RARE EARTH - TRANSITION METAL MAGNETS: THEIR PROCESSING, PROPERTIES AND APPLICATIONS

A.J.Williams and I.R.Harris
School of Metallurgy and Materials
University of Birmingham, UK

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Key words: permanent magnets, sintered magnets, hard magnetic materials, rare eart, processing, magnetic properties, applications, production, Nd-Fe-B magnets, HDDR magnets, hysteresis loops

Abstract: The properties and production of hard magnets are described by particular reference to the NdFeB-type magnets. Thus both the intrinsic properties (e.g. saturation magnetisation Ms) and extrinsic properties (e.g. intrinsic coercivity H_{ci}) are discussed and it is shown how these properties are exploited in sintered magnets and their applications.

Magneti kovin prehoda in redkih zemelj: proizvodnja, lastnosti in uporaba

Ključne besede: magneti trajni, magneti sintrani, materiali trdomagnetni, zemlje redke, procesiranje, lastnosti magnetne, uporaba, proizvodnja, Nd-Fe-B magneti, HDDR magneti, zanke histerezne

Povzetek: V delu opisujemo lastnosti in uporabo trdih magnetov s posebnim poudarkom na NdFeB magnetih. Prikazane so tako nasičenjska magnetizacija, Ms, kakor tudi koercitivna sila, H_c, še posebej glede na izdelavo in uporabo sintranih magnetov.

Introduction

The term hard magnet is used as an alternative to the term permanent magnet and describes a magnetic material which can be permanently magnetised by the application of a magnetic field. This behaviour is illustrated by the hysteresis loop and a typical loop for a good hard magnet is shown in Fig. 1. In production the objective is to produce a square hysteresis loop with as large a value as possible of the remanence, Br, and as high a value as possible of the intrinsic coercivity, Hci. Such properties ensure a large value of the maximum energy product, $(BH)_{max}$, which is a useful figure of merit for hard magnets. Essentially the higher is (BH)max the smaller is the volume of the magnet required to produce a given magnet flux. Thus the progress in hard magnetic technology over this century can be illustrated by the change in (BH)max as a function of time (Fig.2). In the early part of this century, gradual progress was made and magnets were made from steels. These were followed by the alnicos (Al-Ni- Co) which were discovered in the thirties and were improved significantly over a period of some thirty years by a process of "alloy engineering". (Alnicos are still used extensively but are being replaced in many applications by the rare earth-transition metal-type magnets). The next major step was the appearance of the

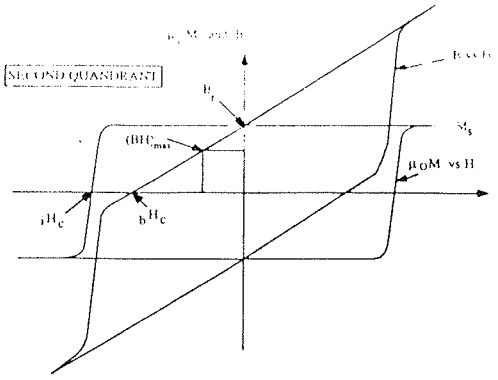


Fig. 1: A hysteresis loop for a good hard magnet.

ceramic magnets based on strontium (and barium) ferrite ($SrFe_{12}O_{19}$) in the fifties and this represented the first significant exploitation of magnetic materials exhibiting the intrinsic property of magnetocrystalline anisotropy the significance of which will be discussed later. These magnets are still used extensively and have the enormous advantage of being extremely cheap.

Perhaps the most exciting development in hard magnetic materials this century (equivalent in superconducting technology to the appearance of the high Tc superconductors) was the development of the $SmCo_5$ magnets by Strnat and co-workers (1,2). This lead to a steep

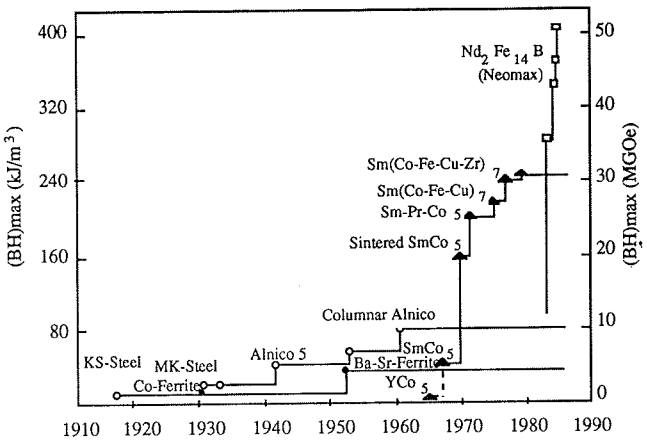


Fig. 2: The variation of $(BH)_{max}$ with time over this century

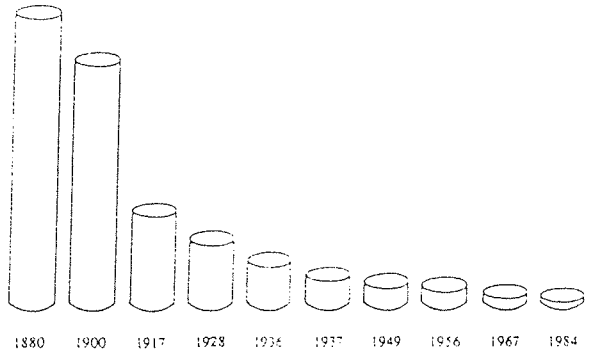


Fig. 3: These magnets all develop the same magnetic flux and the reduction in size is achieved by increasing values of $(BH)_{max}$

rise in $(BH)_{max}$ values with the subsequent development of the $Sm_2(Co,Fe,Cu,Zr)_{17}$- magnets (2,3) and most recently, the NdFeB-magnets (4,5). A consequence of these spectacular improvements in $(BH)_{max}$ is a dramatic reduction in the size of the magnets required to produce a particular magnetic flux and this is illustrated in Fig. 3. The intrinsic and extrinsic properties of magnetic materials will now be considered with particular reference to the NdFeB- magnets.

More recently magnetic materials based on Sm-Fe-N (6) have been developed where nitrogen in the interstitial sites of the Sm_2Fe_{17} structure raises the Curie point from 120°C to 480°C and the anisotropy field of the nitride is twice as high as $Nd_2Fe_{14}B$.

Intrinsic Magnetic Properties

The value of the remanence (Br) depends on the value of the saturation magnetisation(Ms) and the squareness of the hysteresis loop (see Fig. 1). The Ms depends predominantly upon the magnetic moment on the transition metal atoms (Fe,Co). The ferromagnetic phase in the NdFeB-type magnets is the tetragonal compound

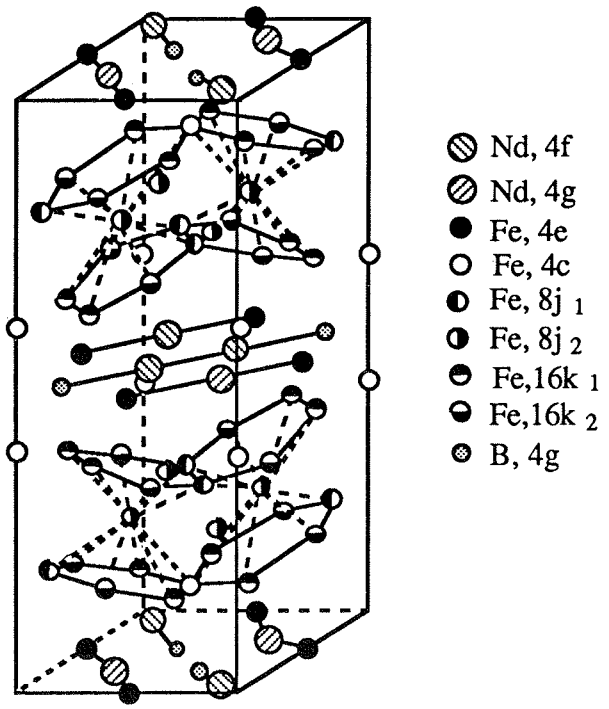


Fig. 4: The structure of the tetragonal compound $Nd_2Fe_{14}B$.

$Nd_2Fe_{14}B$ (Fig.4) with a mean Fe-moment of 2.50μ_B. The Curie-point of this compound is around 585K which means that it can be heated to this temperature before the ferromagnetism disappears. An essential characteristic of the compound with regard to magnet production is that it exhibits easy magnetisation along the c-axis of the tetragonal cell i.e. uniaxial magnetocrystalline anisotropy. This arises largely from the rare earth neodymium atoms where the 4f spin-orbit - lattice interactions produce the anisotropy in the magnetisation behaviour. This is the reason for the presence of the expensive and reactive rare earth metal and the practical significance of this behaviour is that fine single crystal particles of the compound can be aligned preferentially along their c-axis. The particles can be locked into this configuration by sintering and this, together with the development of an appropriate microstructure (see later), is the basis for the production of a NdFeB-hard magnet.

Extrinsic Magnetic Properties

It is not sufficient just to have the necessary intrinsic magnetic properties in order to make an effective hard magnet, it is also necessary to develop the essential extrinsic property of coercivity. Thus, once the magnetic domains are aligned along the favourable c-axis orientation then it should be made as difficult as possible for reverse domains to form and to demagnetise the magnet. How is this achieved?

The theoretical maximum value of the coercivity is the same as the anisotropy field H_A for a particular ferromagnetic phase which is given by the expression:

$$H_A = \frac{2K_1}{Ms}$$

where K1 is the anisotropy constant.

In reality the coercivity values of rare earth-transition metal hard magnets are much less than the appropriate H_A values and this behaviour can be ascribed to the nucleation of reverse domains from imperfections within particular magnetic materials. The reduced coercivity Hc at temperature T is given by the general expression:

$$Hc(T) = \alpha\,(T)\frac{2K_1}{Ms} - NMs$$

where α (T) is a temperature dependent microstructural parameter, and N takes account of demagnetising fields. The formation of reverse domains can be retarded by a pinning or a nucleation mechanism. In the case of the $Sm_2(CoFe,Cu,Zr)_{17}$- type magnets (2,3), the first mechanism operates and the favourable domain configuration is "pinned" by fine precipitates so that a pinning potential well has to be overcome before a reverse domain can form and a series of obstacles have then to be overcome for the domains to propagate throughout the bulk of the material. This behaviour is reflected in a distinct kink in the first quadrant magnetisation behaviour of these magnets (Fig. 5). In the case of the NdFeB-type magnets (5) it is believed that it is the nucleation mechanism which predominates and this is reflected in the first quadrant magnetisation behaviour where a high initial permeability and easy c-axis magnetisation is achieved (Fig.6). Having produced a favourable alignment of the domains, the microstructure of the magnet is such that high reverse fields are required to nucleate, sustain and propagate reverse domains. Electron microscope studies (7) have shown that the $Nd_2Fe_{14}B$ matrix is free of any imperfections and it is thought that reverse domains originate at irregularities at the grain boundaries. A typical composition of the NdFeB-type magnet is $Nd_{15}Fe_{77}B_8$ (atomic percent) whereas the composition of the $Nd_2Fe_{14}B$ compound is $Nd_{11.8}Fe_{82.3}B_{5.9}$. The excess neodymium in the former forms predominantly a Nd-rich grain boundary phase

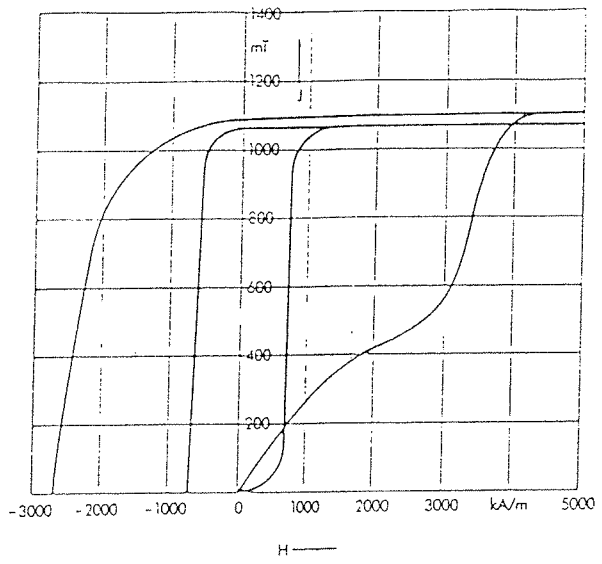


Fig. 5: The magnetisation behaviour of a 2/17-magnet.

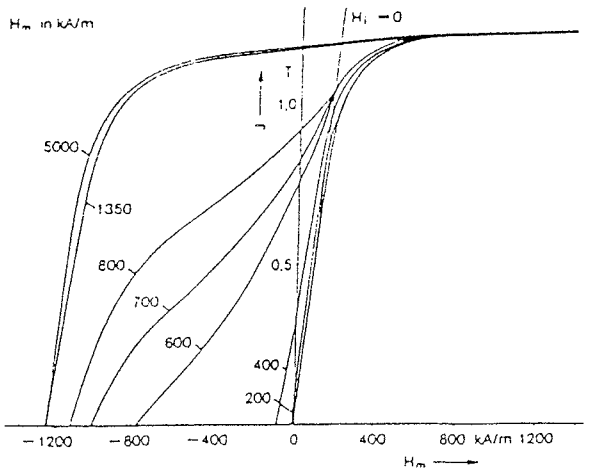


Fig. 6: The magnetisation behaviour of a NdFeB-magnet.

(part of a eutectic which melts at 903K) which is therefore liquid at the sintering temperature of around 1320K. The influences of the grain boundary material are at least three fold in character:

(1) it produces liquid phase sintering with the attendent densification.

(2) it produces smooth grain boundaries and hence reduces the incidence of irregularities (e.g. steps) for reverse domain nucleation. It is known that sharp corners act as nucleation sites for reverse domains.

(3) It provides a barrier to the propagation of reverse domains between grains i.e. it provides the grains with magnetic isolation.

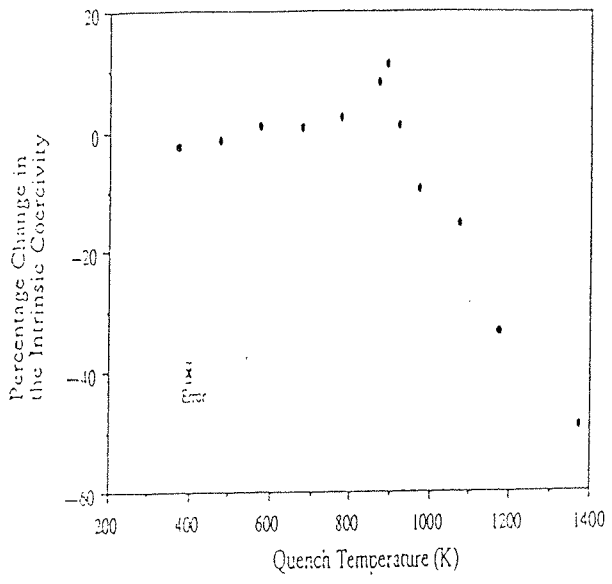


Fig. 7: The effect of quenching on the H_{ci} values of a NdFeB magnet initially slowly cooled from the sintering temperature.

There might also be an element of domain pinning by grain boundary phases and the constitution of the boundary material is complex (7) and sensitive to heat treatment.

The importance of the grain boundary materials is shown in the effect of quenching (8) on the magnetic properties of the sintered NdFeB-type magnets. This is shown in Fig.7. and it can be seen that quenching an initially slowly cooled magnet from above the melting point of the grain boundary material results in a marked deterioration in the values of H_{ci} which become progressively worse with increasing quenching temperature. This was attributed to the incomplete coverage of the grain boundaries by the Nd-rich material on quenching but it was also possible that subtle changes in the constitution also had some influence. The original properties could be recovered by annealing the quenched magnets at 903K.

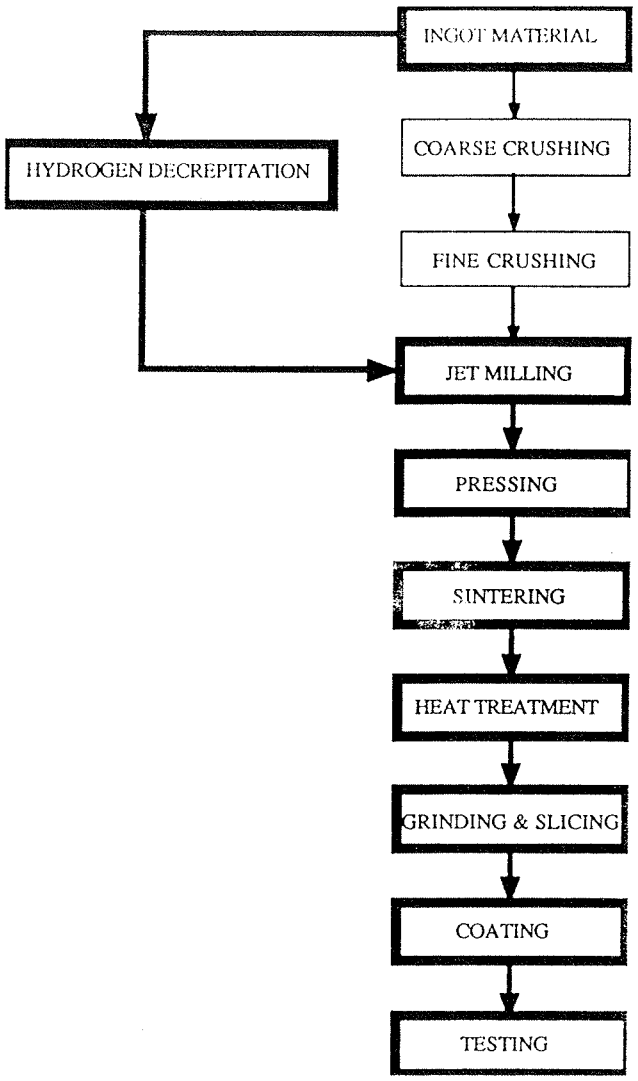
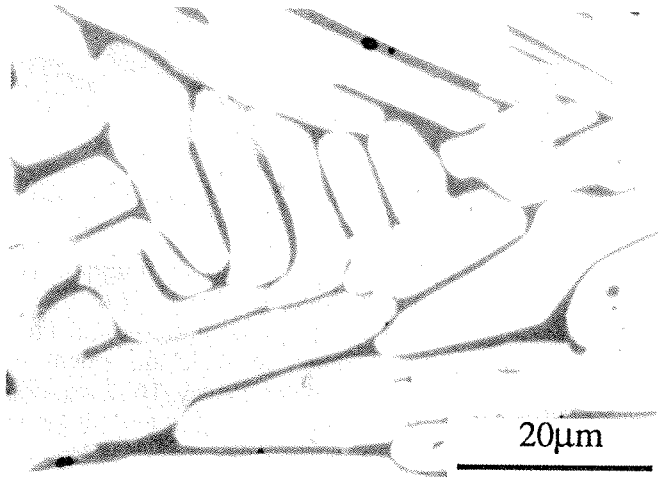


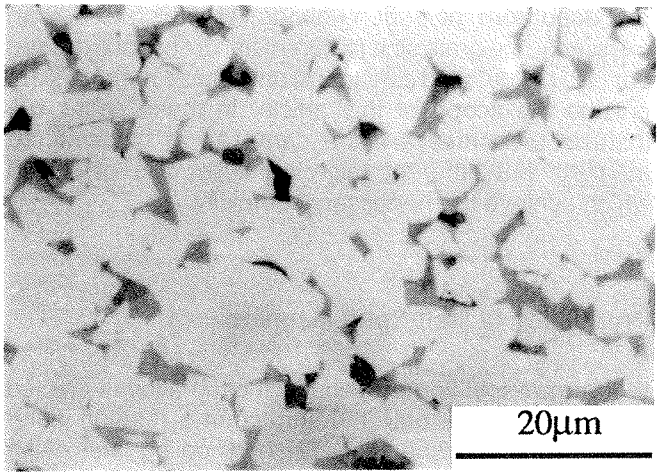
Fig. 8: The production sequence of a NdFeB-magnet.

Production of Sintered Magnets

The previous considerations have shown that the production of an effective sintered magnet depends upon obtaining the appropriate intrinsic properties, Ms and H_A (uniaxial) by the selection of a suitable compound and obtaining the necessary coercivity by the formation of a suitable microstructure. The production sequence for a sintered NdFeB-type magnet is show in Fig. 8. and a very similar procedure is adopted for the production of the strontium ferrite, $SmCo_5$ and $Sm_2(Co,Fe,Cu,Zr)_{17}$ magnets (although the latter also requires a step ageing treatment). The process consists of converting the coarse grained randomly oriented cast ingot into a fine grained, highly oriented sintered magnet; the change in microstructure is shown in figure 9. The hydrogen decrepitation (HD) process (9) provides an effective and convenient means of providing particulate material which is very suitable for jet milling. This process depends on the affinity of the $Nd_{15}Fe_{77}B_8$ and related alloys for hydrogen and the subsequent desorption of hydrogen during vacuum sintering. The decrepitation process is represented schematically in Fig. 10.



(a)



(b)

Fig. 9: The microstructures of the NdFeB (a) cast ingot and (b) sintered magnet.

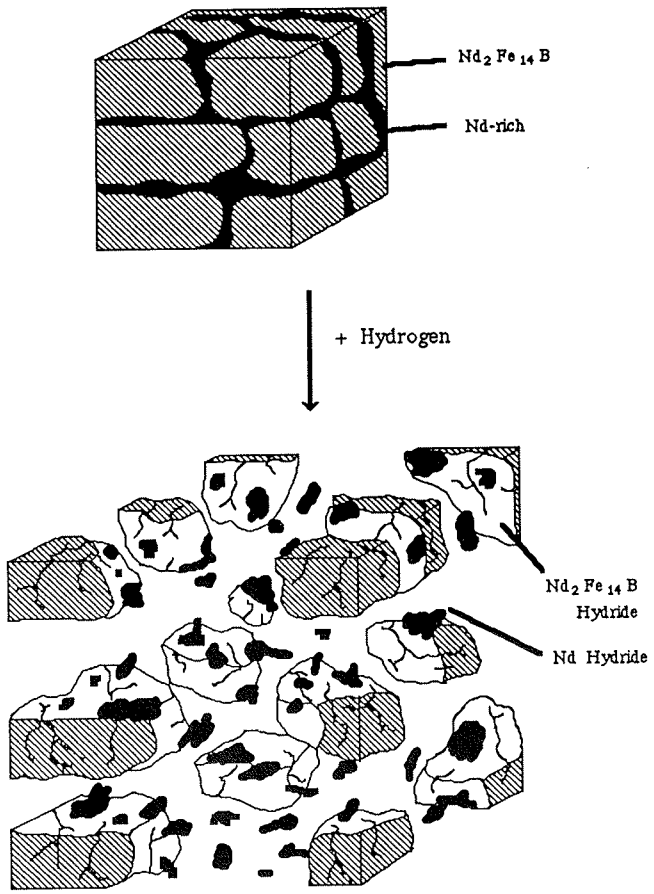


Fig. 10: A schematic representation of the HD-process.

The production of fine grained sintered magnets requires the formation of fine jet-milled powder of ≅ 2μm particle size and the sintering temperature and time have to be controlled carefully to avoid the growth of large grains which degrade the coercivity. The influence of the grain size distribution (10) on the H_{ci} values is illustrated in Figure 11.

It should be noted that NdFeB - magnets can also be produced from melt-spun ribbons (11) which exhibit an extremely fine grain size (≅ 20nm) and from hot extruded bar (12) but detailed consideration of these materials are outside the scope of this article. In these cases the intrinsic properties are the same as in the sintered magnets but different microstructures are produced which achieve the necessary coercivity.

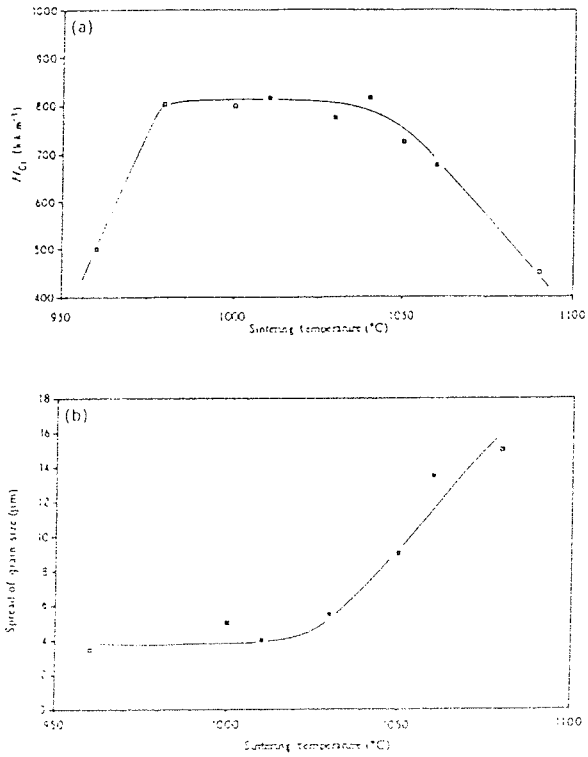


Fig. 11: The influence of the grain size distribution of a NdFeB magnet on the value of H_{ci}.

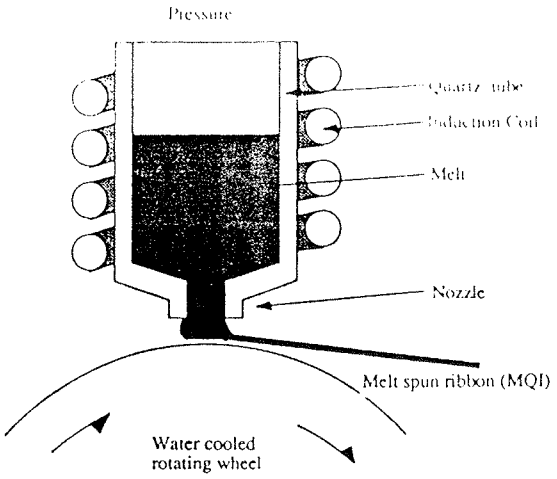


Fig. 12: A schematic representation of the melt spinning process.

Production of Melt-Spun Magnets

In the melt-spinning procedure, molten alloy is ejected through an orifice onto the surface of a rotating water cooled substrate wheel (fig. 12), and cooling rates of the order of one million °C/s are achieved. The microstructure and magnetic properties of the NdFeB ribbons formed by melt- spinning are very sensitive to the quench rate (13). High quench rates produce essentially amorphous ribbons having negligible intrinsic coercivity. Optimum quench rates yield ribbons with the highest coercivities; they are comprised of roughly spherical $Nd_2Fe_{14}B$ grains (20- 100 nm in diameter) (fig.13). At wheel velocities below the optimum, the slow cooling rate produces ribbons that consist of larger grains and are characterised by low coercivities. Ribbon melt-spun at high rates have an amorphous or partially crystalline structure, but can be annealed to nearly duplicate the properties of the optimally quenched materials (14).

Fabrication of the magnet requires consolidation of the magnetically isotropic ribbons. The processes for this

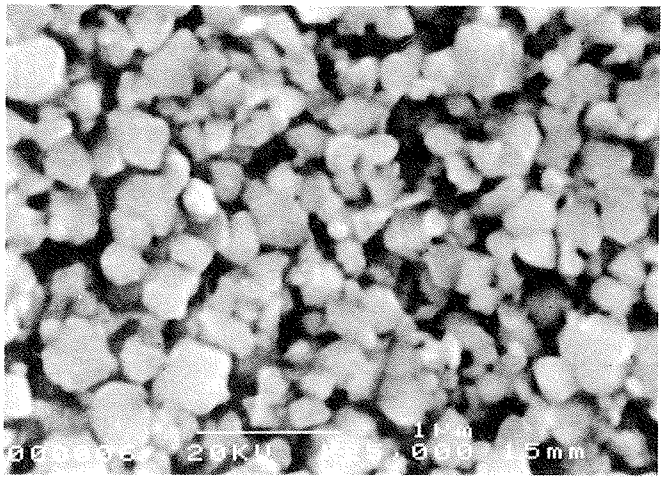


Fig. 13: SEM micrograph of a polished and etched melt spun flake.

have been developed by the Delco Remy Division of General Motors. They have named the magnet material Magnequench and there are three grades. The first and simplest procedure is to cold press, optimally quenched ribbons with a bonding agent. The resulting bonded magnet which remains magnetically isotropic, is commonly referred to as an "MQI" type magnet.

The crystals of MQI material are randomly oriented so that the magnets are isotropic and can be magnetised along any axis. A considerable flux density of about 3T is required to magnetise the magnets to 99% of saturation. The isotropic nature of the material limits the (BH)max to 56-80 kJm^{-3} (7-10 MGOe).

Improved densification of melt-spun ribbons is afforded by the second procedure, hot pressing. Appropriate temperatures and pressures vary with composition; but for compositions near $Nd_{13.5}Fe_{81.7}B_{4.8}$, full density is achieved for T ≅970K and P ≅100 MPa. If optimally quenched ribbons are used, grain growth is not excessive at these temperatures. To ensure the most desirable grain size, however, it is preferable to hot press over- quenched ribbons, which are either amorphous or consist of undersized grains. These "MQII" type magnets exhibit only slight (≅10%) magnetic alignment and require a flux density of about 3T for magnetisation to 99% of saturation. They are 100% dense and this gives them a higher (BH)max than "MQI" of 100-120 kJm^{-3} (12-15 MGOe).

Substantially greater alignment (>75%), and hence greater energy products, can be obtained by the third procedure, in which an initial hot press is followed by another in a die cavity having a larger diameter. This second hot press, termed die upset forging, produces bulk lateral plastic flow and a reduction in ribbon thickness. Such magnets are 100% dense, and have been obtained with energy products as large as 320 kJm^{-3} (37 MGOe). The required magnetising flux density of 2.5T is lower than for the isotropic MQ magnets. A review of the processing and properties of Magnequench has been given by Carlisle (1986) and more recently by (13).

Production of HDDR Magnets

An alternative to the production routes already mentioned is the Hydrogen Disproportionation Desorption and Recombination (HDDR) process (16,17). In this case the intrinsic properties are achieved, in the same way as sintered magnets, with the use of $Nd_2Fe_{14}B$ as the magnetic phase, however the extrinsic properties are generated by a very different method to that used for sintered NdFeB magnets.

A schematic representation of the HDDR process is illustrated in figure 14. The first stage is hydrogen decrepitation of the ingot material, producing a hydrided powder. This powder is then heated in a 1bar pressure of hydrogen up to 800°C, with the effect of disproportionating the Nd2Fe14B phase to Nd hydride, iron and ferroboron. After 2 hours at 800°C the powder is placed in a vacuum for a further hour before cooling. This causes the desorption of the Nd hydride, with the result that recombination of the $Nd_2Fe_{14}B$ occurs. The microstructure of the powder is now very different to the as cast starting material because nucleation of the Nd2Fe14B occurred at many sites within the origin grains and now the average grain size is ≅0.3μm (fig.15). This grain size is approximately the same as the critical grain size for single domain particles in $Nd_2Fe_{14}B$. This means that it is energetically favourable to have only one domain in each grain, hence making it difficult to form reverse domains.

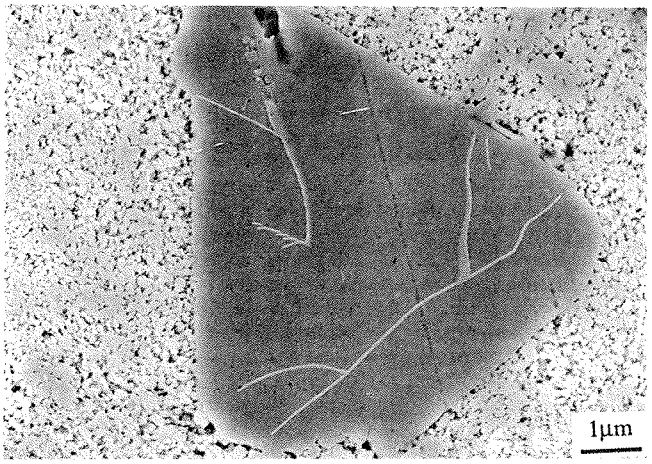


Fig. 15: SEM micrograph of a polished and etched HDDR particle, showing a large grain surrounded by fine grained material.

The powder cannot be sintered because the grains would grow and the coercivity would be lost. Therefore the powder must be bonded or alternatively hot pressed, which is a process rapid enough to avoid grain growth.

The powder produced is isotropic, i.e. its magnetic properties are the same when magnetised in any direction. This is because the powder particles consist of many grains which have random orientation. However, it is possible to make anisotropic powder by adding various elements e.g. 0.1 at% Zr to the alloy, and in this case the fine grains have an overall preferred orientation

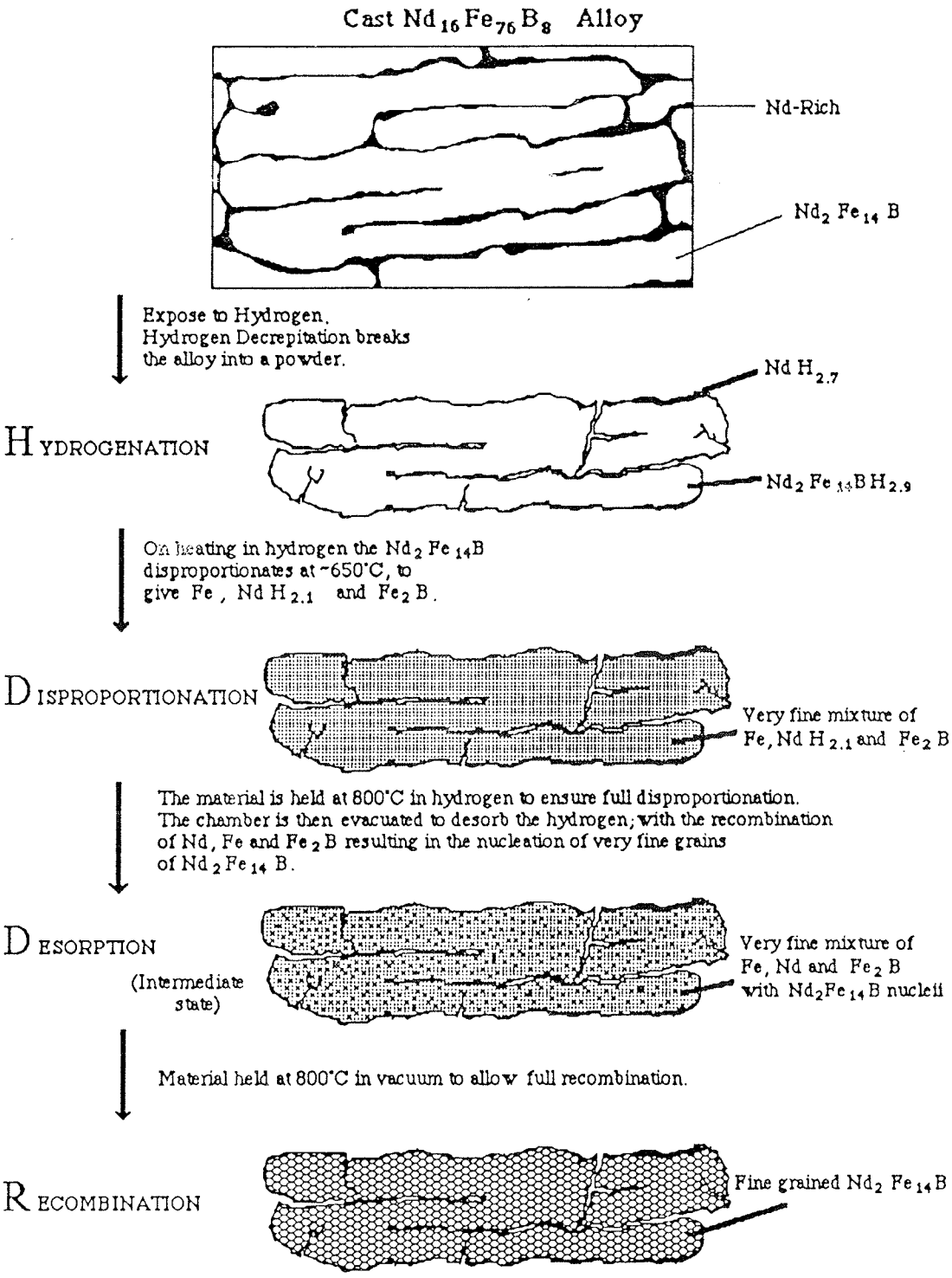


Fig. 14: A schematic representation of the HDDR-process.

related to the orientation of the original $Nd_2Fe_{14}B$ grain. The best energy product of 34MGOe has been achieved by hot pressing anisotropic HDDR powder (18).

Applications

Due to the increased energy product provided by rare earth-transition metal magnets new and miniaturisation of existing applications have become possible. Electric motors with increased power or reduced size / weight are perhaps one of the major advantages of these magnetic materials, for example hand held power tools and small ear phones are now possible. The use of voice coils to generate precise movement is utilised for example in a compact disc player for the scanning and focusing of the laser beam.

Permanent magnet body scanners are now possible, where previously liquid helium cooled superconductors have been required to generate the magnetic fields

required. Medical applications include magnetic clasps for sealing wounds, holding dental crowns in place and to assist in correcting misaligned teeth.

Future Prospects

There is still considerable scope for the development of NdFeB-type magnets to give improved temperature performance and improved corrosion resistance. This is illustrated by recent work (19, 20) on the beneficial influences of V and Mo additions. There is also scope for the discovery of new hard magnets with improved Curie temperatures and perhaps (BH)max values when compared to NdFeB. A particular challenge is the development of magnets based on Mn-rich alloys which would exploit the enhanced magnetic moment of Mn compared with that of Fe. A major problem here is the propensity of Mn to form anti-ferromagnetic alloys but efforts should be encouraged by the prospect of much enhanced (BH)max values.

Acknowledgements

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A.J.Williams and I.R.Harris
School of Metallurgy and Materials
University of Birmingham,
Edgbaston, Birmingham, B15 2TT, UK
tel. +44 21 414 51 65
fax. +44 21 471 22 07

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