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Optimized Microstructure and Improved Magnetic Properties of Pr-Dy-Al-Ga Diffused Sintered Nd-Fe-B Magnets

Pengpeng Qu ^{1,2}, Feifei Li ^{1,2}, Sajjad Ur Rehman ^{1,2}, Lei He ^{1,2}, Xiaoqiang Yu ^{1,2}, Qingfang Huang ^{1,3}, Munan Yang ^{1,2,4} and Jiajie Li ^{1,2,4,*}

- ¹ Jiangxi Key Laboratory for Rare Earth Magnetic Materials and Devices, Institute for Rare Earth Magnetic Materials and Devices (IREMMD), Jiangxi University of Science and Technology, Ganzhou 341000, China; qppwrx@163.com (P.Q.); lifeifei1997@yeah.net (F.L.); sajjadurehman@gmail.com (S.U.R.); helyangy@163.com (L.H.); yuxiaoqiang@jxust.edu.cn (X.Y.); sduhqf@163.com (Q.H.); yangmunan@jxust.edu.cn (M.Y.)
- ² College of Rare Earths, Jiangxi University of Science and Technology, Ganzhou 341000, China
- ³ Fujian Rare-Earth Function Material Key Laboratory, Longyan 364000, China
- ⁴ National Rare Earth Functional Materials Innovation Center, Ganzhou 341000, China
- * Correspondence: lijiajie@jxust.edu.cn

Abstract: The grain boundary diffusion process (GBDP) has become an important technique in improving the coercivity and thermal stability of Dy-free sintered Nd-Fe-B magnets. The influence of Dy₇₀Al₁₀Ga₂₀ and (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ alloys by the GBDP on sintered Nd-Fe-B magnets are investigated in this paper. After diffusing Dy₇₀Al₁₀Ga₂₀ and (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ alloys, the coercivity (H_{cj}) of the magnets increased from 13.58 kOe to 20.10 kOe and 18.11 kOe, respectively. Meanwhile, the remanence of the magnets decreased slightly. The thermal stability of the diffused magnets was improved by the GBDP. The microstructure shows continuous Rare-earth-rich (RE-rich) grain boundary phases and (Dy, Pr/Nd)₂Fe₁₄B core-shell structures which contribute to improving the coercivity. Moreover, the Dy concentration on the surface of the (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ diffused magnets decreased with the Pr substitution for the Dy element. The openness of the recoil loops for the (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ diffused magnets is smaller than that of the original magnets and Dy₇₀Al₁₀Ga₂₀ diffused magnets. The results show that the (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ alloys can effectively optimize the microstructure and improve the magnetic properties and thermal stability of the sintered Nd-Fe-B magnets.

Keywords: Nd-Fe-B magnets; grain boundary diffusion process; magnetic properties; thermal stability; recoil loops

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1. Introduction

Sintered Nd-Fe-B magnets possessing excellent high intrinsic coercivity and energy products are widely used in wind power, hybrid vehicles, maglev trains, and household appliances, etc. [1,2]. In this application, higher magnetism is required. Since the invention of Nd-Fe-B magnets in 1983, the remanence (J_r) and the maximum energy product $(BH)_{max}$ of the Nd-Fe-B magnets reached the theoretical values, while the H_{cj} is only 30% of the theoretical value [3]. However, the higher H_{cj} is urgently proposed in the face of increasingly harsh working environments, especially in high-temperature and high-humidity climates [4–6]. There are basically two ways to develop high coercivity. One is to improve the inherent temperature dependence of H_{cj} , and the other is to develop higher coercivity at room temperature to resist thermal demagnetization of the magnets when exposed to high temperature. Heavy rare earth elements Dy/Tb can be substituted for Pr/Nd to increase the magneto-crystalline anisotropy field (H_A), causing a substantial enhancement of H_{cj} by a single alloying method. However, due to the antiferromagnetic coupling between Dy and Fe, it is unfavorable to the saturation magnetization [7,8]. In order not to sacrifice the

saturation magnetization, the GBDP (grain boundary diffusion process) technique was proposed by Park et al. [9]. Heavy rare earth elements can be selectively diffused into the magnet interior along the grain boundary (GB), forming a hard core-shell structure surrounding the main grains. Later, researchers successively used heavy rare earth metals/compounds/alloys containing Dy or Tb, such as Dy, Dy₂O₃, DyF₃, DyH₂, and Dy-Cu or Pr-Dy-Cu [10–14] acting as diffusion sources to improve the H_{cj} .

In the GBDP, there are large amounts of the Dy/Tb element enriched on the magnets' near-surface by diffusing the Dy/Tb, which causes thicker Dy/Tb-rich shells. Some findings show that the thickness of the Tb-rich shell can be reduced by controlling the thickness of TbF₃ coatings and Al-aided TbH₂ powders' diffusion [15,16], which can still enhance the H_{cj} increment. Therefore, we can design suitable diffusion resources to decrease the thickness of the Dy/Tb-rich shell on the near-surface of the magnets.

In addition, the non-rare-earth elements Al/Ga/Cu can also increase the H_{cj} of the sintered Nd-Fe-B magnets and reduce the irreversible loss of magnetic flux. These elements mainly enrich in the RE-rich (Rare-earth rich) liquid phase to improve the wettability and increase the coercivity of the magnets [17–19]. Therefore, we select the ternary alloy Pr₇₀Al₁₀Ga₂₀ and Dy₇₀Al₁₀Ga₂₀ and quaternary alloy (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ as the diffusion sources in this work. The (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ alloys inculcate the best properties with a large substitution of Pr for Dy after the GBDP, as shown in Supplementary Material. The magnetic properties and thermal stability of the diffused magnets are analyzed. The relationship between microstructure and recoil loops and diffusion mechanism of the magnets are also discussed.

2. Materials and Methods

The commercial sintered Nd-Fe-B magnet of N52 was selected and wire-cut into small magnets with a size of $\phi 10 \times 10 \times 5 \text{ mm}^3$, and the chemical composition was (Pr, Nd)₃₀Co_{1.0}Cu_{0.15}Zr_{0.12}Ga_{0.3}B_{0.94}Fe_{bal.} (wt.%). The ingots of Pr₇₀Al₁₀Ga₂₀, Dy₇₀Al₁₀Ga₂₀, and (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ (wt.%) were prepared by arc melting under a high-purity argon atmosphere. Then, these ingots were melt-spun into ribbons with 10 mm in width and 0.17 mm in thickness at a speed of 8 m/s. The magnets were polished with 400 mesh, 800 mesh, 1000 mesh, 1500 mesh, and 2000 mesh sandpaper and then ultrasonically washed in alcohol and dried. The ribbons were placed on the top and bottom of the magnet and put in a sintering furnace for diffusion heat treatment. The heat treatments were carried out at 850 °C for 6 h, and then annealed at 490 °C for 3 h in a vacuum (10^{-4} Pa) tubular furnace. The magnetic properties at different temperatures were measured by a boron hydride tracer (NIM-500C, National Institute of Metrology, Beijing, China). The melting points of the alloys were measured by differential scanning calorimetry (DSC250, TA Instruments, USA). Additionally, the microstructure of the magnets was observed by a field emission scanning electron microscope (FESEM, MLA650F, FLIR Systems, Inc., Wilsonville, OR, USA). The irreversible magnetic flux loss at elevated temperatures was measured by pulling Helmholtz coils. The phase constitution of the magnets was determined by the X-ray diffraction with a Cu-K α radiation (XRD, D8 Advance, Bruker, Billerica, MA, USA). The elemental distribution of Nd-Fe-B magnets was explored by using an electron probe microanalyzer (EPMA, JXA-8530F, JEOL, Tokyo, Japan). The recoil loops of the magnets were measured by the Physical Property Measurement System (PPMS-DynaCOOL1-9, Quantum Design, San Diego, CA, USA) in fields up to 5 T at room temperature.

3. Results and Discussion

Figure 1 shows the DSC results of the Dy₇₀Al₁₀Ga₂₀, (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀, and Pr₇₀Al₁₀Ga₂₀ ribbons. Compared with ternary alloys, quaternary alloys have relatively lower melting points. Additionally, the lower melting point may reduce the activation energy of the diffusion and improve diffusion efficiency. Moreover, compared with the ternary alloy Dy₇₀Al₁₀Ga₂₀, the quaternary alloy (Pr₇₅Dy₂₅)₇₀Al₁₀Ga₂₀ contains less heavy rare earth elements; thus, it reduces the costs.

Figure 1. DSC results of $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$, $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$, and $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$ ribbons.

Figure 2 shows demagnetization curves at the room temperature of the original magnets and $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$, $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$, and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. It can be clearly seen that the H_{cj} of the diffused magnets is improved after the GBDP, while the remanence is only slightly decreased. The coercivity increased from 13.58 kOe to 15.34 kOe, 20.10 kOe, and 18.11 kOe, respectively, after diffusing $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$, $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$, and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloys. At the same time, the J_r reduced from 14.3 kG to 14.0 kG, 14.0 kG, and 14.1 kG, respectively. The increase in the H_{cj} is mainly because of the partial substitution of Pr and Dy for Nd to form the core-shell structure of $(\text{Dy}, \text{Pr}/\text{Nd})_2\text{Fe}_{14}\text{B}$. The antiferromagnetic coupling of Dy and Fe atoms reduces the J_r of $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. In addition, the Pr content in the $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnet is higher, and the nonmagnetic volume fraction increases after diffusion, which leads to the decrease in the J_r . The increase in the volume fraction of the grain boundary is another reason for the decrease in the J_r .

Figure 2. Demagnetization curves of the original magnet and $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$, $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets.

Figure 3a shows the coercivity curves of the original magnet and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets at the temperature range of 293 to 453 K. Additionally, the temperature coefficient of coercivity (β) of the magnets can be calculated according to the formula [20,21]:

$$\beta H_{cj}(T_0) = [H_{cj}(T_1) - H_{cj}(T_0)] / (T_1 - T_0) \times 100\% \quad (1)$$

where T_1 is the elevated temperature, and T_0 is the room temperature. The β increased from -0.5341% /K of the original magnets to -0.4609% /K and -0.4939% /K, respectively, for the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. Figure 3b is the irreversible flux loss curve of the original magnet and the diffused $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ magnets at 293–453 K. The irreversible flux loss rates of the original magnet and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy diffused magnets were 75.5%, 48.6%, and 48.7%, respectively. The irreversible flux loss of the magnets was reduced by about 27% after diffusion, which suggests that the diffused magnets have less magnetic irreversible flux losses. The magnetic flux and coercivity are very sensitive to temperature. The structure loss occurs at a high temperature, which leads to demagnetization. The irreversible flux loss is not recoverable when back to room temperature. It is related to the irreversible change of the microstructure of the magnets. The GB microstructure of the diffused magnets was optimized after thermal diffusion treatment. The nucleation of the reverse magnetic domain of the magnets is suppressed, and it is difficult to trigger the magnetization reversal of the magnetic domain due to the hardening of the epitaxial layer of the matrix phase grain [22]. This results in an improvement in temperature coefficients and irreversible magnetic flux losses of the diffused magnets. These results indicate that the thermal stability of the diffused magnets was improved after the GBDP.

Figure 3. (a) the coercivity curves of the original magnets and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffusion magnets in the temperature range of 293–453 K; (b) the irreversible flux loss curve of the original magnets and the diffused $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ magnets at 293–453 K.

Figure 4 shows the XRD of the original magnets and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets (vertical to the c-axis plane, with the observation surface near the surface). As can be seen from the diffraction peaks marked in Figure 4, most of the diffraction peaks are the main phases, and small parts are the RE-rich phase, and no new diffraction peaks appear in the diffused magnets. The characteristic diffraction peaks were located at 29.3, 44.6, 60.8, and 78.5 of 2θ , and Bragg diffraction peaks corresponding to (00l) are compared with JCPDS (Joint Committee on Powder Diffraction Standards) card no. 39-0473. This indicates that the magnets are dominated by 2:14:1 phases before and after the GBDP, and the content of other impurity phases is relatively small. The partially enlarged view of the diffraction peaks of the (006) crystal plane shows that the main phase peak of the magnet shifted to a large angle direction after diffusing

$\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$, while the main phase peak moved slightly to a small angle direction after diffusing $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$. This is because the atomic radius of Dy (0.1773 nm) is smaller than Nd (0.1821 nm). According to the Bragg equation, when the Dy atoms diffuse into the main phase to replace Nd to form the $(\text{Nd}, \text{Dy})_2\text{Fe}_{14}\text{B}$ shell layer, the lattice parameters decrease. For the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnet, the lattice parameters of the main phase increase, which is because the diffusion amount of Pr is greater than that of Dy. Based on the Lanthanide contraction effect, the atomic radius of the Dy element is smaller than that of Pr and Nd. Dy instead of Pr/Nd makes the diffraction peaks move to the large angle; in contrast, Pr and Nd move the peak to a small angle. Consequently, the combined effect is that the diffraction peak shifts to a small angle. The shift of the peak also means that Pr and Dy have entered into the main phase, forming a stronger H_A of $(\text{Dy}, \text{Pr}/\text{Nd})_2\text{Fe}_{14}\text{B}$ shells, thus exhibiting the coercivity enhancement effect.

Figure 4. XRD patterns of the original magnet, and $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy diffused magnets (the surface of observation is the near-surface).

In order to explore the reason for the H_{cj} enhancement, the microstructure of the magnets was observed after the GBDP. Figure 5a–c are BSE-SEM (backscattered electron) images of the original magnets, and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy diffused magnets, respectively. The dark gray parts in Figure 5 correspond to the 2:14:1 matrix phase grains, and the bright white and gray white areas correspond to the RE-rich phases. The bright white and gray white in SEM are caused by the difference in composition of the RE-rich phases. Figure 5a shows that the triple junction RE-rich phases of the original magnets were distributed discretely in the magnet interior, and some adjacent matrix phase grains were in direct contact, which is unfavorable to the H_{cj} . Comparably, the smooth and continuous thin grain boundary RE-rich phases were formed in the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. If all grains are surrounded by thin grain boundary phases, then the grains are magnetically isolated from each other. If the grains are in direct contact with each other, there will be a localized exchange coupling effect, and, as a result, the grains are connected together to form a larger ferromagnetic domain grain group. A small grain inversion will drive demagnetization of adjacent grains in chains, because there is no thin layer RE-rich phase boundary, which will not hinder the displacement of the domain wall [23]. Demagnetization of one grain will drive demagnetization of other grains, thus reducing coercivity; that is, the demagnetization resistance will be reduced.

Figure 5. (a–c) are BSE-SEM images of the original magnet, and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy diffused magnets (the surface of observation is the near-surface), respectively.

Figure 6 shows the EPMA images on the surface (perpendicular to c-axis) of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. The distribution of Dy, Nd, Pr, Al, and Ga elements in the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ magnets are shown in Figure 6 after the GBDP, respectively. Dy elements are mainly distributed in the main phase grain epitaxial layer to form the $(\text{Dy}, \text{Pr}/\text{Nd})_2\text{Fe}_{14}\text{B}$ core-shell structure, which is beneficial to increase the coercivity. During the GBDP, Dy penetrates into the Nd-Fe-B sintered magnets through liquid grain boundaries. The Dy-rich shells are only selectively formed on the low-index lattice plane of the main phase grains. These planes, generated by the partial melting of the main phase grains, offer the low-energy configurations at the $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{GB}$ interfaces [24]. During the subsequent cooling process, the Dy-rich liquid phases precipitate on the edge of the main phase grains and solidify to form $(\text{Nd}, \text{Dy})_2\text{Fe}_{14}\text{B}$ hard shells. As shown in Figure 6a, a large amount of Dy elements accumulated on the surface of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets, while the enrichment on the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets is mitigated. Although the H_{cj} of the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnet is 2 kOe lower than that of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused one, the heavy rare earth content of the quaternary alloy is much lower than the ternary alloy.

The grain boundary channels, and intergranular regions of the sintered Nd-Fe-B magnets, are typically around 100–1000 nm in size, and the high temperature wettability causes enough capillary thrust for these elements to enter the intergranular channels during liquefaction, which in turn causes the uniform distribution of grain boundaries with the matrix grains [25,26]. According to the distribution of Al and Ga in Figure 6b, most of them remain in the grain boundaries and play a role in wetting the grain boundaries [18]. At the same time, a small amount of Al also exists in the matrix grains, which is possible when the surface of the Nd-Fe-B grains is partially decomposed, and Dy replaces Nd atoms. Meanwhile, Al penetrates into the selected grain facets from the grain boundaries with a high concentration at the grain edges. With a cooling effect coming in place, lighter Al atoms get transported inwards due to the low melting point while matrix restructuring happens, known as core-shell morphology [27]. Although the core-shells are not obvious, a higher concentration of Pr at the grain boundaries takes precedence of surface diffusion by the substitution of Nd atoms, resulting in the intergranular region becoming richer with Nd and hard phase grains taking composition $(\text{Pr}, \text{Nd})_2\text{Fe}_{14}\text{B}$. Therefore, under the combined effect of the above elements, the hard core-shell structure and optimized microstructure can explain the reason why the diffused magnets have an increased H_{cj} after GBDP.

To investigate the diffusion depth of Dy in different diffused magnets, the EPMA was performed to determine the distribution of the Dy element along the diffusion direction. Figure 7(a1,a2,b1,b2) show the corresponding EPMA mappings at 0–400 μm of $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. As can be seen from Figure 7(a2,b2), a high concentration of the Dy-rich area is formed on the surface of the magnet, and the Dy-rich area is indicated by the red ellipses in Figure 7(a2,b2). It can be seen from the red rectangular box that the concentration of the Dy element in the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets is higher than that of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. With the diffusion depth increasing, the Dy-rich area gradually decreases. At the depth of 400 μm , the Dy element still exists in the magnet interior. At the same time, it is observed that the concentration of Dy in

the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets is higher than that of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets at the same depth as the dotted lines in Figure 7(a2,b2). Therefore, the quaternary alloy $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ can save the Dy elements and promote its diffusion depth.

Figure 6. The EPMA mappings of the near-surface layer (perpendicular to c-axis): (a) $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ magnet; (b) $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ magnet.

Figure 7. The SEM images and the corresponding EPMA mapping (parallel to c-axis) at 0–400 μm of **(a1,a2)** $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and **(b1,b2)** $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets, respectively.

For sintered Nd-Fe-B, the GB provides a channel for the diffusion source. The melting point of the RE-rich grain boundary phase is about $655\text{ }^{\circ}\text{C}$, which is much lower than the melting point of the main phase of $1185\text{ }^{\circ}\text{C}$ [28]. The element diffusion follows the Fick's second law, which states that in the process of unsteady diffusion, we get

$$c_x = c_0 \times \exp(-x^2/A) + c_s \quad (2)$$

where c_x , c_0 , and c_s are the volume concentrations of the diffusion material (kg/m^3) at the different depths; A is a fixed value (when the surface concentration and time are determined); and x is the distance (m) [7]. Figure 8 shows the fitting curve of the Dy element concentration in the range of different depths in the diffused magnets. Additionally, the diffusion coefficients of the Dy element are approximately $4.988 \pm 0.673 \times 10^{-7} \text{ cm}^2/\text{s}$ and $3.139 \pm 0.101 \times 10^{-7} \text{ cm}^2/\text{s}$ in the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ and $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets, respectively. This also shows that the diffusion efficiency of the Dy elements in the quaternary alloys $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ is improved under the cooperation of the Pr elements. The concentration of the Dy element can be measured by EPMA along the diffusion direction from the $0\text{ }\mu\text{m}$ to $450\text{ }\mu\text{m}$ in a continuous $100 \times 100\text{ }\mu\text{m}^2$ square indicated by the red boxes in Figure 7(a1,b1). As the diffusion depth increases, the concentration of Dy elements decreases, and the diffusion rate slows down.

Figure 9 gives a schematic diagram of the change in the amount of diffusion distinguished from the depth of the diffused magnets [29]. Figure 9a,b show the diffusion mechanism of ternary alloys $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and quaternary alloys $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$, respectively. During the heat treatment, Dy atoms enter the magnet along the grain boundaries. By replacing Nd atoms with Dy atoms, a thin layer with higher Dy concentration is formed on the edge of the main phase grains, which is called the core-shell structure. The quaternary alloys $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ have the coordinated diffusion of the Pr element, so that the Dy element can penetrate deeper into the magnets and form a more core-shell structure. At the same time, the surface Dy concentration of the magnets can be regulated by diffusing $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloys. Due to the magnetic isolation effect of the grain boundaries and the high magnetocrystalline anisotropy field of the core-shell structure, the coercivities of the diffused magnets show improvement after the GBDP treatment.

Figure 8. The fitting curves of Dy element concentration in $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets at different depths.

Figure 9. Schematic diagram of the Nd-Fe-B magnet diffused structure. (a) the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnet; (b) the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnet.

The recoil loops can verify the magnitude of the demagnetization capability and the uniformity of the microstructure [17]. Figure 10 shows the recoil loops of the original magnets, and the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. It shows that the recoil loops' opening of the original magnet is larger, while that of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets are much smaller. This is because the distribution of the RE-rich phase for the original magnet is non-uniform and discontinuous, and the grain boundary of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets are optimized

to be more uniform and continuous after the GBDP. However, a large amount of the Dy element enrichment on the surface of the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets leads to the larger opening of the recoil loops than that of the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. The reduced surface Dy enrichment improves the microstructure uniformity by diffusing the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy; thus, the recoil loops' opening of the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets is smaller than that of the original and $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets. This is also confirmed by the microstructure of the magnets mentioned in Figures 5 and 6.

Figure 10. Recoil loops for (a,b) original magnets, and (c,d) $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and (e,f) $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy diffused magnets.

4. Conclusions

In this paper, the effects of diffusing $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ ternary alloys and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ quaternary alloys on the magnetic properties and microstructure of sintered Nd-Fe-B magnets were investigated.

- (1) The coercivity of the $\text{Pr}_{70}\text{Al}_{10}\text{Ga}_{20}$, $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloys diffused Nd-Fe-B magnets increased from 13.58 kOe to 15.34 kOe and 20.10 kOe and 18.11 kOe, respectively, while the remanence is only slightly decreased.
- (2) The thermal stability of the diffused magnets improves by diffusing $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloys. The β increased from $-0.5341\text{ \%}/\text{K}$ for the original mag-

nets to $-0.4609\text{ \%/K}$ and $-0.4939\text{ \%/K}$ for the $\text{Dy}_{70}\text{Al}_{10}\text{Ga}_{20}$ and $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ diffused magnets, respectively.

- (3) The optimized GB microstructure and $(\text{Dy}, \text{Pr}/\text{Nd})_2\text{Fe}_{14}\text{B}$ core-shell structure hardening around the main grains isolate the 2:14:1 phases, which are the main reasons for the great improvement of coercivity in the diffused magnets.
- (4) The decreased surface Dy enrichment and the optimized grain boundary microstructure lead to the smaller opening of the recoil loops by diffusing the $(\text{Pr}_{75}\text{Dy}_{25})_{70}\text{Al}_{10}\text{Ga}_{20}$ alloy. This indicates that the diffused magnet has a stronger capability for demagnetization.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/ma14102583/s1>, Figure S1: Demagnetization curve of the $(\text{Pr}_{100-x}\text{Dy}_x)_{70}\text{Al}_{10}\text{Ga}_{20}$ ($x = 0, 25, 50, 75, 100$) diffused magnets.

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