the energy product is expected higher than 8.3 MG Oe.

4. Conclusion

In conclusion, $ThMn_{12}$-type materials with a maximum energy product of 8.3 MG Oe have been fabricated by mechanical milling. The results show that the magnetic properties of the compounds can be improved by partial substitution of Co for Fe in the $Nd(Fe, Mo)_{12}N_x$ compounds. These compounds show a significant remanence enhancement with M_r/M_s 0.6−0.7 due to the exchange coupling between $Nd(Fe, Mo)_{12}N_x$ and the α-Fe(Co) grains. A single-phase behavior has been observed in the demagnetization curve of $ThMn_{12}$/α-Fe(Co) compounds.

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