Nd-Fe-B sintered magnets fabrication by using atomized powders

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Abstract.

Nd-Fe-B sintered magnets are required to achieve high coercivity for improvement of their thermal stability. Dy is added to increase coercivity, however, this element decrease magnetization and energy products. Therefore, Dy-lean Nd-Fe-B sintered magnets with high coercivity are strongly demanded. To increase coercivity, it is necessary that microstructure of sintered magnets is consisted of both fine main phase particles and homogeneously distributed Nd-rich phases around the main phase. To meet those requirements, Nd-Fe-B atomized powders were applied to the fabrication process of sintered magnets. Comparing with the case of using strip casting (SC) alloys, jet-milled powders from atomized powders show homogeneous distribution of Nd-rich phase. After optimized thermal treatment, coercivities of sintered magnets from atomized powders and SC alloys reach 1050 kA·m⁻¹ and 1220 kA·m⁻¹, respectively. This difference in coercivity was due to initial oxygen concentration of starting materials. Consequently, Nd-rich phases became oxides with high melting points, and did not melt and spread during sintering and annealing.

1. Introduction

Nd-Fe-B sintered magnets, which have been invented by Sagawa et al. [1], possesses high energy products \((BH)_{max}\) and are used for various applications, for example, voice coil motors for hard disk drives and motors of hybrid electric vehicles (HEVs) or electric vehicles (EVs). Recently, HEVs and EVs are greatly paid attention due to a growing concern about environmental issues and the market of HEVs grows. Although Nd-Fe-B sintered magnets have high \((BH)_{max}\), there are several problems for use of motors in HEV. One is their low Curie temperature and the other is intrinsic coercivity so far realized reaches only 12% of the anisotropy field of Nd₂Fe₁₄B compound, which is the main phase of Nd-Fe-B sintered magnets. Therefore, to maintain high magnetic properties at high temperature environment in HEVs, additive elements such as Dy or Tb are used in the Nd-Fe-B sintered magnets because Dy₂Fe₁₄B and Tb₂Fe₁₄B compounds have higher anisotropy field than Nd₂Fe₁₄B. However, the magnetic moment of Dy is aligned antiparallel with those of Fe and Nd, and addition of Dy decreases remanence and \((BH)_{max}\). Moreover, the natural abundance of these additive elements is quite...
low and their material costs increase very rapidly. If the ideal coercivity of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) is obtained, the thermal stability is considered to be enhanced without these additive elements. Therefore, two methods to achieve high coercivity have been proposed. One is obtaining a uniform distribution of the Nd-rich phase that plays important roles in decreasing the nucleation site of reversed magnetic domains. If there are some defects on the surface of the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains, the reversed magnetic domains appear at low reverse magnetic field. Once a reversed magnetic domain appears in the grain, the domain wall moves and magnetic reversal occurs very easily. Therefore, it is required to decrease defects at the surface of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains in order to increase coercivity. The Nd-rich phase plays an important role in decreasing nucleation sites of the reversed magnetic domain during annealing process, then, contributes to increase the coercivity [2] –[7]. Another approach is controlling grain sizes below the single magnetic domain size [8]–[10] in sintered magnets. These approaches show that the control of microstructures of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) magnets is quite important to achieve high coercivity.

The microstructure of the sintered magnets is influenced by each production process such as melting, casting, hydrogen decrepitation (HD) treatment, jet milling, magnetic pressing, sintering, and heat treatments. When the distribution of Nd-rich phase is not homogeneous, the Nd-rich phase segregates, and hence the decreasing the nucleation sites of the reversed magnetic domains occurs partially during the sintering or subsequent annealing process. The degree of increase in coercivity of \( \text{Nd-Fe-B} \) magnets is small in such a case. When the distribution of Nd-rich phase is homogeneous, which means the Nd-rich phase does not segregate, it is easy for the Nd-rich phase to spread between main phase grains during the sintering or subsequent annealing processes. In this case, the Nd-rich phase spreads along grain boundaries and decreases the nucleation sites. Then high coercivity may be obtained. Therefore, the distribution of Nd-rich phase is an important factor to achieve high coercivity for \( \text{Nd-Fe-B} \) sintered magnets.

In our previous report, the relationship between the microstructure of strip casting (SC) alloys, which was the conventional starting material, and distribution of the Nd-rich phase in the jet-milled \( \text{Nd-Fe-B} \) powder particles, have been evaluated [11]. The relationships between the lamella interval of SC alloy and jet-milled \( \text{Nd-Fe-B} \) powder size were evaluated. The Nd-rich phase is aggregated and the distribution of Nd-rich phases becomes worse when the average diameter of \( \text{Nd-Fe-B} \) jet-milled powders decreases. It is caused by the fact that the powder size of \( \text{Nd-Fe-B} \) jet-milled powder is much smaller than the average lamella interval of strip cast alloys.

To achieve small lamella interval, we focused on atomized powders. Sakaguchi et al. [12] have been reported microstructure of \( \text{Nd-Fe-B} \) atomized powders. When the diameter of atomized powder is less than 40 µm, the interval of Nd-rich phase becomes less than 2 µm, which is close to the diameter of \( \text{Nd-Fe-B} \) jet-milled powders. If \( \text{Nd-Fe-B} \) atomized powders use as the starting materials, it is expected to improve Nd-rich phase distribution by using atomized powders. However, there are few reports about microstructure during the fabrication processes using \( \text{Nd-Fe-B} \) atomized powders as a starting material. In this report, \( \text{Nd-Fe-B} \) atomized powders were applied to the fabrication process of sintered magnets with small grain size.

2. Experimental

Atomized powders were prepared as a starting material to fabricate \( \text{Nd-Fe-B} \) sintered magnets. The composition was \( \text{Nd}_{14.49}\text{B}_{0.13}\text{Cu}_{0.03}\text{Al}_{0.66}\text{Fe}_{8.17} \) (at%). SC alloys with same composition that are used as conventional sintering materials were also prepared. Fine powders were fabricated by a jet milling after rough pulverization by the conventional HD process. Fine powders were packed into a mold by press-less process (PLP) [13] and aligned by pulse magnetic field. The mold in which powders were packed through the PLP was sintered in furnace. The base pressure of the furnace for sintering was less than 2.4 x 10⁻⁴ Pa. After sintering, two step annealing were promoted. The temperature of first annealing was 700 and 800 °C and annealed for 1 hour. The temperature of secondary annealing was varied from 450 to 600 °C. After annealing, samples were quenched in vacuum.

The powder size of the \( \text{Nd-Fe-B} \) jet-milled powders was evaluated by the laser diffraction method. The lamella interval of atomized powders and SC alloys and the distribution of Nd-rich phase of jet-
milled powders were observed and evaluated by Scanning Electron Microscope (SEM) - Energy Dispersive X-ray Spectroscopy (EDS) and Wave-length Dispersive Spectroscopy (WDS). The distribution of Nd-rich phase was evaluated by the ratio of grains that contained the Nd-rich phase. Magnetic properties of sintered magnets were measured by the pulsed magnetometer.

3. Results and discussion

Microstructures of starting materials were evaluated [14]. The lamellar interval of SC is 3.9 µm. The Nd-rich interval of atomize powder depends on the particle size of atomized powders. The lamellar interval is smaller than 2 µm when the diameter of the atomized powder becomes smaller than 40 µm. Consequently, atomized powders of whose diameter was less than 40 µm were used to fabricate sintered magnets. Both starting materials were pulverized by the jet milling after the HD. The diameter of Nd-Fe-B powders was evaluated. The average diameter of Jet-milled powders from atomized powders and SC alloys were 1.32 µm and 1.42 µm, respectively. For jet-milled powders from SC alloys, the maximum diameter of Nd-rich phase was 1.33 µm and this value was comparable to average diameter of jet-milled powders as we evaluated in previous paper [11]. However, for jet-milled powders from atomized powders, the maximum diameter of Nd-rich phase was only 0.41 µm. This value was about a third compared to the case in SC alloys. Moreover, the ratio of the jet-milled powders containing Nd-rich phases shows 71% by using atomized powder and it is higher than the powders from SC alloys. These Nd-rich phase distribution shows that decreasing the difference between Nd-rich phase interval in starting materials and particle size achieved homogeneous microstructure in jet-milled powders.

Jet-milled powders were sintered after packing through PLP method. Sintering temperatures were fixed at 930 °C and 950 °C for jet-milled powders pulverized from SC alloys and atomized powders, respectively. Each sintering temperature was decided on condition that it should be the lowest temperature that keeps the density of sintered bodies over 7.5 g/cm³. In spite of smaller average diameter of jet-milled powders from atomized powders, sintering temperature for atomized powders is higher than that for SC alloys. This discrepancy is discussed later. Coercivities of as sintered magnets were 710 kA·m⁻¹ and 640 kA·m⁻¹ for SC alloys and atomized powders, respectively. Saturation magnetization is almost 1.44 T for both sintered magnets. For sintered magnets fabricated from each starting materials, squareness ratio, that is ratio of remanence to saturation magnetization, is about 0.96. This shows that atomized powders were sufficiently pulverized. If jet-milled powders contains atomized powders that is not pulverized, jet-milled powders do not aligned by the magnetic field because atomized powders are consisted of several Nd-Fe-B grains with randomly aligned.

Coercivity change after secondary annealing is shown in figure 1. Open and closed markers show the coercivity of magnets from SC alloys and atomized powders, respectively. Over 525 °C, magnets which were annealed lower temperature, show higher coercivity. Coercivity increases after secondary annealing. The highest coercivity is obtained after annealed at 550 °C, and coercivity of magnet that is fabricated from atomized powders and SC alloys reach 948 kA·m⁻¹ and 1120 kA·m⁻¹, respectively. The demagnetization curves for sintered magnets from atomized powders and SC alloys are shown in figure 2 and 3, respectively. Only the magnet from SC alloys annealed at 800 °C show the highest coercivity after annealing at 575 °C. However, the coercivity is lower than magnets annealed at 700 °C.
To improve magnetic properties, the cooling rate of thermal treatments was also compared. The first and secondary annealing temperature was fixed at the 700 °C and 550 °C, respectively. Cooling in furnace was promoted as a low speed cooling process and quenching under inert gas atmosphere was promoted as a high speed cooling. For sintered magnets from atomized powder, coercivities become 808 kA·m⁻¹ for low speed cooling and 1050 kA·m⁻¹ for high speed cooling, respectively. After high speed cooling, high coercivity was obtained for magnets from SC alloys and it becomes 1220 kA·m⁻¹. However, atomized powders have small Nd-rich interval, coercivity of magnets fabricated from atomized powders is lower than magnets from SC alloys. One reason is that the oxygen concentration of sintered magnets fabricated from atomized powders is about 2200 ppm and it was almost 1.5 times those from SC alloys. In starting materials, oxygen concentration of atomized powders was 460 ppm, which was about twice as large as that in the SC alloy. It shows that decreasing the oxygen content in initial atomized powders for reduction of oxygen concentration in sintered bodies. Therefore the fabrication condition of atomized powders, especially control of fabrication atmosphere is required. High oxygen content in Nd-rich phase results in increasing melting point of Nd-rich phase. Consequently, Nd-rich phases did not melt and spread during sintering and subsequently annealing. From this reason, it is considered that the optimized sintering temperature for jet-milled powders from atomized powders was higher than that from SC alloys.

Microstructure observation was promoted to discuss the increase in coercivity. Microstructures of sintered magnets from atomized powders and SC alloys are shown in figure 4. Dark and bright regions show Nd-Fe-B and Nd-rich phases respectively. Although size and distribution of Nd-rich phase are similar in microstructure for both starting materials, it was observed that Nd-rich phase spread into two grain boundaries for sintered magnet from SC alloys. Due to high oxygen concentration, better

**Figure 1.** Secondary annealing temperature dependence of coercivity. Open and closed markers show the coercivity of magnets from SC alloys and atomized powders, respectively. Shapes of marker shows intermediate annealing temperature. Squares and triangles show that first annealing temperatures are 700 °C and 800 °C, respectively.

**Figure 2.** Demagnetization curves for sintered magnets fabricated from atomized powders. Dashed and solid line shows as-sintered and secondary annealed at 550 °C, respectively.

**Figure 3.** Demagnetization curves for sintered magnets fabricated from SC alloys. Dashed and solid line shows as-sintered and secondary annealed at 550 °C, respectively.
Nd-rich phase distribution did not contribute effectively in atomized powders during sintering and annealing. Figure 5 shows Nd and Cu mapping by WDS. For as sintered magnets, Cu is aggregated. After annealing, aggregated Cu regions were disappeared and divided small sizes in Nd-rich phases. After sintering, samples were cooled in furnace. Consequently, equilibrium phases were appeared. Because Cu-Nd binary system has a low melting point, the phase contained Cu is remained as liquid phase at low temperature and aggregated in Nd-rich phase. After annealing and quenching, aggregated Cu was dispersed into Nd-rich phases in the sintered body.

Figure 4. Microstructure of sintered magnets from (a) atomized powders and (b) after secondary annealed at 550 °C.

Figure 5. Cu (left) and Nd (right) mapping of sintered magnets from atomized powders for (a) as-sintered and (b) annealed at 550 °C.

4. Summary
Comparing with the case of SC alloys, jet-milled powders from atomized powders show homogeneous distribution of Nd-rich phase. However, after sintering and optimized thermal annealing, coercivities of sintered magnets from atomized powders and SC alloys reach 1050 kA·m⁻¹ and 1220 kA·m⁻¹, respectively. This difference in coercivity was due to initial oxygen concentration of starting materials. Because the Nd-rich phase became oxide, its melting point raised and Nd-rich phase did not melt and spread during sintering and annealing.

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