Powder metallurgy of rare earth permanent magnets

by J Ormerod*

Rare earth permanent magnets account for more than 10% of the total world permanent magnet market, valued at £950 million in 1987 and projected to increase at 10% per annum over the coming years. This article outlines the general powder metallurgical processing of both samarium–cobalt and neodymium–iron–boron based magnets. Typical application areas are described and the improvement and future developments of rare earth permanent magnets are also considered.

Permanent magnets today are used in a wide range of industrial, domestic, automotive and aerospace applications. Their special technological importance derives from the ability to act without contact on ferromagnetic material, either by attraction or repulsion, and to provide a permanent magnetic flux with no energy input, and hence at no operating cost. The current usage of permanent magnets in domestic applications averages 50 per household in Western Europe.

The vast majority of rare earth permanent magnets (REPMs) are produced by powder metallurgical processing routes. Commercial REPMs, based on the SmCo₅ intermetallic compound, have been produced since the early 1970s. Shortly after the development of SmCo₅ permanent magnets, alloys containing copper as well as the rare earths and cobalt emerged. These become known as the precipitation hardened family of R(CuCo) alloys and eventually led to the development of high energy Sm(CoCuFe)₅ magnets (where TM is Zr, Ti or Hf).

Since mid 1983, several permanent magnet manufacturers in Europe, the USA and Japan have announced their intention to begin commercial production of permanent magnets based on the Nd–Fe₁₂B intermetallic compounds. These new materials combine high polarisation coercivity, Hcₓ, with the highest known maximum energy product, (BH)ₘₑₓ. These parameters are considered to be the two most important indicators of permanent magnet performance.

The improvement in primary magnetic properties of the NdFe based magnets over the existing high energy SmCo based magnets is illustrated in Table 1. The properties of a typical ferrite permanent magnet, the type of permanent magnet material produced in the largest tonnage, are included in the table for comparison. The greatly enhanced magnetic properties of the NdFe based materials will allow the further miniaturisation of permanent magnet circuit designs and broaden the range of permanent magnet applications. In addition, the basic raw materials required for NdFe based magnets have considerable price advantages and fewer supply restrictions than either Sm or Co which together form the main components of the established rare earth permanent magnets. This could allow NdFe based magnets to be produced for, and used in, large volume applications.

Philips Components Ltd manufactures a wide range of REPM grades based on either the Nd₁₂Fe₁₄B system or (NdDy)₂Fe₁₄BNb system and marketed under the trade name Neodure, fig 1. Table 2 illustrates the typical magnetic characteristics of the Neodure grades currently available.

Table 1: Comparison of the composition and properties of some permanent magnets manufactured by Philips Components Ltd

<table>
<thead>
<tr>
<th>Composition</th>
<th>Nd₁₂Fe₁₄B RES 270</th>
<th>SmCo₅ RES 190</th>
<th>SrFe₁₂O₃ FXD 380</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br typical (T)</td>
<td>1.1</td>
<td>0.89</td>
<td>0.39</td>
</tr>
<tr>
<td>BHₘₑₓ typical (kJ m⁻³)</td>
<td>215</td>
<td>154</td>
<td>28.2</td>
</tr>
<tr>
<td>Hcₓ typical (KA m⁻¹)</td>
<td>1000</td>
<td>1100</td>
<td>275</td>
</tr>
<tr>
<td>Temperature coefficient of Br (20 to +150°C) (‰K⁻¹)</td>
<td>-0.13</td>
<td>-0.04</td>
<td>-0.2</td>
</tr>
<tr>
<td>Temperature coefficient of Hcₓ (20 to +150°C) (‰K⁻¹)</td>
<td>-0.6</td>
<td>-0.05</td>
<td>0.34</td>
</tr>
<tr>
<td>Recoil permeability</td>
<td>1.05</td>
<td>1.05</td>
<td>1.1</td>
</tr>
<tr>
<td>Curie point (°C)</td>
<td>310</td>
<td>720</td>
<td>450</td>
</tr>
<tr>
<td>Max continuous operating temperature (°C)</td>
<td>120</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Density (× 10³ kg m⁻³)</td>
<td>7.4</td>
<td>8.3</td>
<td>4.75</td>
</tr>
</tbody>
</table>

Fig 1 Examples of the REPM product range manufactured by Philips Components Ltd

DEVELOPMENT OF RARE EARTH PERMANENT MAGNETS

Several comprehensive reviews¹–⁵ exist which extensively cover the development of rare earth magnets and the factors determining their magnetic properties. REPMs can be defined as a group of permanent magnet materials containing the magnetically active components rare earth–transition metal (R–T) where R is one or more of the elements having atomic numbers 57 (La) to 71 (Lu) and the group 3B element of atomic number 39 (Y). Up to the advent of NdFe based materials, the commercially most important REPMs were based on Sm and Co.

Rare earth–cobalt magnets can be divided into four types depending on whether the primary phase is of the RCo₅ or RECo₁₇ type and whether a precipitate phase (for domain wall pinning) is present or absent within the grains. The latter types are referred to as multi-phase and...
single-phase magnets respectively, although in practice all commercial sintered permanent magnets have complex multi-phase microstructures. All four types are generally prepared by powder metallurgical processing.

 Historically, the development of RFe based permanent magnets by powder metallurgical processing has been hindered for several reasons. Firstly, iron forms fewer intermetallic compounds with the rare earths than cobalt. Secondly, stable compounds of the RFe composition are absent, and thirdly, compounds which are stable, e.g. R₂Fe₁₇, have low Curie temperatures and planar preference anisotropy. Two alternative approaches have been used in the search for RFe permanent magnet materials. These are:
1 By extending the study to metastable/ non-equilibrium phases instead of being limited to the equilibrium phases, and
2 By extending the study to ternary/ quaternary systems for stable phases.

These two approaches have been followed, independently by several workers⁴-⁶. The former method takes its lead from Clark⁶, who demonstrated that amorphous materials provided a starting point from which a fine grained metastable structure could be obtained by an annealing treatment. Most of the investigators who followed this approach used a melt-spinning technique to produce the amorphous precursor or the fine grained metastable structure directly. The typical method of melt-spinning, fig 2 consists of melting the alloy or elements in a quartz tube under either vacuum or inert gas. The melt, under argon pressure, is sprayed through an opening in the quartz tube onto a rotating, water cooled, copper wheel or disc. Cooling rates in excess of 10⁶ Ks⁻¹ are produced.

More recently, the search for new RFe compounds has shifted to a study of stable phases formed in the ternary/quaternary system based on NdFeB. Sagawa and co-workers⁷ have made studies of the light rare earths, iron and boron ternary systems, and have found a ternary compound in the NdFeB system, with a composition in the range 12 at % Nd, 6 at % B and 82 at % Fe, to have excellent potential as a permanent magnet material. The compound has a tetragonal structure, with a high uniaxial anisotropy and a Curie temperature of 585 K. Permanent magnets have been produced by standard powder metallurgical processing from an alloy composition of 15 at % Nd, 8 at % B and 88 at % Fe, with a (BH)ₘₐₓ value in excess of 279 kJ m⁻³.

**POWDER METALLURGICAL PROCESSING**

The high reactivity of the rare earths and their alloys, and the critical dependence of the magnetic properties on the chemical composition, requires the effective suppression of contamination during the alloy preparation and subsequent powder metallurgical processing. In particular, oxidation of the rare earth components by O₂/ H₂O must be kept to a minimum through all fine powder handling and heat treatment stages.

The main process steps taken during the production of REPMs are shown in fig 3. The general process consists of alloy preparation, pre-milling, milling, composition control and adjustment, particle alignment and pressing, sintering and heat treatment, machining, coating and finally magnetising.

**Alloy preparation**

Rare earth-3d transition metal alloys can be produced on an industrial scale by two methods. These are vacuum induction melting and calciothermic reduction.

**Fig 4 Typical microstructure of an as-cast ingot of the alloy Nd₁₀Fe₇B₄ showing three main phases: primary columnar grains of NdFe₂, a boron rich phase NdFe₆B₈, and a Ni rich grain boundary phase (magnification ×100).**

The vacuum induction method has the advantage that it can produce a wide range of rare earth alloy compositions with very low oxygen contents (less than 200 ppm). The typical microstructure of an as-cast ingot of Nd₁₀Fe₇B₄ is shown in fig 4.

The calciothermic production of rare earth alloys was developed independently by two groups working at General Electric, USA⁸ and Thomas Goldschmidt, W Germany⁹. In the General Electric process, cobalt powder, calcium granules and rare earth oxide powder are blended together and then reacted under hydrogen at 1423K. The reaction can be represented by the equation:

\[
\text{NdO}_3 + 10\text{Co} + 3\text{Ca} \rightarrow 2\text{NdCaO}_3 + 3\text{CaO}
\]

After cooling, the excess calcium and calcium oxide are removed from the reacted product by reacting with moist nitrogen, then washing with water and dilute acid. This is known as the reduction-diffusion (R-D) process.

The Goldschmidt process, known as co-reduction, is a variation of the R-D process in that the reaction is carried out under vacuum at 1273K and both cobalt powder and cobalt oxide powder are used as raw materials.

The main advantages of the calciothermic reduction process are the use of rare earth oxides as raw material and the direct production of alloy powder suitable for milling. However, both the oxygen content and calcium content are higher than alloys prepared by melting.

**Pre-milling**

Depending on the method used to prepare the alloy, the material may require a size reduction stage prior to final milling. For example, after vacuum melting and casting, the NdFeB alloy is in the form of chill cast lumps. These are crushed, under a nitrogen atmosphere in a high energy hammer mill, to a particle size range of less than 500 microns.

An alternative chemical method of pre-milling the alloy has been developed in
co-operation with the group of Dr Rex Harris at the University of Birmingham. This process is known as hydrogen decrepitation. It has been shown that NdFeB alloys react readily with hydrogen at moderate pressures exhibiting a strongly exothermic reaction. Measurements on the desorption behaviour of hydrogen from a Nd₄Fe₁₄B₃ alloy indicated that the vacuum degassing consisted of two stages whereby hydrogen was first desorbed from the NdFe₁₄B₃ matrix phase below 300°C, with the remainder being evolved from the Nd rich phase at higher temperatures.

The formation of two hydrides is consistent with the observed decrepitation behaviour where the initial activation process corresponds with the hydriding of the intergranular neodymium rich material, resulting in transgranular fracture. This is followed by the hydriding of the matrix phase with the attendant transcrysalline cracking of the individual crystallites, fig 5. This technique of hydrogen decrepitation is exploited to produce a friable premilled material with a particle size less than 500 microns directly suitable as input material for the fine milling stage.

**Milling**

The object of milling the REPM alloys is to produce a narrow size distribution of single crystal particles, i.e., individual particles containing no grain boundaries and therefore only one preferred axis of magnetisation. In addition, sufficient particle surface area must be present for high sinter reactivity. For single phase magnets, where the coercivity is controlled by domain nucleation and wall pinning at grain boundaries, the particle size and surface condition play a critical role in determining the coercivity of the sintered magnet. The critical parameters to be controlled during milling are particle size, particle size distribution, damage to crystal structure, and oxidation.

The milling process can be carried out by either ball milling in an organic liquid under an inert gas, e.g., attritor milling in cyclohexane, or by jet milling, fig 6. The jet mill is a dry milling process in which the attrition action is mainly due to high velocity particle-particle collision. Figures 7 and 8 show micrographs of typical NdFeB powders produced by attritor milling and jet milling respectively. The classifying action of the jet mill system is evident from the narrower particle size distribution shown in fig 8.

**Composition control and adjustment**

The magnetic properties of rare earth permanent magnets are critically dependent on the chemical composition. Any contamination, particularly oxidation, of the alloy during processing depletes the alloy of the rare earth components. This results in a shift in composition to the T-rich side of the phase diagram, which may cause a magnetically unfavourable phase distribution.

In the case of SmCo₅ magnets production, the optimum properties are found to occur over a composition range of 0.5 wt% Sm; this corresponds to a mere 0.08 wt% oxygen pick up. In order to prevent excessive dilution of the magnetic material by Sm₂O₃, a maximum oxygen content of 0.6 wt% would not be exceeded in the finished magnet. The Sm₂O₃ formation is compensated for by introducing a corresponding excess of Sm over the stoichiometry of SmCo₅. This can be done during the alloy preparation stage or by blending a samarium rich milled alloy with the SmCo₅ milled alloy. The latter method is used during the manufacture of RES 190 magnets since it allows easier correction for slight variations in oxygen pick-up from batch to batch of milled powder.

For NdFeB, the composition range for optimum magnetic properties is less critical than that for SmCo₅. The critical R content for NdFeB magnets is greater than that for SmCo₅ magnets by a factor of about ten. This enables NdFeB magnets, with careful processing control, to be prepared by the single powder method.
pressing or at right angles. In large scale production, multi-impression tooling is generally used. High homogeneous field levels are required to produce a high level of uniformly aligned particles.

The applied field can be DC or some combination of DC and pulse. The degree of alignment is influenced by particle shape and particle size distribution, magnitude of aligning field and pressing pressure. The pressing pressure should be sufficient to give the powder compact enough strength to withstand handling and chipping. Magnetic chucks are tougher and less susceptible to breakage and chipping. Magnetic chucks are therefore not used to hold pieces down directly.

For magnets that are typically used in uniaxial die pressing, the pieces are moved between two grinding wheels set the required distance apart. Small blocks tend to be slit using diamond impregnated wheels. Machined surfaces are required to give the necessary magnetic contact with the associated components in the final assembly.

Coating
Magnets based on the Nd$_2$Fe$_{14}$B intermetallic are susceptible to corrosion and require a corrosion resistant coating for normal applications. The optimum coating and coating technology has to fulfil several criteria:

- The coating must be thin to minimise air gaps in the magnetic circuit.
- The coating must be uniform and provide complete coverage of all magnet surfaces.
- The coating must be glueable to other parts of the magnetic circuit.
- The coating technology must evolve little or no hydrogen.
- The coating technology has to be applicable to wide range of magnet shapes and sizes.

Machining
During the sintering operation, the pressed product volume reduces to the final magnet body. This shrinkage depends upon production factors and the final magnet size and shape. This results in some variation in magnet size and therefore a machining operation is necessary.

REPMs are in general hard and brittle, although NdFeB magnets are rather tougher and less susceptible to breakage and chipping. Magnetic chucks are therefore not used to hold pieces down directly.

Sintering and heat treatment
The sintering of rare earth permanent magnets is carried out in inert gas atmospheres, reducing atmospheres or under vacuum. The sintering treatment should result in a magnet with a high density and high coercivity, they may be magnetised prior to assembly without flux loss. However, because of the difficulty of handling magnetised and brittle material it is common for the user to carry out magnetisation during the system assembly.

Fig 9. The effect of aligning field and pressing method on remanence of RES 190

Fig 10. Effect of temperature on demagnetisation characteristics of RES 255

These criteria have been met by two coating techniques which are applied to the Neodur range of magnets. These are:

- a Ion vapour deposition of aluminium, which produces a coating thickness of 10±3 µm. The products can either be barrel or jig coated during this process.
- b Cathodic electropaint (epoxy), which produces a thicker coating of 23±5 microns and can only be applied to jigged products.

Both these coatings have guaranteed performance of seven days resistance to accelerated humidity testing.

Magnetisation
Since most REPMs combine relative recoil permeabilities close to unity and high coercivity, they may be magnetised prior to assembly without flux loss. However, because of the difficulty of handling magnetised and brittle material it is common for the user to carry out magnetisation during the system assembly.

Effect of temperature on magnetic properties
The working induction of a magnet falls with increasing temperature, fig 10. This reduction can be caused by three effects: reversible, irreversible and irrecoverable changes. Reversible changes occur because the relevant structure-insensitive properties of saturation magnetisation and anisotropy constant are both temperature dependent. In the case of NdFeB magnets, the temperature coefficient of remanence is −0.13% K$^{-1}$ and the average temperature coefficient of coercivity is −0.6% K$^{-1}$.

Irreversible changes are due to thermal fluctuations causing domain reversal by irreversible rotations or wall movements. Remagnetisation is required to restore the original value.
Irrecoverable changes cannot be recovered by remagnetisation and are caused by structural changes such as oxidation, phase changes or grain growth. As remagnetisation is rarely practical the maximum recommended temperatures of operation for the various magnet grades should never be exceeded.

**APPLICATIONS**

The earliest commercial applications of rare earth magnets were in stepper motors for electronic watches, in the replacement of AlNiCo magnets in electron beam focusing systems such as travelling wave tubes, and in some medical applications. Subsequent applications made greater use of the potential in weight and volume reduction made possible by the high magnetic energy available.

Typical new applications were in magnetic bearings, servomotors, switches and actuators. The real breakthrough happened after 1975 when many new types of motor, generator, couplings, etc were designed to use rare earth permanent magnets. Over the past few years, the application of REPMs has extended, particularly in the Far East, to audio-visual and other consumer products.

A new market opportunity has recently developed due to the growth in Information Technology. Disk file systems have been developed which use a voice coil motor actuator to position the read/write heads over the hard disk. The use of REPMs in these devices has enabled access times to be dramatically reduced.

**CONCLUSION**

The powder metallurgical processing of REPMs produces materials with the highest known magnetic properties. At their present stage of development NdFeB magnets are distinctly superior to SmCo materials in terms of their performance at room temperature. However, at temperatures in excess of 140°C they are inferior.

To ensure that NdFeB magnets find applications in as many fields of modern technology as possible, their operating temperature must be extended to 200°C without risk of demagnetisation. Improvements in the temperature dependence of magnetic properties require both an increase in the Curie temperature and improved thermal stability of the coercivity. Increases in Curie temperature can be achieved by substituting some Fe by Co, eg a substitution of 10% of the Fe by Co produces an increase in Curie temperature from 585K to 671K with a reduction in TK Br to 0.08% K⁻¹.

Increases in HcJ can be obtained by the addition of certain heavy rare earths, eg Tb, Dy or Ho. The addition of other elements, such as Ti, Mo, Zr, Nb and Hf, all produce increases in HcJ.

Corrosion and oxidation problems are mainly associated with the free neodymium present in the grain boundary eutectic phase. It may be possible to reduce the amount of free Nd by the addition of cobalt or a heavy rare earth which forms a rare earth compound in favour of free Nd in the eutectic phase. However, currently available coatings, eg ion vapour deposited aluminium, have guaranteed performance in excess of 200°C.

Finally, increased use of all REPMs will be achieved by the economics of reducing manufacturing costs during powder metallurgical processing. Since all REPMs exhibit high values of HcJ this results in magnetic circuit design requiring components with short magnetic axes.

Such components present particular problems in minimising grinding allowances. This requires the careful control of pressing conditions and powder dosing in the die cavities, the minimisation of distortion during sintering and heat treatment and the choice of suitable finishing methods. Similarly, because of the high raw material costs, the control at all process steps must be such that a zero defect failure rate is guaranteed.

**References**