

# The Origin of Coercivity Enhancement of Sintered NdFeB Magnets Prepared by Dy Addition

N. J. Yu, M. X. Pan\*, P. Y. Zhang, and H. L. Ge

Magnetism key laboratory of Zhejiang Province, China Jiliang University, Hangzhou 310018, China

(Received 17 December 2012, Received in final form 1 July 2013, Accepted 1 July 2013)

The effect of Dy addition on the microstructure and magnetic properties of the sintered NdFeB magnets was investigated. The results of the microstructure analysis showed that Dy-free and Dy-doped samples are composed of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  ( $P42/mnm$ ) and a trace of Nd-rich phase. Dy addition reduces significantly the pole density factor of (004), (006) and (008) crystal faces as estimated by the Horta formula. Accordingly, the coercivity of the Dy-doped sample increases from  $2038 \text{ kA}\cdot\text{m}^{-1}$  up to  $2288 \text{ kA}\cdot\text{m}^{-1}$ . The  $H_{\text{cj}}(T)/M_s(T)$  versus  $H_N^{\text{min}}/M_s(T)$  (Kronmüller-plot) behavior shows that the nucleation is the dominating mechanism for the magnetization reversal in these two kinds of magnets, and two microstructural parameters of  $\alpha_k$  and  $N_{\text{eff}}$  are obtained. The Kronmüller-Plot gives evidence for an increase of the  $\alpha_k$  responsible for an increase of the coercivity as the result of the increase of the magnetic field as the magnetic domain reversed.

**Keywords:** sintered magnet, coercivity, nucleation mechanism

## 1. Introduction

Since the development of the NdFeB magnets, it attracts much attention due to the high anisotropy and coercivity. As compared to the SmCo magnets, the NdFeB magnets have higher magnetic properties, such as coercivity  $H_{\text{cj}} = 5572 \text{ kA}\cdot\text{m}^{-1}$ ,  $B_r = 1.22 \text{ T}$ , and  $(BH)_{\text{max}} = 400 \text{ kJ}\cdot\text{m}^{-3}$  [1]. A high coercivity is always expected for the sintered NdFeB magnets in terms of the high magnetic crystalline anisotropy, but the experimental value of the coercivity, amounting to about 2000 kA/m-3000 kA/m only, is considerably smaller than the theoretical predictions  $H_{\text{cj}} = 7164 \text{ kA}\cdot\text{m}^{-1}$  [2]. Therefore, many efforts have been worked towards refining the microstructure and optimizing the manufacturing method.

It is well known that the coercivity of NdFeB magnets can be improved by adding a small amount of dopants, such as Co, Ga, Zn, Al or some other refractory elements. For example, Kanekiyo *et al.* [3] have reported that the addition of 3 at. % V to NdFeB alloys can increase the coercivity significantly. Harrison *et al.* [4] also showed that the addition of Ti and C to alloys can modify the microstructure. The main reason for the improvement of

coercivity is attributed to the refinement of the microstructure of the sintered magnets by adding metal elements. Presently the hydrogen decrepitation (HD) technique is an effective manufacturing technique to refine the grain size of the NdFeB alloys and has been widely used in the sintering process.

In this work, we reported the effects of Dy addition on the microstructure and magnetic properties of the sintered NdFeB magnets prepared by HD method. The coercivity mechanism of both Dy-free and Dy doped NdFeB samples were studied by Kronmüller-Plot behavior.

## 2. Experimental

The compositions of the sintered magnets were  $\text{Nd}_{14.63}\text{Fe}_{77.48}\text{Cu}_{0.16}\text{Al}_{1.47}\text{Nb}_{0.21}\text{B}_{6.03}$  and  $\text{Nd}_{14.63}\text{Fe}_{76.98}\text{Cu}_{0.16}\text{Al}_{1.47}\text{Nb}_{0.21}\text{Dy}_{0.5}\text{B}_{6.03}$  (at. %), respectively. Metals of Nd, Fe, Dy, Cu, and Al with purity of 99.9%,  $\text{Fe}_3\text{B}$  (B 19.3 at. %), and NbFe (Nb 66.3 at. %) were used. The samples were fabricated using the following technique: The alloys were melted about 30 min by an induction furnace, then the ingots were prepared in rectangular water-cooled copper moulds. In order to eliminate the  $\alpha$ -Fe phase, these alloys were placed into vacuum anneal furnace at 1000 for 10 h under vacuum ( $\leq 10^{-3} \text{ Pa}$ ). The annealed ingot was crushed into powders, and placed in a furnace and then heated from room temperature to  $850^\circ\text{C}$  for 1 h in a high purity

©The Korean Magnetism Society. All rights reserved.

\*Corresponding author: Tel: +8618668232700

Fax: +86-571-28889526, e-mail: pan\_minxiang@yahoo.com

hydrogen atmosphere of 1.2 atm. This pressure of the hydrogen gas, higher than ambient pressure of the hydrogen gas at room temperature, is favorable for observing the absorption and desorption processes of hydrogen gas. After cooling to room temperature, the powder was placed in a spiral type jet mill to produce the powder (average particle size = 4.8  $\mu\text{m}$ ) under a high purity nitrogen atmosphere. The powders were aligned magnetically in an external field of 1.8T, then pressed isostatically and vacuum sintered at high temperature of 1180 $^{\circ}\text{C}$  for 3 h. Finally, single phase sintered NdFeB magnets were achieved. The microstructure of these magnets was examined by X-ray diffraction (XRD) with a Cu K $\alpha$  radiation. Magnetization measurement was accomplished by using a BH loop tracer in the perpendicular direction of the magnetic field.

To study the intensity of crystal texture, the pole density factor  $P_{(hkl)}^H$  was calculated according to the Horta method [5]:

$$P_{(hkl)}^H = \frac{\left[ \sum_1^n M_{(hkl)} \right] \cdot I_{(hkl)} / I_{R(hkl)}}{\sum_1^n [M_{(hkl)} \cdot I_{(hkl)} / I_{R(hkl)}} \quad (1)$$

where  $I_{(hkl)}$  is the measured intensity of the  $(hkl)$  crystal face,  $M_{(hkl)}$  is the multiplicity of the  $(hkl)$  crystal face.  $I_{R(hkl)}$  represents the equational intensity of the  $(hkl)$  crystal face, which can be calculated as follows:

$$I_{R(hkl)} = \frac{\sum I}{\sum C} \cdot C_{hkl} \quad (2)$$

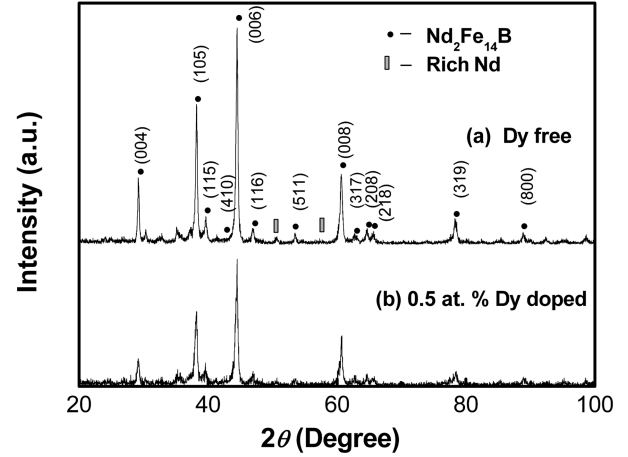
$C_{(hkl)}$  is a factor determined by:

$$C = \frac{1}{V_0} F_{HKL}^2 \frac{1 + \cos^2 2\theta \cos^2 \theta_c}{\sin^2 \theta \cos \theta} e^{-2M} \quad (3)$$

where  $V_0$  is the volume of unite cell,  $F$  is the structure factor,  $P$  is the multiplicity,  $(1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta)$  is the Lorentz-Polarization factor and  $e^{-2M}$  is the temperature factor.

### 3. Results and Discussion

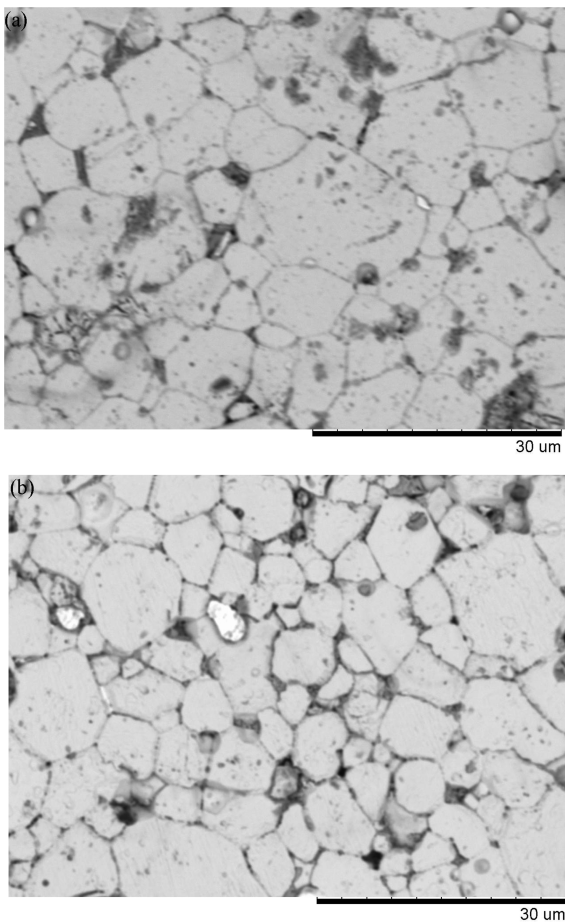
Fig. 1 shows the XRD patterns of Dy-free and Dy-doped NdFeB magnets obtained in the perpendicular direction of the magnetic field. A detailed analysis of the XRD patterns shows that both alloys with Dy-free and Dy doping are composed of hard magnetic phase Nd<sub>2</sub>Fe<sub>14</sub>B ( $P42/mnm$ ) and a trace of the Nd-rich phase. By com-



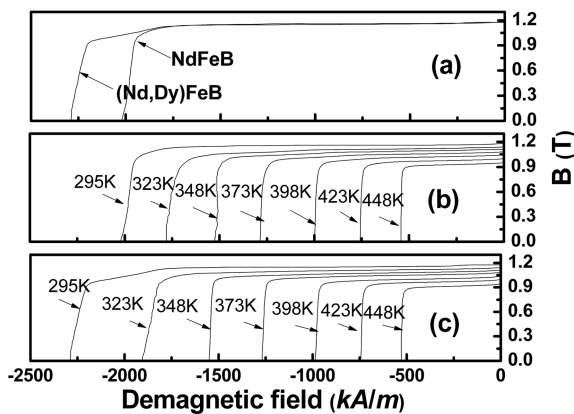
**Fig. 1.** XRD patterns of Dy-free and 0.5 at. % Dy doped NdFeB sintered magnets in the perpendicular direction of the magnetic field.

paring of Fig. 1(a) and (b), it is found that the ratio of  $I_{(410)} / I_{\text{Nd-rich}} = 0.53$  ( $I_{\text{Nd-rich}}$  is at  $2\theta = 50.4^{\circ}$  for Nd-rich phase) for the Dy-doped alloy was slightly lower than that of the Dy-free alloy (0.77). Also, in the case of the Dy-doped sample, the half-width of the diffraction peaks is larger while the intensity is lower than that in the Dy-free sample. This result indicates that the grain size in the Dy-doped alloy was refined and the volume fraction of Nd<sub>2</sub>Fe<sub>14</sub>B phase changes as a consequence of the Dy addition. The refined grain size in Dy-added alloy is further confirmed by SEM observations shown in Fig. 2. Where the average grain size of the NdFeB phase in Dy-free (Fig. 2(a)) and Dy-doped (Fig. 2(b)) the sample is determined to be 22.3  $\mu\text{m}$  and 16.8  $\mu\text{m}$ , respectively. Additionally, the intensities of the (004), (006) and (008) crystal faces of the Nd<sub>2</sub>Fe<sub>14</sub>B crystal are much stronger as compared with the main diffraction intensity of (410) crystal face (See Fig. 1(a) and (b)), indicating a strong (00 $l$ ) texture occurring in the both NdFeB and (Nd,Dy)-FeB alloys. For quantitative analysis of the crystal texture (00 $l$ ) in Dy-free and Dy-doped NdFeB magnets, the pole density factors of (004), (006) and (008) crystal faces were calculated in term of Horta-formula (Eq. 1). The results show that the pole density factors of (004), (006) and (008) crystal faces in the Dy-free NdFeB sample were 2.9, 3.5 and 4.3 respectively, slightly higher than the value (2.4, 3.6 and 4.0) for the Dy-doped NdDyFeB sample. The reduced pole density factor indicates that the Dy addition could result in the decrease of crystal texture in the alloys.

Fig. 3 displays the demagnetization curves of NdFeB and (Nd,Dy)FeB magnets measured at different temperatures. It can be seen that, compared to the Dy-free sample



**Fig. 2.** SEM micrograph Dy-free and 0.5 at. % Dy doped NdFeB sintered magnets.



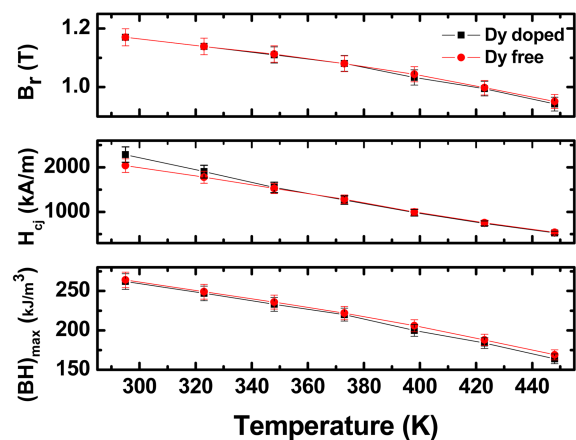
**Fig. 3.** (a) The demagnetization curves of NdFeB and (Nd,Dy)FeB magnets at room temperature. (b) The demagnetization curves of NdFeB magnets measured at different temperatures. (c) The demagnetization curves of (Nd,Dy)FeB magnets measured at different temperatures.

(see Fig. 3(a)), the addition of Dy results in a strong increase of coercivity  $H_{cj}$  from  $2038 \text{ kA}\cdot\text{m}^{-1}$  up to  $2288$

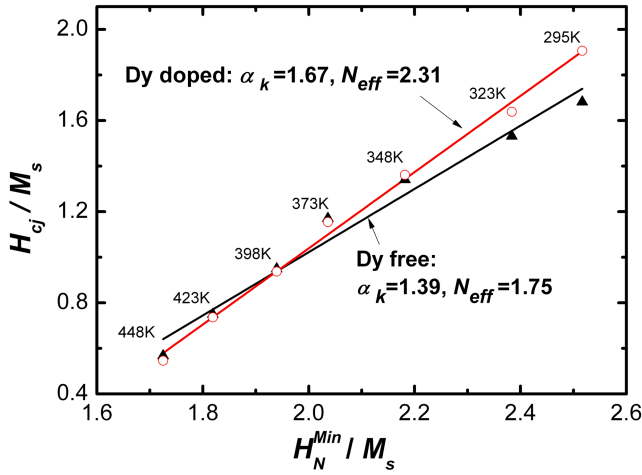
$\text{kA}\cdot\text{m}^{-1}$  without sacrificing the remanence, the remanence  $B_r$  is both close to 1.14 T. This result is different from our previous result [6] that the addition of other heavy rare earth Tb element improve the coercivity but with sacrificing the remanence. Some studies have been carried out on the effect of Dy substitution in the Nd-Fe-B system [7]. The results show that the magnetocrystalline anisotropy field ( $H_A$ ) is improved since the  $H_A$  of  $\text{Dy}_2\text{Fe}_{14}\text{B}$  ( $H_A = 12577 \text{ kA}\cdot\text{m}^{-1}$ ) is much higher than that of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  ( $H_A = 5572 \text{ kA}\cdot\text{m}^{-1}$ ) [8]. On the other hand, Dy substitution can optimize the microstructure of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  matrix and decrease the grain size, which are important for producing magnets with high coercivity ( $H_{cj}$ ) [9]. Similar results were observed in the magnets with Zr [10] and Ga [11] addition.

In order to study mechanism of the coercivity in Dy-free and Dy-doped samples in more detail, the temperature dependence of the demagnetization curves for the NdFeB and (Nd,Dy)FeB magnets were measured and shown in Fig. 3(b) and (c). With the increase of the temperature, two magnets show a rapid decrease of the magnetic properties. It can be seen more clearly by the plots of  $B_r$ ,  $H_{cj}$  and  $(BH)_{max}$  of the NdFeB and (Nd,Dy)FeB magnets versus the temperature (see Fig. 4). For the (Nd,Dy)FeB magnet, as the temperature rises from 295 up to 448 K,  $B_r$  reduces from 1.14 T down to 0.94 T,  $H_{cj}$  from  $2288 \text{ kA}\cdot\text{m}^{-1}$  to  $528 \text{ kA}\cdot\text{m}^{-1}$ , and  $(BH)_{max}$  from  $262 \text{ kJ}\cdot\text{m}^{-3}$  to  $164 \text{ kJ}\cdot\text{m}^{-3}$ .

Generally, the coercivity of the conventional sintered NdFeB magnets is usually dominated by nucleation mechanisms [12]. The nucleation process is defined by the formation of a small reverse domain upon the application of a reverse field. Once the nucleus is formed, it rapidly propagates through the whole volume resulting in a rapid



**Fig. 4.** (Color online) The temperature dependence of the remanence, the coercivity and the energy product of the NdFeB and (Nd,Dy)FeB magnets.



**Fig. 5.** (Color online) The plots of  $H_{cj}(T)/M_s(T)$  versus  $H_N^{\min}(T)/M_s(T)$  for the NdFeB and (Nd,Dy)FeB alloys.

total magnetization reversal [13]. According to a modified form of the Brown model [14]

$$\frac{H_{cj}(T)}{M_s(T)} = \alpha_k \frac{H_N^{\min}(T)}{M_s(T)} - N_{eff} \quad (4)$$

the microstructural parameter  $\alpha_k$  describes the reduced surface anisotropy of nonperfect grains,  $N_{eff}$  is an effective demagnetization factor describing the internal stray fields acting on the grains. The minimum nucleation field  $H_N^{\min}$  denotes the value for the nucleation field of the most unfavorably aligned grains belonging to misalignment angle of  $45^\circ$  according to the Stoner Wohlfarth model [15].  $M_s$  is the saturation magnetization obtained from a  $Nd_2Fe_{14}B$  single crystal. The result of the experimental data  $H_{cj}(T)/M_s(T)$  versus the theoretical values  $H_N^{\min}/M_s(T)$  (Kronmüller-plot) shows a linear behavior (see Fig. 5), indicating that the nucleation of reversed domains is the dominant process for the magnetization reversal in these magnets. The fitting results of the magnets show that the values of the  $\alpha_k$  according to Eq. (4) is 1.39 for the Dy-free sample and 1.67 for the Dy-doped sample, and the values of  $N_{eff}$  is 1.75 for the Dy-free sample and 2.31 for the Dy-doped sample, respectively. The results show that Dy addition to the sample results in a large values of  $\alpha_k$  and  $N_{eff}$ . However, as we know, only the large value of  $\alpha_k$  and small value of  $N_{eff}$  are helpful for the enhancement of the coercive field in the sintered NdFeB magnets. The question now arises of which microstructural parameters play the leading role in the sample with respect to an enhancement of the coercivity. A quantitatively calculation for the samples is favorable for understanding this question. The enhancement of the coercivity due to the increase of  $\alpha_k$  is  $\alpha_\phi H_N(\alpha_k^* - \alpha_k) = 0.84 \text{ MA}\cdot\text{m}^{-1}$ , and the enhancement of

the coercivity due to the increase of the  $N_{eff}$  is  $M_s((-N_{eff}^*) - (-N_{eff})) = -0.15 \text{ MA}\cdot\text{m}^{-1}$  [16]. Here, microstructural parameters  $\alpha_k^*$  and  $N_{eff}^*$  represents the case of Dy addition. The large difference in the value of  $0.84 \text{ MA}\cdot\text{m}^{-1}$  and  $-0.15 \text{ MA}\cdot\text{m}^{-1}$  indicates that the enhancement of the coercivity of the Dy-doped magnet is mainly due to the increase of the parameter  $\alpha_k$ .

## 4. Conclusion

High coercivity sintered Dy-doped NdFeB magnets were prepared by HD method. Dy addition results in a significant reduce of pole density factor of (004), (006) and (008) crystal faces of the sintered (Nd,Dy)FeB magnets estimated by Horta formula. The coercivity  $H_{cj}$  increases from  $2038 \text{ kA}\cdot\text{m}^{-1}$  up to  $2288 \text{ kA}\cdot\text{m}^{-1}$  as a result of 0.5 at. % Dy doping. The  $H_{cj}(T)/M_s(T)$  versus  $H_N^{\min}/M_s(T)$  (Kronmüller-plot) behavior shows that the nucleation is the dominant mechanism for the magnetization reversal in these two kinds of magnets, and two microstructural parameters of  $\alpha_k$  and  $N_{eff}$  are obtained. The Kronmüller-Plot tells us that an increase of the  $\alpha_k$  is responsible for the increase of the coercivity .

## Acknowledgements

This work was supported by Project of Zhejiang Province Innovative Research Team (no. 2010R50016), Provincial Major Science and Technology Project (no. 2009C21010), the Provincial Natural Science Foundation (nos. Z4090462 and Y6100640), the Science and Technology Project of Jiangsu Province (no. BE2011114), the National Science Foundation of China (no. 51001092) and the National Public Interest Research Special (no. 201210107).

## References

- [1] I. Wnuk and J. J. Wyslocki, *J. Mater. Processing Tech.* **175**, 433 (2006).
- [2] D. Goll, M. Seeger, and H. Kronmüller, *J. Magn. Mater.* **185**, 49 (1998).
- [3] H. Kanekiyo, M. Uehara, and S. Hirose, *Mater. Sci. Eng. A.* **A181/A182**, 868 (1994).
- [4] N. J. Harrison, H. A. Davies, and I. Todd, *J. Appl. Phys.* **99**, 08B504 (2006).
- [5] P. L. Wu, X. H. Li, W. Li, H. Y. Sun, Y. Chen, and X. Y. Zhang, *Mater. Lett.* **62**, 309 (2008).
- [6] M. X. Pan, P. Y. Zhang, X. J. Li, H. L. Ge, Q. Wu, Z. W. Jiao, and T. T. Liu, *J. Rare. Earth.* **28**, 399 (2010).
- [7] X. Fang, Y. Shi, and D. C. Jiles, *IEEE Trans. Magn.* **34**, 1291 (1998).

- [8] S. G. Kim, M. J. Kim, K. S. Ryu, Y. B. Kim, C. S. Kim, and T. K. Kim, *IEEE Trans. Magn.* **36**, 3316 (1999).
- [9] Z. W. Liu and H. A. Davies, *J. Magn. Magn. Mater.* **290**, 1230 (2005).
- [10] J. Z. Han, S. Q. Liu, C. S. Wang, H. Y. Chen, H. L. Du, and Y. C. Yang, *J. Magn. Magn. Mater.* **321**, 1331 (2009).
- [11] S. Sugimoto, H. Murai, N. Koike, H. Nakamura, D. Book, N. Tezuka, T. Kagotani, M. Okada, M. Homma, and Inomata, *J. Magn. Magn. Mater.* **239**, 444 (2002).
- [12] J. Bauer, M. Seeger, A. Zern, and H. Kronmüller, *J. Appl. Phys.* **80**, 1667 (1996).
- [13] P. Y. Zhang, R. Hiergeist, M. Albrecht, K. F. Braun, S. Sievers, J. Lüdke, and H. L. Ge, *J. Appl. Phys.* **106**, 073904 (2009).
- [14] H. Kronmüller, *Phys. Stat. Sol.* **144**, 385 (1987).
- [15] E. C. Stoner and E. P. Wohlfarth, *Phil. Trans. Roy. Soc.* **240**, 599 (1948).
- [16] X. C. Kou and H. Kronmüller, *J. Phys. C.* **6**, 6691 (1994).