Research articles

Significantly enhancing the coercivity of NdFeB magnets by ternary Pr-Al-Cu alloys diffusion and understanding the elements diffusion behavior

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ABSTRACT

Low melting point Pr-Al-Cu alloys were employed in grain boundary diffusion for sintered NdFeB magnets. The coercivity of the $7 \times 7 \times 2$ mm magnet was enhanced from 1000 kA/m to 1360, 1615, and 1714 kA/m by diffusing $Pr_{70}Al_{10}Cu_{20}$, $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ alloys, respectively, at 800 °C for 2 h followed by 500 °C for 3 h. The optimized microstructure with strip-like grain boundary phase was evident in diffused magnets, which helps to reduce the magnetic exchange interaction between the hard magnetic grains and improve the coercivity. Under the same diffusion process, the coercivity of the diffused magnets decreased with increasing sample thickness, but 27% coercivity enhancement can still be obtained in the magnet with 6 mm in height. A $\Phi 10 \times 10$ mm block magnet was diffused by $Pr_{70}Al_{20}Cu_{10}$ alloy at 800 °C for 2–10 h. Up to 49% enhancement in coercivity was achieved, which confirms the diffusion ability of Pr-Al-Cu alloy. The diffusion behavior of Pr, Al and Cu elements has been analyzed by Fick's law. Based on the diffusion coefficients obtained at 800 and 900 °C, Pr diffuses faster than Cu and Al along the grain boundary. The current results demonstrated that Pr-Al-Cu alloys can effectively optimize the grain boundary structure and improve the coercivity of NdFeB magnets.

1. Introduction

NdFeB permanent magnets have found a wide range of applications in engineering, electronics, information and energy industries for their high maximum energy product (BH)$_{max}$ [1–3]. To meet the requirements for the hybrid electric vehicles (HEVs) and wind power generators, many efforts have been made to further improve their coercivity and thermal stability. A common approach to enhance the magnetic properties of NdFeB magnets is to add heavy rare earth (HRE) elements like Dy and Tb into the magnet during alloying [4]. In this case, Dy or Tb partially substitutes Nd and increases the anisotropy field H_a of $Nd_2Fe_{14}B$ (2:14:1) phase, which is beneficial to coercivity and thermal stability. However, Dy or Tb substitution generally reduces the saturated magnetization M_s of 2:14:1 phase due to the antiferromagnetic coupling of Fe and Dy/Tb moments [5]. Moreover, resource scarcity and high price of HRE also make them unfavorable for preparing high performance magnets.

Recently, the grain boundary diffusion (GBD) process has been proposed to prepare high performance NdFeB magnets with reduced HRE content. In this process, the elements of diffusion source can selectively diffuse into the magnet along grain boundary, to modify the microstructure and enhance the coercivity without decreasing the remanence J_r [6]. Up to now, the coercivity enhancement by GBD has been successful based on different diffusion sources. In early time the Dy containing compounds like Dy_2O_3 [6], DyF_3 [6,7], Dy-H [8] and Dy-Ni [9] were employed by researchers. The formed Dy-rich hardening layer along 2:14:1 grain surface increases the magnetic anisotropy and reduces the magnetic interactions. Later on, some eutectic alloys like Nd-Cu [10] and Pr-Cu [11] were employed as the diffusion sources. These low melting point alloys show fast infiltration into the magnet when treated at the elevated temperature. The wettability of these alloys to NdFeB magnet is better than that of the previous Dy/Tb ones, and thus a smoothing afflux from the surface to the interior of the magnet can be easily obtained. The coercivity improvement is achieved by decoupling the magnetic grains and by decreasing the local demagnetization field through dissolving the edges and corners of the hard grains during liquid diffusion.

In addition, the effects of the low melting point metals on diffusion process are considerable. Pandian et al. [12] once reported that the alloying addition of non-rare earth elements Al, Ga, Cu, and Nb could also improve the coercivity of sintered NdFeB magnet. The doping elements Al and Cu have also positive effects on optimizing the

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distribution of grain boundary phases [13]. In our present work, Al has been chosen to partially substitute Cu in Pr-Cu eutectic alloy for GBD. The contributions of Al and Cu to coercivity enhancement have also been explored.

On the other hand, in most of the previous researches, the GBD process is employed in the small and thin magnets for limited diffusion depth. While for industrial application, large and thick block magnets are essential. Thus, fabricating the block magnets with high coercivity makes even more sense. In this work, we evidently optimized the coercivity of the Φ10×10 mm block magnet by Pr-Al-Cu alloy diffusion, and the height dependent coercivity has also been illustrated.

Heat treatment process plays a vital role in GBD process. Enhancing the coercivity of NdFeB magnet by simple post annealing is achieved by optimizing Nd-rich grain boundary phase distribution [14,15]. Diffusion depth is also an important parameter for achieving good results in GBD process. Therefore, controlling the diffusion process is very crucial for coercivity improvement. On HRE diffusion process, Gutfleisch et al. [16,17] calculated the diffusion coefficients of HRE elements in grain boundary, which gives references to diffusion rates of the elements and also provides the ideas to roughly determine the diffusion depth. However, the determination of diffusion coefficients of the elements in low melting point alloys during GBD has not been well studied yet. The diffusion kinetics and diffusion behavior of different diffusion sources in GBD process have not been well studied either. In this work, the diffusion rates and diffusion coefficients of various elements in Pr-Al-Cu alloy were investigated, which provide guidelines for designing an optimized diffusion process and obtaining an expected diffusion depth.

2. Experimental

A commercial sintered NdFeB magnet with the composition of $Nd_{26.74}Pr_{4.68}Fe_{67.16}Co_{0.72}Mn_{0.17}Al_{0.12}Ga_{0.11}Si_{0.11}Cu_{0.09}Zr_{0.09}B_{bal}$ (wt. %) (JingYueSanHuan Co. China) was used as the original magnet. The magnet was cut into Φ10×10 mm cylinders and 7 × 7 × h mm cuboids, where h ranges from 2 to 6 mm. The Pr-Al-Cu alloys with compositions of $Pr_{70}Al_{10}Cu_{20}$, $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ (at%) were prepared by arc melting in the protection of argon atmosphere. These alloys were cut into flakes with the same square as diffused magnets (c plane) and thickness of 0.4 mm as the diffusion sources. The mass ratios of the diffusion sources to the magnets are about 7–20 wt% and 4 wt% for the 2–6 mm thick blocks and 10 mm cylinders, respectively. The actual ratio in the magnets after diffusion is much less than these values since only a part of source was diffused into the magnets. The diffusion treatments were carried out at 800 °C ~900 °C for 2–10 h and followed by subsequent annealing at 500 °C for 3 h in the vacuum (10^{-2} Pa) tube furnace. The Φ2 mm cylindrical samples with the initial height were cut from the cuboid diffused magnets for vibrating sample measurement (VSM, PPMS-9, Quantum Design Co.). The magnetic properties of the GBD processed block cylinder Φ10×10 mm magnets were measured by a BH tracer (NIM-500C). The melting point of the alloys was characterized by differential scanning calorimetry (DSC). The microstructure was observed by scanning electron microscope (SEM, Zeiss Co.). The energy disperse spectroscopy (EDS) was used for quantitative analysis of element distributions.

3. Results and discussion

Fig. 1 shows the DSC results for diffusion source of $Pr_{70}Al_{10}Cu_{20}$, $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ alloys. The melting points of three alloys were determined as ~435 °C, and no significant difference was found. There are two exothermal peaks in the curve of $Pr_{70}Al_{20}Cu_{10}$ alloy, indicating the deviation of eutectic composition. Based on these results, the heat treatment temperature higher than 450 °C was employed for GBD process.
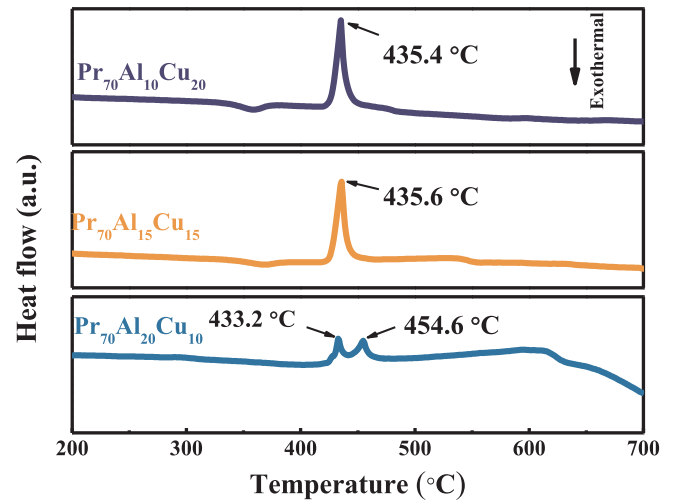

Fig. 1. DSC results of the $Pr_{70}Al_{10}Cu_{20}$, $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ diffusion alloys.

3.1. Magnetic properties and microstructure of thin magnets

The thin magnets with size of 7 × 7 × 2 mm were covered by the diffusion alloy flakes on top and bottom surfaces perpendicular to the easy axis (c plane) as a diffusion couple, then underwent diffusion heat treatment of 800 °C for 2 h followed by 500 °C for 3 h. Fig. 2(a) shows the room temperature demagnetization curves of the original magnet and Pr-Al-Cu diffused magnets. After diffusion treatment, the significant coercivity enhancement is obtained. The coercivity was enhanced from 1000 kA/m for the original magnet to 1360, 1615, and 1714 kA/m for the $Pr_{70}Al_{10}Cu_{20}$, $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ diffused magnets, respectively. The increments in H_c are 36%, 62% and 71%, respectively. At the same time, the remanence J_r drops from 1.36 T to 1.33, 1.20 and 1.14 T, respectively. The improved coercivity is attributed to the modified microstructure. The unexpected J_r decrease is suggested to be caused by the substitution of Pr for Nd as well as the increase volume fraction of non-magnetic phases in grain boundary [11]. More details will be discussed later based on the microstructure. The results demonstrate that the ternary low melting point Pr-Al-Cu alloys can work as ideal diffusion sources for the GBD process of NdFeB magnets. For applications in new energy industry like HEVs, the magnets with both high coercivity and high remanence are required. The high coercivity of the diffused magnets obtained in this work finally meets the requirement for HEVs.

Fig. 2(b) shows the temperature dependent remanences J_r and coercivities H_c at 300–450 K for the original magnet and Pr-Al-Cu diffused magnets. The temperature coefficients of remanence α and coercivity β at 300–390 K and 300–450 K were listed in Table 1. The temperature coefficients of remanence α do not seem to improve compared to the original magnet both at 300–390 K and 300–450 K, and the reason is attributed to the increased non-magnetic phase in the diffused magnets. However, the temperature coefficients of coercivity β show different behavior compared to coefficients of α. At low temperature range of 300–390 K, the value of β was improved from −0.74%/K for the original magnet to −0.73%/K and −0.71%/K for the $Pr_{70}Al_{15}Cu_{15}$ and $Pr_{70}Al_{20}Cu_{10}$ diffused magnets. The optimized microstructure of the diffused magnets is responsible for the improved temperature stability of coercivity at low temperature, which can be related to the BSE-SEM images in the next part. While at high temperature range of 300–450 K, the temperature coefficients of coercivity show no significant improvement for the diffused magnets. The reasons can be that, at temperature above 110 °C, the anisotropy field of $(Nd,Pr)_2Fe_{14}B$ phase which is formed by the substitution of Nd by Pr, is lower than the $Nd_2Fe_{14}B$ phase [11].