Featured Articles

Analysis Technique for Improving Coercivity of Nd-Fe-B Magnets and Development of Dy-free Magnet

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OVERVIEW: Hitachi is working to improve the performance of the Nd-Fe-B magnets that help make people's way of life more energy efficient and reduce the load it places on the environment. To study the factors that govern coercivity, an important parameter of magnet performance, Hitachi used a combination of advanced measurement techniques for evaluating the magnetic properties of a magnet's internal structure and simulation techniques for analyzing magnetization reversal behavior. This analysis found that the properties of the grain boundary phase have a strong influence on coercivity. By working on material developments that focused on the grain boundary phase, Hitachi Metals, Ltd. has commercialized the NEOMAX Low Dy Series, a new range of Nd-Fe-B magnets developed to significantly reduce the use of Dy, a rare element.*

INTRODUCTION

SINTERED magnets made from neodymium (Nd), iron (Fe), and boron (B) (hereinafter referred to as Nd-Fe-B magnets) are the most powerful permanent magnets currently available. They are used in information technology (IT) equipment, home appliances, electric vehicles (EVs), and a wide range of products such as industrial electric motors that underpin social infrastructure(1) (see Fig. 1). Demand has been rising in recent years amid moves to make people's way of life more energy efficient and reduce the load it places on the environment, particularly for the Nd-Fe-B magnets used in the drive motors in hybrid electric vehicles (HEVs) and EVs.

Coercivity is an indicator of a magnet's stability in the presence of a magnetic field. A key challenge for the magnets used in HEVs and EVs is to improve this coercivity without compromising high remanent magnetic flux density that generates the strong magnetic force. While the addition of dysprosium (Dy), a rare element, is one way of improving coercivity, Dy poses a significant procurement risk in terms of its security of supply and price fluctuations. This has created an urgent need to develop ways of achieving high coercivity while also reducing the quantity of Dy in the magnet.

The Research & Development Group at Hitachi, Ltd. is working on the research and development of high-performance Nd-Fe-B magnets in collaboration with Hitachi Metals, Ltd., which is responsible for the magnet business. If magnets are to be developed with high coercivity but without relying on Dy, it is particularly important to identify the factors that determine coercivity. This article describes analysis techniques for magnets that combine measurement

Nd: neodymium Fe: iron B: boron

Fig. 1—Nd-Fe-B Magnet Product Range(1).
Hitachi supplies Nd-Fe-B sintered magnets in a variety of shapes and sizes to suit different applications.

* NEOMAX is a trademark of Hitachi Metals, Ltd.

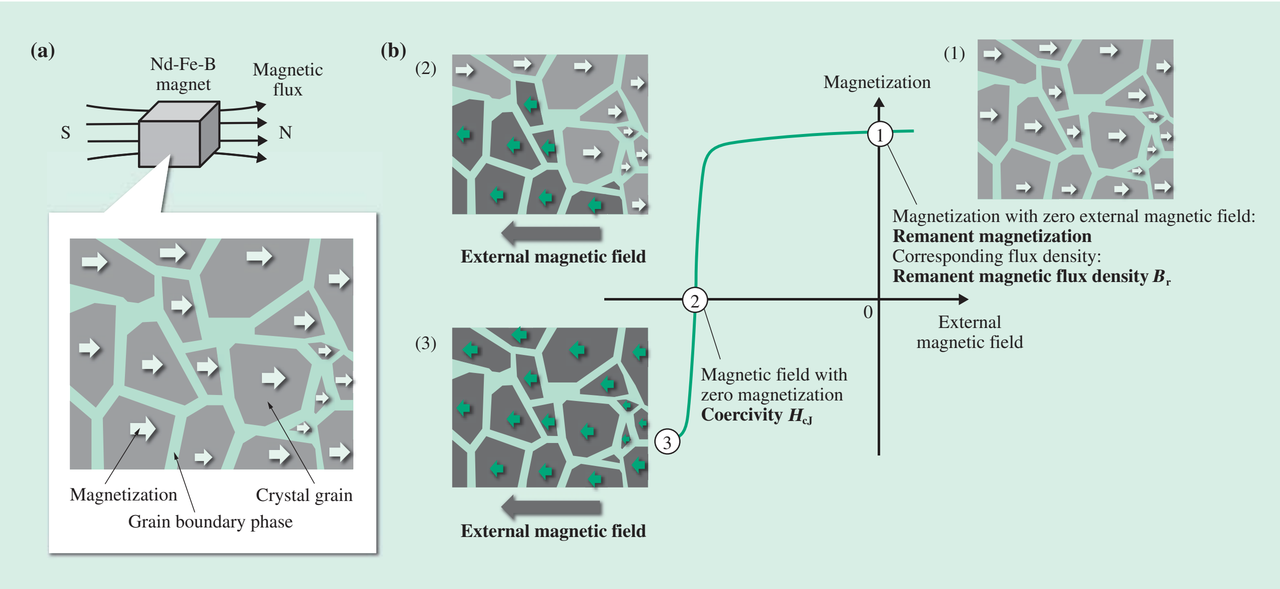


Fig. 2—Schematic Diagrams of Microstructure and Magnetic Properties of Nd-Fe-B Magnets.
(a) The magnet is made of micrometer-sized crystal grains, each of which has magnetization. (b) The magnetization of the grains can be flipped by the application of an external magnetic field, and this polarity reversal occurs if the magnetic field exceeds the material's coercivity.

and simulation to elucidate the mechanisms involved in coercivity, and the new Dy-free Nd-Fe-B magnets developed by Hitachi Metals.

STRUCTURE AND MAGNETIC PROPERTIES OF ND-FE-B MAGNETS

The properties of a magnet, including the remanent magnetic flux density and coercivity described above, are closely related to the magnet's internal microstructure. Fig. 2 shows schematic diagrams of the microstructure and magnetic properties of Nd-Fe-B magnets. Nd-Fe-B magnets have a multi-grain structure made up of Nd-Fe-B crystal grains separated from each other by a grain boundary phase with a thickness of several nanometers. These grains have individual magnetization, and they as a whole generate a unidirectional magnetic flux. Fig. 2 (b) shows how the magnetization changes when an external magnetic field is applied to a magnet. The density of magnetic flux when there is no external magnetic field present is called the remanent magnetic flux density (B_r), [diagram (1) in Fig. 2 (b)], which is equivalent to the strength of magnetization present at that time (remanent magnetization). When an external magnetic field is applied, the magnetic orientations of some of the grains in the magnet reverse [indicated by the transition from diagram (1) to (2) in Fig. 2 (b)], and this continues until all grains have switched their magnetization directions [diagram (3) in Fig. 2 (b)]. The coercivity (H_{cJ}) is the absolute value of the external magnetic field that causes half of the grains in the magnet to reverse their magnetization, resulting in net magnetization of zero [diagram (2) in Fig. 2 (b)]. In other words, coercivity is an indicator of how well the magnet can withstand magnetization reversal due to an external magnetic field, with HEV and EV applications in particular requiring high coercivity.

Coercivity is dependent on a number of factors in the magnet's microstructure, and the mechanisms by which it manifests are not yet well understood. To elucidate the factors that determine coercivity, it is necessary to understand both how magnetization reversal occurs in single grains and how it propagates across grain boundaries. The following sections describe the results of this study.

MEASUREMENT OF MAGNETIZATION REVERSAL IN SINGLE GRAINS

The theoretical coercivity of a magnetic grain can be determined by assuming uniform magnetization rotation throughout the grain, which corresponds to the anisotropy field for the material (5.7 MA/m in the case of Nd-Fe-B). However, the actual coercivity of Nd-Fe-B magnets is only between 20 and 30% of this value. Furthermore, the grains are much larger than would be needed to satisfy the theoretical assumption of uniform rotation taking place simultaneously throughout the grain. That is, rather than magnetization reversal in magnet grains happening all at once, it was assumed that each grain contained a number of magnetic domains (regions of uniform magnetic orientation) and that the mechanism for the reversal of the entire grain involved the movement of the boundaries between these (the domain walls). However, no direct observations had been made to confirm this.

Accordingly, this research included an experiment that directly observed magnetization reversal of single-crystalline grains. An X-ray magnetic microscope was used to perform measurements on microscopic grains of similar size to the crystal grains in magnets. Fig. 3 shows the experimental method. First, particles of single-crystalline Nd-Fe-B were prepared with a similar size to the grains in magnets (6 μm in diameter, 6 μm high) and attached to the tip of a tungsten (W) shaft, over which a W cap was formed, as shown in Fig. 3 (a). These Nd-Fe-B particles were obtained from a single-crystalline sample using a microsampling technique based on focused ion beam fabrication. The sample was measured using an X-ray magnetic microscope installed in the BL16XU industrial consortium beamline at the SPring-8 synchrotron radiation facility. This performed measurements based on the X-ray magnetic circular dichroism (XMCD) principle. When circularly polarized X-rays are directed at a magnetic material, the interaction between the X-rays and magnetism causes the amount of X-ray absorption to be different depending on the polarization (left- or right-handed). This difference in absorption (XMCD intensity) depends on the angle of the incident X-rays relative to the magnetization of the material. Measuring the XMCD intensity while sweeping the external magnetic field, as shown in Fig. 3 (b), can determine the change in magnetization due to the external magnetic field and obtain the magnetization curve shown in Fig. 2 (b). Furthermore, by rotating the sample to change the relative orientation of the magnetization and the external magnetic field,

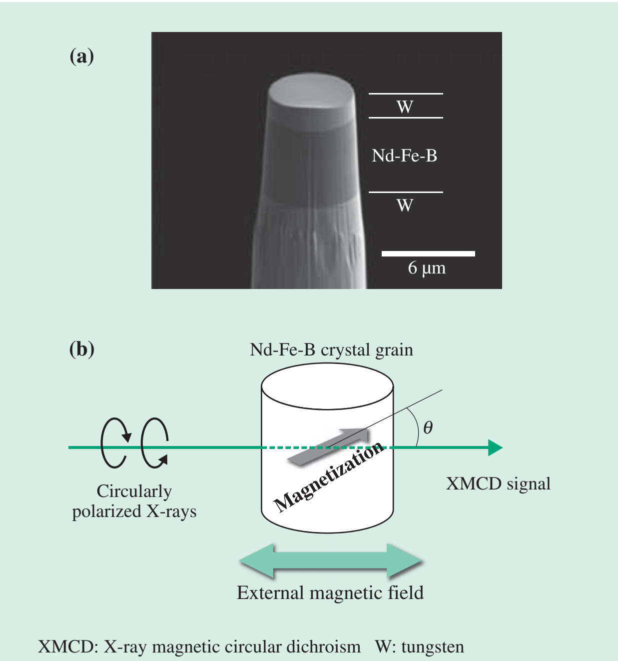


Fig. 3—Method for Measuring Magnetization Reversal in Microscopic Nd-Fe-B Crystal Grains.
Fig. (a) shows an electron microscope image of sample. Fig. (b) shows how the magnetization of the sample can be determined from the XMCD signal obtained through the interaction between the magnetization of the Nd-Fe-B crystal grain and the incident circularly polarized X-rays.

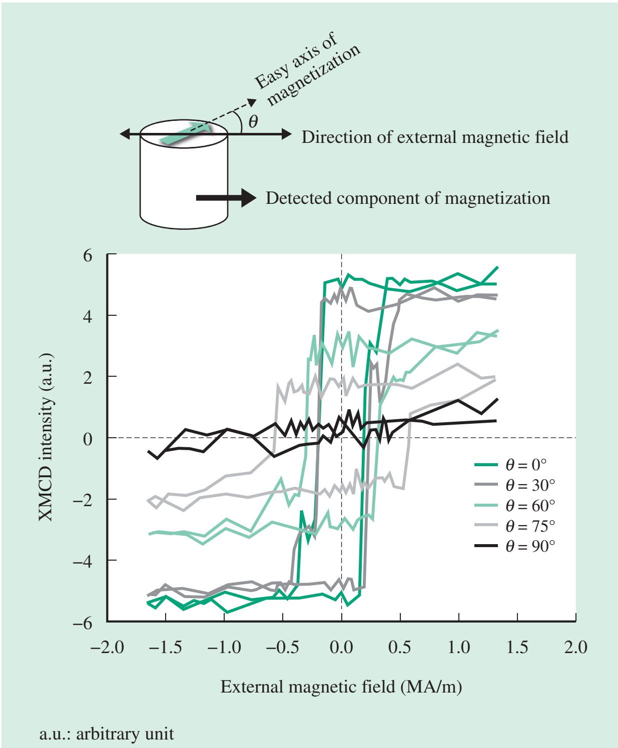


Fig. 4—Dependence of Magnetization Curve of Microscopic Nd-Fe-B Crystal Grains on Angle of Applied Magnetic Field.
The XMCD intensity (vertical axis) indicates the degree of magnetization. The magnetization curve is measured by varying the angle (θ) of the applied magnetic field relative to the easy axis of magnetization. The detected component of magnetization falls as θ becomes larger, representing higher coercivity, which indicates that the mechanism of magnetization reversal in crystal grains involves domain wall motion rather than occurring all at once.

it is possible to measure the dependence of the magnetization curve on the angle of the applied magnetic field, and thereby to determine the nature of the magnetization reversal mechanism.

Fig. 4 shows the results of the experiment in terms of the change in the magnetization curve due to changing the angle of the applied magnetic field. As the angle between the external magnetic field and the magnetization becomes larger, the switching field (coercivity) increases and the XMCD intensity (remanent magnetization) for zero external magnetic field becomes weaker. This indicates that rather than the magnetization reversal of Nd-Fe-B crystal grains occurring all at once, it occurs through the typical domain wall motion mechanism. Furthermore, the way in which magnetic domains form during magnetization reversal is indicated by the magnetization maps obtained from the magnetization curve and XMCD signal, which are shown in Fig. 5. The maps are color-coded to show the direction of magnetization. The figures show how, starting from an initial state in which all of the magnetizations are in the positive direction [Fig. 5 (c)], the distribution of internal magnetizations gradually changes as the applied magnetic field is increased, with reversal occurring progressively rather than all at once [as shown in Fig. 5 (d), (e), and (f)]. These direct measurements indicate that the mechanism for magnetization reversal in the Nd-Fe-B crystal grains of magnets involves domain wall motion rather than simultaneous reversal.

GRAIN BOUNDARY PHASE CHARACTERISTICS AND RELATIONSHIP WITH MAGNETIZATION REVERSAL

Evaluation of Grain Boundary Phase Magnetization

The process of magnetization reversal across the entire magnet involves not only the reversals within individual crystal grains but also their propagation from grain to grain. It is anticipated that the grain boundary phase will exert a strong influence on this process. The magnetism of this phase has been a subject of interest because recent research has suggested the possibility that the grain boundary phase contains high concentration Fe and is ferromagnetic(2). This research

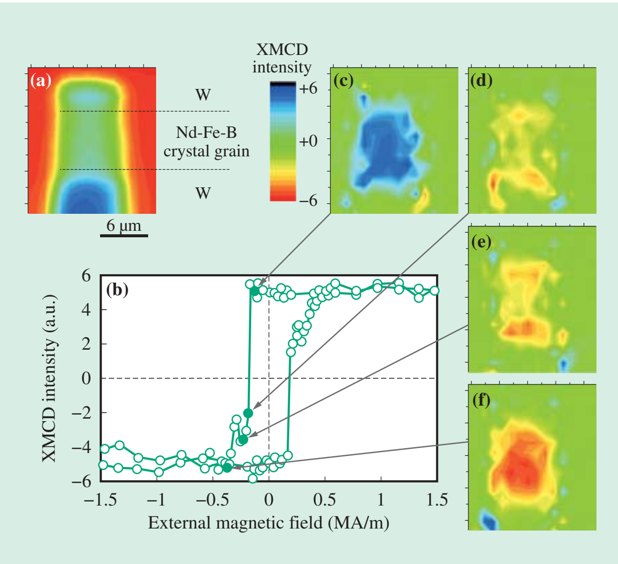


Fig. 5—Magnetization Map during Magnetization Reversal in Microscopic Nd-Fe-B Crystal Grain.
Mapping magnetization shows the process of magnetization reversal when an external magnetic field is applied to a Nd-Fe-B crystal grain. Image (a) is color-coded to show the differences in material-dependent X-ray absorption. The magnetization curve in graph (b) and the magnetization maps in (c), (d), (e), and (f) show that the change in magnetization during reversal does not occur all at once, but rather progressively through the crystal grain.

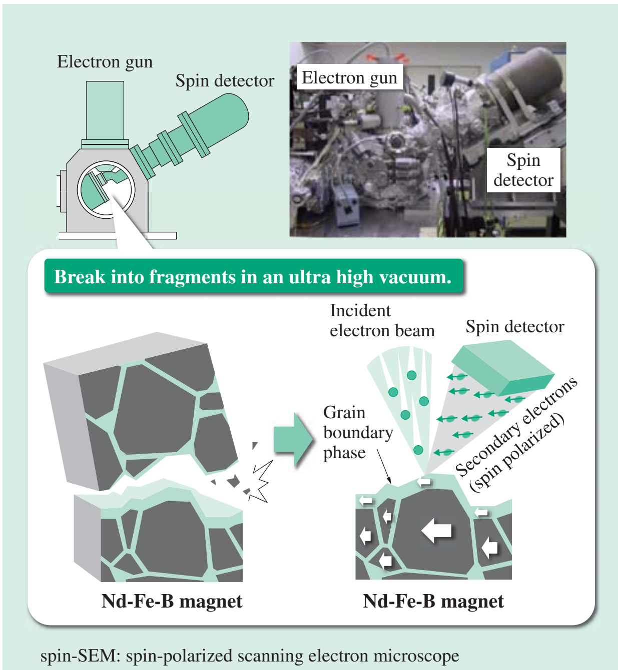


Fig. 6—Magnetization Measurement of Grain Boundary Phase Using Spin-SEM.
The figures show how the spin-SEM is used to perform measurements. Breaking up a magnet in an ultra high vacuum leaves the grain boundary phase exposed on the surface of the fragments. The magnetization of this grain boundary phase can then be determined from the spin polarization of secondary electrons generated by directing an electron beam at the grain boundary phase.

involved using a spin-polarized scanning electron microscope (spin-SEM), a type of electron microscope specifically developed by Hitachi for measuring magnetization, to make direct measurements of the magnetism of the grain boundary phase[3]. Fig. 6 shows how a spin-SEM is used to make measurements. First, a sample Nd-Fe-B magnet is mechanically fractured inside a chamber held in a state of ultra high vacuum. As most fracturing occurs preferentially along grain boundaries, this causes the grain boundary phase to be exposed on the surface of the resulting fragments, as shown in the figure. When an electron beam is directed at such surfaces, secondary electrons generated inside the grain boundary phase carry information about the magnetization of this material (spin polarization). Accordingly, quantitative measurements can be made of the magnetization of the grain boundary phase by detecting these electrons in a spin detector.

Fig. 7 shows the results of measuring the grain boundary phase magnetization for an Nd-Fe-B magnet using a spin-SEM. A series of magnetization measurements were performed accompanied by milling of the fractured surfaces using argon (Ar) ions. As indicated by the measurement results in the figure, the spin-SEM image taken immediately after fracture (0 nm of milling) shows a clear black and white pattern of magnetic domains in those places where the Nd-Fe-B crystal grain (Nd-Fe-B phase) is exposed, whereas the image for the region marked as being a grain boundary phase has poor contrast. As the amount of milling is increased, however, the contrast between black and white gradually sharpens in the grain boundary phase region. This is because the grain boundary phase coating the surface is progressively milled away, eventually leaving the underlying Nd-Fe-B phase exposed. The graph at the bottom of Fig. 7 shows a plot of this change in terms of the magnetization of the grain boundary phase region (the region initially coated with the grain boundary phase immediately after fracturing). The magnetization immediately after fracturing and during initial milling (milling of 0 to 1 nm) remains constant, this being the magnetization of the grain boundary phase. The results indicate this magnetization is 37% that of Nd-Fe-B phase. The results thereby demonstrate that the grain boundary phase in typical Nd-Fe-B magnets is ferromagnetic. This ferromagnetic grain boundary phase strengthens the magnetic coupling between Nd-Fe-B crystal grains and is a cause of lower coercivity because it encourages the propagation of magnetization reversal between crystal grains.

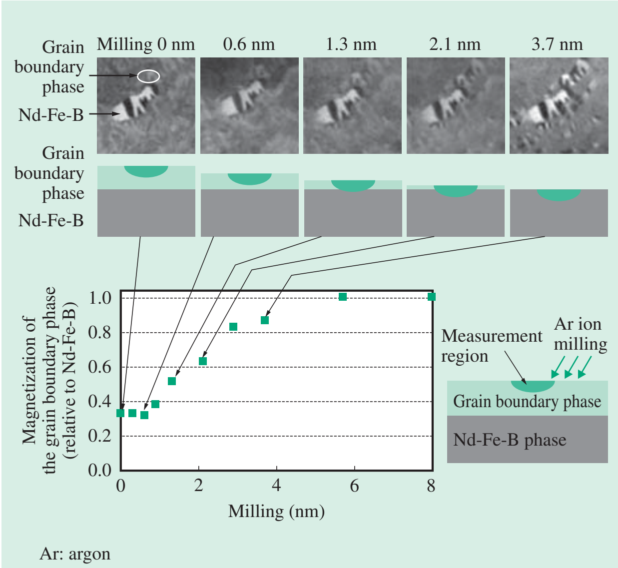


Fig. 7—Results of Magnetization Measurement of Grain Boundary Phase Using Spin-SEM.
The magnitude of detected magnetization changes as progressive milling of the grain boundary phase exposed on the fractured surfaces gradually uncovers the underlying Nd-Fe-B phase, in which the magnetic domains appear sharply contrasted. The measurements made initially and in the early stages of milling represent the magnetization of the grain boundary phase, which is 37% that of Nd-Fe-B phase.

Simulation Analysis of Magnetization Reversal

The simulation of magnetization reversal provides an effective way of systematically studying how it is influenced by the properties of the grain boundary phase. The research team has developed an analytical simulation technique based on micromagnetics theory that provides tools for analyzing the dynamics of magnetization. This technique is called Landau–Lifshitz–Gilbert (LLG) simulation because it uses the LLG equation to calculate how magnetization behaves in a magnetic field. Hitachi used this to calculate and compare the differences in magnetic reversal that result from changing the properties of the grain boundary phase.

First, a two-grain model was formulated consisting of two Nd-Fe-B crystal grains separated by a grain boundary phase. This was then used to study how the strength of magnetic coupling between the grains varied in response to changes in the thickness of the grain boundary phase and its magnetization. As shown in Fig. 8 (a), the strengths of magnetic coupling between the grains via the grain boundary phase were calculated for the planes perpendicular to and parallel to the direction of crystal grain magnetization (series coupling and parallel coupling, respectively). The calculation results are shown in Fig. 8 (b) and (c). As shown in Fig. 8 (b), the magnetic coupling between grains was dependent on the grain boundary phase thickness, becoming stronger as the grain boundary phase becomes thinner. The magnetic coupling between grains also tends to become stronger as the magnetization of the grain boundary phase increases, as shown by Fig. 8 (c). The stronger this magnetic coupling between grains, the easier it is for the magnetization reversal of one grain to propagate to the other. In other words, it encourages magnetization reversal across the entire magnet and therefore implies that coercivity will be reduced.

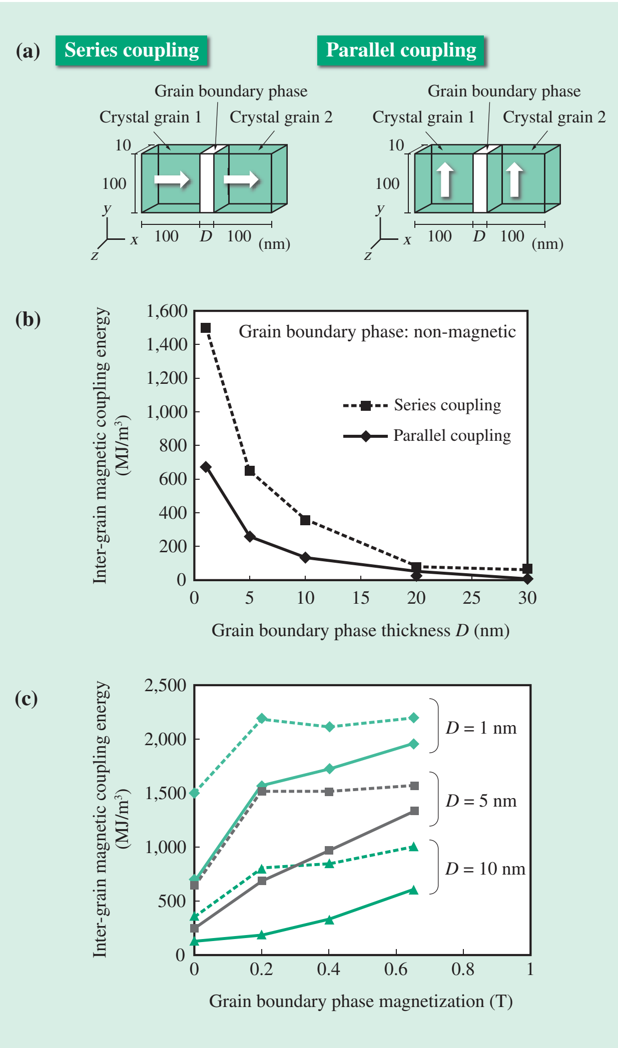


Fig. 8—Results of Calculating Magnetic Coupling across Grain Boundary Phase Using Two-grain Model.
Fig. (a) shows the model used to calculate the magnetic coupling across a grain boundary phase for planes perpendicular to and parallel to the direction of magnetization (series coupling and parallel coupling respectively). Graphs (b) and (c) respectively show how the strength of magnetic coupling between the grains increases when the grain boundary phase is thin and when it has high magnetization. The dotted lines in the graphs represent the calculated values for series coupling and the solid lines are for parallel coupling.

To test this, Hitachi prepared a three-dimensional model with multiple grains to investigate how the properties of the grain boundary phase influenced the propagation of magnetization reversal. Fig. 9 shows the results of calculating how magnetization reversal occurs for a model of four crystal grains under two different grain boundary phase conditions with different levels of magnetization. The grain boundary phase for case A is non-magnetic (no magnetization) and for case B is ferromagnetic with magnetization of 0.65 T (40% of Nd-Fe-B phase). In both cases, the grain boundary phase is 3 nm thick. The figures are color-coded to show the direction of magnetization, with red indicating right-handed and blue indicating left-handed magnetization. Although not shown in the figure, rather than being in a vacuum, the model treats the four grains as being surrounded by magnet grains. That is, the model simulates the situation in the interior of a magnet. As shown in Fig. 9, when the external magnetic field is low (–2.5 MA/m), the magnetization across the entire region is uniformly right-handed. As the field strength is then increased, magnetization reversal starts to occur at some locations inside the grains, indicated by the increase in blue regions (left-

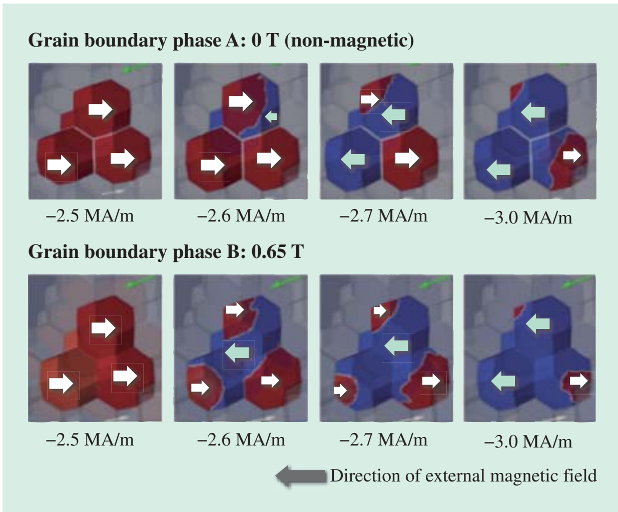


Fig. 9—Results of Calculating Magnetization Reversal Process Using Four-grain Model.
The region where magnetization reversal has occurred (blue regions with left arrows) grows as the external magnetic field increases. The progress of magnetization reversal is faster for case B (grain boundary phase is ferromagnetic) than for case A (grain boundary phase is non-magnetic).

handed magnetization). The behavior is consistent with the magnetization reversal measurements for single-crystalline grains described previously, namely that the grains contain two magnetic domains (with left- and right-handed magnetization respectively) separated by a domain wall that moves over time. A comparison of the two cases A and B shows that magnetization reversal proceeds more easily in case B where the grain boundary phase is ferromagnetic.

Fig. 10 shows this process of magnetization reversal in the form of a magnetization curve. The vertical axis represents the sum of the magnetizations of the four-grain model normalized to the saturation magnetization of Nd-Fe-B. From Fig. 9, the right-handed component of magnetization is treated as positive and the left-handed as negative. The magnetic field at which the total magnetization becomes zero (the coercivity) is lower for case B than for case A.

As the measurements of the grain boundary phase magnetization made using the spin-SEM and the results of LLG simulation analysis both indicate that the grain boundary phase in a typical Nd-Fe-B magnet is ferromagnetic, this indicates that this magnetization is a cause of lower coercivity. Furthermore, LLG simulation analysis indicates that reducing the magnetization of the grain boundary phase and increasing its thickness will improve coercivity.

DEVELOPMENT OF DY-FREE MAGNET[4]

Noting that the grain boundary phase is a major factor in improving coercivity, Hitachi Metals succeeded in significantly reducing Dy content by studying the range of compositions and alloying elements in ways that had not previously been considered, and by various fine tuning, including of the manufacturing conditions.

The new magnets were released in April 2014 as the NEOMAX Low Dy Series, with the product range extending from the NMX-46F to the 35F, and have been increasingly adopted for use. The magnets have similar remanent magnetic flux density (B_r) and coercivity (H_{cJ}) to the previous NMX-50 Series but a significantly lower mass-percentage (mass %) of Dy (mass of Dy as a percentage of the mass of the entire magnet) (see Fig. 11). For example, the 46F is "Dy-free," with similar characteristics to previous magnets despite only containing approximately 2% Dy by mass. Hitachi Metals has also developed a range of low-Dy magnets (NMX-S49F to S38F) similar to its previous NMX-S52 Series of high-performance magnets. These entered mass production in FY2015.

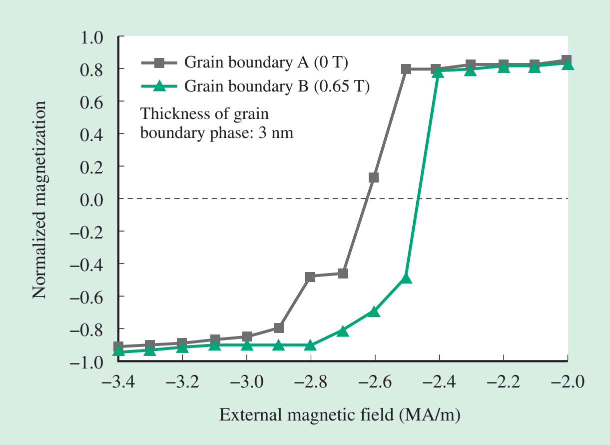
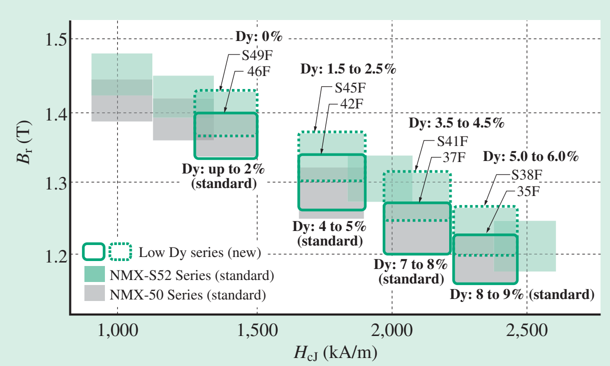


Fig. 10—Results of Calculating Magnetization Curve Using Four-grain Model.
Magnetization reversal is initiated at a lower external magnetic field (coercivity is lower) for case B (grain boundary phase is ferromagnetic) than for case A (grain boundary phase is non-magnetic).



Dy: dysprosium

Fig. 11—Characteristics Map of Dy-free Nd-Fe-B Magnet[4].
Hitachi has developed magnets that maintain high performance despite using significantly less Dy.

CONCLUSIONS

Permanent magnet materials such as Nd-Fe-B play an essential role in underpinning Hitachi's social infrastructure business. While it goes without saying that ongoing material identification and process development based on the accumulation of knowledge and experience in materials science is vital for developments like this, it is also becoming more and more necessary in today's increasingly competitive environment to analyze the phenomena that govern performance and use this to suggest ways of improving characteristics, and to incorporate this knowledge into materials design, as described in this article. The Research & Development Group intends to continue contributing to materials development at Hitachi by making further advances in analysis techniques that combine materials analysis, magnetism measurement, and simulation.

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