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REVIEW ARTICLE

Permanent magnets and hard magnetic materials

H R Kirchmayr

Institute for Experimental Physics, Technical University Vienna,
Wiedner Hauptstrasse 8–10, A-1040 Vienna, Austria

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Abstract. This review deals with the definition and development of hard magnetic materials with special emphasis on more recent developments in this field. After discussing the fundamental properties of all hard magnetic materials, based on the intrinsic and extrinsic properties, some remarks on the history of hard magnetic materials and permanent magnets are given. The important hard ferrites are only briefly treated. Emphasis, however, is laid on the rare earth (RE) intermetallics and the hard magnetic materials based on them. Experimental techniques for the measurement of the basic properties of hard magnetic materials, e.g. the ordering temperature, the magnetization, the anisotropy field, the physical and technical hysteresis loop and the properties, derived from this loop are discussed.

Examples of modern permanent magnets, based on RE–cobalt alloys, on RE–Fe–B alloys and RE–Fe–nitrides, etc are explained. The principles of the production of sintered and bonded magnets are given. Finally some typical applications of these modern permanent magnets are discussed with respect to the different properties of the materials.

Future developments and the possibility of superconducting permanent magnets are briefly discussed. Concluding remarks are concerned with the possibility and necessity of still larger energy products at elevated temperatures and the benefits of high-tech permanent magnets for modern and energy saving devices.

1. Introduction

Permanent magnets are the basis of an ever increasing number of devices of modern life. The development of permanent magnets during this century has shown a continuous increase of quality, strength and the ability to store energy, characterized by the so-called energy product $(\mathbf{B} \cdot \mathbf{H})_{\max}$. A permanent magnet can be considered as a passive mechanical device analogous to a spring which also stores mechanical energy. Therefore the magnetic energy which can be used, namely $(\mathbf{B} \cdot \mathbf{H})_{\max}$, is essential. For electromechanical devices usually the volume, in which a given magnetic field can be established, is important. Different technical requirements on the permanent magnets therefore have to be met for different applications. Furthermore, many devices operate at elevated temperatures. For this multitude of applications special permanent magnets have been tailored in recent years. In this review article we discuss the possibilities and limitations of modern permanent magnets.

2. Fundamentals

2.1. Introduction

Magnetized bodies, such as the traditional horseshoe magnet or a compass needle, exert a force on another magnet or a bar of iron, etc. This was for centuries the most important property of a magnet. In the last century formulas have been established, similarly to electrostatics, for these forces, assuming (negative and positive or North and South) ‘poles’ acting on each other. These forces are proportional to $1/r^2$ —similar to Coulomb’s law of electrostatics. Since Maxwell, however, we know that magnetism and electrostatics are not equivalent, because no magnetic monopoles exist, resulting in the equation $\text{div} \mathbf{B} = 0$. The correct description of magnetism is based on currents—either ‘free currents’ (which can be directly measured) or ‘molecular’ currents (already proposed by Ampère). In the case of permanent magnets these can be identified with atoms with inner unfilled shells, as present in the 3d metals Fe, Co or Ni or the 4f metals, i.e. the rare earth (RE) metals, Ce to Yb.

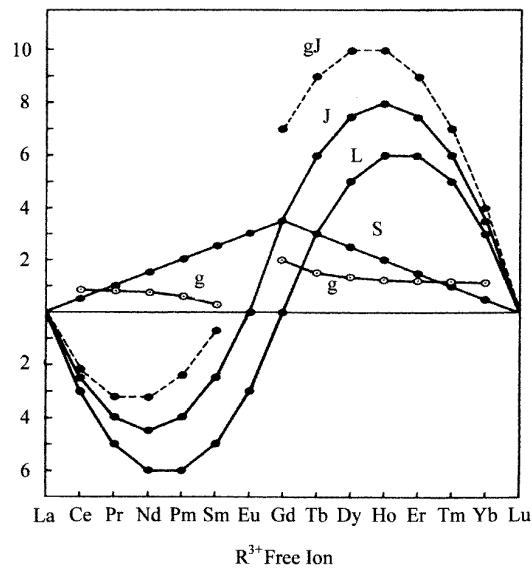


Figure 1. The theoretical construction of the gJ values of the trivalent lanthanides (Kirchmayr and Poldy 1979).

2.2. Magnetic moments

Modern quantum physics is able to explain and calculate the magnetic moments of atoms, ions and molecular complexes. Modern permanent magnets contain either ions, as in the ferrites, or atoms, embedded in a sea of electrons, as in the metallic Sm-Co or Nd-Fe-B magnets. In these magnets the interaction of the magnetic moments of the 3d elements (Mn, Fe, Co and Ni) with the magnetic moment, associated with the RE elements constitute the basis of the magnetic ordering and of the magnetic crystal anisotropy, essential for these modern magnets. The magnetic moments of the 3d atoms are mainly based on the spin of electrons, because the angular magnetic moments are usually quenched and therefore annihilated.

In figure 1 the coupling of the 4f electrons of the rare earth metals (in the trivalent state), the resulting quantum numbers and the total magnetic moment gJ are depicted. The continuous change of the values is remarkable. The light RE La-Gd is clearly distinct from the heavy RE Gd-Lu. Mainly the light REs are of technical importance, but all REs are the scope of scientific investigations.

2.3. Energy relations

Magnetic systems must be stable (or at least metastable) not only with respect to the phase stability, but also with respect to the magnetic energy stored in the material. Therefore, in these systems the magnetic energy W , which is given by

$$W = - \int_V \mathbf{B} \mathbf{M} dV$$

where $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$, is an essential part of the total energy (see Craik 1995, p 313) (\mathbf{B} is the magnetic induction or magnetic field in the material, \mathbf{M} the magnetization, \mathbf{H} the internal field, equal to the external or applied field \mathbf{H}_0 corrected by the demagnetizing field $\mathbf{H}_D = -N\mathbf{M}$ due

to the variation of the magnetization and the geometry of the sample: $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_D$: The demagnetizing factor N varies between 0 and 1 and is 1/3 for a spherical sample. For cylindrical samples see Chen *et al* (1991). Because of their small contribution to the total energy, usually, however, magnetic energies (in particular the above mentioned Zeeman energy due to the external field including the shape anisotropy of the sample) are not taken into account as an additional term for the free enthalpy of metals and alloys, which defines the stability of alloys and phases. However, the appearance of long-range magnetic order is caused by magnetic exchange interactions described phenomenologically in terms of an exchange field $\mu_0 \mathbf{H}_{EX}$ (of about 100 T or more for Fe-Co- and Ni-based alloys metals) that yields, together with the magnetization, the magnetic exchange energy as a significant contribution to the total energy and influences the volume and the stability of the magnetic compounds with respect to their theoretically calculated paramagnetic counterparts. As an example, the magnetic moment-volume instabilities appear to be responsible for the magnetic, magnetovolume and structural properties of Invar-type alloys (Wassermann 1991).

2.3.1. Free energy and free enthalpy. The free energy F and the free enthalpy G are usually defined as $F = U - TS$ and $G = \mathcal{H} - TS$, where U is the inner energy and \mathcal{H} is the enthalpy ($\mathcal{H} = U + PV - \mu_0 \mathbf{H} \mathbf{M}$) (T and S are the temperature and the entropy, respectively). Since the contributions of the volume changes $P\Delta V$ are usually small, the free energy F is a good approximation for the free enthalpy G . The magnetic energy, just defined above, is not taken into account for ordinary metallurgical considerations.

2.3.2. Stable and metastable systems. Stable and metastable systems are important for the preparation of alloys and compounds. A permanent magnet can usually be regarded as a metastable system, although it may be stable as an alloy. By thermally demagnetizing a permanent magnet, i.e. heating beyond the Curie point and subsequent cooling, the stable 'non-magnetic' (or more correctly magnetically compensated) system, consisting of a multitude of small (Weiss-) domains, is obtained. The interplay between different magnetic configurations and the activation energies between different magnetic states determines the actual magnetic configuration. This interplay is reflected in the so-called hysteresis loop.

2.4. Magnetic anisotropy

Magnetic anisotropy can be described in the following manner (Kirchmayr 1991). The mean magnetic moment of a ferro- or ferrimagnetic substance is directed, in the absence of an external magnetic field, in the crystallographic direction, in which the absolute minimum in the free energy F is achieved. This direction is called the easy magnetization direction or 'easy axis'. A part of the total free energy therefore depends on the direction of magnetization with respect to the different crystallographic directions and is called the magnetocrystalline free energy,

F_a , or the 'magnetic anisotropy'. Usually, F_a is expressed in terms of simple sine or cosine functions. For hexagonal crystals,

$$F_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K'_3 \sin^6 \theta \cos 6\phi$$

and for tetragonal crystals,

$$F_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^4 \theta \cos 4\phi$$

where θ is the angle between the c -axis and the vector of magnetization, ϕ is the angle between the projection of the magnetization vector in the basal plane of the crystal and one of the a -axes. K_1 , K_2 , K_3 , and K'_3 are the coefficients of anisotropy in SI units, J m^{-3} , or the alternative cgs-emu unit, G Oe, where one MG Oe is 7.9577 kJ m^{-3} or approximately 8 kJ m^{-3} . The anisotropy constants reflect the magnetic anisotropy only phenomenologically and have no direct connection with the physical origin of magnetic anisotropy. The basis of the magnetic ordering and the magnetic anisotropy in metallic compounds of rare earth RE metals with transition metals T are the RE-RE, T-T, and RE-T interactions. In the $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds the situation is even more complex, because of the presence of a third element. Naturally, in a metallic system most of the interactions are mediated by the electrons, especially the conduction electrons, which means that the full band structure has to be taken into account. While the RE-RE anisotropy is mainly governed by crystal field effects, the T-T and RE-T anisotropies are complex and less well understood. All these interactions are also responsible for other magnetic transitions and peculiarities, such as first-order magnetization processes, critical fields, non-collinearity of ferrimagnetic structures, etc.

If an external magnetic field H is applied to a crystal, an additional term appears in the free energy F , which is given by

$$F = F_a - M_s H \cos(\theta - \beta)$$

where M_s is the saturation magnetization, β is the angle between H and the c -axis, and $(\theta - \beta)$ is the angle between M_s and H . In this equation the stray field energy, which depends on the size and shape of the sample, has been neglected. Equilibrium is achieved, when F reaches a minimum, hence

$$\partial F / \partial \theta = \partial F_a / \partial \theta + M_s H \sin(\theta - \beta) = 0$$

or

$$-\partial F_a / \partial \theta = M_s H \sin(\theta - \beta) = |M \times H|$$

where $M \times H$ is the torque exerted by the crystal anisotropy and is counterbalanced by the external field. For small deviations from the easy axis, $\Delta\theta = 0$, the term

$$(1/M_s) \cdot (\partial^2 F_a / \partial \theta^2)|_{\Delta\theta=0} = H = H_A$$

is equivalent to a field, called the anisotropy field, H_A . As can be seen from the above discussion, the anisotropy field, H_A , is deduced from small deviations from the easy axis and therefore for small applied fields. It must be distinguished from the anisotropy field, H_A^* , which can be directly measured by the singular point detection (SPD) method, as described below.

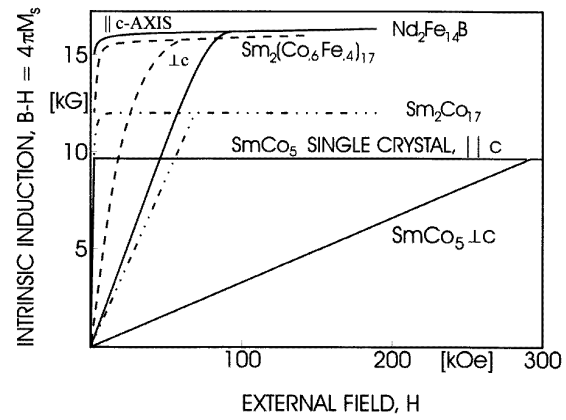


Figure 2. Easy- and hard-axis magnetization curves of several high-anisotropy compounds on which practical permanent magnets are based (Strnat 1988, p 149).

2.4.1. Intrinsic properties. The magnetic anisotropy is intimately linked to the crystal structure. Therefore only non-cubic crystal structures are interesting for permanent magnets. Mainly hexagonal and tetragonal crystals are used for permanent magnets.

Figure 2 shows the easy- and hard-axis magnetization curves of several high-anisotropy compounds, on which practical permanent magnets are based. The discovery of such a curve for YCo_5 (see figure 3) by Hoffer and Strnat in 1966 was the starting point of all RE magnets. Usually, if new alloys are prepared, the crystal structure must be determined by x-ray diffraction. Then the intrinsic magnetic properties, e.g. the Curie point, the magnetization versus field and temperature etc, are measured. If there seems to be scope for a hard magnetic material, a powder of the alloy is prepared and aligned in a magnetic field. If this is possible, the anisotropy field is determined, either on a polycrystal or, if possible, on a small single crystal. In the case of the Nd-Fe-B magnets, however, this sequence was reversed and magnets were available before the correct composition ($\text{Nd}_2\text{Fe}_{14}\text{B}$) and the crystal structure were known.

2.4.2. Extrinsic properties. Extrinsic properties are those, which depend on the history of the sample. This includes anything depending, e.g., on the size or the texture of the grains and is especially reflected in the hysteresis loop. Most of the development work takes place in this area of extrinsic properties and is necessary to produce and establish a practical permanent magnet after the initial optimistic finding of a new hard magnetic material. The extrinsic properties can be modified by heat treatments, mechanical work, surface treatments of the alloy powders and of the finished magnets, etc.

3. Experimental techniques

3.1. Introduction

Some typical experimental techniques for characterizing magnetic materials and permanent magnets are listed here,

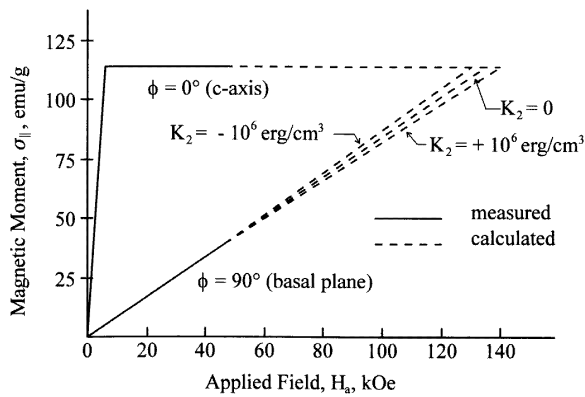


Figure 3. The measured and calculated room temperature magnetic moment of YCo₅ versus applied field in its easiest and hardest magnetic directions (Hoffer and Strnat 1966, from Kirchmayr 1991).

but not treated in detail. Some references for further reading are given. Many very important properties are still not covered by international standards.

3.2. Ordering temperature

The most important ordering temperature to be determined is the Curie temperature. For first scans usually the susceptibility of a small sample of any shape is measured. This can be done in the same kind of susceptometer which is used for detecting superconductivity. In the temperature region above room temperature, slightly larger samples in an appropriate furnace equipped with pick-up coils are used. More sophisticated methods include the measurement of the magnetization versus temperature and extrapolation of the magnetization to zero. If an accurate determination of the ordering temperatures or of other magnetic transition temperatures is necessary (accuracy better than $\pm 1^\circ\text{C}$), in some cases very sophisticated methods are essential.

3.3. Magnetization

For measuring the magnetization of hard magnetic materials, fields in the range of 5–10 T are usually necessary. This is now no problem in research laboratories, where superconducting coils abound. In industry, however, the accurate measurement of the magnetization approaching saturation, may pose a problem. A special solution is the use of pulsed fields in excess of 10 T. The development of accurate techniques to measure saturation magnetization in transient fields is the subject of some projects on a pan-European level. For the measurement of magnetization between 4 K and 700 K commercial equipment is available.

3.4. Anisotropy field

The anisotropy fields H_A and H_A^* , as defined above, are one of the most important intrinsic properties of modern permanent magnets. H_A^* defines the upper limit for the intrinsic coercive field H_c or $M H_c$, which is, however,

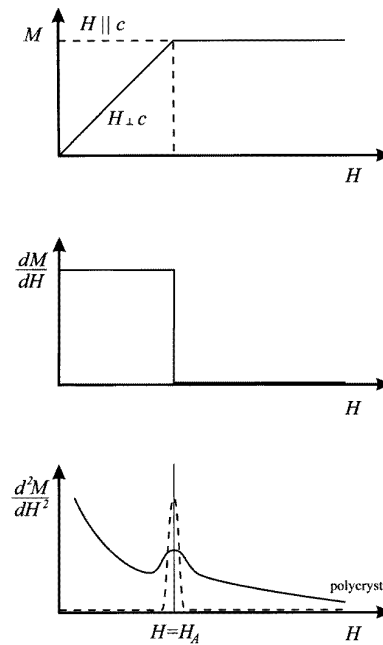


Figure 4. Principle of the SPD (singular point detection) method with M versus H for H parallel and perpendicular to the c -axis (upper), and the first (middle) and second (lower) derivatives (Kirchmayr 1991).

never approached in practical magnets. H_A is sometimes called the nucleation field, H_A^* the saturation field.

3.4.1. Extrapolation techniques. By measuring the magnetization M versus field H in small fields, which can be done in ordinary electromagnets, H_A can be determined by extrapolation (see figure 3). In many cases even with an aligned powder, measured with respect to different directions, a rough idea of the anisotropy field H_A can be gained. The physically important field, however, is H_A^* , which has to be measured in an appropriately high magnetic field, which usually necessitates the use of superconducting or pulsed magnets.

3.4.2. Direct determination by SPD (singular point detection). The SPD method has its merits because it may be applied on polycrystalline samples and in pulsed fields. It yields the anisotropy field H_A^* directly. In figure 4 the principle of the SPD method is given. Many different materials have been measured with respect to the anisotropy field H_A^* versus temperature (see e.g. Kirchmayr 1991 or Asti and Solzi 1994).

3.5. Hysteresis loop

Two different hysteresis loops are available, namely the magnetic induction B versus H and the magnetization M versus H . Both are directly connected by the formula $B = \mu_0(H + M)$. This necessitates, however, knowledge of the internal field $H = H_0 - NM$ via the correction of the external field H_0 by the strayfield NM which may be difficult to determine for specimens of arbitrary shape in an

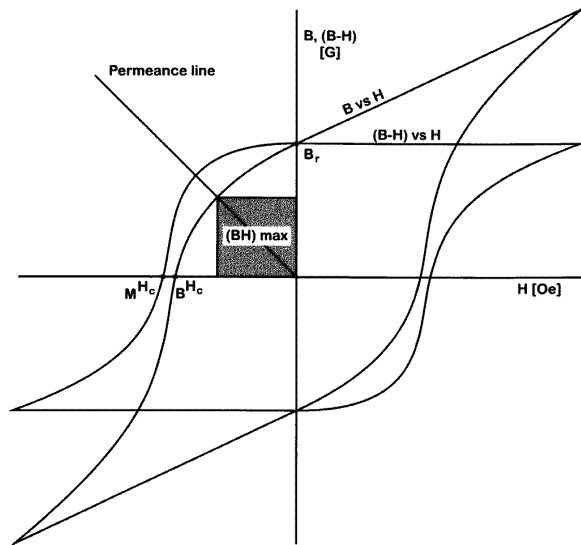


Figure 5. The hysteresis loop in the B/H and M/H representation.

open magnetic loop. Only effective demagnetization factors N can be derived for samples with a geometry deviating from ellipsoids of revolution (Chen *et al* 1991).

3.5.1. Static methods. Using commercially available standard techniques one can usually determine the hysteresis loop in fields up to 2 T. This is sufficient for detecting the virgin curve and to measure the second quadrant in samples, premagnetized to saturation in pulsed fields. For a true measurement of the full hysteresis loop, fields of 5 T to 10 T are necessary, which can be produced by superconducting magnets or in pulsed coils. (The few specialized laboratories, e.g. in Grenoble or Tallahassee, for creating steady magnetic fields in this range without use of the mentioned methods are here neglected.)

3.5.2. Dynamic methods. By dynamic methods we mean non-static fields. These can be achieved either in installations similar to the Amsterdam installation or in pulsed fields. In the first case access to an energy supply in the megawatt range is necessary, in the latter case the energy may be stored in a large condenser bank with typically 100 kJ. Dynamic methods are more subtle with respect to the size of the samples and the data acquisition, however, these problems have been solved to a large extent.

3.5.3. Temperature dependence of the hysteresis loop. The temperature dependence of the hysteresis loop is only measured for scientific reasons or if a permanent magnet has to be used at elevated temperatures. Since, however, permanent magnets always operate at elevated temperatures in power applications, e.g. medium sized motors or in the hood area of automobiles, the hysteresis loop at elevated temperatures becomes more and more important. Naturally such a measuring problem is more demanding, but can be solved.

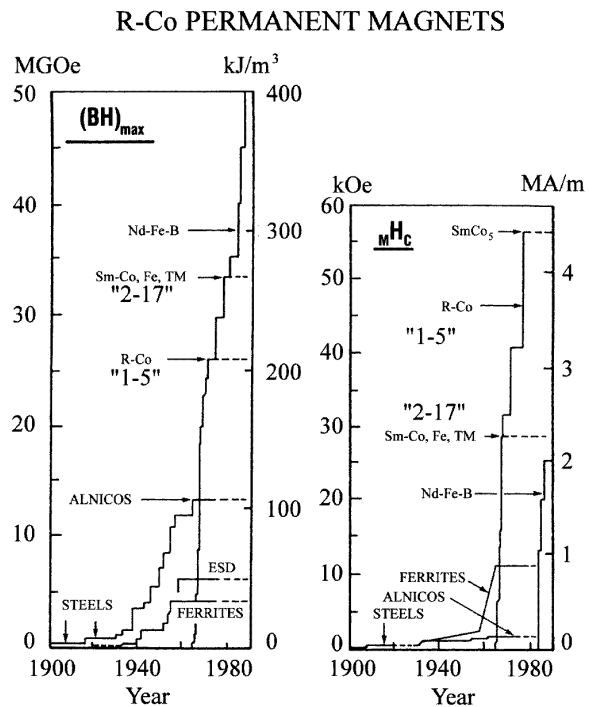


Figure 6. Chronology of magnet development since 1900: best reported laboratory values for the static energy product and intrinsic coercive force (Strnat 1988).

3.5.4. Technical hysteresis loop ($B-H$ curve). The main features of the hysteresis loop are given in figure 5. Two different plots have to be distinguished, namely the B/H or M/H plot. For most technical applications the second quadrant is essential. Therefore in most technical leaflets on permanent magnets only the second quadrant of the B/H representation is given. For a deeper understanding of the physical phenomena occurring in permanent magnets, however, we need the full hysteresis loop, which sometimes is difficult to measure because of the large magnetic fields necessary. Commercial equipment is available for characterizing permanent magnets, however, this equipment is usually not sufficient for scientific investigations.

3.5.4.1. Energy product. The most important single value to characterize a technical permanent magnet is the so-called energy product. This is defined in the second quadrant of the B versus H hysteresis loop (see figure 5). Another quantity of great importance is the intrinsic coercive force M^H_c or I^H_c . In fact the development of permanent magnets during the last century was mainly directed to increase the intrinsic coercive force and therefore also the energy product. This tremendous success is visible in figure 6.

3.5.4.2. Working point. Figure 5 also shows the working point, which is the intersection of the permeance line with the B/H hysteresis loop. The working point in an actual device should be near the ideal working point, defined by

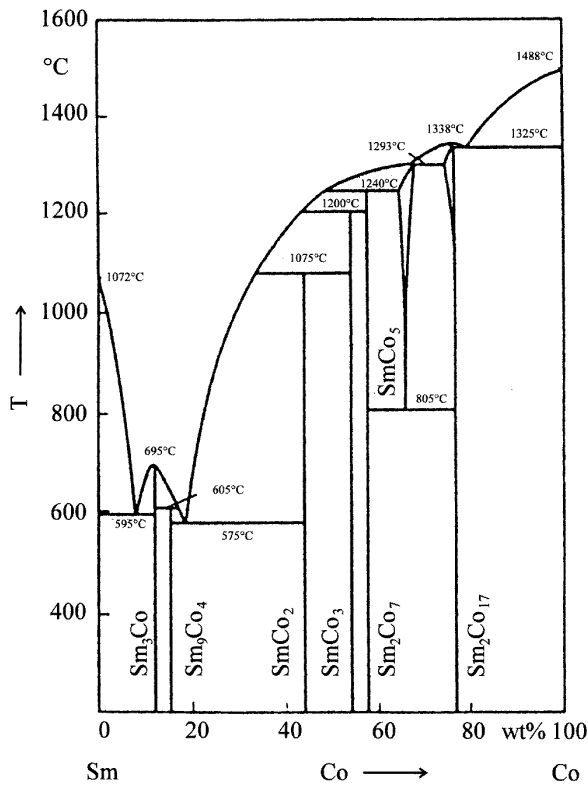


Figure 7. Phase diagram of the Sm–Co system (Kirchmayr and Burzo 1990, p 3).

the energy product, if full use of the magnetic material with respect to the energy stored in the magnet is to be made. In practice, however, many deviations from this ideal working point are necessary because of the design and production of the device and also because of commercial considerations.

4. Magnetic materials for permanent magnets

4.1. Introduction

Permanent magnets have been the subject of materials science long before the term ‘materials science’ was known. Natural loadstone, the mineral magnetite (Fe_3O_4), was known to the ancient Greeks. Carbon steels as permanent magnets have been exclusively used as permanent magnets since 1200 until the end of the 19th century and are sometimes still used today. The status of magnets in 1950 is given in the classic book by Bozorth (1951). Modern permanent magnets, however, are the result of science, research and innovation of the 20th century (see e.g. McCaig and Clegg 1987, Wohlfarth and Buschow 1988, Evetts 1992, Buschow 1994, Campbell 1994, Grandjean *et al* 1995).

4.2. Iron and cobalt steel

Iron-based tungsten steels (up to 6% W) had been invented at the end of the 19th century. By 1917 cobalt steels as permanent magnets had been discovered in Japan. They can contain up to 40% Co, but mostly 35% Co is used.

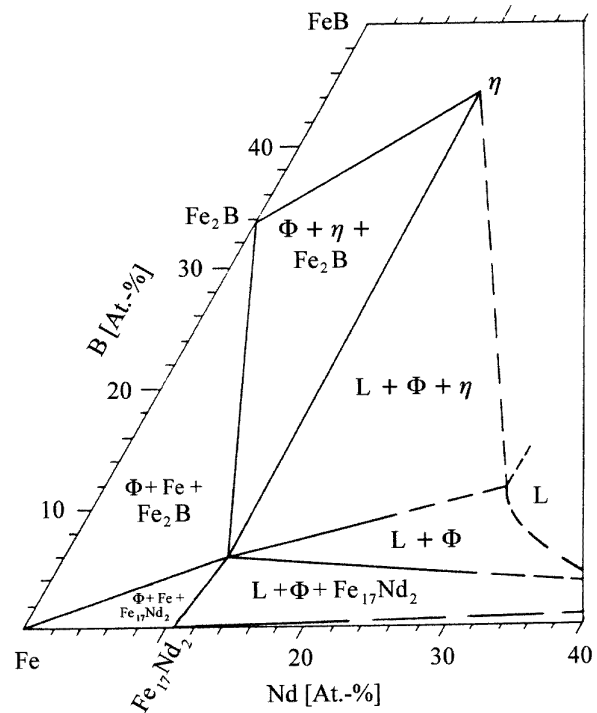


Figure 8. Isothermal section of Nd–Fe–B at 1000°C (The phase ϕ is $\text{Nd}_2\text{Fe}_{14}\text{B}$) (Schneider *et al* 1987).

In an annealed state these steels can be hot worked and machined. To achieve coercivity the steel is heat treated in the austenite region and quenched, therefore yielding martensite. The resulting magnet is brittle and cannot be machined. Few uses are left for these materials.

4.3. Nickel and cobalt alloys

In 1931 Mishima invented the Al–Ni–Fe and Al–Ni–Co–Fe magnets, which are usually known as ‘Alnicos’, irrespective of whether they contain Co or whether they are isotropic or anisotropic. They can be made by casting and by sintering. The cobalt content varies between 12 and 30%. With increasing Co content the coercivity increases. A variety with the composition 7 Al, 14 Ni, 34 Co, 5 Ti, 5 Cu, balance Fe (wt %) achieves by precipitation hardening and field annealing an energy product of up to 8 MG Oe and is therefore called ‘Alnico 8’. Some Alnicos are still produced, but in most cases have been replaced by ferrites and RE magnets.

4.4. Oxides

The most important oxide used in permanent magnets is Ba-hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) and related compositions. Discovered in 1950 in the Philips laboratories, these materials revolutionized the use of permanent magnets in everyday life. An overview of ferrite magnets can be found in the literature (e.g. McCurrie 1994). The production of ferrite magnets surpasses any other magnet material in volume terms, however the production of RE-based permanent magnets is slowly approaching that of ferrites with respect to the total value.

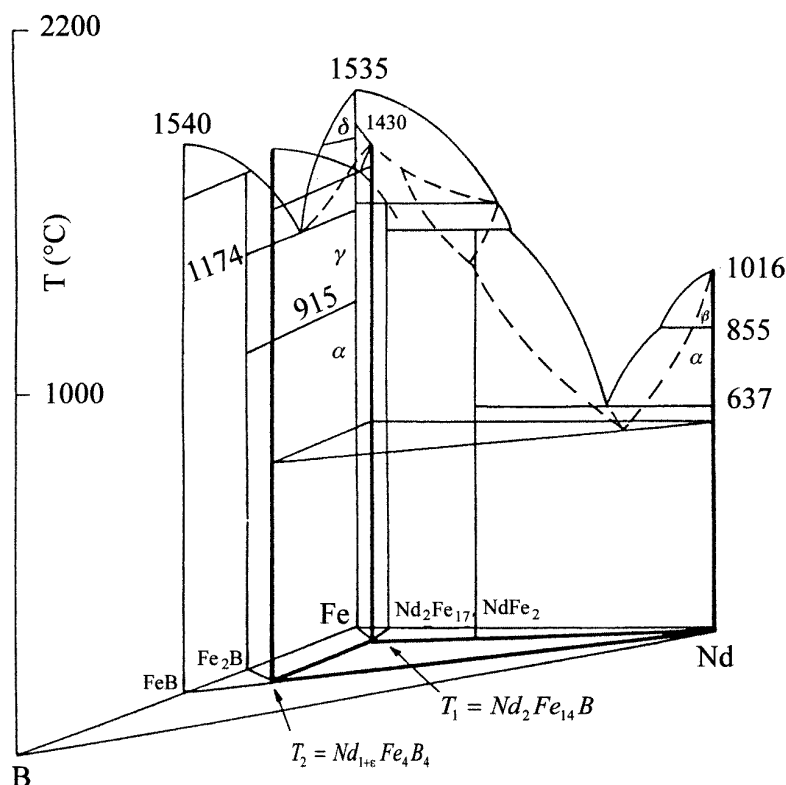


Figure 9. Phase diagram of Nd-Fe-B system (Burzo and Kirchmayr 1989).

4.5. Rare earth intermetallic compounds

Rare earth (RE) intermetallics have been used since 1907 as flint stones. The research on RE alloys and intermetallics was slow until the end of the Second World War, when pure RE metals became available, partly because of research on the actinides. These are chemically and metallurgically similar to the REs and have mainly been investigated at the Ames Laboratory, Iowa. Systematic studies on RE alloys and compounds for properties related to their use in permanent magnets have been performed since the 50s in the USA. Hubbard and Adams (Naval Research Laboratory), Nesbitt, Wernick and Geller (Bell Labs), Wallace (University of Pittsburgh) and Strnat (Wright-Patterson Air Force Base, Dayton) have been major forces in these studies which culminated in the finding of the large crystal anisotropy of YCo_5 (see figure 3).

4.5.1. Systematics of rare earth intermetallics. The magnetic properties of the RE alloys with the 3d elements Mn, Fe, Co and Ni have been the subject of many investigations. A systematic compilation gives more than 3500 references (Kirchmayr and Burzo 1990). No compounds are known between the RE elements and the 3d elements Ti, V and Cr. The 3d elements Mn, Fe, Co and Ni, however, form literally thousands of intermetallic compounds with the RE elements. Modern permanent magnet alloys are located within this area. Furthermore many modern magnetic recording materials are also RE-3d

intermetallic compounds. Seen with the eyes of a crystal chemist, the RE-intermetallics show many interesting features with respect to phase stability, stoichiometry and crystal structures. By no means all existing phases and prospective magnet alloys are known.

The phase diagram of the important system Sm-Co is shown in figure 7. The part of the phase diagram of Nd-Fe-B which is relevant for Nd-Fe-B magnets is shown in figure 8. A representation of the Nd-Fe-B system including temperature is given in figure 9.

4.5.2. YCo_5 and related compounds. The structure of YCo_5 (and most other RECo_5 compounds, including SmCo_5 , which is the most important of all RECo_5 compounds) is the well known CaCu_5 structure (see figure 10). Because of its hexagonal structure strong magnetic anisotropy is possible. Starting from YCo_5 (or SmCo_5) many different 1:5 compounds or pseudo-binary compounds of the general formula $(\text{RE}^1\text{RE}^2)(\text{M}^1\text{M}^2)_5$ have been prepared and magnetically characterized (RE^x = rare earth metal, M^y = 3d metal, especially Mn, Fe, Co or Ni) (see Kirchmayr and Burzo 1990).

4.5.3. Y_2Co_{17} and related compounds. The crystal structure of the $\text{Th}_2\text{Ni}_{17}$ -type and $\text{Th}_2\text{Zn}_{17}$ -type structures is given in figure 11; the position of carbon (C) or nitrogen (N) as a possible interstitial is also shown. The basic structures are important for magnets of the type ' $\text{Sm}_2\text{Co}_{17}$ ', while the interstitials form hard magnetic

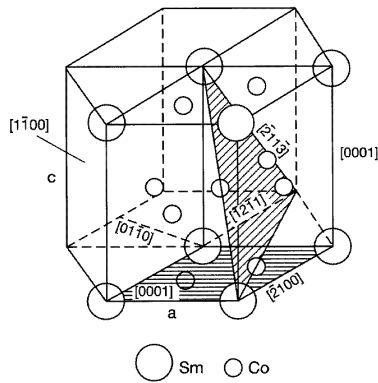


Figure 10. Crystal structure of SmCo_5 (CaCu_5 -type). The predominant slip plane is the (0001) plane with a slip direction parallel to $[2110]$.

materials based on ' $\text{Sm}_2\text{Fe}_{17}$ '. Also in this case many different 2:17 compounds or pseudo-binary compounds of the general formula $(\text{RE}^1\text{RE}^2)_2(\text{M}^1\text{M}^2)_{17}$ have been prepared and magnetically characterized.

4.5.4. $\text{Nd}_2\text{Fe}_{14}\text{B}$ and related compounds. In 1935 Drozzina and Janus reported in a short note the high coercivity of Nd-Fe alloys (probably with an impurity of B). This finding was neglected. The phase diagram of Nd-Fe-B was investigated by Chaban *et al* (1979) and a phase near the composition 2:14:1 was reported, but no magnetic measurements have been made. In 1984 work by Sagawa *et al* opened the field of sintered Nd-Fe-B magnets. Soon afterwards the composition and crystal structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ was confirmed independently by several groups. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure, which is identical to the $\text{Nd}_2\text{Fe}_{14}\text{C}$ structure, is shown in figure 12.

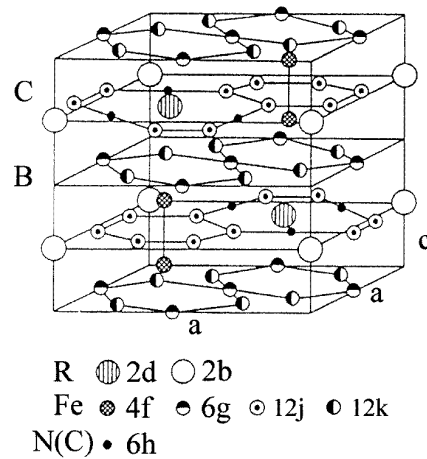
The anisotropy field H_A^* of different $\text{RE}_2\text{Fe}_{14}\text{B}$ compounds, detected by the SPD method, as a function of temperature is shown in figure 13. As can be seen, mainly the Nd- and Pr-alloys are suited for permanent magnet purposes. The Curie temperatures are also clearly visible.

5. Examples of modern permanent magnets

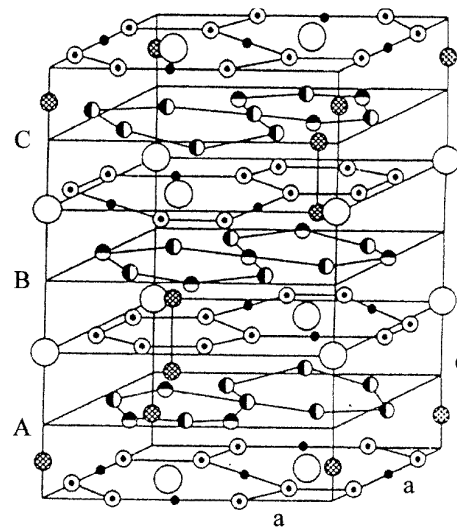
Modern permanent magnets are based on highly anisotropic RE-3d alloys. The first practical permanent magnet with high coercivity and an energy product in excess of 20 MG Oe was SmCo_5 produced in 1970. Such magnets proved a challenge to engineers, because a reassessment of all magnet circuits in many devices was necessary. This took some time, but when Nd-Fe-B magnets became available, they could immediately replace the ' SmCo_5 '- and ' $\text{Sm}_2\text{Co}_{17}$ '-type magnets in many applications. The penetration of the market was fostered in 1974 by the International Workshops on Rare-Earth Magnets, founded by K Strnat.

5.1. RE-cobalt magnets

5.1.1. SmCo_5 -type magnets. SmCo_5 -type magnets are based on alloys of this stoichiometry, but with small



(a)



(b)

Figure 11. Schematic representation of (a) hexagonal $\text{Th}_2\text{Ni}_{17}$ -type structure and (b) rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type lattice relevant to $\text{R}_2\text{Fe}_{17}\text{N(C)}_x$ compounds. The N(C) atoms occupy interstitial sites (Burzo and Kirchmayr 1992, p 271).

additions of other RE metals, Fe, etc. Usually an alloy is molten and milled. An alternative route is the calciothermic reduction, where an alloy, suitable for alignment in a magnetic field, pressing and sintering is directly obtained.

5.1.2. $\text{Sm}_2\text{Co}_{17}$ -type magnets. $\text{Sm}_2\text{Co}_{17}$ -type magnets are more advanced and have better magnetic properties. The development of coercivity in $\text{Sm}_2\text{Co}_{17}$ magnets with different sintering and heat treating cycles can be seen in figure 14. Today in Japan mainly $\text{Sm}_2\text{Co}_{17}$ -type magnets are produced, while in the USA SmCo_5 -type magnets are commonly used. The main magnetic properties of Sm-Co magnets are given in figure 15.

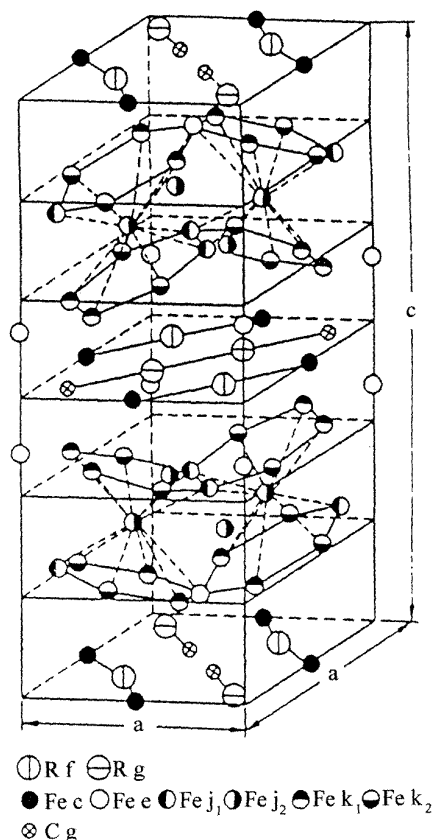


Figure 12. Crystal structure of the $R_2Fe_{14}C$ ($Nd_2Fe_{14}B$)-type compound (Burzo and Kirchmayr 1992, p 233).

The high coercivity of $SmCo_5$ - and Sm_2Co_{17} -type magnets is based on the high anisotropy field H_A^* of the main component of the alloys combined with a correct metallurgical structure. This structure can be achieved by adequate milling of the alloy powders, pressing to a green compact and sintering and annealing. In the case of the Sm_2Co_{17} -type magnets a special microstructure is essential. This structure is metastable, but nevertheless the sintered magnets can be operated up to 300 °C.

5.1.3. Bonded RE-cobalt-magnets. At the beginning of the RE-Cobalt-magnet era Strnat made attempts to fabricate experimental magnets by binding magnetic powders with resin. A great problem was always the stability of the magnets against degradation of the properties, e.g. by time, at elevated temperatures or by corrosion. Furthermore, the coercivity of powders prepared by milling was low. An increase in coercivity could be achieved by etching away the distorted upper layer of the powder (using a 'Becker cocktail' consisting of a mixture of alcohol, formic acid, nitric acid, etc). The introduction of liquid phase sintering therefore stopped the development of bonded RE-cobalt magnets for some time. Meanwhile, however, especially in Japan, bonded RE-cobalt-magnets (as well as bonded Nd-

Fe-B magnets) became an essential part of the total RE magnet market.

Bonded Sm-Co magnets can be based on $SmCo_5$ as well as on Sm_2Co_{17} . In the first case Sm-Co alloys are milled down to a grain size near 10 μm , pressed in (or without) a magnetic field and impregnated with epoxy. This technique, pioneered by the company Recoma, yields very homogeneous magnets with energy products in excess of 10 MG Oe. $SmCo_5$ powder can also be mixed with resin and pressed in a die or extruded.

Precipitation hardened Sm_2Co_{17} alloy offers the possibility to mill grains down to only 100–300 μm , therefore avoiding most problems of corrosion because of the smaller specific surface area. These bonded magnets have the advantage of a higher energy product, but are more difficult to fabricate to a given shape and to magnetize. Therefore a number of properties (as well as the cost of the different fabrication steps) determines the ultimate choice of a bonded $SmCo_5$ or Sm_2Co_{17} magnet. The advantages of all bonded magnets (see below), however, result in their ever increasing market share.

5.2. Nd-Fe-B magnets

The field of Nd-Fe-B magnets was opened in 1984 by Sagawa *et al* and Croat *et al*, although earlier papers by Drozzina and Janus (1935) and especially by Koon *et al* (1981) hinted at the possibility of these magnets. In 1984 it became clear that at least two distinctly different processes to prepare Nd-Fe-B magnets exist, namely by sintering and by melt spinning. In the meantime other possibilities to prepare Nd-Fe-B magnets emerged, e.g. by hydrogen treating Nd-Fe-B alloys, by mechanical alloying or by hot working. Today Nd-Fe-B magnets are the leading RE permanent magnets as can be seen from the proceedings of the different International Workshops on RE Magnets and Their Applications, the most recent of which was held in 1994 in Birmingham, UK (REM IX 1987, REM XIII 1994).

5.2.1. Sintered Nd-Fe-B magnets. The production of sintered Nd-Fe-B magnets is shown schematically in figure 16. The starting point is a Nd-Fe-B alloy with the approximate composition $Nd_{15}Fe_{77}B_8$ (in atomic per cent). This composition is rich in Nd compared to $Nd_2Fe_{14}B$ (see figure 8). The progress in recent years to achieve higher energy products was partly based on successful attempts to go as near as possible to the stoichiometry $Nd_2Fe_{14}B$ in actual permanent magnets. The limit of 50 MG Oe has been passed at room temperature in sintered Nd-Fe-B magnets. Other improvements are aimed at higher temperature stability and operating temperatures in excess of 200 °C. This goal has been achieved mainly by the addition of cobalt. The simultaneous addition of dysprosium decreases the energy product, but increases the coercivity and therefore also the temperature performance. Also improvements in corrosion resistance have been made possible by the addition of cobalt as well as other alloying elements. A typical composition of such an alloy is $Nd_{13.5}-Dy_{1.5}-Fe_{67.5}-Al_{0.5}-Co_5-V_4-B_8$ (REM XIII 1994 p 292).

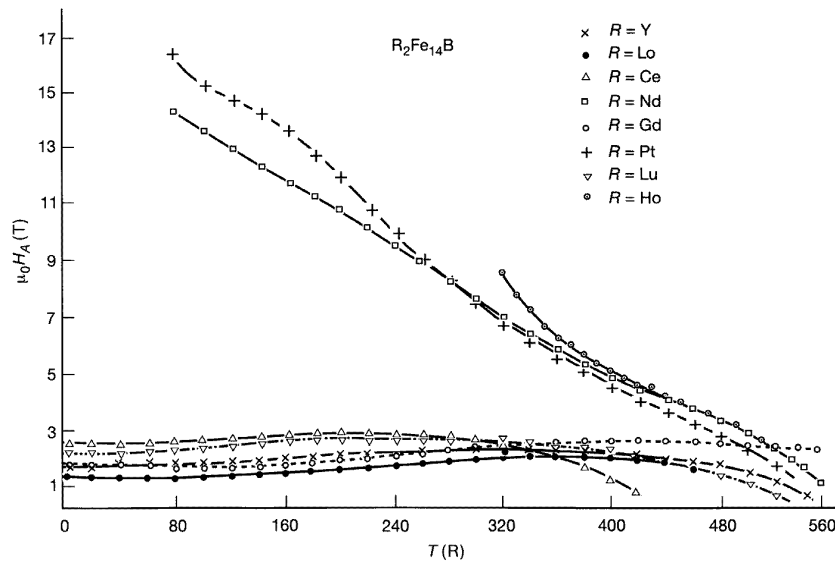


Figure 13. Temperature dependence of the anisotropy field, $\mu_0 H_A$, for various $R_2Fe_{14}B$ compounds (Kirchmayr 1991).

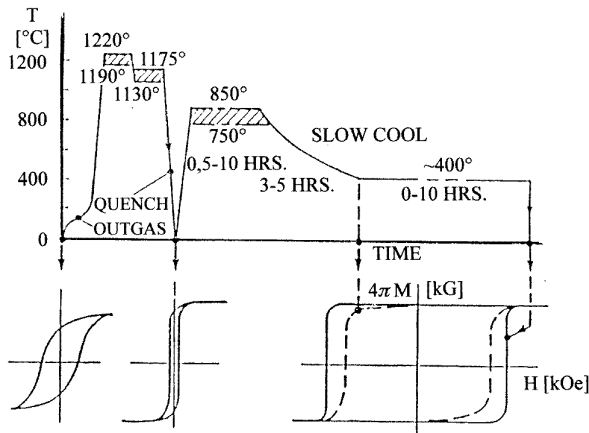


Figure 14. Development of coercivity in 'Sm₂Co₁₇' magnets (REM IX 1987, p 242).

5.2.2. Melt spun Nd-Fe-B magnets. The melt spinning process for Nd-Fe-B magnets was originally thought to be too expensive and not commercially feasible. However, it could be upgraded to a process which is now the leading mechanism for the preparation of magnet powders, suited for bonded magnets. This is important, because a Nd-Fe-B alloy and also sintered Nd-Fe-B magnets cannot be milled to a powder with sufficient coercivity. This is in contrast to Sm-Co alloys and magnets. At present different grades of 'Magnequench' are available, different by the Co content and the coercivity. In some cases a lower coercivity is necessary, if complicated structures or pole arrangements are to be magnetized. Starting from melt spun powder, by compacting and 'squashing' isotropic and anisotropic solid magnets can be produced.

The process developed by General Motors (Delco Remy-Magnequench) to prepare isotropic and anisotropic magnets and powder is schematically shown in figure 17

and figure 18.

Bonded Nd-Fe-B magnets can be produced in a similar fashion to Sm-Co bonded magnets (see above). By using anisotropic magnet powder, which recently became available (see below), anisotropic bonded magnets based on Nd-Fe-B can also be produced. The resulting energy product is in the range of 15–18 MG Oe. A comparison of the losses of bonded NdFeB magnets (polyamide and epoxy) is shown in figure 19.

Comparison of the different qualities of magnets shows that bonded anisotropic magnets fill an important gap. Since all the advantages of bonded magnets (near shape technologies, production of combinations of magnets with e.g. an axle for small motors, etc) are retained, it is obvious that bonded anisotropic Nd-Fe-B magnets, based either on melt spun alloys or on HDDR powder (see next section), will claim an important segment of all magnet applications.

5.2.3. HD (hydrogen decrepitation) and HDDR (hydrogen desorption disproportionation recombination) magnet powder for bonded magnets. Recently the hydrogen decrepitation process has not only been used to support or replace the milling of Nd-Fe-B alloy for further sintering, but also to prepare magnet powder for bonded magnets. Two distinct processes are used today.

(a) The HD process. In this case a compacted or sintered Nd-Fe-B magnet, prepared from Magnequench powder or from ordinary alloy powder, is decrepitated by hydrogen. The resulting powder is fairly coarse and after a heat treatment free of hydrogen and it possesses high coercivity. If an anisotropic magnet has been used, the resulting powder is also anisotropic and can be used to prepare anisotropic bonded magnets.

(b) An alternative process is the HDDR process, mainly developed by Mitsubishi. In this case an alloy of special composition (e.g. Nd-Dy-Fe-Zr-Ga-Hf-B) is treated in

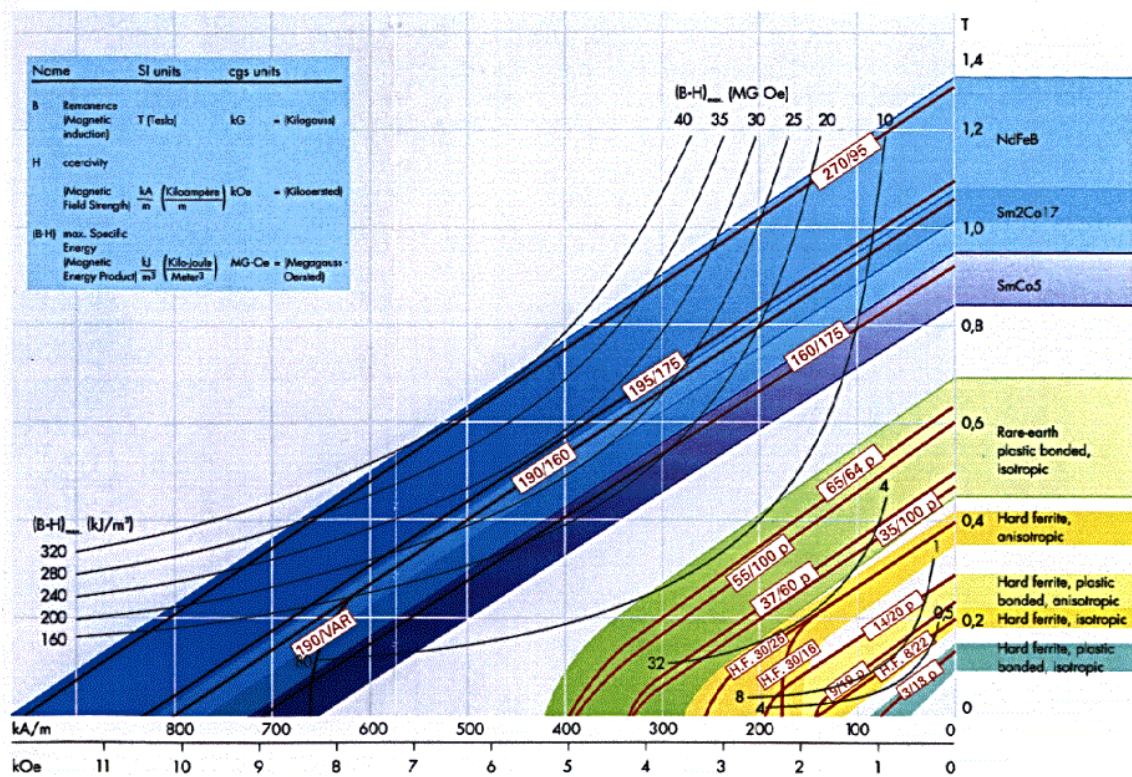


Figure 15. Comparison of demagnetization curves of different permanent magnets (Magnetfabrik Schramberg catalogue 10/95).

hydrogen at temperatures near 800 °C and subsequently heated in vacuum and furnace cooled. The resulting alloy can be anisotropic (depending on the microstructure of the starting alloy).

Two different anisotropic alloy powders for anisotropic bonded magnets are therefore now available from the company Magnequench, which has practically a monopoly on such alloys.

The preparation techniques for bonded magnets are summarized in figure 20.

6. Typical applications of modern permanent magnets

6.1. Introduction

Permanent magnets are an essential part of modern life, although we are usually not aware of how many different permanent magnets we make use of every day. The following discussion therefore just gives some examples.

Typical applications of modern permanent magnets, depending on the energy density $(B \cdot H)_{max}$, are given in figure 21. Bonded and sintered ferrites and AlNiCos are not included in this figure.

6.2. Static devices

The most simple static devices just pass forces from the permanent magnet to another magnetic material. In a static

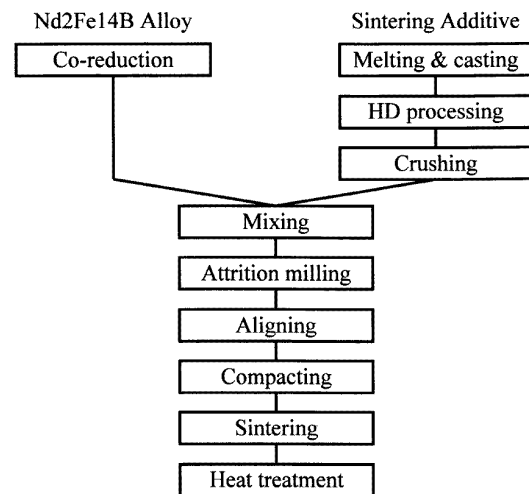


Figure 16. Production scheme of 'Nd₂Fe₁₄B-type' magnets (REM XIII, 1994 p 303).

device, a permanent magnet resembles an energy storage system, similar to a spring, but without the necessity of touching the object. Since magnetic forces interact via vacuum and through non-magnetic walls, magnets can be used in sealed magnet locks together with magnetic keys or, e.g. in special pumps for chemical installations, where the complete separation of different media is necessary. Literally thousands of similar uses are known and used

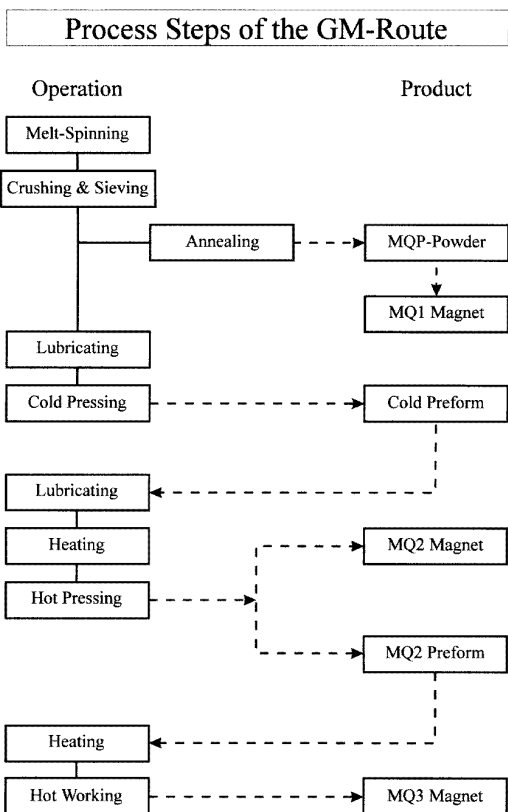


Figure 17. Process steps of the GM route.

abundantly. By using modern permanent magnets some of these applications became possible for the first time or the size of the device using the magnet could be reduced dramatically. Many suggestions for the meaningful use of permanent magnets can be found in the proceedings of relevant conferences and in literature of magnet producers[†].

6.3. Dynamic devices

Dynamic devices are understood to cover applications where an interaction between a permanent magnet and a current exists, resulting in a movement. Therefore all rotating or linear motors, positioning devices, etc, fall into this category.

6.3.1. Low-power devices. By low-power devices we understand from near zero to a few watts. The commercially most important application today, namely the permanent magnets for floppy disk and optical disk drives fall in this category. A classical permanent magnet as a ferrite could not be used, since the access time, the size of the device, etc are crucial for its performance and value.

Small motors, e.g., in video cameras, also make use of modern permanent magnets—otherwise, the small size and low weight of these cameras could not be achieved.

[†] e.g. Magnetfabrik Schramberg, D-78713 Schramberg-Sulgen, Germany. 1995 Catalogue, edition 10/95.

High-quality microphones and speakers also use modern permanent magnets, mainly of the Nd-Fe-B type, in huge numbers. In this case the magnets are small and therefore the price of the unit is still reasonable. All analogue quartz watches also contain small permanent magnets (usually Nd-Fe-B).

6.3.2. High-power devices. Nearly all engineers and scientists agree that modern permanent magnets would find a prominent place in medium sized motors (or even large motors in the 100 kW range), if the price of the magnets could be decreased considerably. While in small devices the advantages of the permanent magnet outweighs the cost, in medium size or large installations the price of the magnets is dominant. Nevertheless, if size or weight has to be reduced or if the efficiency must be high, modern permanent magnets consistently show superiority. In many cases modern electronics in combination with permanent magnets yields technical solutions of problems which otherwise cannot be solved. This is especially valid for special stepping motors, linear motors, etc. In all cases where electrical energy must be converted into mechanical energy or force or vice versa with high efficiency, modern permanent magnets also have a prominent position. Therefore energy saving devices necessitate permanent magnets in ever increasing amounts.

6.4. Other applications

Permanent magnets are now also used in medicine to produce homogeneous fields for MR (magnetic resonance) tomography, unless a higher magnetic field available in superconducting coils is necessary. Another application of high-quality permanent magnets is in travelling wave tubes, where the introduction of RE-Co magnets made possible a drastic increase in performance. Today Nd-Fe-B magnets are used in wigglers and undulators for the electron beam in synchrotrons, resulting in a much better collimated 'light ray' of high brilliance.

6.5. Production figures

The importance of Nd-Fe-B based permanent magnets can be seen in figure 22. Japan at present is the leading producer in the field of permanent magnets, followed by the USA. In the long term China may increase production further, partly because the majority of all RE resources are based in China. The production figures for all types of permanent magnets are steadily increasing with respect to tonnage, number and value. This trend will continue for the foreseeable future (figure 22).

7. Future developments

7.1. Introduction

The three basic ingredients of modern permanent magnets are magnetization (based on large moments), ordering temperature and anisotropy (leading to coercivity). A good modern permanent magnet is feasible only if

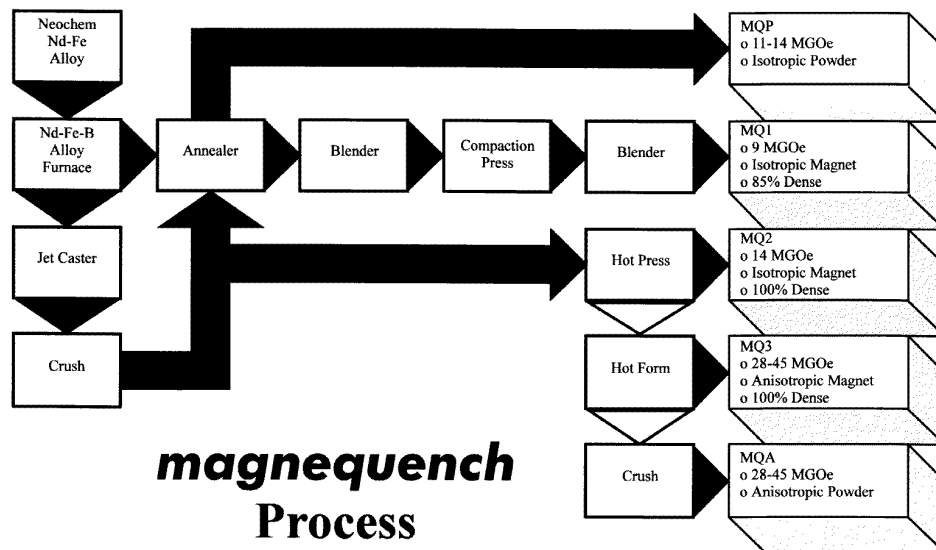


Figure 18. Magnequench process developed by General Motors (Delco Remy-Magnequench) (Rashidi 1989).

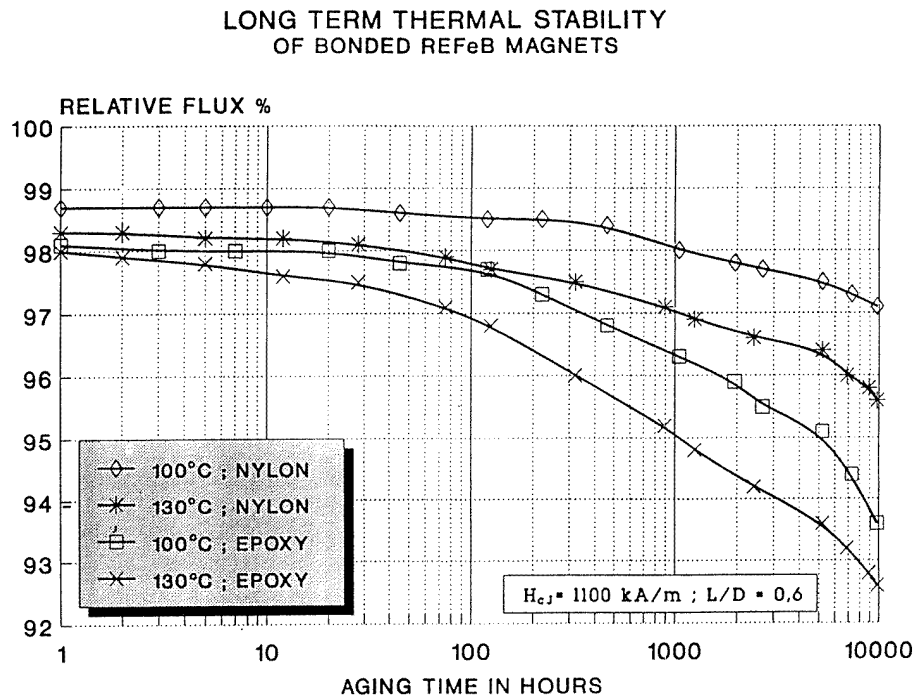


Figure 19. Comparison of losses of bonded NdFeB magnets (nylon and epoxy) (Fernow *et al* 1992).

all three factors are well balanced and are sufficiently large. There exist materials where one or two of these parameters is better than in existing magnets, but it is very difficult to imagine a material which is significantly better overall than existing materials. Research, however, is continuously inventing new materials and techniques toward the goal of more advanced permanent magnets.

7.2. Transition metal alloys

Alloys consisting mainly of Fe or Co can be prepared by advanced techniques e.g. sputtering, CVD, etc with high ordering temperatures and a magnetization surpassing the $\text{Nd}_2\text{Fe}_{14}\text{B}$ level. One example is Fe_4N , which shows a saturation magnetization of $\sigma_s(0 \text{ K}) = 210 \text{ emu g}^{-1}$, close to that of $\alpha\text{-Fe}$ (Andriamandroso *et al* 1993). Other preparation techniques are feasible, but in many cases these techniques do not allow the production of bulk magnets.

Processing of Bonded Magnets with Improved Bending Strength

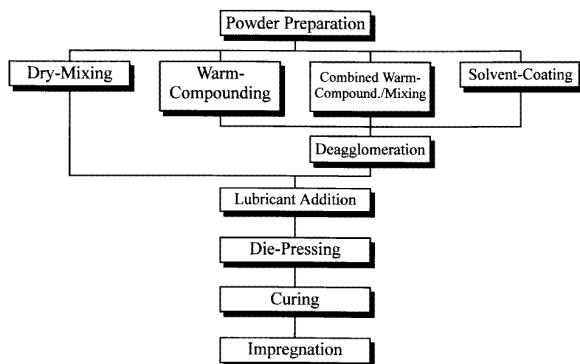


Figure 20. Preparation techniques for bonded magnets (Reppel *et al* 1992).

7.3. Modern rare earth intermetallics research

7.3.1. General overview. Rare earth metals are an indispensable ingredient of modern permanent magnets, because only with specific RE metals the necessary high anisotropy and therefore the necessary value of the coercivity can be achieved. There exist general rules and laws for the development of the anisotropy (axial anisotropy, basal anisotropy, etc) in crystalline materials with a given crystal structure. These properties are based on the nature and electronic structure of the individual RE atoms and are fairly well understood. To some extent the anisotropy of a given system can now even be calculated from first principles. There is therefore little space left for changing the anisotropy at will.

Over the past 50 years a huge number of binary and ternary alloy systems containing REs has been investigated with respect to the phase diagrams, the existing compounds and crystal structures present. RE systems of higher order (quaternary, quinary, etc) have not been investigated systematically. Also, the many metastable systems which must exist are not well known. In many cases the magnetic properties of the alloys and compounds have not been measured in detail. Only in a few cases have these measurements been performed on single crystals. There is therefore still much scope left for scientific research on new phases or compounds not sufficiently investigated to date.

7.3.2. CEAM (concerted european action on magnets).

Startled by the invention of Nd-Fe-B magnets in Japan and the USA, the Commission of the European Communities organized a workshop—Nd-Fe permanent magnets: their present and future applications—(Mitchell 1985) in Brussels on October 25 1984. This workshop was the starting point of CEAM (Concerted European Action on Magnets), which operated for nearly ten years and was guided in the beginning by R Pauthenet and then by M Coey. The original idea of bringing together most of the European scientists and as many as possible of the engineers

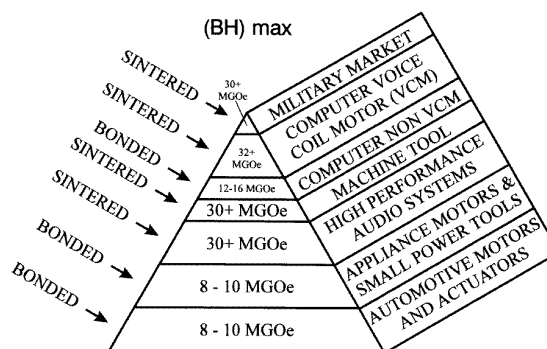


Figure 21. Typical applications of permanent magnets depending on the energy density $(BH)_{max}$ (Rashidi 1989).

interested in modern permanent magnets was met at least with respect to research, maybe not to applications.

CEAM organized many workshops and conferences, tried to coordinate the research sponsored by the EU and achieved altogether a broad cooperation within Europe. Scientifically many new compounds have been found and investigated, but in terms of technology, a breakthrough similar to the finding of $Nd_2Fe_{14}B$ was not achieved. The results of the CEAM program are well documented in conference proceedings (e.g. EMMA '95 1996, REM IX 1987, REM XIII 1994, REM XIV 1996) and in books.

7.3.3. Future possibilities. The drastic increase in the quality of permanent magnets during this century, documented by the energy product, cannot be continued forever. However, new phases and compounds, still not known, may exist which may still allow a doubling of the energy product. Therefore scientific research in this direction is appropriate in the foreseeable future. The most important task, however, is, in our opinion, the systematic scientific penetration of existing systems for better understanding of the principles leading to modern permanent magnets. The best technical product could then be developed based on existing technologies. Therefore, not a revolution in permanent magnets, but a smooth continuous development based on scientific work, will probably be the best idea in the near future for the full exploitation of the still unused enormous possibilities of modern permanent magnets.

8. Concluding remarks

Within the range of magnetic materials (soft magnetic, semi hard magnetic, e.g. recording materials, and hard magnetic materials) permanent magnets have a prominent position. Many devices in industry, medicine and in everyday life rely on high-quality permanent magnets.

8.1. The quest for higher energy products

One of the most important quantities to characterize a permanent magnet is the energy product. During the 20th

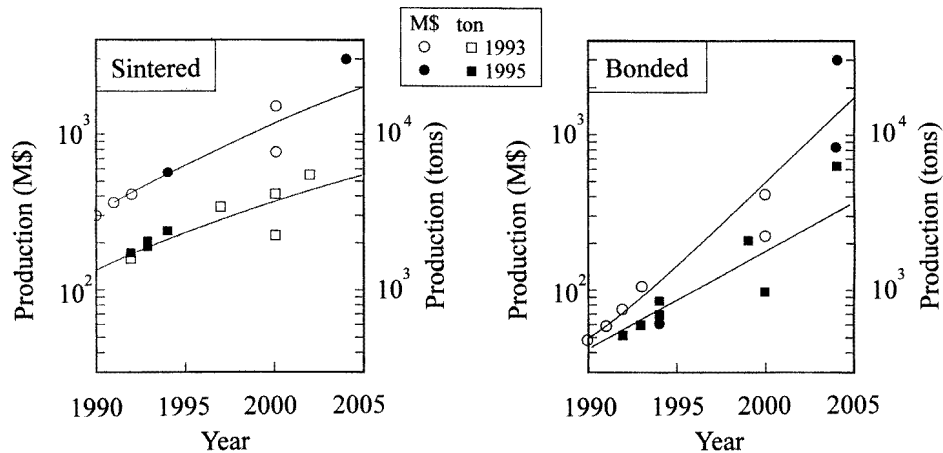


Figure 22. Annual world production of sintered and bonded NdFeB using data presented at the Gorham conferences of 1993 (open symbols) and 1995 (filled) (Fastenau and van Loenen 1996).

century it has been increased tremendously by increasing the coercive field. Now, however, the coercive field has already reached its optimum and an increase in the energy product is only possible by increasing the saturation magnetization. This quantity, however, is limited by the magnetic moments present in a given volume. An increase of the energy product is therefore only possible by increasing the density of magnetic moments, while retaining the ordering temperature well above room temperature as well as the anisotropy field. To achieve all these tasks simultaneously is a difficult problem. The personal opinion of the author is that dramatic increases of the energy product cannot be expected in the future.

8.2. Higher operating temperatures

The main disadvantage of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets is the Curie temperature near 310°C . An increase is naturally possible by the addition of cobalt. A systematic search for materials with higher ordering temperatures is limited by poor understanding of the basic interactions in magnetic materials and therefore of the origin of the magnetic ordering and the possibilities to calculate Curie points. If progress is made in this field, 'man made' magnetic materials with higher ordering temperatures may be possible.

8.3. Economic benefits of better permanent magnets

Over recent years the economic benefits of permanent magnets also became clear to non-scientists and within European research programs (Brite/EuRam, etc) permanent magnets had their position. The CEAM program (see above) was also established. Now, however, there seems to be a change of direction within the EU. This is counterproductive for European research and industry. The important position of permanent magnets within modern high-tech materials, however, is documented by the steady research policy in Japanese government and industry, which has brought Japan to the forefront in the field of modern permanent magnets.

8.4. Permanent magnets based on high- T_c Superconductors

'Permanent magnets' based on high- T_c superconductors already exist. The saturation approaches 8 T, which corresponds to an energy product of 1600 MG Oe or 12800 kJ m^{-3} which is 30 times that of the best $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets. The main disadvantage, naturally, is the operating temperature, which is near 80 K. If this obstacle can be overcome by inventing room-temperature superconductors, then completely new permanent magnets may be feasible. Room-temperature superconductors, however, would revolutionize not only the field of permanent magnets, but also all kinds of industry and everyday life.

8.5. Permanent magnets will never die

We are living in the magnetic field of a huge permanent magnet called Earth. Since the book by William Gilbert *De Magnete*, published in 1600 and describing the still valid basic properties of permanent magnets, nearly 400 years have passed. In the last 100 years the energy product of permanent magnets has been increased by a factor of 100. Permanent magnets have penetrated all aspects of industrial and private life. Therefore it seems very unlikely that in the next century permanent magnets will be superseded by a completely new non-magnetic system. On the contrary, we can assume that permanent magnets are still on the upswing and that the science and technology of permanent magnets will continue to be a fascinating subject in the coming decades.

Acknowledgments

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