Overview of Nd–Fe–B magnets and coercivity (invited)

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High performance Nd$_2$Fe$_{14}$B-based permanent magnets are produced with different composition and various processing techniques. The composition and the processing route influence the complex, multiphase microstructure of the magnets, such as grain size, alignment, and distribution of phases. Grain sizes in the range between 10 and 500 nm are obtained by melt spinning, mechanical alloying, and the HDDR process. Sintered and hot worked magnets exhibit grain sizes above 1 µm. The coercive field is determined by the high uniaxial magnetocrystalline anisotropy as well as the magnetostatic and exchange interactions between neighboring hard magnetic grains. The dipolar interactions between misaligned grains are more pronounced in large-grained magnets, whereas exchange coupling reduces the coercive field in small grained magnets. Transmission electron microscopy has been used to study the influence of substituent and dopant elements on microstructure, coercivity, and corrosion resistance of advanced (Nd,S1)–(Fe,S2)–B:(M1,M2) magnets. The replacement of the Nd-rich intergranular phase by secondary phases formed after doping by M1 and M2 type elements improves the corrosion resistance, especially in large-grained magnets. Secondary, nonmagnetic phases reduce the remanence and the energy product. In addition to the characterization of the microstructure, special attention has been paid to the computer modeling of the interaction between microstructure and coercivity. The simulation of the magnetization reversal process based on the real microstructure reveals a good agreement with experimental values. It is shown that the coercive field depends on grain size, distribution, and misorientation of grains. A strong exchange coupling between hard magnetic grains is desired in nanostructured magnets in order to improve the remanence. This effect is further increased by secondary, soft magnetic phases. Nanocrystalline, composite Nd–Fe–B based magnets show a remanence enhancement, both in experiments and in model calculations. © 1996 American Institute of Physics. [S0021-8979(96)38608-2]

I. INTRODUCTION

Different types of rare-earth permanent magnets, which show excellent hard magnetic properties, are based on SmCo$_5$, Sm$_2$Co$_{17}$, Nd$_2$Fe$_{14}$B, and Sm$_2$Fe$_{17}$N$_x$ alloys with a high magnetocrystalline anisotropy of the hard magnetic phase. Recent developments on iron-rare-earth magnets have been made in order to increase coercivity and corrosion resistance and to decrease material and production costs. Attempts are made to change the composition and to optimize the various preparation techniques, such as the powder metallurgical sintering process, the melt-spinning route, the mechanically alloying process and the hot working technique, in order to obtain Nd$_2$Fe$_{14}$B-based permanent magnets with high remanence, coercivity, and energy product. In addition to the primary hard magnetic phase, various secondary phases also occur, depending on the composition and the processing conditions. This is because of the complex phase relations and phase diagrams involved. The multicomponent composition of the magnets leads to the formation of nonmagnetic and soft magnetic phases. Generally, two types of substituent elements, which replace the rare-earth element or the transition element sites in the hard magnetic phase, and two types of dopant elements are distinguished. Substituent elements mainly change the intrinsic properties, such as spontaneous magnetic polarization, Curie temperature, and magnetocrystalline anisotropy. Depending on the type, the dopant elements, which show a low solubility within the hard magnetic phase, form additional intergranular rare-earth-containing or boride phases. These phases change the coupling behavior between the hard magnetic grains. Nonmagnetic intergranular phases eliminate the direct exchange interaction and also reduce the long-range magnetostatic coupling between the hard magnetic grains, both effects lead to an increase of the coercive field. On the other hand, the decrease of the volume fraction of the hard magnetic phases within the magnet decreases the remanence. Insufficient temperature stability and poor corrosion resistance are the main factors limiting applications of Nd$_2$Fe$_{14}$B-based magnets. Secondary nonmagnetic phases, which replace the Nd-rich intergranular phase, considerably improve the corrosion resistance and are of great technological interest.

The activities in permanent magnetism are mainly concentrated on the improvement of the magnetic energy density product, the corrosion resistance and the temperature coefficient of the coercive field of Nd–Fe–B-based magnets. The optimization of nitried magnets, bonded magnets, and composite nanocrystalline magnets are prospective activities.
The main emphasis of this paper is to distinguish different types of Nd$_2$Fe$_{14}$B-based magnets and to show the influence of the microstructure on the coercivity.

II. MICROSTRUCTURE OF (Nd,S1)-(Fe,S2)–B:(M1,M2) MAGNETS

Nd–Fe–B-based permanent magnets exhibit a complex multiphase microstructure. According to the ternary phase diagram at least three equilibrium phases occur: the hard magnetic Nd$_2$Fe$_{14}$B phase ($\phi$), the boride phase Nd$_{1,5}$Fe$_X$B$_Y$, and the low melting Nd-rich phase (n). Other phases, such as Fe rich and Nd oxides, and pores are found depending on the composition and processing parameters. Selected substituent elements replace the Nd atoms (S1 = Dy, Tb) and the Fe atoms (S2 = Co, Ni, Cr), respectively, in the hard magnetic $\phi$ phase and considerably change intrinsic properties, such as the spontaneous polarization, Curie temperature, and magnetocrystalline anisotropy. The formation of intermetallic, soft magnetic Nd–Fe–(S1,S2) phases, such as the Laves-type Nd(Fe,S2)$_2$-phase, deteriorate the coercivity of the magnets. If dopant elements M1 or M2 are added to Nd–Fe–B, in some cases the coercivity is increased and the corrosion resistance is improved. Our previous, systematic transmission electron microscopy studies performed on sintered, melt spun, mechanically alloyed, and hot worked magnets have shown that two different types of dopants can be distinguished independently of the processing route. Both types influence the microstructure in a different way: (i) Type 1 dopants (M1 = Al, Cu, Zn, Ga, Ge, Sn) ⇒ form binary Nd–M1/ternary Fe–Nd–M1 phases, (ii) Type 2 dopants (M2 = Ti, Zr, V, Mo, Nb, W) ⇒ form binary M2-B or ternary M2-Fe–B phases.

The main difference between substituent and dopant elements is the solubility range within the Nd$_2$Fe$_{14}$B phase. The doping changes the microstructure of Nd–Fe–B sintered magnets in the following way: If a solubility exists at the high temperature (1100 °C), the dopant element is partly dissolved in the hard magnetic Nd$_2$Fe$_{14}$B phase ($\phi$). This is the case for most of the M1-dopant elements (Al and Ga). The dopant element replaces the Fe atoms and therefore changes the spontaneous polarization, Curie temperature, and anisotropy field. If the solubility at sintering temperature is low, precipitation within the $\phi$-phase occurs. This is mainly the case with M2 dopants. The main effect of the addition of dopant elements is the formation of new intergranular phases.

In order to understand the formation of the microstructure and the enhancement of coercivity, various Dy- and Co-free Nd–Fe–B magnets containing a combination of type 1 and type 2 additives, such as (Ga,Nb) and (Cu,Nb), were prepared by the conventional powder metallurgical route from hydrogen decrepitated (HD) powder and were investigated by means of transmission electron microscopy (TEM) after the magnetic characterization. In order to compare these results, we also studied the influence of the (Al,V) and (Al,Mo) additions on the microstructure of Nd–(Fe,Co)–B and (Nd,Dy)–(Fe,Co)–B magnets, respectively.

Type 1 dopants influence the wetting behavior of the liquid phase during the sintering or the hot working process and therefore affect the magnetic decoupling of the grains. After cooling from high temperature, the formation of additional Nd-containing intergranular phases like Nd$_{1,5}$Fe$_{14}$B:M1$_1$ [for M1 = Al, Ga, Cu (\$\delta$ phase)], Nd$_{1,5}$(Ga,Fe) + Nd$_1$(Ga,Fe)$_2$, and Nd$_1$(Ga,Fe)$_3$ occurs. The better separation and decoupling of the hard magnetic grains leads to the enhancement of the coercivity of the magnets. The replacement of the Nd-rich intergranular phase by new dopant-containing phases improves the corrosion resistance of the magnet. Type 2 dopants like V and Mo as well as W and Nb show a low solubility within the hard magnetic phase and form precipitates within the $\phi$ phase and intergranular borides, such as (V,Fe)$_2$B$_2$, (Mo,Fe)$_2$B$_2$, NbFeB, and WFeB, Ti and Zr doping lead to TiB$_2$ and ZrB$_2$ precipitates, respectively. In Nd–(Fe,Co)–B:M1-doped magnets the magnetic properties of the Nd(Fe,Co,M1)$_2$ phases are changed and the coercivity is increased. In Nd–(Fe,Co)–B:M2-doped magnets the formation of the soft magnetic Nd(Fe,Co)$_2$ phase is suppressed and the intergranular Nd-rich phase is partly replaced by the Nd$_1$Co phase. This main effect of this addition is to improve the coercivity and the corrosion resistance.

The TEM micrograph of Fig. 1 shows a typical two-phase intergranular region in the sintered Nd$_{15,4}$Fe$_{75,7}$B$_{11}$Ga$_{1}$Al$_{1}$Mo$_{1}$ magnet. The Nd-rich phase is replaced by the Nd$_1$Co phase (\$i$NC) and by the intergranular boride (Mo,Fe)$_2$B$_2$($i$B). In addition to these phases the Nd$_{14}$Fe$_{13}$Al$_{1}$ phase was also identified as an intergranular phase. A more detailed investigation of this magnet revealed the influence of the Al content on the coercivity and the formation of the Nd$_1$Co phase. A similar and comparable microstructure was previously observed by TEM investigations of the Nd–(Fe,Co)–B:(Al,V) sintered magnet. Various additional phases were identified in the intergranular region in the sintered Nd$_{15,4}$Fe$_{75,7}$B$_{11}$Ga$_{1}$Nb$_{1}$ (Ref. 10) and Nd$_{15,4}$Fe$_{75,7}$Be$_{11}$Cu$_{13}$Nb$_{0,9}$ (Ref. 11) magnets, such as Ga or Cu-containing Nd phases and Nb-containing boride phases. In accordance with the binary Ga–Nd phase diagram, the two phases were characterized as eutectoidal mixture of Nd$_2$(Ga,Fe) and Nd$_6$(Ga,Fe)$_3$. A similar result was obtained in the Nd$_{15,4}$Fe$_{75,7}$B$_{11}$Cu$_{13}$Nb$_{0,9}$ magnet. Individual NbFeB...
depends on the sintering parameters, such as temperature and avoidance of the formation of microstructural changes. The advantage of the Nb addition is a region between the hard magnetic grains. The combination of Ga- and Cu-doped magnets due to their phase relationship in the ternary phase diagram M1–Fe–Nd.

The processing route of the magnet strongly influences the grain size and grain size distribution. Optimized, sintered magnets with high remanence (1.38 T) and energy density product (360 kJ/m³) (Ref. 20).

Precipitates with diameters of less than 100 nm were identified within the grain interior of the ϕ phases of both magnets. Large NbFeB precipitates occur in the intergranular region between the hard magnetic grains. The combination of (Ga,Nb)- and (Cu,Nb)-doping shows both of types 1 and 2 microstructural changes. The advantage of the Nb addition is avoidance of the formation of α-Fe, which easily occurs in Ga- and Cu-doped magnets due to their phase relationship in the ternary phase diagram M1–Fe–Nd.

The processing route of the magnet strongly influences the grain size and grain size distribution. Optimized, sintered magnets with a maximum density exhibit an average grain size in the order of 5–10 μm. The coercive field strongly depends on the sintering parameters, such as temperature and time (Fig. 2).20 Nanocrystalline and submicron magnets show a grain size in the range of 10–500 nm and are obtained by the melt-spinning route,21 or by mechanically alloying,22 or by the HDDR (hydrogenation, disproportionation, desorption, and recombination) process.23 TEM investigations of Nd–Fe–B ribbons show that the microstructure and the magnetic properties sensitively depend on the composition and the quench rate (wheel speed). The electron micrographs of Fig. 3 show the inhomogeneous grain size distribution from the free to the wheel surface side of the ribbon. For ribbons of the thickness of about 30 μm the average grain size of 20 nm near the wheel side increases to 500–700 nm near the free side. For low quenching rates different morphologies of the ϕ grains are observed. Preferential orientation of the grains is only found in equiaxed small grains and disappears for very large grains, as well as for dendritic structures. The most evident texture is observed in columnar grains which crystallized with the c-axis perpendicular to the ribbon plane.24 The formation of intergranular phases between the hard magnetic Nd2Fe14B grains is more pronounced in the large grained regions of the ribbon.25 A magnetically anisotropic behavior has been found in HDDR processed, Co-substituted and Ga-, Zr-doped magnets.26 The mechanism for the preferential orientation of Nd2(Fe,Co)14B grains with an average diameter of about 300 nm after recombination is not yet clear. It is suggested that finely dispersed undecomposed Nd2(Fe,Co)14B particles play an important role by acting as nuclei for the growth or recrystallization of the hard magnetic phase during the desorption process.27 These particles can be formed under controlled hydrogenation conditions together with additives to decelerate the decomposition.

III. COERCIVITY

In Nd2Fe14B based magnets, prepared by the sintering, the melt spinning, the mechanically alloying, or the hot working processing route the hard magnetic grains behave like single domain particles after magnetic saturation. The nucleation and the expansion of reversed magnetic domains control the coercive field during the magnetization reversal process. Micromagnetic calculations by Brown showed that the coercive field of an ideal, homogeneously magnetized material is given by the nucleation field expressed by28

$$H_n = \frac{2K_1}{J_s} - \frac{(N_i - N_p) J_s}{\mu_0}$$

(1)

where $K_1$ and $J_s$ are the first anisotropy constant and the spontaneous magnetic polarization, respectively, and $N_i$ and $N_p$ denote the demagnetization factors parallel and perpendicular to the rotational symmetry axis of an ellipsoidal particle.

Several authors have shown that the experimental results for the temperature dependence of the coercive field $H_c(T)$ of Nd2Fe14B based magnets can be described independently by the processing route by the equation29–31

$$H_c(T) = cH_A(T) - \frac{n J_s(T)}{\mu_0},$$

(2)

where $H_A$ is the anisotropy field, which is 5340 kA/m for Nd2Fe14B at room temperature.32 The temperature indepen-
dent constants $c$ and $n$ take into account the deteriorating effects of the real microstructure. A typical value of $0.2–0.5$ was found for the parameter $c$, depending on the composition and processing parameters of the magnet. The parameter $n$ ($0.8–1.7$) is related to the local demagnetizing field arising from free stray fields at internal phase and grain boundaries. The angular and the temperature dependence of $H_c$ of sintered, melt spun and hot worked Nd$_2$Fe$_{14}$B based magnets has been described by Givord and co-workers$^{33}$ by a different model. These authors consider that the magnetization reversal is initiated in a volume equal to the activation volume $V_a$ determined from magnetic viscosity measurements. The coercive field is given by

$$H_c = c' \frac{\sigma_w}{V_a^{1/3}} \frac{J_1}{\mu_0 J_s} - \frac{n J_s}{\mu_0 J_s V_a} - \frac{25kT}{\mu_0 J_s V_a},$$

(3)

where $\sigma_w$ is the domain wall energy and $k$ is the Boltzmann constant.

A detailed micromagnetic treatment of the nucleation field was carried out by Kronmüller et al.$^{34,35}$ and leads to the equation

$$H_n = \alpha_k \alpha_\phi \frac{2K_1}{J_s} \frac{J_s}{\mu_0},$$

(4)

where $\alpha_k$ describes the inhomogeneity of the magnetocrystalline anisotropy in grain boundary regions with anisotropy lower than that of the matrix phase and in which reverse domain nucleation is supposed to occur. $\alpha_\phi$ accounts for misaligned grains, and $N_{\text{eff}}$ is an average effective local demagnetization factor. Experimental measurements$^{36}$ of the angular dependence of $H_c$ of oriented sintered Nd$_2$Fe$_{14}$B magnets showed that the factor $\alpha_k$ differs from the predictions of the Stoner–Wohlfarth theory$^{37}$ of noninteracting, single domain particles. MQI and MQIII types of magnets show a similar magnetization reversal behavior and temperature dependence of $H_c$ compared with sintered magnets.$^{35}$ A classical domain wall pinning behavior has not been found in such magnets. An increase of the magnetocrystalline anisotropy of the hard magnetic phase leads to an enhancement of the coercive field according to Eqs. (1), (2), and (4). Substituting Nd by Dy by a small amount considerably increases the anisotropy field and slightly decreases the spontaneous polarization.$^{35}$

A conventional, ideal, anisotropic Nd–Fe–B magnet consists of well-aligned grains which are completely separated by a nonmagnetic intergranular phase. Two conditions must be fulfilled for a complete surrounding of the hard magnetic grains. First, the dihedral angle,$^{39}$ which was found to be in the order to $10^\circ–30^\circ$ and decreases with the amount of doping,$^6$ must become zero. Second, the volume fraction of the liquid phase during sintering must exceed a certain value ($\approx 20\%$). Both criteria are not fulfilled in Nd–Fe–B magnets. Thus, the typical microstructure consists of two types of grain boundaries, one containing intergranular phases especially at grain junctions and corners and one in direct contact to each other. Our studies are in good agreement with the theoretical consideration of the liquid phase sintering process.$^{39}$ The incomplete separation of the hard magnetic $\phi$ grains by a low-melting intergranular phase, lead to the fact that even in doped Nd–Fe–B magnets the $\phi$ grains are not completely magnetically decoupled. These magnetic interactions therefore consist of long range magnetostatic or dipolar interactions and of the short range exchange coupling between misaligned grains. Both interactions determine the coercivity of Nd$_2$Fe$_{14}$B-based magnets.$^{40}$ The contribution of exchange coupling between misaligned grains becomes more dominant with decreasing grain size.

**IV. ROLE OF MICROSTRUCTURE ON COERCIVITY**

Computer simulation of the magnetization reversal process has become an important tool for the investigation of microstructural effects on coercivity.$^{31–44}$ The lack of the hysteresis models based on Eqs. (1)–(4) lies in the fact that they describe the behavior of angular and temperature dependence of the coercive field of magnets, but do not allow any predictions of the influence of a certain, real microstructure on the coercivity. Moreover, for a complete understanding of the influence of the microstructure on coercivity it is important to know the effect of microstructural parameters, such as grain size, shape of grains, misalignment of grains, etc., and of different distributions of these parameters on the coercive field. For the two- and three-dimensional, micromagnetic, finite element calculations a realistic grain structure was built by the assumption of different models of grain nucleation and growth.$^{41,45}$ Corresponding to electron micrographs (Figs. 1 and 3) a real homogeneous or inhomogeneous distribution of phases and grain diameters was assumed for the calculations. The method of minimizing the total magnetic Gibb’s free energy with respect to the magnetic polarization has been described previously.$^{46,47}$ The creation of the microstructure starts with a random or preferential seeding for the nucleation of grains, followed by a uniform grain growth in all directions or a preferred growth in one direction, the triangulation of the grains for finite element calculation, and the distribution of hard, soft, and nonmagnetic grains. In our calculations, the total structure of 30–64 grains is divided into 20 000 meshes.

Figure 4 shows the calculated dependence of the coercive field as a function of the average misorientation of the hard magnetic Nd$_2$Fe$_{14}$B grains. The deviation of the misalignment from the average value is in the order of $\pm 5^\circ$.  

![Graph](image)
Similar results are obtained for small (50 nm) and large (5 \(\mu\)m) grained magnets. The upper limit for the coercive field of a real magnet with about 20° misorientation is only 1/3 of the maximum theoretical value of the anisotropy field. From theoretical considerations it is obvious that an improvement of the alignment by changing the processing steps increases both the remanence and coercive field.\(^{48}\) The dependence of the nucleation field on the average grain diameter is shown in Fig. 5. The nucleation field is defined at the field \(H_n(\pm H_n)\) at which irreversible magnetization reversal processes first occur after saturation. The nucleation field increases with decreasing grain diameter. This observation corresponds to coercive fields obtained after varying sintering temperatures and times (Fig. 2). The calculations predict that in an isotropic mechanically alloyed or melt-spun magnet the maximum coercive field is obtained for a mean grain diameters of 20 nm. The effect of an inhomogeneous distribution of grains with different diameter, simulating the case of the cross section of a melt-spun ribbon with different grain sizes at the wheel and free surface side (Fig. 3) is shown in Fig. 6. The demagnetization curve of the inhomogeneous microstructure shows a lower coercive field compared to the homogeneous one (Fig. 7). The current and previous numerical micromagnetic calculations reveal that the interplay of the magnetostatic and exchange interactions between neighboring grains limit the coercive field considerably. Soft magnetic grains in composite permanent magnets cause a high polarization, and hard magnetic grains induce a large coercive field provided that the particles are small and strongly exchange coupled.\(^{49–53}\)

Micromagnetic calculations, which were obtained for a composite material of nanocrystalline SmCo\(_5\), Nd\(_2\)Fe\(_{14}\)B, and Sm\(_2\)Fe\(_{17}\)N\(_{2.7}\) grains, and \(\alpha\)-Fe as soft magnetic phase, show that remanence, coercivity, and coercive squareness sensitively depend on microstructural features, such as the grain size and the volume fraction of the soft magnetic phase.\(^{47,54}\) Interparticle exchange interactions enhance the remanence by about 60% with respect to noninteracting particles for a mean grain size of 10–20 nm. The remanence enhancement and energy produce increases with decreasing grain size and increases with increasing \(\alpha\)-Fe content. Because of their remarkably high magnetocrystalline anisotropy, novel nitried intermetallic compounds have a large potential for composite permanent magnets.

V. CONCLUSIONS

Rare earth permanent magnets exhibit a complex, multiphase microstructure, which considerably influences the coercivity and the remanence of the magnets. Nd\(_2\)Fe\(_{14}\)B based hard magnets can be distinguished by different processing routes, by microstructural differences, or by the kind of elemental substitution or addition. There exist metallurgical reasons for long range dipolar interaction and short range exchange coupling between neighboring hard magnetic grains. The doping of elements changes the phase relation and favors the formation of new phases. Additional secondary nonmagnetic intergranular phases decrease the remanence and interrupt the magnetic interactions between the grains, thereby improving the coercivity of large grained sintered or hot worked magnets. Soft magnetic secondary phases, such as \(\alpha\)-Fe, destroy coercivity in large grained magnets. The additional intergranular phases partly replace the Nd-rich phase and considerably improve the corrosion resistance of the magnet. Numerical, micromagnetic calculations have shown that microstructural parameters, such as
grain size, misorientation, and distribution of grains and phases control coercive field. The dipolar interactions considerably reduce the coercive field of ideally oriented particles by about 20% with respect to $H_c$ of an isolated particle, and exchange coupling between misaligned grains drastically reduces the coercive field to about 30%–40% of the ideal nucleation field. Contrary to the situation found in large-grained magnets, the strong coupling between the hard magnetic grains is desired in nanostructured, composite rare earth permanent magnets. The excellent hard magnetic properties of isotropically oriented grains are attributed to inter-grain exchange interactions, which enhance the remanence by more than 40% as compared to the remanence of noninteracting particles, if the grain size is in the order of 10–30 nm. The content of soft magnetic phases up to 20% is favorable for increased remanence enhancement and sufficient high coercive fields. The advantage of the nitrided Sm$_2$Fe$_{17}$, compared to Nd$_2$Fe$_{14}$B, is the better temperature stability of the permanent magnetic properties.

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