Influence of additional nanoparticles on coercivity of sintered Nd–Fe–B magnets

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Abstract
In this work, we investigated the influence of concentration of the additional nanoparticles of Dy₄₀Nd₃₀Al₃₀ and Nd₃₀Al₃₀ on the coercivity of the sintered Nd₁₆.₅Fe₇₇B₆.₅ magnets. Composition and concentration of the additional compounds clearly influence magnetic properties of the magnets. The coercivity \( H_C \) increases linearly from 8 kOe to 13 kOe with increasing the weight fraction of the Dy₄₀Nd₃₀Al₃₀ nanoparticles from 0 to 5%. Meanwhile, the \( H_C \) of the Nd₃₀Al₃₀ added magnets reaches a maximal value of 10 kOe at the optimum addition of 3 wt%. The quite high maximum energy products, \( (BH)_{max} \) > 30 MGOe, were also obtained for the magnets added with the nanoparticles.

Keywords: sintered Nd–Fe–B magnet, high coercivity, maximum energy product, nanoparticles
Classification numbers: 2.01, 4.02, 5.02

1. Introduction

The further enhancement of magnetic properties and optimization of fabrication technology of anisotropic sintered Nd–Fe–B magnets are still concerned to study because this kind of magnets is more and more applied in practice, especially for generators and vehicle motors [1, 2]. However, the temperature of the sintered Nd–Fe–B magnets in the motors and generators is high (~ 200 °C) during operating time [3]. When increasing temperature, the coercivity of the magnets is decreased rapidly due to the thermal demagnetization, leading to the reduction of efficiency in the high-temperature environments. In order to enhance the \( H_C \) of the Nd–Fe–B magnets to meet the application requirements in these devices, Dy is usually replaced partially for Nd [4–6]. However, Dy is expensive and scarce. Therefore, a number of scientists have been investigating to improve the quality of the sintered Nd–Fe–B magnets without using or using a small amount of the heavy rare earth element. Previous works have indicated that the coercivity of this type of Nd–Fe–B magnets can be enhanced by addition of some elements other than the main components of Nd, Fe and B such as Al, Cu, Co... or by improving technology [7–10]. Especially, the addition of non-ferromagnetic compounds to grain boundary not only enhances the coercivity but also reduces amount of heavy rare earth [11–16]. Each additional compound contains the elements which differently affect to the magnetic properties of the magnets. With Dy-addition, the coercivity is significantly
increased because the anisotropy field $H_A$ of Dy$_2$Fe$_{14}$B of 278 kOe at room temperature is much higher than that of Nd$_2$Fe$_{14}$B, $H_A = 75$ kOe. In addition, the adding Dy also avoids oxygenation for the magnets. However, antiferromagnetic coupling with Fe leads to reduction of remanence $B_r$ and the maximum energy product ($BH_{max}$). It is known that the coercivity of the sintered Nd–Fe–B magnets is sensitive to the microstructure. The addition of Al-containing compounds can improve microstructure such as smoothness of grain boundaries, uniformity of the particles of the magnets [17–19]. Pandian et al reported that the addition of Al of 1~2 wt% decreases remanence $B_r$ of 5% but increases the coercivity $H_C$ of about 20%.

Our previous study reported that, by adding 2 wt% of Dy$_{40}$Nd$_{30}$Al$_{30}$ nanoparticles to grain boundaries, the coercivity of the magnets could be considerably improved [20]. In this work, we investigated the influence of weight fractions of the additional nanoparticles of Dy$_{40}$Nd$_{30}$Al$_{30}$ and Nd$_{30}$Al$_{30}$ on the coercivity of the sintered Nd–Fe–B magnets.

2. Experimental

The pre-alloys of Nd$_{18.5}$Fe$_{77}$B$_{6.5}$ were prepared from Nd, Fe and FeB by induction melting under Ar gas to avoid oxidation. The obtained ingots were pulverized for 8 h to obtain powder with grain size of 3~5 μm by ball milling method in industrial white gasoline. The addition alloys Dy$_{40}$Nd$_{30}$Al$_{30}$ and Nd$_{40}$Al$_{30}$ were prepared by arc-melting furnace under argon atmosphere. After that the resulted alloys were pulverized by high energy ball milling method with milling time of 4 h to obtain nanoparticles with average size of about 50 nm. The solvent/material and ball/powder ratios are 1/1 and 4/1, respectively. The additional nanoparticles with various weight fractions from 1 to 5% were mixed into the Nd–Fe–B powder thoroughly. The mixed powder was pressed under a pressure of 15 MPa in an orientated magnetic field of about 20 kOe. The pressed magnets were sintered at 1080 °C for 1 h. A two-stage heat treatment process was chosen and carried out using a vacuum furnace. At the first stage, the magnets were heat-treated at 820 °C for 1 h and then rapidly quenched to room temperature by argon atmosphere. The second stage, the magnets were heat-treated at 540 °C for 1 h and rapidly quenched by argon atmosphere. For both the stages, the heating and quenching rates were 30 °C min$^{-1}$ and 50 °C min$^{-1}$, respectively. The structure of the samples was thoroughly analyzed by using scanning electron microscope (SEM). The specimens of cylinders with 3 mm diameter and 3 mm height were cut to investigate magnetic properties on a pulsed high field magnetometer. In order to determine the maximum energy product ($BH_{max}$) of the magnets, a demagnetization factor was estimated through a semi-experimental data sheet.

3. Results and discussion

Figure 1 shows the SEM images of powder of the additional compounds with milling time of 4 h. We can see that the particles of the samples are relatively uniform with the average size smaller than 50 nm. However, for both the samples still contains region which is difficult to observe individual grains by their coalescence. With high surface energy, the first melting of nanoparticles during sintering process makes homogeneous distribution of the intergranular phase, leading to a decrease of exchange interaction of the Nd$_2$Fe$_{14}$B grains [21]. This is one of the reasons for the enhancement of coercivity $H_C$ and maximum energy product ($BH_{max}$). Nano-scale sized particles are desired to mix with the Nd–Fe–B micropowder.

Figures 2 and 3 show the hysteresis loops of the magnets added with various weight fractions of Dy$_{40}$Nd$_{30}$Al$_{30}$ and Nd$_{40}$Al$_{30}$ nanoparticles before and after heat treatment. We can realize that, the coercivity of the magnets depends on both the nanoparticle addition and heat treatment process. The influence of addition of Dy$_{40}$Nd$_{30}$Al$_{30}$ nanoparticles is stronger than that of Nd$_{30}$Al$_{30}$ ones. With the Nd$_{30}$Al$_{30}$ added magnets, the change of the coercivity on large concentration of nanoparticles is not considerably. After heat treatment the coercivity was significantly enhanced. This probably is due to the improvement of microstructure of the magnets after heat treatment such as controlling particles size, creating the suitable grain boundary phase… However, the squareness of the hysteresis loops of the magnets is slightly decreased. A little dip was observed in the second quadrant demagnetization curves of the annealed magnets. This can be explained by the wide distribution of the grain size after heat treatment. At the same time, the addition of elements can change the structure and distribution of phases, leading to the inhomogeneity of demagnetization field. On the other hand, heterogeneous grain boundaries can lead to the formation of the soft magnetic $\alpha$-Fe phase which plays a role as nucleation centre of reversal domains to cause magnetization of the magnets at lower external magnetic field [22].

Magnetic characteristic curves of the heat-treated magnets added with 5 wt% of Dy$_{40}$Nd$_{30}$Al$_{30}$ and 3 wt% of Nd$_{30}$Al$_{30}$ are presented in figure 4. The obtained results show that, the coercivity of the magnets added with Dy$_{40}$Nd$_{30}$Al$_{30}$ is higher than that of the one added with Nd$_{30}$Al$_{30}$. However, the squareness of hysteresis loop of the former is worse than that of the latter one, leading to the decrease of maximum energy product ($BH_{max}$) which has been obtained to be 36 MGOe and 37 MGOe, respectively. In general, the enhancement both the coercivity $H_C$ and the maximum energy product ($BH_{max}$) of the magnets is difficult. Because the magnetic properties of the magnets are not only dependent on Nd$_2$Fe$_{14}$B phase, but also on the microstructure. Optimization of microstructure depends on parameters of technological conditions such as particle size, sintering temperature, sintering time, annealing time, annealing temperature… Controlling of manufacture technology to create the sintered magnets with suitable magnetic properties for practical applications is required.

Figure 5 shows the dependences of the coercivity $H_C$ of the magnets on various weight fractions of nanoparticles of Dy$_{40}$Nd$_{30}$Al$_{30}$ and Nd$_{30}$Al$_{30}$ before and after heat treatment. We can see that $H_C$ depends almost linearly on the concentration of Dy$_{40}$Nd$_{30}$Al$_{30}$ (figure 5(a)). Its value
Figure 1. SEM images of the Dy$_{40}$Nd$_{30}$Al$_{30}$ (a) and Nd$_{40}$Al$_{30}$ (b) powder with milling time of 4 h.

Figure 2. Hysteresis loops of the magnets added with various fractions of nanoparticles of Dy$_{40}$Nd$_{30}$Al$_{30}$ before (a) and after (b) heat treatment.

Figure 3. Hysteresis loops of the magnets added with various fractions of nanoparticles of Nd$_{30}$Al$_{30}$ before (a) and after (b) heat treatment.

Figure 4. Magnetic characteristic curves of the heat-treated magnets added with 5 wt% of Dy$_{40}$Nd$_{30}$Al$_{30}$ (a) and 3 wt% Nd$_{30}$Al$_{30}$ (b) nanoparticles.
increases from 5.3 to 10kOe for the as-sintered magnets and from 8 to 13 kOe for the heat-treated magnets when weight fractions of Dy40Nd30Al30 nanoparticles increases from 0 to 5%. This is agreed with the result reported by Liu et al [6]. The coercivity enhancement of the magnets added with Dy-containing compounds is due to Dy diffusion from the grain boundaries to the 2:1 4:1 grain during sintering and heat treatment process, leading to the formation of the (Nd, Dy)2Fe14B shell. Because $H_A$ of Dy2Fe14B is higher than that of Nd2Fe14B, the formation (Nd, Dy)2Fe14B shell might make magnetic anisotropy of the outer layer higher than that of the interior. As a result, the formation and propagation of a reverse domain would be inhibited more than in the normal grains. When the reverse nucleations are inhibited at the surface of the grains, an external magnetic field must be large enough for the formation and growth of them, meaning that the magnets have high coercivity. However, the effect of the coercivity enhancement for the magnets by adding Dy40Nd30Al30 nanoparticles in this work is weaker than that obtained in our previous investigation [20]. This probably is due to the change of milling solvent, whose contaminations might affect to the quality of the additional nanoparticles.

As for the magnets added with Nd30Al30 nanoparticles, their coercivity slightly increases from 5.3 to 7.3 kOe before heat treatment, and from 8 to 10 kOe after heat treatment as weight fraction of the additional compound increases from 0 to 3% (figure 5(b)). After that, the $H_C$ decreases when the additional fraction is further increased. Thus, the optimal additional weight fraction of Nd30Al30 nanoparticles is 3%. The increase of the coercivity is good agreement with the result reported by Mottram et al [19]. The formation of disadvantage phases at grain boundaries is reason for reduction of the coercivity with additional fractions of 4%. On the other hand, the optimal sintering temperature might be changed by large fraction of the additional compound, which has melting temperature far from that of the Nd–Fe–B phase, leading to the undesired microstructure for the magnets.

The dependence of maximum energy product $(BH)_{\text{max}}$ of the heat-treated magnets on various additional fractions of the Dy40Nd30Al30 and Nd30Al30 nanoparticles is shown in figure 6. We can see that, the $(BH)_{\text{max}}$ decreases with increasing the fraction of both the additional compounds, agreeing with the results reported in [12]. The reduction of the $(BH)_{\text{max}}$ of the added magnets is due to a decrease of saturation magnetization by additional of non-ferromagnetic nanoparticles. Although the $(BH)_{\text{max}}$ is reduced but its value is still high enough ($> 30$ MOe) for practical application. Especially, the enhancement of the coercivity is necessary for electric generators and motors. On the other hand, the less use or unused of the heavy rare earth of Dy is important for lowering the cost of the magnets.
4. Conclusion

The influence of concentration of the additional nanoparticles of Dy$_{40}$Nd$_{30}$Al$_{30}$ and Nd$_{30}$Al$_{30}$ on the coercivity $H_C$ of the sintered Nd$_{16.5}$Fe$_{77}$B$_{6.5}$ magnets has been investigated. The $H_C$ is considerably improved by adding nanoparticles to the grain boundaries of magnets. The effect of the Dy$_{40}$Nd$_{30}$Al$_{30}$ nanoparticles on the coercivity enhancement for the magnets is stronger than that of the Nd$_{30}$Al$_{30}$ ones. While the $H_C$ reaches a maximal value of 10 kOe at 3 wt% of Nd$_{30}$Al$_{30}$ addition, it increases linearly from 8 kOe to 13 kOe with increasing the weight fraction of the Dy$_{40}$Nd$_{30}$Al$_{30}$ nanoparticles from 0 to 5%. The $(BH)_{max}$ of the magnets is still retained high enough (> 30 MOe). The obtained hard magnetic parameters of the magnets can be applied in practice.

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References

[1] Matsuura Y 2006 J. Magn. Magn. Mater. 303 344
[2] Coey J M D 1996 Rare–Earth Iron Permanent Magnets (Oxford: Oxford Science Publications)
[3] Hono K and Sepehri-Amin H 2012 Scr. Mater. 67 530
[4] Yu N J, Pan M X, Zhang P Y and Ge H L 2013 J. Magn. 18 235
[5] Pandian S, Chandrasekaran V, Markandeyulu G, Iyer K J L and Rao Rama K V S 2004 J. Alloys Compd. 364 295
[6] Liu Q, Zhang L, Xu F, Dong X, Wu J and Komuro M 2010 Japan. J. Appl. Phys. 49 093001
[7] Sepehri-Amin H, Une Y, Okhubo T, Hono K and Sagawa M 2011 Scr. Mater. 65 396
[8] Kim T H, Lee S R, Kim J W, Kim Y D, Kim H J, Lee M W and Jang T S 2014 J. Appl. Phys. 115 17A770
[9] Kobayashi K, Urushibata K, Une Y and Sagawa M 2013 J. Appl. Phys. 113 163910
[10] Liu X, Ma T, Wang X and Yan M 2015 J. Magn. Magn. Mater. 382 26
[11] Park S E, Kim T H, Lee S R, Namkung S and Jang T S 2012 J. Appl. Phys. 111 07A707
[12] Liang L, Ma T, Zhang P, Jin J and Yan M 2014 J. Magn. Magn. Mater. 355 131
[13] Lee M W, Dhakal D R, Kim T H, Lee S R, Kim H J and Jang T S 2015 Arch. Metall. Mater. 60 1407
[14] Liang L, Ma T, Zhang P, Jin J and Yan M 2014 J. Magn. Magn. Mater. 384 133
[15] Zhang Y, Ma T, Liu X, Liu P, Jin J, Zou J and Yan M 2016 J. Magn. Magn. Mater. 399 159
[16] Lee S, Kwon J, Cha H R, Kim K M, Kwon H W, Lee J and Lee D 2016 Met. Mater. Int. 22 340
[17] Pandian S, Chandrasekaran V, Markandeyulu G, Iyer K J L and Rao Rama K V S 2002 J. Appl. Phys. 92 6082
[18] Ni J J, Ma T Y, Wu Y R and Yan M 2010 J. Magn. Magn. Mater. 322 3710
[19] Mottram R S, Williams A J and Harris I R 2000 J. Magn. Magn. Mater. 222 305
[20] Dan N H, Thanh P T, Yen N H and Hung L T 2014 IEEE Trans. Magn. 50 2102204
[21] Cui X G, Yan M, Ma T Y and Yu L Q 2008 Physica B 403 4182
[22] Muller K H, Handstein A, Eckert D and Schneider J 1987 Phys. Status Solidi 99 K61