Paper

Synthesis of Hard Magnetic Nd-Fe-B Powders by a Thermochemical Process

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SYNOPSIS

Fabrication of Nd-Fe-B magnetic powders by R-D process using spray-dried precursors was tried. Due to stable formation of α -Fe as a primary phase as same as that in ingots, the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was not formed in the alloy powder with the composition of stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ unless excessive amount of Nd precursor or Ca was added in the process. However, this excessive addition, especially for Ca, led to abnormal grain growth of $\text{Nd}_2\text{Fe}_{14}\text{B}$. On the contrary, $\text{Nd}_2\text{Fe}_{14}\text{B}$ was successfully obtained as a major phase from the alloy powder with the composition of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ without such excessive addition. The size of spherical shape $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles mostly consisted of one or more subgrains was less than $1\text{ }\mu\text{m}$. The coercivity measured from this powder was relatively low ($\sim 3\text{ kOe}$) mostly due to residual CaO and soft magnetic phases.

KEYWORDS

Nd-Fe-B, R-D process, Spray drying, Magnetic powder

1 Introduction

Nd-Fe-B magnetic powders for making sintered or bonded Nd-Fe-B magnets are commonly prepared by crushing Nd-Fe-B ingots or melt-spun flakes, which need additional energy and increase the production cost because of using high-purity metals as starting materials. One inexpensive alternative way is to prepare the Nd-Fe-B powders by reduction-diffusion (R-D) process¹⁻³⁾ that was originally applied for the preparation of SmCo_5 alloys. Typically, in this process, neodymium oxides are reduced by calcium in the presence of iron or iron oxide and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is formed simultaneously by solid state diffusion. The reacted alloy powder is then washed with water or dilute acid to remove calcium oxide and dried. Currently, this method is applied to prepare magnetic powders only for making sintered Nd-Fe-B magnets.

Meanwhile, spray drying has been widely use for preparing granulated powders of ferrites, carbides, nitrides, titanates, and other electrical ceramics. Not only it provides uniformly dispersed components, allowing exact composition control of a desired compound, but also it is possible to obtain fine particles of the final product. It has been shown that the size of final Nd-Fe-B product of R-D process depends on the size of starting iron powder^{4,5)}. Furthermore, when superfine precursors were employed in

R-D process, the reaction temperature and the reaction time were significantly reduced, resulting in small particulate powders ($\sim 6\text{ }\mu\text{m}$ in diameter) of Nd-Fe-B alloys⁵⁾. It implies that uniformly distributed ultrafine Nd-Fe-B powders could be obtained if the spray-dried precursors are used as starting materials for R-D process.

Therefore, using spray-dried precursors, we attempted to fabricate Nd-Fe-B magnetic powders with the target composition of stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$, a typical composition of a commercial sintered magnet, by the R-D process in this paper, and the phase evolution in each process step and the magnetic properties of the final products were investigated.

2 Experimental

The raw materials used were $\text{Nd}(\text{NO}_3)_6\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, and H_3BO_3 . They were weighted and dissolved into deionized water to make the solutions for spray drying, with the target composition of $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ (stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$) and $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$. 10% excess neodymium hydrate was weighted in to compensate neodymium loss during the reactions. Spray drying was performed at $250\text{ }^\circ\text{C}$ with nozzle rotation velocity of 11,000 rpm and feed rate of aqueous solution of 20 ml/min. so that Nd, Fe, and B components could be uniformly dispersed in the spray-dried

precursors. These precursors were debound at 900 °C for 2 hours in air to remove all of the volatile components and to form oxides. To obtain finer final products⁹, the debound oxide powders were milled for 20 hours under a vacuum in a sealed steel vial with steel balls 6.3 mm in diameter. The milled oxides were then hydrogenated at 800 °C for 2 hours to reduce iron oxide to α -Fe. The hydrogen-reduced powders were mixed with granular calcium, with the mixing ratio of Ca to powder of 2:1, and compressed into compacts. The reduction-diffusion of the compacts was carried out at 1,000 °C for 3 hours under a flowing Ar atmosphere. The reacted compacts were stirred in deionized water into a slurry state. The slurry was washed repeatedly using dilute acetic acid and water. Eventually, the Nd-Fe-B alloy powders were recovered and dried in a vacuum.

Phase identification of the powders was performed by Cu K α X-ray diffraction. Morphologies and microstructures of the powders were examined with a SEM and a TEM. The magnetic properties of the final powders were measured with a VSM with a maximum applied field of 20 kOe.

3 Results and Discussion

Fig. 1 shows X-ray diffraction patterns of the powders

Fig. 1 X-ray (Cu K α) diffraction patterns of Nd₂Fe₁₄B powders after (a) spray-dried, (b) debound at 900 °C for 2 hrs., (c) ball milled for 20 hrs., (d) H₂ reduced at 800 °C for 2 hrs., (e) Ca reduced at 1000 °C for 3 hrs. with Ca: powder = 2:1, and (f) washed and dried.

obtained from the first step (i.e., spray drying) to the final one (i.e., washing and drying) of R-D process for Nd₁₂Fe₈₂B₆ (stoichiometric Nd₂Fe₁₄B). As shown in Fig. 1 (a), the spray-dried precursor was amorphous whose morphologies were spherical shells 5 ~ 40 μ m in diameter. After debinding, as shown in Fig. 1 (b), NdFeO₃ and Fe₂O₃ (Hematite) were mainly formed with small NdOCl, B₂O₃, and NdBO₃. In fact, the debound product was mostly well-dispersed oxides of Nd, Fe, and B with finer particle size of < 2 μ m⁹. This chemical mixture of oxides is one of the advantages of the present fabrication method because the chemically mixed one is more active for subsequent treatment than the mixture of coarser and/or mechanically mixed powders of oxides used as starting materials in previous work⁷. As can be seen in Fig. 1 (c), the minor phases such as NdOCl, B₂O₃, and NdBO₃ were not detected after milling. They seemed to be decomposed due to the mechanical stress generated during long-time milling. It has been shown that the milling before or after H₂ reduction is a necessary step to obtain well-dispersed Nd₂Fe₁₄B particles as final products⁹. After H₂ reduction (Fig. 2 (d)), FeNdO₃ was still maintained, but α -Fe was completely separated out from aggregated Fe₂O₃ (Hematite).

In R-D process, Nd-oxides are reduced by Ca in the presence of iron or iron oxide and Nd₂Fe₁₄B phase is formed simultaneously by solid state diffusion²). Therefore, Nd₂Fe₁₄B and CaO should be only remained after Ca reduction. However, as shown in Fig. 1 (e), α -Fe was still

Fig. 2 X-ray (Cu K α) diffraction patterns of Nd₂Fe₁₄B powders after Ca reduced at 1000 °C for 3 hrs. The mixing ratio of Ca to powder of (a), (b), and (c) are 3:1, 5:1, and 7:1, respectively, with the addition of 25% excess Nd.

sustained as a major phase with CaO after Ca reduction, and other oxides such as Nd_2O_3 (A type, hexagonal) and soft magnetic Fe_2O_3 (Maghemite) were also formed, all due to insufficient reduction and diffusion. Consequently, the final powders obtained after washing and drying were mostly α -Fe with small amount of Nd_2O_3 . It was found that it is necessary to add more Ca and/or Nd in order to obtain $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase from the stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ composition.

In fact, when 25% excess Nd-hydrate was added to the starting materials and the mixing ratio of Ca to powder increased as 3 : 1, 5 : 1, and 7 : 1, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was successfully formed as a major phase as shown in Fig. 2. However, with the mixing ratio of Ca to powder of 3 : 1, α -Fe still coexisted with $\text{Nd}_2\text{Fe}_{14}\text{B}$ (Fig. 2(a)), even when excessive amount of Nd was 30%. And α -Fe disappeared

completely only with the mixing ratio of more than 5 : 1. Unfortunately, as shown in Fig. 3, particles in the final products were grown abnormally with the increase of calcium dose, resulting in polyhedral particles with the size of $\leq 10\text{ }\mu\text{m}$. It shows that excessive dose of Ca enhances the formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$, but is harmful to obtain fine particles. Eventually, it deteriorates the magnetic properties of Nd-Fe-B powders (See Fig. 5(b)).

Above results suggest that it will not be easy to obtain the Nd-Fe-B powder consisted of $\text{Nd}_2\text{Fe}_{14}\text{B}$ single phase,

(a)

(b)

(c)

Fig.3 SEM images of $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders after Ca reduced at 1000°C for 3 hrs. Ca: powder=(a) 3 : 1, (b) 5 : 1, and (c) 7 : 1, with the addition of 25% excess Nd.

(a)

(b)

(c)

Fig.4 (a) X-ray ($\text{Cu K}\alpha$) diffraction pattern, (b) SEM image, and (c) TEM image of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ powder.

whose composition is stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$, because $\alpha\text{-Fe}$ is crystallized as a stable primary phase in the alloy powder as same as that in the ingot of the stoichiometric composition⁸⁾. As demonstrated below, therefore, to fabricate the Nd-Fe-B powders mainly consisted of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and exhibit reasonably high magnetic properties by the thermochemical process, it is desirable to choose a composition in which Nd is richer than that in the stoichiometric one.

When the target composition was $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$, in fact, the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ was formed as a major phase without the aid of too much excess Nd or Ca. Fig. 4 (a) shows x-ray diffraction pattern obtained from the $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ powder fabricated with 10% excess Nd and the mixing ratio of Ca to powder of 2 : 1. As shown in the figure, the powder was mostly composed of $\text{Nd}_2\text{Fe}_{14}\text{B}$ with some residual CaO. As shown in Fig. 4(b) and (c), particles of $\text{Nd}_2\text{Fe}_{14}\text{B}$ with the size of $< 1 \mu\text{m}$ were aggregated to form clusters. And each particle was composed of one or more subgrains of $\text{Nd}_2\text{Fe}_{14}\text{B}$.

Fig. 5 shows magnetization curves of above mentioned $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ powders. As shown in Fig. 5(a), Nd-Fe-B powders in which the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase were coexisted with the soft magnetic $\alpha\text{-Fe}$ yielded very low coercivity and remanence (See Fig. 2 (a)). Unfortunately, increase of the mixing ratio of Ca to powder more than 5 : 1 to obtain fully developed $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in the stoichiometric composition deteriorated the magnetic properties further, as shown in Fig. 5(b), even though the major phase in the powder was $\text{Nd}_2\text{Fe}_{14}\text{B}$ (See Fig. 2(b)). On the other hand, as shown in Fig. 5(c), the coercivity of $\sim 3.0 \text{ kOe}$ was obtained from $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ powders without the aid of too much excess Nd or Ca. Constriction of the loop in Fig. 5(c) at low applied field was mainly due to the residual soft magnetic phases.

4 Conclusions

Nd-Fe-B magnetic powders were fabricated by R-D process using spray-dried precursors. Unless excessive amount of Nd precursor or Ca was added, the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was not formed in the alloy powder of stoichiometric $\text{Nd}_2\text{Fe}_{14}\text{B}$ because the soft magnetic $\alpha\text{-Fe}$ was formed as a primary phase. However, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was fully developed in the alloy powder of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ without such excessive addition. The particle size of $\text{Nd}_2\text{Fe}_{14}\text{B}$ in $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ powder was less than $1 \mu\text{m}$. Magnetic properties of this powder was relatively poor, resulting in the coercivity of $\sim 3 \text{ kOe}$, mainly due to residual CaO and soft magnetic phases.

Fig.5 Hysteresis loops of Nd-Fe-B powders Ca reduced at 1000°C for 3 hrs. The mixing ratio of Ca to powder is (a) 3 : 1 and (b) 5 : 1, with the addition of 25% excess Nd to $\text{Nd}_2\text{Fe}_{14}\text{B}$ composition. (c) The mixing ratio of Ca to powder is 2 : 1 with the composition of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$.

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