OPTIMIZING FABRICATION CONDITIONS IN PILOT SCALE FOR SINTERED Nd-Fe-B MAGNETS

Pham Thi Thanh*, Nguyen Hai Yen, Nguyen Huy Dan

Institute of Materials Science, Vietnam Academy of Science and Technology

18 Hoang Quoc Viet, Cau Giay, Ha Noi, Vietnam.

*Email: *thanhpt@ims.vast.ac.vn*

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ABSTRACT

In this report, we present the results of study on fabrication technology for sintered Nd-Fe-B magnets. Influence of grinding, pressing, sintering and heat treatment processes on magnetic properties of the anisotropic Nd-Fe-B permanent magnets was investigated systematically. By applying wet-pressing technique and two-stage heat treatment process the technology and performance of the magnets can be significantly improved. The optimal technological conditions were found. A low cost, practical applicable technological process has been established to manufacture sintered Nd-Fe-B magnets in pilot scale with their coercivity larger than 7,5 kOe and maximum energy product above 35 MGOe.

Keywords: anisotropic sintered magnet, coercivity, maximum energy product $(BH)_{max}$, Nd-Fe-B alloy, hard magnetic material.

1. INTRODUCTION

Nowadays, Nd-Fe-B magnets occupy an important position in the market of the permanent magnets in the world because these materials are applied widely in practice such as motors, generators, ore-separators, magnetic cushions... To full-fill requirements of various aspects of practical applications, further enhancement of magnetic properties and optimization of fabrication technology of these magnets are still concerned to study. There are several methods such as sintering, melt-spinning and high energy ball milling, which are used to fabricate Nd-Fe-B magnets. Recently, the exchange-spring magnets or nanocomposites of the Nd-Fe-B material have attracted a lot of scientists. However, the sintered magnets are currently considered as an advanced hard magnetic material with the highest actually achieved maximum energy product $(BH)_{max}$ (above 50 MGOe). Many researchers continue to study this type of Nd-Fe-B magnets to reach the theoretical value for $(BH)_{max}$ (64 MGOe) and lower the cost of the material [1, 2, 3, 4, 5, 6]. In Vietnam, the sintered Nd-Fe-B magnets with $(BH)_{max}$ over 30 MGOe were obtained in laboratory by several research groups [7, 8, 9]. Nevertheless, it is difficult to have a technology which can be applied in practice as well as to raise the energy product $(BH)_{max}$ closed to the theoretical limit for sintered Nd-Fe-B magnets. In this work, we optimize technological conditions for fabrication of anisotropic sintered Nd-Fe-B magnets in pilot scale. Influence of grinding, pressing, sintering and annealing processes on magnetic properties of sintered Nd-Fe-B magnets was investigated.

2. EXPERIMENTAL PROCEDURES

The pre-alloys with nominal composition of $Nd_{16.5}Fe_{77}B_{6.5}$ and mass of 5 kg were prepared from Nd, Fe and FeB (18 % B) on an induction furnace under Ar gas to avoid oxidation. The alloys were induction-melted for about 30 minutes before casting in a water-cooled mold with inner size of 4 cm. The obtained alloy was crashed into small pieces with size smaller 2 centimeters and coarsely milled with amount of 0.5 kg per batch. The coarse powder was then finely milled with amount of 1 kg per batch using industrial white gasoline as a solvent to avoid oxygenation. The obtained powder with average grain size of several μm was pressed, with a pressure of 15 MPa, into rectangular parallelepiped tablets (6.5×5.5×3.5 cm^3) in an oriented magnetic field, yielded by an electromagnet, of about 20 kOe. For this stage, the wet pressing technique was used instead of the dry one. The pressed magnet tablets were then sintered at 1050, 1080 and 1100 °C for 0.5, 1 and 2 h in vacuum. After that, these magnets were heat-treated in various conditions to improve their coercive force. In order to investigate magnetic properties of the sintered magnets on a pulsed high field magnetometer with maximum magnetic field of 90 kOe, the cylinders with 3 mm diameter and 3 mm height were cut from the magnets by means of spark-cutting. To calculate the maximum energy product $(BH)_{max}$ of the magnets the following relations were used:

$$(BH) = B.H_{eff} \tag{1}$$

$$H_{eff} = H_{ext} - 4\pi\rho M_m D \tag{2}$$

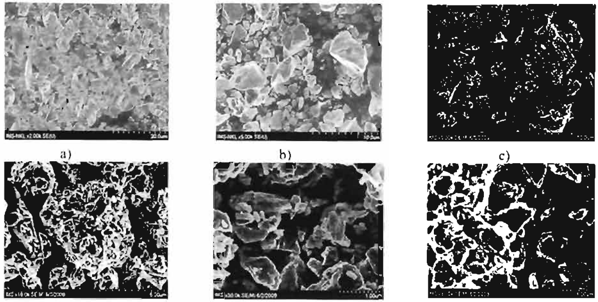
$$B = 4\pi\rho M_m + H_{eff} \tag{3}$$

where: H_{ext} - external magnetic field, H_{eff} - effective magnetic field, ρ - mass density of the material (ρ = 7.6 g/cm^3), M_m - mass magnetization (obtained from magnetic hysteresis measurement), D - demagnetization factor depending on ratio of length l and diameter d of sample.

Demagnetization factor was determined based on a semi-experimental data sheet of D = f(l/d) in a monograph book for magnetism and magnetic materials.

3. RESULTS AND DISCUSSTION

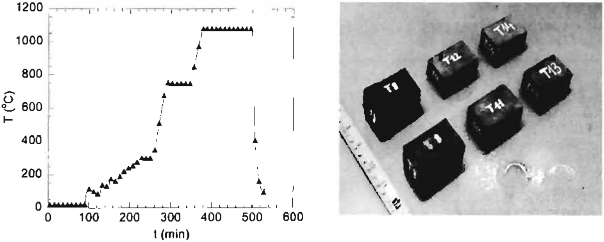
We investigated influence of milling time, in the range of 1   12 h, on size and size-distribution of particles of the materials. The power X-ray diffraction shows that the milling process does not degrade the $Nd_2Fe_{14}B$ phase. The grain size of the milled powder was determined by scanning electron microscopy (SEM). Figure 1 shows SEM images of the powder with the milling time from 1 to 12 h. The SEM images reveal that the grain size decreases from about 15 μm to 1 μm when increasing milling time from 1 to 12 h.



a) b) c)

d) e) f)

Figure 1. SEM images of the Nd-Fe-B powder with milling time of 1 (a), 2 (b), 3 (c), 6 (d), 9 (e) and 12 hours (f).



a) b)

Figure 2. Typical sintering diagram (a) and view of sintered Nd-Fe-B magnets (b).

With our old technology, the most disadvantage of the conventional dry pressing is that an additional time and labour consuming step of mixing is required to evaporate the gasoline solvent. In addition, dried Nd-Fe-B powders suffer to be oxygenated easily and it is difficult to be preserved. Consequently, we had to improve pressing technique. In this work, a wet pressing technique was used instead of the dry one. With the wet pressing technique, the wet magnetic powder can be pressed into tablets immediately after being separated from gasoline solvent by using cloth bags. Two felt layers (~ 2 mm) were used to cover the bottom and the top of pressing samples to drip out gasoline during pressing. If these felt layers were not used, the magnetic powder would be splashed out with gasoline. By using the wet pressing technique, we can save not only time and labour but also the magnetic powder, which are easily scattered in case of the dry pressing. After sintering, the wet pressed magnets are still reliable good mechanical properties, no crack nor distortion. Figure 2 presents a typical sintering diagram and a picture of the fabricated magnets with mass of about 0.5 kg per tablet.

In comparison with the conventional dry pressing, it is required to carried out with slower heating rate at low temperature range (about 2 h) to avoid the cracking caused by escaped gasoline (Fig. 2a). Thus, for fabrication of sintered Nd-Fe-B magnets by using the wet pressing instead of the conventional dry one, the magnets can be produced at large scale with a significant reduction in pressing time as well as oxidation.

Figure 3 exhibits the hysteresis loops of $Nd_{16.5}Fe_{77}B_{6.5}$ magnets prepared by the same sintering process but with different milling time. With milling time in the range of 1 to 6 h, the highest coercivity of 4.7 kOe was obtained for the magnets with milling time of 3 h as shown in Fig. 3. It is agreed with the results from SEM measurements that showed a homogeneous distribution with grain sizes found in desired range of 3 to 5 μm [1]. The coercivity of the investigated magnets varies as a function of the milling time. As for sample with the milling time of 6 hours, its coercivity is low due to the fact that its grains are too small. For magnets with the milling time of 1 and 2 h, their coercivity also did not reach the highest value because of relative large grains. Thus, the optimal milling time of 3 h is selected to fabricate magnets.

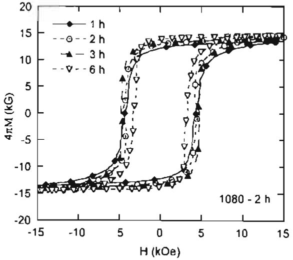
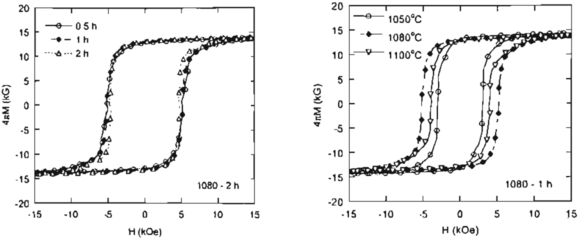


Figure 3. Hysteresis loops of $Nd_{16.5}Fe_{77}B_{6.5}$ magnets with different milling time prepared by the same sintering process.

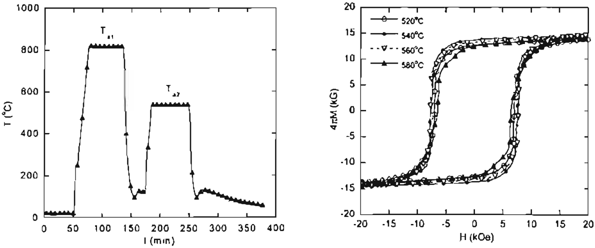
The effects of sintering time and temperature on magnetic properties of the magnets were also studied (Fig. 4). For magnets sintered at 1080 °C for 0.5, 1 and 2 h, the change in coercivity is not significant with coercivity values of 4.7, 5.3 and 5.1 kOe (Fig. 4a). However, the value of coercivity of fabricated magnets depends strongly on sintering temperature (Fig. 4b). This can be explained that the percolation of secondary magnetic phases existed around each grain and the diffusion rate of Nd-rich phase at grain boundary is controlled by sintering temperature. The sintering temperature is selected to decrease re-crystallization of grains. If the sintering temperature is selected unsuitably, the coercivity value will decrease because of large grain size caused by re-crystallization process. Thus, the choice of sintering temperature is very important in fabrication of sintered Nd-Fe-B magnets. From these results, the sintering temperature of 1080 °C and the sintering time of 1 h are optimal.



a) b)

Figure 4. Hysteresis loops of Nd-Fe-B samples prepared with different sintering times (a) and temperatures (b)

The sintered magnets were then heat-treated to enhance energy product $(BH)_{max}$. This stage is rather complicated with many parameters involved such as heating steps, time, method of fast cooling... In this work, a two-stage heat treatment process was chosen and carried out using RVS-260 furnace. At the first stage, the magnets were heated at T_{a1} = 820 °C for 1 h and then fast cooled down to room temperature. For the second stage, magnets were heated at different temperatures, T_{a2}, namely, 520 °C, 540 °C, 560 °C and 580 °C for 1 h and quenched rapidly by Ar gas. Figure 5a showed a typical two-stage heat treatment process for Nd-Fe-B magnets. For both the stages, the samples were heated with the rate of 30 °C/min and quenched rapidly with the rate of about 50 °C/min.



a) b)

Figure 5 Typical Two-stage heat treatment process (a) and hysteresis loops of of Nd-Fe-B magnets with different heat treatment regimes (b).

Figure 5b exhibits hysteresis loops of the samples with different heat treatment regimes. Their coercivities were significant higher than those of untreated magnets and almost unchanged with annealing temperatures in the range of 520 to 560 °C. However, the coercivity of the magnet with T_{a2} = 540 °C is highest (7.7 kOe). The values of remanence B_r, coercivity H_c and maximum energy product $(BH)_{max}$ were listed in table 1. Thus, the two-stage heat treatment process is optimal with the follows: in the first stage, magnets were heated at T_{a1} = 820 °C for 1 h and then fast cooled down to room temperature (rate of 30 °C/min) and in the second stage, magnets were heated at T_{a2} = 540 °C for 1 h and quenched rapidly by Ar gas (rate of 50 °C/min).

Table 1 B_r, H_c, $(BH)_{max}$ values of $Nd_{16.5}Fe_{77}B_{6.5}$ magnets heat-treated by two-stage processes.

T_{a2} (°C)	520	540	560	580
B_r (kG)	12.7	13.7	13.2	12.5
H_c (kOe)	7.1	7.7	7.6	6.4
$(BH)_{max}$ (MGOe)	30.3	36.2	34.5	24.4

Figure 6a exhibits hysteresis loops of $Nd_{16.5}Fe_{77}B_{6.5}$ magnets before and after heat-treatment with T_{a2} = 540 °C. The heat-treatment increases the coercivity but slightly decreases the remanence of the magnet. To simultaneously increase coercivity and remanence of the magnets needs further studies. Figure 6b shows the magnetic characteristic curves of the best fabricated magnet. With the obtained parameters, our fabricated sintered Nd-Fe-B magnets can be applied in practice.

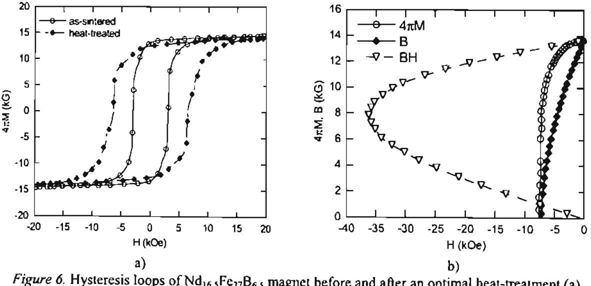


Figure 6. Hysteresis loops of $Nd_{16.5}Fe_{77}B_{6.5}$ magnet before and after an optimal heat-treatment (a) and their magnetic characteristic curves (b).

4. CONCLUSION

The influences of grinding, sintering and annealing processes on magnetic properties of $Nd_{16.5}Fe_{77}B_{6.5}$ magnets were investigated. We have established a stable technological processes to fabricate Nd-Fe-B magnets by sintering method. With the optimized sintering and using two-stage heat- treatment conditions, Nd-Fe-B magnets with $(BH)_{max}$ over 35 MGOe can be achieved.

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REFERENCES

1. Brown D., Bao-Min M. and Chen Z. - Development in the processing and properties of NdFeB-type permanent magnets, J. Magn. Magn. Mat. **248** (2002) 432-440.

2. Park S. E, Kim T. H., Lee S. R., Namkung S. and Jang T. S. - Effect of sintering conditions on the magnetic and microstructural properties of Nd–Fe–B sintered magnets doped with DyF_3 powders, J. Appl. Phys. **111** (2012) 07A707-1-07A707-3.

3. Fukunaga H., Yamamoto I., Nakano M. and Yanai T. - Magnetic properties of Dy-diffused Nd-Fe-B powder prepared by crystallization from amorphous state, J. Appl. Phys. **111** (2012) 07A733-1-07A733-3.

4. Nakamura H., Hirota K., Ohashi T. and Minowa T. - Coercivity distributions in Nd-Fe-B sintered magnets produced by the grain boundary diffusion process, J. Phys. D: Appl. Phys. **44** (2011) 064003-1-064003-5.

5. Sepehri-Amin H., Une Y., Ohkubo T., Hono K. and Sagawa M. - Microstructure of fine-grained Nd-Fe-B sintered magnets with high coercivity, Scripta Materialia **65** (2011) 396-399.

6. Kim S. H., Kim J. W., Jo T. S. and Kim Y. D. - High coercive Nd-Fe-B magnets fabricated via two-step sintering, J. Magn. Magn. Mat. **323** (2011) 2851-2854.

7. Do Vuong Hoanh, Le Cong Quy, Vu Van Hong, Chi Van Chiem, Nguyen Hong Quyen, Vu Huu Tuong, Do Khanh Tung, Vu Hong Ky and Nguyen Tuan Minh - Investigation of fabrication technology of sintered Nd-Fe-B materials and magnets, Proceedings of the 4th National Conference of Solid State Physics, Nui Coc, Thai Nguyen, 2003, pp. 638-642.

8. Do Khanh Tung, Vu Huu Tuong, Le Cong Quy and Do Vuong Hoanh - Some results of analyses of composition and structure of Nd-Fe-B magnetic materials, Proceedings of the 4th National Conference of Solid State Physics, Nui Coc, Thai Nguyen, 2003, pp. 634-637.

9. Pham Dinh Thinh, Do Tran Huu, Vu Huu Tuong, Vu Hong Ky, Do Khanh Tung, Nguyen Thi Thanh Huyen, Phung Anh Tuan, Duong Dinh Thang and Nguyen Huy Dan - Influence of technological conditions on magnetic properties of sintered Nd-Fe-B magnets, Proceedings of The 6th National Conference of Solid State Physics and Materials Science, Da Nang, 2009, pp.154-157.

TÓM TẮT

TỐI ƯU HÓA ĐIỀU KIỆN CHẾ TẠO NAM CHÂM THIÊU KẾT Nd-Fe-B QUY MÔ BÁN CÔNG NGHIỆP

Phạm Thị Thanh*, Nguyễn Hải Yến, Nguyễn Huy Dân

Viện Khoa học vật liệu, Viện Hàn lâm KHCNVN, 18 Hoàng Quốc Việt, Cầu Giấy, Hà Nội

*Email: *thanhpt@ims.vast.ac.vn*

Trong bài báo này, chúng tôi trình bày những kết quả nghiên cứu công nghệ chế tạo nam châm thiêu kết Nd-Fe-B. Ảnh hưởng của quá trình nghiền, ép mẫu, thiêu kết và chế độ xử lí nhiệt lên tính chất từ của nam châm vĩnh cửu dị hướng Nd-Fe-B đã được khảo sát một cách hệ thống. Với công nghệ ép ướt và chế độ xử lí nhiệt hai giai đoạn, phẩm chất từ của nam châm được cải thiện đáng kể. Điều kiện công nghệ tối ưu đã được tìm thấy. Nam châm thiêu kết Nd-Fe-B quy mô bán công nghiệp với lực kháng từ lớn hơn 7,5 kOe và tích năng lượng từ trên 35 MGOe được sản xuất với giá thành thấp, có thể ứng dụng trong thực tế.

Từ khóa: nam châm thiêu kết dị hướng, lực kháng từ, tích năng lượng từ $(BH)_{max}$, hợp kim Nd-Fe-B, vật liêu từ cứng.