

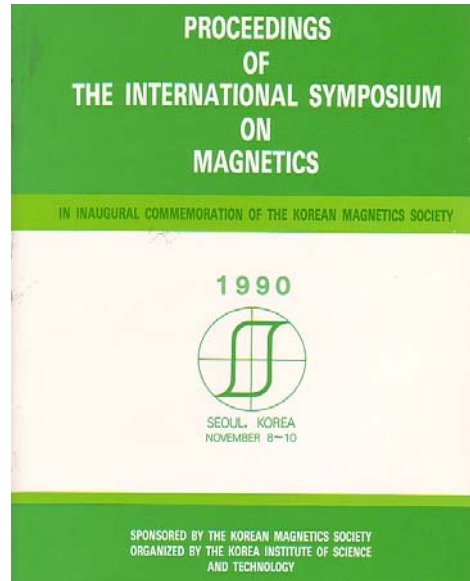
# PERMANENT MAGNETS BASED ON THE LANTHANIDES

Raw Materials, Processing and Properties

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## Abstract

Lanthanide based permanent magnets, Sm-Co and Nd-Fe-B type magnets are reviewed. The historical progression of materials over the last fifty years is traced. The lanthanides and their idiosyncrasies are covered. Processing technologies are discussed and some observations about the future of these materials are made.



## Introduction

Permanent magnets based on the lanthanides, Sm-Co and Nd-Fe-B, are exciting additions to the family of magnetic materials, from many perspectives. To the materials scientist, they are a new generation of lanthanide-based intermetallic materials, with excellent magnetic properties. To the electrical engineer, they are powerful components in designing new devices with greatly enhanced performance. To the magnet producer, they are new permanent magnet materials, with improved magnetic properties and several processing options.

## History

Using a lanthanide element in permanent magnets is hardly a new concept. The first work in this area was published in 1935, when Urbaine, et al. reported that gadolinium is ferromagnetic. [1] Some of the lanthanides have record magnetic moments, but unfortunately their Curie temperatures are at or far below room temperature. Commercialization of the lanthanides occurred as a result of the Manhattan Project, when the technology for large scale separation of the lanthanides, as well as the actinides, was developed. Since the end of the Second World War, scientists and engineers have had access to reasonable quantities of high purity lanthanide elements and have systematically studied the many unique properties, not just magnetic, of these elements

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and their alloys.

By the mid 1960's,  $\text{LnCo}_5$  compounds (Ln being any lanthanide) had been recognized as excellent candidates for permanent magnet materials, due to their high magnetocrystalline anisotropy and moderate saturation magnetization. [2, 3, 4] Primary interest focused on the light lanthanides, i.e. La, Ce, Pr, Nd, Sm and Y, even though the light lanthanide generally have smaller magnetic moments than the heavy lanthanides. In the  $\text{LnCo}_5$  structure, the heavy lanthanide moment couples antiferromagnetically with the cobalt moment, reducing the saturation magnetization. The first  $\text{SmCo}_5$  magnets appeared in the late 1960's and early 1970's, due to the research and development efforts of several organizations, most notably: General Electric, Raytheon, Bell Telephone Laboratories, Wright Patterson Air Force Base, N. V. Philips and Brown Boveri et Cie.

As soon as  $\text{SmCo}_5$  became a commercially viable permanent magnet, research began in two directions. One direction was to replace or reduce the amount of samarium in the alloy, by substituting one or more of the more abundant and less expensive lanthanides: Ce, La, Nd, Pr and MM, where MM is mischmetal. The other direction was to replace the cobalt with iron, since iron is less expensive and has a slightly larger magnetic moment per atom than cobalt. In both cases, the goal was to reduce the cost of the magnet, by reducing the raw material cost, without adversely affecting the magnetic properties. Four distinct alloys have evolved from this research.

The first material is  $\text{MMCo}_5$ . Mischmetal is far less expensive than samarium, by about a factor of 15. However, the magnetic properties of  $\text{MMCo}_5$  magnets are drastically poorer than  $\text{SmCo}_5$  magnets, to the point that the tradeoff of magnetic properties versus alloy cost is unfavorable for  $\text{MMCo}_5$ . Similar behavior was also observed for  $\text{CeCo}_5$ ,  $\text{LaCo}_5$  and  $\text{NdCo}_5$ . [3] The main fault is that the anisotropy is much lower for these compounds, making difficult to obtain acceptable  $H_{ci}$  levels. [5]

The second material is  $\text{Sm}_x\text{Pr}_{(1-x)}\text{Co}_5$ . Praseodymium is more abundant, less expensive and has a slightly larger magnetic moment than samarium. A partial substitution of Pr for Sm actually improves  $B_r$  and  $(BH)_{\text{max}}$ . However, as the Pr/Sm ratio increases above 1, the stability of the alloy above room temperature is reduced and it is difficult to keep  $H_{ci}$  as high as it is in  $\text{SmCo}_5$ . Therefore, most commercial materials have a Pr/Sm under 0.5, for a good combination of magnetic properties and raw material cost. Some research continues to try to make a  $\text{PrCo}_5$  magnet, but nothing is commercial as of this writing. [6, 7]

The third material is the  $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr}$  or  $\text{Hf})_{17}$  alloy system, here after referred to a 2-17 magnets. This is a metallurgically complicated alloy system, with high  $H_{ci}$  based on precipitation hardening. In these alloys, both the samarium and the cobalt levels are reduced, while the magnetic properties are generally superior to  $\text{SmCo}_5$ . The major drawback to 2-17 magnets is their complicated processing, due in part to the fact that the alloy has at least 5 components, which must be held to tight tolerances. In production, it is difficult to obtain the desired microstructure for the best magnetic properties. Also, the heat treatments are much longer and more complicated than the heat treatment of  $\text{SmCo}_5$ . The limited availability of 2-17 magnets stem from these complications. [8]

The fourth material is  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , which achieves the original goals of replacing Sm

and Co in SmCo<sub>5</sub> magnets. The magnetic properties of the binary lanthanide-iron compounds, including Nd-Fe, were examined at about the same time as the lanthanide-cobalt systems, in the 1960's and early 1970's. However, all the binary lanthanide-iron alloys have at least one of the following problems, making them unsuitable as permanent magnets. The problems are: 1) a Curie temperature near or below room temperature, 2) unfavorable anisotropy, usually an easy cone or an easy plane, or 3) antiferromagnetic coupling between the lanthanide and the iron magnetic moments, resulting in low saturation magnetization. The critical addition of the metalloid element boron to the Nd-Fe alloy, results in a slightly expanded crystal structure, overcoming the above mentioned drawbacks of the lanthanide-iron alloys. At almost the same time in 1983, several groups reported independently, excellent permanent magnet properties based on the Nd-Fe-B alloy system. [9, 10, 11, 12, 13] Commercial production of these materials started almost immediately thereafter.

### The Lanthanides

The lanthanides consist of elements number 57, lanthanum, through 71, lutetium, at the bottom of the periodic table. These elements have historically been called the rare earths, but this name is misleading, as they are neither rare like gold or earths like magnesium or calcium. At the time these elements were discovered, rare was an apt term. However, several large deposits are found all over the world. Figure 1 shows the relative abundance of some of the lanthanides compared to other elements. Cerium, the most abundant lanthanide, is more common in the earth's crust than nickel. Lanthanum, the second most abundant lanthanide, is more common than lead or tin. [14, 15]

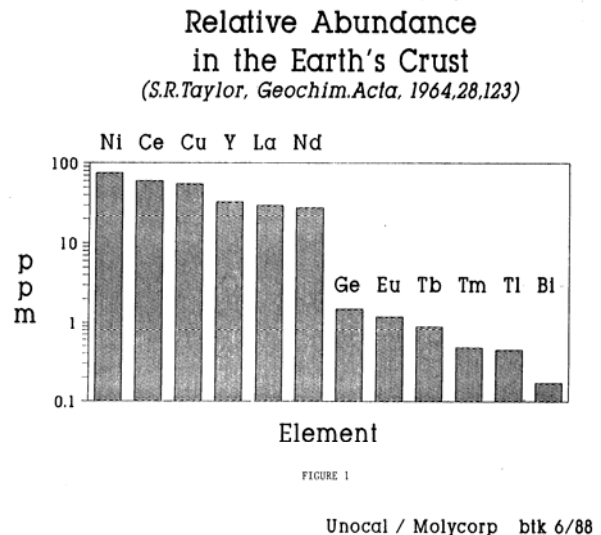


Figure 1. Relative abundance of various elements in the earth's crust

Lanthanides are unusual in that they are all found together in the ore. Figure 2 shows the breakdown of the most common lanthanide ores, Bastnasite and Monazite. In both ores, two general observations can be made about relative abundance. The abundance of the even atomic numbered elements is greater than the odd atomic numbered elements on either side and abundance diminishes with increasing atomic number, odd or even.

The periodic table shows that in the lanthanide series, the inner 4f electron shell is being filled from lanthanum to lutetium. This in part explains some of the facts known about the lanthanides.

1. Chemically the lanthanides are all very similar since there is little difference in the outer electron configuration.
2. The lanthanide oxides are extremely stable since the outer electrons are easily removed from the metals. The metallic form of any lanthanide is not found in nature. Lanthanides are always found as compounds, usually a complex oxide or fluoride.
3. Because the lanthanides are chemically similar and are found together in the ore, their separation is difficult.

Use of separated lanthanides, as oxides, metals or salts, has grown tremendously in the last 25 years. There are two principal methods for separating lanthanides, solvent extraction and ion exchange. Purities as high as 99.999% can be obtained with either technique.

Comparison of the Lanthanide Content  
Bastnasite vs. Monazite

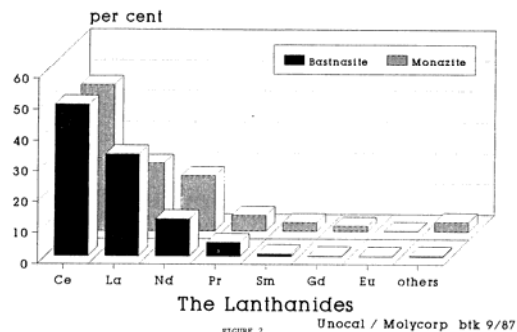


Figure 2. Breakdown of the lanthanides in the two most common ores.

Lanthanide metals are generally reduced by calciothermic reduction of a salt, usually fluoride or chloride. The exceptions are samarium and europium, which due to their low boiling point are distilled in the presence of mischmetal.

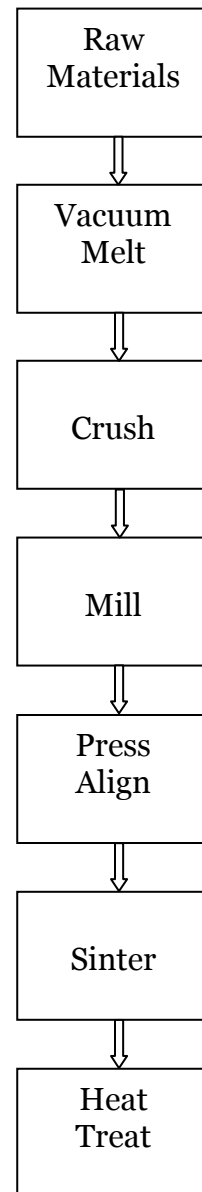
Electrolytic techniques may also be used to produce the metals. This technique is cost effective only at relatively large production volumes. Historically, electrolytic reduction of the lanthanides to metals has been used mainly to produce mischmetal.

### Processing

There are several ways to make lanthanide based permanent magnets. We will start with the conventional powder metallurgy method, concentrating on Nd-Fe-B, and compare the other processing methods to the powder metallurgy approach.

A block diagram of the powder metallurgy process is shown in figure 3. The first step is the vacuum melting of neodymium, iron and ferrobaboron to the correct composition. Melting in an inert atmosphere is required since molten neodymium is readily oxidized when exposed to air. The desired composition is just slightly richer in Nd than the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  stoichiometry, to offset the preferential oxidation of Nd and to retain a small amount of an Nd-rich phase in the grain boundaries of the magnet. During vacuum melting, the iron and ferrobaboron are melted first in vacuum. Neodymium is added after the iron and ferrobaboron are molten and after the atmosphere has been changed to argon. The argon atmosphere is necessary to reduce the vaporization of the molten Nd. The molten alloy is poured into

Figure 3. Powder Metallurgy Method



a mold.

Like most lanthanide-transition metal alloys, as-cast Nd-Fe-B is brittle and is easily broken with a hammer, as the first step in making powder. The broken pieces are crushed to about 250  $\mu\text{m}$  by a pulverizer and reduced to final size by milling. The optimum particle size is in the 2 to 4  $\mu\text{m}$  range, as measured by the Fisher Sub Sieve Sizer. A jet, ball or vibratory mill can be used for this step. Both crushing steps are done in an inert atmosphere, usually argon or nitrogen. The critical point is that at the optimum particle size nearly all the powder consists of particles that are single crystals. This is a necessary condition for magnetic aligning. Powder milled to less than the optimum particle size is more prone to oxidation, sometimes rapid, making it difficult to handle and not suitable for magnet making.

Magnets are shaped and the powder is aligned by die pressing. In one operation, the powder is aligned and pressed in a three step process. In step one, the powder is filled into the die cavity. The tooling is moved to the top of the die cavity, but no pressure is applied. In step two, a magnetic field is applied to the powder. Because the particles are nearly all single crystals, each particle rotates so that its easy direction is nearly parallel to the applied magnetic field. In step three, the powder is compacted by the tooling and the magnetic field is reversed to demagnetize the tooling.

Pressing begins the process of making the magnet material dense. The densification process is completed by sintering, typically a density of 7.4 to 7.5  $\text{g}/\text{cm}^3$  can be achieved, compared to the theoretical density of 7.6  $\text{g}/\text{cm}^3$ . Typical sintering conditions are vacuum, 1080  $^\circ\text{C}$  for 2 hours, followed by a quench to room temperature. Sintering completes the process of densification, but does not develop the optimum magnetic properties. As figure 4 shows,  $H_{ci}$ ,  $H_k$  and  $H_c$  can all be improved by a post sintering heat treatment. A typical heat treatment is one hour at 600  $^\circ\text{C}$ , followed by a rapid quench to room temperature.

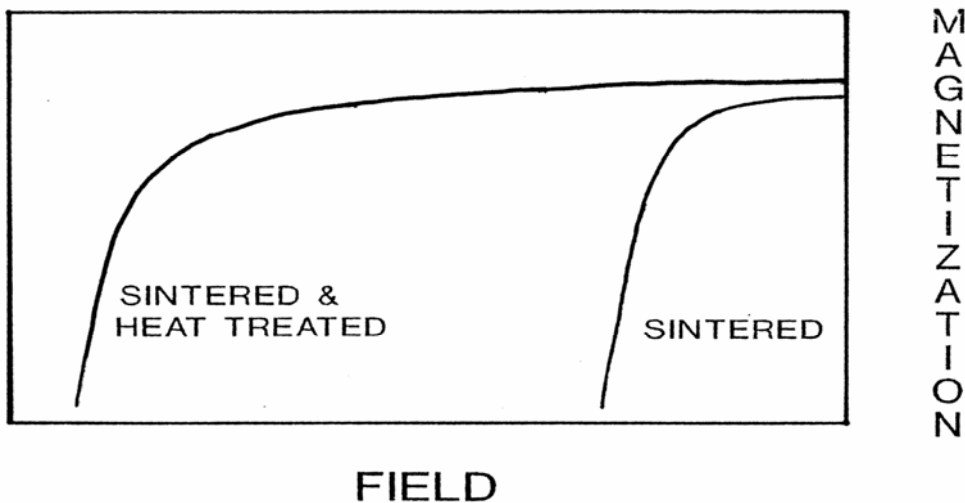


Figure 4. Effect of heat treatment on demagnetization curves for a typical Nd-Fe-B magnet.

## Hydrogen decrepitation (hydriding)

While the as-cast Nd-Fe-B alloy is brittle and easily broken, ductility is readily apparent during the crushing step. Crushing as-cast alloy to a size less than 250  $\mu\text{m}$  is not easy. As a result, the alloy can oxidize excessively during this step. An improvement on the conventional powder metallurgy process is hydrogen decrepitation or hydriding. [16] Alloy is exposed to hydrogen gas, usually at a slightly elevated temperature and/or elevated pressure, to increase the reaction rate. Hydrogen diffuses into the alloy, making it brittle and causing it to literally fall apart. The resulting material is a coarse powder and with very little effort, it can be crushed to a size less than 250  $\mu\text{m}$ , before milling. Hydrogen decrepitation was applied earlier to Sm-based alloys by Harris, but the approach is more useful in the Nd-Fe-B alloy system. [17]

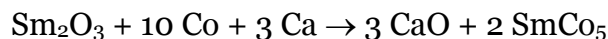
The principal advantage of hydriding is that the difficulty of the crushing step is greatly reduced. Since hydriding greatly reduces the ductility of the material, far less mechanical work is required to crush the alloy, reducing the extent of alloy oxidation. Some work has been done on using hydriding to replace both crushing and milling. However, it is difficult to obtain a particle size below 5  $\mu\text{m}$  by hydriding alone, with a particle size distribution as narrow as other milling methods. With a combination of hydriding and conventional grinding techniques, it may be possible to make further improvements in powder making. The mechanism of hydriding is not completely understood, however the most likely explanation is that hydrogen rapidly diffuses through the grain boundaries of as-cast alloy. The absorbed hydrogen expands the lattice of the grain boundary phases and fractures the alloy from within. Alloys that are slightly rich in Nd, which contain an Nd-rich phase in the grain boundary, seem to hydride with greater ease. Rapidly quenched materials which are generally nearer the stoichiometric composition do not hydride as easily.

## Reduction/Diffusion

The reduction/diffusion (R/D) process was developed for the production of  $\text{SmCo}_5$  alloys by Cech. [18] A very similar process called co-reduction was developed by Herget and Domazer. [19] Both processes are in commercial use today.

The first  $\text{SmCo}_5$  alloys were made by vacuum melting in a fashion similar to the process described in figure 3. There are two important differences between Nd-Fe-B and  $\text{SmCo}_5$  in the alloy making process. First samarium metal cannot be made by the direct reduction of its oxide or salts; it must be sublimed in the presence of mischmetal and condensed on a tantalum cone. This is a more expensive process than calciothermic reduction. Second roughly 10% of the samarium is vaporized and lost during vacuum melting. Thus the production of  $\text{SmCo}_5$  by vacuum melting the metals is expensive.

The R/D method overcomes both of these problems and also has the advantage that the alloy is produced in a powder form, ready for milling. The reaction is



The reaction takes place at 1100 °C for 1 to 4 hours in a hydrogen atmosphere. Usually an excess amount of Ca is added, typically 20 to 40% to assure that the reaction goes to completion.

The R/D method has also been applied to the Nd-Fe-B system with limited success. A major problem has been the solubility of Nd in the water used by the washing step to remove the reacted Ca. [20, 21]

### Atomization

Atomization combines to alloying and powder making steps, by spraying the molten Nd-Fe-B alloy into small particles before quenching them in a suitable media, usually a cryogenic fluid, nitrogen or argon. The spraying allows the particles size to be well controlled. The quenching permits rapid solidification without time for segregation of secondary phases. Although the quenching does not take place at a fast enough rate to create amorphous material. The particle size after atomization is in the 10 to 40  $\mu\text{m}$  range. Further grinding is necessary to obtain the optimum particle size. Atomization seems to have the advantage of delivering a narrow range of particle sizes, but it has the disadvantage of being a capital intensive process.

### Rapid solidification

Rapid solidification has been used for many years for making a wide variety of materials. The original patents for this technique were issued around 1900. Molten alloy is forced onto a moving surface, quenching the liquid into a solid with cooling rates of  $10^6$  K/second. A popular use of rapid solidification has been to make the magnetically soft amorphous alloys. Rapid solidification was applied by several groups to Nd-Fe-B. [10, 11, 12]

Rapidly quenched Nd-Fe-B usually is produced in the form of microcrystalline flakes. The grains are isotropically oriented and several hundred Angstroms in diameter. Usually annealing is required to obtain the optimum grain size. The Nd-Fe-B rapidly quenched flakes can be bonded, hot pressed or hot worked into magnets. The bonded and hot pressed magnets are isotropic, while hot worked magnets are oriented.

### The effect of individual alloying elements

One of the more interesting aspects of the development of Nd-Fe-B magnets has been the usefulness of small additions of several alloying elements. Most of the periodic table has been tried to improve the performance of the basic alloy, in some respect. Table I summarizes the most popular alloying elements and attempts to assign a mechanism on their influence. Many elements are effective at very low addition levels, up to 1% by weight, indicating that these elements are influencing the grain boundary phases. Other elements like Co and Dy require larger substitutions to be useful and seem to be substituting in the matrix phase for Fe and Nd, respectively.

Table I  
Common Alloying Additions

Element	Typical Addition (%)	Cause	Effect	Reference
Dy, Dy <sub>2</sub> O <sub>3</sub>	0-5	Increase K	Increases H <sub>ci</sub> Decreases B <sub>r</sub>	22
Co	0-10	Increase T <sub>c</sub>	Increases operating temperature	22
Al	0-1	Grain boundary modification?	Increases H <sub>ci</sub>	
Ga	0-1	Grain boundary modification?	Lower losses	23
V	0-1	Grain boundary modification?	Corrosion	24
Mo	0-1	Grain boundary modification?	Corrosion, Lower losses	25
Nb	0-1	Grain boundary modification?	Lower losses	26
O <sub>2</sub>	0-1.2	Grain boundary modification?	Corrosion	27
C	0-.14	Grain boundary modification?	Corrosion	27
N <sub>2</sub>	0-0.1	Grain boundary modification?	corrosion	27

### Properties

Table II contains a comparison of the typical magnetic properties of the common permanent magnets. One key point is that each material has at least one area where it is clearly superior.

Table II  
Common Permanent Magnets

Material	$B_r$ (kG)	$H_{ci}$ (kOe)	$(BH)_{max}$ (MGOe)	$T_c$ (°C)
Ceramic 8	3.8	3.5	3.6	450
Alnico 5	13.5	0.6	7.0	890
SmCo <sub>5</sub>	9.0	20	18	727
2-17	10.5	10	26	800
Nd-Fe-B	12.8	12	35	320
Nd-Dy-Fe-B	11.6	20	32	320
MQ1	6.1	15	8	320
MQ2	7.9	16	13	320
MQ3	11.8	13	32	320

### The Future

Lanthanide based permanent magnets have been a very popular area of research in the recent past. Their development has been rapid and their commercialization has been extraordinarily rapid. Yet many challenges remain unanswered.

The first is what improvements are possible with the basic Nd-Fe-B system. There are several areas to explore. The first is the topic of alternative processing technologies. Since these magnets can be made by rapid quenching, hot working or powder metallurgy, there is still some exploring to be done as to which method is preferable for a given application. Hot pressing is preferred for very thin magnets. Extrusion is preferred for radial orientation or for magnets with complicated cross sections. An example of this application might be a stepper motor with radial orientation and an irregularly shaped cross section.

Corrosion resistance is a primary concern with Nd-Fe-B magnets. Since the neodymium easily reacts with oxygen and the iron component also is somewhat reactive, at least compared to the SmCo<sub>5</sub> magnets, there has been much research to improve the corrosion resistance of these materials in the 100 to 200 °C range. Many alloy variations have been tried, adding V, Ga or Nb, with some partial success. The rapidly quenched magnets have an advantage that their composition is closer to the Nd<sub>2</sub>Fe<sub>14</sub>B stoichiometry, meaning that there is little or no Nd-rich phase present. However, the manufacturers of all types of Nd-Fe-B magnets have been using epoxy, other types of coatings, or surface treatments to improve corrosion resistance.

Another area of interest is raising the maximum operating temperature of these materials. The common alloying additions to help at elevated temperatures have been Dy, Co, Ga and Nb. Heavy lanthanide additions, especially Dy and Tb, increase the anisotropy, increase  $H_{ci}$ , but decrease  $B_r$  and  $(BH)_{max}$ . Cobalt additions moderately affect the Curie temperature. The later two seem to be helpful at enhancing the effect of Dy on coercivity, by controlling the grain boundary phases.

A third area of interest would be in lower costing raw materials for these magnets.

The most expensive element used in these alloys is dysprosium. At the same time, adding Dy decreases  $B_r$  and  $(BH)_{max}$  slightly. One would like to be able to remove or reduce the amount of Dy, maintain the same values of  $H_{ci}$ , and increase  $B_r$  and  $(BH)_{max}$ .

Another approach to lower cost raw materials is the substitution of less expensive lanthanides for neodymium. There are three possible substitutions, cerium, lanthanum, or a mixed lanthanide. Cerium substitution seems to be out of the question because of the lower magnetic moment of Ce and the decrease in  $H_{ci}$  that would result. Lanthanum substitutions are not as bad as cerium, but are not well supported by the literature, since there are data showing that  $La_2Fe_{14}B$  does not have uniaxial anisotropy. However, partial substitutions of La-rich mixtures for part or all of the Nd may work and raise the possibility of using a Ce-reduced or a Ce-free mischmetal as a substitute for neodymium.

Since the introduction of the  $Nd_2Fe_{14}B$  system, a new permanent magnet alloy system has been introduced, namely  $SmFeTi_{10}$ . [28] This seems to be a similar crystal structure as  $Nd_2Fe_{14}B$ , but has the problem of using samarium as the lanthanide component. It does have the advantage of a higher Curie temperature and may well be capable of much better performance than Nd-Fe-B, either because of higher operating temperatures, or lower cost, if the Sm can be replaced with a less expensive lanthanide.

Another area of future interest and concern is the handling of scrap materials, falling into three main categories. One is material left in the furnace after vacuum melting, atomizing or rapid quenching. The second is rejected finished magnets. The third is the residue from the grinding operations used to fabricate the magnets to their final physical dimensions.

The reasons for interest in these materials are twofold. They have some commercial value due to the content of Nd and in some cases Dy. Without any way to recycle them, scrap materials are handled as hazardous wastes, which add to the cost of manufacture.

Several recycling methods have been proposed, but the economics and viability of them has, so far, proven unsatisfactory. The first is to try to remelt these materials, attempting to recover the metallic, unoxidized, lanthanide content. In general, the yield from this process is very low from any of the three types of scrap. Although for melting residue, there may be enough of a recovery to be economical. The second approach is to try to reduce the scrap materials completely to the oxide state and recover the lanthanide component chemically. This approach and its variations are not completely tested, but appear to be the only way to handle these materials, meaning their commercial value is nearly zero.

In short, there are a few problems to be addressed, but we have many exciting opportunities with permanent magnets based on the lanthanides.

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