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Strategic coating of NdFeB magnets with Dy to improve the coercivity of permanent magnets

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Abstract. We present a method, supported by theoretical analysis, for optimizing the usage of the critical rare earth element dysprosium in $Nd_2Fe_{14}B$ (NdFeB)-based permanent magnets. In this method, we use Dy selectively in locations such as magnet edges and faces, where demagnetization factors are largest, rather than uniformly throughout the bulk sample. A 200 nm thick Dy film was sputtered onto a commercial N-38, NdFeB magnets with a thickness of 3 mm and post-annealed at temperatures from 600-700°C. Magnets displayed enhanced coercivities after post-annealing and as much as a 5 % increase in the energy product, while requiring a total Dy content of 0.06 wt. % - a small fraction of that used in the commercial grade Dy-NdFeB magnets. By assuming all Dy diffused into NdFeB magnets, the improvement in energy product corresponds to a saving of over 1% Dy (critical element). Magnets manufactured using this technique will therefore be higher performing which would potentially broaden the application space of these magnets in the traction motors of hybrid and pure electric vehicles, and wind generators.

Keywords: NdFeB magnets; sputter deposition; selective Dy diffusion; magnetic properties; theoretical analysis

1. Introduction

Sintered ($Nd_2Fe_{14}B$) Nd-Fe-B magnets are commonly used for various magnetic applications including motors, generators, medical instruments, hard disk drives, and measuring devices because of their high magnetic performance (Sugimoto 2011). While Nd-Fe-B magnets have excellent hard magnetic properties for applications at or below 120 ˚C, their performance quickly degrades at higher temperatures (Sagawa *et al*. 1984, Croat *et al*. 1984). In order to increase the high temperature coercivity of sintered $Nd_2Fe_{14}B$, dysprosium (Dy) can be substituted for Nd in the magnets (Tenaud *et al*. 1984). This enhancement occurs because $(Nd_{1-x}Dy_x)_2Fe_{14}B$ has a larger magnetic anisotropy than pure $Nd_2Fe_{14}B$. Previous studies show that the formation of a core-shell microstructure which is formed by the segregation of Dy along the grain boundaries by grain boundary diffusion is the driving force for this enhancement in coercivity (Xu *et al*. 2011, Doser *et*

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al. 1988, Kianvash *et al*. 1999). However, the main disadvantage of this process is the supply risk and consequential high price of heavy rare earth (HRE) elements (Hirosawa *et al*. 1986, Boltich *et al*. 1985). Rapidly increasing demand for permanent magnets coupled with supply restrictions and the potential for the ever rising costs of critical elements makes a strong economic case for developing alternative techniques that would use less Dy without compromising the magnetic performance. Global production of Dy is about 1700 Mt (metric tonnes) annually (US DOE, critical materials strategy 2011). For high temperature applications, Dy may comprise as much as 5 wt. % in order to improve the high temperature coercivity, though at a significant penalty to the magnetization. It would be helpful to achieve this higher coercivity with less Dy; both to minimize use of the costly rare-earth element and also to negate the performance loss (i.e. BH_{max}) associated with the magnetization penalty. Researchers attempted to reduce the use of Dy by facilitating the formation of a $(Nd,Dy)_2Fe_{14}B$ hardening shell surrounding the 2:14:1 phase grains instead of direct alloying (Nakamura *et al*. 2011, Komuro *et al*. 2010). The question we are exploring in this study is the following: Can one *selectively* use Dy, at optimal sample locations, to improve coercivity? It is well known that demagnetization effects in a given sample are strongly dependent on the shape of the sample. For example, the reverse domain nucleation that leads to demagnetization and thereby the destruction of magnetic performance frequently begins at the corners of the magnet (Kronmuller *et al*. 1987, Buschow 2005), so that a selective application of Dy might begin in such areas. A key question is: *where are sample demagnetization factors largest?* To answer this question we must first specify which demagnetization factors are relevant. In this study, we investigate the optimum areas for Dy coating that might yield the same or better energy performance in NdFeB magnets.

2. Experimental procedure

We compare seven magnet samples, with dimensions of 1mm×1mm×3mm, sintered commercial grade N-38, Nd-Fe-B magnets in this study. Prior to sputtering treatment, no additional treatment was done on any of the magnets such as adding a protective layer or grinding the pieces. The samples that we studied would be described as below, along with their short hand notation that was used throughout this study: as received magnet which underwent no annealing treatment, and was used as a baseline in this study (as-received); 2 magnets which were sputtered with a Dy film thickness of 200 nm on the whole surface of the sample using an rf-magnetron sputtering unit (AJA International Inc., N. Scituate, MA, USA), followed by a heat treatment at 600-700 °C for 4 hours to promote Dy diffusion in sealed quartz ampoules (600 and 700 °C surface). Here, the whole surface implies the usage of no carbon tape such that the whole surface of the magnet specimen in Fig. 1 is exposed to the Dy treatment; 2 magnets which were also sputtered and heat treated at 600-700 °C for 4 hours, except for these samples, we used carbon tape to mask the central portion of the surface so that the Dy coating is only performed on the edges as schematically shown in Fig. 1 (600 and 700 °C edge). Lastly, 2 magnets which were heat treated at 600-700 °C for 4 hours without the Dy coating to see the influence of annealing treatment only (600 and 700 °C not-coated). In this study, 600 °C surface, 600 °C edge, 600 °C not-coated magnet samples all underwent the same heat treatment (same heating and cooling history) to observe only the influence of Dy on the magnetic properties. Magnetization was measured in a SQUID magnetometer with the magnetic field applied parallel to the magnetization direction.

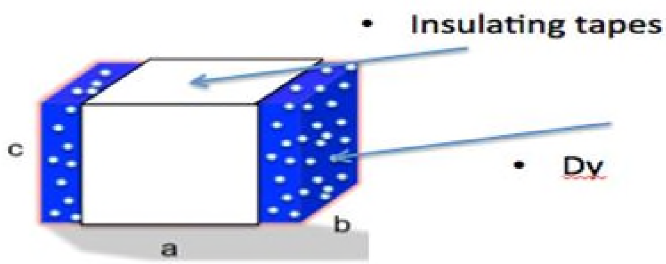

Fig. 1 Schematic of the N-38 Dy-free Neo magnet surfaces where Dy was sputter-coated onto the edges (other areas were masked).

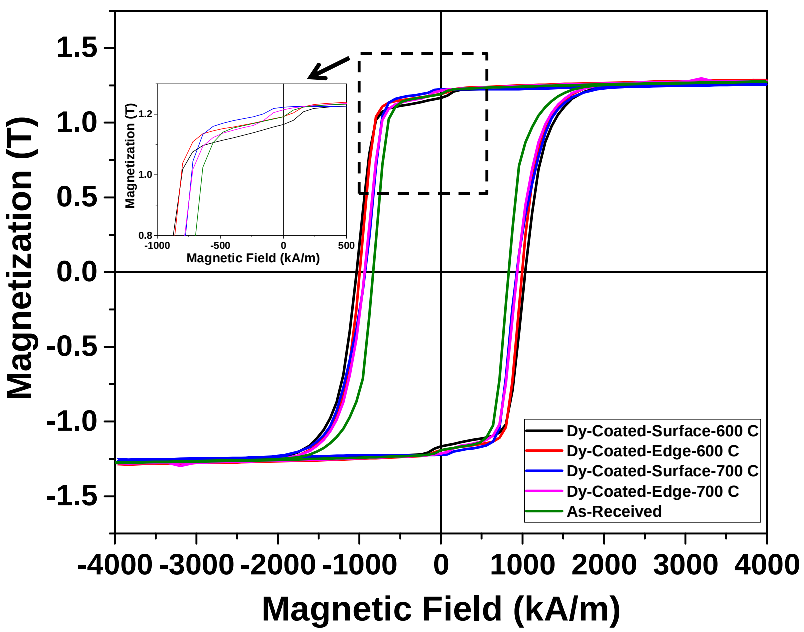

Fig. 2 Hysteresis loops after sputter deposition of Dy films onto both edges and whole surface of the magnet followed by post-annealing at 600 and 700 °C

3. Results

Based on calculation of the areas of high flux concentration on a magnet surface, the commercial magnets were coated as described in the experimental section. Fig. 2 shows the hysteresis loops for a series of samples where those coated with Dy possess an increased coercivity relative to the pristine samples. This can be readily explained by the enhanced magnetocrystalline anisotropy due to the diffusion of dysprosium (Soderznik *et al*. 2012, Tang *et al*. 2012). Also, the coercivities of the samples annealed at 600 ^{o}C are higher than those annealed at 700 °C. The energy product (shown in Fig. 3) of the sample coated only on the edges increased more than that of the whole surface treated magnet, at 600 ˚C annealing temperature. However, for the samples annealed at 700 °C , we achieved an increase of 5% in energy product for a total Dy

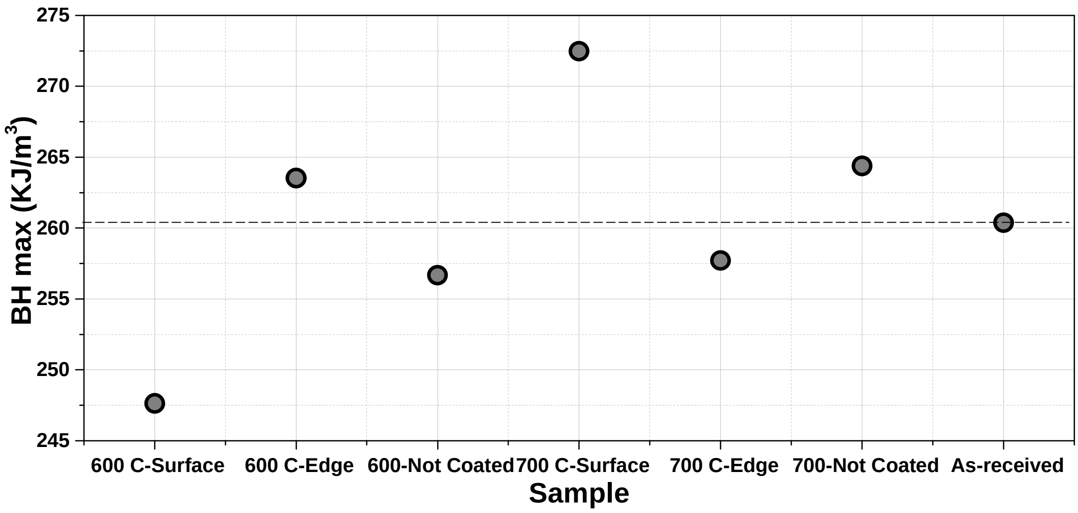

Fig. 3 Plot of energy product, BH_{max} vs. samples (after sputter deposition of Dy films onto both edges and whole surface of the magnet followed by post-annealing at 600 and 700 °C).

wt. % of 0.06. By assuming all Dy diffused into NdFeB magnets, the improvement in energy product corresponds to a saving of over 1% Dy (critical element). In other words, the performance of the magnet is superior for the one that was sputtered on the whole surface as compared with the one which was sputtered on the edges.

4. Discussion

In general, a ferromagnetic sample with magnetization **M** exposed to a uniform external magnetic field $\mathbf{H_0}$ will experience a torque (due to the demagnetization field) $\boldsymbol{\tau}$ given by

$$\boldsymbol{\tau} = \boldsymbol{M} \text{ x } \boldsymbol{H_{eff}}$$

where $\boldsymbol{H_{eff}} = \mathbf{H_0} - \mathbf{N} \bullet \mathbf{M}$. Here **N** is the spatially varying demagnetization tensor **N(r)**, whose six independent components for a parallelepiped, as we consider here, are given in explicit form in Smith *et al*. 2010. The boundary condition for this calculation is the assumption of a uniform magnetization **M** throughout the parallelepiped. Assuming both **M** and $\mathbf{H_0}$ to be parallel to the z-axis, the demagnetization torque (tending to misalign the sample magnetic moments from the z-axis, and ultimately causing moment reversal under sufficient field) will be given by

$$\boldsymbol{\tau} = (-\boldsymbol{N_{yz}M^2}, \boldsymbol{N_{xz}M^2}, \mathbf{0}).$$

Hence it is the spatial dependence of the transverse demagnetization factors $N_{yz}(\mathbf{r})$ and $N_{xz}(\mathbf{r})$ that is relevant for this problem. For specificity we now consider a parallelepiped of relative dimensions (2a,2a,a), which are comparable to the right cylinder with h=(1/3)d of the maximum-energy product shape for a hard magnet. We now consider the spatial dependence of these transverse demagnetization factors. The demagnetization factor $N_{yz}(r)$ along the surface x=a

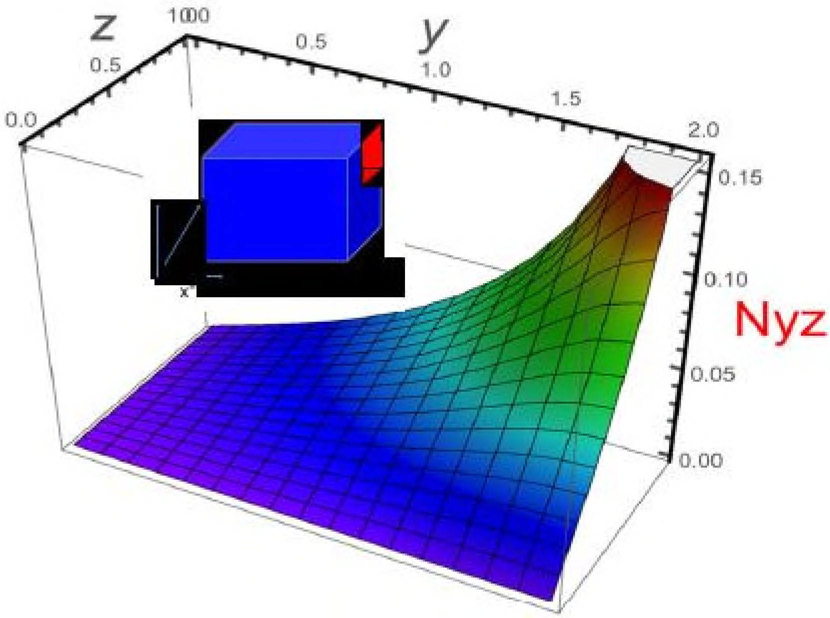

Fig. 4 The calculated demagnetization factor Nyz along the x=a (side) surface of the body indicated in the inset.

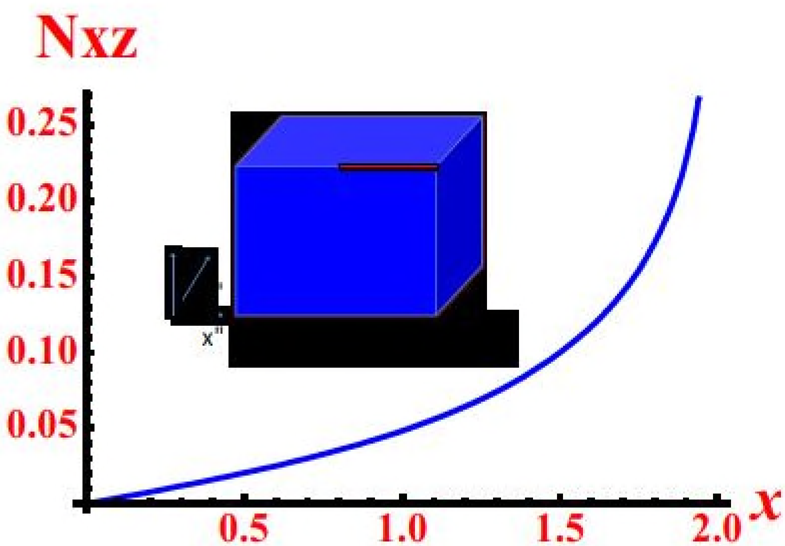

Fig. 5 The calculated demagnetization factor Nxz along the top edge of the sample. X=0 corresponds to midpoint of edge and x=2 to corner (see inset)

of the parallelepiped body is shown in Fig. 4, which we have plotted using Mathematica from Eq. A12 of Smith *et al.* 2010. Only the upper right quadrant of this area is depicted so that the face center is at lower left.

As depicted in Fig. 4 corner, the demagnetization factor is largest at the corners of the magnet, and smallest at the center of the face. This demagnetization factor is also larger on the edges than on the main surface of the body. In general, sharp features in the magnet body correspond to large demagnetization factors. This is due to the demagnetizing effects of stray magnetic fields at sharp edges. It was reported that stray fields can reduce the coercive field of Nd-Fe-B magnets by as much as 795.77 kA/m (Buschow 2005). Fig. 5 further depicts the calculated demagnetization factor N_{xz} on the top edge of the sample (z = a/2, y = a). It illustrates a demagnetization factor exceeding 0.25 at the corner and increasing rapidly on the edge up to this point. These results reconfirms that demagnetization processes are higher at the corners of the magnet.

These results demonstrate that the edges of a parallelpiped magnet experience the greatest demagnetization fields and therefore are the most beneficial locations for selective application of Dy. It is important to note that such regions comprise a small fraction of the surface area of a rectangular magnet body. In practice, this means that the surfaces in the near vicinity of the corners and edges are the locations for optimal application of Dy to reduce demagnetization. For magnets used in electrical machines such as motors and generators where they experience rotating magnetic fields along a single axis, these regions will expand along that direction. However, these results suggest that Dy can be selectively applied to portions of the surface which will provide maximal benefit.

5. Conclusions

Theoretical calculations indicate that the relevant demagnetization factors are at a maximum on the corners of a rectangular magnet. Based on this information, we used a sputtering technique to selectively coat commercial Nd-Fe-B magnets with Dy. Our results agree with what the theory predicts at 600 ˚C annealing temperature. However, it seems to deviate from the theoretical calculations at a slightly higher temperature (700˚C). We will investigate the underlying reasons for this discrepancy and also detailed microstructure analysis in our future studies.

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