

High-Thermostability Nd-Fe-B Magnet Formed by Binderless Net-Shaping

Toru MAEDA*, Asako WATANABE and Koji YAMADA

The recent needs for safe and secure automobiles and energy-saving appliances have increased the demand for high-efficiency motors and high-sensitivity sensors. While the performance of these devices largely depends on the intrinsic properties of the magnet materials used in such devices, it is also important to improve the flexibility and durability of the magnet in order to form them into complicated shapes and use them in high temperatures or severe environments. Although resin-bonded Nd-Fe-B magnets are known for their good formability, they lack in durability due to the poor heat resistance of resin. To overcome this challenge, we have developed a new process that enables the net-shaping of plastic deformable magnet powder and created a resin-free bonded Nd-Fe-B magnet with a high heat resistance.

Keywords: rare-earth magnet, bonded magnet, high heat resistance, net shape, thin-walled

1. Introduction

Permanent magnet materials (hereafter, “magnets”) are an important part used in a wide variety of devices and machines, such as hard disk drives, home appliances, automobiles, air conditioners, and wind power systems, affecting their conversion efficiency or detection sensitivity. The market for magnets is forecast to further expand in the future, driven by the growing demand for electric motors and generators due to the rising popularity of electric vehicles, the increasing use of wind power and other clean energy schemes, and globally widespread use of inverter-controlled air conditioners.

For these applications, small size, light weight, and low price are essential requirements. For example, one key consideration in the development of motors is a high torque density. Measures proposed to achieve this^{(1),(2)} are magnetic circuit designs incorporating arc-shaped magnets instead of conventional flat ones. It is forecast that there will be a growing demand for complex-shaped magnets. Accordingly, expectations are high for the net-shaping technique,^{*1} which offers an efficient method for creating magnets with complex geometries to meet specific design requirements at low cost. At the same time, it is equally important to improve the heat resistance of magnets. In conventional applications, magnets have been used typically at temperatures below 100°C. In recent years, however, they have been increasingly used in higher-temperature environments, such as in the engine bays of vehicles.

Ordinary magnets are manufactured by sintering.^{*2} However, complex-shaped sintered magnets require expensive machining due to the hardness of the raw material powder, and this is not possible with net-shaping. Meanwhile, bonded magnets, produced by binding the raw material powder with resin, are compatible with net-shaping. However, the use of resin poses heat-resistance problems, and so currently available bonded magnets fail to fully meet market needs.

This paper reports on our newly developed neodymium (Nd)-iron (Fe)-boron (B) magnet that meets both complex-shape and thermostability requirements using neither machining nor a binder.

2. Bonded Magnets and the Challenges Facing Them

The raw material most widely used in the manufacture of bonded magnets is an NdFeB^{(3),(4)} powder that exhibits high magnetic performance. Normally, the coercivity^{*3} of the NdFeB material is low, exhibiting a substantial decrease in magnetic functionality around 100°C. Consequently, to use an NdFeB magnet at high temperatures over 100°C, it is necessary to improve its coercivity. One possible technique for achieving this is to add a further element like dysprosium (Dy) to improve the coercivity.⁽⁵⁾ However, because Dy is an extremely rare material, other approaches to improving NdFeB powder for bonded magnets have been commercialized, including the rapid quenching⁽⁴⁾ and hydrogenation decomposition desorption recombination (HDDR)^{(6),(7)} processes, which make the crystal grains in the powder particles finer for improved coercivity. The resultant raw materials enable magnets to be used in high-temperature conditions above 100°C.

The above-mentioned NdFeB powder is too hard to be molded. It does not solidify when placed under pressure. As a solution to this challenge, bonded magnets are molded by blending the NdFeB powder with a resin, effectively binding the magnetic particles together. With this process, using a mold constructed to the desired geometric requirements enables the net-shaping of a complex-shaped magnet without the need for machining. This allows low-cost manufacturing of complex-shaped magnets. Depending on the pressure-application technique used, bonded magnets fall into two types: compression-molded and injection-molded.⁽⁸⁾

Compression-molded magnets are manufactured by: filling the mold with magnet powder and thermosetting resin such as epoxy; applying pressure by a compressor; and heat-curing the resin. The magnet produced by this process contains a high percentage of magnet powder, and accordingly, its strength (remanence^{*4}) is high in proportion to the percentage of the magnet powder filled. In contrast, injection-molded magnets are produced by: preparing a mixture of magnet powder and thermoplastic resin such as nylon resin; turning the mixture into slurry at

a temperature above the melting point of the resin; injecting the slurry into a mold constructed to achieve the end-product shape; and allowing the product to cool and solidify. Injection molding offers a high flexibility in mold shapes, enabling more complex magnet shapes than compression molding. However, to obtain the necessary fluidity of the slurry, the process requires a high amount of resin and a reduced percentage of magnet powder, resulting in lower remanence.

Epoxy and nylon resins soften and diminish in strength at around 100°C. Hence, ordinary bonded magnets lack the structural heat resistance required to be suitable for long-term use in high-temperature conditions above 100°C. To overcome this problem, it is necessary to use a resin with better thermostability. Recently, polyphenylene sulfide (PPS) and other thermoplastic resins that meet the requirement for excellent long-term stability in environments above 100°C have been commercialized for use in injection-molded magnets.⁽⁹⁾ However, when heated and melted, PPS resin is lower performing in slurry fluidity and in homogeneous dispersion of magnet powder compared with nylon resin. This leads to the need to use a substantially increased amount of resin. Consequently, on the one hand, the use of the PPS resin ensures improved structural heat resistance; on the other hand, the resulting magnet will suffer even lower remanence, in which injection-molded magnets are inherently inferior to compression-molded magnets. Meanwhile, with compression-molded magnets that exhibit high remanence, no thermosetting resin has yet been commercialized that sufficiently fulfills long-term stability requirements. These features are summarized in Table 1.

Table 1. Types and features of bonded magnets

	Pressure-application method	Typical binder	Percentage of magnet powder filled	Remanence	Structural heat resistance (>100°C)
Compression-molded magnet	Powder compression molding machine	Thermosetting resin (e.g. epoxy)	65 to 70 (vol%)	Excellent	Poor
Injection-molded magnet	Melting and injection	Thermoplastic resin (e.g. nylon)	50 to 60	Average	Poor
		Thermoplastic resin (PPS)	40 to 50	Poor	Excellent

Given the design goal of improving magnet performance through net-shape formability and arrangement of magnet shapes, any attempt to create a bonded magnet for use under high-temperature conditions would necessarily lead to the use of a PPS resin-based injection-molded magnet, despite its low remanence. The limitations would offset the benefits of the design. Consequently, with current bonded magnets, it is impossible to fully meet the requirements for high remanence and structural heat resistance in the desired temperature range at the same time.

3. Concept of the Newly Developed Magnet

As discussed in the previous section, bonded magnets are subject to a tradeoff between structural heat resistance and remanence. We studied molding methods characterized by the softening of the hard NdFeB powder in order to avoid the use of resin (the cause of the tradeoff). In short, we explored an innovative method that allowed the NdFeB powder to undergo plastic deformation under pressure so as to render strength to the molded product, thus enabling the net-shaping of complex geometry. To soften the NdFeB powder, we employed the HDDR process, which is a technique used to improve the coercivity of NdFeB. Figure 1 shows the concept behind the HDDR process.

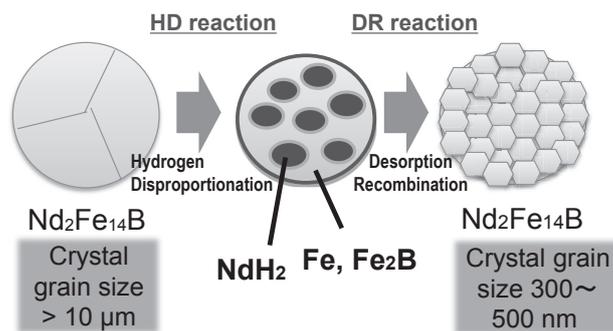


Fig. 1. Conceptual schematic of HDDR reactions

When cast through an ordinary casting process, the NdFeB powder would form coarse crystals with the grain size exceeding 10 μm. In general, coercivity increases with decreasing crystal grain size. In the aforementioned coarse condition, the product will lose its magnetic functionality at around 100°C. However, by heating the NdFeB powder in a hydrogen gas atmosphere at 700°C to 900°C, Nd dissociates from Fe and Fe₂B and reacts with hydrogen to form neodymium hydride (NdH₂). This is known as the hydrogenation decomposition (HD) reaction. Heat treatment of this substance under vacuum removes the hydrogen, allowing it to return to Nd₂Fe₁₄B. This is known as the desorption recombination (DR) reaction. During this reaction, the crystal grain size decreases to 300 to 500 nm, which improves the coercivity. After this process, the substance retains its magnetic functionality up to a temperature range of 150 to 200°C even without the addition of Dy. HD and DR reactions are generally processed consecutively, and hence, it is called the HDDR process.

In the state of dissociation following the above-mentioned HD reaction, in the structure of the powder, the neodymium hydride is dispersed in the parent phase of soft Fe, which accounts for approximately 60% of the total volume, and Fe₂B. With this structure, the powder is believed to be plastically deformable. Consequently, the design concept we embraced was to deform the powder under pressure for molding into a bulk body without the use of any resin. If it is possible to return this bulk body to Nd₂Fe₁₄B through a DR process, the result would be an

NdFeB magnet that features binderless forming of complex shapes, structural heat resistance, and improved coercivity owing to finer crystal grains.

A test was conducted on a method developed based on this design concept (Fig. 2).

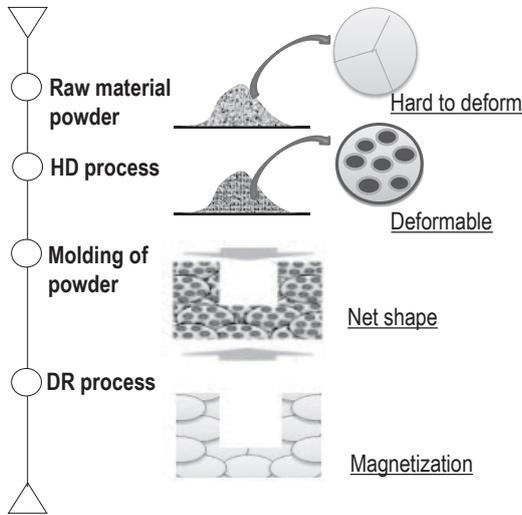


Fig. 2. Basic process of the newly developed method

4. Experimental Method

The starting material was a strip-casting (flakes approximately 300 μm in thickness) commonly used as a raw material for sintered magnets. The composition of the starting material was 62.9Fe-30.5Nd-5.0Co-1.1B-0.5Ga (wt%). The HD process comprised heat treatment in a hydrogen gas flow (at atmospheric pressure) in a temperature range between 750°C and 900°C for 2 hours. This was followed by pulverizing the strip cast material to an average particle size range between 50 and 500 μm to obtain molding powder. Subsequently, the obtained powder was molded at room temperature under a surface pressure of 1000 MPa. A 10 mm diameter mold (7 mm in height) was used to make samples for the evaluation of magnetic properties. To assess complex-shape molding, stack molds and those with features for forming thin-walled sections were used. The molded products were subjected to a DR process under vacuum (reachable minimum pressure: 1×10^{-2} Pa) at a temperature of 825°C. In this process, the temperature increased in a hydrogen atmosphere, and evacuation started when the prescribed temperature was reached.

Material structures were evaluated by observation with a scanning electron microscope (SEM) and phase identification by X-ray diffraction (XRD). Magnetic properties were evaluated with a BH tracer.

5. Experimental Results

5-1 Feasibility study of the new method

As the first step, analyses were conducted on the relationships between the HD process temperature and the

structural texture and between the HD process temperature and the formability. Figure 3 shows SEM images taken before and after the HD process. The latter SEM images were taken after HD processing at 750, 850 and 900°C. When examined by XRD, each sample revealed dissociation into NdH_2 , Fe, and Fe_2B . Fe and Fe_2B , which are indicated as gray portions, formed a parent phase. Spheroidized NdH_2 , indicated as white portions, was dispersed in the Fe. This structure replicates the report by Sugimoto et al.⁽⁷⁾

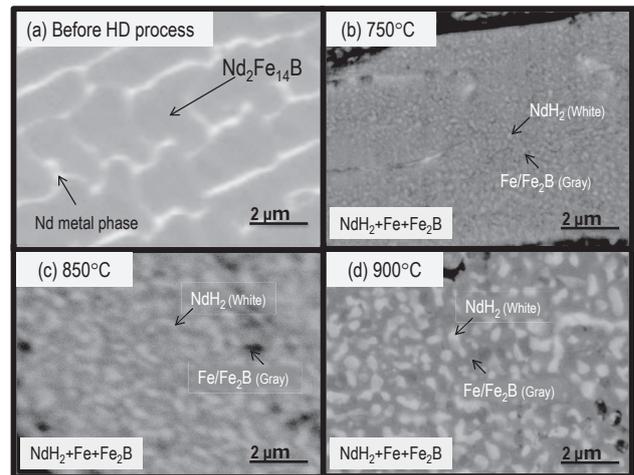


Fig. 3. SEM images taken before and after HD process

These powders were each formed into molded products. Figure 4 shows photos of the molded products, along with their relative densities. Without the HD process, the molded products failed to solidify and broke. In contrast, materials that had undergone the HD process at 750°C or higher successfully solidified. However, at 750°C, the HD process resulted in a low relative density of the molded product, chipped edges, and degraded formability. Consequently, it is highly probable that sufficient softening of the powder does not occur under 750°C HD process conditions.

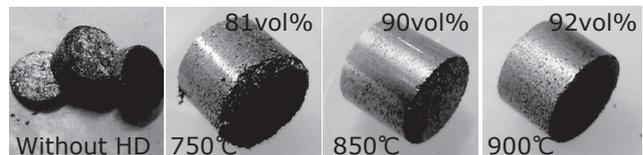


Fig. 4. Appearance of molded products (10 mm dia. \times 7 mm)

The samples subjected to the HD process at 850°C and 900°C exhibited favorable formability. Figure 5 shows SEM images of the samples that underwent the DR process at 825°C.

In the HD process at 850°C, the Fe and NdH₂ disappeared and all surfaces returned to Nd₂Fe₁₄B, successfully removing hydrogen. White dots represent an Nd metal phase originating from the raw alloy material. Meanwhile, the HD process performed at 900°C resulted in Nd₂Fe₁₄B being present in most areas. However, Fe seen as black portions and NdH₂ seen as white portions were observed, revealing an incomplete DR reaction. This suggests that a large distance between spherical NdH₂ phases before the DR process suspends the DR reaction due to the loss of contact between the NdH₂ phase and the Fe/Fe₂B phase. To be more specific, it is evident that NdH₂ must be, to some extent, finely dispersed in the parent phase. Consequently, an upper limit should be imposed on the HD process temperature. The present experiment revealed that the optimal temperature is 850°C.

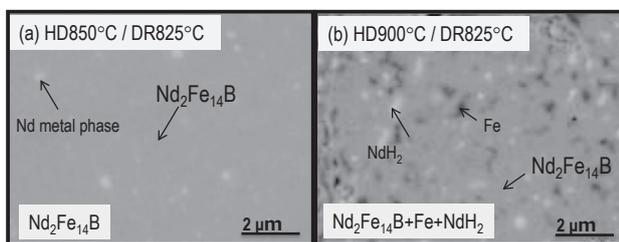


Fig. 5. SEM images of structures after DR process

Fracture surfaces of the samples were observed to check whether the HDDR process was effective for making finer crystal grains in the newly developed material. The result is shown in Photo 1.

The average particle size was approximately 400 nm. Even when the HD and DR processes were conducted separately, submicron fine crystals specific to the HDDR process were obtained.

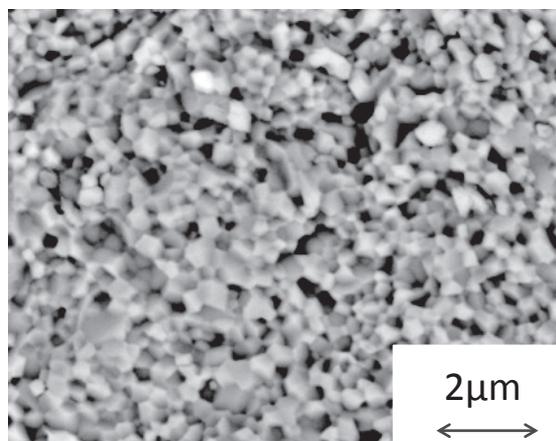


Photo 1. SEM image of fracture surface of product after DR process

Meanwhile, the DR process exhibited no problems such as bulges on molded products, with all molded products maintaining their shapes. The newly developed material proved itself to be compatible with net-shaping and adaptable to mold geometry. Thus, the new concept-based method turned out to be feasible.

5-2 Magnetic properties of prototype magnet

Table 2 compares the magnetic properties of the prototype magnet and bonded magnets. The properties of the bonded magnets were cited from data sheets (calculated estimates)⁽¹⁰⁾ provided by Molycorp, Inc. on compression-molded magnets (epoxy resin) and injection-molded magnets (nylon and PPS) formed from NdFeB rapid quenching powder (MQP-B).

Table 2. Remanence of prototype magnet

	Remanence (25°C) [T]
Prototype magnet	0.65
Bonded magnet (compression-molded/77.5 vol% epoxy)	0.69
Bonded magnet (injection-molded/60 vol% nylon)	0.53
Bonded magnet (injection-molded/50 vol% PPS)	0.44

The prototype magnet exhibited a remanence of 0.65 T at room temperature, which is comparable to the best performing compression-molded bonded magnets. Moreover, while, as shown in Table 1, bonded magnets incorporating epoxy resin for compression molding appear not to meet the need for long-term structural heat resistance above 100°C, the prototype magnet exhibited no dimensional change or deformation after measurement at 200°C. Hence, the prototype magnet provides better structural heat resistance than bonded magnets of the same level of remanence. Consequently, the prototype magnet achieves both the required structural heat resistance and compatibility with net-shaping without compromising remanence. This implies that the prototype magnet is not subject to the tradeoff that offsets the improvements achieved by well-arranged magnet geometry.

Next, Figs. 6 and 7 show a demagnetization curve for the prototype magnet and the temperature dependence of

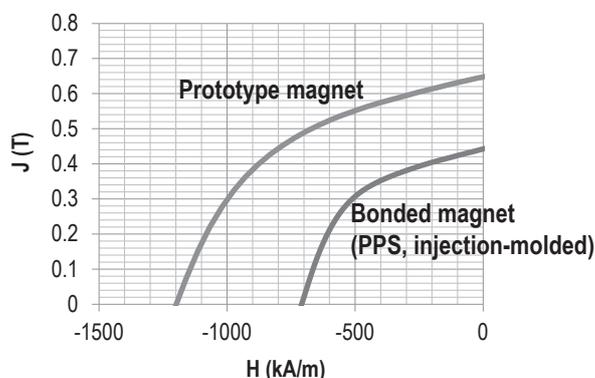


Fig. 6. Demagnetization curves at room temperature

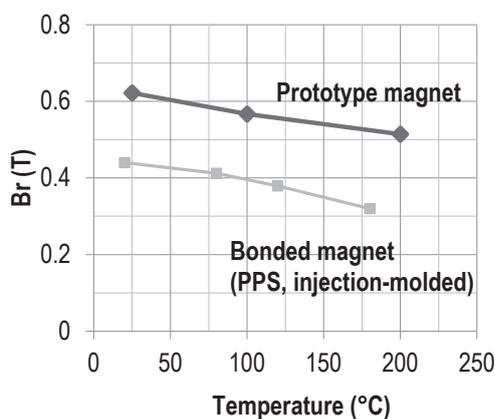


Fig. 7. Temperature dependence of remanence

remanence, respectively. Both figures also show the properties of injection-molded magnets⁽¹⁰⁾ for comparison. These injection-molded magnets incorporate PPS resin and, exhibit high structural heat resistance among bonded magnets. The prototype magnet exhibited approximately 50% higher remanence (the intercept on the vertical axis in Fig. 7) than the injection-molded magnet. The difference remained up to high temperatures around 200°C. These results prove that the prototype magnet is suitable for net-shaping and offers both high structural heat resistance and remanence.

5-3 Molding considerations for complex-shaped parts

Photo 2 shows prototype products of various geometries obtained by the use of molds with irregularities, curved surfaces, and thin-walled sections (about 1 mm in thickness). These molded products developed no cracks or chipping, demonstrating their suitability for net-shaping. Important factors involved in the molding of complex shapes include the fluidity of the powder, as well as high strength of the molded product. To be more specific, poor fluidity results in uneven mold filling, bridging in the mold, or powder build-up. These in turn result in locally low magnet powder filling rates and therefore low-strength portions, which can lead to cracks or chipping. While powder particle shape, friction between powder particles and various other factors are involved in fluidity, the most significant factor is powder particle size. In the case of



Photo 2. Various shapes of prototypes

sintering, crystal grains are generally pulverized to a particle size of 5 μm or smaller for coercivity purposes. The fluidity of this pulverized powder is extremely low to the extent that it is impossible to achieve a homogenous molded product using a complex-shaped mold. This is a reason why sintering is not suitable for net-shaping. In comparison, the newly developed method employs the HDDR process to achieve fine crystal grains for improved coercivity. One feature of this process is that it enables the control of the particle size of the powder within a range not affecting the progress of the HD and DR reactions. More specifically, this method allows a particle size of 50 μm or larger for enhanced fluidity. As a result, complex-shaped molding is possible. Regarding achievable height differences and thicknesses, additional improvements can be made by optimizing the powder fluidity and mold design.

Thus, we have explored the possibility of molding complex-shaped parts, such as those with height differences and thin-walled rings, without the use of resin or machining. The new concept-based method enables the production of NdFeB magnets that meet the demand for complex shapes, heat resistance and environmental resistance.

6. Conclusion

In this study we developed an innovative high-heat-resistance magnet that differs from conventional sintered or bonded magnets. The newly developed magnet is suitable for net-shaping of complex geometries, eliminating the need for a binder such as resin. This innovative magnet utilizes the property of soft Fe and Fe₂B, which turn into a parent phase in the intermediate stage of creating an NdFeB magnet in the HDDR process. Our findings are summarized below.

- (1) High-hardness NdFeB magnet powder is unsuitable for pressure molding. Treating the magnet powder in a hydrogen atmosphere at 850°C enables its pressure-molding without a binder such as resin. Molded products produced through this treatment exceeded 90 vol% in density.
- (2) Magnets produced from these molded products through heat treatment under vacuum were free of dimensional changes and deformation even at 200°C. The remanence of these magnets was approximately 50% higher (at 0.65 T) than those of conventional heat-resistant bonded magnets (incorporating PPS resin).
- (3) The newly developed method enables net-shaping of complex geometries such as irregularities and curved surfaces, along with rings with thin-walled sections and arcs.

These results suggest that the newly developed magnet will meet the complex-shape requirements of magnetic circuit design calculated for reducing the size, weight and cost of motors.

Future tasks include additional improvements to the degree of freedom of geometry, assessment of variation in

dimensions and magnetic properties on a mass-production scale, and evaluation of the long-term reliability of the magnets, such as their thermostability and environmental resistance. Through these research and development activities, we intend to respond to specific user needs.

Technical Terms

- *1 Net-shaping: A molding process characterized by the use of a raw material powder, a mold, and a pressing or injection machine, which is designed to directly achieve an end-product shape without using machining or other subsequent processes.
- *2 Sintering: A magnet manufacturing method that compacts a raw material powder to a low-density solid at 40 to 50 vol% and then heat-treats the solid at a high temperature above 1000°C to closely pack it nearly to the full density (> 95 vol%). With sintering, it is difficult to perform net-shaping for complex shapes due to the low strength of low-density solidified bodies and substantial dimensional shrinkage.
- *3 Coercivity: A measure of magnet performance; the higher the coercivity of a magnet, the higher the temperature range in which the magnet continues to be functional (producing magnetic lines of force).
- *4 Remanence: A measure of magnet performance; the higher the remanence of a magnet, the stronger the magnetic lines of force produced by the magnet (an advantage in terms of motor torque enhancement).

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Contributors The lead author is indicated by an asterisk (*).

T. MAEDA*

- Dr. Eng
Assistant General Manager, Advanced Materials Laboratory



A. WATANABE

- Assistant Manager, Advanced Materials Laboratory



K. YAMADA

- Group Manager, Advanced Materials Laboratory

