

Permanent Magnet Materials—Developments During the Past 12 Months

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Information about real and potential permanent magnet materials continues to grow at a rapid pace, and developments in the following areas are discussed. Co-Zr, although not comparable to the best high-performance magnets, has attracted interest as a rare earth free alloy. Carbon and nitrogen are becoming more prominent as the metalloid in iron-rare earth magnets. This leads to cast magnets based on Fe-Nd-C, bonded magnets based on $\text{Fe}_{17}\text{Sm}_2\text{N}_x$, a renewed interest in the tetragonal phase $(\text{Fe,Ti})_{12}\text{Nd}$, now with added nitrogen, and a nitrogen treatment for sintered $\text{Fe}_{14}\text{Nd}_2\text{B}$ that raises the Curie temperature by more than 100 K. Alloying additions to $\text{Fe}_{14}\text{Nd}_2\text{B}$ improve the coercivity. Finally, developments in corrosion protection and processing are highlighted.

1 Introduction

If one excludes alnicos and hexaferrites, the term "permanent magnets" comprises mostly alloys of Fe and Co with rare earth metals. Exceptions, such as Mn-Al-C or Co-Pt, are of lesser commercial importance, yet attempts to achieve high magnetocrystalline anisotropies with alloying elements that are not taken from the lanthanides have continued, witness the recent activities around Co-Zr alloys. A richness of characteristics can be found by adding further components to a simpler transition metal-rare earth metal system, and a well-known example of such a multicomponent alloy is the magnet based on $\text{Co}_{17}\text{Sm}_2$ with additions of Fe, Cu, and Zr. The elements selected for further alloying are often suggested by earlier magnet formulations. Thus, Cu, Zr, and Al, which have been used in previous magnet systems, reappear in the new magnets. Chemical similarity is suggestive, so elements are also replaced by ones in the same or a neighboring group in the periodic system. A novel classification is emerging that is based on the interstitial metalloid: B, C, N. Interstitial atoms are being introduced into known magnet materials, including old ones such as CoPt. As one observes the magnetism conferences and the permanent magnet literature, one senses that new developments are driven by some theoretical insight and much empiricism based on unique skills and facilities. It is not possible, in the available space, to cover all of the deserving developments, so the work described here is a subjective selection. The account begins with lanthanide-free materials followed by metalloid-free Fe-rare earth alloys, then discusses nitrides, carbides, and borides. It concludes with some notes on corrosion and processing.

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2 Rare Earth Free Materials

2.1 Update on Cobalt-Zirconium(-Boron)

The recent description of these alloys^[1] stands in its essential conclusions, but can be supplemented with regard to the magnetically hard phase. Now there is good evidence that the magnetically hard phase has a Co:Zr ratio near or at 5:1 in both Co-Zr and Co-Zr-B alloys, but that it is pseudohexagonal (orthorhombic) in the binary and hexagonal in the ternary alloys.^[2] There is no reason to believe that $\text{Co}_{11}\text{Zr}_2$, a formula first introduced by Pechin *et al.*,^[3] is the correct one for the magnetically hard binary phase. The binary and ternary phases are both structurally related to the familiar CaCu_5 type that is found in Co-Sm magnets. Although they do not have identical structures, the Curie temperatures of the Co-Zr and the Co-Zr-B magnetic phase are close to each other and near 500 °C. The anisotropy field is comparable in both phases,^[2] and it is reported to be 34 kOe in the ternary phase.^[4] The best coercivities that can be derived from this moderate crystal anisotropy have been obtained by melt spinning.^[4-6] In the case of Co-Zr-B-Si, the melt spinning to form an amorphous ribbon of $\text{Co}_{76}\text{Zr}_{18}\text{B}_3\text{Si}_3$ is followed by annealing for a few minutes at 650 °C to form a microcrystalline material with a coercivity of 6.7 kOe.^[7] Unfortunately, the processing required to achieve a high coercivity is not conducive to a preferred crystal orientation so that a considerable fraction of the potential remanence can be lost. On the other hand, ratios of remanence to saturation magnetization that exceed by far the value 0.5 expected for a random orientation of the crystallites have been reported.^[5] They are probably due to exchange coupling effects between the very small particles, in the manner described by Clemente *et al.*^[8]

2.2 Tetragonal $L1_0$ Types MnAl and CoPt; Hexagonal MnBi

These materials are of increasing interest in thin films. Films of τ -MnAl can apparently be grown at low substrate temperatures (150 to 200 °C) without adding the carbon that is introduced to stabilize the phase in extruded magnets. Although the phase has been characterized as metastable by Köster and Wachtel,^[9] their thermal and microstructural data suggest oth-

erwise, and τ might well be a stable low-temperature phase. One method of making thin films of τ -MnAl is RF sputtering.^[10] Single crystal films of τ have been grown on GaAs substrates by molecular beam epitaxy.^[11] Superlattices of Co-Pt are becoming an interesting model substance, exhibiting perpendicular anisotropy when grown on GaAs by molecular beam epitaxy.^[12] The high-anisotropy compound MnBi has been known as a magnet under the name Bismanol and has the hexagonal NiAs structure. It possesses one of the largest known magneto-optical Kerr rotations and is therefore being discussed for magneto-optical storage. Thin films of this material have been grown by evaporation on to a glass substrate.^[13] By doping with aluminum, the change from room-temperature easy axis to low-temperature planar anisotropy can be shifted to transition temperatures well below the 200 K found in undoped MnBi.^[13] The Al addition also reduces the polycrystalline grain size.^[13]

3 Fe₁₇R₅

3.1 Binary Fe-Nd and Fe-Sm

Because Fe₁₇R₅ was first recognized in binary Fe-Nd,^[14] it is useful to review briefly some points of the early work on rapidly solidified binary Fe-Nd by Croat.^[15] At that time, his X-ray diffraction patterns suggested that the principal phase in magnetically hard rapidly solidified Fe-rich alloys (e.g., Fe₆₀Nd₄₀) was Fe₁₇Nd₂. Because the 17:2 phase is known to have easy-plane anisotropy and therefore cannot be the source of the magnetic hardness, it is reasonable to assume that the phase is really Fe₇Nd, which is known to form by rapid solidification^[16] and to share strong X-ray reflections with Fe₁₇Nd₂. The magnetic ordering temperature of the magnetically hard phase was shown by Croat to vary with the Nd content of the alloy.^[17] It drops with decreasing Nd content and clearly approaches the value for Fe₇Nd (370 K) reported by Stadelmaier *et al.*^[16] Annealing above 750 K leads to a complete loss of the high coercivity in the melt spun alloy Fe₆₀Nd₄₀, and one of the phases that can be identified in the diffraction pattern of Croat^[15] is known to be magnetically soft.^[14] A comparison between the pattern of Croat^[15] and X-ray powder diffractions calculated by Stadelmaier *et al.*^[18] from the crystal structure of Fe₁₇Nd₅ determined by Moreau *et al.*^[19] allows positive identification of this phase as Fe₁₇Nd₅. Recently, the anisotropy in this compound has been determined to be the basal-plane type.^[20] Furthermore, the agreement between the pattern of Fe₁₇Nd₅ and the patterns of magnetically hard Fe-Ti-Sm alloys obtained by sputtering^[21] and also by mechanical alloying^[22] has shown that Fe₁₇Nd₅ and (Fe,Ti)₁₇Sm₅ are isostructural.^[18] Based on the cell constants of (Fe,Ti)₁₇Sm₅ and the apparent lack of expansion resulting from the substitution of the larger Ti atom, it was suggested that the Ti content in (Fe,Ti)₁₇Sm₅ might be much lower than the assumed 10 at.%.^[18] In the meantime, Cadieu *et al.*^[23] were able to establish by X-ray diffraction that Fe₁₇Sm₅ exists as a binary compound and requires no third element. Its volume expansion for a Ti substitution of 11% turns out to be 1.67% (compared to an estimated 2% for 10% substitution^[18]). The room-temperature value of coercivity obtained by sputtering followed by crystallization of Fe₁₇Sm₅ is 12

kOe.^[24] In the interest of historical fidelity, it should be mentioned that, while the first report of binary Fe₁₇Sm₅ is credited to Cadieu *et al.*,^[23] it is quite likely that this phase was present in melt spun Fe₆₀Sm₄₀ as described by Croat in 1982^[25] and that it was responsible for its very high coercivity (24 kOe). For Fe₁₇Sm₅ to form in this manner would require that the stable phases Fe₂Sm and Fe₃Sm be suppressed at the particular cooling rate that is responsible for the high coercivity.

3.2 Ternary (Fe,Ti)₁₇Sm₅

The Ti substituted phase has received several names since it was first introduced as Fe₇₃Ti₈Sm₁₉ in sputtered films.^[26] It was designated ω -Fe₇₀Sm₂₀Ti₁₀ by Katter *et al.*,^[27] then "A2" (near Fe₇₅Ti₄Sm₂₁),^[28] following the name introduced by Schneider *et al.*,^[14] for the isostructural Fe-Nd phase. It is now recognized to be (Fe,Ti)₁₇Sm₅.^[18] It can be formed by mechanical alloying, and after a short anneal above 500 °C, it yields the exceptionally high room-temperature coercivity of 64 kOe.^[29] The hexagonal phase has an [001] easy axis, an anisotropy field greater than 200 kOe, and a Curie temperature of 305 °C.^[28] Its remanence is below 4 kG because the saturation magnetization is low and because the samples were magnetically isotropic.^[28] Successful alloying with Ti suggests that V should be equally effective, as seen in the tetragonal 12:1 phases (see below). However, the 17:5 phase with Fe-V-Sm appears to lose the competition against the 12:1 phase at compositions that produce 17:5 in equivalent Fe-Ti-Sm alloys.^[28]

4 Fe₃Sm and Fe₇Sm

The rhombohedral structure type of Fe₃Sm(Ni₃Pu type) is familiar in isostructural Co₃Sm. The Fe compound has high uniaxial magnetocrystalline anisotropy, and by melt spinning or mechanical alloying, it produces high coercivities.^[28] Replacing some of the Sm by Zr changes the hysteresis loop, and the highest reported coercivity for a resin-bonded sample prepared by mechanical alloying was 14.8 kOe.^[27] The highest remanence (5 kG) was found in Fe_{3.8}Sm_{0.57}Zr_{0.43}, but for this composition the coercivity dropped below 10 kOe.^[28] It was mentioned above that the Cu₇Tb structure type can be formed in Fe-Nd by rapid solidification,^[16] and it is also stabilized by adding Ti or V to Fe-Sm.^[30] Cadieu *et al.*^[31] have shown that it forms in sputtered films of Fe-Sm by adding Zr. Because of the high Sm content of 20 at.%, one might assume that this phase is being mistaken for rhombohedral Fe₃Sm. However, in reviewing the diffraction pattern shown by Cadieu *et al.*,^[31,32] one verifies that the structure type is indeed Cu₇Tb (or Co₅Sm). In view of the composition, the transition metal to rare earth atom ratio is likely to be closer to 5:1 than to 7:1. The coercivity at 293 K for a sputtered film of 72.0 at.% Fe, 8.1 at.% Zr, and 19.9 at.% Sm is 6.7 kOe, but the magnetization $4\pi M$ is low, measuring only 6.2 kG in a field of 18 kOe.^[32] Binary "Fe₇Sm" (with an assumed stoichiometry of Fe₉Sm) has been reported by Katter *et al.*^[33] It is obtained by melt spinning at high wheel velocities and has a Curie temperature of 210 °C and a saturation polarization of 12.5 kG.

5 Mn₁₂Th-Type Phases

5.1 Binary Fe₁₂Sm

In a paper on magnetic coupling in (Fe, V)₁₂R, where R ≡ Ho and Er, it was stated that compounds Fe₁₂R did not exist.^[34] An observation that was also repeated in a recent review.^[35] This assertion can no longer be upheld because Cadieu *et al.*^[36] succeeded in stabilizing Fe₁₂Sm in thin films that were RF sputtered on Al₂O₃ substrates preheated to 400 to 550 °C. The Fe₁₂Sm films have a saturation magnetization of 14.5 kG and an anisotropy field of ~ 130 kOe.^[36] The structure may be metastable or possibly stabilized by some impurity whose amount would have to be minor. Coercivities of the sputtered films were on the order of 6 kOe when 4% of the Fe was replaced by Ti.^[36]

5.2 Ternary (Fe, M)₁₂Sm

From a survey of these tetragonal phases by Buschow and de Mooij,^[37] one gathers that when *M* is Ti or V, the Curie temperatures are reasonably high—585 K for Ti and 610 to 620 K for V—whereas for Mo it is only 510 K. The Curie temperature can be increased by small additions of Co.^[38] It was previously pointed out^[11] that making permanent magnet materials from the 12:1 phases was only possible by rapid solidification or mechanical alloying, resulting in isotropic magnets. This will produce fine-grained structures of < 200 nm in the case of mechanically alloyed Fe-V-Sm.^[28] By staying on the Sm-rich side of the phase composition, one obtains a microstructure containing a thin grain boundary phase (of apparent Fe₂Sm), leading to coercivities as high as 11.8 kOe in Fe₇₀V₁₅Sm₁₅.^[29] When *M* is Ti or Mo, only half the coercivity attainable with V is reached,^[28] although for (Fe, Mo)₁₂Sm the anisotropy field is 90 kOe and therefore higher than that of Fe₁₄Nd₂B.^[29] The remanence of these isotropic magnets is typically between 4.5 and 5.5 kG.^[28] In the case of mechanically alloyed and hot pressed, fully dense, isotropic Fe₇₈Mo₁₀Sm₁₂ magnets, the grains had a high concentration of defects (stacking faults, twins), which by pinning the domain walls were assumed to be responsible for the coercivity of 3.8 kOe.^[38] Also present in these mechanically alloyed magnets were crystallites and polycrystalline clusters of the oxides SmO and Sm₂O₃, the latter in the form of high-temperature modifications that had to originate at the hot pressing temperature.^[38] Contrary to Fe-V-Sm, no grain boundary phase is observed in the (Fe, Mo)₁₂Sm magnets.^[38]

6 Nitrogen

An authoritative review of the status of the new iron rare earth (R) nitrides as of October 1990 has been given by Coey *et al.*^[39] The recent survey of permanent magnet developments^[1] also highlighted the new findings on Fe₁₇R₂ phases in which the addition of interstitial carbon or nitrogen atoms leads to interesting values of magnetocrystalline anisotropy and magnetic ordering temperature. An outstanding composition is Fe₁₇Sm₂N_{2.3}, for which the anisotropy field is 140 kG and the Curie temperature 476 °C.^[40] Unfortunately, Sm is the only one

of the rare earth elements that exhibits the desired easy-axis anisotropy in the nitride,^[41,42] whereas the others lead to easy-plane anisotropy. Binary Fe₁₇Sm₂ is also an easy-plane material, unlike easy-axis Co₁₇Sm₂, on which a family of permanent magnets is based. In a sense, the addition of interstitial nitrogen has pushed the substitution of Fe for Co in Co₁₇Sm₂ to the Co-free limit.

6.1 Magnets Based on Fe₁₇Sm₂N₃₋₈; Nitrided “Fe₉Sm”

The notation used here reflects a hypothetical maximum of three interstitial atoms per formula unit and follows Coey *et al.*^[39,40] The anisotropy field of Fe₁₇Sm₂N₃₋₈ was reported first to be comparable to that of Fe₁₄Nd₂B, which was 140 kOe, and most recently, 200 kOe.^[42] Although this and the high Curie temperature identify the material as a potential permanent magnet, suggestions for the preparation of actual magnets do not abound. At present, the material offers itself as a bonded magnet made of mechanically alloyed powder subjected to a two-step heat treatment, the first step to form binary Fe₁₇Sm₂ (several hours at 650 to 800 °C) and the second step, nitriding at 400 to 500 °C in nitrogen gas.^[42] The resin-bonded magnet has a room-temperature coercivity as high as 30 kOe.^[42] So far, it remains isotropic with a remanence that is about half the saturation magnetization, the latter reported to be about 15.4 kG by Otani *et al.*^[40]

A method of preparing individual crystallites to permit orienting of the particles in the bonded magnet is desirable, and a means of increasing the nitriding rate in larger particles for this purpose by prior charging with hydrogen has been described by Fukuno *et al.*^[43] The main difficulties in preparing fully dense magnets with nitrided Fe₁₇Sm₂ result from the complete decomposition of the nitride above 650 °C. In the case of exactly two N atoms per formula unit of the reactant, it proceeds by the simple reaction Fe₁₇Sm₂N₂ → 17 Fe + 2SmN. Whether the magnetic nitride is stable or, as suggested by Schnitzke *et al.*,^[42] metastable, is immaterial for the arguments to follow. Any temperature for which sintering is realistically possible is well above 650 °C, so that sintering is not an obvious path to consolidation of the nitride powder. To sinter the nitrogen-free Fe₁₇Sm₂ and then nitride the bulk material rather than a powder requires long nitriding times. Even if that difficulty could be overcome, one would want to orient the powder in a magnetic field before pressing, and this is problematic because of the easy-plane anisotropy of the binary compound. It is obvious why the discovery of the Fe-Sm nitride was not promptly followed by the production of a commercially competitive magnet: The best prescription for a suitable process has yet to be worked out. Bonded magnets are already feasible, and cold pressing with zinc powder, followed by an anneal near the melting point of zinc, has been described by Coey *et al.*^[39] In this case, a coercivity of 6 kOe and an energy product of 10.5 MGOe were achieved with Fe₁₇Sm₂N_{2.3}. Nitriding melt spun Fe₉Sm with the Cu₇Tb structure produces a material with a Curie temperature of 470 °C, an anisotropy field of 86 kOe, a coercivity of 6.2 kOe, remanence of 8.6 kG, and an energy product of 8.7 MGOe.^[33]

6.2 Nitrogen in 12:1 Magnets

With the observation that the metalloids B, C, and N readily enter the crystal structure of $\text{Fe}_{17}\text{Sm}_2$, it is a logical conclusion that they should dissolve in crystallographically related structures, including the Mn_{12}Th type. Nitriding proceeds by exposing the alloys to nitrogen gas in a temperature range around 500 °C. The alloys first investigated include Fe with the transition metals Ti, V, and Mo and the rare earth atoms Y, Nd, Sm, and Dy. All studies agree that the 12:1 structure is retained after nitriding,^[44-47] whereas it decomposes below 1000 °C without nitrogen.^[47] It is generally assumed that one interstitial nitrogen atom per formula unit enters the structure,^[45] leading to a lattice volume expansion of 3% and an increase in Curie temperature by as much as 200 K. The anisotropy is strongly affected, and in the particular case of $\text{Fe}_{11}\text{TiNdN}_{1.8}$, the improvement in anisotropy is sufficient to make it a potential permanent magnet material.^[44,46] In Fe-Ti-Sm and Fe-V-Sm, however, nitriding changes the uniaxial to undesirable planar anisotropy.^[46] Therefore, Fe-Ti-Nd, which had been written off as unpromising, warrants renewed consideration. The increase in Curie temperature can be quite dramatic. For $\text{Fe}_{11}\text{TiNd}$, the Curie temperature increases from 551 to 723 K^[46] and for Fe_{11}TiY by more than 230 K from 521 to 756 K.^[45] One of the problems associated with Mo-stabilized $\text{Fe}_{10}\text{Mo}_2\text{Nd}$ was the very low Curie temperature (410 K). Now nitriding has raised it to 577 K.^[47]

6.3 Nitrogen in $\text{Fe}_{14}\text{Nd}_2\text{B}$

In a paper dealing with the milling in water and gas passivation of Fe-Nd-B powders,^[48] a corrosion-resistant powder is described. The passivation step consists of treatment at 125 to 300 °C in carbon dioxide and/or nitrogen gas.^[48] The good corrosion resistance, measured by weight gain in a humid atmosphere at elevated temperature, continues to be high after sintering the passivated powder. The most surprising aspect of this treatment is the reported increase, by more than 100 K, in the Curie temperature of the sintered magnets. Inasmuch as carbon, when it replaces boron, is known to lower the Curie temperature of the 14-2-1 phase, the effect would have to be attributed to nitrogen pickup (and in the case of the CO_2 treatment, additional carbon that is interstitial). Full details of the circumstances leading to the high Curie temperature are not disclosed in Ref 48, but the nitriding of $\text{Fe}_{14}\text{Nd}_2\text{B}$ has also been investigated by Chin *et al.*,^[49] who found that the Curie temperature did indeed increase, in this case to 370 °C. Nitrogen pickup and retention begins at temperatures as low as 300 °C and continues up to the sintering temperature, although with decreasing amounts as the temperature increases.^[49] The nitrogen pickup is accompanied by a 15% increase in anisotropy and saturation magnetization.^[49] It is known that the tetragonal compound exists as one continuous single-phase region from $\text{Fe}_{14}\text{Nd}_2\text{B}$ to $\text{Fe}_{14}\text{Nd}_2\text{C}$,^[50] and it is therefore not unreasonable to assume an Fe-Nd-B-N series (terminating well before $\text{Fe}_{14}\text{Nd}_2\text{N}$) that is isoelectronic with $\text{Fe}_{14}\text{Nd}_2\text{B}_{1-x}\text{C}_x$. The assumption inherent in the formula $\text{Fe}_{14}\text{Nd}_2\text{BN}_x$ used by Chin *et al.*,^[49] however, is that the nitrogen atoms do not replace boron but are interstitial. Interstitial nitrogen would explain the rise in

Curie temperature, whereas simple substitution of nitrogen for boron would not.

7 Carbon

Carbon stands between nitrogen and boron in the periodic table and in the very real sense that, on one hand, it enters the Fe_{17}R_2 phases interstitially (as does nitrogen) and, on the other hand, that it stabilizes the 14-2-1 structure type (as boron). In this intermediate position, carbon does not reach the full potential of either boron or nitrogen: The magnetic moments and Curie temperatures of the $\text{Fe}_{14}\text{R}_2\text{C}$ phases lie somewhat below those of the borides; the moments and Curie temperatures of easy-axis $\text{Fe}_{17}\text{Nd}_2\text{C}_x$ lie below those of $\text{Fe}_{17}\text{Nd}_2\text{N}_x$. Contrary to the nitrides, which exist only at low temperatures (below 650 °C in the case of $\text{Fe}_{17}\text{Nd}_2\text{N}_x$), the carbides $\text{Fe}_{17}\text{R}_2\text{C}_x$ are found at high temperatures and tend to decompose at low temperatures in favor of the ϕ phase $\text{Fe}_{14}\text{R}_2\text{C}$. This transformation from high-temperature $\text{Fe}_{17}\text{Nd}_2\text{C}_x$ to low-temperature $\text{Fe}_{14}\text{Nd}_2\text{C}$ can be exploited to control the microstructure and obtain high coercivities without rapid solidification or sintering.

7.1 Cast Fe-Nd-C Isotropic Magnets

In cast ingots, the transformation to $\text{Fe}_{14}\text{Nd}_2\text{C}$ (ϕ) from the parent $\text{Fe}_{17}\text{Nd}_2\text{C}_x$ phase is extremely slow. It can be accelerated by transforming from melt spun flakes.^[51] The idea of producing a simple isotropic magnet based on Fe and Nd without the added steps of melt spinning or powder metallurgical processing is nevertheless attractive. Basically, the method relies on an enhanced nucleation rate of ϕ gained by adding a very small amount of boron.^[52] Considerable progress in the fabrication of these magnets has been made by Grieb *et al.*^[53] The transformation, which is normally too sluggish to make Fe-Nd-C alloys useful,^[54] can be accelerated to reasonable rates by adding as little as 0.05 mass % boron.^[53] This effect of boron is already implied in the first report on Fe-R-C magnets.^[50] The new feature in Ref 53 is the addition of Cu, which changes the phase relations in Fe-Nd-C dramatically by forming Cu-Nd intermetallic compounds. This provides a fully dense magnet in which hydrolyzable carbides are absent so that a feared corrosion problem is avoided. A similar problem is the hydrolyzable carbide Al_4C_3 in Mn-Al-C magnets, where it is solved by strictly limiting the total carbon content. The addition of Cu is also significant in that it increases the growth rate of $\text{Fe}_{14}\text{Nd}_2\text{C}$ grains.^[52] For the coercivity, the effects of the newly added Cu-Nd phases and the small size of the ϕ particles are synergistic. Without the Cu, it has not been possible to obtain really high coercivities in Fe-Nd-C unless a considerable fraction of Nd was replaced by Dy.^[50] Inasmuch as the loss of coercivity suffered by dropping the Dy additive could be correlated with magnetically soft free Fe in the microstructure,^[55] the increase in coercivity must be due to the reduction of the free Fe fraction. By introducing Cu, coercivities as high as 6 kOe are readily obtained in a cast alloy of 68 at. % Fe, 20 at. % Nd, 9.5 at. % C, 0.5 at. % B, and 2 at. % Cu. The magnets are isotropic and as such comparable to unoriented melt spun Fe-Nd-B. It is to be expected that they can be oriented by hot forming below the transformation temperature, or that the transformation to magnetically hard ϕ

can be coupled with hot forming. When 10% of the Nd is replaced by Dy, the coercivity exceeds 10 kOe.^[53]

7.2 Oriented (Die Upset) Fe-Nd-C Magnets

Melt spun ribbons containing Fe₁₄Nd₂C have been produced by Coehoorn *et al.*^[54] and coercivities over 10 kOe have been reported. The normally sluggish formation of ϕ becomes quite rapid in the melt spun flakes, which start out with crystallites of Fe₁₇Nd₂C and free Fe, as well as an amorphous phase.^[54] The amorphous phase reportedly first goes to metastable 17-2, even though the temperature is in the range of stable ϕ . Hot pressing Fe₇₅Nd₁₆C₉ followed by die upsetting has yielded the best energy product (22.4 MGOe). In that case, the remanence was 10.2 kG, up from 7.1 kG in the hot pressed precursor, and the coercivity was 9 kOe.^[56] Further enhancement of the coercivity by low-level alloying additives has not been successful,^[56] although this effect can be observed in cast magnets, as shown above.

7.3 Carbon in Fe₁₇Sm₂

The enhancement of permanent magnet properties in Fe₁₇Sm₂ by adding interstitial nitrogen (see above) suggests that interstitial carbon should have a similar effect. A room-temperature anisotropy field of 70 kOe is reported for the carbide by Grössinger *et al.*,^[57] and the maximum Curie temperature is given as 251 °C for the composition Fe₁₇Sm₂Co_{0.9}. Similarly, Wang and Hadjipanayis^[58] show a Curie temperature of 247 °C for Fe₁₇Sm₂C_x with $x = 1.5$. By mechanical alloying, a coercivity approaching 20 kOe was found in Fe₁₇Sm₂ with added carbon.^[59] Furthermore, the anisotropy of Fe₁₇Sm₂N_x can be improved by carbon addition to form Fe₁₇Sm₂(C,N)₃.^[59] The question of stability of the carbide is intriguing because in the cast alloys it is replaced by Fe₁₄R₂C at low temperatures, yet it can be formed at 550 °C by carburization of binary Fe₁₇Sm₂ in hydrocarbon gases (methane, acetylene, and butane).^[60] With this method, the carbon uptake is higher ($x \approx 2$), the anisotropy is easy-axis, and the Curie temperature is 400 °C, making the Fe-Sm carbide another viable candidate for permanent magnet applications.^[60]

8 Boron; Fe-Nd-B Magnets

The improvement of Fe-Nd-B magnets continues to occupy a prominent place in permanent magnet research efforts. Of particular interest is the effect of alloying additions that go beyond the original substitutions of Co (for Fe) and Dy (for Nd). A peculiar application of boron has been in CoPt magnets where it increases the coercivity well above the typical values around 5 kOe.

8.1 Alloying in Fe-Nd-B; Aluminum and Gallium

Here one has to distinguish between elements that enter the principal magnetic phase Fe₁₄Nd₂B and affect its intrinsic magnetic properties (saturation magnetization, magnetic ordering temperature, anisotropy) and those that operate chiefly by their influence on the region between the grains of Fe₁₄Nd₂B. Some elements, such as Al, do both. Additions are introduced by dif-

ferent methods— alloying in the melt, additions made during powder processing, and admixing of powdered compounds that react during sintering. Al and Ga have been known to increase the coercivity of sintered Fe-Nd-B magnets, but the mechanism is just beginning to be understood. With a judicious choice of composition, the intergranular Nd-rich eutectic is replaced by an Fe-Nd-Al or Fe-Nd-Ga phase that apparently leads to a better separation of the magnetic crystallites,^[61] whereas improved wetting by the liquid phase during sintering is now assumed to be of secondary importance. That less Ga than Al is required to achieve the same beneficial effect on coercivity follows directly from the lower solubility of Ga in Fe₁₄Nd₂B so that more Ga ends up in the intergranular region. Underdoping with Ga causes the retention of free Nd, whereas overdoping can introduce (Fe,Ga)₁₇Nd₂ and a solid solution of Ga in α -Fe, both detrimental to coercivity.

8.2 Nickel, Copper, Zinc

The amounts of additives are not large, and the technology is peculiar to the General Motors process. Therefore, it may or may not work for conventional powder metallurgical preparation. Fuerst and Brewer^[62] show that diffusion-alloyed zinc is capable of doubling the coercivity in die upset Nd-Fe-B magnets. In their work, melt spun Fe-Nd-B ribbons were crushed and mixed with powders (10 to 100 μ m) of elemental Ni, Cu, or Zn before hot working into fully dense anisotropic magnets. At the temperatures required for densification the additives diffused through the ribbon matrix and presumably into the Nd-rich grain boundary regions. In concentrations of 0.5 to 0.8 wt.%, the addition of Ni, Cu, and Zn increased the coercivities of die upset magnets by 53, 77, and 100%, respectively, without affecting the remanence significantly. In the case of zinc, it is suggested that the zinc attaches itself to the Nd-rich regions between the grains. Zinc, incidentally, has been mentioned previously as an additive to die upset Fe-Nd-B magnets by Nozawa *et al.*^[63] There it was introduced into the ingot prior to melt spinning and a coercivity increase by about 50% was achieved. One of the new phases is Fe₆₅Zn₄Nd₃₁, which is assumed to be a Zn-stabilized Laves phase.^[62] It might also be related to the Al-stabilized phase (Fe_{1-x}Al_x)₂Nd, $0.025 < x < 0.05$, which is not a Laves phase.^[64] This reopens the question of the effect of small quantities of disperse phases at or near the boundaries of the Fe₁₄Nd₂B crystallites. Could it be that the alloying elements that enhance coercivity in Fe-Nd-B magnets simply precipitate a pinning phase in the region that is liquid at the processing temperature? Rather than being in the Nd-rich eutectic, such a phase could be found inside the rim of Fe₁₄Nd₂B that grows during the drop from the processing temperature.

8.3 Tin

The importance of phases located between the grains of Fe₁₄Nd₂B has been emphasized repeatedly by advocates of both the nucleation and pinning model of coercivity in sintered magnets. An interesting method of modifying the intergranular structure to improve coercivity is due to Velicescu,^[65] who added Fe₂Sn and CoSn powders during milling. In the case of Fe₂Sn, he achieved an increase of its coercivity by 25% at room

temperature and 75% at 150 °C, a considerable improvement in the temperature dependence of H_c . The Sn does not go into the main phase $\text{Fe}_{14}\text{Nd}_2\text{B}$, but forms a separate phase identified as $\text{Fe}_{13}\text{Sn}_1\text{Nd}_6$, which is tetragonal, $a = 0.8$ nm, $c = 2.3$ nm. It is located between the grains of $\text{Fe}_{14}\text{Nd}_2\text{B}$, exhibits a domain pattern, and is described as isotypic with $\text{Fe}_{11}\text{Ga}_3\text{Nd}_6$, reported as a new ternary compound by Li *et al.*^[66] Actually, the structure is most likely that of $\text{Fe}_{13}\text{Si}_1\text{Nd}_6$, which has recently been determined to be an ordered variant of the $\text{Fe}_{11}\text{Ga}_3\text{Nd}_6$ structure with the same unit cell dimensions as given above.^[67]

8.4 Rare Earth Substitution

The use of dysprosium to improve coercivity, and its temperature dependence has become an accepted procedure. Total replacement of Nd by another lanthanide with high anisotropy and low magnetic moment has been investigated in sintered magnets made of Fe-Tb-B. This provides a model sintered magnet that has coercivities exceeding 50 kOe.^[68]

8.5 Boron in Cobalt-Platinum

Large improvements in the coercivity of CoPt, an old and expensive but ductile material, have been reported as the result of boron additions and rapid solidification techniques.^[69] Normally, CoPt has intrinsic coercivities just above 5 kOe. In this case, an alloy of composition $\text{Pt}_{42}\text{Co}_{45}\text{B}_{13}$, processed by double anvil splat quenching followed by annealing 30 min at 600 °C, showed an intrinsic coercivity of 14 kOe.^[69] It can be assumed that the boron atom, which is small compared to Pt, is interstitial. The high coercivity has to be seen against an older report in a book on permanent magnets^[70] referencing a French patent, where it is stated that a CoPt alloy powder prepared by hydrogen reduction of the metal salts produced an intrinsic coercivity of 20 kOe.

9 Corrosion

The sensitivity of Fe-Nd-B sintered magnets to corrosion is a serious problem that is inherent in the constitution of these alloys. The mechanism is intergranular corrosion by preferential oxidation of the Nd-rich phases that reside between the $\text{Fe}_{14}\text{Nd}_2\text{B}$ grains, the principal corrosion product being $\text{Nd}(\text{OH})_3$.^[71] An obvious method of combatting corrosion is to coat the surface with a metallic barrier, such as nickel plate, or an organic protective layer. Corrosion beneath these layers, accompanied by blistering or peeling, is an irritating problem that originates in the large volume increase attending the formation of $\text{Nd}(\text{OH})_3$. Attempts to reduce the susceptibility to this attack follow two paths: (1) to make the coating more impervious to moisture and (2) to modify the microstructure of the Nd-rich intergranular region to enhance its inherent resistance to corrosion. The second approach is really the more fundamental one, and it ought to precede any concern with coating behavior, but it is here that a certain amount of confusion is found. One paper concludes that alloy composition is of minor significance,^[72] whereas another one claims that the most effective way to improve the corrosion resistance of Fe-Nd-B type sintered magnets is to control the composition, *e.g.*, by adding Co.^[73] On the

other hand, Tenaud *et al.*^[71] denies the efficacy of Co in controlling corrosion unless it is combined with V. Here it is assumed that Co-Nd phases and a network of FeV_2B_2 in the grain boundary region retard oxidation.^[71] The effect of carbon, nitrogen, and oxygen content of Fe-Nd-B sintered magnets has been studied by Kim *et al.*^[74] Individually, these elements cause the corrosion rate to go through a minimum at a critical content. Taken together, they yield a minimum corrosion rate for concentrations of 0.06 to 0.14% C, 0.05 to 0.10% N, and 0.6 to 1.2% O.^[74] An interesting speculation concerns the effect of large particles in the milled powder, which are assumed to promote localized corrosion and, ultimately, blisters and ruptures in protective coatings.^[75] In this case, the particles were prepared by hydrogen decrepitation of the ingot, followed by milling to a mean size of 10 μm and homogenization by annealing. Particles exceeding 20 μm were observed to have composition segregations ranging from free Fe to elemental Nd. When such particles were deliberately added to the powder, the sintered body showed preferential oxidation at the site of the large particle. It is further assumed that poor adhesion of the coating occurs over such particles, leading to blistering.^[75] The presence of free Fe results either from metastability during solidification of the ingot or, more likely, from preferential oxidation of Nd accompanied by reduction to Fe in the particles during one or several of the powder processing stages. The large composition gradient in the particle represents a large electrochemical potential difference that would explain the poor corrosion resistance of such particles when moisture is available. In this connection, one is reminded that melt spun powders with their extremely small grain size have good corrosion resistance that carries over to the fully dense hot pressed magnets.^[76]

For sintered magnets made from powders prepared by the reduction-diffusion process, an interesting dependence of the deterioration of magnet properties on oxygen content in a humid atmosphere has been reported.^[77] Good long-term stability was found for magnets with less than 0.75 mass percent O, whereas magnets with 0.95 mass percent O deteriorated rapidly. Magnets with 2.5 mass percent O had the lowest oxidation rate (but also had negligible coercivity).^[77] In the reduction-diffusion process, significant oxidation occurs during leaching of the powders, and the oxygen content increases with immersion time.

On the other hand, Fe-Nd-B alloys can be milled in water with very good results, as shown in a recent account by Bogatin *et al.*,^[48] and one obtains sintered magnets with high corrosion resistance. As mentioned earlier, the process includes a passivation stage for the powder that follows the water milling. In it, the powders are annealed at 125 to 300 °C in CO_2 and/or N_2 and acquire surface layers that protect them from corrosion.^[48] However, the assertion made in Ref 48 that Nd_2C_3 and NdC_2 phases in the passivated layers protect the powder particles from corrosion has to be viewed with suspicion because these carbides are known to be hydrolyzed by water. An overview of magnet coatings for corrosion protection is given by Bloch *et al.*^[72]

Among the metallic coatings, one has to distinguish between those, such as Ni or Sn, that are cathodic with respect to the Fe-Nd-B magnet, and anodic coatings, such as Zn and Al. The former must be free of pores and defects to protect the un-

derlying magnet, whereas the latter effect their protection by becoming a sacrificial anode. Manipulation of the intergranular phases in sintered Fe-Nd-B has been discussed earlier, and the beneficial effect on coercivity was emphasized.^[61] Ideally, the highly corrosive Nd phase in the intergranular region should be replaced in its entirety by an intermetallic compound of Fe-Nd-Al or Fe-Nd-Ga. The elimination of free Nd achieved in this way has improved the corrosion resistance substantially.^[61]

10 Processing

It has been shown that Fe-Nd-B ingots can be hot extruded successfully to produce a radial orientation of the easy-axis of magnetization with respect to the extrusion direction.^[78] An interesting trick that produces a radial orientation in a conventionally sintered magnet is described by Lin *et al.*^[79] Hydrogen absorption changes the direction of easy magnetization of Fe₁₄Pr₂B from axial to planar. Therefore, the tetragonal *c*-axis comes to lie perpendicular to the field direction during magnetic alignment of hydrogen decrepitated Fe-Pr-B powder. To obtain an axial orientation in iron-rare-earth-boron magnets processed directly from ingots, die upsetting is known to work in the case of Fe-Pr-B alloys doped with copper. Die upsetting alloys that approach the Fe-Nd-B system (composition Fe_{78.6}Cu_{1.4}Nd_{12.7}Pr_{4.1}B_{3.8}) has been able to produce magnets with H_c of 11 kOe and B_r of 11.5 kG.^[80] The requirements of this process are (1) chill-cast for grain refinement and some alignment, (2) die upset transverse to the chill direction (to take advantage of the available orientation), and (3) heat treat to increase coercivity by modifying the grain boundary phases.^[80] Further work will be required to make this process competitive. For Fe-Nd-B materials used in bonded magnets, only powders made by rapid solidification are able to retain their coercivity after comminution, but they cannot be magnetic field oriented, and therefore the magnets are isotropic. The performance and applications of these isotropic powders have been reviewed by Croat.^[76] The desire to utilize Fe-Nd-B powders in anisotropic bonded magnets has always foundered on the coercivity problem. Ground ingots have essentially no coercivity to begin with, and crushing and grinding presintered alloys of high coercivity into alignable particles causes an unacceptable coercivity loss. One method of preserving coercivity in anisotropic powders is by grinding hot pressed magnets derived from melt-spun ribbons,^[76] but this may turn out to be the least economical of the available options. Significant recovery of coercivity and hysteresis loop shape of ground presintered Fe-Nd-B is experienced with a double vacuum anneal of 1 hr/890 °C followed by 1 hr/570 °C.^[81] A commonly applied material for bonded magnets, Co-Sm "17-2" alloy, has been studied using lead as a binder in cold compaction. The best results, yielding the highest remanence (6 kG) and energy product (8.6 MGOe), were achieved when the pressing direction and the direction of the alignment field were perpendicular to each other, with results that surpassed isostatic pressing.^[82] In these experiments, the magnetic fill factor was low because the magnetic powders were limited to a single size fraction, and therefore, higher energy products are still feasible. Finally, it has been mentioned in an earlier section that Fe₁₇Sm₂N_{2.3} as a nitrided powder is suitable for making (isotropic) bonded mag-

nets. Cold pressing with powders of soft metals improves the coercivity to about 4 kOe and annealing below the melting point of the binder is possible, but only with the zinc binder has a further increase in coercivity to 6 kOe been possible.^[39]

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