
New Material for Permanent Magnets on a Base of Nd and Fe

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Abstract

A new compound composed of Nd, Fe, and a small quantity of B (about 1% weight) has been found, which has a tetragonal structure with lattice constants $a = 0.880$ nm and $c = 1.221$ nm. This phase, which has the approximate composition, 12 atom % Nd, 6 atom % B and balance Fe, possesses remarkable magnetic properties. From the approach to saturation an anisotropy constant of about 3.5 MJ/m³ can be calculated, while saturation magnetization amounts to 1.35 T. The magnetization versus temperature curve shows a Curie temperature of 585 K, which is much higher than those of the Fe and light rare earth binary compounds. Based on the new compound, sintered permanent magnets have been developed which have a record high energy product. Permanent magnet properties and physical properties of a typical specimen which has the composition Nd₁₅B₈Fe are as follows: $B_r = 1.23$ T, $H_{cb} = 880$ kA/m, $H_{cl} = 960$ kA/m, $(BH)_{max} = 290$ kJ/m³, temperature coefficient of $B_r = -1260$ ppm/K, density = 7.4 Mg/m³, specific resistivity = 1.4 μΩm, Vickers hardness = 600 , flexural strength = 250 MPa.

Introduction

Production of Sm-Co permanent magnets has been increasing steadily. They have become widely applied to the fields of the electronics industry. To obtain larger scale adaptation, for example, in the automotive industry, it is necessary to develop a material containing little or no Sm and Co which are less abundant resources. As alternative materials, there have been a growing interest in rare earth (R)-Fe alloys, especially those containing large amounts of the abundant light rare earths (LR).^{1,2,3,4,5}

The LR and Fe binary compounds have high saturation magnetizations as a result of the ferromagnetic coupling of LR and Fe moments. Through the action of crystal field, a huge magneto-crystalline anisotropy is expected if R carries an orbital moment. The LR-Fe compounds

are strong candidates for high performance permanent magnets rivaling SmCo magnets.

However, the R-Fe permanent magnet has not been realized yet. This is thought to be mainly due to three reasons:

- (1) The Curie temperatures of R-Fe compound containing LR are too low;
- (2) The LR and Fe form few stable inter-metallic phases;
- (3) No R-Fe compound shows a uniaxial magnetic anisotropy.

Adhering to the equilibrium R-Fe binary phases does not appear promising. Two alternative approaches may possibly achieve a breakthrough.

- (1) Extending the search to metastable or non-equilibrium phases instead of limiting it within the equilibrium phases. Actually, Croat *et al.*^{1,3} and Koon *et al.*^{4,5} have already developed R-Fe alloys having high coercivity by utilizing melt spinning which tends to form metastable phases.
- (2) Extending the search to ternary or quaternary systems instead of limiting it within the binary system. Even though the LR and Fe form few stable compounds, a variety of stable phases might exist in ternary or quaternary systems.

We have synthesized numerous compounds composed of LR, Fe and small quantities of other elements and have found that various kinds of equilibrium phases exist in the ternary systems. Of these phases, we have found a new ternary compound consisting of Nd, B, and Fe which shows remarkable magnetic properties for a permanent magnet material. Based on this compound, a powder metallurgical process has been developed to obtain permanent magnets having a record high energy product.

Experimental Procedure

Induction melts of the nominal compositions $\text{Nd}_x\text{B}_y\text{Fe}_{100-x-y}$ with $x = 13-19$ and $y = 4-17$ were made in an alumina crucible under an argon gas atmosphere. The ingots were crushed in a nitrogen atmosphere to a particle size ~ 1 mm by a jaw crusher, to ~ 100 μm by a disk mill, and then, pulverized in 1,1,2-trichloro-1,2,2-trifluoroethane to about 3 μm by a ball mill with a stainless-steel container and balls. The powders were aligned in a magnetic field of 800 kA/m and pressed perpendicular to the aligned direction at a pressure of 200 MPa. The green compacts were sintered in an argon gas atmosphere at temperatures from 1310-1430 K for 1 hour and then, cooled rapidly in a cooling chamber. The sintered samples were given a post-sintering heat treatment for 1 hour at 400-1400 K and cooled rapidly.

The x-ray diffractometer measurements were carried out on powders with average particle size smaller than 100 μm which were obtained by grinding the ingots as described above. We employed Cu-K α radiation in combination with an x-ray monochromator. The rotating-crystal method was used on the single crystal fragments which were obtained from a crushed ingot which had been slowly cooled in the temperature range from just above to just below the melting point of the alloy.

Magnetization versus temperature curves from room temperature to above the Curie temperature were measured on the sintered specimens using vibrating-sample magnetometer (VSM). A magnetic field of 800 kA/m was applied to the sintered specimen parallel to its magnetically oriented direction. The Curie temperature was estimated from low field measurements. The virgin magnetization curves were measured on the same specimen parallel and perpendicular to the magnetically oriented direction using VSM. The maximum magnetizing field was 1200 kA/m. Specimens used for VSM measurements were disks, 2 mm in diameter and 1 mm thick, cut from sintered blocks.

Permanent magnet properties were measured by a magnetic flux meter with a maximum magnetizing field of 1600 kA/m. The microstructures of the sintered specimens were investigated by an optical microscope and an electron probe microanalyzer.

Results

Figure 1 shows the variation of the x-ray powder spectra with increasing the addition of B, y in $\text{Nd}_{15}\text{B}_y\text{Fe}_{85-y}$ alloys. The spectrum of $\text{Fe}_{85}\text{Nd}_{15}$ alloy comprises the Bragg reflections of $\text{Nd}_2\text{Fe}_{17}$ and $\alpha\text{-Fe}$. With the addition of B, a set of unknown reflections appears. The intensity of these reflections increases with increasing B addition. For the alloy containing 6 atoms % B, only the set of unknown reflections is detected and $\text{Nd}_2\text{Fe}_{17}$ and $\alpha\text{-Fe}$

Bragg reflections disappear. With the aids of the measurements of rotating crystal-method of the single crystal fragments, the set of unknown reflections were indexed to a tetragonal crystal structure with lattice parameters, $a = 0.880$ nm, and $c = 1.221$ nm.

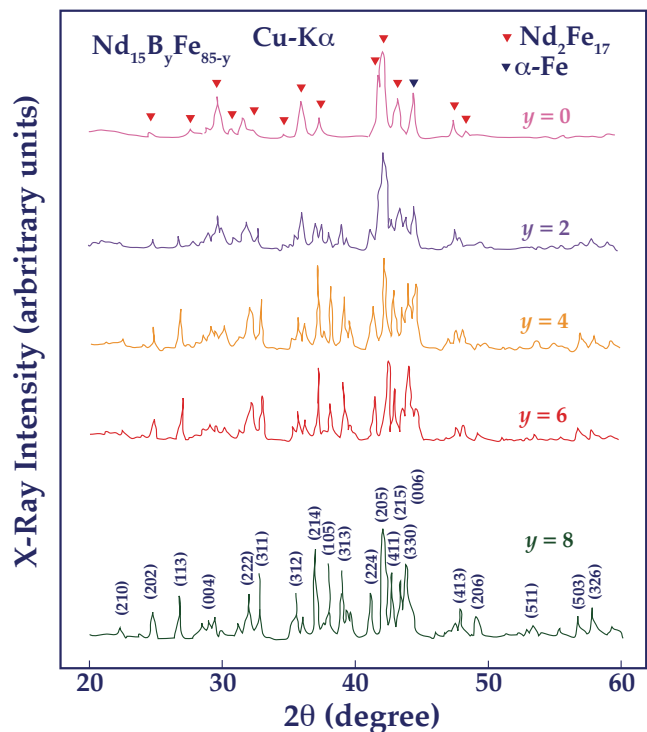


Figure 1 — X-ray diffraction spectra on five alloys containing different percentages of boron in $\text{Nd}_{15}\text{B}_y\text{Fe}_{85-y}$ system. \diamond and \blacktriangledown indicate the reflections from $\text{Nd}_2\text{Fe}_{17}$ and $\alpha\text{-Fe}$, respectively.

A few reflections left unindexed in these spectra are considered to be of the minor phases in the alloys. As the Nd content increases, the intensity of the reflections from minor phases increases. The alloys containing Nd less than 10 atoms % exhibit strong $\alpha\text{-Fe}$ reflections. It is likely that the single phase region of the tetragonal structure exists in the vicinity of 12 atoms % Nd, 6 atoms % B and balance Fe.

Figure 2 shows the magnetization versus temperature curves for $\text{Nd}_{15}\text{B}_y\text{Fe}_{85-y}$ with $y = 0-8$. The magnetization of $\text{Nd}_{15}\text{Fe}_{85}$ binary alloy, having about 0.8 T at room temperature, decreases with increasing the temperature to a very small value at about 400 K. From a low field measurement, the Curie temperature of the Nd-Fe alloy was estimated about 310 K. The magnetization of the alloy increases with increasing B addition, and reaches the maximum at around 6 atoms % B. This increase is caused by the formation of tetragonal phase having a high Curie temperature. The low field measurement showed the Curie temperature of this phase to be 585 K.

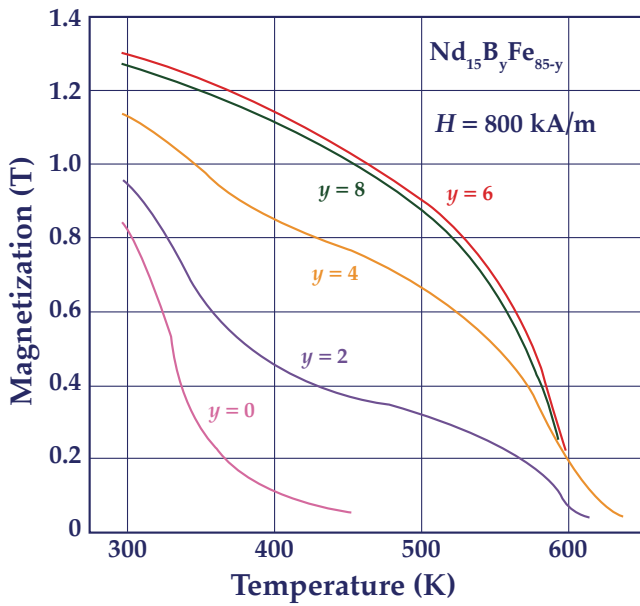


Figure 2 — Magnetization vs temperature curves for $H = 800$ kA/m on five alloys containing different percentages of boron in $\text{Nd}_{15}\text{B}_y\text{Fe}_{85-y}$ system.

X-ray diffraction measurements were made on the specimens aligned in a magnetic field and then, sintered. For the alloys containing B, it was found that the c axis of the tetragonal structure is aligned parallel to the magnetic field, while for Nd-Fe binary alloys, the c plane of the rhombohedral $\text{Nd}_2\text{Fe}_{17}$ is aligned.

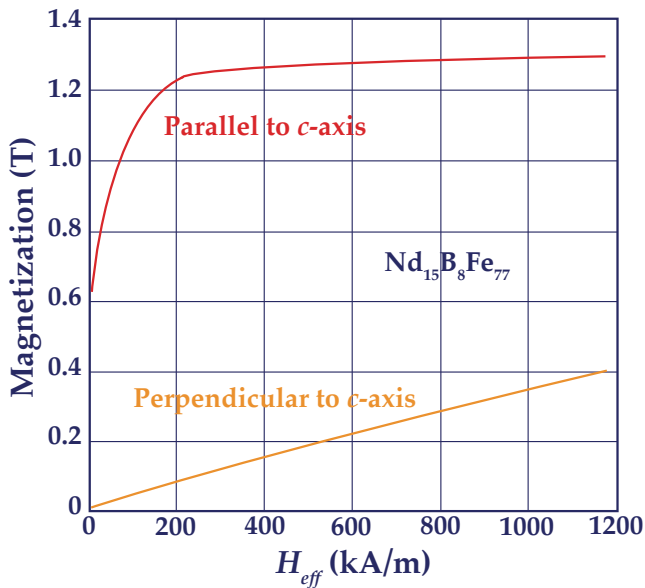


Figure 3 — Magnetization at room temperature in the easy and hard directions as a function of applied field for $\text{Nd}_{15}\text{B}_8\text{Fe}_{77}$.

Figure 3 shows the virgin magnetization curves of the sintered $\text{Nd}_{15}\text{B}_8\text{Fe}_{77}$ specimen measured parallel and perpendicular to the easy axis. In the maximum field of 1200 kA/m, the magnetization in the easy direction

amounts to 1.3 T, while, in the hard direction, it is only 0.4 T. It turns out that the tetragonal compound has a high uniaxial magnetic anisotropy. A preliminary measurement of the magnetization curves was carried out using Bitter-type electromagnet with the maximum field of 8 MA/m. This showed that the anisotropy field of the tetragonal phase was approximately 8.8 MA/m, which corresponds to an anisotropy constant K_j as high as 3.5 MJ/m³. Saturation magnetization was estimated at 1.35 T. Thus we have a remarkable new compound as a material for high performance permanent magnets.

Based on this Nd-Fe-B tetragonal phase, a powder metallurgical process has been developed to produce permanent magnet.

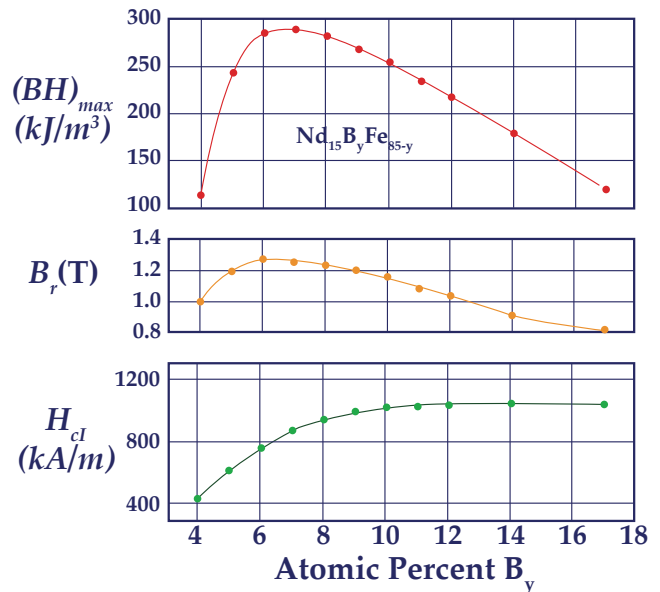


Figure 4 — Permanent magnet properties versus percentage of boron in $\text{Nd}_{15}\text{B}_y\text{Fe}_{85-y}$ system.

Figures 4 and 5 show the compositional dependence of the permanent magnet properties for the sintered specimens. All of the specimens were given a post-sintering heat treatment at 870 K which, as shown later, raised the intrinsic coercivity H_{cl} . Excellent magnetic properties are obtained on the Nd-rich side as well as B-rich side of the composition thought to be the single phase. The highest $(BH)_{max}$ is attained in the vicinity of 6-8 atoms % B and 14-15 atoms % Nd, reaching 280-290 kJ/m³, which is the highest record of all magnets including Sm-Co magnets. H_{cl} increases with increasing the amount of B up to 10 atoms % and Nd up to 16 atoms %. Further increases of B and Nd give only a small change in H_{cl} .

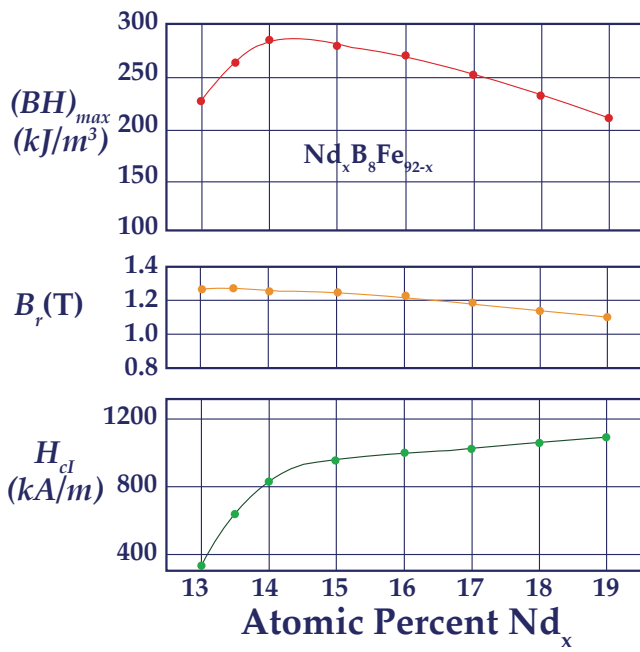


Figure 5 — Permanent magnet properties vs percentage of neodymium in $Nd_xB_8Fe_{92-x}$ system.

Figure 6 shows the variation in the density and the permanent magnet properties of the sintered $Nd_{15}B_8Fe_{77}$ alloy annealed at 870 K for 1 hour after sintering. Density as high as 98-99% of that of the cast alloy are obtained at temperatures about 1350 K. H_{cl} decreases gradually with increasing sintering temperature. It should be noted that high magnetic properties are obtained over a wide range of the sintering temperature.

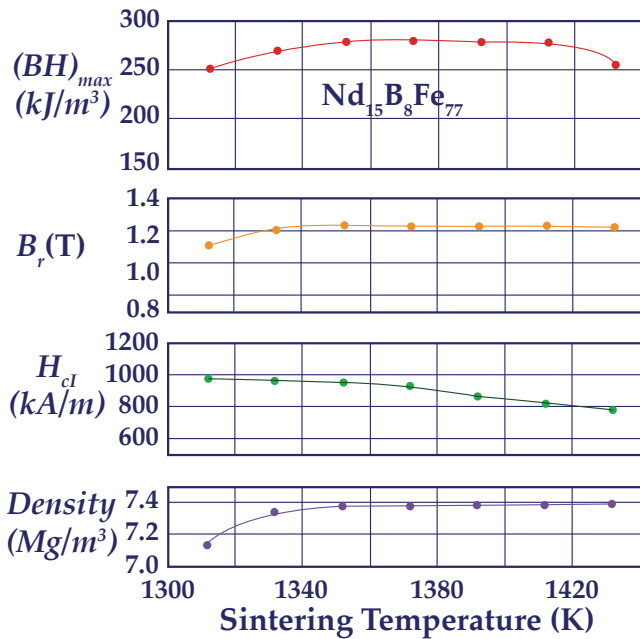


Figure 6 — Permanent magnet properties and density as a function of sintering temperature for $Nd_{15}B_8Fe_{77}$ magnet.

Figure 7 shows a plot of H_{cl} versus temperature of the post sintering heat treatment for a $Nd_{15}B_8Fe_{77}$ alloy. As

the temperature is increased, H_{cl} begins to increase from 700 K, reaches a maximum value at 870-890 K and then, decreases, taking a shoulder at around 1100-1200 K.

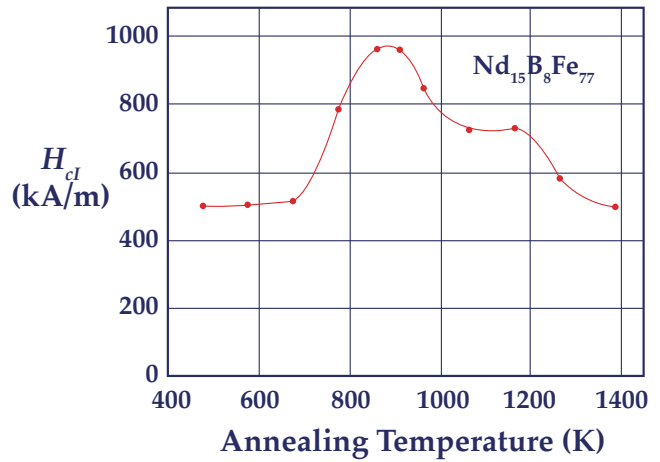


Figure 7 — Variation of intrinsic coercivity with temperature of post sintering heat treatment for a $Nd_{15}B_8Fe_{77}$ magnet.

Metallographic studies have shown the following results:

- (1) The alloy consists of mainly two phases, that is, tetragonal major phase and Nd-rich minor phase;
- (2) The average grain size of the tetragonal phase is about 15 μm ;
- (3) The Nd-rich phase which contains more than 80 atoms % Nd is scattered along the grain boundaries of the tetragonal major phase.

Figure 8 shows an x-ray composition image of the $Nd_{15}B_8Fe_{77}$ sintered alloy, where the dark areas correspond to the tetragonal phase and the white areas correspond to the Nd-rich phase.

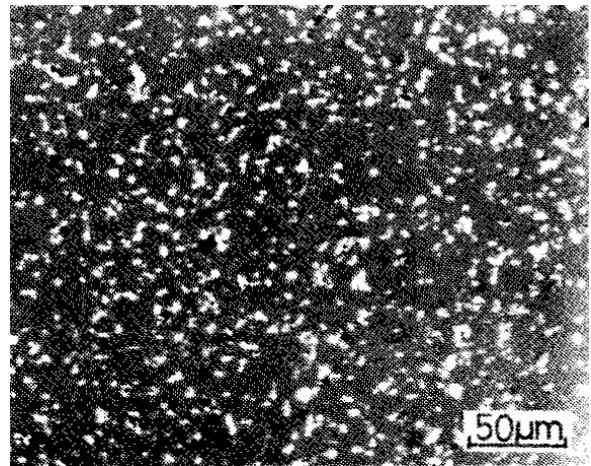


Figure 8 — X-ray composition micrograph of a sintered $Nd_{15}B_8Fe_{77}$ magnet.

Magnetization curves in the first and second quadrants for the $Nd_{15}B_8Fe_{77}$ alloy are shown in Figure 9. The fig-

ure at each demagnetization curve gives the strength of the maximum magnetizing field. Each magnetization curve is obtained for a specimen thermally demagnetized at a temperature higher than the Curie temperature before each measurement. It can be seen from Figure 9 that H_{cl} increases with increasing the magnetizing field and as the magnetizing field is increased more than 600 kA/m, the squareness of the curve in the second quadrant is improved with a slight increase in H_{cl} .

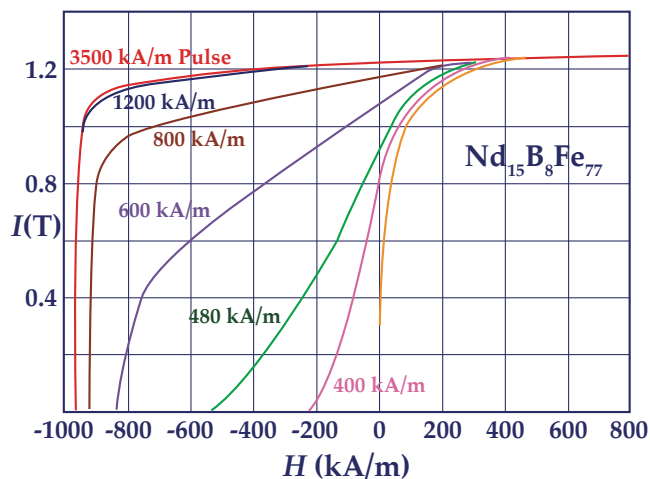


Figure 9 — Magnetization and demagnetization curves with different magnetizing fields for a $\text{Nd}_{15}\text{B}_8\text{Fe}_{77}$ magnet.

Magnetic and physical properties of a typical specimen which has the composition $\text{Nd}_{15}\text{B}_8\text{Fe}_{77}$ are as follows: $B_r = 1.23$ T, $H_{cB} = 880$ kA/m, $H_{cl} = 960$ kA/m, $(BH)_{max} = 290$ kJ/m³, temperature coefficient of $B_r = -1260$ ppm/K, temperature coefficient of $H_{cl} = -6000$ ppm/k, density = 7.4 Mg/m³, specific resistivity = 1.4 $\mu\Omega\text{m}$, Vickers hardness = 600, flexural strength = 250 MPa, tensile strength = 80 MPa, thermal expansion coefficient = $3.4 \times 10^{-6}/\text{K}$ (parallel to c axis), $-4.8 \times 10^{-6}/\text{K}$ (perpendicular to c axis).

Discussion

It has often been pointed out that the Curie temperatures in R-Fe compounds, extremely low compared with RCo compounds, increase with increasing Fe-Fe interatomic distances and with decreasing the number of Fe nearest neighbors.⁶

This is thought to be related to a high degree of localization of the Fe moment compared with the Co moments. For R-Fe compounds, the magnetic properties are mainly determined by the Fe-Fe interatomic distances and the number of Fe nearest neighbors, whereas for R-Co compounds, the magnetic properties are determined by the conduction electron transfer from the rare earth to the $3d$ band of Co.⁶

In the Nd-B-Fe tetragonal compound, it seems that B atoms play a role in expanding the Fe-Fe interatomic distances and/or decreasing the number of Fe nearest

neighbors, leading to a high Curie temperature compared with Nd-Fe binary compounds. Since the B concentration is less than 1/10 of the Fe concentration for the composition thought to be the single phase, it is likely that B atoms do not directly expand the interatomic distances and/or decrease the number of nearest neighbors, but act to stabilize the tetragonal phase which has long interatomic distances and/or few nearest neighbors compared with Nd-Fe binary compounds. To understand the relation between the magnetic properties and atomic environments, it is necessary to determine the precise atomic positions in the tetragonal unit cell. We have already started the analysis of the crystal structure and will present the result in the near future.

Since Nd^{3+} carries an orbital moment, it might be expected that the Nd-B-Fe tetragonal phase possesses a huge magnetic anisotropy through the action of crystal-line field. It is fortunate, however, that the tetragonal phase has a uniaxial anisotropy parallel to the c axis.

In addition to the remarkable magnetic properties of the Nd-B-Fe tetragonal compound, the metallographic condition in the ternary system also favored the realization of the practical permanent magnets. On the Nd-rich side of the stoichiometric composition of the tetragonal phase, there exist a nonmagnetic phase with a low-melting point which contains Nd more than 80 atoms %. This low-melting point phase acts as a sintering aid at a relatively low temperature and enables a liquid phase sintering. As a result, densification occurs without significant grain growth. The liquid phase formed might act to etch the damaged layer in the particle surfaces, leading to enhance the coercivity of the magnet.

The melting point of the Nd-rich phase is considered to be near the eutectic temperature of the Nd-Fe binary alloy, approximately 910 K,⁷ although it would be slightly modified by the addition of B. The enhancement of the coercivity by the post-sintering heat treatment at around 900 K is considered to be related to the eutectic reaction of the Nd-rich phase.

The steep rise in the virgin magnetization curve indicates a type of nucleation controlled coercivity mechanism. However, a simple nucleation model of magnetization reversal cannot explain the demagnetization curves shown in Figure 9. To understand the increase in both coercivity and the rectangularity of the I - H curve with increasing magnetizing field, it is necessary to assume pinning zones locally distributed in each grain with different depths of trapping against domain wall motion.

Since the saturation magnetization of the Nd-B-Fe tetragonal compound amounts to 1.35 T, permanent magnets having $(BH)_{max}$ of 330-340 kJ/m³ may be developed before long. The high mechanical strength of Nd-B-Fe based magnets, approximately twice that of the Sm-Co magnets, makes the treatment of the magnet

easy during machining work and assembly work. The low specific gravity compared with Sm-Co based magnets is effective in reducing the weight of magnetic circuits.

On the other hand, the high temperature-coefficients of B_r and H_{cl} of the Nd-B-Fe based magnets are significant disadvantages. From our latest research, it has turned out that 10-20 atoms % Co addition is effective in reducing the temperature coefficient of B_r , while small addition of heavy rare earths can practically improve the temperature coefficient of H_{cb} due to the increase of H_{cl} as high as 1600 kA/m, although the coefficient itself is not reduced.

The newly developed Nd-B-Fe magnets do not necessarily need less abundant Co. Common ores of rare earth contain 13-19 weight % Nd,⁸ which is 5 - 10 times more abundant than Sm. Therefore, as the reduction cost of Nd metal is decreased the Nd-B-Fe magnets will be able to compete with any other permanent magnets.

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Publishing History

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References

- ¹ John J. Croat; "Observation of large room-temperature coercivity in melt-spun $\text{Nd}_{0.4}\text{Fe}_{0.6}$," *Applied Physics Letters* 39, pp. 357 (1981), doi:10.1063/1.92728
- ² John J. Croat and Jan F. Herbst; "Melt-spun $\text{R}_{0.4}\text{Fe}_{0.6}$ alloys: Dependence of coercivity on quench rate," *Journal Applied Physics* 53, pp. 2404 (1982), doi:10.1063/1.330826
- ³ John J. Croat; "Magnetic hardening of Pr-Fe and Nd-Fe alloys by melt-spinning," *Journal Applied Physics* 53, pp. 3161 (1982), doi:10.1063/1.331014
- ⁴ N. C. Koon and B. N. Das; "Magnetic properties of amorphous and crystallized $(\text{Fe}_{0.82}\text{B}_{0.18})_{0.9}\text{Tb}_{0.05}\text{La}_{0.05}$," *Applied Physics Letters* 39, pp. 840 (1981), doi:10.1063/1.92578
- ⁵ N. C. Koon, B. N. Das. and J. A. Goehagan; "Composition dependence of the coercive force and microstructure of crystallized amorphous $(\text{Fe}_x\text{B}_{1-x})_{0.9}\text{Tb}_{0.05}\text{La}_{0.05}$ alloys," *IEEE Transactions on Magnetics* 18, pp. 1448 (1982), doi:10.1109/TMAG.1982.1061968
- ⁶ Hans R. Kirchmayr and Carl A. Poldy; *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gshneidner, Jr. and L. Eyring. (North-Holland, Amsterdam, 1979); Chapter 14.
- ⁷ William G. Moffatt, editor; *The Handbook of Binary Phase Diagrams* (General Electric, 1978), Volume 2.
- ⁸ Rare Earths, U.S. Bureau of Mines, Mineral Commodity Profiles (1979).