Recycling of Nd-Fe-B magnets by hydrogen processing and re-sintering

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Abstract
In this work, sintered neodymium-iron-boron-type (Nd-Fe-B) magnets, from voice coil motors (VCM) of hard disk drives (HDD), were recycled using the hydrogen processing of magnet scrap (HPMS) route previously described. A hydrogenated NdFeB powder was generated from the VCM magnets, which was milled and sieved to a range of particle sizes. The powder was subsequently re-sintered into new magnets at 1060 °C in vacuum. The magnets produced from smaller particle sizes demonstrated an increase in remanence, density and maximum energy product compared to those from larger particle sized powders. However in all cases the re-sintered Nd-Fe-B magnets showed a decrease of density, remanence, coercivity and maximum energy product in comparison to the starting material. The decrease in magnetic properties has previously been reported to be due to a loss of Nd-rich grain boundary phase as a result of oxidation. In order to alleviate this effect and to optimise magnetic properties, neodymium hydride (NdH₂) was systematically added to the recovered hydrogenated Nd-Fe-B powder in this study to replace the grain boundary phase and to allow for liquid phase sintering. At between 2 to 3 at% NdH₂ additions the coercivity was fully recovered, at the expense of remanence which fell by 12.4-13.4 % respectively.

Keywords
Hydrogen decrepitation, Nd-Fe-B, permanent magnet, recycling, sintering, powder metallurgy

1. Introduction
The biggest market for rare-earth elements (REEs) is in rare earth magnets based upon neodymium-iron-boron. These magnets are used in high tech and clean energy applications such as hard disk drives, electric vehicles and wind turbines [1]. The great majority of Nd-Fe-B magnets are produced in fully dense form as sintered Nd-Fe-B magnets.

The European Commission has highlighted that the rare-earth elements are at highest supply risk of all metals for clean technologies and as a result these materials are now at the top of the European Union (EU) critical materials list [2]. It is expected that the demand for rare earths will grow at between 6 and 9 % per year, reaching 20 and 50 % growth by 2017 and 2020 respectively [2,3]. As the world moves towards a cleaner, greener future, demand for rare-earth-based materials will continue to increase. To alleviate the supply risk for REEs then multiple solutions will be required, including (1) substitution of critical REEs by less critical metals; (2) investing in sustainable primary mining from old or new REE deposits; (3) recycling of REE containing end-of-life (EOL) products such as hard disk drives (HDDs) and (4) using alternative technologies which do not contain rare earths. It should be noted that these solutions are not mutually exclusive.

HDDs have been identified as one of the most abundant and readily available forms of Waste Electronics and Electrical Equipment (WEEE) scrap containing Nd-Fe-B [4,5] which are available for recycling today. They are easy to identify and have a rapid turnover at about 5 years. Each 2½ inch HDD, mainly in laptops, contains 2.5 g of Nd-Fe-B whereas each 3½ inch HDD, mainly in desktop PCs, contains between 10 and 20 g [4,5]. However the separation of the magnet is difficult because the magnet is glued into its functional position, it is fully magnetised, and coated with e.g. Ni for corrosion protection. The VCM assembly is then held together with screws.

1.1. Use of hydrogen for separation of Nd-Fe-B magnets from electrical assemblies
Workers at the University of Birmingham (UoB) have shown that hydrogen can be used to efficiently separate Nd-Fe-B magnets from hard disk drives scrap. During the HPMS process the magnets are broken down into friable, demagnetised, hydrogenated Nd-Fe-B powder [5]. In doing so the nickel coating peels away from the surface of the magnets and the powder can be liberated from the
electronics. By mechanically processing the separated powder using mills and sieves it is possible to reduce the nickel content down to 400 ppm using a 90 µm sieve. At this nickel content, it should be possible to reprocess the magnets in alloy form into a new material avoiding its adverse effect on the re-sintering process.

1.2. Re-processing of Nd-Fe-B powder

The first description for the use of the hydrogen decrepitation (HD) process for re-processing of sintered Nd-Fe-B was initially proposed by Rivoirard et al. who used hydrogen to break down a demagnetised uncoated magnet into an anisotropic powder [6]. This route was later investigated by Zakotnik et al. who produced recycled sintered magnets from demagnetised uncoated Nd-Fe-B scrap. This was performed at the University of Birmingham by processing the material in hydrogen, then milling, aligning, pressing and re-sintering [7,8].

The magnetic properties of the re-sintered magnets showed a general decrease compared to the starting material (coercivity by 20 %, remanence by 10 % and maximum energy product by 15 %) as a result of the adverse effects of oxidation. During the sintering process for the primary production of Nd-Fe-B magnets, the Nd-rich grain boundary phase melts resulting in liquid phase sintering. When sintered material is used as the feedstock then the grain boundary phase has a higher oxygen content and therefore it does not all melt on re-sintering, resulting in a lower density magnet and a reduction in coercivity, remanence and maximum energy product.

It has previously been reported that by powder blending neodymium hydride into hydrogenated primary cast Nd-Fe-B alloys, then it is possible to produce fully sintered magnets which a higher coercivity [9]. The increase in coercivity was attributed to improved magnetic isolation of the Nd₂Fe₁₄B grains as a result of the increased proportion of the Nd-rich phase. Subsequently powder blending of NdH₂₋₇ was performed with secondary hydrogenated Nd-Fe-B powders from end of life sintered magnets. Zakotnik et al. studied the effect of blending 1 at% NdH₂₋₇ after the first cycle of re-sintering [10]. It was determined to be beneficial in recovering the loss in coercivity due to the fact that the Nd-rich phase was replaced on the second, third and fourth cycles. However, the addition of neodymium hydride was not included on the first recycling cycle and the quantity of neodymium hydride was not optimised. Zakotnik et al. subsequently reported the addition of rare earth material by blending with RE alloys [11].

At present, when the HPMS process is used to separate Nd-Fe-B magnets from electronics, then sieving to 90 µm is sufficient to remove all the nickel impurities [5]. To reduce the particle size of the material closer to near single crystal particles (around 10 µm) then further milling and sieving would be required which increases the time, energy consumption and therefore cost of this step.

At 90 µm, the HD powder will contain multiple Nd₂Fe₁₄B grains, which may still be aligned from the starting sintered magnet. It may be possible to align the 90 µm particles, with all the grains pointing in the c-axis direction during pulse magnetisation prior to re-sintering into a new magnet. If good alignment can be achieved in the final magnet then it may not be necessary to sieve the material down to near single crystal particles. Therefore the first aim of this paper was to investigate the effect of decreasing the particle size of the HD powder (90 microns – 45microns), produced from HD processed sintered Nd-Fe-B magnets, on the subsequent magnetic properties of re-sintered magnets.

The second aim of this work was to determine the optimum level of neodymium hydride additions to HD powder in order to maximise the magnetic properties of the final re-sintered magnets.

2. Experimental

The starting material was in the form of nickel coated arc segments obtained from scrap VCM magnets from the former Philips factory, in Southport UK. The composition, minor additions excluded, is Nd₃.₆₁Dy₁.₅₆Fe₁.₅₉P₁₄.₃₁Al₀.₇₅Co₁.₄₄Cu₀.₂₉B₅.₇₁ and was determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

The nickel coating layer was removed from the surface of the VCMs by scoring and peeling using a scalpel. The magnets were then hydrogenated at 4 bar pressure for 1 hour at room temperature. When the HD reaction was complete the remaining hydrogen was evacuated from the vessel, which was then transferred into an argon filled glove box.

Half of the HD powder was then burr milled inside the glove box, whereas the other half remained non-milled. The non-milled or burr milled powder was then sieved through either a 90 µm or a 45 µm mesh sieve.

Neodymium hydride was produced by roller ball milling for 20 hours and passed through a 45 µm sieve. The neodymium hydride was blended with VCM magnet hydrogenated powder by sieving the <45 µm neodymium hydride, from 0-5 at%, and the <45 µm burr milled HD powder together through a 45 µm mesh sieve several times to ensure a homogeneous mixture.

All sintered magnets produced during this work were made via the HD powder metallurgy route, at optimum conditions.
3. Results and discussion

3.1. Sintering with different particle sizes

The milling and sieving procedures used in the HPMS process will consume energy and require time for the powder to pass through the sieves stages [5]. The first part of this study was aimed at determining whether milling and sieving was required to below 45 µm where it has previously been shown that near single crystal particles are produced [15]. The demagnetisation loops for a range of sieved and milled or non-milled samples are presented in the Figure 1. The results are also presented in Table 1, which also includes the values of density and maximum energy product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( p ) [g cm(^{-3})]</th>
<th>( H_r ) [kA m(^{-1})]</th>
<th>( B_r ) [mT]</th>
<th>((BH)_{\text{max}}) [kJ m(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCM magnet</td>
<td>7.59</td>
<td>1,191</td>
<td>1,140</td>
<td>242</td>
</tr>
<tr>
<td>Non-milled &lt;90 µm</td>
<td>7.09</td>
<td>1,005</td>
<td>843</td>
<td>128</td>
</tr>
<tr>
<td>Burr milled &lt;90 µm</td>
<td>7.33</td>
<td>971</td>
<td>942</td>
<td>162</td>
</tr>
<tr>
<td>Non-milled &lt;45 µm</td>
<td>7.37</td>
<td>951</td>
<td>1,011</td>
<td>189</td>
</tr>
<tr>
<td>Burr milled &lt;45 µm</td>
<td>7.46</td>
<td>860</td>
<td>1,059</td>
<td>203</td>
</tr>
</tbody>
</table>

It is clear when comparing the magnetic properties of the starting VCM magnet to all the recycled materials that the density, remanence, coercivity and maximum energy product values decrease after re-sintering as can be seen in Figure 1 and Table 1. This result is consistent with previous studies which showed the same effect on magnetic properties after re-sintering of hydrogen processed Nd-Fe-B powder [7,8,10].

The oxygen content of this starting material is around 5,000 and 6,000 ppm which is much higher than a primary source (typically 300-400ppm). As mentioned previously, the Nd-rich grain boundary phase is the most reactive phase and therefore a proportion of this phase is more likely to have formed an oxide. Due to the oxidation of the Nd-rich grain boundary phase, there is a decrease in the total amount of liquid phase during the re-sintering process which results in incomplete sintering, and hence increased porosity. Consequently, the magnetic properties decrease as shown in Figure 1 and Table 1, as there are a high number of reverse nucleation sites in the recycled magnet compared to the starting material.

By decreasing the particle size of the hydrogenated Nd-Fe-B powder, the coercivity of the resultant magnets decreases, however, there is an increase in both the remanence and the maximum energy product. This would indicate that better alignment of the magnetic Nd\(_2\)Fe\(_{14}\)B grains is achieved when the material is reduced to near single crystal particles. It also implies that either the larger, multigrained particles from the sintered magnets cannot rotate in the pulsed magnetic field or that they are breaking apart during pulsing and pressing which leads to a significant degree of misalignment. The coercivity could also be affected by the packing factor, and pressing behaviour of the larger Nd-Fe-B powder particles during processing.

Figure 2 shows back-scattered electron images obtained from the SEM of the recycle sintered Nd-Fe-B magnets subjected to this study.
It is clear that more porosity is observed when larger starting particle sizes are used when comparing the SEM images in Figure 2 of the different recycled magnets. This is confirmed by lower density values in the larger particle sized materials. This reduction in density is likely to be a major cause for the loss in remanence due to the non-magnetic volume which this occupies. It is also interesting to note that for both 90 µm and 45 µm materials the milling improves the density.

Table 1 show that the recycling process results in a reduction in density when comparing the starting sintered material with the recycled materials. However, the density can be recovered when decreasing the particle size of the hydrogenated powder. From values in Table 1 and images in Figure 2 the recycled magnets with different particle sizes and processing can be ordered from the highest to the lowest density as follows: Burr milled <45 µm, Non-milled <45 µm, Burr milled <90 µm and Non-milled <90 µm. These results indicate that the smaller the particle size, the better the packaging arrangement of the particles, resulting in more dense green compacts prior to sintering.

Kerr effect imaging was performed using an optical microscope with a polarising filter in the direction perpendicular to the magnetisation axis of the recycled re-sintered NdFeB magnets. It was found that more misalignment of the grains occurred in the re-sintered magnets from larger particle sizes. The magnets made from smaller particles sizes demonstrated the highest degree of alignment which is accompanied by the greater remanence demonstrated by these magnets in Figure 1 and Table 1. These results are in accordance with previous studies [16-19], which described a sharp decrease in intrinsic coercivity and an increase in remanence and maximum energy product with the enhancement of the degree of alignment.

### 3.2 Neodymium hydride additions

By adding NdH₂.₇ to the hydrogenated Nd-Fe-B powder by powder blending it has been previously shown that it is possible to recover much of the coercivity lost during the recycling process [10]. However, in previous work the NdH₂.₇ additions were not studied systematically to map the improvement in coercivity with increasing NdH₂.₇ content from the first cycle or to optimise the quantity which should be added. Consequently, different percentages of NdH₂.₇ have been added to systematically study the influence of this addition on the magnetic properties.

As the best results were achieved above using hydrogenated powder milled and sieved below 45 µm then this was used for the starting materials. The demagnetisation loops of the recycled sintered Nd-Fe-B magnets blended with different NdH₂.₇ contents are shown in Figure 3.

![Figure 3 - Demagnetisation curves of recycled Nd-Fe-B based sintered magnets blended with 0 at%, 1 at%, 2 at%, 3 at%, 4 at% and 5 at% neodymium hydride](image)

The magnetic results are also presented in Table 2, which includes the values of density, relative density and maximum energy product. In Figure 4 the back-scattered electron micrographs obtained using the SEM of the starting material and recycle sintered NdFe-B magnets blended with NdH₂.₇ are displayed.
Table 2 - Properties of starting material and recycle sintered Nd-Fe-B-based magnets blended with neodymium hydride.

<table>
<thead>
<tr>
<th>NdH$_{2.7}$ content [at%]</th>
<th>$\rho$ [g cm$^{-3}$]</th>
<th>$\rho_{rel}$ [%]</th>
<th>$H_c$ [kA m$^{-1}$]</th>
<th>$B_r$ [mT]</th>
<th>$(BH)_{max}$ [kJ m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting material</td>
<td>7.59</td>
<td>99.98</td>
<td>1.191</td>
<td>1.140</td>
<td>242</td>
</tr>
<tr>
<td>0 at%</td>
<td>7.46</td>
<td>98.59</td>
<td>860</td>
<td>1.059</td>
<td>203</td>
</tr>
<tr>
<td>1 at%</td>
<td>7.54</td>
<td>99.84</td>
<td>1.138</td>
<td>1.016</td>
<td>194</td>
</tr>
<tr>
<td>2 at%</td>
<td>7.52</td>
<td>99.72</td>
<td>1.155</td>
<td>999</td>
<td>189</td>
</tr>
<tr>
<td>3 at%</td>
<td>7.50</td>
<td>99.68</td>
<td>1.246</td>
<td>987</td>
<td>183</td>
</tr>
<tr>
<td>4 at%</td>
<td>7.48</td>
<td>99.59</td>
<td>1.381</td>
<td>984</td>
<td>182</td>
</tr>
<tr>
<td>5 at%</td>
<td>7.46</td>
<td>99.44</td>
<td>1.400</td>
<td>975</td>
<td>179</td>
</tr>
</tbody>
</table>

It is clear that recycling results in a loss in density in all samples investigated. However, the relative density measurements remained above 98%. The addition of NdH$_{2.7}$ results in an increase of at least 1% in the relative density of the recycled sintered magnets compared with the sample with no additions. The measured density decreases from 1-5 at% NdH$_{2.7}$ as the neodymium hydride has a lower density than the starting material.

The remanence of the re-sintered magnets decreased with the addition of NdH$_{2.7}$ as can be seen in Table 2 and Figure 3, reaching a minimum of 975 mT in recycled magnets blended with 5 at% neodymium hydride. This was expected as the proportion of magnetic Nd$_2$Fe$_{14}$B matrix phase, which is the only phase contributing to the remanence, decreases with the addition of non-magnetic NdH$_{2.7}$. This is in good agreement with previous investigations [8,10]. The decrease in remanence results in a subsequent drop in maximum energy product.

The coercivity increased with increasing NdH$_{2.7}$ content reaching a maximum 1,440 kA m$^{-1}$ in recycled magnets blended with 5at% neodymium hydride. This increase can be attributed to better smoothing and isolation of the Nd$_2$Fe$_{14}$B grains due to the increased proportions of grain boundary phase as previously reported by Mottram et al [9]. The backscattered SEM images in Figure 4 clearly show less porosity with increasing NdH$_{2.7}$, larger triple points and better connectivity of the grain boundary phase.

It is especially interesting to note that the coercivity values obtained by the addition of 3, 4 and 5 at% NdH$_{2.7}$ are 4.6 %, 15.9 % and 17.5 %, respectively, higher than those exhibited by the starting material, as observed in Figure 3.

4. Conclusion

When hydrogen is used to separate Nd-Fe-B magnets from electronic waste in the HPMS process then the powder is sieved down to 90 µm to remove the Ni. At this size the separated particles may contain multiple aligned grains from the starting material. When 90 µm HD powder was used as the feedstock to produce sintered magnets then the coercivity, remanence and maximum energy product of the re-sintered magnets were inferior to magnets produced from HD powder which had been milled and sieved below 45 µm. It is therefore clear that further milling is required beyond that used to purify the hydrogenated Nd-Fe-B during the HPMS process.

By re-sintering of HD processed sintered Nd-Fe-B VCM material, the resultant magnets displayed a reduction in density, remanence, coercivity and maximum energy product in every case where no NdH$_{2.7}$ was added to the HD powder. This loss of...
coercivity, remanence and maximum energy product is attributed to a lack of Nd-rich material to provide liquid phase sintering. The optimum quantity of NdH$_{2.7}$ required in order to provide the liquid phase and to recover the coercivity of the sintered magnets was between 2 and 3 at%. Higher NdH$_{2.7}$ quantities resulted in coercivities which were in excess of the starting material at the expense of remanence. It should be noted that higher Nd ratios are likely to adversely affect the corrosion resistance of the magnets and this is the focus of further work.

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