Effects of Dy diffusion time on magnetic properties of Nd–Fe–B sintered magnets

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Abstract

In recent years, significant research efforts were undertaken to enhance coercivity ($H_{cj}$) of Nd–Fe–B sintered magnets. One of the methods is Dy diffusion, which is very effective in improving $H_{cj}$ while maintaining the same level of remanence ($B_r$). Experiments reported in this work revealed that Dy diffusion differently affected $H_{cj}$ of Nd–Fe–B sintered magnets at three diffusion stages: (1) from 0 to 4 h of Dy diffusion, $H_{cj}$ increased rapidly from 32.3 to 36.5 kOe as Dy content increased rapidly from 0 to 0.27 wt%; (2) from 4 to 24 h, when Dy content changed from 0.27 to 0.56 wt%, $H_{cj}$ increased from 36.5 to 38.7 kOe; (3) from 24 to 30 h, $H_{cj}$ and Dy content barely changed. Thus, extending Dy diffusion time beyond 24 h period would not yield any improvements. From 0 to 30 h, $B_r$ slightly decreased from 12.40 to 12.22 kGs. During Dy diffusion, intergranular grain boundaries became continuous and homogeneous, and some micro-defects were repaired. As a result, from 0 to 24 h, $H_{cj}$ enhanced significantly while $B_r$ barely changed. Thus, the Nd-Fe-B sintered magnets with high properties ($B_r = 12.22 \text{ kGs}, H_{cj} = 38.9 \text{kOe and } (BH)_{max} = 36.87 \text{ MGOe}$) were obtained.

1. Introduction

Since the discovery of outstanding properties of Nd-Fe-B sintered magnets in 1984 they became and remained very popular in a variety of practical applications [1, 2]. However, low coercivity values ($H_{cj}$) and unsatisfactory thermal stability limit their high-temperature applications above 200 °C (e.g., wind turbines for electricity generation, traction motors of electrics, etc). To eliminate these drawbacks, significant research efforts were undertaken to enhance $H_{cj}$ of Nd-Fe-B sintered magnets in recent years. One approach to increase $H_{cj}$ is to substitute directly some of neodymium (Nd) with heavy rare-earth (HRE) elements such as dysprosium (Dy) or terbium (Tb). However, low supplies and high costs of Dy and Tb used to fabricate (Pr,Nd,Dy)Fe$_{14}$B or (Pr,Nd,Tb)$_2$Fe$_{14}$B sintered magnets create economic and production obstacles. Another disadvantage of Nd substitution by HRE is low remanence values ($B_r$) caused by anti-ferromagnetic coupling between Fe and Dy (or Tb) atoms [3–5]. Dy diffusion by vapor deposition or intergranular addition by mixing Nd-Fe-B material powders with DyF$_3$, DyH$_3$, Dy$_{82.3}$Co$_{17.7}$, Dy$_{71.5}$Fe$_{28.5}$ and Dy$_2$O$_3$ are very effective for improving $H_{cj}$ while maintaining the same level of $B_r$ [6–10]. However, diffused Dy affects $H_{cj}$ of Nd-Fe-B sintered magnets differently at various Dy diffusion annealing stages. Thus, the mechanism of Dy diffusion into Nd-Fe-B sintered magnet matrix to fully utilize valuable Dy needs to be studied.

This work reports three stages of $H_{cj}$ enhancement as a function of Dy content. Two approaches were used to induce Dy diffusion into the magnet grains by vapor deposition. During the first approach 1 and during the first diffusion stage, Dy diffused from the surface into the magnet along the liquid grain boundaries (GBs), which resulted in continuous and homogeneous intergranular grain boundaries and well-isolated neighboring ferromagnetic grains. All of these factors significantly improve $H_{cj}$. During approach 2 and during the second diffusion stage, Dy diffused from the grain boundaries into the grain surface regions and partially substituted Pr...
or Nd in the (Pr,Nd),Fe₁₄B lattices, the (Pr, Nd, Dy),Fe₁₄B hard magnetic shell formed and some micro-defects were repaired. These factors also enhanced \( H_{cj} \). During the third stage, Dy diffusion path became gradually blocked, which extended Dy diffusion time without any improvement in \( H_{cj} \). The magnets with excellent properties (with \( B_r = 12.22 \) kGs, \( H_{cj} = 38.9 \) kOe, \( (BH)_{max} = 36.87 \) MGOe) were obtained by Dy diffusion at 900 °C for 30 h in 2 kPa of Ar.

2. Experimental

Starting material with the composition of \((\text{Pr},\text{Nd})_{12.47}\text{Ti}_{1.05}\text{Fe}_{60}\text{Al}_{0.49}\text{Co}_{1.67}\text{Cu}_{0.16}\text{Nb}_{0.14}\text{Ga}_{0.19}\text{B}_{0.06}\) (at%) was prepared by induction melting, followed by strip casting (SC). The strips were crushed into coarse powders with 10–100 μm particles by hydrogen decrystallization (HD). These HD powders were ground to ~3.0 μm by jet-milling (JM) in the N₂ atmosphere, and then homogenized for 4 h using a 3D-mixer (also in N₂). The resulting materials were compacted under a 1.7 T magnetic-field and 6 MPa pressure, and then isostatically pressed at 190 MPa. The green compacts were sintered at 1080 °C for 4 h, and then annealed at 890 °C for 3 h and at 465 °C for 5 h. Sintered magnets were cut into cylinder \( \Phi 10 \times 5.5 \) mm, and then cleaned by HNO₃. Metallic Dy for grain boundary diffusion experiments was prepared by induction melting in Ar. During Dy diffusion tests, the magnets were annealed at 900 °C for 4, 5, 12, 16, 24 and 30 h in 2 kPa of Ar using a special furnace. 900 °C was chosen based on our preliminary experiments. Finally, the samples were heated at 460–500 °C for 3.5 h in vacuum.

Particle size distribution was measured using HELOS-RODOS laser diffraction particle size analyzer. The density of the samples was determined using the Archimedes method. Magnetic properties were obtained by Hirst PFM-12 pulse magnetic field equipment. The whole sample was broken into pieces and dissolved completely in HNO₃. Then, metal contents in the samples were determined using IY-ICP ULTIMA 2 spectroscopy instrument. Compositions and microstructures of grain boundaries were analyzed using field emission microscopy (FE-SEM) coupled with the energy dispersive x-ray spectroscopy (EDS). The elemental distribution map was conducted using a JEOL JXA-8530F electron probe micro-analyzer (EPMA).

3. Results and discussion

\( H_{cj} \) of Nd-Fe-B sintered magnets is controlled by the nucleation of reverse magnetic domains at the Nd₂Fe₁₄B grain surfaces. Nucleation of reverse magnetic domains depends on (1) continuous and homogeneous intergranular grain boundaries, on (2) magnetic anisotropy field \( H_A \) at the surface region of the Nd₂Fe₁₄B grains and on (3) the surface micro-defects [3–7]. Discontinuous intergranular grain boundaries, which imply that the neighboring ferromagnetic grains are not well-isolated, cannot decouple Nd₂Fe₁₄B grains well enough, which leads to low \( H_{cj} \) of the starting magnets. Since the presence of surface micro-defects enlarges the stray field of the area adjacent to the non-ferromagnetic grains, anisotropy field \( H_A \) at these regions is much lower than that of the Nd₂Fe₁₄B grains. Therefore, the resulting \( H_{cj} \) values are significantly below theoretical values [11]. Dy introduced into the magnet grain surface forms a thin (Pr, Nd, Dy),Fe₁₄B hard magnetic shell and repairs micro-defects. Since \( H_{cj} \) of Dy,Fe₁₄B (15.8 T) is higher than those of Nd₂Fe₁₄B (7.3 T) and Pr₂Fe₁₄B (7.5 T) [6], (Pr, Nd, Dy),Fe₁₄B shell can enlarge \( H_{cj} \) of the 2:14:1 phase grain surface, and improves \( H_{cj} \). The saturation magnetization (\( M_s \)) of Dy,Fe₁₄B (0.71 T) is lower than those of Nd₂Fe₁₄B (1.60 T) and Pr₂Fe₁₄B (1.56 T). Additionally, \( M_s \) of the main phase covered by the (Pr, Nd, Dy),Fe₁₄B magnetic hard shell is decreased, which reduces both \( R \) and \( (BH)_{max} \) [12, 13].

Figures 1(a) and (b) demonstrate the two approaches of how Dy can be introduced into the magnets. Yellow arrows in figure 1(a) show that Dy diffuses from the magnet surface into the magnets along the liquid grain boundaries (Approach 1). Blue arrows in figure 1(b) show that Dy migrates from the grain boundaries into the grain surface regions (Approach 2), which helps to repair micro-defects (see figure 1(c)) [14].

Figure 2 shows SEM images of the fractured microstructure of Nd-Fe-B sintered magnets obtained upon Dy diffusion performed at 900 °C for 0, 4, 12 and 24 h. The average particle size of the dark-gray Nd₂Fe₁₄B grains distribution did not change significantly. Contents of impurities and voids were very small. Thus, the sintering effect was optimum. As diffusion time was increased from 0 to 24 h, the agglomeration of RE-rich phases in the triple junctions became more obvious. The silver-gray RE-rich phases, which expanded due to the diffused Dy, isolated the neighboring Nd₂Fe₁₄B grains and increased decoupling effect.

Compared to the maps (EPMA) and the area ratio of Dy distribution obtained 0.2 mm below the magnet surface (figure 3(a)) and in the core (figure 3(c)) of magnets diffused at 900 °C for 30 h, the green (including red islands) Dy distribution bands around the blue 2:14:1 phases in figure 3(a) were obviously thicker than those in figure 3(c), the area ratios of Dy decreased from 43.2% in figure 3(a) to 19.3% in figure 3(c). These confirmed that Dy diffused from the surfaces to the magnets and Dy content gradually decreased from the surface to the
The core of the magnets [3, 15]. The green (including red islands) Dy bands (figure 3(a)) were obviously thicker than the silver-gray grain boundaries (figure 3(b)) around the dark-gray 2:14:1 phases. The area ratios of Dy (43.2 %) in figure 3(a) were larger than those of grain boundaries (10.3 %) in figure 3(b). Those indicated that Dy diffused from grain boundaries to grain surface regions. The grains showed a remarkable Nd$_2$Fe$_{14}$B / (Pr, Nd, Dy)$_2$Fe$_{14}$B core-shell structure, and the thickness of the shells decreased with increasing distance from the magnet surface [16]. The EDS line scan analysis (figure 4) illustrated the graded distribution of some elements across the RE-rich phases and the 2:14:1 phase grains. The concentration distributions of Nd (the pink lines), Tb (the red lines), Fe
(the green lines) and Pr (the yellow lines) were the same as those of conventional magnets, but the concentration distributions of Dy (the blue lines) gradually decreased from the grain boundaries to the grains. This also suggested a (Pr, Nd, Dy)\(_2\)Fe\(_{14}\)B shell had been formed surrounding the 2:14:1 phase grains.

Comparison of Dy distribution maps (EPMA) of the magnet cores (figure 5) obtained upon Dy diffusion performed at 900 °C for 4, 5, 12 and 24 h, the thickness of the green (including red islands) Dy distribution bands noticeably increased as diffusion time increased from 4 to 24 h, the area ratio of Dy distribution in figure 5 increased from 8.5 % to 18.5%. Thus, extended Dy diffusion time could increase the thickness of the (Pr, Nd, Dy)\(_2\)Fe\(_{14}\)B shell (shown in green color) [16] and resulted in continuous and homogeneous intergranular grain boundaries in the magnet core.

Initial magnets were off-stoichiometric Nd\(_2\)Fe\(_{14}\)B. Dy diffusion underwent three stages (see figure 6(c)). Inflection points occurred at 4 and 24 h. From 0 to 4 h, Dy content increased from 0 to 0.27 wt%. In this case, Dy diffusion mainly occurred by approach 1, namely, Dy diffused along the liquid grain boundaries of the magnet,
which contained less Dy, which allowed Dy to diffuse relatively easy. From 4 to 24 h, because liquid grain boundaries were near the Dy saturation limits, Dy diffusion by approach 1 slowed down. Simultaneously, contact of Dy in the grain boundaries with grain surfaces rapidly increased, Dy diffusion occurred by approach 2, namely, Dy diffused from the grain boundaries into the magnet surface regions, Dy content increased from 0.27
to 0.56 wt%, and some micro-defects were repaired. From 24 to 30 h, grain boundaries and grain surface regions became saturated by Dy. The path for Dy diffusion gradually became blocked, and Dy content change barely, it increased from 0.56 to only 0.58 wt%. Therefore, extending Dy diffusion time would not result in higher Dy content.

Equation (1) shows mathematical expression for $H_{cj}$ [17]:

$$H_{cj}(T) = \alpha H_A(T) + N_{eff} M_s(T),$$

where $\alpha$ is degradation constant, $H_A$ is the anisotropy field, $N_{eff}$ is an effective demagnetization factor, $M_s$ is saturated magnetization. $H_{cj}$, $H_A$ and $M_s$ are temperature dependent. $N_{eff}$ depends on microstructure as well as on the continuity and smoothness of the grain boundaries.

During Dy diffusion, as Dy content increased, $H_{cj}$ underwent three stages (see figure 6(a)). The inflection point appeared at 4 and 24 h. From 0 to 4 h, at Dy content <0.27 wt%, $H_{cj}$ rapidly increased from 32.3 to 36.5 kOe. From 4 to 24 h, at Dy content in the 0.27–0.56 wt% range, $H_{cj}$ increased from 36.5 to 38.7 kOe. During these two stages, grain boundaries containing higher Dy amounts were more continuous and homogeneous, and their $N_{eff}$ decreased. At the same time, Dy diffused from the grain boundaries into the grain surfaces, (Pr, Nd, Dy)$_2$Fe$_{14}$B hard magnetic shells formed, and surface micro-defects were repaired while $H_A$ value increased. According to equation (1), $N_{eff}$ decreased and $H_{cj}$ increased, which resulted in $H_{cj}$ increasing from 32.3 to 38.7 kOe. From 24 to 30 h, Dy content was in the 0.56–0.58 wt% range, a path for Dy diffusion was gradually blocked. However, $H_{cj}$ barely increased from 38.7 to 38.9 kOe. Thus, longer Dy diffusion time would not improve magnetic properties any further.

We also analyzed the relationship between Dy content and $B_r$ values. Equation (2) shows mathematical expression for $B_r$ [18]:

$$B_r \propto (M_s \cdot \beta) \cdot (\rho \cdot \rho_b) \cdot (1 - \alpha)^{2/3} \cdot f,$$

| Table 1. Comparison of magnetic properties of Nd-Fe-B sintered magnets diffused and non-diffused Dy. |
|---------------------------------|----------|----------|
| $B_r$ (mT) | 1240 (12.40 kGs) | 1222 (12.22 kGs) |
| $H_{cj}$ (kA · m$^{-1}$) | 2571 (32.3 kOe) | 3096 (38.9 kOe) |
| $(BH)_{max}$ (kJ · m$^{-3}$) | 295 (37.13) | 293 (36.87) |
| $H_s/H_{cj}$ | 94.2 | 86.7 |

Figure 7. Demagnetization curves at 20 ºC for Nd-Fe-B sintered magnets diffused and non-diffused Dy.
where $M_s$ is saturated magnetization, $\beta$ is the temperature coefficient of saturation magnetization, $\rho$ is magnet density, $\rho_f$ is the theoretical density of Nd$_2$Fe$_{14}$B, $\alpha$ is the volume fraction of the non-magnetic phase, and $f$ is the orientation degree.

During 30 h Dy diffusion into the magnet, (Pr, Nd, Dy)$_2$Fe$_{14}$B hard magnetic shell formed and $M_s$ decreased. Grain boundaries containing more diffused Dy increased orientation degree.

During Dy diffusion, $H_{cj}$ significantly increased and $B_r$ barely changed. Thus, during Dy diffusion, $H_{cj}$ significantly increased and $B_r$ barely changed.

Results shown in table 1 and figure 7 confirmed that the magnet with high magnetic properties ($B_r = 12.22$ kGs, $H_{cj} = 38.9$ kOe and $(BH)_{max} = 36.87$ MGOe) was successfully obtained in this work.

4. Conclusion

Based on the data obtained in this work, the following conclusions were made:

1. During Dy diffusion, $H_{cj}$ of Nd-Fe-B sintered magnets underwent three distinct stages judging by Dy content change: from 0 to 4 h, $H_{cj}$ increased rapidly as Dy content increased. From 4 to 24 h, both $H_{cj}$ and Dy content increased slowly. From 24 to 30 h, $H_{cj}$ and Dy content barely changed. Thus, extending Dy diffusion time beyond 24 h period did not yield any improvement in desired magnetic properties.

2. Dy diffusion also resulted in more continuous and homogeneous intergranular grain boundaries and repaired surface micro-defects. Thus, from 0 to 30 h, $H_{cj}$ was enhanced significantly from 32.3 to 38.9 kOe while $B_r$ barely changed (from 12.40 to 12.22 kGs).

3. Nd-Fe-B sintered magnets with high properties ($B_r = 12.22$ kGs, $H_{cj} = 38.9$ kOe, $(BH)_{max} = 36.87$ MGOe) were obtained.

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