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Coercivity enhancement in Nd–Fe–B sintered permanent magnet by Dy nanoparticles doping

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ABSTRACT

Nd–Fe–B permanent magnets with a small amount of Dysprosium (Dy) nanoparticles doping were prepared by conventional sintered method, and the microstructure and magnetic properties of the magnets were studied. Investigation shows that the coercivity rises gradually, while the remanence decreases simultaneously with increased Dy doping amount. As a result, the magnet with 1.5 wt.% Dy exhibits optimal magnetic properties. Further investigation presumed that Dy is enriched as (Nd, Dy)$_2$Fe$_{14}$B phase in the surface region of the Nd$_2$Fe$_{14}$B matrix grains indicated by the enhancement of the magnetocrystalline anisotropy field of the Nd$_2$Fe$_{14}$B phase. As a result, the magnet doped with a small amount of Dy nanoparticles possesses remarkably enhanced coercivity without sacrificing its magnetization noticeably.

1. Introduction

Sintered Nd–Fe–B permanent magnets have been widely used due to their outstanding magnetic performance [1]. Up to now, however, their undesirable thermal stability is still a major concern in some practical application such as high temperature motor. It is well known that addition of heavy rare earths of Dy or Tb is effective to enhance coercivity and consequent thermal stability of the Nd–Fe–B magnets because Dy or Tb increases the magnetic anisotropy field of the Nd–Fe–B compound [2–6], but this method simultaneously results in considerable degradation of the remanence of the magnets. Recently, techniques for enhancement of coercivity of sintered Nd–Fe–B magnets by diffusing a continuous layer of Dy or Tb onto the surface of the Nd$_2$Fe$_{14}$B matrix grains without obvious reduction of the remanence have been developed by different researchers [7–10], but the detailed mechanism for the improving coercivity is unclear. Furthermore, these techniques can only be used to prepare small size magnets since the diffusion of Dy or Tb into the magnet is confined within 5 mm. In our previous study, a sintered Nd–Fe–B magnet with enhanced coercivity by Tb nanoparticles doping was prepared [11]. Here we report the effect on microstructure and magnetic properties of sintered Nd–Fe–B magnets with Dy nanoparticles doping.

2. Experiment

Alloy ingot with nominal composition of Nd$_{10.2}$Pr$_{3.0}$Fe$_{\mathrm{bal}}$B$_{5.8}$ was prepared by induction melting. The ingot was then prepared into flakes via strip casting technique. Subsequent hydrogen decrepitating and jet milling were applied to obtain Nd–Fe–B powders with good size distribution from the flakes. On the other hand, Dy nanoparticles were prepared by inert gas condensation method. The Nd–Fe–B powders and the Dy nanoparticles were mixed homogeneously and pressed together with rubber isotropic pressing (RIP) [12,13]. The amount of the Dy nanoparticles was set as 0.5–2.5 wt.% of the Nd–Fe–B powders. In the RIP process, the cavity of the rubber mold inserted in the stainless steel die was filled with mixed powders. After that, magnetic alignment was carried out in a pulse magnetic field of 5 T, and then the die with the powder-filled mold was placed on a pressure of 0.4 T/cm^2. The green compacts were then sintered at 1060 °C for 3 h and subsequently annealed at 900 °C and 480 °C for 2 h and 1 h, respectively. For comparison, Nd–Fe–B magnet without Dy nanoparticles doping was also prepared under same processing condition. The microstructure and composition of the magnets were analyzed using scanning electron microscope (SEM) with energy dispersive X-ray detector (EDX). The magnetic properties of the magnets were measured by B–H loop-line instrument.

3. Results and discussion

Fig. 1(a) shows the ideal doping model of Dy nanoparticles onto the surface of the Nd–Fe–B powders [11]. In this model, Dy nanoparticles (small grey round circles) distribute homogeneously on the surface of the Nd–Fe–B powder (big half round circle). Fig. 1(b) and (c) show the micrographs of Nd–Fe–B powders and the Dy nanoparticles, respectively. It is observed that the Nd–Fe–B powders are fine and uniform, and their average diameter is about 5 μm. On the other hand, the Dy nanoparticles possess a rather wide size distribution ranging from 20 to 100 nm. Investigation on preparation of nar-

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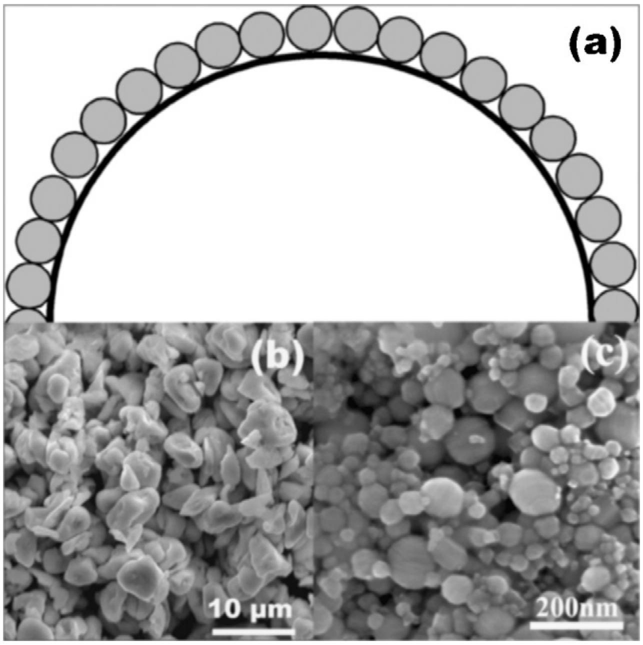

Fig. 1. Ideal doping model of Dy nanoparticles on the surface of Nd–Fe–B powders (a) and micrographs of Nd–Fe–B powders (b) and Dy nanoparticles (c).

row size distribution Dy nanoparticles via optimizing processing conditions is underway.

Fig. 2 shows the magnetic properties of sintered magnets as a function of Dy nanoparticles doping amount. As we expected, the coercivity of the magnets remarkably increases by 27.8% when the Dy content increases from 0 to 1.5 wt.%. When the Dy content increases further to 2.5 wt.%, however, the coercivity (H_{ci}) of the magnet exhibits only 2.6% increment, indicating that the optimal amount of Dy nanoparticles is no more than 1.5 wt.%. On the other hand, the remanence (B_r) and the maximum energy product ($(BH)_{max}$) of the magnets reduce slightly with increasing Dy. When the Dy content is 1.5 wt.%, the B_r and the $(BH)_{max}$ of the magnet drops only by 2.9% and 5.4% compared with those of the Dy-free magnet. It is therefore concluded that by proper amount Dy nanoparticles doping, the magnet exhibits remarkable improvement in its coercivity without obvious sacrificing its remanence and maximum energy product.

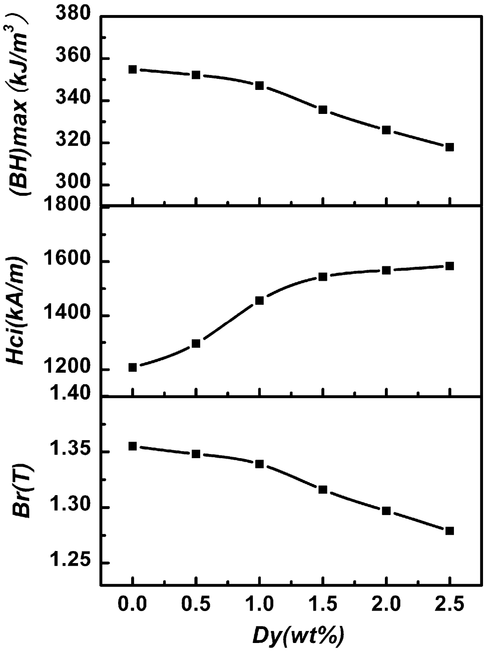

Fig. 2. The magnetic properties of sintered magnets as a function of Dy contents.

Table 1
Energy dispersive X-ray analysis in Nd-rich phase (1), grain surface region (2), and center of the $Nd_2Fe_{14}B$ grains (3) in the Nd–Fe–B magnets doped with Dy nanoparticles (wt.%).

Position	Fe		Nd		Pr		Dy	
	5.21		67.29		26.89		0.61	
	4.98		69.09		25.34		0.59	
1	4.84	5.10	69.06	68.51	25.47	25.79	0.63	0.60
	5.02		68.18		26.12		0.68	
	5.42		68.91		25.15		0.52	
	69.34		21.61		6.58		2.47	
	71.48		20.42		5.74		2.36	
2	70.40	70.78	21.32	20.73	5.87	6.07	2.41	2.42
	71.72		19.75		6.02		2.51	
	70.95		19.56		6.12		2.37	
	73.82		19.89		5.72		0.57	
	71.99		21.35		6.07		0.59	
3	72.38	72.90	21.12	20.74	5.87	5.77	0.63	0.59
	72.89		20.75		5.77		0.59	
	73.4		20.57		5.42		0.61	

To clarify the distribution of the doping Dy element in the Nd–Fe–B magnet, the microstructure as well as the concentration distribution of Fe, Nd, and Dy elements going through the Nd-rich grain boundary phase and the $Nd_2Fe_{14}B$ matrix phase grains were examined, and the result was shown in Fig. 3. It is found that the doping Dy element exhibits similar distribution as Fe, indicating that most Dy exists in the matrix phase grains, but not in the Nd-rich phase. Further quantitative investigation of Dy distribution in Nd-rich phase, grains surface region, and center of the $Nd_2Fe_{14}B$ grains, which were respectively indicated by number 1, 2, and 3 in Fig. 3, shows that Dy element enriches mainly into the surface region of $Nd_2Fe_{14}B$ grains where the Dy concentration is four times higher than that in both Nd-rich phase and the center of $Nd_2Fe_{14}B$ grains (Table 1). Furthermore, the enriched Dy element in the grains surface region of the $Nd_2Fe_{14}B$ grains was expected to exist as $(Nd, Dy)_2Fe_{14}B$ phase which has the larger H_A than that of the $Nd_2Fe_{14}B$ phase, so H_{ci} of the Nd–Fe–B magnets was remarkably enhanced.

For conventional sintered Nd–Fe–B magnet, its coercivity will increase to some extent with the addition of Dy element since the H_A of 15.8 T for $Dy_2Fe_{14}B$ compound is much higher than that of 6.7 T for $Nd_2Fe_{14}B$ compound [14]. In the present Dy nanoparticles doped Nd–Fe–B magnet, however, the special distribution of the $(Nd, Dy)_2Fe_{14}B$ phase in the $Nd_2Fe_{14}B$ grains surface region, which may results from the substitution of Dy to Nd atoms during the sintering and subsequent heat treatment process, was expected to enhance the coercivity of the magnet via an additional way. As Kronmüller pointed out [15], the crystal anisotropy of the magnetic grains surface region, which is always lower than that of inside the grains, may lead to an obvious reduction of the magnetic reversal nucleation field, H_N, and subsequent coercivity of the magnet. The H_N of the $Nd_2Fe_{14}B$ phase, for example, usually drops obviously because of the reduction of crystal anisotropy of the surface regions where the stoichiometry has changed due to diffusion process, and the coercivity of the magnet is therefore reduced with the decrease of H_N. In our case, on the contrary, the surface regions of the $Nd_2Fe_{14}B$ grains were enriched with $(Nd, Dy)_2Fe_{14}B$ phase with higher crystal anisotropy. The H_N and the coercivity of Nd–Fe–B compound doped with Dy nanoparticles were therefore enhanced noticeably.

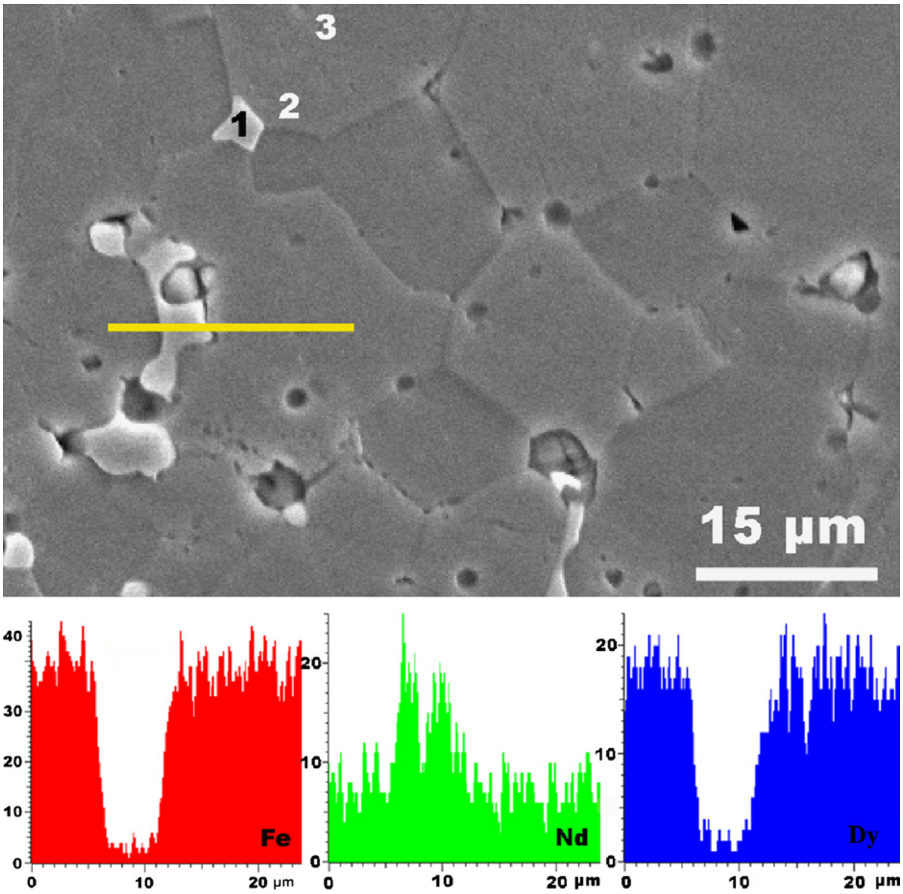

Fig. 3. SEM micrograph of the Dy doped Nd–Fe–B sintered magnet (back scattered mode) and the EDX results of concentration distribution of Fe, Nd, and Dy going through the Nd-rich phase and $Nd_2Fe_{14}B$ matrix phase grains (indicated by the short bar in the figure).

4. Conclusions

In summary, Dy nanoparticles had been used for doping sintered Nd–Fe–B permanent magnets. The doping Dy element was expected to enrich as $(Nd, Dy)_2Fe_{14}B$ phase in the surface region of the $Nd_2Fe_{14}B$ matrix grains. The special distributed $(Nd, Dy)_2Fe_{14}B$ phase was expected to improve the coercivity of the Nd–Fe–B magnet by enhancing both the H_A and the H_N of the Nd–Fe–B compound during demagnetization process. As a result, the magnet doped with a small amount of Dy nanoparticles possesses enhanced coercivity without obvious sacrificing its magnetization.

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References

[1] M. Sagawa, S. Fujimura, N. Togawa, Y. Matsuura, J. Appl. Phys. 55 (1984) 2083.
[2] N.C. Koon, B.N. Das, M. Rubinstein, J. Tyson, J. Appl. Phys. 57 (1985) 4091.
[3] S. Hirosawa, Y. Matsuura, H. Yamamoto, S. Fujimura, M. Sagawa, J. Appl. Phys. 59 (1986) 873.
[4] J.J. Croat, F. Herbst, R.W. Lee, F.E. Pinkerton, J. Appl. Phys. 55 (1984) 2078.
[5] A.S. Lileev, A.G. Ayuyan, W. Steiner, M. Reissner, J. Magn. Magn. Mater. 157/158 (1996) 373.
[6] M. Sagawa, S. Fujimura, H. Yamamoto, K. Hiraga, IEEE Trans. Magn. 20 (1984) 1584.
[7] K.T. Park, K. Hiraga, M. Sagawa, Proceedings of the Sixteenth International Workshop on Rare-Earth Magnets and Their Applications, Sendai, Japan, 2000, p. 257.
[8] H. Nakamura, K. Hirota, M. Shimao, T. Minowa, M. Honshima, IEEE Trans. Magn. 41 (2005) 3844.
[9] K. Hirota, H. Nakamura, T. Minowa, M. Honshima, IEEE Trans. Magn. 42 (2006) 2909.
[10] N. Watanabe, M. Itakura, N. Kuwano, D. Li, S. Suzuki, K. Machida, Mater. Trans. 48 (2007) 915.
[11] M. Yue, W.Q. Liu, D.T. Zhang, Z.G. Jian, A.L. Cao, J.X. Zhang, Appl. Phys. Lett. 94 (2009) 092501.
[12] H.R. Madaah Hosseinia, A. Kianvashb, M. Seyyed Reihania, H. Yoozbashi Zadeha, J. Alloys Compd. 298 (2000) 319.
[13] A.M. Gabay, Y. Zhang, G.C. Hadjipanayis, J. Magn. Magn. Mater. 238 (2002) 226.
[14] S. Hirosawa, K. Tokuhara, Y. Matuura, H. Yamaoto, S. Fujimura, M. Sagawa, J. Magn. Magn. Mater. 61 (1986) 363.
[15] Kronmüller, Phys. Stat. Sol. B 144 (1987) 385.