POWDER METALLURGY AND ITS APPLICATION IN THE PRODUCTION OF PERMANENT MAGNETS

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ABSTRACT
In this article, some aspects of powder metallurgy have been reported. Powder metallurgy technique has been used in the production of permanent magnets since 1700s, and found to be the best method of fabrication of this sort of magnets. Most of high performance permanent magnets have been fabricated by employing powder metallurgy. Magnetic properties are so dependent on starting materials, microstructures, magnetic alignment, and heat testament process, therefore powder metallurgy represents an ideal route to control most of these factors.

Keywords: Powder Metallurgy, Permanent Magnets, Magnetic Alignment, Rear Earth Magnets.

HIGHLIGHTS
Powder metallurgy is a route of fabrication without full melting. Some aspects of this method of production have been discussed. The application of powder metallurgy in the production of permanent magnets has been reported. Magnetic properties are very sensitive to the chemical composition and microstructure of the products.

1. INTRODUCTION: WHAT IS POWDER METALLURGY?
Powder metallurgy is a means of manufacturing, without full melting, objects having properties which cannot be obtained by any other process. It is a technique that is applied for consolidation and formation of materials into useful products with different shapes, starting with powder mass. Powder metallurgy has played a vital role in solving many production problems, especially with those materials having very high melting points. During the last period of time powder technology has made remarkable progress for many fundamental reasons:
(i) It can be used to manufacture articles which cannot be made by any other route, such as porous bearing, filters, abrasive tools, electric lamp filaments, dynamo brushes, and a variety of soft and hard magnets, etc.

(ii) High purity material can be produced through this technique by controlling the production processes.

(iii) It may be used for products which may be made by other methods, but for which powder metallurgy is more convenient and cheaper with better quality.

The development of powder metallurgy is due to its great advantages over other routes in certain applications. It has now become the basis for the production of refractory metals, heat resistances materials, cutting tools, especial alloys which cannot be produced by conventional melting method, ceramic materials and most of magnets either in micro-scales or in nano-scales. The aim of this article is to give a general idea about powder metallurgy and its employment in the production of permanent magnets with especial specification according to their use.

2. SOME ASPECTS OF POWDER METALLURGY

a- Compaction

Compaction may be defined as the process for fabricating a desired shape by applying pressure to a powder in a die. The pressures which are used for this purpose are either of a mechanical or hydraulic type. The strength of the compacts made by pressing should be sufficient to withstand transportation to the next metallurgical operation. More information about this subject has been reported by Kuhn and Lawley 1978 [1]. There are many compacting techniques which have been used for fabricating different shapes;

(i) Die compaction         (ii) Isostatic compaction
(iii) Explosive compaction (iv) magnetic compaction
(v) Compaction by rolling  (vi) Compaction by extrusion
(vii) Compressing shearing method which was successfully developed by Tetsuji et al. [2].

There are two kinds of isostatic pressing equipment, these are known as Cold Isostatic Pressing (CIP) and Hot Isostatic Pressing (HIP) and both of them are either wet bag tooling or dry bag tooling. Fig. 1 illustrates the principles of the both types of tooling [3]. The use of any compaction technique depends on the shape of the magnet, and which one of these techniques is suitable for the production process to reach the desirable magnet.

![Fig. 1. Wet and dry tooling isostatic pressing](image-url)
b- Green density

Green density is an expression given to the density of the part after pressing by any powder metallurgy route in which the starting material is a powder. One of the most useful properties to be specified in the powder metallurgy process, generally the green density increases with:

(i) Increasing compaction pressure according to the type of the starting powder.
(ii) The use of a wide range of particle size.
(iii) Decreasing the hardness of the particles.
(iv) Addition of lubricants.

The green density distribution is much dependent on the length to the diameter (L/D) ratio of the compact [4]. If this ratio decreases, the green density becomes more homogeneous. A schematic illustration is given in Fig. 2 for high and low (L/D) ratios.

![Single End Compaction](image)

**Fig. 2.** Schematic illustration of green density distribution for high and low L/D ratios

c- Solid state sintering

In most cases, a green density compact cannot be used as the finished article because of low strength and brittleness. Sometimes a compact is required with a certain amount of porosity, but even in this case mechanical properties need to be improved by means of a heat treatment, which increases the cohesion between the particles of the green compact, or within a loose powder confined to a required shape. This heat treatment is known as "sintering". Many authors have discussed the phenomena occurring during sintering and it is agreed that sintering can occur in the solid state, normally taking place at a temperature below the melting point of the main component [5-7]. The Metals Handbook. Vol.7, American Society for metals, 1984, defines sintering as "the bonding of adjacent particles in a powder mass or compact by heating below the melting point of the main constituent". Six stages are considered during the sintering process; initial bonding, neck growth, pore channel closure, pore rounding, pore shrinkage and pore coarsening [8].

d- Liquid phase sintering

Liquid phase sintering (LPS) can be defined as "sintering of a compact or loose powder to produce consolidation under condition where a liquid is present during part of the sintering cycle". This process is widely used for consolidating metallic powder, ceramic powder, or both of them together, into final shapes. Liquid phase sintering is an important technological process for the production of hard metals, ceramic materials, soft and hard magnets, which is very essential to approach a value of about 99% of the theoretical density of the product. The advantages of production by this sintering method are a very fast densification rate, and production of microstructures which often provide mechanical and physical properties superior to those produced by solid state sintering.
Three stages in the liquid phase sintering process have been identified [9-11]; rearrangement, solution-reprecipitation and solid-phase bonding. One case should be noted; that is the liquid phase does not wet the solid particles because there is no reaction between them. This condition is often termed "sweating" and is shown by the presence of droplets on the compact surface. Fig. 3 shows high magnification fracture surface of sintered magnet of Nd$_{16}$Fe$_{76}$B$_8$ which was fabricated by hydrogen decrepitation (HD) process, and the sintering temperature was within the liquid phase sintering of this magnet. It is very clear to recognize the Nd-rich phase at the grain boundaries, surrounding almost all the particles of the hard phase Nd$_2$Fe$_{14}$B.

Fig. 3. SEM micrograph showing fracture surface of sintered specimen of Nd$_{16}$Fe$_{76}$B$_8$ made from powder of (HD) process [12, p. 171].

e- Sintering density

The density of the sintered mass is normally compared with the theoretical density of the basic material. In general, the maximum value of this sintered density is usually considered as a criterion of the quality of the sintering process, unless otherwise is specified.

3. THE ADVANTAGES OF POWDER METALLURGY IN THE PRODUCTION OF PERMANENT MAGNETS

Powder metallurgy techniques have been found to offer advantages in the fabrication of permanent magnets. It seems that the best magnetic properties probably often achieved by employing Powder metallurgy routes rather than casting processes. Although in some cases a combination between them is used in the manufacturing of permanent magnets. Careful control of particle size and particle orientation, using a magnetic field to align the starting particles, are among two of the greatest advantages of the powder metallurgy process.

Chemical composition, impurities, and metallic and non-metallic inclusions probably controlled by using powder techniques. Additionally, extremely pure powders and freedom from inclusions are easy to attain by powder metallurgy processing. Composition of the permanent magnets may be limited in precision by the purity with which powder can be produced. In fact, all these factors mentioned above play a vital role in controlling and enhancing the magnetic properties of permanent magnets and soft magnets as well.
The products of powder metallurgy almost semi-finished produced to specifications with different shapes and sizes, so from this point of view the powder metallurgy technique is very advantageous as the machining stage can be dispensed with, thus decreasing costs and saving materials.

4. HARD MAGNETIC MATERIALS

Hard magnetic materials remain permanently magnetised after they are pulse magnetised in a magnetic field. These materials are hard to magnetise and demagnetise. Magnetic hardness is obviously related with the microstructure, heat treatment and chemical composition of the starting material. Magnetically hard substances are made into permanent magnets which provide magnetic field in working air, or vacuum gaps. The distinguishing characteristics of hard magnets are large hysteresis loops, high remanence and coercivity with different Curie temperatures. Permanent magnets are fundamentally energy storage systems when they are magnetised. Development of hard magnetic materials is in the direction of obtaining improved magnetic properties, reducing the cost of production and the volume of material required. Hard magnets are used to perform a wide variety of magnetic functions, such as in electrical machines, motors, computers, direct drive motors, electro-dynamic braking, clamping and holding devices for ferrous materials, loudspeakers, magnetic sealing, head-phones, focusing and steering of charged particles, medical equipment, etc.

5. POWDER METALLURGY AND PERMANENT MAGNETS

In fact, powder magnets have been known for a long time, the first development was made by Gowin Knight (1713-72), an English gentleman who stirred continuously a large amount of iron in water until he got a suspension of divided of finely iron oxide. This was mixed with linseed oil, the paste moulded into shape and baked hard. The resulting blocks were then magnetised and formed strong magnets for that time, reputedly [13]. The beauty of this story shows that the beginning of the development of the first permanent magnet by powder metallurgy primitive technique.

In the 1960's, the idea of this process of surrounding hard phase particles with non-magnetic material has been strongly re-introduced for producing permanents magnets [14, 15]. Some ferrites tend to be dissociated during heating at elevated temperature, so that the conventional route of melting and casting is impractical for ferrites, and ferrites are normally fabricated by Powder metallurgy [16].

6. MAGNETIC ALIGNMENT

(i) Magnetic field alignment

It is well known that magnetic alignment is one of the most important factors in the manufacturing of magnetic materials and articles made from them. If a magnetic filed is applied during the cooling or tempering while the temperature is just below the Curie point, a crystallographic growth along the direction of the applied filed which is nearest to the easy axis is encouraged. This process called magnetic annealing, the first attempt of this process was carried out at Sheffield (UK), and in 1938 it was found that heat treatment in a suitable magnetic field could enhance the magnetic properties of Alnicos permanent magnets [17]. This process was also used in the production of Sm-Co permanent magnets to solidify the ingots from the liquid state in a magnetic field produces oriented polycrystalline materials [18].

The production of magnets, by employing powder metallurgy technology probably give improved products because of the simplicity of aligning most of the powder particles along the easy direction at room temperature, and hence producing anisotropic compacts. These are manufactured
by pressing fine particles of the materials in a strongly aligning magnetic field and then sintering to near theoretical density. The degree of alignment is influenced by particle shape, particle size distribution, magnitude of aligning field, and pressing pressure. The remanence and the energy product are thereby sharply enhanced [19]. Magnetic alignment of Nd-Fe-B hydride powder using a flexible bag is shown in Fig. 4.

In 2007, synthesis of magnetite particle-chain microwires by applying magnetic field during the fabrication process has been firstly reported by Fashen et al. [20]. Their conclusions were that \( \text{Fe}_3\text{O}_4 \) microwires are successfully produced under external magnetic field, and the connection of the particles is very tight with each other. Fig. 5 shows the morphology of \( \text{Fe}_3\text{O}_4 \) magnetic powder, from which we can see the chain agglomeration of the particles and the particle size is within the range of 0.25 \( \mu m \).

**Fig. 4.** Magnetic alignment using a flexible bag [12, p. 120]

(a) Schematic diagram

(b) Flexible bag filled with (HD) powder wetted with some cyclohexane
(ii) Magnetic alignment by cold rolling

This method is limited to ductile ferromagnetic materials. Many of them exhibit a fairly strong tendency to orientate their crystals when they are cold rolled or worked, depending upon the fabricability of the materials. Plastic deformation can produce a grain orientation which gives improved magnetic properties. An investigation of this phenomenon utilising a single crystal of Ni$_3$Fe was made by Chikazumi, et al. [21]. They found that the anisotropy is strongly dependent on the crystallographic orientation during the rolling process. Textured anisotropic FePd /$\alpha$-Fe nanocomposite foils have been produced by combination between cold rolling process and magnetic alignment under high magnetic field, after being annealed at 450–600°C for 2h [22]. Their conclusions were that magnetic anisotropy could be induced in the magnetically annealed FePd /$\alpha$-Fe nano-composites due to their textured nanostructures.

(iii) Magnetic alignment by Thermo-mechanical route

Magnetic alignment may be achieved by Thermo-mechanical alignment means. Crystallographically orientated or anisotropic magnets can be prepared by this route, which consists of hot pressing followed by hot deformation. This was discovered in 1985 by R. W. Lee, Physics Department, General Motors Research Laboratories (USA) and applied in the production of Nd-Fe-B permanent magnets [23]. This method could be applied for many magnetic materials to see the results of it to fabricate anisotropic magnets. Magnets prepared by this means have been further improved by Croat [24, 25] who announced values of (BH)$_{\text{max}}$ up to 350 kJ/m$^3$ and $H_c$ of about 1080 kA/m. The relation between the % of height reduction and remanence of Nd-Fe-B permanent magnets is shown in Fig. 6.

The great advantages of this technique include the fact that:
(i) Magnetic alignment may be induced with no magnetic field.
(ii) The product is almost in the final shape required.
(iii) The process is ideally suited to radial alignment, either for ring or arc shapes.
Fig. 6. Magnetic remanence versus % die upset for hot deformed Nd-Fe-B magnets [25]

7. POWDER METALLURGY OF CERAMIC PERMANENT MAGNETS

Powder metallurgy has been used in the production of ceramic permanent magnets since 1950s by Philips Company (USA) [26-28]. In general, these ferrites are based on Ba, Sr, Pb and have a formula MFe$_{12}$O$_{19}$, where M is Ba, Sr, Pb. The representatives of this class of ferrites, which have been given the name of Ferroxdure, have a hexagonal structure (the easy axis being along the c-axis). Ferroxdure is manufactured either as a solid permanent magnet or in the form of ferrite particles dispersed in plastic (bonded ferrites), which is the same idea of Gowin Knight. Production of SrFe$_{12}$O$_{19}$ powders by direct use of celestite as a source of strontium has been reported by Mortaza and Jamshid [29]. Their results were compared with those of powders fabricated by normal ceramic route. They showed that their process is more covenant for production of SrFe$_{12}$O$_{19}$ powders than the conventional one. Synthesis and orientation of barium hexaferrite ceramics by magnetic alignment was studies by Denis AUTISSIER, who showed that the magnetic properties strongly depends upon the structural quality of the produced ceramic, magnetic alignment, particle size and the density of the sintered magnets [30]. Starting powder of BaFe$_{12}$O$_{19}$ and the production route of these hexaferrite permanent magnets by powder injection molding have been reported by Zlatkov et al. [31]. Production and characterization of SrFe$_{12}$O$_{19}$ powder obtained by hydrothermal process at 180°C for 24h have been investigated by Malick Jean et al. [32]. Their results were shown that to produce a quasi-pure SrFe$_{12}$O$_{19}$ phase, it is necessary to start with a solution that contains a ratio of Fe/Sr equal to 8.

8. POWDER METALLURGY AND REAR EARTH MAGNETS

(i) The first generation

Over the last four decades, permanent magnets based upon Rear Earths have been dramatically developed. The first generation of rear earth permanent magnets depends on SmCo$_5$ and
Sm (Co, Cu, Fe, Tm)$_{7-8}$ alloys, where Tm≡Zr, Ti, of Hf. Several intermetallic phases of the type RCo$_5$ where R≡Y, Ce, Pr, Sm, or Y-rich, Ce-rich mischmetal were investigated by Srrnat et al. [15]. They concluded that these alloys promising candidates for fine particles permanent magnets with high anisotropy. Magnets fabricated by compacting fine powders of SmCo$_5$ in a magnetic field gave different maximum energy products $(BH)_{\text{max}}$ according to the production factors [14, 33]. In 1969, Das [34] reported a "Twenty Million Energy Product Samarium-Cobalt Magnet" with a value of $(BH)_{\text{max}}$ of 158kJ/m$^3$ (about 20MGOe). This result was achieved by improving the magnetic alignment and reducing the particle size below $10\ \mu m$.

In the 1970s, the preparation and enhanced properties of SmCo$_5$ magnets produced by liquid phase sintering were reported by Benz et al. [35]. Their conclusions were that this route gives improved magnetic properties and eliminates porosity. After the development of SmCo$_5$ permanent magnets in the early of 1970's, alloys with some quantity of copper as well as rare earth and cobalt emerged. These alloys became known as the precipitation hardened family of R(Cu, Co) and eventually led to the development of Sm (Co, Cu, Fe, Tm)$_{7-8}$ [36].

(ii) The second generation

The Sm$_2$Co$_{17}$ compounds have emerged as second generation rare earth permanent magnets and these were developed with some addition of Fe to become Sm$_2$ (Co, Fe)$_{17}$ [37]. The effects of various additive elements on magnetic hardness of the Sm-Co-Fe-Cu system studied Ojimo et al. [38]. The formula was Sm$_2$ (Co, Cu, Fe, M)$_{17}$, where M≡Nb, V, Ta, or Zr. It was found that Zr addition to the Sm-Co-Fe-Cu system improves the hard magnetic properties whilst a post-sintering annealing process enhances the coercivity. Production and development of these magnets have been reviewed by Strant and Ormerod [39, 40].

(iii) Nd-Fe-B permanent magnets, the third generation

In the middle of 1983, new rare earth permanent magnets were discovered, and this led to extensive research on these materials in many countries. These magnets based on Nd-Fe-B alloys could be looked upon as the third generation of Rare-Earth permanent magnets. At the beginning, and independently, two routes were developed for fabricating these new magnets, and these have continued to be used.

The first is a conventional powder metallurgy route which was developed by Sagawa et al. [41] in Sumitomo Special Metals Company Ltd (SSMC), Japan. This route is the well established powder metallurgy technique traditionally employed for the production of ferrite magnets. It is used by most magnets manufactures and was successfully employed by Sagawa and his colleagues to produce sintered Nd-Fe-B permanent magnets, starting from an as-cast ingot. After preparing the ingots, the following steps were used for making magnets:

(i) The ingots were crushed to a particle size of about 1mm by using a jaw crusher under an inert gas atmosphere.
(ii) Using a disc mill, a particle size of around $100\ \mu m$ was achieved.
(iii) Pulverization by ball milling in a stainless steel container with an inert solution produced a particle size of about $3\ \mu m$.
(iv) The powders thus obtained were aligned in a magnetic field at 200kA/m and pressed at a pressure of 200MPa, giving a green compact.
(v) The green compacts were then sintered in argon gas at temperature of $1000-1125^\circ C$ for 1h and then rapidly cooled. The sintered specimens were given a post-sintering to enhance the coercivity.

In the end of these steps, an energy product $(BH)_{\text{max}}$ of about 290kJ/m$^3$ was obtained. Further improvements which gave $(BH)_{\text{max}}$ values as high as 380kJ/m$^3$ were later reported by Sagawa et al.
[42]. Liquid phase sintering is widely used in the fabrication of Sm-Co and Nd-Fe-B magnets. In the case of Nd-Fe-B, a Nd content in excess of stoichiometric Nd$_2$Fe$_{14}$B is normally used for LPS of Nd-Fe-B magnets [43]. Many fundamental investigations have been reported on this type of rare earth permanent magnets [19, 44-47].

The second route for the production is rapid solidification to give an isotropic permanent magnet, this method being announced by the General Motors Corp. (GM) USA. They announced in 1983 the fabrication of isotropic Nd-Fe-B hard magnets by employing the rapid solidification technique [48, 49]. At the beginning the energy product of the magnets produced by this method was about 114 kJ /m$^3$. Later, magnets prepared by employing thermomechanical deformation route have been further improved by Croat, 1989 [24, 25], who announced a value of $(BH)_{max}$ of around 350kJ/m$^3$ starting from stacks of ribbons, or fragments of ribbon material which were produced by rapid solidification process.

9. HYDROGEN DECREPITATION (HD) PROCESS

In 1979, Harris et al. patented the hydrogen decrepitation (HD) process as a means of producing powder of SmCo$_5$ alloys (British patent 1554384, October 1979). Large lumps can be crumbled up readily to obtain an extremely friable produced which is consequently very amenable to further reduction in particle size. After the discovery of Nd-Fe-B permanent magnets, the (HD) process was successfully re-applied to decrepitate as-cast ingots of the Nd$_{15}$Fe$_{77}$B$_8$ alloy and related compositions [50]. This subject has been fully reviewed by Harris, Harris and McGuiness, and Ragg et al. [51-53]. The production of rare-earth-sintered magnets by a low-cost has been published by Takiishi et al. [54]. They showed that sintered Nd- based permanent magnets can be produced without using glove box. In 2012, combination between the HD and HDR has been used in the recycling of Nd-Fe-B magnets [55]. The procedure for the use the (HD) method can be briefly summarised as follows:

(i) The as-cast ingot is broken into pieces of about 20mm or less in diameter.
(ii) The broken lumps are exposed to hydrogen in a stainless steel vessel at room temperature, the vessel being evacuated initially to avoid the oxidation problem. One bar of hydrogen pressure can be used to decrepitate the Nd$_{15}$Fe$_{77}$B$_8$ alloy.
(iii) The hydride is then removed from the vessel and milled by any milling technique available, under protective atmosphere.
(iv) The particles obtained within a certain particle size are magnetically aligned and pressed. The green compacts are heat treated in vacuum to remove the dissolved hydrogen and then sintered to produce permanent magnets.

Very small particle size required probably achieved following decrepitation by different technique of milling within a relatively short time, thus replacing the time consuming conventional route. This reduction in processing time should decrease the oxygen content of the powder, which leads to enhancement of the magnetic properties. Comparison between magnets produced by the (HD) process and the conventional route has been made by Moosa et al. [56]. Fig. 7 shows the effect of the hydrogen pressure on particle size at a certain milling time, whilst Fig .8 shows the microstructures of Nd$_{16}$Fe$_{76}$B$_8$ magnet produced by the two methods. The demagnetisation curve for an example of a magnet produced from Nd$_{16}$Fe$_{76}$B$_8$ alloy after a post-sintering anneal at 640°C for 1h, together with magnetic parameters are shown in Fig. 9. The curve shows very good squareness, which indicates that, the hydride particles were well aligned by using powder metallurgy techniques.
Fig. 7. Micrographs showing the variation of particle size at the same milling time (30min.) for different hydrogen pressure, (a) 2bar, (b) 10bar [12, P.154]

Fig. 8. SEM micrographs: (a) Magnet made by the (HD) process, (b) Magnet produced by the conventional route [56]
Mechanical alloying normally starts with mechanical milling of the elemental powders, which are repeatedly welded together and sheared until mixing on a microscopic scale has occurred. This is followed by pressing and sintering causes a solid state reaction within and between the compacted particles, hence creating the required alloy and structure. In general the results obtained depend on starting particle size, powder impurities, milling time, and heat treatment. Mechanical alloying is one of the methods which has been employed in the production of Nd-Fe-B permanent magnets [57-59]. This route has also been used in the production of Sm-Fe-N permanent magnet [60]. The main drawback of this magnet is the sintering process at high temperature, because Sm$_2$Fe$_{17}$N$_3$ compound is not stable at high temperature and decomposes into $\alpha$Fe and SmN phases above 600°C. Recently, Sm-Fe-N bulk magnets have been produced utilizing nonconventional consolidation techniques of compaction such as deformation- shearing process and shock compression route [2, 61, 62]. Mechanical alloying can be employed in the production of soft magnets as well, so as the magnetic properties more easy to be controlled [63].

The vast of majority of the rare earth permanent magnets are fabricated by powder metallurgy techniques. The general process steps are alloys preparation, milling, composition control, particles alignment, pressing, sintering and post-sintering treatment, machining or grinding, and magnetizing of the products as shown in the metallurgical process diagram, which represents the production steps of sintered magnets with attainable magnetic properties.
11. CONCLUSION

At the end, we can see the significance of using powder metallurgy techniques in the fabrication of permanent magnets. Important things should be concluded here; that by employing powder metallurgy techniques, superior magnetic properties can be achieved. The properties of permanent magnets are critically dependent upon chemical composition, particle size of the hard phase, magnetic alignment, pressing technique, type of materials, and heat treatment. Almost all these parameters can be easily controlled by using powder metallurgical processing methods, and hence enhancing the magnetic properties of the produced magnets. Most of the permanent magnets are preferred to be fabricated by this route because the products are almost semi-finished to a certain specifications, so as the machining can be avoided during the production process.

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