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Coercivity Enhancement of Sintered Nd-Fe-B Magnets by Grain Boundary Diffusion with DyH_3 Nanoparticles

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Grain boundary diffusion technique with DyH_3 nanoparticles was applied to fabricate Dy-less sintered Nd-Fe-B permanent magnets with high coercivity. The magnetic properties and microstructure of magnets were systematically studied. The coercivity and remanence of grain boundary diffusion magnet were improved by 60% and reduced by 7% compared with those of the original magnet, respectively. Meanwhile, both the remanence temperature coefficient (α) and the coercivity temperature coefficient (β) of the magnets were improved after diffusion treatment. Investigation shows that Dy is preferentially enriched as $(Nd, Dy)_2Fe_{14}B$ phase in the surface region of the $Nd_2Fe_{14}B$ matrix grains indicated by the remarkable enhancement of the magneto-crystalline anisotropy field of the magnet. As a result, the magnet diffused with a small amount of Dy nanoparticles possesses enhanced coercivity without remarkably sacrificing its magnetization.

Keywords : grain boundary diffusion, DyH_3 nanoparticles, coercivity, thermal stability

1. Introduction

Sintered Nd-Fe-B permanent magnetic alloys are widely used in many fields including electric, electronic, instrument, and medical devices because of their excellent magnetic properties [1]. However, this kind of magnets can usually be used below 100 °C owing to their undesirable thermal stability, which is still a major concern in some practical application such as high temperature electromechanical devices. It is well known that the addition of heavy rare earths (Dy or Tb) is effective to enhance coercivity (H_{ci}) [2-6]. Unfortunately, this method simultaneously results in considerable degradation of the remanence of the magnets and increase of the cost due to more Dy or Tb contents. Recently, techniques for enhancement of coercivity of sintered Nd-Fe-B magnets by diffusing a continuous layer of Dy or Tb onto the surface of the $Nd_2Fe_{14}B$ matrix grains without obvious reduction of the remanence have been developed by different researchers [7-9]. Previous investigations focus on micro-size Dy_2O_3, DyF_3 and TbF_3 powders diffusion. However, little is known concerning effects of nano-particles diffusion on the magnetic property of the Nd-Fe-B permanet magnets. Here we report the effect on the magnetic property of sintered Nd-Fe-B magnets by grain boundary diffusion with DyH_3 nano-particles.

2. Experiments

Nd-Fe-B powders with nominal composition of $Nd_{22.5}$-$Pr_{6.6}Dy_{0.7}Fe_{bal}Cu_{0.1}Co_{0.8}Ga_{0.1}B_{1.0}$ were prepared by induction melting, hydrogen decrepitating, jet milling, and magnetic alignment. The green compacts were then sintered at 1060 °C for 3 hours and subsequently annealed at 900 °C and 480 °C for 2 hours and 1 hour, respectively. Blocks of Nd-Fe-B sintered magnets were cut into thin slices with the dimension of 1 mm × 3 mm × 4 mm. Then the magnets were etched with a nitric acid solution. DyH_3 nano-particles were prepared by inert gas condensation method, and then were mixed with ethyl alcohol in a ratio of 50:50 in weight. Fig. 1 shows the TEM images of DyH_3 nanoparticles. Most of DyH_3 nanoparticles are 50-100 nm in diameter. The magnets were immersed in the mixture with applying ultra sonic for two minutes, and dried immediately by a hot air. Powder coated magnets were heat-treated at 600-950 °C for 7 h under Ar atmosphere. Magnetic properties were measured using a vibrating sample magnetometer after applying a pulsed field of 3 T. The microstructure the magnets were

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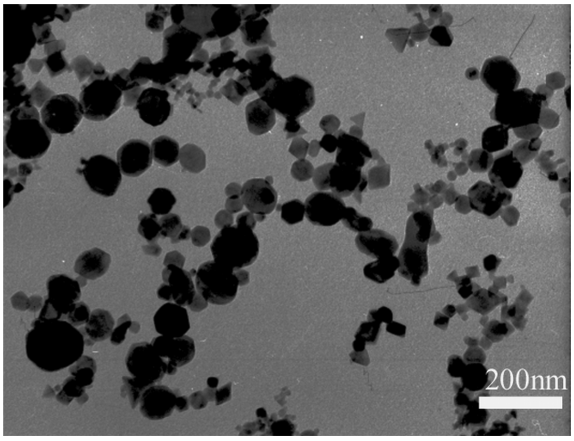


Fig. 1. The TEM images of DyH_3 nanoparticles.

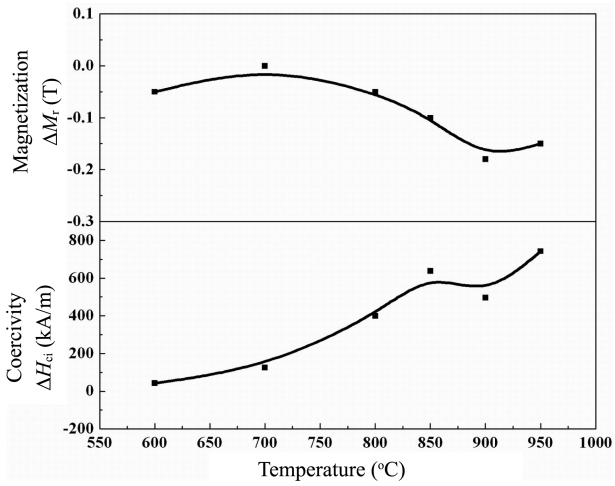


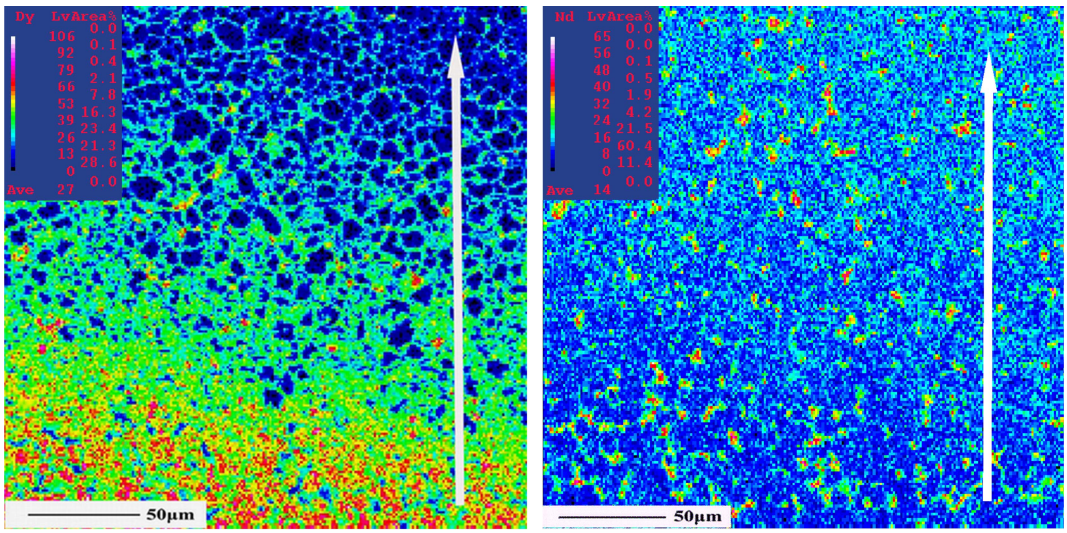
Fig. 2. The influence of heat treatment temperature on the magnetic properties of the magnets after grain boundary diffusion process with DyH_3 nanoparticles.

analyzed using Electron Probe Microanalyzer (EMPA) and Energy Dispersive X-Ray Spectroscopy (EDX). To investigate the influences of Dy content and distribution on the magnetic properties of the magnets, different thickness of the surface of grain boundary diffusion processed magnets were removed by abrasive paper and the magnetic properties were measured by VSM. The thickness of the samples were measured by micrometer and the measurement error was less than 5%.

3. Results and Discussion

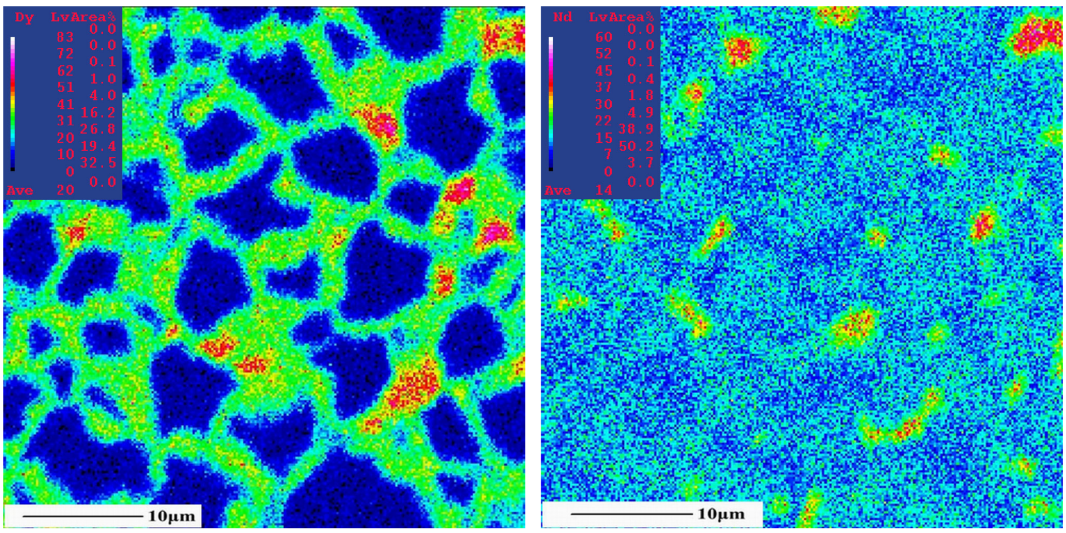
Figure 2 shows the influence of heat treatment temperature on the magnetic properties of the magnets after grain boundary diffusion process with DyH_3 nanoparticles. It shows that increasing the heat treatment temperature results in gradual augment of the coercivity of the magnets, while the remanence of the magnets drops simultaneously. Considering the factors of the coercivity and remanence, the heat treatment temperature was optimized at 850 °C. The coercivity of the magnets increases 637 kA/m (60%), while the remanence of the magnets reduces 0.1T (7%) compared to the original magnets.

To clarify the distribution of the Dy element in the Nd-Fe-B magnet, the concentration distribution of Nd and Dy elements was examined, and the results were shown in Fig. 3 and Fig. 4. The Dy content of the magnets form the surface to the internal was analyzed by EDX quantitative as



(a) (b)

Fig. 3. (Color online) The corresponding compositional profiles of a) dysprosium and b) neodymium taken from a portion of a magnet after grain boundary diffusion process with DyH_3 nanoparticles at the depth from 0ìm to 200 μm.



(a) (b)

Fig. 4. (Color online) The corresponding compositional profiles of (a) dysprosium and (b) neodymium taken from a portion of a magnet after grain boundary diffusion process with DyH_3 nanoparticles at a depth of 100 μm from the surface.

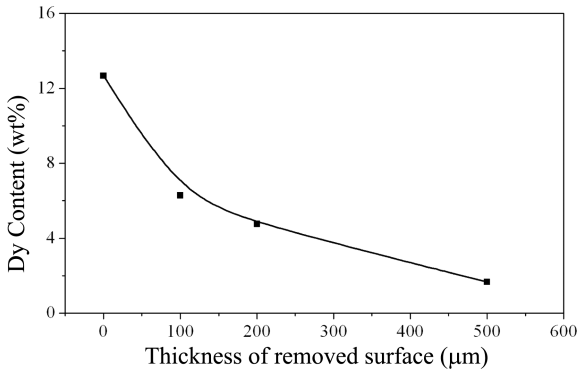


Fig. 5. Dy content changes in the magnet after grain boundary diffusion process with DyH_3 nanoparticles.

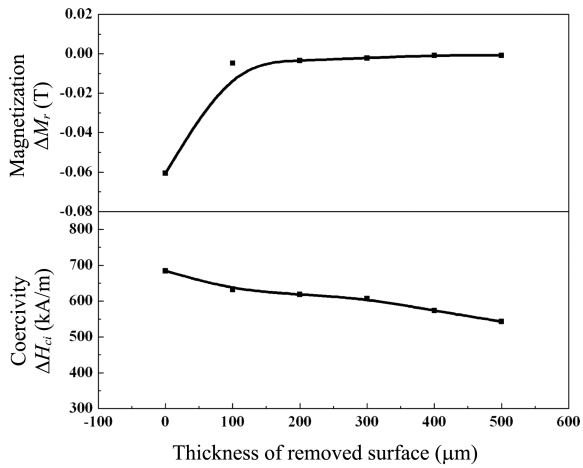


Fig. 6. Remanence and coercivity plotted against a thickness of removed surface of the grain boundary diffusion processed magnets with DyH_3 nanoparticles.

shown in Fig. 5. It is found that Dy diffuses into the inside of the magnet through the grain boundary phase, and forms Dy-rich shells around the grain boundary of the $Nd_2Fe_{14}B$ grains by substituting Nd. The Dy content is about 12.7 wt. % in the surface of the magnet. Dy element enriches in the main phase grain, resulting in significantly reducing of the remanence. As the diffusion depth increasing, Dy content gradually reduces form the surface to the internal. At the 100 μm depth position, Dy content is about 6.28 wt. % and most Dy element enriches in the surface region of $Nd_2Fe_{14}B$ grains and is expected to exist as $(Nd, Dy)_2Fe_{14}B$ phase. This result confirms that Dy elements diffuse into the internal along the grain boundary and preferentially distribute in the surface region of the main phase. At the 500 μm depth position, Dy content is only 1.7 wt. %.

Remanence and coercivity plotted against a thickness of removed surface of the grain boundary diffusion processed magnets with DyH_3 nanoparticles were shown in Fig. 6. The remanence after removing the surface layer of 100 μm showes same value as that of the original magnet. It is considered that the degradation of the remanence of the magents is due to a large number of Dy substituting Nd in the surface of the magnets and forming $(Nd, Dy)_2Fe_{14}B$ phase bearing lower M_s compared to $Nd_2Fe_{14}B$ phase. As the diffusion depth increasing, the amount of Dy element diffusion into the $Nd_2Fe_{14}B$ phase gradually decrease and no longer cause significant on remanence. On the other hand, the improvement of coercivity gradually reduces as the depth increasing. Even though the surface layer of more

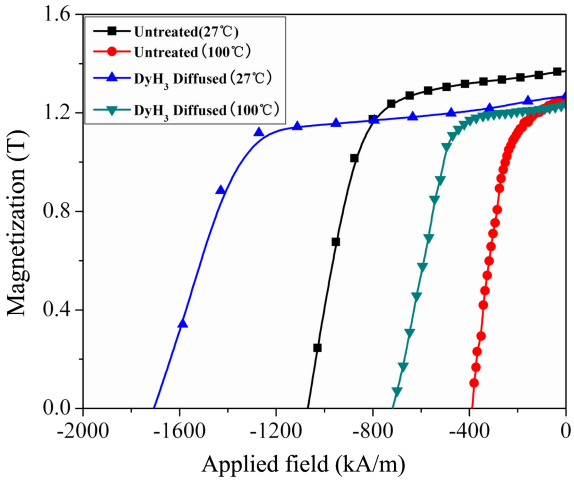


Fig. 7. (Color online) Demagnetization curves of the original magnet and magnet after grain boundary diffusion process with DyH_3 nanoparticles at different temperatures.

than 500 μm is removed, the improvement of the coercivity is also 543 kA/m (50%). At the internal position, the Dy element enriches in the surface region of $Nd_2Fe_{14}B$ grains and is expected to exist as $(Nd, Dy)_2Fe_{14}B$ phase. As Kronmüller pointed out [10], the crystal anisotropy of the magnetic grains surface region, which is always lower than that of inside the grains, may lead to an obvious reduction of the magnetic reversal nucleation field, H_N, and subsequent the coercivity of the magnet. In our case, the surface regions of the $Nd_2Fe_{14}B$ grains were enriched with $(Nd, Dy)_2Fe_{14}B$ phase with strong crystal anisotropy. The H_N and the coercivity of the Nd-Fe-B sintered magnet diffused by Dy nano-particles were therefore enhanced noticeably. It can be considered that the improvement of coercivity depends on the forming of $(Nd, Dy)_2Fe_{14}B$ phase in not only $Nd_2Fe_{14}B$ grains but also the surface region of the $Nd_2Fe_{14}B$ grains and the later plays an important role.

Demagnetization curves of the magnets before and after grain boundary diffusion process with DyH_3 nanoparticles at different temperatures were measured. As shown is Fig. 7, both magnets exhibit lower magnetic properties at 100 °C than those at 27 °C. The magnets after grain boundary diffusion process with DyH_3 nanoparticles possess higher coercivity than that of original magnet at 27 °C and 100 °C. Reversible temperature coefficients were calculated in Table 1. The results show that the remanence temperature coefficient (α) and the coercivity temperature coefficient (β) of magnets after grain boundary diffusion process are reduced from –0.11 to –0.03%/°C and from –0.87 to –0.79%/°C between 27 °C and 100 °C, respectively. It is concluded that the grain boundary diffusion magnets exhibit better thermal stability than original magnets.

4. Conclusions

In summary, high coercivity magnets without obvious degradation of the remanence were fabricated by applying grain boundary diffusion technology with DyH_3 nanoparticles. The coercivity increased by more than 637 kA/m (60%) compared to original magnets. Meanwhile, both the remanence temperature coefficient (α) and the coercivity temperature coefficient (β) of the Nd-Fe-B magnet were improved after diffusion treatment. The diffusion Dy element was found to preferentially enrich as $(Nd, Dy)_2Fe_{14}B$ phase in the surface region of the $Nd_2Fe_{14}B$ matrix grains. The special distributed $(Nd, Dy)_2Fe_{14}B$ phase was expected to improve the coercivity of the Nd-Fe-B magnet by enhancing both the H_A and the H_N of the magnet during demagnetization process.

Acknowledgments

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Table 1. The magnetic properties and temperature coefficient of the original magnet and magnet after grain boundary diffusion process with DyH_3 nanoparticles.

	H_{ci} [kA/m]		M_r [T]		α [%/°C]	β [%/°C]
Temperature	27 °C	100 °C	27 °C	100 °C	27-100 °C	27-100 °C
Untreated	1068	386	1.37	1.26	-0.11	-0.87
DyH_3 Diffused	1705	717	1.27	1.24	-0.03	-0.79

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