JOURNAL OF MATERIALS SCIENCE 21 (1986) 4107–4110

The production of a Nd–Fe–B permanent magnet by a hydrogen decrepitation/attritor milling route

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A bulk ingot of a Nd–Fe–B alloy has been powdered by a combination of hydrogen decrepitation and attritor milling. The powder was aligned and pressed in the hydrided condition and the green compact sintered at 1080° C for 1 h after an appropriate heating rate. Excellent densities were achieved after this procedure and the magnets produced by this method exhibited energy products in the region of 250 kJm^{-3} (32 M GOe).

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1. Introduction

Since 1978, the use of hydrogen in the processing of rare-earth-based magnets has been studied in the Department of Metallurgy and Materials, University of Birmingham. The earliest work [1] was mainly concerned with the hydrogen decrepitation of the intermetallic $SmCo_5$ and good quality sintered and polymer-bonded magnets were produced from the hydrogen decrepitated (HD) powder. In the case of this compound the hydrogen could be readily absorbed and desorbed at room temperature prior to the magnetic alignment and compaction procedure.

The hydrogen decrepitation process was extended to the production of 2–17 ($Sm_2(Co, Fe, Cu, Zr)_{17}$)-type magnets [2] and in these cases the process required the combination of a high hydrogen pressure and a slightly elevated temperature of around 200° C. In the case of the sintered magnets the powder was magnetically aligned in the hydrided condition and the hydrogen was subsequently removed during the vacuum sintering process [3].

More recently we have reported [4] the hydrogen decrepitation of a bulk "Neomax" alloy (composition $Nd_{15}Fe_{77}B_8$) on exposing the alloy to hydrogen at room temperature. These studies showed that the desorption of hydrogen from the Nd–Fe–B alloy on vacuum degassing consisted of two stages whereby most of the hydrogen was desorbed in the temperature range 150 to 260° C and a smaller amount was desorbed in the range 350 to 650° C. This behaviour was interpreted in terms of the loss of hydrogen from the $Nd_2Fe_{14}B$ matrix phase during the first stage and from the neodymium-rich grain-boundary phase during the second stage. The loss of hydrogen from the matrix phase was confirmed by X-ray diffraction studies. The formation of two hydrides was consistent with the decrepitation behaviour where the initial activation process corresponds with the hydriding of the intergranular, neodymium-rich material resulting in transgranular failure, followed by the hydriding of the matrix phase with the attendant transcrystalline cracking of the individual crystallites. These studies also showed that hydrogen charging the sample at around 300° C produced a disproportionation of the sample and X-ray diffraction showed the presence of very finely divided iron after this reaction. The loss of hydrogen from the matrix phase in the lower temperature range is consistent with observations [5, 6] on the $Nd_2Fe_{14}B$ compound.

Harris *et al.* [4] made an aligned compact from the (HD) powder and in this condition no obvious coercivity was exhibited, but after vacuum sintering and an appropriate ageing treatment, the sample exhibited a value of H_{Ci} which was comparable with those of magnets produced from the standard milled material. These observations are consistent with other studies [6] which showed a remarkable reduction of the coercivity of $Nd_2Fe_{14}B$ on forming the hydride.

The hydrogen absorption/desorption behaviour of a $Nd_{15}Fe_{77}B_8$ alloy has been studied by Cadogan and Coey [7] using a thermomanometric analyser (TMMA). These workers showed that desorption of hydrogen from a hydrided sample heated in vacuum reached a maximum at 300° C and a disproportionation reaction was also observed. The composition, structure and magnetic properties of the $R_2Fe_{14}B$ hydrides have been reported in [8–10].

In this paper we report the application of the hydrogen decrepitation process to the production of a Nd–Fe–B magnet from a bulk alloy, based on the "Neomax" [11] composition ($Nd_{15}Fe_{77}B_8$).

2. Materials and experimental results

The bulk alloy was prepared by induction melting the

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constituents and the microstructure of the alloy was investigated by polishing a section and examining in a "Neophot" optical microscope and in a scanning electron microscope (SEM) using secondary electron and back-scattering electron imaging.

In order to produce the fine powder necessary for the production of the sintered magnets, the following procedure was adopted:

(i) The bulk ingot was broken-up into smaller pieces of ~1 to 2 cm^3 and then placed in a stainless steel hydrogenation vessel. The hydrogen pressure was monitored by means of a Budenberg gauge.

(ii) The vessel was evacuated to backing-pump pressure.

(iii) Hydrogen (white spot) was introduced to the vessel through a liquid nitrogen trap to remove water vapour.

(iv) The hydrogen pressure was raised to 40 bar at room temperature.*

(v) The hydrogen absorption process occurred and this was accompanied by audible clicks and a rise of temperature. The former was consistent with the decrepitation of the bulk material and the latter with the exothermic nature of the hydrogen absorption process.

(vi) After the hydrogen decrepitation process the powder (particle size < 1 mm) was transferred to an attritor mill and milled under cyclohexane for 25 min.

(vii) The milled powder was then dried prior to the production of the magnets.

The level of oxygen in the powder is a critical parameter in the production of the magnets and the oxygen content of the HD and HD/milled powder was determined by a LECO analyser.

The HD/attritor milled (HD/AM) powder was then pressed into an aligned "green compact" using a load of 750 kg cm^{-2} and a perpendicular alignment field of 955 kA m^{-1}. The "green compacts" were then placed in a tantalum boat and gradually heated to the sintering temperature of 1080° C. There was a marked degradation of the vacuum starting around 200° C due to the evolution of the hydrogen from the matrix phase. A smaller effect was observed at higher temperatures due to the second stage of desorption as reported by Harris *et al.* [4]. The samples were maintained at 1080° C for 1 h and then slowly cooled to room temperature. The densities of the sintered compacts were determined using a mercury displacement system which measured the densities to an accuracy of ± 0.03 g cm^{-3}.

The samples were magnetized in a magnetic field of 2388 kA m^{-1} prior to the determination of the second quadrant demagnetization loop. In order to compare the alignment fields required for the HD/AM powder with that of the standard milled powder, the remanence (*Br*) of the sintered magnets have been determined as a function of the alignment field.

3. Results and discussion

3.1. Characterization of the bulk alloy

A typical microstructure of the carefully polished bulk alloy is shown in Fig. 1 and the neodymium-rich regions and the $NdFe_4B_4$ (approximate composition) phase are observed mainly at the columnar grain boundaries.

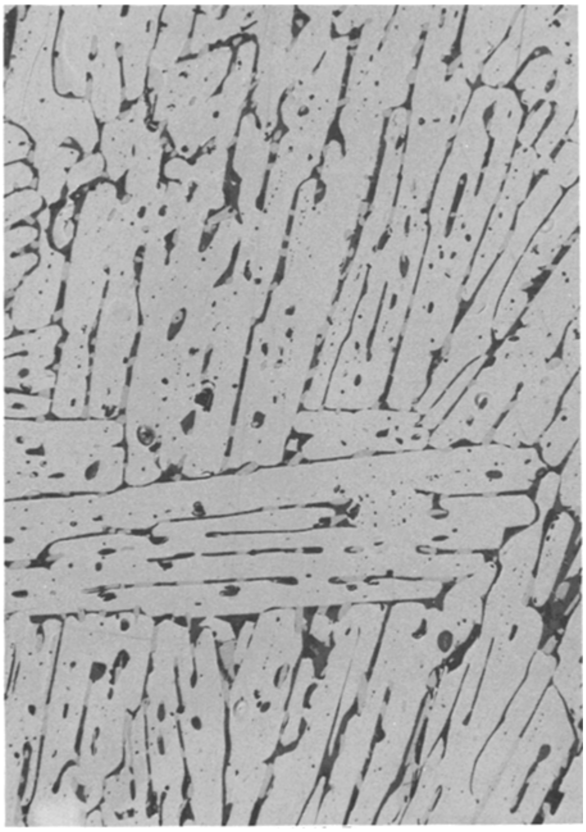

Figure 1 Optical metallograph showing the typical microstructure of the Nd–Fe–B alloy with the neodymium-rich regions and boride mainly at the grain boundaries. Magnification × 100.

3.2. Characterization of the HD powder

The morphologies of the HD powder are shown in Figs 2a and b the particles are largely flake-like in appearance. Unlike the standard milled powder, there is no fine debris clinging to the surfaces of the HD powder; a similar characteristic has been reported for the HD powder of a 2–17 alloy [2] and $SmCo_5$.

An oxygen analysis of the HD powder indicates a value of 0.28 wt %.

3.3. Characterization of HD/AM powder

The morphologies of the HD/AM powder are shown in Fig. 3 and compared with Fig. 2 there is an appreciable reduction in size. There is still an absence of fine debris compared with standard milled powder. An oxygen analysis of this material indicates a value of 0.45 wt % and Fisher sub-sieve measurements indicate an average particle size of 2.1 μm.

3.4. Characterization of the "green compacts" and sintered magnets

Unlike in our previous studies [4], we observed that the aligned green compacts exhibited a slight coercivity. Because of the change in the magnetic properties of the HD powder compared with that of the standard

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*More recent studies have shown that much lower pressures of around 1 bar can be employed.

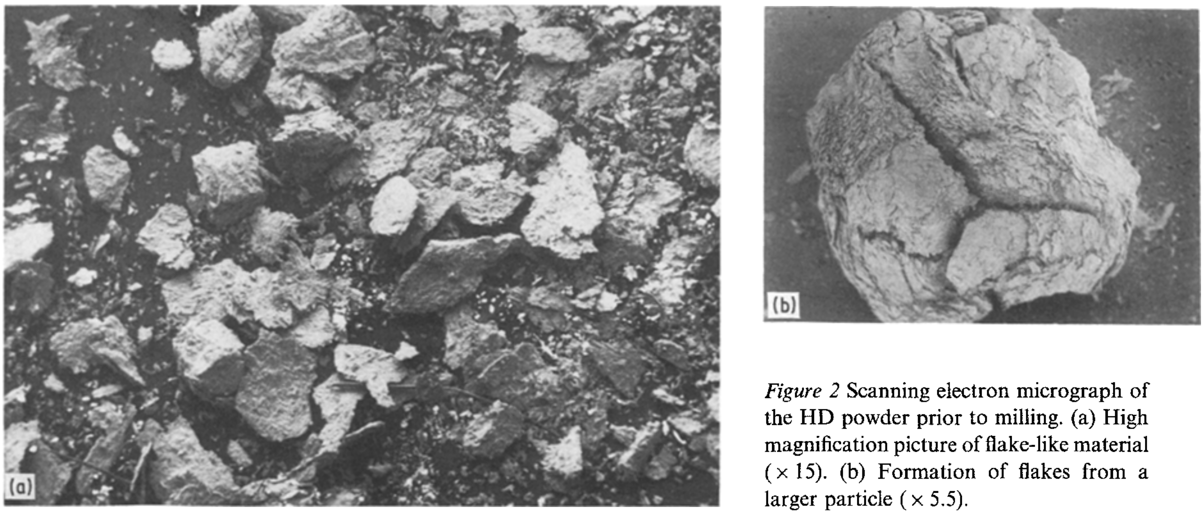

Figure 2 Scanning electron micrograph of the HD powder prior to milling. (a) High magnification picture of flake-like material (× 15). (b) Formation of flakes from a larger particle (× 5.5).

milled material, the alignment characteristics of the HD/AM powder have been determined in the present investigation. This was carried out to ensure that uniaxial anisotropy was maintained and to establish the optimum value of the alignment field. The remanence (*Br*) was employed as a measure of the degree of alignment and the variations of *Br* with alignment field (perpendicular and parallel to pressing direction) are shown in Fig. 4. The magnets were in the as-sintered and slowly cooled state (i.e. no ageing treatment) and were magnetized with a magnetic field of 2388 kA m^{-1}. These measurements show that the best properties are achieved for an alignment field perpendicular to the pressing direction and in this case a field of around 320 kA m^{-1} is required to achieve the maximum value of *Br*. For the alignment field parallel to the pressing direction, a field of around 800 kA m^{-1} is required. Typical *B* against *H* and (*B–H*) against *H* curves for an as-sintered magnet made from HD/AM powder using a perpendicular alignment field are shown in Fig. 5. The value of *Br*, H_{CB}, H_{Ci} and $(BH)_{max}$ are summarized in Table I together with the oxygen content of the magnet and the density.

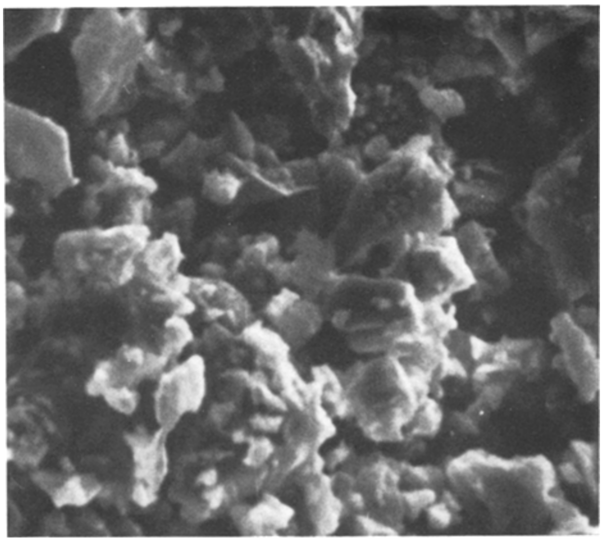

Figure 3 Scanning electron micrograph of the HD/AM powder, × 320.

4. Conclusions

The present studies demonstrate clearly that the hydrogen decrepitation process in conjunction with attritor milling can be used to produce suitable powder for the preparation of high energy product, Nd–Fe–B magnets. However, some important questions still need to be answered, such as (i) is it possible to use ordinary grade hydrogen? (ii) how effective is the process at lower neodymium contents? (iii) is it possible to dispense with the attritor milling stage by suitable manipulation of the hydrogenation factors (pressure, temperature, cycling)? (iv) what is the economic viability of the process?

Our current opinion is that the hydrogen decrepitation process would be more effective if combined

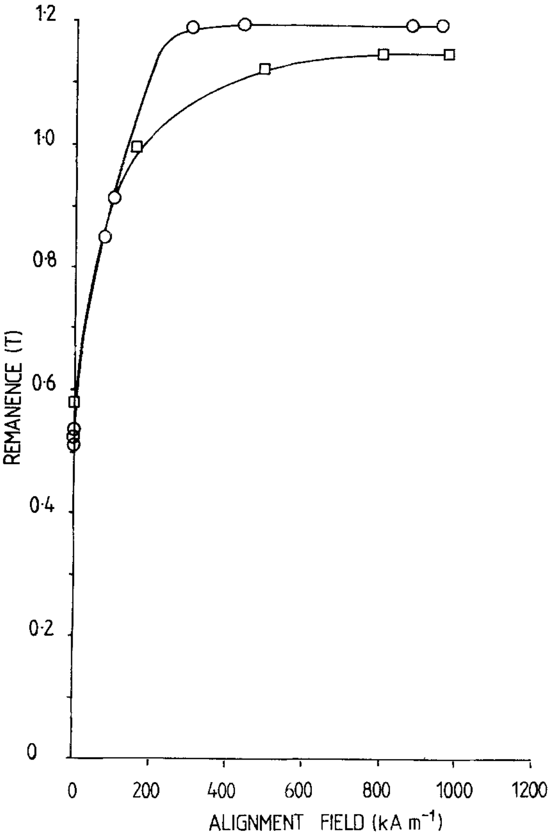

Figure 4 The remanence (*Br*) plotted against alignment field (H_A) for magnets made from HD/AM powder. (□) Parallel alignment field, (○) perpendicular alignment field.

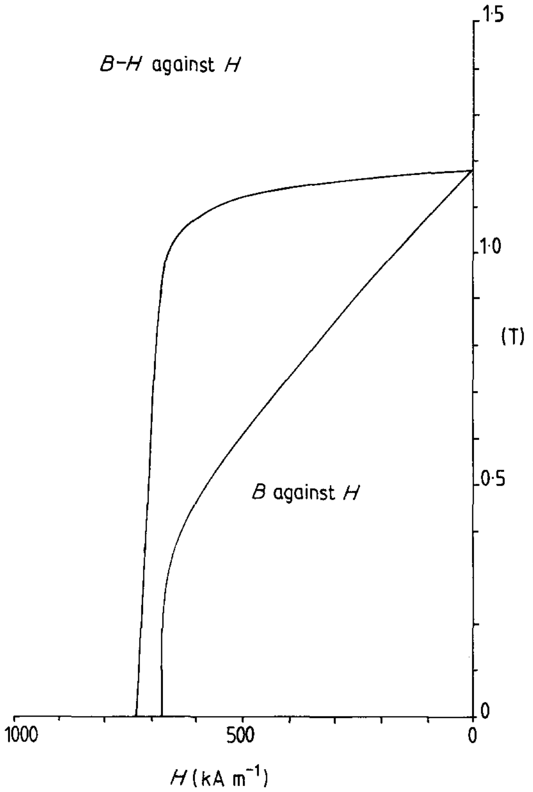

Figure 5 B against H and (B–H) against H curves for an as-sintered magnet (slowly cooled) made from HD/AM powder.

with jet milling and we propose to study such a hybrid process.

Possible advantages of hydrogen decrepitation as a pre-milling technique can be summarized as follows:

1. Large pieces of the bulk alloy can be decrepitated readily to fine powder. Difficulties with breaking-up the bulk ingot are sometimes encountered in the conventional process because the bulk alloy can exhibit toughness associated with the presence of free iron. These difficulties are removed by the use of hydrogen.
2. Intergranular failure should ensure the production of single-crystal particles.
3. There should not be a significant pick-up of oxygen or water during the process.
4. The HD particles have very clean surfaces suitable for subsequent sintering or bonding with, for example, soft metals.
5. The desorption of high-purity hydrogen from the powder particles should produce a non-oxidizing environment during the annealing process.

TABLE I Characteristics of HD/AM Nd–Fe–B magnet

Intrinsic coercivity (H_{Ci})	= 740 kA m^{-1}
Normal coercivity (H_{CB})	= 690 kA m^{-1}
Remanence (Br)	= 1.175 T
$(BH)_{max}$	= 250 kJ m^{-3}
Density	= 7.18 g cm^{-3}
Oxygen content	= ~0.4 wt %

Acknowledgements

Many thanks are due to the Commission of the European Communities for the support of the programme Concerted European Action on Magnets (CEAM) of which this work forms a part. Thanks are also due to M. A. Hixon for useful discussions and J. Knight for help with the metallography.

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Received 24 March
and accepted 3 April 1986