Microstructure evolution and coercivity enhancement of sintered Nd–Fe–B magnets by grain boundary diffusion with Cu aided TbF$_3$

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Abstract

Compared with the TbF$_3$ grain boundary diffusion (GBD) magnet, in this study, Cu aided TbF$_3$ GBD was applied to Nd–Fe–B magnets to further improve the coercivity. It is found that the coercivity increased sharply from 17.42 kOe to 25.43 kOe when the diffusion source is the mix powders of Cu and TbF$_3$, higher than 21.25 kOe with single TbF$_3$ as the diffusion source. The wettability of the grain boundary phases were improved owing to the accumulation of Cu in grain boundary. The grains were uniformly enveloped by grain boundary phase with the help of Cu addition. The microstructure analysis indicated that the diffusion depth of Tb increased significantly due to the modified grain boundaries which offered better tunnels for the diffusion of Tb.

1. Introduction

Due to their superior magnetic properties, sintered Nd–Fe–B magnets have been widely used in engineering applications such as motors, generators, actuators etc, since they were discovered in 1983 [1–4]. These application areas require magnets have an ability to work at high temperatures, so enhancing the coercivity is imperative to satisfy the thermal stability of sintered Nd–Fe–B magnets [3, 5, 6]. Adding heavy rare earth elements (HRE) [1] like Dy or Tb to the base alloy is a common method to improve the coercivity of a sintered Nd–Fe–B magnets, because the magnetic anisotropy field $H_A$ of Dy$_2$Fe$_{14}$B and Tb$_2$Fe$_{14}$B are 22 T and 14 T respectively, which is higher than that of Nd$_2$Fe$_{14}$B [7]. However, it is unsustainable to keep the overuse of Dy/Tb-added sintered magnets due to the high price and scarcity of Dy/Tb. In addition, adding heavy rare earths will dramatically reduce the remanence, because Dy/Tb could couple anti-ferromagnetically with the Fe in the RE$_2$Fe$_{14}$B lattice [8]. The grain boundary diffusion process is one of the effective and useful methods to enhance the coercivity of the Nd–Fe–B magnets with a small quantity of heavy rare earth and little sacrifice of remanence [9–12]. By HRE GBD, the (Nd, HRE)$_2$Fe$_{14}$B shell magnetically hardened the grains due to its higher anisotropy field [13]. However, the depth of HRE diffusion was restricted by the insufficient grain boundary phase which played as diffusion tunnels, and led to accumulation of HREs in the surface region [14]. It is a meaningful work to solve the problem.

The study of Pandian et al [15] indicated that introducing Al, Cu and Nb in grain boundary phase (GBP) can enhance the coercivity to optimize the wettability and continuity of the GBP. Goto et al [16] have demonstrated that addition of Cu into Nd–Fe–B magnet can promote the wettability of Nd-rich phases and then optimize boundary structure. It is well acknowledged that Cu element appeared mainly in grain boundary phases which can reducing the melting temperature of grain boundary phases then improved the flowability of Nd-rich phases [5, 17–19]. It is hopeful to optimize the boundary structure and improve the diffusing depth of Tb by introducing of Cu.

It is systematically considered that how the coercivity and the microstructure of sintered Nd–Fe–B magnets will be affected by the Cu aided TbF$_3$ grain boundary diffusion in this study. The reason for the significant coercivity enhancement will be discussed based on the observation.
2. Experimental

The original N52H sintered magnets were cut into $\Phi 30 \times 3$ mm cylinder. The magnets were cleaned in distilled water for 5 min ultrasonically, and then put into the nitric acid and alcohol (3 wt%) for 50 s. The samples after acidizing were washed by the distilled water and alcohol for 1 min, respectively. Finally, samples were dried by hot air. The magnet dip-coated in the TbF$_3$ powders with the average particle size of 1.7 $\mu$m mixed in alcohol was sample A. The Cu powder (Cuprum, 1-2 $\mu$m, 99.5% purity) and TbF$_3$ powder were evenly mixed in the ratio of 20:80 in wt% in alcohol and the magnet dip-coated in it was called sample B. The dip-coated samples were dried immediately. All the concentration of suspension was set as 20%. The coated samples in Al$_2$O$_3$ crucible were diffused at 920 $^\circ$C for 5 h diffusion treatment and subsequently annealed at 500 $^\circ$C for 3 h under a high vacuum of $10^{-3}$ Pa. And the reference sample underwent the same heat treatment process without GBD. Specimens of $\Phi 10 \times 3$ mm cylinder in size for measurement were cut close to the diffusion surface by wire-electrode cutting machine. The magnetic properties were measured by using an AMT-4 instrument. Backscattered electron images and the element compositions distribution were conducted by scanning electron microscopy (FESEM, Inspect F50) equipped with an energy dispersive spectrometer (EDS). The elements mappings determined by Electron probe microanalyzer (EPMA-1720H).

3. Results and discussion

The demagnetization curves and magnetic properties of the A magnet, B magnet and the reference magnet are shown in figure 1. It can be seen that the remanence of both A and B magnets reduce a little compared with the reference magnet, and this result is principally induced by the anti-ferromagnetic coupling between Tb and Fe atoms in the (Nd, Tb)$_2$Fe$_{14}$B shell [20, 21]. The coercivity of the A magnet shows a distinct increase from 17.42 kOe to 21.25 kOe compared with the reference magnet. As for the B magnet, surprisingly, there was a noteworthy increase of coercivity (17.42 kOe to 25.43 kOe). It would be of interest to unveil the reason, by which the Cu aided can affect the properties of the sintered magnets, through microstructure investigation.

Figure 2 shows cross-sectional SEM images and EPMA mapping images of Cu, Nd and Tb elements in A and B samples, at 20 $\mu$m from the diffusion surfaces. As shown in figure 2(a), the region with the dark contrast is the Nd$_2$Fe$_{14}$B main phase and the brighter region is the RE-rich phase in the A magnet. The bright intergranular phases are not obvious between the adjacent grains. However, the phenomenon is quite different in B magnet shown in figure 2(b). The matrix grains are fully surrounded by the continuous Nd-rich phase due to the thicker intergranular phases. As shown in figure 2, the distinct core–shell structure in the BSE image was well developed at the A magnet and B magnet, the Tb-rich phase are surrounding the dark Nd$_2$Fe$_{14}$B grains. Nd element mainly distributes in the core structure. From the distribution of Cu element, it is obvious to observe the Cu enrichment in the GBs, which can improve the wettability of the grain boundary phases due to the low melting temperature of grain boundary phases [16]. So Tb-rich shells distribute clearly among GBs and then reduce the magnetic coupling of Nd$_2$Fe$_{14}$B grains and impede effectively the propagation of reversed domain walls through the magnetic phase grains. The better separation and decoupling of hard magnetic grains contribute to the enhancement of
The coercivity of Nd–Fe–B magnets [22–24]. The Cu and Tb enrichment in the grain boundaries shows that the grain boundary diffusion has been promoted with the help of Cu. This suggests that the optimized boundary phase isolating 2:14:1 grains by Cu addition is helpful to enhance the coercivity.

Figure 3 shows cross-sectional EPMA Tb mapping images of (a), (b) the A magnet, and (c), (d) B magnet. It is obvious to see in figure 3(b), Tb was principally distributed in the surface of the magnet and surround the main phase in the A magnet. In contrast, it was observed that the Tb element has a deeper diffusion depth in B magnet (figure 3(d)). As the diffusion depth increases, the GBs and the shell structures become thinner in both the A and the B magnet. The Tb-rich shell disappeared in 50 μm from the diffusion surface in the A magnet, whereas in about 200 μm from the diffusion surface in the B magnet. It implies that grain boundary phases as diffusion tunnels markedly affect the diffusion depth of Tb and Tb element diffused deeper in B magnet than the A magnet, indicating that TbF₃ and Cu co-addition can improve the coercivity more effective than individual pure TbF₃ addition, as shown in figure 1. Consequently, the coercivity was enhanced by adding Cu during the dip-coating owing to the deeper diffusion depth of Tb.

The Tb concentrations along the diffusing direction were characterized EDS analysis (figure 4). Figure 4 shows that as the depth increase, Tb concentrations has a sharply decrease in the A magnet. However, the variation of Tb concentration in B magnet gently decrease with increase of the distance, the diffusing depth of B magnet is deeper than that of A magnet. It indicated that the sufficient diffusion of Tb during the grain boundary diffusion was strongly dependent on mobility of the grain boundary phases.

Figure 5 shows the cross-sectional BSE images and EDS line profile of A and B magnet, with GB diffusion of Tb at a depth of 20 μm from the surface. The Tb-rich shells in A magnet is thinner than that in B magnet, and there are little variation of the elements content in A magnet (figure 5(a)). As shown that in figure 5(b), Tb diffuses into the surface of the magnet through the grain boundaries, and forms Tb-rich shells around the grain boundaries of the main phase by substituting for Nd. The thickness of the Tb-rich shell is about 1–2 μm. Tb
content between the shell and core areas was considerable difference, this higher content of Tb in the shell could be conducive to the coercivity improvement, because it is generally believed that the mechanism of magnetic reversal in the sintered Nd$_2$Fe$_{14}$B magnet is nucleation of reverse magnetic domains in the grain boundary area [25–27]. Tb diffusion into the magnet became difficult when the GBs of the magnets were not optimal. However, the GBs can be modified by Cu aided, leading to the increasing diffusion depth of Tb. As the result, the coercivity of sintered magnets could enhance by GBD with the Cu added.

4. Conclusions

It is an effective way to enhance the coercivity of sintered Nd–Fe–B magnets by grain boundary diffusion process with Cu and Tb. On the one hand, it is beneficial to enhance the coercivity due to the formation of the core–shell structure in the magnet. On the other hand, the microstructure of the magnet was optimized with Cu aiding. By Cu aided, the grain boundaries adequately isolate the adjacent grains owing to the homogeneously distributing of Cu, and the diffusion depth of Tb was significantly improved. Improvement of decoupling with the continuous grain boundary phase and forming the (Nd, Tb)$_2$Fe$_{14}$B phase in the outer region of the matrix grain both contribute to enhancing the coercivity.

**Figure 4.** Tb content variation depth of A magnet and B magnet after GBD process.

**Figure 5.** The BSE-SEM image of A and B magnet with the EDS line scan profiles of Fe, Nd, Tb and Cu taken from line 1 and line 2 in (a), (b).
The coercivity was increased from 17.40 kOe to 25.29 kOe for the Cu aided TbF₃ grain boundary diffusion magnet, significantly higher than 21.25 kOe of TbF₃ grain boundary diffusion magnet with nearly no reduction of the remanence. Due to the restriction of Tb diffusion depth, it will be helpful to enhance the coercivity of the sintered Nd–Fe–B magnets by Cu aided TbF₃ grain boundary diffusion process which can improve the utilization of Tb.

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