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Grain boundary diffusion of different rare earth elements in Nd-Fe-B sintered magnets by experiment and FEM simulation

K. Loewe [a, *], D. Benke [a], C. Kübel [b], T. Lienig [a], K.P. Skokov [a], O. Gutfleisch [a]

[a] TU Darmstadt, Department of Material- and Geosciences, Functional Materials, Alarich-Weiß-Str. 16, 64287 Darmstadt, Germany
[b] Karlsruhe Institute of Technology, Institute of Nanotechnology, Karlsruhe Nano Micro Facility, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

In the present work, we explore the influence of a surface-bulk coercivity gradient in Nd-Fe-B magnets produced by the Grain Boundary Diffusion Process (GBDP) on the overall coercivity. In our systematic and comprehensive study we diffused four different rare earth elements (Dy, Tb, Ce and Gd) in two different kinds of commercial Nd-Fe-B magnets, one very Dy-lean and one Dy-rich. By means of cutting the magnets into thin slices we obtain lateral coercivity profiles, from which diffusion constants are extracted. We find that in both magnets Tb diffuses significantly faster than Dy. The diffusion is generally slower in the Dy-lean magnet, which is attributed to the different chemistry and a smaller grain size. Ce diffuses slightly slower than Dy and the overall coercivity decrease is similar for Ce and Gd. With scanning electron microscopy it is revealed that, contrary to the magnets diffused with the heavy rare earths, the microstructure in the magnets treated with Ce show no (Nd,Ce)-Fe-B shells in the surface regions. While not of practical importance this allows some interesting insights into the metallurgy of (Nd,Ce)-Fe-B system. High-resolution scanning transmission electron microscopy coupled with electron probe microanalysis show the nano-scale distribution of Tb around the grain boundaries located in the bulk of the magnet. Finally, a simple model for the magnetization reversal in grain boundary diffusion processed gradient Nd-Fe-B magnets was developed and implemented into a FEM software. Our calculated demagnetization curves correspond very well for the Dy and Tb samples, but deviate significantly for Ce and Gd.

1. Introduction

A common method to increase the temperature stability and coercivity of Nd-Fe-B permanent magnets is the addition of heavy rare earth (HRE) elements like Dy or Tb to the base alloy [1–3]. The HRE atoms are partially substituting the Nd atoms in the Nd-Fe-B lattice and lead to an enhancement of the anisotropy field H_a. Unfortunately, this also leads to a decrease in saturation magnetization M_S as well as of the energy product $(BH)_{max}$ [4]. Other drawbacks are the price volatility of HRE and their relatively high supply risk because of the monopolistic market situation with China being the only global supplier of significance [5–7]. A materials science approach to overcome these problems is the so-called grain boundary diffusion process [8]. The working principle is to let heavy rare earth (HRE) elements diffuse along the grain boundaries from the surface into the volume of the magnet during a heat treatment. As a result, the HRE are deposited selectively around the grain boundaries, which magnetically hardens the whole magnet. In addition to HRE elements [9,10], the GBDP in sintered magnets has been investigated for many other systems, e.g. HRE-fluorides [11] and eutectic compositions [12]. Also, the diffusion in nanocrystalline hot-deformed Nd-Fe-B magnets has gained a lot of attention in recent years [13–15].

Macroscopically and microscopically, the diffusion process creates an inhomogeneous distribution of HRE, and therefore coercivity, within the magnet, with high values at the surface and lower values at the center [16]. The diffusion depth is only several mm, which geometrically limits the maximum size a diffusion treated magnet can have if a relatively homogeneous coercivity is desired. The question arises, whether it is necessary to magnetically harden the whole magnet or if for some applications a surface hardening is sufficient. To answer the question we diffuse four different rare

* Corresponding author.
E-mail address: loewe@fm.tu-darmstadt.de (K. Loewe).

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earth (RE) elements into Nd-Fe-B: the “traditional” HRE Dy and Tb used in industry, as well as Ce and Gd.

Gd-rich grain boundaries are of interest because they relate to the concept of increasing coercivity by adding a ferrimagnetically exchange-coupled surface layer to the Nd-Fe-B grains. This *superferrimagnetism* concept was suggested by Akdogan et al., in 2014 [17]. In their thin film approach a GdFe layer was deposited on NdFeB, which leads to an antiferrimagnetic (i.e. antiparallel) coupling of the magnetic moment of Gd to the moments of Fe and Nd in the $Nd_2Fe_{14}B$ phase. Under an applied field that tends to reverse the magnetization of the grain, the surface layer, with a magnetization parallel to the applied field, works against reversal and impedes the nucleation of reverse domains.

As a result of different valance states of Nd in $Nd_2Fe_{14}B$ and Ce in $Ce_2Fe_{14}B$ (3 vs. 3.44 [18]), their magnetism is distinct. At room temperature, the saturation magnetization of $Ce_2Fe_{14}B$ is 26% lower than of $Nd_2Fe_{14}B$, and the anisotropy field is 3 times lower [4]. Consequently, Ce substitution leads to deterioration of the intrinsic properties of the $Nd_2Fe_{14}B$ phase and grain boundaries enriched by Ce should induce an adverse effect on coercivity. A quantitative analysis of this effect in our experiments can provide a comprehensive view on the GBDP.

After the diffusion we determine lateral coercivity profiles of the produced gradient magnets. To quantify the respective diffusion speeds, diffusion constants are determined from fitted data. This helps to evaluate necessary heat treatment times to achieve wanted diffusion depths. The findings are correlated with FEM simulations, which give a guideline for the necessary diffusion parameters to tailor specific demagnetization curves.

Two Nd-Fe-B sample materials were chosen: one with Dy addition for high temperature applications and for comparison one nearly Dy-free. To our knowledge, so far only a single study exists, which also investigates the diffusion of Dy in Nd-Fe-B magnets with high Dy contents [19].

2. Experimental

Commercial Dy containing sintered magnets with a composition of $Nd_{13.3}Dy_{1.1}Fe_{bal}B_{6.1}Co_{1.0}Cu_{0.1}$(at.%) or $Nd_{29.0}Dy_{2.6}Fe_{bal}B_{1.0}Co_{1.0}Cu_{0.1}$(wt.%), a typical remanent polarization of 1.3 T, a coercivity of 1.8 T and a size of 8 mm (length) x 5 mm (width) x 5 mm (depth) were used as sample material. For comparison a nearly Dy-free commercial magnet with 0.3 at.% Dy and a typical remanent polarization of ~1.42 T and a coercivity of 1.2 T with the same dimensions was used.

The source material for the diffusion treatment are rare earth (RE) thin film foils (Alfa Aesar) with 99,9% purity and a thickness of 25 μm, which were attached to the magnets. The diffusion occurred along the length side, i.e. always with an 8 mm distance. The samples were protected with Molybdenum foil and the diffusion heat treatment was conducted in protective Argon atmosphere. It consisted of a step at 900 °C with varied length and a low temperature annealing step at 500 °C for 2 h. The magnets were cut into slices of about 500 μm thickness using a wire saw. Magnetic measurements were performed with a high field hysteresis meter HyMPulse (Metis Instruments) in open circuit conditions. The microstructure observations were carried out with an XL30 FEG (Philips) electron microscope equipped with an Si(Li)-EDX detector. The TEM measurements were conducted on a Jeol JEM 2100F (scanning) transmission electron microscope (STEM) equipped with an Oxford X-max80 EDX detector. The simulation of the magnetization reversal in the gradient magnets was done with the commercial FEM-software Comsol Multiphysics.

3. Results and discussion

3.1. Magnetic properties

Fig. 1 shows the demagnetization curves of the Dy-rich sample magnets, which were diffusion treated with Dy, Tb, Ce and Gd, respectively. These samples will be labeled “Dy”, “Tb”, ”Ce” or ”Gd” magnets in the following. While the former two rare earths (RE) lead to an increase in coercivity, the latter two decrease it. The striped bars mark the coercivity and magnetization range of 10 reference samples, which underwent the same heat treatment as the respective samples (900 °C, 1.5–10 h and 500 °C, 2 h) but without diffusing RE. Depending on the heat treatment time the coercivity difference $\mu_0{*}\Delta H_c(Dy)$ after the diffusion ranges from 0.15 T to 0.35 T (Fig. 2). $\mu_0{*}\Delta H_c(Tb)$ is almost twice as large with 0.2 T–0.6 T. The diffusion treatment with Ce leads to a decrease of $\mu_0{*}\Delta H_c(Ce)$ from −0.1 T to −0.15 T, which is similar to the Gd values. The coercivity changes follow the same trend as the literature values for the anisotropy fields $\mu_0{*}H_a$ of the $RE_2Fe_{14}B$ compounds. At room temperature these values for RE = Tb, Dy, Nd, Ce and Gd are 22 T, 15 T, 7.3 T, 2.6 T and 2.4 T, respectively [4]. The magnetization for all samples is almost the same before and after the annealing.

Selected samples from Fig. 1 have been cut into slices perpendicular to the diffusion direction. The coercivity of the slices has been measured and lateral coercivity distributions have been

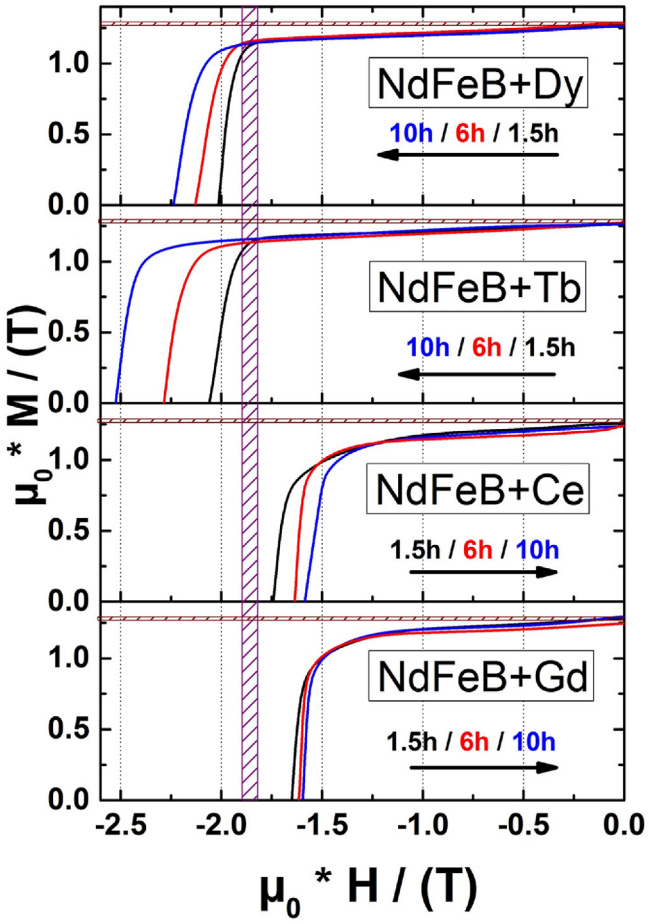

Fig. 1. Demagnetization curves of the Dy-rich Nd-Fe-B magnets after diffusion for different annealing times at 900 °C. The shaded bars mark the coercivity and remanence range for 10 reference samples heat treated without diffusing RE.