THE USE OF HYDROGEN IN THE PROCESSING AND IN THE CHARACTERIZATION OF Nd-Fe-B MAGNETS AND ALLOYS: AN UPDATE

Rex Harris, Paul McGuiness, Carolyn Short, David Book, Oliver Gutfleisch, Akira Fujita, Marc Verdier and Hartmut Nagel[a]

School of Metallurgy and Materials Science, University of Birmingham, Birmingham B15 2TT, UK.

[a] NKE GmbH, Wedelstrasse 38, Dortmund 30, Germany.

Hydrogen can be used very effectively in the processing and characterization of Nd-Fe-B type magnets and alloys. The first use of hydrogen was in the Hydrogen Decrepitation (HD) process, a method of producing fine particles of $Nd_{15}Fe_{77}B_8$ type material suitable for jet milling as part of the powder metallurgy route for producing sintered magnets. The hydrided powder was found to be extremely friable, a techno-economic analysis revealing that a considerable saving can be made in processing costs in comparison with the conventional mechanical crushing route.

Hydrogen absorption and desorption measurements also provide useful information on the nature of these materials. Mass spectrometry and thermopiezic analysis (TPA) has been used to determine the hydrides formed during the process in a number of alloy compositions as well as the way in which they desorb hydrogen.

More recent developments involving hydrogen and the Nd-Fe-B material include the Hydrogenation Disproportionation Desorption Recombination (HDDR) process, which produces highly coercive material via a hydrogen induced structural change within the alloy. The basic nature of the process is discussed in addition to the relationship between initial microstructures, processing conditions, additional elements and final magnetic properties. The process has been characterized with the aid of TPA and in-situ resistance measurements.

1. THE HD PROCESS

The HD process for the production of Nd-Fe-B sintered magnets is now well established and is used by many manufacturers around the globe. The process involves exposing $Nd_{15}Fe_{77}B_8$-type alloys to <1 bar of hydrogen at room temperature, the material absorbs large quantities of hydrogen in an exothermic reaction; the resultant expansion of the crystal lattice combined with it's extremely brittle nature results in heavy cracking and the formation of a powder with a broad range of particle sizes from <1μm to >1mm. This powder is then jet milled in the same way as conventional jaw crushed & hammer milled powder, although due to the highly friable condition of the HD powder, the feed rate of the pre-milled material can be increased substantially. A techno-economic study of the process has shown that jet milling costs can be halved and that a reduction can be made in magnet costs, depending on the size of the magnet, of between 15 and 25% .

The variations of the final grain size of the sintered magnets with the jet mill feed rate for conventional and hydride powder are shown in Fig.1.

The hydriding process takes place in two stages. An initial reaction between the neodymium rich phase and hydrogen

results in the formation of $NdH_{\sim3}$ and subsequent to this, the main $Nd_2Fe_{14}B$ phase forms a hydrogen containing compound $Nd_2Fe_{14}BH_{\sim2.8}$. During vacuum sintering, the hydrogen is removed from the material in three stages. Between 50° and 300°C the $Nd_2Fe_{14}BH_{\sim2.8}$ hydrogen containing compound is completely desorbed, between 200° and 400°C the $NdH_{\sim3}$ is partially desorbed to form the more stable $NdH_{\sim2}$ and in the range 600° to 800°C, the final desorption of the di-hydride takes place leaving the hydrogen free alloy to sinter at ~1040°C , some 50°C below the temperature required for the sintering of conventionally milled materials.
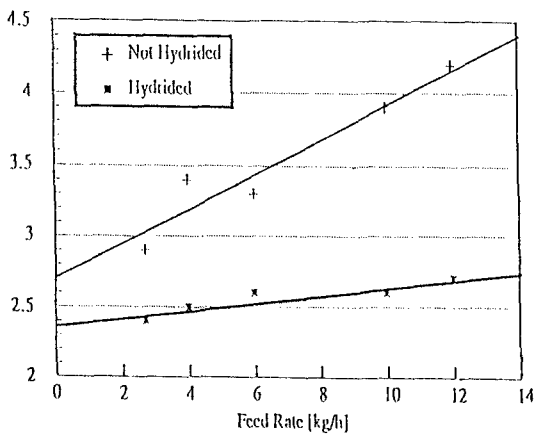

Fig.1. Final grain size vs jet mill feed rate.

Using a TPA, the interaction of $Nd_{15}Fe_{77}B_8$ alloys with hydrogen gas was investigated for different alloy additions of Nb and V. The TPA consists of a sample enclosed in a small volume with a fixed quantity of gas. As the temperature is raised and the material absorbs or desorbs gas, the pressure changes and these changes are detected, recorded and analysed via a microcomputer.

An alloy of $Nd_{15}Fe_{76.5}Nb_{0.5}B_8$ (Nb has been observed to enhance the coercivity) was heated to determine whether the Nb had any effect on the amount of hydrogen absorbed. No change in comparison with an undoped alloy could be determined except that the disproportionation temperature was found to be higher, possibly indicating that an increased stability results from the solubility of Nb in the $Nd_2Fe_{14}B$ phase.

Vanadium is also used to improve coercivity and to avoid the formation of the $NdFe_4B_4$ phase. Fig.2. shows the increased amount of hydrogen absorbed as a function of V concentration. The increase in the amount of hydrogen absorbed is due to an increase in the amount of Nd-rich material which is itself a result of the formation of the V_2FeB_2 phase which consumes Fe and B, thus increasing the amount of Nd rich material available to absorb hydrogen. The absence of any significant change in the disproportionation temperature points to little substitution of V in the matrix phase.
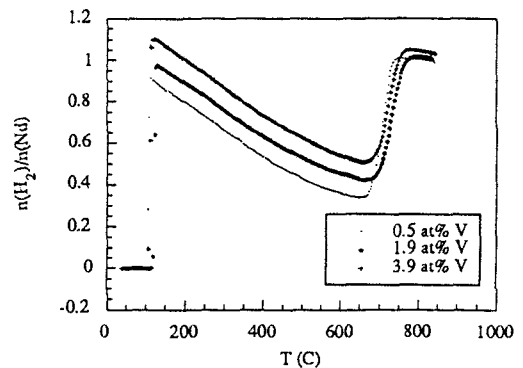

Fig.2. Effect of Vanadium additions on the hydrogen absorption properties of $Nd_{15}Fe_{77-x}B_8$ alloy

THE HDDR PROCESS

The Hydrogenation Disproportionation Desorption Recombination (HDDR) process has been reported [1&2] as a method of producing highly coercive

powder without the need to proceed through complex and expensive jet milling/sintering or melt spinning procedures. In it's simplest manifestation the process consists of hydriding the material, with a composition not dissimilar to that used for sintered or melt spun magnets, then heating the hydrided alloy in a hydrogen atmosphere to ~750°C. After holding at this temperature for a short time the material is then out-gassed in a vacuum again at ~750°C and allowed to cool to room temperature.

McGuiness *et al* [3] explained the induction of coercivity in terms of a disproportionation reaction which was known to occur in hydrogen at these temperatures. This disproportionation reaction on cooling to room temperature can be represented as follows:

$Nd_2Fe_{14}B + 2.7H_2 -> 2NdH_{2.7} + 12Fe + Fe_2B$ Eq.1.
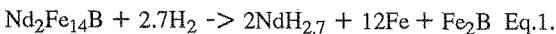
The nature of the high temperature disproportionation reaction and the identification of the reaction products were revealed by Curie point measurements, X-ray diffraction and hydrogen desorption via mass spectroscopy.

Thus the development of the very fine grain size, (compare Fig.3. the as-cast material with Fig.4. the same material subjected to the HDDR process), can be understood in terms of an initial hydriding which proceeds to a disproportionation with the external application of heat.

The finely divided disproportionated material: Nd-hydride, Fe_2B and Fe remains stable until the hydrogen atmosphere is replaced by vacuum conditions whereupon, the Nd-hydride desorbs, the Nd, Fe_2B and Fe mixture becomes thermodynamically unstable and recombines to form the $Nd_2Fe_{14}B$ phase, this time as very fine grains typically of the size ~0.3μm if optimum conditions are used.
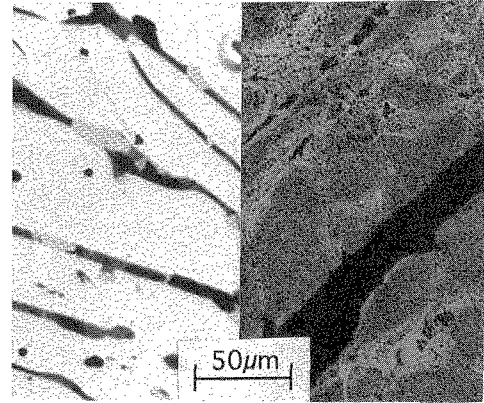

Fig.3. As cast   Fig.4. HDDR
$Nd_{16}Fe_{76}B_8$

It has been observed that the HDDR grains are susceptible to grain growth with the formation of relatively large faceted grains when processing temperatures higher than that required for optimum properties are used. This can result in low coercivities.

The poor coercivities at lower processing temperatures can be attributed to the presence of unrecombined iron, whereas the fall off in coercivity at higher temperatures can be ascribed to grain growth.

In an attempt to monitor and to understand the HDDR process we have looked at the various stages of the process using TPA, magnetic, and *in situ* resistance measurements[4,5&6].

TPA measurements[7] have been carried out on a number of Nd-Fe-B materials which exhibit a wide range of grain sizes. The heating rate used for these experiments was constant at 1°C min^{-1}, and the starting pressure for each experiment was 1bar.

Results indicate that the disproportionation temperature is sensitive

to grain size, particularly when the grain size is below 1μm. The difference in the onset temperature of disproportion for cast material and nano-crystalline melt spun material is some 250°C.

Fig.5. shows a schematic diagram of a HDDR experiment monitored by measuring the electrical resistivity. Resistivity, hydrogen pressure and temperature are shown as a function of time.

The $Nd_{14.68}Dy_{.94}Al_{.62}Fe_{76.47}Nb_{.5}B_{6.79}$ samples were heated under vacuum to elevated temperatures (T=700-850°C) and then hydrogen was introduced into the system (p(H2)=0.1-1.0 bar). Introduction of hydrogen at lower temperatures would result in the decrepitation of the material (the HD process), whereas, at T~800°C, disproportionation occurs during hydrogenation with the absence of cracking.

The rapid decrease in resistivity after the introduction of hydrogen corresponds to the disproportionation process (Eq.1.) with the formation of free iron. After a certain time, no further change in resistivity can be observed, indicating that the material is completely disproportionated. The equilibrium value of resistivity after disproportionation depends upon the hydrogen pressure in the system. On evacuating the system, the $NdH_{~2.2}$ phase desorbs hydrogen and the sudden decrease in resistivity can be attributed to the dissociation of Nd-hydride into Nd which subsequently recombines with the other constituents. Thus the intimate mixture of iron, ferro-boron and neodymium becomes thermodynamically unstable and recombines to form the thermodynamically more stable $Nd_2Fe_{14}B$ phase.

The appreciable increase in resistivity after recombination compared with that before disproportionation, could be due to

enhanced scattering of electrons at the grain boundaries, as well as to the reduction in anisotropy in comparison with the cast structure.
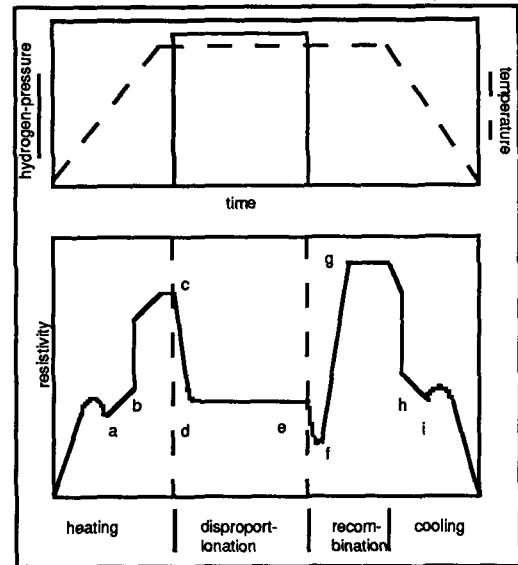

Fig.5. Schematic representation of resistivity changes taking place during HDDR process

To provide microstructural evidence of the nature of the HDDR-process, a sample (~1cm³) was processed. Fig.6 shows an optical micrograph of the sample which was exposed to hydrogen p(H2)=0.7 bar for 3 hrs at T=750°C. The sample was cut across a 'transition zone' where the original as-cast grains are partly disproportionated. Using the Kerr-effect, this phenomenon can be observed more clearly because no domain pattern can be seen in the sub micron sized disproportionated grains. Embedded in the dark Nd-rich phase (A) is the grey 1-4-4 phase (B) and a light phase (C) which is Fe- and Nb-rich. Towards the edges of the cubes most of the grains are fully disproportionated and towards the centre, the grains are still in the original state.

The micrograph indicates that the Nd-rich grain boundaries act as a diffusion path for the hydrogen and moreover, as the hydrogen will be transported quickly along transgranular microcracks in the sample, no sharp front of a disproportionated zone can be observed. The disproportionation occurs from the outside of each $Nd_2Fe_{14}B$ as-cast grain towards the centre. These observations are in agreement with phase transformation studies during HDDR by Xiao et al [8] and by Book & Harris [9]. In the 'transition zone' a ring of disproportionated material encloses the centre of the original grain.
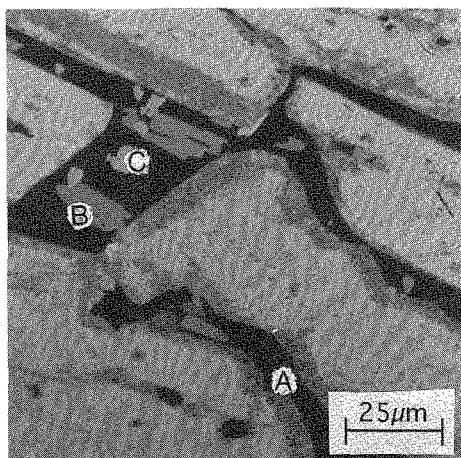

Fig. 6. Optical micrograph using the Kerr-effect of a $Nd_{14.68}Dy_{0.94}Al_{0.62}Fe_{76.47}Nb_{0.5}B_{6.79}$ alloy which was exposed to hydrogen at 750°C for 3 hrs under a pressure of $p(H_2)=0.7$ bar (cubic sample cut across the 'transition zone' where the 2-14-1 as-cast grains are partly disproportionated)

In cubes which were exposed to lower hydrogen pressures such as $p(H_2)=0.2$ bar for 3 hrs, it was observed that only the regions close to the surface disproportionate.

In an attempt to understand the role of Zr in producing anisotropic material, a thorough investigation of Zr substituted alloys with composition $(Nd_{2.2}Fe_{14}B)_{100-X}Zr_X$ has been undertaken [10 & 11]. Alloys were annealed at around 1040°C for 24hrs. Solid HDDR materials were prepared from both the cast and homogenized alloys with Zr concentrations in the range $0 \leq X \leq 1.0$. The magnetization values of the samples were measured using a VSM. In this experiment the arc melted samples were cut in a direction perpendicular to the surface of the copper hearth and then shaped to plate like specimens about 4mm in diameter and 1mm thickness.

It was found that, the greater the Zr content, the lower the concentration of iron dendrites, this was found to be particularly true for alloys with a relatively rapid cooling rate. After annealing, grain growth was observed in the sample without Zr while the columnar structures were preserved in the samples 0.3 - 0.7 at% Zr without significant grain growth. Figs.7&8. show clearly the difference in grain growth between the 0% and 0.5% at% Zr alloys.
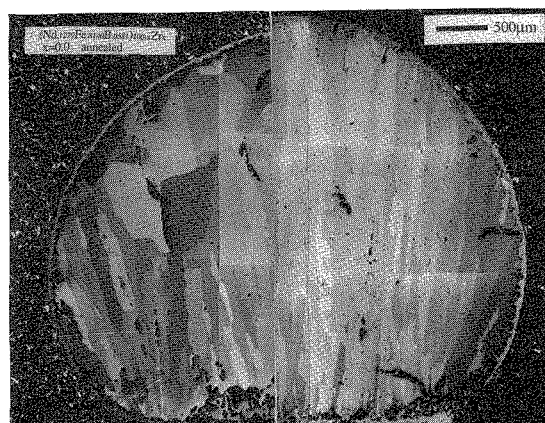

Fig.7. 0% Zr   Fig.8. 0.5% Zr

Thus, in this concentration range, the Zr seems to inhibit grain growth and this could indicate the presence of grain

boundary precipitates. The VSM measurements in directions both parallel and perpendicular to the cooling surface revealed no evidence of anisotropy in the HDDR sample produced from the cast ingot, even with 1at% Zr. The magnetic properties indicated a random orientation of the c - axis unlike the initial condition. Thus it can be concluded that the crystalline directions are not memorised after the HDDR process. In contrast however,when the HDDR treatment was applied to annealed samples with more than 0.5% Zr, anisotropic behaviour was observed. These results indicate that, in the HDDR process, Zr plays some role in preserving the c- axis orientation of the initial grains. The extent of the aligned fine grains seems to depend not only on the concentration of additional elements but also on whether the ingots were annealed before the HDDR treatment

CONCLUSIONS

1. The HD process results in substantial savings in the production cost of sintered magnets largely because of the much improved jet milling characteristics of the hydrided powder.
2. TPA can be used to characterise effectively $Nd_{15}Fe_{77-X}Nb_XB_8$ and $Nd_{15}Fe_{77-X}V_XB_8$ alloys. TPA shows that Nb additions inhibit disproportionation and V additions increase the amount of Nd-rich phase.
3. TPA studies show that the disproportionation temperature is sensitive to the grain size of the initial alloy, particularly when the grain size is $<1\mu m$.
4. The disproportionation reaction in solid samples can be followed very effectively by resistivity measurements after introducing the hydrogen at elevated temperatures.

5. In solid samples the Nd-rich grain boundaries act as diffusion paths for the hydrogen.
6. After the HDDR treatment, Zr additions to annealed $(Nd_{2.2}Fe_{14}B)_{100-X}Zr_X$ alloys result in the retention of the preferred alignment of the cast solid samples

REFERENCES

1. IR Harris., 12th Int. Workshop on Rare Earth Magnets and their Applications, Canberra, Aus. (1992) 347.
2. R Nakayama & T Takeshita., J. Alloys and Compounds, 193(1993)259.
3. PJ McGuiness, XJ Zhang, XJ Yin and IR Harris., J. Less-Common Metals.,162(1990)359.
4. O Gutfleish, M Verdier and IR Harris., Journal of Alloys and Compounds, 196(1993)L19.
5. O Gutfleish, M Verdier, IR Harris and AE Ray., Presented at Intermag '93 Stockholm, Sweden.
6. O Gutfleisch, C Short, M Verdier and IR Harris, Presented at EMMA '93 Kosice, Slovakia.
7. D.Book & I.R.Harris., IEEE Trans. Magn. Vol. 5 (1992)2145
8. Y Xiao, J Liu, B Qiu, and M Liu., 12th Int. Workshop on Rare Earth Magnets and their Applications, Canberra, Aus. (1992)258.
9. D Book & IR Harris,. To be published.
10. A Fujita & IR Harris., Presented at Intermag '93, Stockholm, Sweden.
11. A Fujita & IR Harris., Presented at EMMA '93 Kosice, Slovakia.

ACKNOWLEDGEMENTS