Most Production routes of Nd-Fe-B permanent magnets

Iessa Sabbe Moosa, Chiraz ZIDI

Abstract- A vital information about the most used production routes of Nd-Fe-B magnets has been reported. Very significant details about these routes were given, as well as manufacturing procedure of Nd15Fe77B8 and near compositions permanent magnet. Seven methods of production have been summarized, starting with the conventional powder metallurgy route and ending by the Hydrogen Decrepitation (HD) route, as they are the most applicable routes in this field. The advantages and disadvantages of the reported routes were mentioned. In fact, the HD method was found to have the following advantages in the production of Nd-Fe-B magnets: simplicity, reducing the sintering temperature, and improving the coercivity of the formed magnets. Two designed units related with the HD route has been drawn. Furthermore, some microstructures of SEM images of decrepitated polished surfaces were given to show the advantage of using the HD route in the production process of Nd-Fe-B.

Key words: Powder metallurgy, Thermal-Mechanical Deformation, Reduction / Diffusion route, Hydrogen Decrepitation (HD).

I. INTRODUCTION

The announcement of high performance permanent magnets based on Nd-Fe-Bin 1983 generated much scientific and technological interest [1] [2]. It was shown that these magnets were superior to Sm-Co material in terms of their magnetic properties at room temperature, while at service temperature higher than 1500°C they were inferior to Sm-Co magnets because of the strong draw-back of their properties like larger temperature coefficients and low corrosion resistance which reduced the possibility of using those magnets in many technical fields [3]. Thus, much effort has been made to solve these problems [4] [5] [6] [7]. The great interest in the material resulted from both its magnetic properties and from the fact that its raw material, Nd and Fe are more abundant than Sm and Co.

The high magnetic anisotropy associated with the tetragonal structure of the Nd2Fe14B hard phase is now known to be the origin of the excellent magnetic properties [1] [8]. After the discovery of Nd-Fe-B magnets, Koon et al. reported that they had successfully grown a single crystal of Nd2Fe14B and this had a saturation induction at room temperature of 1.62T, which places a theoretical upper limit of about 2.0T for the Nd2Fe14B magnets. This was calculated using the relation \((BH)_{\text{max}} \leq B_r^2 / 4\mu_0\). However, the presence of porosity, imperfect magnetic alignment, and other phases will give a value of the energy product lower than the theoretical value.

This article reviews what has been learnt about the basic of the most production routes which have been applied and their effect on the magnetic properties of Nd-Fe-B magnets. In reality, these production methods could be classified according to the techniques that have been used during the production process:

II. CONVENTIONAL ROUTE

This route is well established powder metallurgy traditionally employed for the production of ferrite magnets [1] [10]. It is used by most magnet manufacturers and was successfully employed to produce sintered Nd-Fe-B permanent magnets, starting from an as-cast ingot. In order to optimize the magnetic properties of the Nd-Fe-B, many alloys were prepared. The general formula for the chemical composition is Nd_xB_yFe_{100-x-y}, where x and y are the atomic percentages of Nd and B respectively. These alloys were melted in an alumina crucible under a protective gas atmosphere in an induction furnace. After preparing the ingots, the following steps were used for producing permanent 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 100μm was achieved.
(iii) Pulverization by ball milling in a stainless steel container with an inert solution produced a particle size of about 3μm.
(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°C for 1h and then rapidly cooled. The sintered specimens were given a post-sintering to enhance the coercivity.

At the end of these steps, an energy product \((BH)_{\text{max}}\) of about 290kJ/m³ was obtained [1]. Further improvements which gave \((BH)_{\text{max}}\) values as high as 380kJ/m³ were later reported by Sagawa et al. [11]. Liquid phase sintering (LPS) 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 of the hard phase Nd₃Fe₁₄B is normally used for LPS of Nd-Fe-B magnets [12]. At the beginning, typical characteristics reported for magnets produced by the conventional production means are given in Table I.

Iessa Sabbe Moosa and Chiraz ZIDI are current working in University of Buraimi, College of Engineering, Sultanate of Oman, P. O. Box 890, P. C. 512, Al-Buraimi
Many fundamental investigations have been reported on this type of rare earth permanent magnets [13] [14] [15]. Powder metallurgy and its application in the manufacturing of permanent magnets has been almost comprehensively reviewed by the author [16]. This route is well recommended in the mass production process.

III. RAPID SOLIDIFICATION PROCESS

This method of permanent magnet production based on Nd-Fe-B has been investigated almost fully by the group at General Motors Research Laboratories in the U.S.A. They announced in the 1983 the production of isotropic Nd-Fe-B permanent magnets by employing the raid solidification technique [17] [18]. The starting ingots were prepared by arc melting commercially available constituents. These ingots were then melt spun in an argon atmosphere by ejecting molten alloys through an orifice in a quartz crucible onto the edge of a rotating substrate disc, as schematically shown in Fig. 1. The quench rate can be varied by changing the substrate, hence controlling the grain size of the product which subsequently affects the magnetic properties. The result was ribbons about 40μm in thickness and 1.5mm wide.

![Fig. 1. Diagram of a typical melt-spinning apparatus](image)

Magnetic measurements were then made on mechanically compacted powdered samples and it was found that \( H_c \) was strongly dependent upon the quenching rate of the produced ribbons. The characteristics of magnets with composition of \( \text{Nd}_{13}\text{Fe}_{83}\text{B}_4 \) fabricated by this route are summarized in Table II.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remanence (Br)</td>
<td>1.23 T</td>
</tr>
<tr>
<td>Intrinsic coercivity (( H_c ))</td>
<td>969 kA/m</td>
</tr>
<tr>
<td>Normal coercivity (( H_{Nc} ))</td>
<td>880 kA/m</td>
</tr>
<tr>
<td>Energy product (BH)_{max}</td>
<td>290 kJ/m³</td>
</tr>
<tr>
<td>Density</td>
<td>7.40 g/cm³</td>
</tr>
<tr>
<td>Vickers Hardness</td>
<td>600 HV</td>
</tr>
<tr>
<td>Curie temperature (Tc)</td>
<td>312 °C</td>
</tr>
</tbody>
</table>

Later, Livingston reported that the peak properties occur at an optimum wheel speed, i.e. optimum quenching rate, that produces \( \text{Nd}_2\text{Fe}_{14}\text{B} \) hard phase with grain size of about 20-80nm in diameter [19]. The isotropic nature of the melt-spun ribbons gives limited remanence and energy product values and the problem which had to be overcome was how to achieve crystallographic alignment. Because of the extremely fine grain size of this material, crystallographic orientation by grinding followed by magnetic alignment as in the case of the conventional route was not practical [20]. This method has also been experienced in the recycling of rare earth sintered magnets of Nd-Fe-B to produce as isotropic bonded magnets [21].

IV. THERMAL-MECHANICAL DEFORMATION ROUTE

In 1985, Lee showed that a magnetic anisotropy could be induced by high temperature plastic deformation, and hence well aligned Nd-Fe-B magnets could be fabricated from rapidly quenched ribbons [22]. The first stage is to obtain full density by hot pressing stacks of ribbons at a pressure of about 200MPa and a temperature of about 750°C. The second stage was hot pressing of the products at almost as in the first stage, in a large die cavity to accommodate deformation transverse to the press (die upsetting). The feedback of this process is to create a preferred magnetization direction parallel to the press direction. A degree of magnetic alignment of about 75% probably approached with 50% die-upset (half of the original thickness). Magnets produced by this method have been enhanced by Croat [20]. He announced values of (BH)_{max} up to 350kJ/m³, with \( H_c \) of about 1080kA/m, and \( H_{ci} \) of around 900kA/m. This route has been reviewed by Croat et al. [23]. The value of \( B_r \) as a function of the height % reduction is shown in Fig. 2.

![Fig. 2](image)
Mechanical alloying normally starts with mechanical milling of the elemental powder, which are repeatedly welded together and sheared until mixing on a microscopic scale has occurred. This process is followed by pressing and sintering which causes a solid state reaction within and between the compacted particles, hence creating the required structure. In general, the results obtained depend on starting particle size, powder impurity, milling time, and critically upon heat treatment.

Mechanical alloying is one of the methods which has been used in the production of Nd-Fe-B permanent magnets [24]. They showed that a sintered magnet of tetragonal Nd₃Fe₁₄B hard permanent magnet phase can be produced from mechanically alloyed material starting from elemental Nd and Fe powders, and master alloy of Fe₃B powder, which was previously prepared by arc melting under a high purity argon gas atmosphere and crushed. All powders were milled, compacted in air at a pressure of about 700MPa, and the green compact then sintered in a sealed quartz glass capsule, which was evacuated to 10⁻² Pa. However, the authors did not report full magnetic properties of magnets produced by this route. The maximum value of H₆ obtained was about 577kA/m for Nd₁₅Fe₇₇B₈ composition. This value is much less than that reported by Sagawa et al.[1], and may the other magnetic properties were not that good not compared with results of above authors because of the oxidation process during the fabrication procedure.

Later, magnetically isotropic Nd₁₅Fe₇₇B₈ powder was prepared from elemental powders by mechanical alloying route combined with solid-state reaction [25]. Pure powders were used, the Fe powder size varying from 5μm to 40μm while the Nd was smaller than 500μm, and the amorphous B was less than 1μm. The prepared powders were mixed to give an average composition of Nd₁₅Fe₇₇B₈, and then sealed under argon gas in a stainless steel container prior to ball milling action. Two stages of reaction were recognized, the first was diffusion between the Fe and the Nd particles which develop after milling time of about 30h at room temperature. This process leads to the formation of FeNd interfaces which increased in depth with milling time and resulted in FeNd powder particles with submicron B particle embedded between them. The second stage was a solid state, or interdiffusion reaction produced by heating in which the hard phase of Nd₃Fe₁₄B formed because of the dissolution of the B particles in the FeNd powder. The best magnetic properties were achieved after heat treatment at about 700°C for 30min., they were as follows: Bₜ=0.8T, (BH)ₜmax=1011kJ/m³, and Hₑ=1014kA/m. These values can be compared with the results of the rapid quench route (see TABLEII). The method was also used to prepare Dy₁₅Fe₇₇B₈ magnets as well as Nd₁₅Fe₇₇B₈ [25]. The results obtained by employing this route showed that mechanical alloying can be advantageously used to fabricate of permanents magnets of Nd-Fe-B, and this method should be able to be developed to convert the isotropic magnets to anisotropic by magnetically aligning and pressing the obtained powders.

This method is characterized by simplicity of production instead of using the casting method to produce Nd₁₅Fe₇₇B₈ alloy first, and then going to the conventional powder metallurgy to complete the production process which probably lead to increase the produced magnets cost. Very important details about mechanical alloying and its application have been reported [27] [28] [29]. Nanocrystalline Nd-Fe-B magnet prepared by mechanically has been published by Liu et al. [30]. The disadvantage of this method is the difficulties to control on the content of oxygen as very important factor affects the magnetic properties of these magnets.

VI. REDUCTION/DIFFUSION (R/D) METHOD

The main advantage of using the (R/D) route is that the production process begins with the elemental powders of Fe, B, or Fe and FeB (ferro-boron particles), together with commercial Rare Earth oxides, as starting materials, so that the cost of fabrication could be reduced. In 1985 Hereget first reported success in using this method in the production of the Nd-Fe-B magnets [31]. He suggested that the process can be divided into two steps, a reduction step (I), and leaching step (II). Calcium was used as reducing material. The reaction equations for this process are as follows:

\[
\begin{align*}
\text{(I)} & \quad \frac{15}{2} \text{Nd}_2\text{O}_3 + 72 \text{Fe} \rightarrow \frac{4}{30} \text{Fe}_{30} + \frac{45}{2} \text{Ca} \\
& \quad \text{at } 1200 \degree \text{C, vacuum, } 4h \quad \text{Nd}_{15}\text{Fe}_{77}B_8 + \frac{45}{2} \text{CaO} \\
\text{(II)} & \quad \text{Ca (solid) + CaO (solid)} \rightarrow \text{Ca (OH)₂ (Liquid), *Excess Ca} \\
\end{align*}
\]

Where * iron powder and ⁰ commercial powderized ferro-boron.

The rout consists of a reduction of Rare- Earth oxide, and in the presence of transition metal powder is immediately followed by a diffusion process, and hence leads to the formation of the required alloys.
Elsewhere, the R/D method was also studied and successfully employed to produce Nd-Fe-B magnets [32].

The starting materials were Nd₂O₃, Fe, and FeB particles which were mixed with an amount of calcium 2-3 times the stoichiometric value, the diffusion process was represented by the following equation:

\[ 8 \text{Nd}_2\text{O}_3 + (76 - \frac{8x}{y}) \text{Fe} + \frac{8}{y} (\text{Fe} \times \text{By}) + 24 \text{Ca} \xrightarrow{860-1120 \degree \text{C, vacuum}} 4-6 \text{h} \rightarrow \text{Nd}_{17} \text{Fe}_{77} \text{B}_8 + 24 \text{CaO} \]

The excess calcium and the calcium oxide were leached out of the obtained powder by using water, and then rinsed with alcohol. The particle size was refined to that needed for fabrication of magnets by milling as in the conventional route. The magnetic properties obtained by this method were: \(B_r = 1.3T, H_{cj} = 240kA/m\), and \((BH)_{max} = 286.5kJ/m^3\).

This calco-thermic route was also used and reviewed by other workers to prepare sintered \(\text{Nd}_{17}\text{Fe}_{77}\text{B}_8\) permanent magnets to achieve higher energy product of about 306kJ/m³ [33] [34]. More information of applying this method can be obtained in US patent No. 4990307, Inventors Floyd E. Camp. Feb. 1991.

VII. LIQUID DYNAMIC COMPACTION ROUTE

Liquid dynamic compaction (LDC) is a method of production in which a thick ribbon sheet can be made by consolidating a stream of atomized particles directly on a cooled substrate. The LDC route has been used to produce isotropic permanent magnets of Nd-Fe-B which can react with hydrogen gas to form hydrides, and that rendered the alloys very friable and hence convert them very easy to mill to get the required particle size. During this process, hydrogen gas reacts with the Rare Earth rich phases in the ingots of Rare Earth magnets to form hydride compound. Therefore volume expansion occurs due to the creation of the hydride, and the product is very brittle, so that producing very fine powder is done by employing any milling method.

In 1978, Harris et al. discovered and patented the Hydrogen Decrepitation (HD) process as a new method of preparing powder of SmCo5 alloy [39]. In 1983, and after the discovery of Nd-Fe-B Rare Earth permanent magnets, the HD route was immediately re-applied on as-cast alloys of Nd_{17}Fe_{77}B_8 and near compositions to produce needful powder of these alloys. This really amazing work was done in the School of Metallurgy and Materials at Birmingham University, Magnetic Materials Group, UK [40] [41].

![Schematic diagram showing the LDC process](image)

Fig. 3. Schematic diagram showing the LDC process [34, redrawn]

Generally, LDC is based upon the process of gas atomization in which a stream of molten alloy is broken into a spray of very fine particles by a jet of high velocity gas, and the rapidly solidified particles are collected. In this route, a cooled substrate just beneath the atomization cone at a distance such that most of the sprayed particles are immediately solidified. Fig. 3 illustrates this process.

It can be concluded that this route may lead to the elimination of the handling of powders and their compaction and sintering, but there may be difficulties in producing different shapes required of magnets. Nanocomposite bulk magnets of \(R_2\text{Fe}_{14}\text{B} / \alpha-\text{Fe} (R = \text{Nd or Pr})\) with almost full density have been successfully fabricated by shock compaction starting from melt-spun powders [38]. In this attempt, the addition of \(\alpha-\text{Fe}\) is to increase the magnetization of the product.

VIII. THE HYDROGEN DECRIPITATION (HD) ROUTE

Hydrogen Decrepitation (HD) is a method to crumble alloys which can react with hydrogen gas to form hydrides, and that rendered the alloys very friable and hence convert them very easy to mill to get the required particle size. During this route, hydrogen gas reacts with the Rare Earth rich phases in the ingots of Rare Earth magnets to form hydride compound. Therefore volume expansion occurs due to the creation of the hydride, and the product is very brittle, so that producing very fine powder is done by employing any milling method.

In 1978, Harris et al. discovered and patented the Hydrogen Decrepitation (HD) process as a new method of preparing powder of SmCo5 alloy [39]. In 1983, and after the discovery of Nd-Fe-B Rare Earth permanent magnets, the HD route was immediately re-applied on as-cast alloys of Nd_{17}Fe_{77}B_8 and near compositions to produce needful powder of these alloys. This really amazing work was done in the School of Metallurgy and Materials at Birmingham University, Magnetic Materials Group, UK [40] [41].
Fig. 4. (b) Unit for HD with heating facility [42, pp. 98-99]

Fig. 4 shows the designed units related with the HD route, in which it can be seen that there are two types of HD processes, one of them can be conducted at room temperature (a) to decrepitate Nd$_{15}$Fe$_{77}$B$_{8}$ and near ingots, whereas the other one with heating facility (b) to decrepitate Nd$_{2}$Fe$_{14}$B alloy [42]. Fig. 5 reveals fracture surface and decrepitated polished surface of Nd$_{15}$Fe$_{77}$B$_{8}$ with different hydrogen pressures.

Fig. 5. SEM micrographs of hydride, (a) fracture surface, 20 bar, (b) decrepitated polished surface, 4 bar after 10 min [42, P. 149]

From the manufacturing point of view, the HD method was found to have the following advantages over other routes:
- Preparing of the starting powder is easy compared with other routes
- Reducing the sintering temperature, and controlling the starting particle size
- Enhancing the coercivity because of uniformity distribution of the Rare Earth rich-phase around the grain boundaries during sintering process
- The HD process has been intensively applied in the recycling of the sintered Rare Earth magnets, and therefore reducing the cost of production and supporting environmental balance [43] [44] [45].

Also, mechanical alloying method can be conjugated with the (HD) route to enhance magnetic properties of Nd-Fe-B by controlling the particle size of the obtained powders. Comparison between magnets based on Nd-Fe-B alloys fabricated by the conventional process and the HD method have been investigated by Moosa et al. [46]. In 2016, more vital technical details and history of the HD have been almost comprehensively reported by the author [47].

IX. CONCLUSION

In this article, the most production routes of Nd-Fe-B permanent magnets have been summarized. Many fabrication methods were employed to produce these types of magnets, as they are classified the strongest permanent magnets. It seems that the most applicable routes are the conventional and the (HD) in the mass production process. The chosen method of fabrication depends on the required magnetic properties and the needed shapes. In general, the advantages of using the conventional and the (HD) can be specified as follows:

- Simplicity in the preparing of the required powder starting form as cast lumps
- Producing different shapes of magnets
- Controlling the particle size of the compacted powder, and hence producing the needed magnetic properties
- Controlling the quantity of oxygen

ACKNOWLEDGMENT

The author would like to thank Mr. Kalyan Baddipudi of the UoB for proofreading and kind support.

REFERENCES

International Journal of Computation and Applied Sciences


First Author: Dr. Iessa Sabbe Moosa was born in Baghdad, IRAQ. He obtained the B. Sc. degree in physics, Basrah University, south of IRAQ, 1977, and the Ph.D. degree from The University of Leeds, 1991, UK, in magnetic properties of Nd-Fe-B.

The Author has published six books in different physics topics.In addition, he is very expert in using electron microscopy, TEM and SEM with EDS and WDS facility for chemical analysis. Also, he has some researches in the field of selective surfaces for solar heating system applications. He is currently working in the University of Buraimi, at College of Engineering in a position of Assistant Professor since 2011.

Second Author: Assistant Prof. Dr. Chiraz ZIDI, Chemical Engineer, PhD and Master's in Analytical Chemistry, almost 10 years of academic experience in teaching and research.

Acting Chair of Research and Innovation Department at the University of Buraimi, Sultanate of Oman.