Low Melting-point Diffusion Salts of Heavy Rare-earth for Enhancing Coercivity of Grain-boundary-diffusion-processed Nd-Fe-B-type Magnet

J. Y. Choi[1], H. W. Kwon[1]*, B. A. Kim[1], and J. G. Lee[2]*

[1]*Pukyong National University, Busan 48513, Republic of Korea*
[2]*Korea Institute of Materials Science, Changwon 51508, Republic of Korea*

Effective low melting-point Dy-diffusion for grain boundary diffusion treatment for enhancing coercivity in Nd-Fe-B-type magnet was found in the DyF$_3$–LiF binary system. Efficacy of the low melting-point (DyF$_3$–LiF) diffusion source as Dy-diffusion source for enhancing coercivity in the diffusion processed Nd-Fe-B-type magnet was investigated. Speedier and more profound coercivity enhancement in the Nd-Fe-B-type magnet was achieved by grain boundary diffusion using the low melting-point (DyF$_3$–LiF) diffusion source with respect to solid DyF$_3$ single salt. Since the liquid in the (DyF$_3$–LiF) mixture contained plenty of Dy atoms already freed from DyF$_3$ and they were in better contact with magnet, speedier and profuse diffusion of Dy atoms through Nd-rich grain boundary was possible in the magnet coated with low melting-point (DyF$_3$–LiF) diffusion source.

Keywords : Nd-Fe-B magnet, grain boundary diffusion, liquid diffusion source

1. Introduction

Nd-Fe-B-type magnet has been almost exclusively used for rotor magnet in traction motor of HEV and EV, but it still has one big drawback: poor thermal stability (large temperature coefficient of coercivity (β)) due to low Curie temperature (T_c = 312 °C). Operating temperature (> 150 °C) of the rotor magnet is overly high given the unsatisfactorily low T_c. Current standard approach for solving this problem is sufficiently enhancing room temperature coercivity mostly by means of grain boundary diffusion (GBD) of heavy rare-earth (HRE), such as Tb or Dy [1-6]. Commonly used diffusion sources of the HRE for GBD are HRE fluoride or oxide salts. As these salts exist as solid during GBD process, diffusion of HRE towards interior of magnet is bound to be inherently sluggish. We have been hard to escape the idea that more homogeneous and speedier diffusion of HRE would be achievable if the HRE diffusion sources in liquid form is available. By a lucky chance, we could find good candidate of Dy-diffusion source in DyF$_3$–LiF binary salt system, which became liquid in the course of GBD annealing. In

this study, efficacy of using liquid phase Dy-diffusion source for enhancing coercivity in the GBD-processed Nd-Fe-B-type magnet was investigated.

2. Experimentals

Dy-diffusion source, which became partially liquid, was searched in two-phase region (solid DyF$_3$ + liquid (DyF$_3$–LiF)) above peritectic line in the DyF$_3$–LiF binary system [7]. The (DyF$_3$–LiF) mixture with composition placed on the peritectic line (measured to be 806 °C) contains varying amount of DyF$_3$ diffusion source depending on its composition and is considered to be the perfect fit for the present study. DyF$_3$ and LiF salts (particle size: ~1 μm) were thoroughly mixed in ethanol to prepare salt suspension (salts : alcohol = 5 g : 50 ml) for coating. Commercial (Nd,Pr)-Fe-B-Si-Al sintered magnet (12 × 12 × 2 mm^3) was coated using the salt suspension by dip-coating technique. Amount of coated salts was controlled to be approximately 2 wt.% relative to magnet mass. Magnet coated with the salts was dried and annealed at 820 °C in vacuum and quenched, and then followed by aging at 550 °C for 1 hr. Annealing temperature (820 °C) was chosen on the basis of necessity that not only it has to be above the peritectic temperature for having liquid phase, but also it has not to be too high so as to avoid the risk of undesirable grain growth during annealing. Magnetic

measurement was performed using a vibrating sample magnetometer (VSM) after magnetizing with 5 Tesla pulsing field. Microstructure and elemental analysis were performed by a scanning electron microscope (SEM) and an electron probe microanalysis (EPMA).

3. Results and Discussion

The (DyF$_3$–LiF) mixtures used as Dy-diffusion source have varying amount of liquid depending on its composition at GBD-annealing temperature of 820 °C. In order to find (DyF$_3$–LiF) mixture with optimum amount of liquid, starting magnet was coated with the (DyF$_3$–LiF) mixtures with varying amount of liquid and annealed at 820 °C for 9 hrs. Amount of liquid in the (DyF$_3$–LiF) mixtures was estimated according to lever rule on the tie-line at annealing temperature (820 °C) in the (solid DyF$_3$ + liquid (DyF$_3$–LiF)) two-phase region above peritectic line. Figure 1(b) shows dependence of magnetic performance of the GBD-treated magnet on the amount of liquid in coated (DyF$_3$–LiF) mixtures. The (DyF$_3$–LiF) mixtures having 10 vol.% liquid appeared to be the most efficient Dy-diffusion source in regard with enhancing coercivity, which is the primary purpose of GBD. Figure 2 shows comparison of efficacy of solid DyF$_3$ single salt and (DyF$_3$–LiF) mixture (10 vol% liquid) on performance enhancement of the magnet. Also included is variation of magnetic performance of the magnet without salt coating for comparison. It was apparent that GBD using both the Dy-containing single salt and salt mixture had markedly improved coercivity at the little cost of remanence and energy product. Noteworthy finding was that speedier and consistently more profound coercivity enhancement was achieved by the low melting-point (DyF$_3$–LiF) diffusion source with respect to solid DyF$_3$ single salt.

For better discussion on the speedier and more pro-

found coercivity enhancement by the liquid Dy-containing diffusion source, understanding of origin of coercivity enhancement in Nd-Fe-B-type magnet by GBD using HRE (Dy, Tb) can be of great assistance. It has been known that coercivity enhancement by GBD using Dy is attributed to substitution of Nd atoms by Dy atoms near surface of the Nd$_2$Fe$_{14}$B-type grains in the magnet [3-5]. By the substitution, Dy-substituted (Nd,Dy)$_2$Fe$_{14}$B shell forms near surface of the Nd$_2$Fe$_{14}$B-type grains, and this shell region has highly enhanced anisotropy field [8, 9]. Thanks to the shell region with high anisotropy field, nucleation of reverse domain and/or domain wall propagation across the Nd$_2$Fe$_{14}$B-type grains under opposite applied field is profoundly suppressed, hence enhancing coercivity. Since Dy, Li fluorides were used as Dy-source and liquid forming agent, a concern regarding the effect of lithium and fluorine on magnetic performance of the GBD-treated magnet would arise. In relation to influence of Li and F in the coated mixture, it has been known that they barely influence magnetic performance of the GBD-treated magnet [10, 11]. For speedy and profuse diffusion of Dy atoms, quick and unlimited supply of Dy atoms from the Dy-source (DyF$_3$) in coated salt is critically needed. As for how Dy atoms separate from the coated DyF$_3$ and migrate inward through grain boundary, it has been previously revealed that Dy atoms are separated from the coated Dy salt (DyF$_3$) by exchange reaction with Nd atoms mostly from the Nd-rich grain boundary phase in the magnet, which is liquid during annealing: Nd atoms preferentially bind with fluorine in DyF$_3$ to form NdF$_3$ instead and release Dy atoms [11-13]. Freed Dy atoms then diffuse inward via liquid grain boundary phase (melting point: ~650 °C) to substitute Nd atoms in the surface of Nd$_2$Fe$_{14}$B-type grains and to form (Nd,Dy)$_2$Fe$_{14}$B shell. The low melting-point (DyF$_3$–LiF) diffusion source coated on the magnet was believed to have plenty of Dy
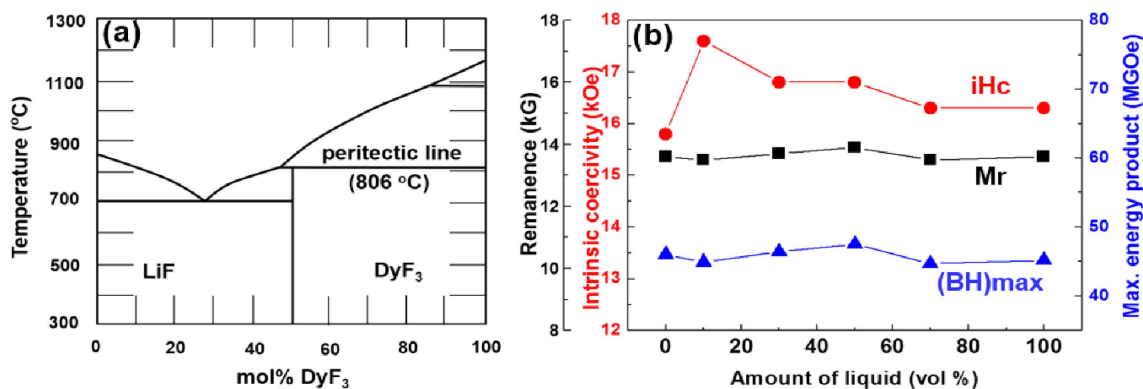

Fig. 1. (Color online) (a) Phase diagram of DyF$_3$–LiF binary salt system redrawn from ref. 7. (b) Dependence of magnetic performance of the GBD-treated (Nd,Pr)-Fe-B-Si-Al sintered magnet on the amount of liquid in coated (DyF$_3$–LiF) mixtures.
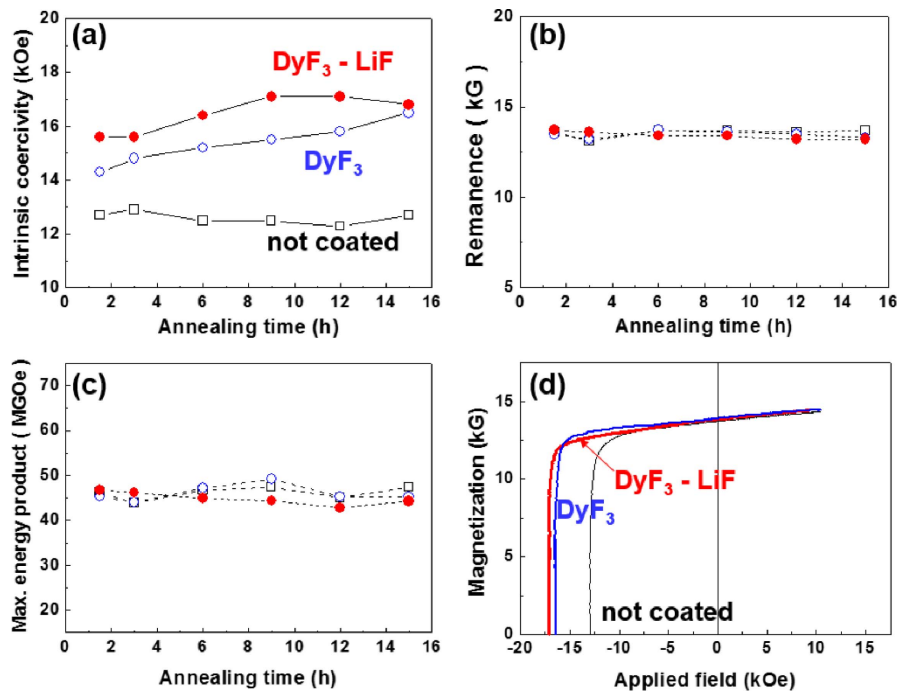
Fig. 2. (Color online) (a, b, c) Comparison of efficacy of solid DyF$_3$ single salt and (DyF$_3$–LiF) mixture (10 vol% liquid) on performance enhancement of the GBD-treated (Nd,Pr)-Fe-B-Si-Al sintered magnet. (d) Demagnetization curves of the magnets with peak coercivity after GBD using the salts.
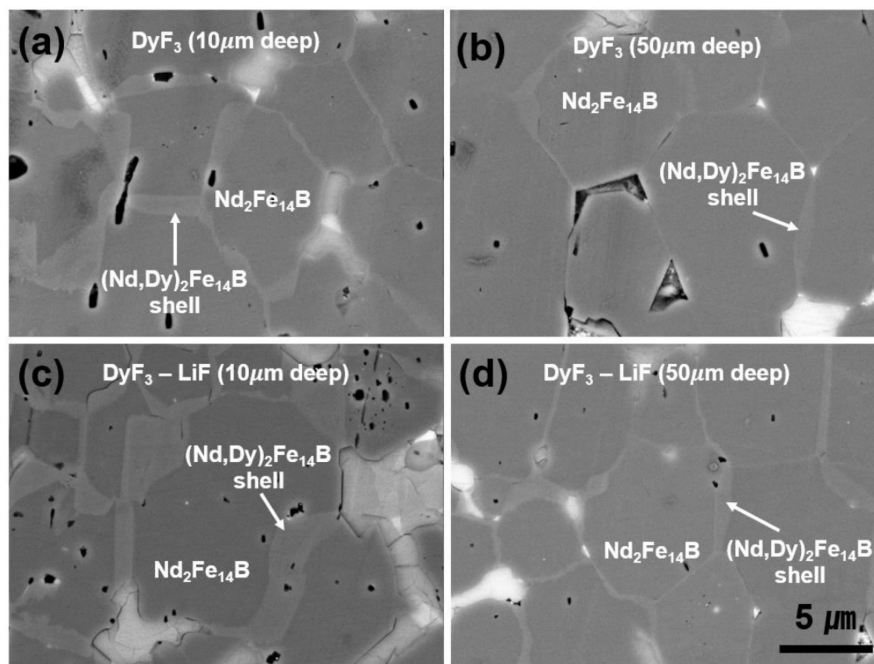

Fig. 3. SEM(BSE) photos showing Dy-substituted (Nd,Dy)$_2$Fe$_{14}$B shell on the surface of Nd$_2$Fe$_{14}$B-type grains in the regions near surface of the GBD-treated (Nd,Pr)-Fe-B-Si-Al magnet coated with (a, b) solid DyF$_3$ and (c, d) low melting-point (DyF$_3$–LiF) diffusion source, respectively. (a, c) 10 μm, (b, d) 50 μm deep from surface.

atoms in it, that were already freed from DyF$_3$ and existed probably as cation. The Dy atoms were in good contact with magnet with help of liquid and could diffuse more

swiftly and actively through the Nd-rich grain boundary which was liquid. On the other hand, since the DyF$_3$ of single salt coated on magnet still existed as solid during
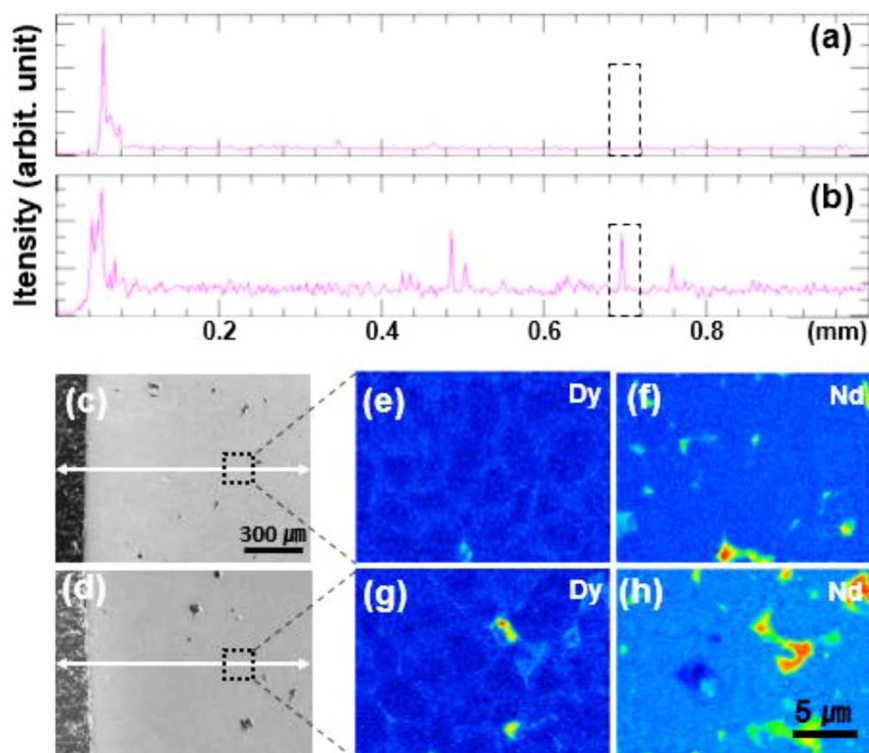
Fig. 4. (Color online) EPMA line analysis, BSE image, and x-ray mapping showing distribution of Dy atoms in the GBD-treated (Nd,Pr)-Fe-B-Si-Al magnet coated with solid DyF_3 (a, c, e, f) and with low melting-point (DyF_3–LiF) diffusion source (b, d, g, h), respectively.

annealing, reaction between solid DyF_3 and Nd atoms from the liquid grain boundary phase to free Dy atoms was first needed to be completed before diffusion started. This reaction made whole diffusion process sluggish. Therefore, speedier, more active and more homogeneous diffusion of Dy had probably been accomplished in the magnet coated with low melting-point (DyF_3–LiF) diffusion source, leading to more profound coercivity enhancement.

Figure 3 shows Dy-substituted $(Nd,Dy)_2Fe_{14}B$ shell formed on the surface of $Nd_2Fe_{14}B$-type grains in the regions near surface of the magnet GBD-treated using solid DyF_3 single salt and low melting-point (DyF_3–LiF) diffusion source. It was apparent that thicker and more homogeneous Dy-substituted shell near surface of the $Nd_2Fe_{14}B$ grain formed in the magnet coated with low melting-point (DyF_3–LiF) diffusion source with respect to the magnet coated with solid DyF_3 single salt. This is surely a telltale evidence clarifying speedier and more active diffusion of Dy in the magnet coated with low melting-point (DyF_3–LiF) diffusion source. Figure 4 shows Dy distribution in the magnet GBD-treated using solid DyF_3 single salt and low melting-point (DyF_3–LiF) diffusion source. Line analysis of Dy atoms was performed along thickness direction from surface to the point near

center of the magnet (2 mm thick). The line analysis evidently revealed that more Dy atoms had diffused farther into interior in the magnet coated with low melting-point (DyF_3–LiF) diffusion source: many Dy atom peaks with high intensity were observed at farther deep points from surface in the magnet coated with low melting-point (DyF_3–LiF) diffusion source. X-ray elemental mapping of Dy also revealed more profuse Dy diffusion in the magnet coated with low melting-point (DyF_3–LiF) diffusion source. X-ray elemental mapping of Dy was analysed on the spot (700 μm deep from surface) where the farthest noticeable Dy peak (indicated with dotted square on Fig. 4(b)) was observed on the line analysis result for the magnet coated with low melting-point (DyF_3–LiF) diffusion source (Fig. 4(g)). Dy, Nd elemental mapping was also analysed on the spot same distance deep (700 μm) for the magnet coated with solid DyF_3 single salt (Fig. 4(e)). For both the magnets, Dy, Nd atoms had diffused deeply into interior and their distribution appeared as dimly visible stripe along grain boundaries. Notably, more profuse diffusion of Dy atoms into deeper interior was observed in the magnet coated with low melting-point (DyF_3–LiF) diffusion source.

4. Conclusion

low melting-point (DyF_3–LiF) diffusion source was verified to be an effective Dy-diffusion source of grain boundary diffusion treatment for enhancing coercivity in the Nd-Fe-B-type magnet. Speedier and more profound coercivity enhancement in the Nd-Fe-B-type magnet was achieved by grain boundary diffusion using the low melting-point (DyF_3–LiF) diffusion source with respect to solid DyF_3 single salt. Since the liquid in the (DyF_3–LiF) mixture contained plenty of Dy atoms already freed from DyF_3 and they were in better contact with magnet, speedier and profuse diffusion of Dy atoms through Nd-rich grain boundary was possible in the magnet coated with the low melting-point (DyF_3–LiF) diffusion source.

Acknowledgement

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