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Invited paper

Rare earth permanent magnets

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Abstract

A survey is given of the state of the art in rare earth permanent magnet research of materials based on Nd₂Fe₁₄B. The magnetic properties of various types of interstitially modified Fe-rich rare earth intermetallics are discussed, including the possibility to apply these materials in permanent magnets.

1. Introduction

It has been slightly over ten years since Sumitomo Special Metals and General Motors announced the discovery of a novel permanent magnet material based on Nd–Fe–B. The manufacturing of sintered Nd–Fe–B has increased enormously in the last decade and completely superseded the production of Sm–Co type magnets, reaching a share of over 20% of the total global permanent magnet market. Current applications comprise automotive, consumer electronic, computer peripheral, medical, office automation and acoustic applications. Further penetration of Nd–Fe–B in the permanent magnet market is expected thanks to improvements in the quality of the magnets. In the initial stage of development the maximum energy product was close to 240 kJ/m³ with coercivities around 1 MA/m but over the years these values have become considerably improved. In this report it will be highlighted how the improvement in quality has gone hand in hand with a better insight into the physical and chemical mechanisms involved.

Interstitially modified rare earth iron compounds form another class of materials that may find an application as permanent magnets. However, many of these materials are still in the predevelopment stage and the study of their physical properties is still a topic of current interest. For this reason the discussion of these materials will include mainly more fundamental than technological aspects.

2. General principles of the magnetism in rare earth permanent magnets

Important characteristics of the magnetism in rare earth permanent magnets (REPM) are a sufficiently high Curie

temperature, a high magnetization and a high magnetic anisotropy. The first two of these properties are provided mainly by the 3d sublattice whereas the rare earth sublattice is mainly responsible for the latter.

The magnetic anisotropy of the rare earth sublattice is a single-ion crystal field induced anisotropy. A strong magnetic coupling between the rare earth sublattice and the 3d sublattice is required in order to extend the anisotropy to the whole lattice and to preserve this anisotropy at elevated temperatures. In most REPM materials the exchange interaction exceeds the crystal field interaction. In this case crystal field theory leads to a simple expression for the lowest order anisotropy constant K_1 :

$$K_1 = -\frac{3}{2}N_R\alpha_J\langle r^2 \rangle \langle O_{20} \rangle A_{20}, \quad (1)$$

where N_R is the rare earth concentration, α_J the second order Stevens factor, $\langle r^2 \rangle$ the expectation value of the squared 4f radius, A_{20} the second order crystal field parameter, and $\langle O_{20} \rangle$ the expectation value of $3J_z^2 - J(J+1)$. The latter quantity has its maximum value at 0 K but, unfortunately, decreases with temperature as m_R^3 , where m_R is the reduced rare earth sublattice magnetization. For applications of rare earth permanent magnet materials at room temperature and above it is therefore necessary that the rare earth moments experience a strong molecular field that keeps m_R at a sufficiently high level. Because the intrasublattice rare earth interaction is almost negligible, the latter molecular field is mainly due to the intersublattice interaction, and is given by the expression

$$B = n_{RT}M_T, \quad (2)$$

where n_{RT} is the intersublattice coupling constant and M_T the 3d sublattice magnetization. This shows that the magnetic anisotropy at elevated temperatures, in contrast to the anisotropy at 0 K, depends on the 3d sublattice magnetization. It follows from Eq. (1) that $K_1(T=0)$ is the larger, the higher the rare earth concentration. By contrast, in compounds of rare earths and Co or Fe one finds that

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$K_1(T=300)$ reaches a maximum at intermediate concentrations. It can also be seen from Eq. (1) that both the magnitude and the sign of K_1 , via A_{20} , are structure dependent. For permanent magnet applications one needs a unique axis of easy magnetization. This means that the corresponding intermetallic compounds should have hexagonal or tetragonal symmetry and that K_1 has to be positive. For a given sign of A_{20} it is always possible to select a rare earth element having the appropriate sign of the second order Stevens factor to make K_1 positive.

In the discussion of the anisotropy we have not yet included the contribution of the 3d sublattice anisotropy. In some of the permanent magnet materials this latter anisotropy can reach quite appreciable values, as for instance in SmCo_5 . In the latter compound the 4f and 3d anisotropies add constructively. However, in $\text{Sm}_2\text{Fe}_{17}$ the 4f and 3d anisotropies compete and the 3d anisotropy ($K_1 < 0$) exceeds the 4f anisotropy ($K_1 > 0$) in absolute value. For this reason $\text{Sm}_2\text{Fe}_{17}$ in pure form is not suited as permanent magnet material. Constructive interaction of both sublattice anisotropies is found in $\text{Nd}_2\text{Fe}_{14}\text{B}$ above $T = 142$ K. Below this temperature higher order terms of the Nd sublattice anisotropy become important and lead to a deviation of the easy magnetization direction from the c-axis. A more detailed description of exchange and anisotropy in these materials can be found in Refs. [1–3].

Permanent magnets are characterized by an extremely wide hysteresis loop, which prevents demagnetizing of the magnet when subjected to strong demagnetizing fields in a magnetic device. The important quantity here is the coercivity H_C (H_{CB}) defined as the demagnetizing field at which the magnetic polarization J (magnetic induction B) becomes zero. The coercivity is intimately connected with the total anisotropy via the relation [4]:

$$H_C = 2\alpha K_1/M_s - N_{\text{eff}}M_s. \quad (3)$$

The microstructural parameter α expresses the fact that alignment of the fine magnetic particles in a magnet body, and the nature and size of the defect regions in which nucleation or pinning of domain walls can take place, are of prime importance. The microstructural parameter N_{eff} takes account of the presence of demagnetizing fields.

3. Research and development of $\text{Nd}_2\text{Fe}_{14}\text{B}$ type magnets

Research and development of $\text{Nd}_2\text{Fe}_{14}\text{B}$ type magnets has been focused on three main aspects:

(1) Sintered magnets with enhanced energy products.

In most of the earlier sintered magnets of this type the composition of the starting alloys was chosen strongly off-stoichiometric in order to suppress the occurrence of primary Fe crystals during solidification of the melt. These primary Fe crystals occur generally near the centre of the grains of the main phase. Because they will act as nucle-

Fig. 1. Schematic representation of a microstructure of a sintered NdFeB type magnet prepared from a precursor alloy of typically off-stoichiometric composition.

ation centers for Bloch walls, and hence will reduce the coercivity, they have to be avoided during casting already as far as possible. In a typical microstructure of magnets prepared from such off-stoichiometric alloys (Fig. 1) one can discern large grains surrounded rather nonuniformly by the eutectic intergranular material. The latter does not contribute to the remanence B_r . Because the energy product depends on the squared remanence, the corresponding magnets had comparatively low energy products BH_{max} , typically 300 kJ/m^3 [3]. In the last few years much attention has been paid to finding means of applying alloys of more stoichiometric composition. Numerous recent investigations have shown that the application of various types of tiny amounts of additives (W, Mo, Nb, V, Co, Al, Ga, Cu) can suppress the formation of primary Fe to some extent, largely inhibit grain growth during sintering and lead to a more uniform distribution of the nonmagnetic intergranular material around the grains. On a laboratory scale permanent magnets can be manufactured having energy products around 400 kJ/m^3 [5]. A typical example of such a magnet is shown in Fig. 2. There is little room left for much improvements since the theoretical upper limit at room temperature for $\text{Nd}_2\text{Fe}_{14}\text{B}$ is about 500 kJ/m^3 . One possibility for improvement is to start from an annealed almost single phase alloy and blend the corresponding powder with small amounts of powder of a nonmagnetic

Fig. 2. Demagnetization curves for energy product enhanced and coercivity enhanced types of permanent magnets.

intermetallic compound from which the intergranular material is formed after sintering. More details can be found in Ref. [5].

(2) Sintered magnets with enhanced coercivity.

The application of permanent magnets in several types of electric motors implies use temperatures which may reach values of about 200°C. The main problem here is the strong temperature coefficient of the coercivity of NdFeB type magnets compared to SmCo type magnets. Several investigations have focused on replacing the more expensive SmCo magnets by improving the coercivity at the cost of the remanence of NdFeB type magnets. The coercivity model as expressed by Eq. (3) offers two possible avenues. If the remanence is not at a premium one may use alloy compositions less close to the stoichiometric composition than in case (1), and a different choice of the additives to reach microstructures of sintered magnets with more favourable α and N_{eff} values [6]. A further coercivity improvement can be reached by increasing K_1 . This can be done by substituting Dy or Tb for Nd in $\text{Nd}_2\text{Fe}_{14}\text{B}$, because these elements have larger values of $\alpha_1 \langle O_{20} \rangle$ in Eq. (1). Room temperature data for a coercivity enhanced permanent magnet are included in Fig. 2.

(3) Bonded magnets.

For many years it has not been possible to prepare coercive powders from cast NdFeB type alloys suitable for application in resin bonded magnets. Success in this area is intimately linked to the attainment of very small grain sizes by means of the so-called HDDR process (Hydrogen Decrepitation Desorption Recombination). When heating $\text{Nd}_2\text{Fe}_{14}\text{B}$ in hydrogen gas the initially formed hydride of this compound decomposes into a very fine grained mixture of Nd-hydride, Fe_2B and Fe. Subsequent heating under vacuum transforms the Nd-hydride into Nd, which then reacts via solid state diffusion to form very fine grained $\text{Nd}_2\text{Fe}_{14}\text{B}$. When very small amounts of additives (Zr or Ga) are used in the starting alloy it is possible to prepare anisotropic powder in which the HDDR grains are aligned to some extent because they have grown in a common direction corresponding to the parent grain in the original alloy [7,8]. This memory effect can be explained by the presence of tiny regions in the original alloy that have escaped hydrogen absorption and which serve as nucleation centres for the formation of the HDDR grains [5].

4. Interstitially modified permanent magnet materials

It has already briefly been mentioned that the Curie temperature of R_2Fe_{17} compounds can be strongly increased by the formation of interstitial solid solutions of nitrogen and carbon. To a somewhat lower extent this is also the case for compounds of the type $\text{RFe}_{12-x}\text{M}_x$ where

M is any of the elements Ti, V, W, Mo or Si. The interstitially modified 2:17 and 1:12 compounds derive their potential as permanent magnet materials less from the Curie temperature enhancement than from the anisotropy enhancement. In permanent magnet materials based on $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ it is primarily the fact that a high magnetic anisotropy is still present at high temperatures which makes this material promising for high-temperature applications, replacing the more expensive SmCo type materials. The high magnetic anisotropy is due to the effect of the interstitial atoms. These atoms occupy positions very close to the R atoms, which leads to strong changes of the A_{20} values in Eq. (1). The reason for these changes is the following: A detailed experimental and theoretical study has shown that the A_{20} values are primarily determined by the degree of asphericity of the on-site valence electrons of the rare atoms [9,10]. These asphericities are strongly changed by bonding with the valence electrons of the interstitial atoms. Information of strong bonding can be derived from results of NMR experiments performed on the compounds before and after charging with interstitial atoms. Results of ^{89}Y spin echo NMR [12] have been used to study the Y hyperfine field in Y_2Fe_{17} as a function of increasing occupancy of the interstitial sites by C, N or H atoms. All these atoms give rise to strong volume expansions, and in all these cases there is only a very modest increase of the Fe moments. The strong decrease of the Y hyperfine field found for the carbides and nitrides (Fig. 3) can therefore be taken as experimental evidence for strong bonding effects. In the case of interstitial hydrides these bonding effects are apparently only very modest. This agrees with the observation that strong anisotropy changes are restricted to interstitial nitrides and carbides.

It is interesting to note that the concomitant changes of A_{20} are large but different in the 2:17 and 1:12 com-

Fig. 3. Dependence of Y hyperfine fields on interstitial site occupation by H, N and C atoms in Y_2Fe_{17} . The results show the change in hyperfine field when $n = 1, 2$ or 3 of the available interstitial sites become occupied.

Fig. 4. Schematic representation of the location of the interstitial atoms around the rare earth atoms in 2:17 and 1:12 type compounds.

pounds. The reason for this is the different arrangement of the interstitial atoms in the two crystal structures, as may be illustrated by means of Fig. 4, and as will be further discussed below.

Because A_{20} takes the form of an electric field gradient at the 4f site it is possible to use rare earth Mössbauer spectroscopy as a local probe of this field gradient. This technique has been proven to be most useful for studying the behaviour of the macroscopic crystal-field induced anisotropy in rare earth materials. From the quadrupole splitting of the corresponding ^{155}Gd Mössbauer spectra [10] it was derived that the value of the electric field gradient at the nuclear site (V_{zz}) in R_2Fe_{17} compounds changes upon nitrogenation from 4.4 to 16.2 (in units of 10^{21} V m^{-2}). By contrast, the strong nitrogen induced enhancement of the field gradient is accompanied by a sign reversal in the case of the 1:12 compounds, where V_{zz} changes from 1.6 to -21.3 [12]. Changes of similar magnitude and sign are expected for A_{20} . This implies that for permanent magnet purposes R elements having a dif-

ferent sign of α_j must be employed in the 2:17 nitrides (Sm) than in 1:12 nitrides (Pr or Nd).

At present the interstitially modified materials are still under development. A major problem is their thermodynamic instability at high temperatures, which hampers application of these materials in fully dense sintered magnets.

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