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The dual trend of diffusion of heavy rare earth elements during the grain boundary diffusion process for sintered Nd-Fe-B magnets

Binghui Wu [a,b], Xuefeng Ding [a,c], Qingke Zhang [a], Lijing Yang [a], Bizhang Zheng [a,d], Fangqin Hu [a], Zhenlun Song [a,*]

[a] CAS Key Laboratory of Magnetic Materials and Devices, Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[b] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China
[c] Baotou Hidyree Technology Co., Ltd., Baotou 014030, China
[d] Jing Ci Material Science Co., Ltd., Beijing 101300, China

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ABSTRACT

Diffusion of heavy rare earth elements (HREEs, Tb and Dy) after being coated on sintered Nd-Fe-B magnets by direct current magnetron sputtering was investigated. The results reveal that gain of the coercivity shows a higher efficiency of HREE consumption compared with other coating methods. The HREE diffuses along the grain boundary phase (GBP) deep into the magnet, an HREE-rich shell forms at the superficial layer of the diffused $Nd_2Fe_{14}B$ grains, and the HREE in the magnets shows a dual-trend distribution. The diffusion of HREE includes a fast diffusion in the GBP and a slow diffusion in the grain phase (GP).

To increase the coercivity of the sintered Nd-Fe-B magnets, a common method is the addition of heavy rare earth elements (HREEs) [1]. The anisotropy field (H_A) of the $HREE_2Fe_{14}B$ compounds is much higher than that of the $Nd_2Fe_{14}B$. At room temperature, the H_A of $Tb_2Fe_{14}B$ and $Dy_2Fe_{14}B$ are 22 T and 15 T, respectively [2]. However, the saturation magnetization (M_S) and the energy product $(BH)_{max}$ of the sintered Nd-Fe-B magnet decreases with increasing content of HREEs [3], and the addition of HREEs will also improve the production costs. A grain boundary diffusion process (GBDP) has been proposed to solve this problem, which has achieved remarkable success, as the minimum content of HREE is precisely used to drastically enhance the coercivity. As a result of the GBDP, a core-shell-type microstructure with HREE-rich regions surrounding the grain is formed, which magnetically hardens the whole magnet [4,5]. The shell structure is resulted by diffusion of Tb or Dy into the $Nd_2Fe_{14}B$ and replaces the Nd to form a $(Nd_{1-x}, HREE_x)_2Fe_{14}B$ shell [2,4,5]. The GBDP has been investigated with oxide, fluoride, hydride, metallic layer and so forth as the HREE sources [1]. A variety of techniques could be used for coating of the magnet, such as sputtering of a metallic HREE [6–8], painting or dipping deposition of HREE compounds [5,9–14], electrophoretic deposition of DyF_3 or TbF_3 [15–21], and evaporation of HREEs [17,22–24]. In this study, a direct current magnetron sputtering method is applied to coat the Nd-Fe-B magnets with HREEs to get a high efficient GBDP, make full use of the HREE and efficiently improve the coercivity. The Nd-Fe-B magnets were sputter coated and then processed by an optimized heat treatment, after that the magnetic properties of the specimens were tested and the microstructures were observed. Although a large amount of HREE distribution data in diffused magnets has been obtained, the diffusion model of HREEs in sintered Nd-Fe-B magnet is still incomplete, therefore a model describing the diffusion of HREE in the magnets was suggested according to the experimental results.

The commercial sintered Nd-Fe-B magnets (52 M, demagnetization state, stated remanent magnetization, 14.32 kG, coercivity, 14.4 kOe, shaped in cylinder along preferred magnetization direction, $\Phi 10$ mm × 5 mm) were used in this study. The Nd-Fe-B specimens were chemically cleaned and placed in a vacuum chamber equipped with ion beam guns and direct current magnetron sputtering sources with Tb or Dy targets (purity: >99.9%). A Tb or Dy coating with a thickness of 6.0 μm was deposited on both the top and the bottom surfaces of the magnet under a pressure of 0.1 Pa with argon as the sputtering gas. The coated specimens were individually wrapped in molybdenum foil, heated to 900 °C and kept for 0.5 h–16 h for diffusion, followed by a low-temperature annealing at 520 °C for 2 h in a high vacuum condition. After that, the magnetic properties were measured by a NIM-500C magnetic measuring device at room temperature, and three specimens were tested for each point. Some specimens were inlaid, ground, polished and observed by Qunta250 field emission Scanning Electron Microscope (SEM). The

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[*] Corresponding author.
E-mail address: songzhenlun@nimte.ac.cn (Z. Song).

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distributions of HREEs were determined by a glow discharge atomic emission spectrometer (GDA, Spectruma 750HP).

The magnetic properties of the HREE-diffused Nd-Fe-B magnets are exhibited in Fig. 1. Fig. 1(a) and (b) show the coercivity, the remanent magnetization and energy product of Tb and Dy-coated Nd-Fe-B magnets as a function of diffusion time, in which the error bar for each point is obtained from the standard deviation value of three specimens testing. It can be seen that the grain boundary diffusion lead to an increase in coercivity, which is increased as the diffusion process goes on. The coercivity increases from 14.4 kOe for the original specimen to 23.4 kOe and 19.3 kOe for the Tb and Dy diffused specimens, respectively. There is a little decrease in remanent magnetization after HREE diffusion, as in Fig. 1(c) and (d), when diffusion time is 16 h the remanent magnetization decreased from 14.32 kG to 14.24 kG and 14.10 kG, respectively. Besides, compared with the original specimen, the squareness (H_k/H_{cJ}) of demagnetization curves of diffused specimen has a little decrease, and then improves with the increasing diffusion time.

Fig. 2 shows the cross-section views of the magnets and the element distribution. The bright part shown in Fig. 2(a) is the Nd-rich phase and the dark part is the grain phase. The coated Tb or Dy film is uniform before the diffusion process, with a thickness of about 6.0 μm, as in Fig. 2(b) and (c). Fig. 2(d) and (e) show the BSE images of the region at a distance of about 120 μm from the surface of the Tb-coated and Dy-coated specimens diffused at 900 °C for 16 h, the bright gray shells are found to form at the superficial layer of the $Nd_2Fe_{14}B$ grains. The liner distribution of Fe, Nd and HREEs along the white lines in Fig. 2(d) and (e) are presented in Fig. 2(f) and (g), respectively. The contents of Tb or Dy decrease from the shell to the core of the grain and from the interface of the bright gray shell to the dark gray core phase, indicating that the HREE-rich shell is not formed by grain phase diffusion from the PVD-coated surface, but formed by diffusion of HREE from the grain boundary phase (GBP) to the grain phase (GP).

The distributions of HREEs with different diffusion times along the depth of the magnet are shown in Fig. 3. As in Fig. 3(a) and (b), with the increase in the distance to the coated surface, the gradients of the HREE concentration showed a dual-trend distribution. At the depth ranging from 0 to approximately 30 μm from the coating surface, the drop of content followed a diffusion rule with a low diffusion coefficient. Inside the magnet at the depth larger than 30 μm, the content drop with a high diffusion coefficient. This dual-trend distribution could be roughly treated as a diffusion contributed by two paths [14]: the GP diffusion and the GBP diffusion. The diffusion of HREE in the GBP is faster than that in the GP. The path from the GP is wider and slower, so the effect of diffusion is shallower. The path from the GBP is narrower and faster, so the effect of diffusion is deeper.

The fitted function of the distributions of HREE alone the GP and GBP path with different diffusion times is constructed in the format of the Grube solution to Fick's second law for semi-infinite solids [25]:

$$C(x,t) = A_1 - A_2\ erf(x/B) \tag{1}$$

where $C(x,t)$ is the concentration of HREE, x is the diffusion depth, t is the diffusion time, A_1 and A_2 are the parameters concerning with the concentration of HREE and B is the parameter concerning with diffusion coefficient. According to stereology laws, the surface fraction of a random distributed second phase should equal to its volume fraction. By analyzing the SEM of the specimen, the surface fraction of GP is about 0.898 and the GBP is 0.102. That is to say, the total contribution of the HREE concentration at a certain depth is 89.8% from GP and 10.2% from GBP. Suppose HREE source is sufficient during the diffusion process, the fitting distribution of HREE can be written as:

$$C(x,t) = \varphi C_{GP}(x,t) + (1-\varphi)C_{GBP}(x,t) \tag{2}$$

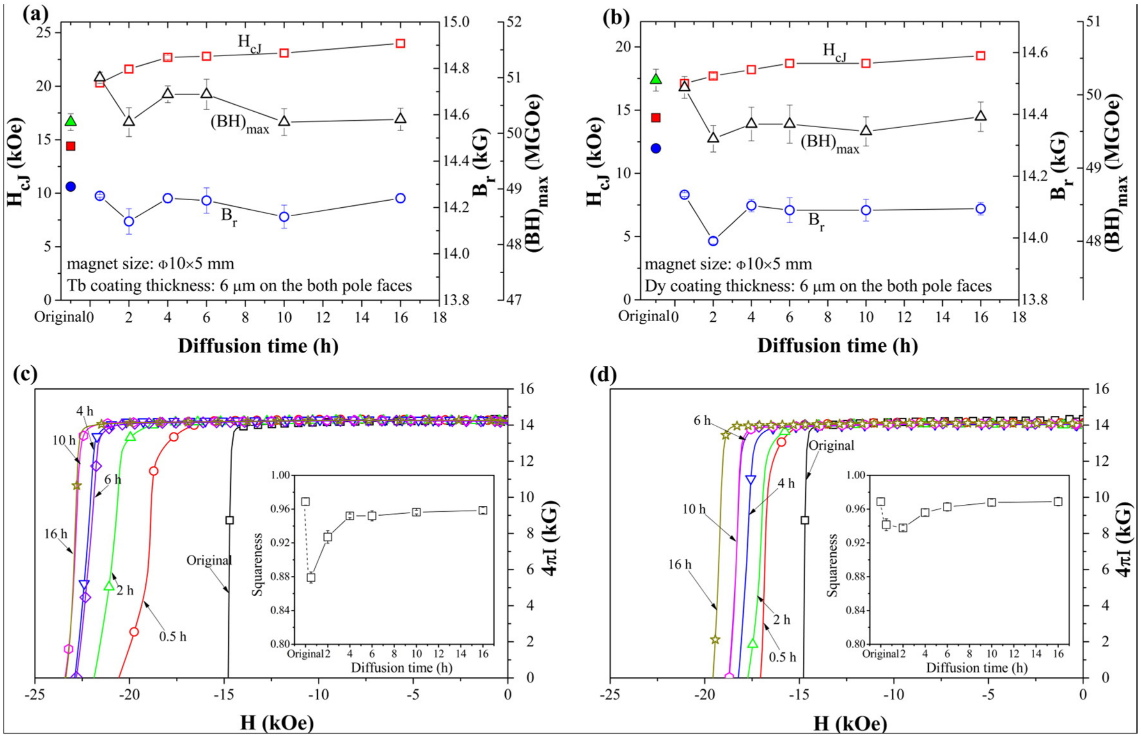

Fig. 1. Coercivity, remanent magnetization and energy product of (a) Tb and (b) Dy-diffused Nd-Fe-B magnets as a function of diffusion time (the error bar for each point is obtained from the standard deviation value of three specimens); demagnetization and squareness of (c) Tb and (d) Dy-diffused Nd-Fe-B magnets.