## Recent Research Trend in Powder Process Technology for High-Performance Rare-Earth Permanent Magnets<sup>†</sup>

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### Abstract

Higher performance is constantly required in rare earth permanent magnets, which are an indispensable component of the motors of electric vehicles. When producing sintered magnets, advanced structural control is necessary in the powder metallurgy process in order to achieve high performance. Especially in recent years, it has become important to develop processes for Sm-Fe-N magnets and metastable phase magnets as next-generation magnets to replace the Nd-Fe-B magnets. Because the crystal grain refinement of sintered magnets is most effective for improving coercivity, production methods for raw powders have evolved from the traditional pulverization to chemical synthesis approaches, and as a result, a submicron-sized Sm-Fe-N powder with huge coercivity has been developed. State-of-the-art physical synthesis methods have also been applied successfully to the synthesis of nanopowders. Since control of the grain boundary is very effective in Nd-Fe-B magnets, this approach has also been evolved to Sm-Fe-N magnets by nano coating. On the other hand, since technologies for crystalline orientation control and high-density sintering are indispensable for improvement of remanence, new low-thermal load consolidation techniques such as spark plasma sintering are being developed for Sm-Fe-N magnets and metastable phase magnets in order to overcome the inherent low thermal stability of these materials.

Keywords: rare earth permanent magnets, powder metallurgy processes, grain refinement, crystalline orientation, grain boundary control

### **1. Introduction**

Rare earth permanent magnets are a typical material produced by powder metallurgy technology, and most of these products are now used in electric motors. Permanent magnet synchronous motors (PMSMs) using rare earth magnets are much more efficient than inductive motors, and were the driving force behind the industrialization of hybrid and electric vehicles in the late 1990s. More recently, higher efficiency has been required in motors in response to the growing need for global CO<sub>2</sub> reduction, and new high-performance permanent magnets are being developed from this viewpoint. Among rare earth magnets, materials based mainly on Nd-Fe-B, Sm-Co and Sm-Fe-N have been industrialized, but most magnets used in motors are Nd-Fe-B magnets. As a practical problem, the prices of the specific rare earth and heavy rare earth elements that are the raw materials for these rare earth magnets, such as the Nd and Dy used in Nd-Fe-B magnets, are easily affected by the international situation due to their strongly uneven

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 TEL: +81-52-736-7561 FAX: +81-52-736-7406 regional distribution (Seo Y. and Morimoto S., 2014). In particular, since the "rare earth shock" of 2010, difficult development aimed at improving magnetic characteristics while considering resource problems has been urgently needed.

Various magnetic properties must be considered when developing permanent magnet materials for motors, but the most important are the maximum energy that can be extracted from the magnet  $(BH)_{max}$  and coercivity, which indicates the resistance to the opposite magnetic field. Although  $(BH)_{max}$  is determined by various magnetic properties such as remanence, coercivity and rectangularity, the most influential factor is remanence. In other words, the first consideration when developing a high-performance magnet is improvement of coercivity and remanence.

The potential for improving coercivity depends on the anisotropic magnetic field, which is an intrinsic property of each magnetic compound, but coercivity very strongly depends on the crystal grain size and grain boundary structure. For example, the anisotropic magnetic field of  $Nd_2Fe_{14}B$  is about 1/3 that of  $Sm_2Fe_{17}N_3$ , but the coercivity of the  $Nd_2Fe_{14}B$  bulk magnet, which is achieved by using advanced microstructural control technology, exceeds that of  $Sm_2Fe_{17}N_3$ . Many studies so far have shown that the basic guidelines for developing high coercivity magnets are selection of a magnetic material with a high anisotropic



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magnetic field, refinement of its microstructure and appropriate control of its grain boundary structure.

On the other hand, the guideline for high remanence is achieving remanence closer to saturation magnetization, which is an intrinsic property of the compound. The easy axis and hard axis of magnetization in a magnetic crystal are mutually orthogonal, and high magnetization is achieved in the direction of the easy axis. This means that a high crystal orientation is necessary in a magnet with a high remanence. Moreover, since the occupied volume ratio of the magnetic phase in a sintered magnet is also important, pores and non-magnetic phase should be reduced to the absolute minimum.

As described above, in the development of highperformance rare earth magnets, various factors such as grain refinement, grain boundary control, crystal orientation and high density must be achieved simultaneously. For this reason, most modern rare earth magnet materials are produced by powder metallurgy technology, which enables advanced microstructural control. However, various restrictions arise in the production process because the rare earth powders which are the constituents of the magnets are more easily oxidized than aluminum and magnesium, and thus, various restrictions arise in the process of passing through powder with an extremely large specific surface area. In order to solve this complex problem, various advanced powder processes from powder preparation to consolidation have been developed in an integrated manner. This paper describes the trends in the development of powder processes for improving coercivity and remanence, focusing on Nd-based and Sm-based magnets. The development and expectations of the powder process for metastable phase magnets and nanocomposite magnets, which are considered to be next-generation magnets, are also described.

Fig. 1 compares the various powder processing tech-



Fig. 1 Comparison of various preparation methods of rare earth magnet powder. The blue and orange areas represent isotropic and anisotropic powders, respectively.

niques in term of coercivity. The traditional mechanical pulverization, mechanical alloying and melt spinning methods were applied in powder preparation with the aim of refining the crystal size to improve coercivity. Grain refinement made it possible to achieve high coercivity in the powders produced by these methods, and coercivity as high as 1.7 MA/m has been achieved in Nd-Fe-B magnets. Therefore, for example, Nd-Fe-B and Sm-Fe-N based powders produced by melt spinning were industrialized at an early stage. However, since these powders have a polycrystalline structure with random crystal orientations, it is difficult to orient the crystals when they are used as bulk magnets, which means they cannot be used directly in high-remanence magnets. The hydrogenationdisproportionation-desorption-recombination (HDDR) process and the reduction-diffusion (R-D) process have been developed in recent years to overcome this problem. The HDDR process is capable of producing polycrystalline powders with a crystalline orientation, and the R-D process make it possible to obtain very fine single-crystal powders. These respective processes realize anisotropic powders with high coercivity of more than 1.5 MA/m and huge coercivity of up to 4.7 MA/m, respectively. Recently, advances in mechanical pulverization methods such as ball milling and jet milling have made it possible to produce submicron-sized powders, and physical synthesis approaches such as the thermal plasma method have been applied successfully to nanopowders.

In addition, as mentioned above, the development of high coercivity magnets by grain boundary control in sintered compact is being actively carried out with Nd-Fe-B magnets. Forming Dy-Fe-B with a high anisotropic magnetic field at the grain boundaries of Nd-Fe-B magnets greatly improves coercivity. Initially, the grain boundary phase was formed by using a mixed powder (two-alloy method), but the development of the grain boundary diffusion method has made it possible to obtain high coercivity magnets. In the Sm-Fe-N magnet, high coercivity of up to 4.7 MA/m has been obtained by adding Zn to the grain boundaries, and more recently, sintered magnets with high coercivity and high remanence have been discovered by combining low oxygen powder metallurgy with powder coating.

Various powder processes have been also examined to improve remanence. Although the current-generation Nd-Fe-B magnets can be densified by liquid phase sintering under atmospheric pressure, since Sm-Fe-N magnets are thermally decomposable, high temperature sintering cannot be applied. Low thermal load sintering techniques such as spark plasma sintering (SPS) have been studied, but remanence is still limited to a low level due to insufficient densification. As a new approach, high strain rate consolidation techniques such as the shear compression method and the powder rolling method are being studied. For



Nd-Fe-B magnets, a special processing method called the hot-deformation method was developed to simultaneously achieve a high crystal orientation and grain refinement, that is, both high remanence and high coercivity at the same time. The strongest Nd-Fe-B bulk magnet to date was produced by this process.

As described above, novel powder processes are constantly being developed for high-performance rare earth magnets. The next chapter introduces the individual powder processes and powder metallurgy processes for high-performance magnets in more detail.

### **2. Powder processes for enhanced coercivity 2.1 Production technologies for fine powder** 2.1.1 Pulverization

The traditional approach to grain refinement in powder metallurgy is pulverization of the material into a fine powder. Currently, the gas flow-type pulverization method (jet milling) is often used for fine pulverization of Nd-Fe-B magnet materials. Unlike ball mills, a crushing medium is not used in jet milling, so impurities can be reduced. As an additional advantage, although the particle surface of the rare earth alloy powder is extremely active, deterioration of magnetic properties due to oxidation of the particle surface can be suppressed if the oxygen concentration of the pulverizing gas is sufficiently reduced. In general production processes for Nd-Fe-B magnets, the powder is refined to a size of several µm by high throughput counter-type jet milling before the sintering process. In recent years, Sagawa et al. have shown that swirling-type jet milling using helium gas, which can generate a high-speed gas flow, can refine the powder down to a size of 1 µm (Sepehri-Amin H. et al., 2011). Nakamura et al. succeeded in producing a Nd-Fe-B magnetic powder with a size of 0.33 µm by helium-gas jet milling using HDDR powder as the raw powder, as show in Fig. 2 (Nakamura M. et al., 2013). By combining the ultrafine powders produced by this type of process with

grain boundary control technology, Nd-Fe-B sintered magnets with coercivity of 1.59 MA/m have been obtained (Sugimoto S. et al., 2015).

Improvement of coercivity by fine pulverization has also been attempted with other alloys. Takagi et al. applied swirling-type jet milling to a Sm-Fe-N alloy and demonstrated that it can be pulverized to 1 µm (Takagi K. et al., 2020). However, the coercivity of the sintered magnets derived from this fine powder was only about 0.8 MA/m, which is much smaller than the coercivity expected from its huge anisotropic magnetic field. This is considered to be is closely related to the mechanical damage introduced during jet milling. That is, crystals which contain defects such as dislocations have a lower anisotropic magnetic field than perfect crystals and tend to become nucleation sites for the reverse magnetic domain. As a result, coercivity is significantly reduced by surface damage in the powder. It may be noted that the coercivity of the Nd-Fe-B powder prepared by the pulverization method is actually very small, but since the Nd-Fe-B sintered magnet can be consolidated by liquid phase sintering, the surface damage can be recovered, resulting in high coercivity in the sintered magnet. However, only solid-phase sintering in the low temperature range is possible with the Sm-Fe-N magnet, as this material is a thermally-decomposable alloy, so the coercivity of the powder is inherited unchanged in the sintered magnet. Hosokawa et al. conducted a detailed TEM investigation of the Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> fine powder produced by jet milling. As shown in Fig. 3, that study revealed that numerous dislocations and nanocrystallization occur on the particle surface, and these types of damage increase as pulverization progresses (Hosokawa A. et al., 2021a). In fact, it was found that the decrease in the crystallinity of the particle surface leads not only to the above-mentioned decrease in coercivity, but also to a decrease in remanence. Although the reason for this decrease in remanence has not yet been clarified, this suggests that some solution, such as



**Fig. 2** BSE image of (a) hydrogen decrepitated HDDR alloy, and SE images of jet-milled powders of (b) HDDR and (c) SC alloys. The median diameter ( $d_{50}$ ) of the jet-milled powder of the HDDR alloy in (b) is about 0.33 µm. Reprinted with permission from Ref. (Nakamura M. et al., 2013). Copyright: (2013) AIP Publishing LLC.





Fig. 3 (a) TEM BF image of a jet-milled powder particle, and (b) and (c) corresponding SADPs. (d) TEM BF image of a UFP and its corresponding SADP. Reprinted with permission from Ref. (Hosokawa A. et al., 2021a). Copyright: (2021) Elsevier B.V.

heat treatment, is required in order to recover the damage.

Besides jet milling, it has often been reported that further pulverization is possible by ball milling using a surfactant. In traditional ball milling, crushing and rewelding are performed repeatedly, so particle size reduction becomes saturated, but addition of a surfactant to the solvent suppresses rewelding, allowing pulverization to progress. As a pioneering study, Chakka et al. pulverized Sm-Co and Nd-Fe-B to sizes of less than 30 nm by surfactant-assisted ball milling (Chakka V.M. et al., 2006). Akdogan et al. and Yue et al. have also produced SmCo<sub>5</sub> nanopowder with a coercivity of 1.4 MA/m and Nd-Fe-B nanopowder with 0.3 MA/m by surfactant-assisted ball milling (Akdogan N.G. et al., 2009; Yue M. et al., 2012). However, as in the case of jet milling, the high coercivity expected from the particle size has not been obtained so far, and this is thought to be the result of mechanical damage induced by the milling process.

#### 2.1.2 Chemical synthesis

As mentioned in the previous section, milling methods have the problem of causing damage to the particle surface and thus are not an appropriate approach for magnetic alloys such as Sm-Fe-N which are not suitable for liquid phase sintering. Moreover, milling cannot be considered an ideal method for producing powders for bonded magnets due to the issue of reduced coercivity. Therefore, chemical powder synthesis processes which enable direct production of high coercivity fine powders have been developed recently. The most successful chemical synthesis method for rare-earth magnet fine powders is the reduction-diffusion (R-D) method, which was originally developed by Robert E. Cech of General Electric in 1969 to produce SmCo<sub>5</sub> magnetic powder (Cech R.E., 1973; 1974). In the R-D method, rare earth magnet alloy powders are produced by heating a mixture of rare earth oxide powders, transition metal powders and Ca in an inert atmosphere. During heating, the rare earth metals that are reduced by Ca diffuse into the transition metal particles, resulting in an alloy powder. Therefore, the particle size of the alloy powder is greatly affected by the particle size of the raw transition metal powder. Conventionally, a fine alloy powder is produced by grinding the R-D powder to the order of tens of microns after synthesis from coarse transition metal and rare earth oxide raw powders. Recent research has demonstrated that micron-sized fine alloy powders can be directly synthesized by the R-D process from fine raw powders synthesized by a wet chemical method, and it has been reported that the powders synthesized by the R-D process exhibit higher coercivity than milled powders because the R-D powders are free of surface damage (Tada S. et al., 2012). Particularly, the last ten years of research have successfully shown that submicron-sized alloy powder can be synthesized by using of nano-sized oxide raw powders prepared by the pyrolysis or sol-gel method, and by using techniques to prevent necking and particle growth during Ca reduction (Ma Z.-H. et al., 2018; Zhang H. et al., 2011a). As mentioned above, the R-D method has high potential for producing fine rare earth magnetic powders and has been energetically studied, especially for Sm-Co and Sm-Fe-N alloys.

SmCo<sub>5</sub> has a large anisotropy field and has been reported to exhibit high coercivity. Fig. 4 summarizes the particle size dependency of coercivity for SmCo<sub>5</sub> fine powders. (Dong Y. et al., 2019; Li C. et al., 2018; Ma Z.-H. et al., 2018; Ma Z. et al., 2019a; Ma Z. et al., 2019c; Ma Z. et al., 2015; Shen B. et al., 2019; Tang H. et al., 2020a; 2021; Tang H. et al., 2020c; Wu Q. et al., 2020b; Zhang H. et al., 2011a). Coercivity improves as the average particle diameter becomes finer, but reaches its maximum at about 400 nm and then decreases in the smaller diameter range. This decrease is considered to be due to the more pronounced effect of particle surface oxidation as the particle size decreases, i.e., as the specific surface area increases. The highest coercive force at room temperature was 5.8 MA/m, as reported by Dong et al. (Dong Y. et al., 2019), when a hydroxide powder synthesized by





**Fig. 4** Particle size dependency of coercivity of  $\text{SmCo}_5$  powder (Dong Y. et al., 2019; Li C. et al., 2018; Ma Z.-H. et al., 2017; Ma Z. et al., 2019a; Ma Z. et al., 2019b; Ma Z. et al., 2015; Shen B. et al., 2019; Tang H. et al., 2020a; Tang H. et al., 2021; Tang H. et al., 2020b; Wu Q. et al., 2020a; Zhang H. et al., 2011b).

coprecipitation of a SmCl<sub>3</sub>, CoCl<sub>2</sub> and CaCl<sub>2</sub> aqueous solution was mixed with KCl and Ca and subjected to a R-D process at a relatively low temperature of 1 133 K. In their study, the CaO coating, which was derived from CaCl<sub>2</sub> and dilution of Ca by KCl, prevented necking and growth between particles, resulting in an ultrafine powder with a narrow particle size distribution.

Of the rare earth magnetic powders produced by the R-D method, the Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> powder is the only raw material powder which is produced commercially for bonded magnets. Fig. 5 shows the relationship between the particle size and coercivity of the Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> powder (Hirayama Y. et al., 2016; Okada S. et al., 2019; Okada S. et al., 2017; Okada S. and Takagi K., 2019; Dong Y. et al., 2019; Tada S. et al., 2012; Takagi K. et al., 2021). Okada et al. revealed that Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> fine powder synthesized by the R-D method exhibited high coercivity even at the submicron size, unlike powders prepared by milling. In particular, they reported that  $Sm_2Fe_{17}N_3$  with a giant coercive force of 2.5 MA/m and an average particle diameter of about 400 nm can be produced by improving various processing steps (Okada S. et al., 2019; Okada S. et al., 2017; Okada S. and Takagi K., 2019; Takagi K. et al., 2021). They employed a synthesis process in which Sm-Fe oxide powders synthesized by coprecipitation were subjected to hydrogen reduction, reduction-diffusion and nitridation. Using a different approach, Dong et al. applied a particle growth suppression technique, which was used to achieve the previously described synthesis of SmCo<sub>5</sub> fine powder with huge coercivity, to the synthesis of Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> fine powder, and reported Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> ultrafine powder with a particle size of about 100 nm. However, the coercive force was only about 1.2 MA/m (Dong Y. et al., 2019).



**Fig. 5** Particle size dependency of coercivity of  $Sm_2Fe_{17}N_3$  powder (Hirayama Y. et al., 2016; Okada S. et al., 2019; Okada S. et al., 2017; Dong Y. et al., 2019; Tada S. et al., 2012; Takagi K. et al., 2021).

Although there have been reports on the synthesis of Nd-Fe-B alloys, coercivity was not outstanding, being limited to around 0.5 MA/m (Jeong J.H. et al., 2016; Swaminathan V. et al., 2013). Since Nd-Fe-B is a ternary system, adjustment of the composition seems to be difficult, especially in controlling the amount of B (Guo Y. et al., 2019). Moreover, because Nd-Fe-B is more easily oxidized than Sm-based materials, decreased coercivity due to surface oxidation is considered to have a serious influence. As for ThMn<sub>12</sub>-type alloys, which are expected to be a new type of magnet, Gabay et al. reported (Sm,Zr)1(Fe,Co,Ti)12 powder with a high coercivity exceeding 1 MA/m by the R-D method using raw powders prepared by a mechanochemical process (Gabay A.M. and Hadjipanayis G.C., 2021). Although TbCu<sub>7</sub>-type Sm-Fe-N is expected to be a next-generation magnet with high saturation magnetization, there had been no reports on production of this material by the R-D route because it is a metastable phase. However, Okada et al. recently developed a low-temperature R-D method using molten salts such as LiCl as a solvent for Ca, which enables a R-D reaction below the melting point of Ca, and succeeded in synthesizing a TbCu7-type Sm-Fe single-crystal fine powder at an R-D reaction temperature of about 873 K (Okada S. and Takagi K., 2021).

### 2.1.3 Physical synthesis

Physical synthesis approaches for rare earth magnetic powders include, for example, vapor phase methods such as an arc discharge method and a high frequency induced thermal plasma method, as well as the cluster beam deposition method. Vapor phase methods are able to synthesize ultrafine particles much smaller than those prepared by the breakdown methods described in **Section 2.1.1**, and these ultrafine particles are also extremely pure, as they



are free of the particle surface contamination which is a drawback of the chemical synthesis processes described in Section 2.1.2. Many reports on nanoparticle synthesis of rare earth-transition magnetic alloys using the gas phase method have been based on the cluster beam deposition method, in which the alloy is deposited on a substrate (Sellmyer D.J. et al., 2015). In particular, many reports have examined the synthesis of Sm-Co nanoparticles. However, while the obtained particle size was smaller than 50 nm, maximum coercivity was only about 0.6 MA/m at room temperature (Abbas N. et al., 2019; Balamurugan B. et al., 2012; Balasubramanian B. et al., 2011; He S. et al., 2013; Landi G.T. and Santos A.D., 2010; Stoyanov S. et al., 2003). Here, the high coercivity expected in nanoparticles is not obtained due to the difficulty of synthesizing nanoparticles with high crystallinity and avoiding surface oxidation due to the large surface area. Recently, Hirayama et al. energetically investigated the synthesis of these metal nanoparticles by a thermal plasma process, especially focusing on easily oxidizable metals such as Al and rare earth alloys. They newly modified a conventional thermal plasma method so that the nanoparticles can be synthesized and handled under an extremely low oxidizing atmosphere, as indicated in Fig. 6. Their research demonstrated that Al nanoparticles obtained by this method form necking under low temperature heating because surface oxidation is minimized (Hirayama Y. et al., 2018; Kim D. et al., 2021), and Fe-Co alloy nanoparticles with reduced surface oxidation exhibited the same saturation magnetization as the conventional bulk alloy without a hydrogen reduction treatment (Hirayama Y. and Takagi K., 2019). In the synthesis of rare earth-transition metal nanoparticles, Hirayama et al. showed the possibility of synthesizing a TbCu<sub>7</sub>-type metastable phase in a Nd-Fe system by this process by taking advantage of its high quenching rate (Hirayama Y. et al., 2021). Synthesis of core-shell particles with a Sm-Co shell/ Co core structure, which could not be obtained until now, has also been reported (Park K. et al., 2021), and is a very

noteworthy new process for raw material powders for the creation of novel permanent magnets in the future.

## **2.2 Grain refinement technologies** 2.2.1 Rapid solidification

The previous section introduced attempts to develop single crystalline powder with the finest possible particle size for production of high coercivity fine-grained sintered magnets. On the other hand, the production methods for polycrystalline powders composed of ultrafine grains accompanied by rapid solidification have also been studied. The most common method is single roll melt spinning, and in fact, magnetic powder production by this method has already been commercialized. Fig. 7 shows a schematic diagram of a melt spinning device and an image of the typical nanostructure (Mishra R.K., 1986). In the melt spinning method, a molten metal is directly poured into a rotating cold copper roll to achieve an extremely rapid quenching effect. Traditionally, this method was used in the development of amorphous and nanocrystalline materials. In the 1980s, it was reported that high coercivity could be obtained by alloying Fe with Tb, Pr, La, etc., and later, similar coercivity enhancement in Re-Fe alloys was also reported. General Motors (GM) was apparently searching for Re-Fe-based hard magnetic materials at the time, and Croat et al. at GM reported that Nd-Fe-B produced an excellent magnetic powder with coercivity of about 1.2 MA/m (Croat J.J., 1982).

The flake powder obtained by melt spinning has the advantage that extremely high coercivity due to the effect of grain refinement can be achieved because fine grains of several 10 nm to several 100 nm can be obtained without pulverization. However, since the orientation of each crystal grain is random, remanence and  $(BH)_{max}$  are inferior to those of anisotropic magnets. In spite of this weakness, this powder has been applied practically in bonded magnets, in which the powder is kneaded with resin and molded, and melt-spun powder is also an indispensable raw material for



**Fig. 6** Experimental set-up of low-oxygen induction thermal plasma process. The cooling rate can be controlled by introducing extra Ar gas at the tail of the plasma, which results in differences in the formed phase. Reprinted with permission from Ref. (Hirayama Y. et al., 2021). Copyright: (2021) Elsevier B.V.





Fig. 7 (a) Schematic illustration of melt spinning apparatus and (b) typical microstructure of as-spun ribbons. Reprinted with permission from Ref. (Mishra R.K., 1986). Copyright: (1986) Elsevier B.V.

hot-deformation magnets, which have attracted attention recently, as will be explained in detail in Section 3.1.

The rapid solidification method also has the advantage of obtaining a non-equilibrium phase. For example, in the TbCu<sub>7</sub> type Sm-Fe-N alloy, it is possible to obtain a supersaturated Fe composition by melt spinning, and a high saturation magnetization of 1.7 T, which exceeds the values of  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , can be obtained (Katter M. et al., 1991; Sakurada S. et al., 1996). This TbCu<sub>7</sub> type Sm-Fe-N melt-spun powder was partially commercialized as a bonded magnet (Morii K. and Hasegawa F., 2008). As another example of melt-spun powders, Toshiba commercialized a 240 kJ/m<sup>3</sup> class sintered magnet using a Sm-Co-Fe-based magnet with a TbCu<sub>7</sub> structure (Horiuchi Y. et al., 2015; Horiuchi Y. et al., 2014), and this magnet is already used in the main motors of railway vehicles.

The single roll melt spinning method is also used for research on nanocomposite magnets, which are candidates for next-generation magnet materials. Nanocomposite magnets, also known as exchange spring magnets, are a new type of magnet. The original concept was first proposed by Kneller and Hawig (Kneller E.F. and Hawig R., 1991). When the hard magnetic phase and the soft magnetic phase are composited at the nano scale, the soft magnetic phase is expected to behave as if it were a hard magnetic phase due to exchange coupling at the interface. Prior to this work, Coehoorn of Philips in fact had performed an experimental work and reported a magnet similar to this concept in which nano-sized  $\alpha$ -Fe was dispersed in the Nd<sub>2</sub>Fe<sub>14</sub>B matrix by melt-spinning Nd-Fe-B powder with a Fe-rich composition (Coehoorn R. et al., 1989). Later, Skomski and Coey predicted that the combination of  $Sm_2Fe_{17}N_2$ and FeCo would yield ultra-strong nanocomposite magnets with  $(BH)_{max} = 1\ 000\ kJ/m^3$  (Skomski R. and Coey J.M.D., 1993). Following those pioneering works, nanocomposite magnets using melt-spun powder were actively investigated (e.g. (Hirosawa S. and Kanekiyo H., 1996; Hirosawa S. et al., 2003; Manaf A. et al., 1993a; Manaf A. et al., 1992; 1993b)), and Hitachi Metals later developed a new spinning is annealed to obtain a hard/soft nanocomposite structure. This class of powder was commercialized under the name Sprax<sup>®</sup>. Nevertheless, the values of  $(BH)_{max}$  for the nanocomposite magnets reported to date have never exceeded that of the single-phase Nd2Fe14B magnet, except for a thin film reported by Cui et al. (Cui W.B. et al., 2015). The work by Zhang et al. (Zhang J. et al., 2005) is another interesting experiment with thin films, wherein the  $(BH)_{max}$ obtained in the SmCo/Fe composite is superior to that of the SmCo hard phase. As indicated by these thin-film experiments, it is definitely important to align the crystal orientations in order to achieve the combined advantages of both the hard phase and the soft phase. Although this precise microstructural control is still difficult by methods other than the thin-film technique, thin films cannot be commercialized as permanent magnets. Thus, it is essential to develop new manufacturing processes that will potentially enable mass production of permanent magnets in a bulk form. Our group is currently energetically conducting research targeting anisotropic nanocomposite magnets by combining the melt spinning method, hot deformation method and addition of low melting point alloys (Hosokawa A. and Takagi K., 2018b; 2019; Hosokawa A. et al., 2019).

process in which amorphous powder obtained by melt

### 2.2.2 Solid synthesis

Another approach for synthesizing a powder consisting of ultrafine crystal grains is mechanical alloying (MA). In many studies on Nd-Fe-B-based, Sm-Fe-N-based and Sm-Co-based alloys, rare earth magnetic powders with crystal grain sizes of several 10 nm to several 100 nm have been synthesized for MA. For example, the mechanical-alloyed Nd-Fe-B powder produced by Zhang et al. had a high coercivity of 1.7 MA/m, which is comparable to the value obtained by the melt spinning method (Zhang Z.-D. et al., 1998), and Teresiak et al. demonstrated that  $Sm_2Fe_{17}N_X$ powders produced by MA exhibited a huge coercivity of 2.8 MA/m (Teresiak A. et al., 1999). However, the MA



process has not been industrialized, as its low productivity makes it unsuitable for mass production.

MA has been used in many studies to explore metastable compounds such as  $\mathrm{Tb}\mathrm{Cu}_7$  type and  $\mathrm{Th}\mathrm{Mn}_{12}$  type alloys because it is possible to synthesize a metastable phase by solid-phase synthesis without melting, and grain refinement is also possible. In particular, MA was actively utilized in research on ThMn<sub>12</sub> type alloys, leading to clarification of the magnetic properties of ThMn<sub>12</sub> type Nd-Fe-M-N alloys and Sm-Fe-M alloys (M: Ti, V, Mo) (Jin Z.-q. et al., 1997; Schultz L. et al., 1990; Shengen Z. et al., 2001). The ThMn<sub>12</sub> type compound has recently been discovered to have magnetic properties superior to those of existing compounds, and has attracted renewed attention (Hirayama Y. et al., 2015; 2017). Nevertheless, MA is rarely used in current development of magnet materials because only polycrystalline powder can be obtained and as mentioned above, it is not suitable for mass production.

### 2.2.3 Gas reaction

As an epoch-making method for producing fine polycrystalline magnetic powders, approaches utilizing the reaction between solids and gases have attracted strong interest. Because rare earth transition metal alloys react with hydrogen and nitrogen to form unique microstructures, research on producing crystallographically-oriented polycrystalline powder by using gas reactions has been widely conducted. The hydrogenation-disproportionation-desorptionrecombination method (HDDR) makes it possible to produce a polycrystalline powder consisting of submicron-sized crystal grains from single crystal powder by using the reaction between a rare earth transition metal alloy phase and hydrogen gas. For example, when an Nd-Fe-B alloy is heated in a H<sub>2</sub> atmosphere, the alloy is temporarily decomposed into an NdH<sub>2</sub> phase, Fe phase, Fe<sub>2</sub>B phase, etc. (decomposition). Subsequently, when dehydrogenation is performed by heating in a reduced pressure environment, the phase returns to the Nd-Fe-B phase (recombination). In this process, the Nd-Fe-B phase forms fine crystal grains with sizes controlled in the range from 0.2 to 0.6 µm, depending on the treatment temperature. In particular, unlike rapid solidification and MA, HDDR treatment under appropriate conditions is capable of producing crystallographically-oriented grains as shown in Fig. 8 (Takizawa R. et al., 2017). That is, although this alloy is a polycrystal, particles close to a single crystal can be produced, which means the powder can be used as a raw material for anisotropic magnets. The latest theory concerning the mechanism of microstructure refinement and crystal orientation is summarized in the literature by Hirokawa et al. (Horikawa T. et al., 2021). The maximum coercivity of the reported HD-DR-processed Nd-Fe-B powder is 1.3 MA/m (Morimoto K. et al., 2003), and coercivity is improved to 1.6 MA/m by diffusing Cu at the grain boundaries in the subsequent



**Fig. 8** Typical microstructure of HDDR-treated Nd-Fe-B powder. (a) TEM-BF image and (b) inverse pole-figure map obtained by TEM-PED. Reprinted with permission from Ref. (Takizawa R. et al., 2017). Copyright: (2017) Elsevier B.V.

process (Sepehri-Amin H. et al., 2010).

HDDR can also be used to produce fine-grained Sm-Fe-N and Sm-Co powders with high coercivity. The internal crystal grain size of HDDR-processed SmCo<sub>5</sub> powder has been refined to less than 100 nm, which achieved a huge coercivity exceeding 3 MA/m (Bulyk I.I. and Panasyuk V.V., 2012). While high coercivity of 1.4 MA/m has also been obtained with HDDR-processed Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> (Arlot R. et al., 1999), crystal orientation has not been realized in any of these alloy systems, and HDDR is currently effective only for Nd-Fe-B alloys. On the other hand, HDDR can also be used to synthesize fine-grained powders of TbCu<sub>7</sub> type and ThMn<sub>12</sub> type alloys (Dirba I. et al., 2019; Takagi K. et al., 2018), suggesting that it may be a very promising process, provided crystal orientation can be realized in alloys other than Nd-Fe-B in the future.

For  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ , a unique grain refinement method employing a nitrogen gas reaction is possible (Saito K. et al., 1994). When nitriding  $\text{Sm}_2\text{Fe}_{17}$  alloy powder, various  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  compound powders with different nitrogen content *x* can be obtained by tuning the nitriding conditions. While it is known that nitriding with a mixed gas of ammonia and hydrogen can overnitride the compound to a maximum nitrogen content of about x = 6, it is also known that the highest saturation magnetization and highest anisotropy are obtained when x = 3. Thus, optimally-nitrided  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  having a small diameter (typically, up to 3 µm) is used in permanent magnet applications.

Overnitriding  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  to the region of x > 3 induces the interesting phenomenon of nanocrystalline cell formation. According to classical TEM results, this microstructure is composed of very fine nanocrystalline cells (30 to 100 nm) and amorphous cell walls dividing the individual cells. Several researchers have reported that this technique makes is possible to obtain reasonably high coercivity even



with coarse powders without reducing the particle size (Imaoka A. et al., 1998; Imaoka N. et al., 1995; Saito K. et al., 1994). In particular, in overnitridation treatment of Mn-added Sm<sub>2</sub>Fe<sub>17</sub>N<sub>x</sub>, excess N and Mn were concentrated on the amorphous cell walls, resulting in the formation of domain walls. A maximum coercivity of about 0.7 MA/m was reportedly obtained by this approach. A group at Osaka University later reported that addition of Ti, V and Cr in addition to Mn had the same effect of increasing coercivity as Mn. A group at Sumitomo Metal Mining reported that a high-performance powder with  $(BH)_{max} = 175 \text{ kJ/m}^3 \text{ was}$ obtained with an Sm<sub>2</sub>(FeMn)<sub>17</sub>N<sub>x</sub> system by combining crushing treatment after overnitriding, and this powder was actually commercialized. Although the coercivity of the  $Sm_{2}Fe_{17}N_{3}$  powder produced by the pulverization method was drastically reduced when exposed to a high temperature environment of about 200 °C, it is noteworthy that the overnitrided coarse powder exhibited excellent thermal stability (Iseki T. et al., 2003; Ito M. et al., 2003; Ito M. et al., 2002; Majima K. et al., 1997; Ohmori K. et al., 2006).

The coercivity mechanism of optimally-nitrided  $Sm_2Fe_{17}N_3$  is normally classified as the nucleation-type, but in contrast, an analysis of the initial magnetization curves of the overnitrided  $Sm_2Fe_{17}N_x$  revealed that its coercivity mechanism is pinning-type (Imaoka et al., 1995). This viewpoint was later supported by the Lorenz microscopy, which directly captured the domain wall being pinned at the Mn- and N-enriched amorphous cell walls in the overnitrided  $Sm_2(FeMn)_{17}N_x$ , as indicated in Fig. 9 (Kim J.J. et al., 2007; Yasuhara A. et al., 2005; Yasuhara A. et al., 2004).

As demonstrated above, while overnitriding method is an excellent approach for obtaining high coercivity magnetic powders, they have the disadvantage that residual magnetization decreases when the nitrogen content reaches x > 5, where coercivity increases. This decrease in remanence was originally thought to be caused by spontaneous rotation of the nanocrystalline cells after cell formation by overnitriding. Therefore, our group initially attempted to develop a new process that would make it possible to control the cell rotation during nitridation. We began by investigating what actually occurs in Sm<sub>2</sub>Fe<sub>17</sub>N<sub>x</sub> during overnitridation treatment. An interesting finding during this investigation was that the formation of this nanocell structure can be observed with a recent high-performance SEM which makes it possible to observe a very large field of view (Hosokawa A. and Takagi K., 2017; Hosokawa A. and Takagi K., 2018a). Coupling SEM and TEM enables multi-scale observation of the  $Sm_2Fe_{17}N_{\chi}$ , and it has been found that a large number of plate-shaped amorphous bands are generated and then form a ladder-like structure, as shown in Fig. 10. These amorphous bands eventually form a cell-like structure inside an initially singlecrystalline coarse particle. Since this investigation also confirmed that the size of the cells decreases as the (local) nitrogen content increases, the degradation of residual magnetization is thought to be due simply to the increased amount of low magnetization amorphous regions (Hosokawa A. and Takagi K., 2017; Hosokawa A. and Takagi K., 2018a). This means that it is not necessary to control the rotation of the crystalline cells, and new, completely different guidelines are needed to improve this process.

### **2.3 Grain boundary engineering**

2.3.1 Nd-Fe-B magnets

The only drawback of Nd-Fe-B magnets is their heat resistance. When used in an onboard vehicle motor, the operating temperature is as high as 150 to 200 °C, and coercivity is significantly reduced by heating. An effective solution to this problem, which will make it possible to withstand use in the high temperature automotive environment, is to increase the absolute value of coercivity or, alternatively, to reduce the temperature dependency of coercivity (temperature coefficient). Since no significant improvement in the temperature dependency of coercivity has been realized in Nd-Fe-B magnets, neodymium magnets which can withstand high-temperature use have been developed by increasing the absolute value of coercivity.

In order to increase coercivity, appropriate control in/ around the grain boundary phase is required. A grain boundary diffusion method for this type of control has been



Fig. 9 (a) and (b) Domain wall pinning at amorphous boundaries captured by Lorenz microscopy and (c) schematic diagram of the pinning mechanism. Reprinted with permission from Ref. (Yasuhara A. et al., 2005). Copyright: (2005) Elsevier B.V.





Fig. 10 Typical microstructural evolution during formation of cell structures. Reconstructed with permission from Ref. (Hosokawa A. and Takagi K., 2017). Copyright: (2017) Acta Materialia Inc. Published by Elsevier Ltd.

developed based on a report by Park et al. (Park K.T. et al., 2000). Since Nd-Fe-B magnets have a new creation-type coercivity mechanism, suppressing the formation of reverse magnetic domains on the surface of crystal particles is extremely effective for improving coercivity. Therefore, a  $(Nd-Dy/Tb)_2Fe_{14}B$  phase having a higher anisotropic magnetic field than the main Nd<sub>2</sub>Fe<sub>14</sub>B phase is formed only in the grain boundary by diffusion of Dy and Tb, resulting in a significant increase in coercivity. In particular, after preparing the sintered compact by the conventional process, metallic Dy and Tb or their oxide/fluoride are applied to the surface of the sintered compact and diffused at 800 to 900 °C. Because only the grain boundary phase becomes a liquid, diffusion of Dy and Tb is limited to the grain boundary.

Another technique for increasing coercivity is the low temperature eutectic alloy diffusion method, which can be mentioned as a method for increasing coercivity by controlling the grain boundary phase. In this method, magnetic decoupling between particles is induced by diffusing a low melting point eutectic alloy into the grain boundaries to increase the thickness of the grain boundary phase, which greatly improves coercivity. Many reports on this technology have appeared in connection with HDDR powders with fine crystal grains and heat-sensitive processed magnets, and significant improvement of coercivity has been achieved. In particular, this method is very important for the development of high coercivity magnets which do not use the heavy rare earth elements Tb and Dy.

#### 2.3.2 Sm-Fe-N magnets

The grain boundary diffusion method described in the previous section cannot be applied to Sm-Fe-N magnets because Sm-Fe-N is thermally decomposed below the diffusion treatment temperature of 800 to 900 °C. Therefore, different approaches are applied to grain boundary control of Sm-Fe-N magnets.

The oldest attempt of grain boundary control in the history of Sm-Fe-N development is the "metal-bonded magnet" proposed by Otani et al. (Otani Y. et al., 1991). Since Sm-Fe-N has a low decomposition temperature (Coey J.M.D. et al., 1991; Katter M. et al., 1992; Zhang D.T. et al., 2007), conventional sintering methods involving high temperature heating cannot be applied. Therefore, use of low melting point metals such as Sn, Bi, Zn, or Al as a binder was proposed to obtain a bulk magnet at a sufficiently low temperature (Huang M.Q. et al., 1991; Otani Y. et al., 1991). However, preparation of a metal-bonded magnet with a Zn bond led to the discovery Zn bonding significantly increases coercivity. As a result, much research has been devoted to Zn-bonded magnets as a technology for improving coercivity, but some critical problems were



discovered in the course of development. Specifically, although coercivity increases monotonically with the amount of Zn added, more than 20 wt% of Zn must be added to achieve coercivity on the order of 1 MA/m, as indicated in **Table 1** (Ito S. et al., 2004; Kuhrt C. et al., 1992; Otani Y. et al., 1991; Prabhu D. et al., 2012). However, the magnetic Sm-Fe-N phase is inevitably diluted by addition of Zn, resulting in a decrease in remanence, and it was also found that heavy Zn addition significantly deteriorates the squareness of the demagnetization curve (Kuhrt C. et al., 1992; Müller K.H. et al., 1996). Therefore, even if coercivity increases, *(BH)*<sub>max</sub> decreases.

The mechanism of coercivity improvement by Zn was initially attributed to soft magnetic  $\alpha$ -Fe crystallites on the particle surface, which remain as an impurity in the raw material preparation process (Kuhrt C. et al., 1992). In

addition, the non-magnetic  $\Gamma$ -FeZn reaction phase spreads to the grain boundaries and was believed to block the magnetic coupling between Sm-Fe-N grains (Wendhausen P.A.P. et al., 1993). Based on a study utilizing microstructural observation, Hiraga et al. explained that Zn reacts with the Sm-Fe-N main phase into the Sm-(Fe, Zn)-N phase on the surface of the grains, which smooths the grain surfaces, and the Sm-(Fe, Zn)-N phase isolates the by-product soft magnetic α-FeZn from the main phase, thereby suppressing the formation of reverse magnetic domains (Hiraga K. et al., 1993). However, certain problems remain unsolved: In particular, this interpretation relies on the assumption that the Sm-(Fe, Zn)-N phase is non-magnetic, and it does not explain why squareness is significantly deteriorated. Recently, Matsuura et al. conducted more detailed microstructure observations (Matsuura M. et al., 2020) (Fig. 11),

 Table 1
 Magnetic parameters of sintered samples for various heat treatment conditions. Reprinted with permission from Ref. (Prabhu D. et al., 2012).

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Zn conc. (wt %)	Coercivity and remanence for various heat-treatment conditions							
	As-sintered		425 °C/1 h		435 °C/1 h		450 °C/1 h	
	$\mu_0 H_{\rm c} \left( {\rm T} \right)$	$B_{\rm r}({\rm T})$	$\mu_0 H_{\rm c} \left( {\rm T} \right)$	$B_{\rm r}({\rm T})$	$\mu_0 H_{\rm c} \left( {\rm T} \right)$	$B_{\rm r}({\rm T})$	$\mu_0 H_{\rm c} \left( {\rm T} \right)$	$B_{\rm r}({\rm T})$
10	0.56	0.67	1.11	0.67	1.39	0.68	1.67	0.69
15	0.42	0.56	1.24	0.62	2.75	0.62	2.33	0.62
20	0.65	0.53	1.54	0.58	1.78	0.59	2.13	0.44

Magnetic properties of the initial SmFeN powder:  $\mu_0 H_c = 1.2$  T and  $\mu_0 M_s = 1.25$  T.



Fig. 11 Schematic diagram of microstructural changes in Sm-Fe-N (SFN) bulk magnets during annealing. Reprinted with permission from Ref. (Matsuura M. et al., 2020). Copyright: (2020) Elsevier B.V.



and concluded that the non-magnetic  $\Gamma$ -FeZn phase surrounds the soft-magnetic  $\alpha$ -FeZn crystallites and breaks the magnetic coupling between the grains.

While the mechanism of improved coercivity by Zn is still unclear, the amount of Zn added should be reduced to suppress the harmful effects of Zn. In order to maximize the effect of Zn with limited addition, it will be necessary to form a thin layer of Zn at the grain boundaries, and this layer should be as thin and uniform as possible. Various thin-film and coating techniques such as vacuum deposition (Fukunaga H. et al., 1996; Makita K. and Hirosawa S., 1997) and photolysis of organic metal complexes (Arlot R. et al., 1997; Izumi H. et al., 1996; Machida K.-i. et al., 1995) have been applied to Sm-Fe-N powders for this purpose. Initial attempts showed meaningful improvements in thermal stability and oxidation resistance, but the improvement in coercivity was modest and coercivity remained inferior to the levels achieved by conventional processes. The problems of these thin-film approaches are considered to be two-fold: (1) Since the original purpose was metal bonding, the research target was biased toward low melting point metals. However, now that other low-temperature consolidation techniques are available, the scope of research should be extended to materials with higher melting points (Imaoka N. et al., 2008; Saito T. et al., 2017). (2) The direct effect on the Sm-Fe-N main phase could not be investigated because the added metals were not in direct contact with the magnetic phase, but were in contact with non-magnetic surface oxides. Thus, a process for forming a coating on a surface without an oxide film can be expected to have a higher coercivity improvement effect with a small amount of Zn addition.

Recent efforts to implement these two approaches simultaneously include a combination of powder coating



Fig. 12 Effects of sputter coating of 20 nonmagnetic metals on surface oxide-free  $Sm_2Fe_{17}N_3$  powders on coercivity. The powders were heat treated at 500 °C for 2 min after coating. Reprinted with permission from Ref. (Yamaguchi W. and Takagi K., 2020). Copyright: (2020) Elsevier B.V.

technology with the low oxygen powder metallurgy process. Sm-Fe-N fine powder without a surface oxide film is produced by pulverization in a low oxygen atmosphere, followed by sputter-coating with continuous stirring (Yamaguchi W. et al., 2020). This is a highly versatile powder coating technique which is capable of forming a direct metal-metal interface, and it can also form a thin and uniform film even on a material with a high melting point. Yamaguchi et al. used this technique to coat Sm-Fe-N powder with 20 kinds of non-magnetic metal elements, and found that, in addition to Zn, addition of metals such as Al, Sn and Ce is also effective for improving coercivity as indicated in Fig. 12 (Yamaguchi W. and Takagi K., 2020). Matsuura et al. also succeeded in producing a Znadded Sm-Fe-N anisotropic sintered magnet with (BH)<sub>max</sub>  $= 179 \text{ kJ/m}^3$  by a similar coating technique (Matsuura M. et al., 2018).

# **3.** Powder technologies for enhancement of remanence

### **3.1 Hot deformation techniques**

To produce a sintered magnet with high residual magnetization, it is important to produce a green compact in which the easy axis of magnetization of the crystal grains is aligned in one direction and to achieve the highest possible densification of the compact by sintering. In addition, as described above, it is also essential to construct a fine grain structure for high coercivity. Since all these simultaneous improvements have become saturated in the conventional powder metallurgy process consisting of magnetic-aligned compaction and atmospheric sintering, the hot deformation process has attracted attention as a new process.

Lee reported that an anisotropic magnet with the easy axis oriented in the press direction was obtained when a sintered compact produced from Nd-Fe-B melt-spun powder was upset at an elevated temperature (Lee R.W., 1985). Mishra and Lee observed hot-deformed anisotropic magnets by TEM and found that the grains were significantly flattened in shape and all the crystal grains were oriented in the *c*-axis // press direction (Mishra R.K. and Lee R.W., 1986; Sepehri-Amin H. et al., 2013) as shown in Fig. 13. Since that time, intensive research has been carried out, and magnets with  $(BH)_{max}$  exceeding 350 kJ/m<sup>3</sup> have been reported (Mishra R.K., 1987; 1989; Mishra R.K. et al., 1988; Mishra R.K. et al., 1990; Mishra R.K. et al., 1993). The formation of this oriented microstructure is not the result of a deformation texture mechanism, but a unique mechanism involving liquid phase formation of an Nd-rich phase at the grain boundaries in the hot working temperature range (Grunberger W. et al., 1997). When the grain boundary phase is liquified at the hot deformation temperature, diffusion between the main phase and the liquid phase becomes extremely active. At this time, high stress is generated in the direction of uniaxial compressive stress, that is, in the





Fig. 13 (a) Typical microstructure of highly textured nanocrystalline structure after die-upsetting and (b) schematic diagram. Reprinted with permission from Ref. (Sepehri-Amin H. et al., 2013). Copyright: (2013) Acta Materialia Inc. Published by Elsevier Ltd.

vertical direction of the crystal grains, while stress is low in the lateral direction. "Dissolution" is promoted at this highstress location, the substance moves toward the low-stress location through the liquid phase, "reprecipitation" occurs, and as a result, the above-mentioned oriented microstructure is formed (Pharr G.M. and Ashby M.F., 1983; Raj R. and Chyung C.K., 1981; Wakai F., 1994). What is important here is that when a liquid phase grain boundary exists between Nd<sub>2</sub>Fe<sub>14</sub>B main phases with a highly anisotropic crystal structure, the rate of dissolution-reprecipitation changes greatly depending on the crystal orientation. In the Nd-Fe-B phase, it is generally thought that only specific crystal grains having an azimuth relationship of stress axis // c axis grow preferentially in the ab axis direction, and an oriented structure is obtained.

Daido Steel succeeded in commercializing hot-deformed magnets (Akiya T. et al., 2014a; b; Liu J. et al., 2014). Another advantage of hot-deformed magnets is that they tend to have improved thermal resistance since the thermal stability of coercivity increases as the crystal grain size decreases. In this connection, studies on hot-worked magnets of the ThMn<sub>12</sub> type using Sm as the main raw material have been reported recently (Schonhobel A.M. et al., 2020; Schonhobel A.M. et al., 2019).

### 3.2 Low-thermal load consolidation

As mentioned in 2-3-2, Nd-Fe-B alloys and Sm-Co alloys can be sintered by high temperature heating, but Sm-Fe-N alloys are thermally decomposed at about 620 °C, making it difficult to produce bulk magnets by sintering. In addition, non-equilibrium alloys such as the TbCu<sub>7</sub> type and ThMn<sub>12</sub> type also transform to a stable phase at high temperatures, so consolidation in a low thermal load environment is considered necessary. Therefore, various low thermal load sintering techniques have been examined for these alloys. Spark plasma sintering (SPS) is a hot-pressing process with rapid heating, and has been applied to Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> alloys and metastable alloys such as TbCu<sub>7</sub> type Sm-Fe-Ne alloys (Saito T., 2008; Zhang D.T.

Fig. 14 Cross-sectional SEM images of (a) Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> anisotropic sintered magnet and (b) TbCu<sub>7</sub> type Sm-Fe-N isotropic sintered magnet produced by high-pressure current sintering. Reprinted with permission

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(a)

et al., 2007). Although these materials cannot be heated to high temperatures, these studies have demonstrated that sintered magnets with a relative density of more than 90 % can be obtained without degrading the magnetic properties of the powder by sintering at a high pressure exceeding 1000 MPa as shown in Fig. 14 (Nakayama H. et al., 2012; Saito T., 2008; Takagi K. et al., 2012a; Takagi K. et al., 2012b; Takagi K. et al., 2020). In particular, Matsuura et al. and Takagi et al. used a low oxygen powder metallurgy process combined with SPS to perform sintering without decreasing coercivity due to surface oxidation, and achieved (BH)<sub>max</sub> exceeding 190 kJ/m<sup>3</sup>, which is the highest value reported for a Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> sintered magnet (Matsuura M. et al., 2018; Takagi K. et al., 2020).

from Ref. (Takagi K. et al., 2012c; Takagi K. et al., 2020). Copyright:

(b

500 nm

Prototype bulk magnets using non-heat forming processes such as shear compression (Saito T. et al., 2005; Saito T. and Kitazima H., 2011; Saito T. and Sato H., 2006; Saito T. et al., 2006) and shock consolidation (Mashimo T. et al., 2000; Mashimo T. et al., 1999) have been reported, and recently, the authors also conducted research that refocuses on powder rolling (Hosokawa A. et al., 2021b). A method called high-pressure torsion processing has also attracted attention in recent years (Edalati K. and Horita Z., 2016; Valiev R.Z. et al., 2000). A schematic illustration of high-pressure torsion is shown in Fig. 15. Since permanent magnets are generally brittle, it is not possible to apply huge strain by shear deformation by ordinary methods. However, high-pressure torsion makes it possible to apply huge shear strain without breaking brittle materials thanks to hydrostatic stress (Hosokawa A. et al., 2014a; Hosokawa A. et al., 2014b). Recently, many applications of this technique to permanent magnet materials have been reported (Gorshenkov M.V. et al., 2020; Popov A.G. et al., 2006; Shchetinin I.V. et al., 2020; Straumal B.B. et al., 2015). It has also been reported that Nd-Fe-B powder can be consolidated without heating by applying a huge strain exceeding 10 in shear strain, and as a result, the internal structure of the magnet can be improved as shown in Fig. 15(b) (Hosokawa A. and Takagi K., 2018b; Hosokawa A. et al.,





Fig. 15 Schematic illustration of high-pressure torsion process. (a) The deformation mode at the perimeter region is essentially simple shear. (b) Example of densification by high-pressure torsion captured by SEM. Porosity decreases with the distance from the center.

2019). Although mass production cannot be expected by the high-pressure torsion route, research in this direction is needed in order to obtain clues for envisioning a new process that utilizes shear processing without relying on high-temperature heating.

### 4. Concluding remarks

In order to improve the efficiency of electric motors, continuous improvement of the performance of the rare earth magnets which are their core component is essential. Research on conventional Nd-Fe-B magnets has provided design guidelines for control of the internal microstructure of sintered magnets, such as grain refinement, nanoscale grain boundary control and crystal orientation, to improve the performance of rare earth permanent magnets, and an advanced powder metallurgy process which can efficiently achieve these types of control is being developed. Especially in recent years, process development for Sm-Fe-N magnets and metastable phase magnets as nextgeneration magnets has become important. In order to improve coercivity, it is necessary to refine the crystal grain size, and for that purpose, refinement of the raw powder is being studied. Research on pulverization is evolving from traditional pulverization approaches such as jet milling to chemical/physical synthesis methods such as the reduction diffusion (R-D) method and the thermal plasma method, and the submicron- and nano-sized Sm-Fe-N powder obtained by these methods have achieved huge coercivity of 2.5 MA/m. Methods for synthesizing nanopolycrystalline powders using gas reactions such as the HDDR method and the overnitriding method have also been examined, and crystal-oriented ultrafine polycrystalline powders have been synthesized successfully. In Nd-Fe-B magnets, it has been found that, in addition to grain refinement, grain boundary phase control is also very effective in improving coercivity. Recently, grain boundary control of Sm-Fe-N sintered magnets by sputter coating on the powder surface has been investigated, and a new grain boundary phase has been proposed. To improve remanence, uniaxial orientation technology for crystal grains and high-density sintering

technology are indispensable. Especially for Sm-Fe-N magnets and metastable phase magnets, which have low thermal stability, new low thermal load consolidation techniques such as rapid hot pressing and large-strain consolidation are being developed. However, for practical use of next-generation magnets, it will be necessary to develop a powder consolidation technique that enables higher densification.

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### **Authors' Short Biographies**



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Kenta Takagi is a senior researcher at the National Institute of Advanced Industrial Science and technology. He obtained his bachelor's degree and master's degree in Materials Science from Tohoku University in 1995 and 1997, respectively. Later he obtained his Doctor of Engineering from Tohoku University in 2003. His latest research interests revolve around permanent magnets. In particular, he is motivated in studying on powder processing for low-sinterable and metastable magnetic alloys.



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![](_page_19_Picture_7.jpeg)

### Shusuke Okada

Shusuke Okada is a senior researcher at the National Institute of Advanced Industrial Science and technology. He obtained his Doctor of Engineering from Osaka University in 2013. His latest research is synthesis of magnetic material powder by wet-chemical process.

![](_page_19_Picture_10.jpeg)

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Akihide Hosokawa is a senior research scientist at the National Institute of Advanced Industrial Science and technology. He obtained his Ph.D. degree 2010 at McMaster University (Hamilton, ON, Canada). His research interest is to develop new generation ultrastrong permanent magnets through development of novel microstructural control techniques.

![](_page_19_Picture_13.jpeg)

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Wataru Yamaguchi is a senior research scientist at the National Institute of Advanced Industrial Science and Technology. He received his doctorate from the University of Tokyo in 1997. He is currently working on methods to improve the performance of a group of rare-earth magnets through grain boundary engineering.