M.-W. LEE[*], D.R. DHAKAL[*], T.H. KIM[**], S.R. LEE[**], H.J. KIM[***], T.S. JANG[*,♯]

EFFECT OF DyMn ALLOY-POWDER ADDITION ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF NdFeB SINTERED MAGNETS

WPŁYW DODATKU PROSZKU DyMn NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MAGNETYCZNE SPIEKANYCH MAGNESÓW NdFeB

Micostructural change and corresponding effect on coercivity of a NdFeB sintered magnet mixed with small amount of DyMn powder was investigated. In the sintered magnet mixed with the DyMn alloy-powder Dy-rich shell was formed at outer layer of the main grains, while Mn was mostly concentrated at Nd-rich triple junction phase (TJP), lowering melting temperature of the Nd-rich phase that eventually improved the microstructural characteristics of the gain boundary phase. The coercivity of a magnet increased more than 3.5 kOe by the mixing of the DyMn alloy-powder.

Keywords: NdFeB sintered magnets, DyMn-alloy powder, Coercivity, Low melting point element

1. Introduction

Magnetic properties, thermal properties and corrosion resistance of NdFeB sintered magnets can be improved by adding several elements. With excellent magnetic properties, NdFeB sintered magnets are used in the driving motor of a hybrid electric vehicle but usually unable to sustain at high temperature operation due to low Curie temperature and high temperature coefficient of the coercivity. This disadvantage can be overcome when their coercivity is enhanced by adding heavy rare-earth elements like Tb or Dy to NdFeB magnets by creating high anisotropy field [1-2]. However, the remanence reduction is always accompanied with the usage of these heavy rare-earth elements for the coercivity improvement. The anti-ferromagnetic coupling between heavy rare earth elements and Fe leads to reduce the saturation magnetization and the energy product $(BH)_{max}$. Moreover, limited resources and expensive price of Tb and Dy drive many researchers to seek a method to save heavy rare earths as much as possible, keeping high coercivity.

The addition of Mn on NdFeB magnet can be another method to enhance the coercivity, because it increases c-axis magneto-crystalline anisotropy by increasing c/a ratio of $Nd_2Fe_{14}B$ lattices [3]. In addition, the wettability and continuity of Nd-rich phase can be enhanced by Mn addition because Mn decreases the melting point of Nd-rich phase [4]. However, large amount of Mn addition on the magnet reduces the saturation magnetization because non-magnetic Mn occupying J_2 site loses ferromagnetic coupling with Fe atoms. In this work, we studied the effect of DyMn alloy powder addition on microstructure and magnetic properties of NdFeB sintered magnets and were abled to improve the coercivity with minimum reduction of the remanence.

2. Experimental

Starting alloy with the composition of $Nd_{14.7}Fe_{76.5}B_{6.0}M_{2.8}$ (M = Cu, Co, Al, Nb, at.%) was prepared by strip casting. The strips were HD treated and jet-milled to produce magnetic powder. The average particle size of the powder was about 5 μm. The jet-milled powder was wet-mixed with 1.2 wt% of DyMn alloy-powder. The solvent was removed by creating vacuum atmosphere. The mean particle size of DyMn alloy powder was about 4 μm. The mixed powder was aligned under the magnetic field of 2.2 T and pressed to form green compacts. The compacts were then sintered at 1070°C for 4 hours in vacuum, followed by a sequential annealing at 850, 530 and 500°C for 2 hours each in vacuum. Microstructural studies were carried out with a Scanning Electron Microscopy (SEM, Hitachi S-3000N). Phases were analyzed with Electron Probe Micro Analyzer (EPMA, SHIMADZU EPMA-1720). Magnetic properties were measured using a B-H loop tracer (Magnet Physik Permagraph C-300).

3. Results and discussion

Fig. 1 shows the magnetic properties of Dy-free magnets, DyMn alloy-powder mixed magnets (Dy 1.0 wt.%), and

[*] DEPT. OF ADVANCED MATERIAL ENGINEERING, SUNMOON UNIVERSITY, ASAN, CHUNGNAM 336-708, KOREA

[**] DEPT. OF MATERIALS SCIENCE AND ENGINEERING, KOREA UNIVERSITY, SEOUL 136-713, KOREA

[***] R&D CENTER OF JAHWA ELECTRONICS CO. LTD, CHEONGWON 363-922, KOREA

[♯] Corresponding author: tsjang@sunmoon.ac.kr

the magnets containing 1.0 wt% Dy added by a conventional method. When Dy was added conventionally, the amount of coercivity increase was about 2.4 kOe, yielding 17 kOe. However, the coercivity was reached to 18.1 kOe, with the increase of 3.5 kOe, when small DyMn alloy-powder was mixed. Furthermore, the decrease of remanance by the mixing was very small (13. 4 kG → 13. 1 kG). In order to figure out why the coercivity was improved more with DyMn alloy-powder mixing, without much decrease of the remanance, EPMA analysis on Dy and Mn distribution was carried out.
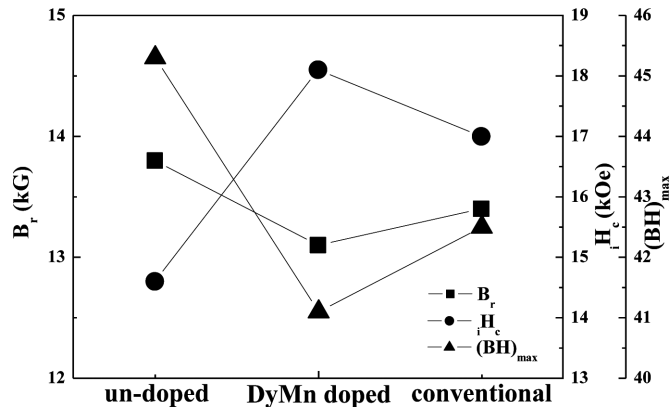

Fig. 1. Magnetic properties of Dy-free NdFeB sintered magnet, a DyMn alloy-powder mixed magnet (Dy 1.0 wt%), and a conventional Dy contained magnet (Dy 1.0 wt%)

Fig. 2 shows EPMA mapping images of some elements in the DyMn alloy-powder mixed magnets. As shown in the figure, most Dy atoms were distributed in nonmagnetic Nd-rich phases and around main grains. The concentration of Dy in the interior of the main grains was 1.2 at% whereas that of the outer area of the grains was 2.9 at%, showing a core-shell type structure. In such structure, magnetic anisotropy of the outer layer would be much higher than that of the interior because the anisotropy field of $Dy_2Fe_{14}B$ is greater than that of $Nd_2Fe_{14}B$ [5,6]. As a result, the formation and propagation of a reverse domain that usually start from the surface of the 2:14:1 main grains would be inhibited more than in the normal grains, creating higher coercivity. On the other hand, Mn was distributed not only in the RE-rich phase area but also in the main grains. The concentration of Mn in the main grains was about 2.0 at%. It is known that c/a ratio of the 2:14:1 lattice increases when Mn atoms replace some Fe atoms in the lattice. This increases the magnetocrystalline anisotropy of the 2:14:1 phase, which also contributes the improvement of the coercivity. The reduction of magnetization values accompanied by the replacement of some Fe by Mn in the 2:14:1 lattice [7,8] is inevitable even though the amount of the reduction is smaller than expected.

As shown in the figure, however, most Mn was segregated at the Cu-rich triple junction phases (TJP) and the RE-rich phases. Typical composition of the Cu-rich TJP and the RE-rich phases was $Nd_{40.2}O_{46.3}Cu_{3.1}Co_{5.0}Mn_{5.3}$ and $Nd_{33.6}Dy_{1.6}O_{60.1}Mn_{4.6}$ (in at%), respectively. According to the previous results [9], the formation of the RE-rich phase deteriorates the coercivity of a NdFeB magnet because the surface energy of the RE-rich phase is very large. When Mn is segregated at the RE-rich phase, however, the surface energy seems to become lower because the melting point of RE-rich phase decreases due to Mn. This may help to reduce the lattice misfit between the RE-rich phases and the main phases. Furthermore, the wettability and the nonmagnetic property of the Cu-rich TJP would be improved by the Mn segregation also due to the low temperature melting behavior of Mn-contained nonmagnetic phases. As a result, the uniformity and continuity of the Nd-rich grain boundary phase (GBP) generated from the Cu-rich TJP would be improved too[10]. These effects are all beneficial to the improvement of the coercivity.
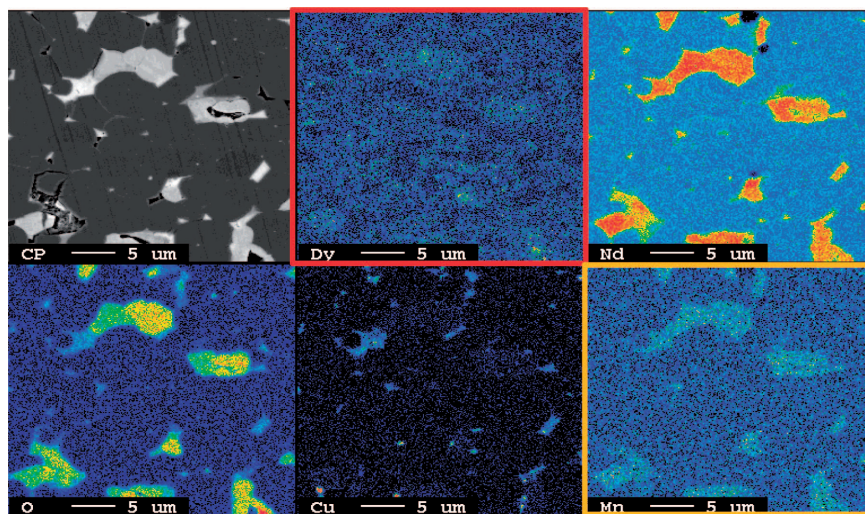

Fig. 2. EPMA mapping images of a sintered magnet mixed with 1.2 wt.% DyMn alloy-powder

(a)

conventional | with DyMn powder mixing
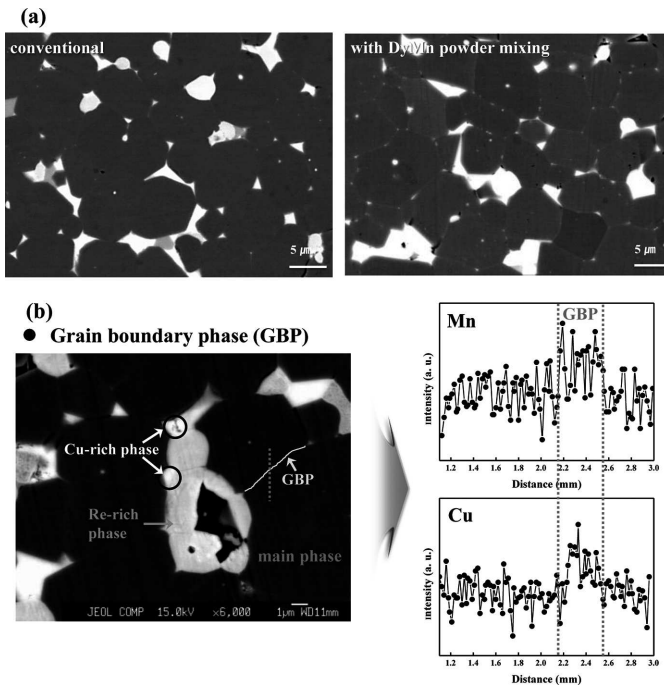
(b)
● **Grain boundary phase (GBP)**

Fig. 3. (a) SEM images of a conventional Dy contained magnet (Dy 1.0 wt%) and a DyMn alloy-powder mixed magnet (Dy 1.0 wt%). (b) BSE images and WDS line profile of DyMn alloy-powder mixed magnet (Dy 1.0 wt%)

Overall microstructures of a conventional Dy-contained sintered magnet (Dy 1.0 wt%) and a DyMn powder-mixed sintered magnet (Dy 1.0 wt%) are shown in Fig. 3(a). It is clearly seen that the magnetic grains are well isolated by continuously and uniformly developed Nd-rich grain boundary phase after DyMn alloy-powder mixing. As shown in Fig. 3(b), along with Cu, Mn is highly concentrated at Nd-rich grain boundary phase that developed from Cu and Mn enriched TJP. Cu-Mn binary phase diagram indicates that Cu and Mn are soluble to each other. Therefore, as Cu does, Mn would also penetrate through the Nd-rich GBP by a capillary action during sintering and improve the formation and microstructural characteristics of Nd-rich GBP[11]. Above results indicate that the coercivity of a NdFeB sintered magnet can be enhanced without much reduction of the remanance if the composition of DyMn alloy-powder source is kept to Dy-rich. Effect of the variation of Mn content in DyMn alloy-powder will be discussed in the near future.

4. Conclusions

The coercivity of a NdFeB sintered magnet mixed with small DyMn alloy-powder (1.2 wt%) increased from 14.6 to 18.1 kOe without much reduction of the remanance. Dy and Mn in the alloy-powder were decomposed during sintering and behaved differently. While Dy was mostly concentrated at the outer layer of the main grains forming a core-shell type structure, Mn was mostly concentrated at (Nd, Cu)-rich TJP and GBP improving the microstructural characteristics of Nd-rich GBP. The enhancement of the coercivity by the mixing of small DyMn alloy-powder was due to this duplicated effect of Dy and Mn although a minor reduction of the remanance arose from the substitution of some Fe with Mn was inevitable.

REFERENCES

[1] K. Hirota, H. Nakumara, T. Minowa, M. Honshima, IEEE Trans. Magn. **42**, 2909 (2006).
[2] M. Komuro, Y. Satsu, H. Suzuki, IEEE Tans. Magn. **46**, 3831 (2010).
[3] L. Pareti, M. Solzi, F. Bolzoni, O. Moze, R. Panizzieri, Solid State Communications **61**, 761 (1987).
[4] C. Abache, H. Oesterreicher, J. Appl, Phys. **60**, 1114 (1986).
[5] Y.C. Yang, W.J. James, X.D. Lo, H.Y. Chen, L.G. Xu, IEEE Trans. Magn. **22**, 757 (1986).
[6] K.H.J. Buschow, New permanent magnet material, J. Mater. Sci. Res. **1**, 1 (1986).
[7] O.A. Pringle, G.K. Marasinghe, G.J. Long, W.J. James, J. Appl. Phys. **64**, 5580 (1988).
[8] M. Jurczyk, W.E. Wallace, IEEE Trans. Magn. **22**, 755 (1986).
[9] T.H. Kim, S.R. Lee, S. Namkung, T.S. Jang, J. Alloys Compd. **537**, 261 (2012).
[10] S. Namkung, M.W. Lee, T.H. Lim, T.H. Kim, S.R. Lee, T.S. Jang, J. Kor. Powd. Met. Inst. **19**, 4 (2012).
[11] J.W. Kim, S.H. Kim, Y.D. Kim, J. Kor. Powd. Met. Inst. **18**, 1 (2011).