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# ALLOY DESIGN AND MICROSTRUCTURE OF ADVANCED PERMANENT MAGNETS USING RAPID SOLIDIFICATION AND POWDER PROCESSING

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### INTRODUCTION

The ability to control magnetic fields and the forces they produce is a cornerstone of modern technology. Long before magnetic fields or magnetic materials were understood, the magnetic compass was a critical tool for early explorers. More recently, the demands of technology have grown significantly for both time-varying and time-independent magnetic fields. Time-independent fields may be generated either by a steady electric current or by a permanent magnet. Since a permanent magnet generates its field without an external source of electric power, it is attractive for many constant-field applications. However, permanentmagnet usage is constrained by the amount of work each magnet can produce<sup>1,2</sup> and the cost and availability<sup>3</sup> of the input materials, primarily the rare earth (RE) metals, needed for the strongest known magnets. All permanent-magnet systems function by using the energy stored in the atomic interactions within the magnetic material and the magnetic field that surrounds it. The permanent magnet is trapped in a high-energy state by barriers created in the structure of the magnet itself, and so long as the force exerted against those barriers is not sufficient to overcome them, the magnetic field is maintained without loss.<sup>1,2,4</sup>

The basis for a permanent magnet is a crystal structure with magnetic moments of the active (ferromagnetic) atoms aligned to produce a large ferromagnetic moment with a strongly preferred direction in relation to the crystal lattice. In a large single crystal of such a material, the magnetic moment will align itself in a series of randomly oriented magnetic domains so as to reduce the amount of energy in the external magnetic field created by the net moment of the crystal. To create a permanent magnet with a high external field, a means must be found to prevent the formation of multiple domains within each crystal by

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Current Nd<sub>2</sub>Fe<sub>14</sub>B magnet alloys exhibit excellent roomtemperature magnetic properties and they are well suited for applications with operating temperatures  $\leq 120^{\circ}$ C, due in part to their low Curie temperature of ~310°C. The poor temperature stability of these rare earth (RE) permanent magnet alloys above 120°C limits their current performance in existing motors and their potential application in advanced drive-motor designs. Consequently, it is necessary to find other compositions to improve the thermal stability of RE<sub>2</sub>Fe<sub>14</sub>B magnets. A systematic study was conducted by melt spinning on the magnetic properties of a series of isotropic nanocrystalline magnet alloys where a yttrium (Y)+dysprosium (Dy) mixture replaced neodymium (Nd) or praseodymium (Pr) as the dominant RE constituent in mixed rare earth  $(MRE)_2 Fe_{14}B$  (MRE = Y+Dy+Nd). The most recent results have shown that the Y+Dy-based MRE<sub>2</sub>Fe<sub>14</sub>B alloy can result in isotropic bonded magnets with superior magnetic properties in competitive commercial isotropic bonded magnets above ~30°C and well beyond 200°C by a judicious combination of Y, Dy, and Nd, along with a minor cobalt substitution for iron. Gasatomized powders of these advanced magnet alloys have also demonstrated improved magnetic strength over existing commercial spherical powders in a finepowder-size range that is suitable for injection molding of bonded isotropic magnets.

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suppressing domain-wall formation.<sup>2,4</sup> Since the domain-wall energy is a surface energy, and the magnetic field is associated with the volume of the crystal, reducing the size of the crystal makes it harder to form a domain wall. In practice, if the size of the crystal is reduced to a few microns, domain walls will not form within the crystal. If the crystal has sharp corners, it is possible to nucleate a domain wall at the corners so the crystal should have smooth edges. Unfortunately, a crystal of a few microns in size produces a small magnetic field so it is necessary to utilize a collection of micron-sized crystals (i.e., a material with a fine-grain microstructure). If we want the fields from all the grains to add up to the maximum possible value, the grains must be perfectly aligned producing what is called an anisotropic magnet that can only be magnetized along one preferred direction. If we are willing to settle for half the maximum field, we can produce a random distribution of fine grains, resulting in an isotropic magnet that can be magnetized in any direction.2

Permanent magnetic fields are used to operate many useful devices, including motors, generators, rotating machines, and sensors. In fact, the average use of permanent magnets in domestic applications is well over 50 per household. Automotive applications include over 200 devices per car, with more than 30 DC electric motors used for starting engines, heating and air conditioning blowers, windshield wiper activation, window lifts, fuel pumps, and more.5 Available hybrid-drive automobiles and experimental fuel cell-powered vehicles also are driving the development of compact and powerful DC traction motors that rely on RE permanent magnets (REPM). Also, a surprising amount of REPMs go into each new large wind-turbine generator unit that is installed, for example, 2,000 kg in a recent model.6 In general, the demand for permanent magnets, particularly for those with a high magnetic-energy density, is steadily increasing.

### Advanced Permanent-Magnet Materials

There are two major alloy families of high-performance permanent magnets that derive their magnetocrystalline anisotropy (magnetic strength) from RE atoms in an ordered intermetallic crystal lattice. They are by far the most powerful permanent magnets available.<sup>1,4</sup> The first REPM alloy family to be discovered is based on two intermetallic compounds of samarium (Sm) and cobalt (Co), SmCo<sub>5</sub> and Sm<sub>2</sub>Co<sub>17</sub>. Sm-Co magnets<sup>4,7</sup> supply the highest coercive fields ( $\mu_0H_C = 3.5$  T at ambient temperature) and the highest Curie point (T<sub>c</sub> > 700°C) of any permanent magnets. Also, Sm-Co magnets have an extremely low temperature coefficient of coercivity, due in part to their high T<sub>c</sub>, which makes them well suited for high-temperature applications. However, Sm-Co magnets suffer not only from the high cost of the RE component, Sm, but also from the high cost and price instability of Co. Thus Sm-Co magnets are limited to those applications where a high cost can be justified.

The second major REPM alloy family is based on a single intermetallic compound,  $RE_2Fe_{14}B$ , where nearly all of the rare earth elements can form a stable version of this ordered intermetallic, Figure 1. At room temperature, fully dense magnets based on  $Nd_2Fe_{14}B$  have the highest maximum energy products, with a  $(BH)_{max} > 55$  MGOe in a well oriented (aligned) sintered magnet and are composed of constituents that are less costly than the Sm-Co magnets. Permanent magnets based on  $RE_2Fe_{14}B$  intermetallic compounds, mostly  $Nd_2Fe_{14}B$ , have had a significant technological impact<sup>5</sup> in the nearly 30 years since their discovery<sup>8,9</sup> and extensive research has been performed to develop and improve their magnetic



**Figure 1.** Crystalline unit cell of the general type of RE<sub>2</sub>Fe<sub>14</sub>B magnetic compound<sup>5,10</sup>—schematic

properties. Commercially, two classes, aligned sintered microcrystalline and isotropic bonded nanocrystalline, Nd<sub>2</sub>Fe<sub>14</sub>B magnets have been successfully developed. The aligned sintered microcrystalline magnets are processed by a casting, crushing, aligning/compacting, sintering, and annealing approach that is similar to that used for SmCo<sub>5</sub> magnets.<sup>4,8</sup> Final magnet shapes typically are machined from large hot-pressed blocks. Also, similar Nd<sub>2</sub>Fe<sub>14</sub>B alloys are processed into bonded isotropic magnets by rapid solidification to produce nanocrystalline particulate that is mixed with a polymer binder and molded into netshape magnets before magnetic alignment.<sup>4,2</sup> Because of their isotropic microstructure and the dilution of the magnetic material by the polymer binder, bonded Nd<sub>2</sub>Fe<sub>14</sub>B magnets exhibit a reduced energy product, but can have significant cost advantages for mass-production applications. Both types of current "2-14-1" magnets exhibit excellent room-temperature magnetic properties and are primary candidates for applications with an operating temperature ≤120°C; but their poor temperature stability above this temperature limits their range of use.

### Aligned Sintered Microcrystalline $RE_2Fe_{14}B$ Magnets

The highest known energy product for a REPM is obtained with Nd<sub>2</sub>Fe<sub>14</sub>B, which has a theoretical maximum of 64 MGOe for a fully dense array of perfectly aligned single-domain particles that are non-interacting.1,2 In order to obtain the highest possible energy product in an aligned sintered microcrystalline magnet, a number of conditions must be met. First, a high volume fraction of the 2-14-1 phase must be obtained in an assembly of ultrafine grains (1-3 µm), which should contain single magnetic domains. Second, a high degree of crystalline texture (alignment) must be achieved in the 2-14-1 phase grains. Third, the magnet must be free of soft magnetic secondary phases, such as  $\alpha$ -iron, whose presence will drastically degrade the coercivity of the magnet. From a practical standpoint, there is a conflict between the first and third criteria that creates a processing challenge. From the phase diagram in Figure 2,11 it is clear that the casting of a large ingot of the stoichiometric 2-14-1 composition that solidifies according to the equilibrium peritectic reaction will result in extensive solute segregation (since iron will nucleate within the L+S region on cool-

Volume 44, Issue 6, 2008 International Journal of Powder Metallurgy ing) and will require an unacceptably long heat treatment at high temperature (<1,180°C) to produce a homogeneous ingot. In practice, to avoid iron formation and attendant degradation of coercivity, compositions higher in neodymium than the peritectic reaction limit of 33 a/o Nd typically are chosen and strip casting is used to limit segregation.<sup>1,8</sup> The neodymium-rich composition is also desirable for magnet consolidation after alignment/compaction, since the presence of some liquid phase (T > 655°C) results in a rapid sintering process that fuses the ultrafine grains metallurgically without time for grain growth.

Processing: One of the most significant problems to overcome before RE<sub>2</sub>Fe<sub>14</sub>B magnets with enhanced maximum-energy product could be produced was the oxygen content of the RE alloy components. While there is a modest amount of oxygen solubility in the liquid alloy, there is almost none in the solidified phase and any residual oxygen reacts during solidification with the neodymium in the remaining liquid to form Nd<sub>2</sub>O<sub>3</sub>, which effectively reduces the neodymium content in an uncontrolled manner and wastes this valuable component. As a result of the demands of the magnet industry, the oxygen content of commercial neodymium metal has been reduced by an order of magnitude in the last 20 years.<sup>4</sup> In order to approach the stoichiometric phase composition, the solidification rate of the casting process also has been enhanced either by the use of "thin strip" casting, producing chill cast





strips of 0.2–0.5 mm in thickness,<sup>12,13</sup> or by the use of relatively coarse gas-atomized powders of 0.2–1 mm dia.<sup>14</sup> These reduced casting sizes can promote a sufficiently high cooling rate and even modest undercooling (into the L + Nd<sub>2</sub>Fe<sub>14</sub>B phase field) to allow the starting neodymium content to closely approach the peritectic limit (33 a/o Nd), enhancing the volume fraction of Nd<sub>2</sub>Fe<sub>14</sub>B phase and the resulting energy product in the finished magnets.

After preparation of the chill-cast ingot, the processing route for RE<sub>2</sub>Fe<sub>14</sub>B microcrystalline aligned magnets is based on the approach developed previously for SmCo5 magnets, namely, liquid-phase sintering, with reference to the ternary Nd-Fe-B phase diagram in Figure 2. Typically, the following procedure is used<sup>8</sup> to fabricate sintered magnets of the prototypical Nd<sub>2</sub>Fe<sub>14</sub>B compound: (i) chill-cast alloy forms are subject to hydrogen absorption and incomplete desorption to promote initial fracture and particulate decrepitation; (ii) the particles are milled to an average particle size ~3-6 mm in an inert atmosphere, producing single-grain particles; (iii) the tap-densified singlegrain particles are oriented magnetically in a 10-30 kOe field and compacted (under the applied field) by uniaxial die pressing in a direction perpendicular to the alignment direction at a pressure of 200 MPa, producing a highly textured powder compact; (iv) the compact is liquid-phase sintered between 1,090°C and ~1,155°C, under an inert argon atmosphere for ~1 h or less, followed by rapid cooling; (v) a solid-state anneal may be performed for several hours at a temperature approaching but <655°C, the eutectic melting temperature of the neodymium-rich phase to relieve cooling stresses and to help suppress reverse domain nucleation.

With reference to Figure 2 as an approximate guide (recognizing that most common compositions are slightly lower in boron than this pseudobinary section), a final sintered magnet microstructure contains the Nd<sub>2</sub>Fe<sub>14</sub>B phase, termed "1," along with the Nd<sub>1.1</sub>Fe<sub>4</sub>B<sub>4</sub> phase, termed "4," and the neodymium-rich solid-solution phase, termed Nd. The ideal 2-14-1 magnet of the sintered aligned microcrystalline type would consist of small, uniform single-crystal grains of Nd<sub>2</sub>Fe<sub>14</sub>B, all with their easy axis of magnetization perfectly aligned in the direction of the applied field, providing the maximum possible remanence.1.2.4 By minimizing the initial size of

the as-milled particles (preferably down to 1-3 µm), the chance of survival of multi-grain 2-14-1 particles is reduced significantly, eliminating internal grain boundaries as one type of active site for reverse domain nucleation to help increase coercivity. As the phase diagram in Figure 2 confirms, liquid-phase sintering at >1,090°C (the  $Nd_2Fe_{14}B$  peritectic temperature) and subsequent continuous cooling are preferred to minimize the as-solidified content of Nd<sub>11</sub>Fe<sub>4</sub>B<sub>4</sub> phase, which can reduce the final content of 2-14-1, the sole permanent magnet phase. The neodymium-rich solid solution, which solidifies as the grain boundary-wetting phase from the liquidphase-sintering process, serves to "smooth" the grain boundaries, eliminating more high-activity grain-boundary sites (re-entrants and sharp corners) for reverse domain nucleation. Another effect of the complete wetting of all of the 2-14-1 grain boundaries is to isolate each grain with a non-magnetic phase, predominantly a neodymium-rich solid solution, preventing the spreading of any reverse domains that manage to nucleate. These combined extrinsic characteristics produce an enhanced coercivity in the smooth rounded grains of 2-14-1 with inherently high intrinsic magnetocrystalline anisotropy.

The pursuit of these ideal characteristics gives rise to the choices of conventional alloying additions to sintered 2-14-1 magnets to aid in the liquid-phase-sintering process. Minor additions of aluminum, copper, and gallium<sup>15,16</sup> are made to  $Nd_{2}Fe_{14}B$  to improve wetting of the grains, thereby promoting a complete distribution of the liquid during liquid-phase sintering. Both niobium and vanadium<sup>17</sup> are added to promote the formation of small, isolated boride particles on the grain boundaries that stabilize the small grain size during liquid-phase sintering. Also, dysprosium is substituted for neodymium (or praseodymium) to enrich the near-grain-boundary regions to further reduce reverse domain nucleation.18 As a substitute for iron, cobalt is added to raise the Curie temperature (for increased operating temperature) of the resulting 2-14-1 magnetic phase and to form isolated Nd<sub>3</sub>Co particles<sup>19</sup> on the grain boundaries, again to stabilize a small grain size. Because of these alloying efforts and the development of an optimized processing sequence, aligned sintered microcrystalline 2-14-1 magnets based on neodymium have set an extremely high standard for room-temperature magnetic strength

and are unsurpassed for applications with an operating temperature  $\leq 120^{\circ}$ C.

### Development of High-Temperature 2-14-1 Permanent Magnets

Our recent efforts to increase the high-temperature tolerance of RE<sub>2</sub>Fe<sub>14</sub>B magnet alloys toward 200°C are based on substitution for the neodymium with a majority of yttrium and dysprosium, to produce a mixed rare earth (MRE) content of about  $(Nd_{0.45}, Y_{0.37}, Dy_{0.18})_2 Fe_{14}B$  as one prototype composition that is shifted toward "heavy" RE dominance. The preference for heavy RE elements in the 2-14-1 phase to promote high-temperature permanent-magnetic performance is discussed subsequently. This unique alloying strategy<sup>20</sup> makes the assumption that any mixture of RE elements will be tolerated as a solid solution in the 2-14-1 phase, which appears to be supported since all RE elements will form the same 2-14-1 phase.<sup>21</sup> However, a major effect of this shift in 2-14-1 magnet alloy composition to  $MRE_{2}Fe_{14}B$  with neodymium in a minority (by atomic fraction) is a shift in the equilibrium ternary phase diagram from the common type in Figure 2 for Nd-Fe-B to the alternate type, shown for example in Figure 3 for Dy-Fe-B.18

A key difference for the heavy RE metal phase diagrams in the composition region of the 2-14-1 phase (Figure 3) is that the  $RE_2Fe_{17}$  intermetallic compound ("2-17") is the primary phase of highest



**Figure 3.** Vertical section through the ternary Dy-Fe-B phase diagram<sup>18</sup> that starts at pure iron and extends through the  $Dy_2Fe_{14}B$  compound, labeled "1" line compound

stability immediately above the stoichiometric 2-14-1 compound, instead of iron (Figure 2). Thus, in contrast to the unavoidable formation of iron primary phase (due to rapid nucleation kinetics) at the 2-14-1 composition in the "light" RE (neodymium-rich) phase diagram (Figure 2), a solidification reaction at the 2-14-1 composition in Dy-Fe-B offers the likelihood that a chill-cast ingot can sustain some undercooling18 and will contain only a minor content of primary 2-17 phase, a complex intermetallic with reduced nucleation kinetics, and a majority of 2-14-1 phase. Analysis of the Dy-Fe-B phase diagram (recognizing that most common compositions are slightly lower in boron than this pseudo-binary section) also indicates that it is advantageous to select an alloy composition that is slightly rich in dysprosium to avoid iron formation, which would increase the volume fraction of 2-14-1 phase above that possible in Nd-Fe-B alloys.

In terms of sintered aligned microcrystalline magnets, the Dy-Fe-Be phase diagram<sup>18</sup> (Figure 3) also shows that it is apparently impossible to completely dissolve any 2-17 (soft magnetic phase) that forms on solidification by high-temperature liquid-phase sintering (similar to step (iii) for Nd-Fe-B) between 1,190°C and ~1,250°C, since the 2-17 phase is within a three-phase equilibrium phase field with L and 2-14-1 phases. However, annealing within a lower-temperature three-phase field that contains DyFe<sub>3</sub>, for example, may allow liquid-phase sintering with a dysprosium-enriched liquid and 2-17 dissolution, but would dilute unavoidably the 2-14-1 magnetic microstructure with some non-magnetic DyFe<sub>2</sub> for slightly dysprosium-rich alloys. Thus, there is no access to a two-phase field with only 2-14-1 and alloy liquid to accomplish the same intrinsic liquid-phase-sintering step8 as in the neodymiumbase REPM alloys for sintered magnets. In spite of the mixed benefits and challenges of the alternative phase equilibria, the potential to pursue hightemperature performance benefits in a MRE<sub>2</sub>Fe<sub>14</sub>B magnet alloy design with a dominant heavy RE content, provides sufficient motivation for ongoing R&D on aligned sintered microcrystalline 2-14-1 magnets.

In order to develop the formulation for improved high-temperature magnetic properties of  $MRE_2Fe_{14}B$  compounds, the individual intrinsic 2-14-1 properties of all of the RE types were analyzed and studied. Table I lists the annotated

TABLE I. SATURATION MAGNETIZATIONS (M <sub>s</sub> ), ANISOTROPY	
FIELD ENERGY (H <sub>A</sub> ), QUANTUM ORBITAL ANGULAR	
MOMENTUM NUMBERS (L), AND CURIE TEMPERATURES (Tc	)
FOR THREE 2-14-1 COMPOUNDS5,19, 22-24	

Compound	4πM <sub>s</sub>	H	L	Тс
	(kG)	(kÕe)		(K)
Nd <sub>2</sub> Fe <sub>14</sub> B	16.0	73	6	585
Dy <sub>2</sub> Fe <sub>14</sub> B	7.1	~150	5	598
Y <sub>2</sub> Ēe <sub>14</sub> B	14.1	26	0	565

properties of the three most promising  $RE_2Fe_{14}B$ compounds.5,19,22-24 Of the three compounds, Nd<sub>2</sub>Fe<sub>14</sub>B has the highest saturation magnetization  $M_s$ , while  $Dy_2Fe_{14}B$  has the largest anisotropy field  $H_a$ . For a solid solution of  $RE_2Fe_{14}B$ , both the magnitude and temperature dependence of the saturation magnetization  $(M_s)$ , and anisotropy energy (H<sub>a</sub>), are expected to follow a rule of mixtures relation in  $MRE_2Fe_{14}B$ . Thus, it appeared promising to combine all three of these RE elements with their outstanding individual magnetic attributes into a single MRE version of a 2-14-1 magnet alloy. While it has been a standard practice to add minor amounts of dysprosium to neodymium in the Nd-Fe-B magnet alloys, as cited above,<sup>18</sup> this attempt to make neodymium the minority RE element in favor of a mixture of yttrium and dysprosium had not been done before.

Figure 4 shows the temperature dependence of anisotropy field energy,  $H_a(T)$ , and magnetic moment,  $M_s(T)$ , of these three  $RE_2Fe_{14}B$  compounds. The anisotropy energy as a function of temperature,  $H_a(T)$ , of  $RE_2Fe_{14}B$  for neodymium and dysprosium<sup>24,25</sup> arises from the large RE

moment with an orbital angular moment (L  $\neq$  0), which results in large crystal field splittings, Figure 4(a). However, H<sub>a</sub> for neodymium and dysprosium has a strong temperature dependence and declines monotonically with increasing temperature. In contrast, a smaller H<sub>a</sub> at room temperature for Y<sub>2</sub>Fe<sub>14</sub>B from the iron lattice exhibits a weak temperature dependence, which initially rises above room temperature before decreasing as the Curie temperature T<sub>c</sub> is approached. Thus, the inclusion of yttrium in solid solution with neodymium and dysprosium in the MRE<sub>2</sub>Fe<sub>14</sub>B phase may decrease Ha, but should improve the temperature dependence of H<sub>a</sub>.

The behavior of  $M_s(T)$  for  $Dy_2Fe_{14}B$  (Figure 4(b)) is similar to that of  $H_a(T)$  for  $Y_2Fe_{14}B.^{22,23}$  This is the result of the anti-ferromagnetic dysprosium-iron coupling that has a widely noted effect on the low M<sub>s</sub> of Dy<sub>2</sub>Fe<sub>14</sub>B at room temperature. However, as the temperature is increased the anti-ferromagnetic interaction decreases, resulting in an increased M<sub>s</sub> for Dy<sub>2</sub>Fe<sub>14</sub>B as the temperature is raised above room temperature. The Ms for Dy2Fe14B decreases again as T approaches  $T_c$ . Thus, a MRE alloy like  $(Y_{1.0}Dy_{1.0})_2Fe_{14}B$  could combine the intrinsic property advantages of  $Y_2Fe_{14}B$  and  $Dy_2Fe_{14}B$ , which may result in compensation for the usual loss of M<sub>s</sub> and H<sub>ci</sub> due to heating for a 2-14-1 magnet alloy dominated by  $Nd_2Fe_{14}B$ . In other words, it is presumed possible to obtain simultaneously a smaller (negative) temperature coefficient for Br and Hci.20

### Nanocrystalline RE<sub>2</sub>Fe<sub>14</sub>B Magnets

In contrast to the limited design space (primari-



**Figure 4.** Temperature dependence of (a) anisotropy field energy  $H_a(T)$  and (b) magnetic moment  $M_s(T)$  of three  $R_2Fe_{14}B$  compounds (After R. Grössinger,<sup>19</sup> S. Hirosawa,<sup>22</sup> E.B. Boltich<sup>23</sup> and D. Givord<sup>24</sup>)



**Figure 5.** Isothermal section at 1,000°C of the general RE-Fe-B phase diagram of the type shown in Figure 2 for Nd-Fe-B, which is accompanied by schematic microstructures for the demagnetized state of the three types of nanocrystalline permanent magnets that can be developed within the three composition ranges indicated<sup>11</sup>

ly optimization of one type of microstructure/ property relationship) of microcrystalline RE permanent magnets that are well equilibrated, the ability to produce amorphous phases and nanocrystalline grains in RE<sub>2</sub>Fe<sub>14</sub>B type magnets by rapid-solidification processing offers several choices. The opportunity is presented by rapid solidification of nanocrystalline magnets to tailor the microstructure and magnetic properties by selection of the base ternary alloy, relative to the stoichiometric 2-14-1 composition, and by minor or major alloying additions, working with highly non-equilibrium processing. The three basic types of nanocrystalline permanent magnets possible in the light RE versions (typically neodymium-rich) of this 2-14-1 alloy system are shown schematically on the right hand side of Figure 5,11 includ-**RE-rich** (decoupled ing nanograins), stoichiometric (single-phase exchange-coupled nanograins), and iron-rich (dual-phase exchangecoupled nanograins). The processing of nanocrystalline RE<sub>2</sub>Fe<sub>14</sub>B magnets based on light RE alloys is considered subsequently, focusing primarily on stoichiometric alloys, in terms of typical microstructures, processing approaches, and magnetic characteristics. Recent experimental developments in high-temperature MRE<sub>2</sub>Fe<sub>14</sub>B magnet alloys dominated by heavy RE metals will follow with a review of minor alloying effects and gas-atomized-powder processing efforts.

### Stoichiometric (Single-Phase, Exchange-Coupled) Nanocrystalline Magnets

Exchange-coupled nanocrystalline magnets were first reported for melt-spun ribbon of stoichiometric Nd<sub>2</sub>Fe<sub>14</sub>B. As the composition of the alloy approaches stoichiometry, it is possible to produce a uniform fine grain (~200 nm) structure with clean grain boundaries, Figure 5. In this case the same interaction that causes the atomic moments to align within a grain will cause magnetization within each grain to rotate away from the easy axis of the grain and to align with neighboring grains. Increases in Mr of the order of 20% have been observed due to this effect and most current melt-spun magnet materials exhibit some degree of remanence enhancement due to interaction between grains. The key to producing exchange-enhanced materials is in the control of the microstructure.<sup>4,11</sup> If the coupling between grains (dictated by the grain-boundary area) approaches the magnetocrystalline anisotropy energy of the grains (determined by the volume of the grains), the effect is to average the anisotropy over the coupled grains. For randomly oriented grains this average rapidly approaches zero. In contrast, the exchange coupling affects only those atomic moments within half of a domain-wall width of the grain boundary. As the grain size increases, the volume of the sample within this distance of a grain boundary decreases rapidly so the effect disappears. Thus it is important to create grains in Nd<sub>2</sub>Fe<sub>14</sub>B that are ~200 nm across (approximately equiaxed) with a narrow distribution in size. (Note: this critical nanocrystalline grain size can change in different 2-14-1 alloys.) As might be expected, in an interacting system, the interaction enhances the properties of the magnet until the first part of the sample starts to reverse. At this point the interaction causes an avalanche effect resulting in a rapid reversal of the remaining parts of the sample. As a result, the coercivity is determined by the weakest part of the sample rather than the average.

Given the stringent nanostructured requirements for stoichiometric exchange-enhanced magnets, a large number of additives have been investigated as grain refining agents. These include refractory metals, their carbides and nitrides, as well as other metallic elements.<sup>26</sup>

### Processing

Processing of the nanocrystalline 2-14-1 mag-

nets of all three basic microstructure types of both light and heavy RE magnet alloy families generally commences with melt spinning to generate the rapidly solidified microstructures. In this process a prealloyed casting is melted inductively under an inert atmosphere in a sealed quartz or alumina tube with a small (1-2 mm dia.) precision-machined orifice. Generally, the surface tension of the melt is sufficiently high to prevent dripping during the rapid melting and superheating cycle. On a laboratory scale, the melt-spinning crucible is located within a larger chamber that is maintained with an inert atmosphere at the same pressure as the crucible during melting. When the molten alloy reaches the designated temperature, an overpressure of the inert gas is introduced into the sealed crucible, forcing the molten alloy out of the orifice and onto the polished outer surface of a rotating metal wheel (surface velocity = 10 to 30m/s), typically copper. The molten alloy is quenched on the contact surface of the wheel, cooling by conduction, and is transported along the surface, before being flung off the wheel. In free flight it finishes cooling by convection in the stagnant chamber atmosphere on both the wheel and free sides of the resulting ribbon, typically 25–50 µm thick and a few mm wide. Since the liquid film is subject to radial heat extraction from the quenching wheel surface, a preferred solidification-morphology alignment can be established that mirrors this unidirectional heat flow over a significant portion of the ribbon thickness, depending on the wheel surface residence time of the solidifying alloy and whether or not crystallization is permitted to occur.4

The solidification process for melt spun ribbons of Nd-Fe-B (and other light RE elements) can be forced by increased wheel speed to be sufficiently rapid to suppress crystallization of the primary iron phase for iron contents >77 a/o (the peritectic limit in Figure 2), and even for stoichiometric 2-14-1 phase compositions, if special alloying is employed, for example, with titanium and carbon.<sup>26</sup> In fact, the most effective commercial method for the production of nanocrystalline 2-14-1 magnets of either RE-rich or stoichiometric compositions is to produce ribbons with a significant amorphous fraction and to promote additional nanocrystalline 2-14-1 grains to crystallize during a subsequent anneal at 700°C-750°C. This method has been found to remove the effects of any variabilities in the melt spinning process, such as trapped porosity on the wheel/ribbon interface, and the magnetic properties that may arise if the nanocrystalline structure is accessed directly from the rapid solidification process.5 In addition, there is a beneficial effect of reduced oxidation and corrosion from an increase in the iron content and a reduction of the RE content in rapidly solidified alloys, especially if a stoichiometric, single-phase alloy can be used. It should be noted that this same "overquenching" melt-spinning approach and ribbon-annealing process at 700°C-750°C is also effective for the RE-Fe-B magnet alloys based on heavy RE elements.20 However, the RE<sub>2</sub>Fe<sub>17</sub> phase (instead of iron) is the soft magnetic phase that is bypassed to form a glassy alloy,18 as represented in the phase diagram of Figure 3. Actually, if the heavy RE-dominated 2-14-1 magnet alloys are doped with titanium and carbon, ribbon annealing temperatures of 800°C can be used without degrading the near-ideal nanocrystalline grain size, as seen in Figure 6.

For light RE versions of 2-14-1 magnet alloys, melt spinning and annealing to promote full crystallization are followed by ribbon chopping or crushing in an inert-atmosphere vessel to produce a flake product that is commercially termed Magnequench "MQP" and is used in bonded isotropic magnets.<sup>27</sup> In fact, isotropic nanocrystalline polymer-bonded magnets (Figure 7) can be made from both light RE and heavy RE particulate of 2-14-1 magnet alloys that have been rapidly solidified and annealed. The use of bonded magnets is growing rapidly as mass production of net-shape isotropic 2-14-1 magnets has become commercially attractive for many consumer and industrial applications.

Close-coupled gas atomization is an alternative



**Figure 6.** Melt-spun ribbon of { $[Nd_{0.45} (Y_2Dy)_{0.55}]$ Fe<sub>12.5</sub>Co<sub>1.5</sub>B}+Ti<sub>0.02</sub>+  $C_{0.02}$  after an 800°C anneal for 15 min, in which the initial ribbon was primarily amorphous

rapid-solidification process to melt spinning that also has been utilized in the experimental production of isotropic nanocrystalline RE-Fe-B magnet alloy particulate,28 targeted for bonded magnet fabrication. Observations of the solidification product phases and segregation patterns in 2-14-1 magnet alloys indicate that the average solidification rate of gas-atomized powders can reach that of melt-spun ribbons (for a moderate wheel speed of 15m/s), if the particle size is reduced below ~15-20 µm.29 It should be noted that atomization with helium gas has a tenfold advantage in convective cooling rate over argon-gas atomization and this pushes the equivalent microstructure of powders to larger sizes (~20-30 µm), compared with ribbons melt spun at 15 m/s. The principal differences between melt spinning and gas atomization are related to the type and directionality of heat transfer and the tendency for melt undercooling. As noted previously, unidirectional conductive cooling dominates initially in melt spinning, followed by mild convective cooling. In contrast, non-directional forced convective gas cooling operates continuously in gas atomization and the outer rim of the spherical droplets is quenched first; it serves to inhibit heat extraction from the particle interior which can solidify at a reduced rate. This difference can be manifested in differences in the continuity and directionality of the resulting solidification microstructure (Figure 8) in spherical gas-atomized particles, which can mirror the isotropic heat flow pattern, especially if cellular or dendritic solidification occurs.30 At gas-atomized droplet sizes smaller than ~5 µm the RE-Fe-B magnet alloys tend to solidify as an amorphous phase due to high undercooling. Alternatively, melt spinning has a minimal ten-



**Figure 7.** Schematic cross section transverse to the pressing direction<sup>27</sup> of a polymer-bonded or compression-molded permanent magnet made from melt-spun ribbon flake particulate

dency for undercooling, and crystallization or glass formation usually occur immediately upon contact of the melt with the metallic wheel surface. However, at high wheel speeds (>25 m/s) the wheel surface results in a highly effective quench that can extend an amorphous phase; for example, throughout the thickness of a 30  $\mu$ m ribbon of a magnet alloy.

Interestingly, gas-atomized droplets ≤5 µm can also experience extreme undercooling, on the order of 0.22T<sub>m</sub> or greater,<sup>31,32</sup> resulting in rapid adiabatic solidification that can produce amorphous particles. Unfortunately, the dimensions of the gas atomized particles that exhibit this extremely rapid solidification effect are typically about five times smaller than the melt-spun ribbon thickness for common magnet alloys<sup>28</sup> and this ultrafine powder has a much higher surface area that is susceptible to oxidation. In spite of the reduced rate of solidification in gas-atomized powder of increased size, the spherical shape of the powder can have important advantages in the molding of bonded magnets. Thus, a second generation of magnet alloy designs have been developed to improve the "quenchability," or glass-forming tendency of Nd-Fe-B magnet alloys permitting gas atomization,33,34 and other atomization processes<sup>35</sup> to produce spherical amorphous powders that can be annealed to achieve improved magnetic properties. These spherical magnet powders are also directly suited to bonded magnet compounding, without any chopping or milling.

### Bonded Nanocrystalline RE<sub>2</sub>Fe<sub>14</sub>B Magnets

Isotropic nanocrystalline RE-Fe-B polymerbonded permanent magnets are a fast growing



**Figure 8.** Gas-atomized spherical powder particle of  $(Y_{1,0}Dy_{1,0})_2Fe_{14}B$  from a 10–20  $\mu$ m-size fraction in the as-atomized condition<sup>30</sup>

market segment, especially in mass-production applications. At this time, the chopped and/or milled form of 2-14-1 melt-spun ribbons (after annealing) is almost universally employed as the magnetic "filler" in a polymer matrix. These nanocrystalline, single-phase, exchange-coupled magnet materials are typically of stoichiometric 2-14-1 composition and use rapid-solidification processing to generate their isotropically oriented nanograin structure, as described previously, and illustrated in Figure 7. The high (BH)max values (compared with ferrites) and relatively low RE content of these isotropic RE-Fe-B materials makes them ideally suited for loading into bonded magnets, since this magnet form will intrinsically have diluted magnetic strength and is sensitive to the raw-material cost. Bonded magnets are processed by blending or "compounding" the fragmented magnetic material with a polymer (e.g., nylon powder or an epoxy resin solution), followed by injection molding or compression molding, respectively, into a finished magnet shape. Unlike conventional metal injection molding (MIM) of high-performance powder metallurgy (PM) parts,<sup>34</sup> the polymer binder is retained in the part and serves as a barrier to corrosion or oxidation of the resulting bonded magnets. To some extent, the polymer binder softening temperature serves as an upper limit to the application temperature of bonded magnets, especially for nylon. Efforts to extend the upper temperature limit and high-temperature strength of bonded magnets has led to development efforts with polyphenyl sulfide (PPS) polymers. However, high compounding temperatures (~300°C) and a narrow "working" viscosity temperature range (~5°C-10°C) have been a barrier to progress. Initial efforts to improve the MRE-Fe-B compositions for high-temperature use were described in the section on sintered magnets and will be described more specifically below for nanocrystalline 2-14-1 magnets. The difficulty of high-temperature compounding is related to powder-particle oxidation and corrosion in the blending atmosphere and polymer medium, especially with corrosive additives. Recent efforts to provide oxidation-resistant surface coatings on RE-Fe-B powders may help address particulate surface degradation (oxidation) during powder handling, PPS compounding,30,37 and long-term use.

In general, net-shaped bonded magnets avoid expensive sawing or grinding operations and the associated waste "swarf" material. Also, compared with sintered aligned microcrystalline RE-Fe-B magnets, the bonded isotropic magnets are less brittle (reduced breakage losses during handling), have low electrical conductivity, and are often molded into a singular magnet assembly that can be magnetized into a multipole configuration, all advantageous for electric motor applications. The major disadvantage to bonded magnets is the reduction in their magnetic properties, compared with the properties of fully dense (e.g., hotpressed) isotropic nanocrystalline RE-Fe-B magnets, their direct, undiluted counterpart.27 For purposes of comparison of laboratory measurements, an unchopped melt-spun ribbon sample of the same nanocrystalline structure may also serve as a standard, if it has the same isotropic crystallinity. The reduction of magnetic strength can be estimated with the so-called filling factor (f), which reflects the volume fraction of the magnetic powder in the bonded magnet according to the relation:

$$[(BH)_{max}]_{bonded} = (f)^2 [(BH)_{max}]_{isotropic}$$
(1)

To illustrate the importance of maximizing the filling factor, a simple analysis based on equation (1) shows that bonded magnets with loadings that range from 50 v/o to 71 v/o can have a  $(BH)_{max}$ that ranges from 25% to 50% of the fully dense value, respectively. In terms of magnetic hysteresis loops, the consequences of bonded magnet dilution are illustrated in Figure 9, which shows the results for isotropic nanocrystalline  $Pr_2Fe_{14}B$ in polymer bonded and isotropic melt-spun rib-



Figure 9. Hysteresis loops of a polymer-bonded Pr<sub>2</sub>Fe<sub>14</sub>B magnet<sup>1</sup>

bon forms.1 The use of anisotropic magnet powder can be effective for boosting the strength of bonded magnets beyond that predicted by the dilution effect, if the increased processing cost is balanced by the magnetic property benefits. For example, in one approach to accomplish this, hot-pressed and forged magnets made from ribbon flake were milled into anisotropic powder and molded under a magnetic field to produce anisotropic nanocrystalline bonded magnets with an increased energy product,38 but the high processing cost made the resulting magnets non-competitive in the marketplace. An alternative processing approach to anisotropic bonded magnets involving hydrogen decrepitation has been more successful commercially, but has a restricted elevated-temperature range.39

To maximize the filling factor and magnetic strength for a given type of isotropic nanocrystalline bonded magnet, the objective is to make the powder as small and round as possible, much



Figure 10. Effect of particle shape on viscosity vs. solids loading for glass particles<sup>36</sup>

like the maximum ideal powder filling in a compound for powder injection molding (PIM).36 This optimum powder filling will minimize the volume fraction of polymer, while still maintaining adequate flow characteristics for molding the compound and sufficient particle bonding for good mechanical properties. From the fundamentals of filled-polymer processing, it is well known that a nonspherical particle shape is detrimental to the viscosity of a powder-binder mixture because of the lower inherent packing density and higher interparticle friction. As illustrated in Figure 10, the infinite viscosity limit is reached at far lower solids loadings for nonspherical particles,36 where chopped magnet alloy flakes could be approximated as a disk shape to relate to this illustration, Figure 11(a). Industrially, injection molded bonded magnets from flake particulate that has been lightly milled, similar to Figure 11(a), can be produced with a volumetric loading limit ~60%. Additional milling of the flake particulate can raise this loading limit to ~70%, in some commercial bonded magnets. Alternatively, spherical gasatomized powders (Figure 11(b)) have been investigated as a promising source of nanocrystalline magnet particulate, especially well suited for bonded magnets.28,30,37 In theory, an ideal dense random packing arrangement of monosized spheres can reach a limit ~63.7% filling, or slightly lower for the optimal molding limit. As a consequence of highly tailored size distributions that provide effective interparticle void filling, spherical-powder packing densities up to 93% can be reached, implying over 90% loading for molding purposes;36 for example, 4-5 size modes and 7:1 dia. ratios. With far more processing simplicity, a



Figure 11. Representative micrographs of (a) flake and (b) gas-atomized powder. SEM

collection of spheres with a broad particle-size distribution, resembling a close-coupled gasatomized powder yield, can reach loadings in excess of 80%.<sup>36</sup> In comparison with flake particulate, high-pressure gas (helium or argon)-atomized powders of similar magnet alloys have a near-ideal spherical shape (Figure 11(b)) and a fine-particle-size distribution with a 65% yield <20  $\mu$ m dia.<sup>29,30</sup> The increased loadings via the use of a spherical-powder-size distribution will enhance the effective (BH)<sub>max</sub> of the resulting isotropic bonded magnets as a consequence of equation (1), if suitable control can be exercised over the nanocrystalline magnetic structure.

### Alternative Isotropic Nanocrystalline MRE<sub>2</sub>Fe<sub>14</sub>B Magnets

The goal of the current research is to develop alloys with low-temperature coefficients that may be prepared by gas atomization, particularly for bonded magnet molding. As explained previously, the spherical powder produced by gas atomization is a much more desirable form for MIM than the flake produced by melt spinning. This advantage is tempered by the reduced convective cooling rates and isotropic heat extraction associated with rapid solidification of gas-atomized droplets. Recently, we have conducted a systematic study on the magnetic properties of a series of alloys in which an yttrium/dysprosium mixture replaced neodymium or praseodymium as the primary RE constituent in  $MRE_2Fe_{14}B$  (MRE = Y+Dy+Nd). Ribbons and powder were fabricated by melt spinning and gas-atomization techniques.20,30,40 Our results show that the YDy-based MRE<sub>2</sub>Fe<sub>14</sub>B alloy can be processed into isotropic nanocrystalline bonded magnets from melt-spun particulate with superior magnetic properties above 115°C by a judicious mixture of yttrium, dysprosium, and neodymium. In addition, a combination of zirconium substitution and ZrC addition has been found to result in adequate microstructural control in both the gas-atomization and melt-spinning techniques, and a new MRE<sub>2</sub>(Fe, Co)<sub>14</sub>B alloy with these modifications was developed.

### Effect of Neodymium Substitution

It is known that  $Nd_2Fe_{14}B$  has the maximum Ms of the three  $RE_2Fe_{14}B$  compounds, Table I. If yttrium and dysprosium in the  $(Y_{1-z}Dy_z)_{2.2}Fe_{14}B$  ribbons are substituted for by the correct amount of neodymium, a substantial improvement in

 $(BH)_{max}$  may be obtained without severely degrading high-temperature behavior. (BH)max as a function of temperature up to 300°C is shown in Figure 12.<sup>20</sup> It is seen that the samples with higher neodymium content exhibit a higher room temperature (BH)<sub>max</sub>, but their (BH)<sub>max</sub> also exhibits a strong temperature dependence.

Figure 13 shows  $\alpha$  and  $\beta$  for annealed  $[Nd_x(YDy)_{0.5(1-x)}]_{2.2}Fe_{14}B$  ribbons from 27°C to 127°C, as a function of neodymium content. The value for  $\alpha$  increases monotonically from -0.045% to -0.106%/°C with increasing x from 0 to 0.8, while  $\beta$  has an essentially constant value of -0.3%/°C when x is below 0.4.20 When x is increased from 0.4 to 0.8,  $\beta$  increases up to -0.38%/°C. These thermal magnetic properties over a wide range of neodymium-based ribbons.

### Effect of Cobalt Substitution

The results cited show that high-performance magnets with superior temperature stability can



Figure 12. (BH)<sub>max</sub> as a function of temperature for annealed [Nd<sub>x</sub>(YDy)<sub>0.5(1-x</sub>]<sub>2.2</sub>Fe<sub>14</sub>B ribbons with different neodymium contents<sup>4</sup>





be developed by adjusting the ratio of yttrium to dysprosium and adding the correct amount of neodymium. If higher-temperature performance is required, thermal stability may be further improved by partial substitution of cobalt for iron in the YDy-based R<sub>2</sub>Fe<sub>14</sub>B alloys. Table II lists the magnetic properties of annealed [Nd<sub>0.5</sub>(YDy)<sub>0.25</sub>]<sub>2.2</sub> Fe<sub>14-v</sub>Co<sub>v</sub>B ribbons with different cobalt-substitution levels. The temperature coefficients in the table are in the temperature range of 27°C to 127°C. With increasing cobalt content, the Curie temperature T<sub>c</sub> increases rapidly, resulting in a corresponding decrease in  $\alpha$ . The (BH)<sub>max</sub> first increases and then decreases slightly. These trends in the change in magnetic properties as a function of cobalt content are consistent with those in Nd<sub>2</sub>Fe<sub>14-y</sub>Co<sub>y</sub>B pseudo-ternary compounds.<sup>19,41</sup> In Nd<sub>2</sub>Fe<sub>14-v</sub>Co<sub>v</sub>B pseudo-ternary compounds, the maximum M<sub>s</sub> is achieved when y is about 1.5. Although the  $H_a$  of  $Nd_2Fe_{14-v}Co_vB$ compound decreases with cobalt substitution, it is noted from Table II that H<sub>ci</sub> declines slightly with increasing cobalt content.40 It indicates that the detrimental effect of cobalt substitution on H<sub>a</sub> in YDy-based compounds is less than in the neodymium-based compound. Increasing the cobalt content also leads to an increase in  $\beta$ .

For comparison, Figure 14 shows  $(BH)_{max}$  as a function of temperature for  $[Nd_x(YDy)_{0.5(1-x)}]_{2.2}Fe_{14-y}Co_yB$  ribbons with different compositions. The highest room-temperature  $(BH)_{max}$  is obtained in sample A with x = 0.8 and y = 0, but  $(BH)_{max}$  exhibits a stronger temperature dependence. When x = 0.4, y = 0, the temperature dependence of  $(BH)_{max}$  of sample B is improved although, the room-temperature  $(BH)_{max}$  is decreased. If cobalt at y = 1.5 is substituted for iron with x = 0.5 (sample C), both room-temperature are improved.<sup>40</sup> Thus, at or above 150°C,  $(BH)_{max}$  of

FE <sub>14-Y</sub>	TABLE II. MAGNETIC PROPERTIES OF ANNEALED [Nd <sub>0.5</sub> (YDy) <sub>0.25</sub> J <sub>2.2</sub> FE <sub>14-Y</sub> Co <sub>Y</sub> B RIBBON: EFFECT OF COBALT SUBSTITUTION <sup>4</sup>					
у	B <sub>r</sub> (kG)	H <sub>cj</sub> (kOe)	(BH) <sub>max</sub> (MGOe)	-α (%/°C)	-β (%/°C)	T <sub>c</sub> (°Č)
0	6.0	22.6	7.9	0.09	0.37	309
1.0	6.1	21.6	7.9	0.08	0.39	374
1.2	6.2	21.3	8.4	0.08	0.38	387
1.5	6.6	19.8	10.0	0.07	0.39	405
2.5	6.6	17.2	9.6	0.05	0.40	455
3.0	6.6	16.3	9.6	0.03	0.43	487



Figure 14. (BH)<sub>max</sub> as a function of temperature for annealed [Nd<sub>x</sub>(YDy)<sub>0.5(1-x</sub>]<sub>2.2</sub>Fe<sub>14-y</sub>Co<sub>y</sub>B ribbon with different neodymium and cobalt contents<sup>4</sup>

sample C is greater than that of sample A in the YDy-based  $[Nd_x(YDy)_{0.5(1-x)}]2.2Fe_{14-v}Co_vB$  ribbons.

### Effect of Zirconium Substitution

Gas atomization is capable of producing spherical rapidly solidified magnet powders. However, the solidification rate using this process is significantly lower than that characteristic of melt spinning. In order to develop magnet alloys for gas atomization, the effect of zirconium substitution on microstructure and magnetic properties in  $[Nd_{0.5}(YDy)_{0.25}]_{2.2-x}Zr_xCo_{1.5}Fe_{12.5}B$  (x = 0-0.7) ribbons melt spun at a low wheel speed (10 m/s) has been systematically studied. The results show that zirconium substitution for RE can significantly refine the grain size in as-spun  $[Nd_{0.5}(YDy)_{0.25}]_{2.2-x}Zr_xCo_{1.5}Fe_{12.5}B$  ribbon. Figure 15 shows the effect of zirconium substitution on H<sub>c</sub>



**Figure 15.** Effect of zirconium substitution on  $H_c$  and (BH)<sub>max</sub> for asspun  $[Nd_{0.5}(YDy)_{0.25}]_{2.2x}Zr_xCo_{1.5}Fe_{12.5}B$  ribbon<sup>4</sup>

and  $(BH)_{max}$  for as-spun  $[Nd_{0.5}(YDy)_{0.25}]_{2.2-x}Zr_xCo_{1.5}Fe_{12.5}B$  ribbon.<sup>40</sup> When x = 0.4, a fine and uniform 2-14-1 type microstructure is formed with an average grain size of 65 nm. The as-spun ribbon has an H<sub>cj</sub> value of 10.6 kOe and a  $(BH)_{max}$ of 9.6 MGOe, and exhibits enhanced high-temperature magnetic properties in the temperature range of 150°C to 300°C. Larger substitution of zirconium for RE further refines the grain size but also leads to the appearance of the 2-17 phase, which severely degrades the magnetic properties.

### Gas Atomized Powder

Based on these alloy design considerations for rapid solidification by melt spinning, an improved alloy composition  $[Nd_{0.45}(Y_{0.66}Dy_{0.33})_{2.2}Zr_{0.1}Co_1Fe_{13}B]_{(1-2x)/17,3} + Zr_{0.01}C_{0.01}$  (termed GA-1-114) was developed for gas atomization.42 Ingots of this composition were prepared by plasma arc melting in an argon atmosphere. The ingot was induction heated to 1,550°C and atomized by high-pressure argon gas at a pressure of 5.5 MPa. Powder was sieved into the major ASTM size fractions. As-atomized powders were annealed in argon over the temperature range 700°C-750°C for 15 min. X-ray diffraction (XRD) was performed with Cu Ka radiation on a Philips X-ray diffractometer. Differential thermal analysis (DTA) was performed with a Perkin-Elmer DTA at a heating rate of 10°C/min. Hysteresis loop measurements were performed using a Quantum Design MPMS SOUID magnetometer with a maximum field of 5.0 T. High-temperature hysteresis loops and magnetization vs. temperature curves were obtained utilizing a vibrating sample magnetometer (VSM) with fields 9T and 1T, respectively.

Microstructural analysis was carried out using

TABLE III. SIEVE RESULTS FOR AS-ATOMIZED POWDER <sup>42</sup>			
Sieve Size (um)	Sieve Weight (g)	Sieve Amount (%)	
106	0.043	0.04	
90	1.187	1.22	
75	2.459	2.52	
63	4.193	4.3	
53	5.76	5.91	
45	4.5229	4.64	
38	9.587	9.83	
32	17.775	18.22	
25	25.882	26.54	
20	12.545	12.86	
<20	13.584	13.93	

a JEOL JSM-5910LV scanning electron microscope (SEM). The sieved results for 100 g of powder are given in Table III. The weight of powder <38  $\mu$ m was 79.4 g, approximately 81.4 w/o of the total powder.

A typical result for magnetization as a function of temperature for as-atomized and annealed powder with a particle size of 20-25 µm is shown in Figure 16.42 Analysis reveals the existence of two ferromagnetic ordering transformations at ~280°C and 400°C for the as-atomized powder. These two transformations coincide with the Curie transformations of the 2-17 and 2-14-1 phases, respectively. After annealing at 700°C for 15 min., the M vs. T curve exhibits only the 2-14-1 phase transition at 410°C, confirming that the phase composition has evolved from a majority 2-14-1 plus a small amount of 2-17 phases to a single 2-14-1 phase (modified by a cobalt addition to raise the Curie temperature) during the annealing process.

Figure 17 shows the X-ray diffraction patterns for powder samples as-atomized and annealed at 700°C for 15 min.<sup>42</sup> Both XRD patterns appear to contain reflections mainly from the crystallized 2-14-1 structure and do not indicate the presence of the 2-17 phase before annealing; however, this evidence does not rule out a small volume fraction of the 2-17 phase. In addition, DTA measurements (Figure 18) of the as-atomized powder show a crystallization (exothermic) transformation around 650°C, indicating that some amorphous phase exists in the powder. Figures 19(a) and 19(b) show typical SEM microstructures of as-



Figure 16. Magnetization as a function of temperature for as-atomized and annealed powders,  $20-25 \ \mu m^{42}$ 

atomized and annealed powder, respectively, with a particle size of 20–25  $\mu$ m. It is seen from Figure 19(a) that the as-atomized powder consists predominately of uniform equiaxed grains with an average grain size of 1.5  $\mu$ m. The amorphous phase is not easily detected by XRD or SEM. After the powder is annealed at 700°C for 15 min, the grains grow slightly and the grain boundaries become narrower, Figure 19(b).

By combining the results of the microstructural observations with those of XRD and DTA, it is concluded that the partial substitutions of zirconium and the ZrC additions result in the formation of a uniform, fine-scale microstructure.<sup>42</sup> After annealing at 700°C for 15 min, the powder is fully crystallized, and the phase structure is transformed to the single 2-14-1 phase from the 2-14-1 and 2-17 phases (trace). These microstructure and phase-structure changes are critical to the final magnetic properties.



Figure 17. XRD patterns for as-atomized and annealed powders, 20–25  $\mu$ m<sup>42</sup>



The magnetic properties of the annealed powder from each size fraction are shown in Table IV.<sup>42</sup> It is seen that  $(BH)_{max}$  first increases with increasing powder size from 5 µm, reaches the peak value at the size range 20–25 µm, and then decreases with further increasing powder size. It is clear that fine powder (<5 µm), with a high surface area, is readily oxidized, resulting in degraded magnetic properties. The highest energy product is observed when the particle sizes are 20–25 µm. With larger particle sizes, a coarser microstructure is observed, which weakens the reversal field strength, reducing the magnetic properties.

Typical demagnetization curves of as-atomized and annealed 20–25  $\mu$ m sizes powders are shown in Figure 20.<sup>42</sup> The curves for the as-atomized powder exhibit a feature consistent with the amorphous phase or magnetically soft phase, which verifies the results revealed by DTA and M vs. T, respectively. Annealing at 700°C for 15 min results in a smoother demagnetization curve and increased "squareness." The temperature depend-



Figure 19. Representative microstructure of powder, 20–25  $\mu$ m, (a) as-atomized and (b) annealed at 700°C for 15 min.<sup>42</sup> SEM

Sieve Size (µm)	B <sub>r</sub> (kG)	H <sub>cj</sub> (kOe)	(BH) <sub>max</sub> (MGOe)
45-53	4.7	4.7	4.8
38-45	5	6	5.6
32-38	5.6	7	7.1
25-32	6.3	9.6	9.0
20-25	6.4	10.5	9.6
-20	6.5	11.2	10.1
10-15	6.3	10	9.8
10-5	6.3	10.7	9.1
-5	5.8	10.7	7.7

ence of the magnetic properties of the annealed powder was also determined, Figure 21. The results confirm that the temperature coefficients of  $B_r$  and  $H_{cj}$  are 0.084%/°C and 0.4%/°C in the temperature range of 27°C to 100°C, respectively.



Figure 20. Hysteresis loops for annealed powder, 20–25 µm<sup>42</sup>



Figure 21. Magnetic energy product (BH)max as a function of temperature for annealed powder <20 μm<sup>42</sup>

 $(BH)_{max}$  values at room temperature and 200°C are 9.6 and 5.6 MGOe, respectively.

Based on a knowledge of the magnetic behavior of the 2-14-1 compound, it is likely that the ability to produce a fine particulate, in which each particle is a highly aligned cellular (nanocrystalline) structure or a single crystal (microcrystalline), can result in a large gain (four times) in magnetic properties, if the ensemble of particulate can be aligned in a bonding matrix to form a bonded or (extrinsically) sintered magnet.<sup>1,2</sup> These concepts are being pursued by focusing on the particulate-production processes as a first step, using a rapid-solidification process as our first choice. To enable the maximum energy product to be realized in high-temperature MRE-Fe-B alloys, development of sintered (full-density) aligned permanent magnets also will be continued. The approach will embrace magnet alloy design and processing of micron-sized (single-crystal) particulate and the development of an extrinsic liquidphase-sintering constituent to lock in the aligned magnetic-particle assembly.

### SUMMARY

A systematic study was conducted by melt spinning to enhance the magnetic properties and to reduce the high-temperature degradation of a series of isotropic nanocrystalline magnet alloys where a Y+Dy mixture replaces neodymium or praseodymium as the dominant RE constituent in  $MRE_{2}Fe_{14}B$  (MRE = Y+Dy+Nd). The most recent results have shown that the Y+Dy based MRE<sub>2</sub>Fe<sub>14</sub>B alloy can result in isotropic bonded magnets with superior magnetic properties compared with competitive commercial isotropic bonded magnets above about 30°C and well beyond 200°C by a judicious combination of yttrium, dysprosium, and neodymium, along with a minor cobalt substitution for iron. A combination of zirconium substitution and ZrC addition also enhances quenchability and yields a preferred microstructure in MRE 2-14-1 base alloys. In a wide particle-size range, gas-atomized powder exhibits desirable magnetic properties at room and high temperature, superior to commercial spherical magnet alloy powders in the temperature range of 27°C to 277°C. (BH)<sub>max</sub> values of 9.6 and 5.6 MGOe for gas-atomized 20-25 µm-size powder were obtained at room temperature and 200°C, respectively. The gas-atomized powders with superior magnetic strength were also in a

fine-powder-size range that is more suitable for MIM of bonded isotropic magnets than commercial spherical powder. A major remaining barrier to high-performance application of these new high-temperature nanocrystalline  $MRE_2Fe_{14}B$  magnet alloys is the development of an aligned magnetic structure in consolidated form (either bonded or sintered) that permits the high level of magnetic strength of aligned sintered microcrystalline magnets to be approached.

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