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Boundary structure modification and magnetic properties enhancement of Nd–Fe–B sintered magnets by diffusing (PrDy)–Cu alloy

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ABSTRACT

The grain boundary diffusion process was applied to the commercial sintered Nd–Fe–B magnets using $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ ribbons as direct diffusion source. The coercivities increased from 1114.4 kA/m for the original magnet to 1642.8 kA/m for the processed magnet by $Pr_{68}Cu_{32}$, higher than 1402.7 kA/m by $Dy_{70}Cu_{30}$. Microstructural investigations showed that the evident coercivity enhancement for the sample by $Pr_{68}Cu_{32}$ was mainly attributed to continuous intergranular layers isolating $Nd_2Fe_{14}B$ grains. Nevertheless, the coercivity enhancement of the sample by $Dy_{70}Cu_{30}$ was mainly resulted from the magnetic strengthening of the extensive layers in $Nd_2Fe_{14}B$ grains.

It is very essential to achieve Nd–Fe–B magnets with high coercivity at room temperature. The nucleation of magnetic domains from grain boundaries is a regular phenomenon, which causes magnetic reversal [1]. So the microstructure and chemistry of the grain boundary play an important role in coercivity of sintered Nd–Fe–B magnets.

The introduction of Dy element is a beneficial procedure to increase the magnetocrystalline anisotropy of the $Nd_2Fe_{14}B$ compound in the extensive layers of the $Nd_2Fe_{14}B$ grains where magnetization reversal starts. Recently, pure Dy metal [2] or its nonmetal compounds like Dy_2O_3 [3], DyF_3 [4], or DyH_2 [5] have been selected to form the so-called core–shell structure. Metal nanoparticles like Al [6], Cu [7], and $Al_{85}Cu_{15}$ [8] were also chosen as the intergranular additions to enhance corrosion resistance of sintered Nd–Fe–B magnets since they have higher standard electrode potentials than that of Nd. These metal or compounds with low melting points can also modify boundary structure by improving the wettability between intergranular phase and matrix phase, which isolates the $Nd_2Fe_{14}B$ grains in the magnet. Some investigations focused on Dy–metal compounds like $Dy_{73}Ni_{9.5}Al_{17}$ [9] and $Dy_{32.5}Fe_{62}Cu_{5.5}$ [10] by intergranular addition or grain boundary diffusion. The core–shell structure and more continuous grain boundary were achieved in the magnet by suitable annealing since these alloys have relatively low melting points. However, the anti-ferromagnetic coupling between Dy and Fe atoms causes reduction in overall remanence and magnetic energy product. The low reserves in the earth and high cost of Dy metal are also the obstacles. Recently, Nd–Cu and Pr–Cu alloys with low melting points were used for improving boundary microstructure and coercivity of HDDR [11], and hot deformed [12,13] and sintered [14,15] Nd–Fe–B magnets.

In this present work, the grain boundary diffusion process was applied to the commercial sintered Nd–Fe–B magnets using $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ alloys, respectively. Especially, the alloy ribbons prepared by melt-spinning technique were directly flatted on the upper and lower surfaces of the commercial magnet as direct diffusion source. The coercivity of the magnet significantly increased after boundary diffusing and annealing treatment. The influence of boundary microstructure modification on coercivity enhancement of the magnet was discussed.

The commercial Nd–Fe–B sintered magnets were used as the original magnets. The magnet was cut into cylinder shape with a dimensional size of Φ 8 × 5 mm^3 by wire-electrode cutting. The ingots used as diffusion source with the composition of $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ (at.%) were prepared by vacuum induction melting. Then the alloy ribbons were prepared by melt-spinning technique using the high vacuum quenching system with the copper roller speed about 8 m/s. The thickness of the ribbons was about 30 μm. The magnets and ribbons were polished by abrasive papers and cleaned by an ultrasonic cleaner in alcohol. The original magnets, covered by pieces of ribbons as diffusion source on the upper and lower surfaces, were set in the ceramic crucible. Then, these magnets were performed the diffusion treatment at 900 °C for 4 h following subsequent annealing at 500 °C for 2 h with the protection of high vacuum following high-purity argon. The alloy ribbons melted into liquid during diffusion treatment, which was beneficial to flow and diffuse, since the melting points of the $Pr_{68}Cu_{32}$ (472 °C), $Dy_{70}Cu_{30}$ (790 °C) and $Pr_{35}Dy_{35}Cu_{30}$ alloys were lower than the diffusing temperature. The room-temperature magnetic properties of the processed magnets by mechanical polishing were

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measured by a magnetic measurement device NIM-200C (National Institute of Metrology, PR China). Microstructural and compositional analyses were conducted by backscattered electron scanning microscopy (Carl Zeiss, Supra55) and electron probe microanalyzer (EPMA, JEOL, JXA-8230).

Fig. 1 shows the demagnetization curves of the original and processed magnets by diffusing $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ alloys following subsequent annealing. From Fig. 1, the intrinsic coercivities of all processed magnets increase significantly. The coercivity for the processed magnet by diffusing $Dy_{70}Cu_{30}$ alloy increases to 1402.7 kA/m from 1114.4 kA/m of the original magnet and the corresponding remanence decreases from 1.19 T to 1.15 T. The introduction of Dy element is beneficial to increase the magnetocrystalline anisotropy of the $Nd_2Fe_{14}B$ compound, especially in the extensive layers of the $Nd_2Fe_{14}B$ grains. Meanwhile, the introduction of Dy element results a slight decrease in remanence of the magnet. The coercivity of the processed magnet by diffusing $Pr_{68}Cu_{32}$ alloy increases from the original 1114.4 kA/m to 1642.8 kA/m and the corresponding remanence decreases from 1.19 T to 1.18 T. It is emphasized that the coercivity enhancement of the sample by diffusing $Pr_{68}Cu_{32}$ alloy is larger than that of the magnet by diffusing $Dy_{70}Cu_{30}$ alloy. It can be inferred that the magnetic hardening in the extensive layers of $Nd_2Fe_{14}B$ grains is not the main factor in the increase of coercivity for the sample by diffusing $Pr_{68}Cu_{32}$ since the anisotropy field of $Pr_2Fe_{14}B$ phase is only a little higher than that of $Nd_2Fe_{14}B$ phase. The coercivity of the processed magnets by $Pr_{35}Dy_{35}Cu_{30}$ alloys is slightly higher than that of the sample by $Pr_{68}Cu_{32}$, which is attributed to the joint advantages of Pr–Cu and Dy–Cu alloys.

To investigate the mechanism of coercivity enhancement, SEM images of the original and processed magnets by $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ alloys are shown in Fig. 2. Shown in Fig. 2 are SEM images of the transverse section about 100 μm from the surface of magnets. The original magnet shows the typical microstructure of sintered Nd–Fe–B magnet (shown in Fig. 2(a, b)), in which the dark gray regions are $Nd_2Fe_{14}B$ matrix phases and the brightly imaged regions correspond to Nd-rich intergranular phases. The interface between the Nd-rich layer and the main phase is not very well defined. These grain boundaries are relatively fuzzy and discontinuous. Fig. 2(c, d) corresponds to the processed magnet by $Pr_{68}Cu_{32}$ alloy. The interface between the (Nd,Pr)-rich layer and the $Nd_2Fe_{14}B$ phases is very clean and continuous. The intergranular phases spread around uniformly in the matrix phase, which is beneficial to diminish magnetic exchange interactions between neighbor grains. The continuous intergranular phase is formed because of the dissolution and diffusion of Pr and Cu elements into the intergranular phase adjacent to the $Nd_2Fe_{14}B$ grains. It is emphasized that the $Nd_2Fe_{14}B$ grains become rounder, indicating the improvement of wettability between intergranular phase and matrix phase. Fig. 2(e, f) corresponds to the processed magnet by $Dy_{70}Cu_{30}$ alloy. The Dy-rich shell microstructure and thicker intergranular phases can be observed, which is consistent with the previous work [16]. The coercivity of the processed magnet by $Dy_{70}Cu_{30}$ alloy is mainly improved due to enhancement of the anisotropy field in the Dy-rich shells. Fig. 2(g, h) corresponds to the processed magnet by $Pr_{35}Dy_{35}Cu_{30}$ alloy. The microstructural characterizations of the processed magnets by Pr–Cu and Dy–Cu alloys can be partly observed.

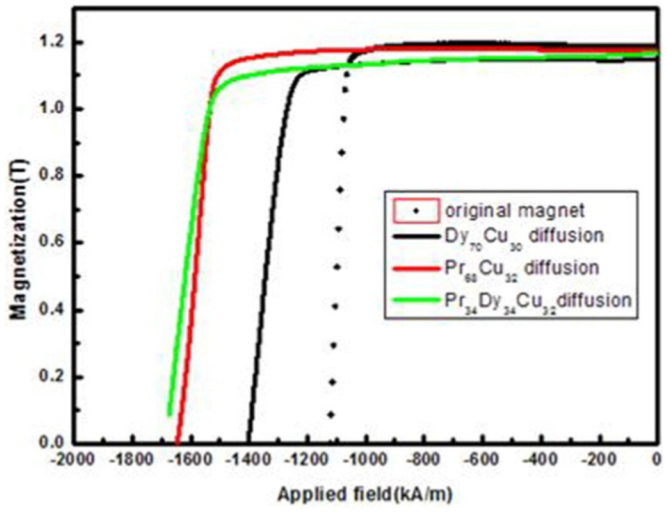

Fig. 1. The corresponding demagnetization curves of the original and processed samples by diffusing $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ alloys at 900 °C for 4 h and subsequent annealing at 500 °C for 2 h.

In order to further investigate the influence of boundary diffusing $Pr_{68}Cu_{32}$ and $Dy_{70}Cu_{30}$ alloys on microstructure and magnetic properties of the magnets, Fig. 3 shows the elemental distributions of Pr, Dy and Cu elements in the processed magnets. It can be observed that Pr distribution shown in Fig. 3(b) is slightly broader than that of Cu shown in Fig. 3(c). It indicates that the replacement of Pr atom occurs. The previous study showed this structure of Nd–Pr–Fe–Cu shell in hot-deformed magnet [13]. However, how these shells distribute along the grains in sintered magnet can't be known in this study. For the processed sample by $Dy_{70}Cu_{30}$ alloy (shown in Fig. 3(e, f)), Dy element enriches in a shell structure and distributes like continuous network and Cu element mainly concentrates in the boundary phase, consistent with the reports [2,9].

The evident coercivity enhancement of the processed magnets by diffusing $Pr_{68}Cu_{32}$, $Dy_{70}Cu_{30}$ and $Pr_{35}Dy_{35}Cu_{30}$ ribbons is achieved. However, the mechanisms of coercivity enhancement of the processed sample are different. The modified boundary microstructure plays a significant role in increasing coercivity of the magnet since the magnetocrystalline anisotropy field of $Pr_2Fe_{14}B$ phase is slightly higher than that of $Nd_2Fe_{14}B$ phase. Show in Fig. 2(c, d), the processed sample by $Pr_{68}Cu_{32}$ shows continuous intergranular phase surrounding $Nd_2Fe_{14}B$ grains, which inhibits magnetic exchange interactions between neighbor $Nd_2Fe_{14}B$ grains. From Fig. 2(e, f), the processed sample by $Dy_{70}Cu_{30}$ shows regular $(Nd,Dy)_2Fe_{14}B$ magnetic hardening shell surrounding the $Nd_2Fe_{14}B$ phase grains. The Dy-rich layer surrounding the $Nd_2Fe_{14}B$ grains has a higher magnetocrystalline anisotropy field, which can suppress the nucleation of reverse magnetic domains on the surface of the $Nd_2Fe_{14}B$ grains during the magnetic reversal process. However, it is worthy of emphasizing that the coercivity of the sample by diffusing $Pr_{68}Cu_{32}$ alloy reach 1642.8 kA/m, obviously higher than 1402.7 kA/m for the sample by $Dy_{70}Cu_{30}$. Meanwhile, as we all know, the reduction of remanence of the magnet is inevitable in process of heavy rare earth Dy element grain boundary diffusion process because of the formation of the Dy-rich shell structure in the surface of the grains adjacent to the grain boundary phase.

Fig. 4 shows the results of the temperature dependency of Hc for original, $Pr_{68}Cu_{32}$ diffusion and $Dy_{70}Cu_{30}$ diffusion magnets. The reversible temperature coefficients of coercivity (β) of the original magnet, $Pr_{68}Cu_{32}$ diffusion magnet and $Dy_{70}Cu_{30}$ diffusion magnet were −0.521%/°C, −0.511%/°C and −0.479%/°C in the range of 25–185 °C. As shown in previous work in hot-deformed magnet [13], when Pr diffuse into $Nd_2Fe_{14}B$ phase, the degradation of Hc at high temperature is slightly larger. Since we have not studied the processed magnets by Nd–Cu alloy, this result was not observed. However, the degradation of Hc by Pr–Cu alloy at high temperature is slightly lower than original magnet, which is consistent with the result shown in Ref. 13. For $Dy_{70}Cu_{30}$ diffusion magnet, the improvement of β can be attributed to the increased intrinsic property H_A, which is consistent with the result shown in previous study [17].

Using the Pr–Cu alloy with low melting point as diffusion source is a promising approach to produce high performance Dy-free Nd–Fe–B sintered magnets. The effect of Cu element on boundary microstructure modification of the magnet is significant. On the one hand, Cu element