Magnetic Materials: Hard Magnets

Hard magnets, also referred to as permanent magnets, are magnetic materials that retain their magnetism after being magnetised. Practically, this means materials that have an intrinsic coercivity of greater than ~10kAm-1.

It is believed that permanent magnets have been used for compasses by the Chinese since ~2500BC. However, it was only in the early twentieth century that high carbon steels and then tungsten / chromium containing steels replaced lodestone as the best available permanent magnet material.

These magnets were permanent magnets due to the pinning of domain walls by dislocations and inclusions. The movement of dislocations within a material is often hindered by the same factors that affect the motion of domain walls and as a consequence these steels are mechanically very hard and are the origin of the term hard magnetic. These magnets had an energy product of approximately 8kJm^{-3}.

Alnicos

In the development of permanent magnets the first improvement over steels came about in the early 1930s with the discovery of the group of alloys called the Alnico alloys. These alloys are based mainly on the elements nickel, cobalt and iron with smaller amounts of aluminium, copper and titanium (Typical weight%: Fe-35, Co-35, Ni-15, Al-7, Cu-4, Ti-4).

The alloy composition and processing were developed over the years and the properties reached a maximum in 1956 with the introduction of anisotropic columnar alnico 9, with an energy product of ~80kJm^{-3}.

These alloys are still used today as they have a high Curie temperature (~850°C), and as a result can operate at higher temperatures as well as having more stable properties around room temperature than some of the more modern alloys.

However, their main disadvantage is that they have low intrinsic coercivity (~50kAm^{-1}) and as a consequence must be made in the form of horseshoes or long thin cylinders, which cannot be exposed to significant demagnetising fields. The magnets are either sintered or directionally cast, and then annealed in a magnetic field.

This processing route develops an oriented microstructure consisting of rods of strongly magnetic Fe-Co (α') in a matrix of weakly magnetic Ni-Al (α). The coercivity derives from the rod shaped nature of the α' phase generating shape anisotropy along with the weak magnetism of the a phase pinning the domain walls.

Hard ferrites

The next advance in the development of permanent magnets came in the 1950s with the introduction of hard hexagonal ferrites, often referred to as ceramic magnets. These materials are ferrimagnetic and considering the proportion of iron within the material have quite a low remanence (~400mT).

The coercivity of these magnets (~250kAm^{-1}), however, is far in excess of any previous material. The low remanence means that the maximum energy product is only ~40kJm^{-3}, which is lower than the alnicos, but due to the high coercivity these magnets can be made into thinner sections.

The magnets could also be exposed to moderate demagnetising fields and hence could be used for applications such as permanent magnet motors. The hexagonal ferrite structure is found in both $BaO._6F_{e2}O_3$ and $SrO._6Fe_2O_3$, but Sr ferrite has slightly superior magnetic properties.

The main advantage of ferrites is that they are extremely low cost, due to the ease of processing and the low cost of raw materials, which makes them the most widely used permanent magnet material.

The magnets are made by a powder metallurgy processing route and there are no problems with oxidation of the powder during processing, as the material is already a stable oxide.

The powder processing route ensures that the magnets comprise of very small grains (<1mm), which is essential for generating coercivity in these magnets. During processing the powder is compacted in a magnetic field in order to align the easy direction of magnetisation of the particles and hence enhances the remanence and the maximum energy product.

SmCo Type

In 1966 the magnetic properties of the $_{YCo5}$ phase were discovered. This was the first phase based on a rare-earth (RE) and a transition metal (TM) to be found to have permanent magnetic properties. The combination of RE and TM is ideal as the RE provides the anisotropy to the phase and the TM provides the high magnetisation and Curie temperature.

The discovery of $SmCo_5$ soon followed in 1967 and this became the first commercial RE/TM permanent magnetic material, which was polymer bonded and had an energy product of ~40kJm^{-3}. It was later (1969) found that $SmCo_5$ sintered magnets could be made with energy products of the ~160kJm^{-3}.

These magnets have excess Sm which forms a smoothing grain boundary phase and coercivity is achieved by prevention of the nucleation of reverse domains.

In 1976 the record maximum energy product was increased to 240kJm^{-3}, with a Sm$_2$Co$_{17}$ based alloy. These materials are based on the general composition Sm$_2$(Co,Fe,Cu,Zr)$_{17}$ and achieve their permanent magnetic properties by careful control of the microstructure.

The magnets are produced by powder metallurgy and are solution treated at ~1100ºC, where they are single phase. This homogenising stage is followed by several aging treatments at lower temperature where a cellular microstructure is formed.

The cells are based on the Sm$_2$Co$_{17}$ type phase, which is enriched in Fe and the cell boundaries comprise of a layer of SmCo$_5$ type phase, which is enriched in Cu. The intrinsic magnetic properties of the cells and the cell boundaries vary such that the magnetic domain wall energy is greatly reduced within the cell boundary and hence pin the domain walls, leading to permanent magnetic properties.

There is still a great deal of interest in these materials as they have the potential for operating at high temperature (~500ºC), making new applications possible, for example as bearings in gas turbine engines.

The main problem with Sm/Co based magnets is the expense of the raw materials. Samarium is much less abundant than other light rare-earth elements, such as La, Ce, Pr and Nd, which account for over 90% of rare-earth metals in typical rare-earth ores. Cobalt is classified as a strategically important metal and hence sales are restricted.

NdFeB Type

In 1984 the magnetic properties of NdFeB were discovered simultaneously by General Motors in the USA, and Sumitomo Special Metals of Japan. Both groups produced materials based on the magnetic phase Nd2Fe14B, but employed different processing routes.

Sintering
In Japan, Sumitomo special metals developed a powder metallurgy processing route, which initially gave the highest ever observed energy product, in excess of 300kJm^{-3}. Subsequently NdFeB based sintered permanent magnets have been produced with maximum energy products of ~450kJm^{-3}, by improved heat treatment, more controlled processing and the use of more iron rich compositions.

Sintered NdFeB based magnets achieve their coercivity by virtue of a Nd-rich phase at the grain boundaries which acts to produce liquid phase sintering, smooth the boundaries and hence prevent nucleation of reverse magnetic domains.

The processing route for sintered NdFeB based magnets is shown in figure 9. The as-cast ingot must first be broken into a powder. This is achieved most conveniently by exposing the ingot to hydrogen, which is absorbed at the surface. The hydrogen enters the material in the spaces

between the atoms and causes the material to expand. The differential expansion generates stress in the ingot and the alloy breaks down into a fine powder. This process is known as Hydrogen Decrepitation (HD). The HD powder is then broken up further by a jet milling stage which reduces the particle size to around 5mm. It must be noted that when the alloy is in a powdered form then it is very flammable and must be handled under an inert gas.
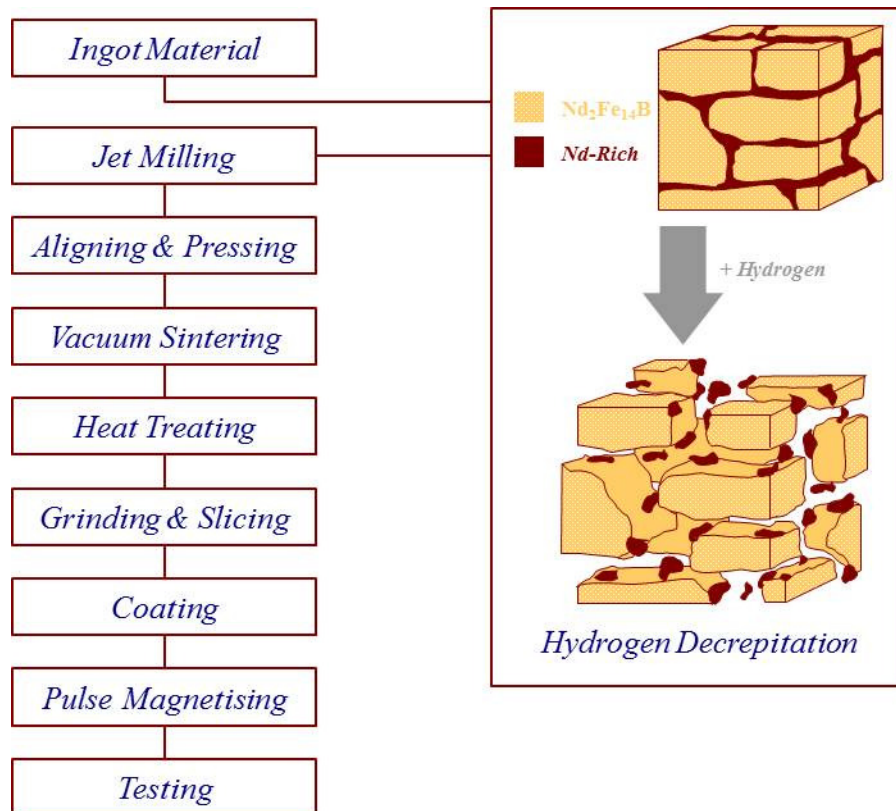

Figure 9: *The processing route for sintered NdFeB magnets.*

When the powder has been broken down to so fine a size, each particle of powder is a single crystal, which can be aligned in a magnetic field. This alignment is held in place by pressing the powder into a green compact, which is about 60% dense. The compact is then heated in vacuum to ~1060ºC for 1 hour. During the heating stage the hydrogen comes out of the material and is pumped away. When held at ~1060ºC for 1 hour sintering occurs and the compact densifies, with the assistance of a liquid formed by the melting of the Nd-rich phase. After sintering the magnets are quenched and then heat treated in order to achieve the optimum magnetic properties.

The magnet must then be machined to the final dimensions required for the intended application. Due to the large degree of shrinkage that occurs during sintering, which is greater in the direction of alignment, it is not possible to press compacts that will shrink to the exact size required. The

machining is a very expensive operation and, particularly for small magnets, a large proportion of the material may need to be machined away.

Due to the highly reactive nature of the Nd-rich phase, the magnets tend to corrode very rapidly, particularly in moist environments. Therefore, the next stage in the processing is to provide a protective barrier on the surface of the magnets. This is usually done with a nickel coating, although aluminium, zinc and epoxy resins are also used. Finally, the magnets are magnetised and tested prior to shipping to the customer.

Melt Spinning

In the USA, melt-spinning was used to produce a ribbon like powdered material. In this process, molten alloy is ejected onto the surface of a rotating water cooled wheel (see figure 10), 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, i.e. the speed of the rotating wheel. High quench rates produce essentially amorphous ribbons (i.e. no crystal grains) 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), which are single domain particles thus have a high coercivity (~1000kAm^{-1}). At wheel velocities below the optimum, the slow cooling rate produces ribbons that consist of larger grains and are characterised by low coercivities. This powder cannot be sintered to produce fully dense magnets without destroying the magnetic properties, but can be employed in one of three ways:

MQ-I

The melt spun ribbon is blended with a resin to produce a bonded permanent magnet . The crystals of MQI material are randomly oriented so that the magnets are isotropic and can be magnetised along any axis. The isotropic nature of the material limits the $(BH)_{max}$ to ~80 kJm^{-3}.

MQ-II

Improved densification of melt-spun ribbons can be achieved by hot pressing at ~750ºC, without adversely affecting the coercivity of the powder. These "MQII" type magnets exhibit a slight (~10%) degree of magnetic alignment and are 100% dense, i.e. the magnetic properties are not diluted by a non-magnetic material, such as a resin. This gives MQII a higher $(BH)_{max}$ than MQI of 100-120kJm^{-3}.

MQ III

Substantially greater alignment (> 75%), and hence greater maximum energy products, can be obtained by an additional processing step. The MQII material is heated to ~750ºC in a die cavity having a larger diameter and then slowly deformed. This second hot press, termed die upset forging, produces plastic flow and a reorientation of the crystals. Such magnets, known as 'MQIII' are 100% dense, and because of the alignment of crystals have maximum energy products of ~400 kJm^{-3}.
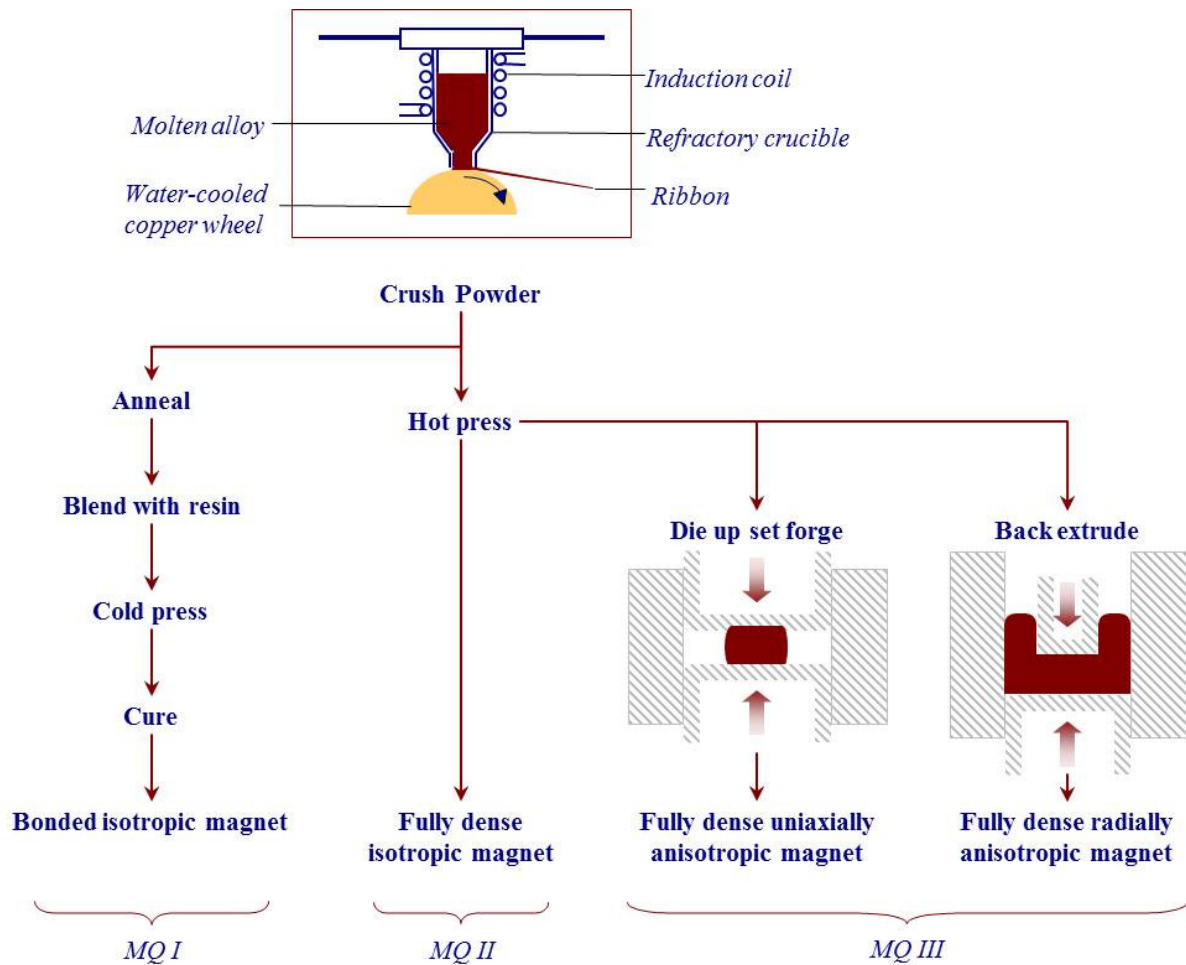
Figure 10: *The processing routes for melt spun NdFeB magnets.*

Applications of Hard Magnetic Materials

The rate of growth in the production of RE-Magnets has continued unabated, despite fluctuations in the world economy. Thus, sintered NdFeB magnets are exhibiting a current growth rate of ~12% whereas the growth rate for bonded NdFeB magnets is in excess of 20%.

The total value of hard magnets now exceeds that of soft magnets and the gap is widening. The reason for this spectacular growth has been due partially to the booming global PC market, as around 60% of NdFeB magnet production goes into disc-drive applications, primarily voice-coil-motors (VCMs).

This is by no means the whole story however and a summary of the very wide range of applications for RE-magnets is given below, with many of these being capable of substantial further growth.

In general terms, permanent magnets are far more important than is generally realised and this is perhaps, best illustrated by their use in the motor car. In the early fifties a car would have one

magnet (the speedometer) whereas some modern cars can have over a hundred permanent magnet motors.

Currently these are almost exclusively based on Sr-ferrite (SrFe12019) and the penetration of NdFeB magnets into this area requires a significant cost reduction, an increase in the maximum operating temperature and improvement in corrosion resistance.

The potential benefits of using NdFeB magnets would be a significant reduction in volume and weight and an improved efficiency. This will probably be a major influence in the use of these magnets in the future.

Growing concern about global warming has scientific and technological implications and many of these impinge on the use of NdFeB magnets. Future uses could include their more widespread use in "white goods" such as washing machines, refrigerators etc, in order to improve energy efficiency and hence reduce CO_2 emissions.

Another large use could be in generators for domestic combined heat and power units and in clean energy production such as windmills. The biggest potential however is in electric vehicles (EVs) which could be hybrid vehicles or totally driven by electricity in the form of batteries or a fuel cell.

There has been an enormous increase of interest and activity in this area over the past 5 years and the Japanese have been the first to commercialise these vehicles.

Examples of applications for permanent magnetic materials:
Automotive: Starter motors, Anti-lock braking systems (ABS), Motor drives for wipers, Injection pumps, Fans and controls for windows, seats etc, Loudspeakers, Eddy current brakes, Alternators.

Telecommunications: Loudspeakers, Microphones, Telephone ringers, Electro-acoustic pick-ups, Switches and relays.

Data Processing: Disc drives and actuators, Stepping motors, Printers.

Consumer Electronics: DC motors for showers, Washing machines, Drills, Low voltage DC drives for cordless appliances, Loudspeakers for TV and Audio, TV beam correction and focusing device, Compact-disc drives, Home computers, Video Recorders, Clocks.

Electronic and Instrumentation: Sensors, Contactless switches, NMR spectrometer, Energy meter disc, Electro-mechanical transducers, Crossed field tubes, Flux-transfer trip device, Dampers.

Industrial: DC motors for magnetic tools, Robotics, Magnetic separators for extracting metals and ores, Magnetic bearings, Servo-motor drives, Lifting apparatus, Brakes and clutches, Meters and measuring equipment.

Astro and Aerospace: Frictionless bearings, Stepping motors, Couplings, Instrumentation, Travelling wave tubes, Auto-compass.

Biosurgical: Dentures, Orthodontics, Orthopaedics, Wound closures, Stomach seals, Repulsion collars, Ferromagnetic probes, Cancer cell separators, Magnetomotive artificial hearts, NMR / MRI body scanner.