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Further studies of anisotropic hydrogen decrepitation in $Nd_{16}Fe_{76}B_8$ sintered magnets

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Abstract

$Nd_{16}Fe_{76}B_8$ sintered magnets were produced in aligned and unaligned forms. The magnets were prepared by isostatic pressing and finished with a centreless grinder; no coatings were applied and the samples were left unmagnetised. These magnets differed only in the orientation of the $Nd_2Fe_{14}B$ grains. Magnets were exposed to hydrogen and the decrepitation behaviour observed. At room temperature the aligned samples were found to decrepitate exclusively from the ends of the rods, with the decrepitation taking place in two distinct stages. It was found that only elevated temperatures, electrolytic charging or application of special coatings could initiate decrepitation away from the ends of the aligned sample. X-ray diffraction data have provided evidence for very high uptakes of hydrogen in the case of electrolytic charging of the aligned sintered sample. As a result of these studies, anisotropic hydrogen decrepitation was attributed to differences in the activities of the ends and sides of the aligned samples.

Keywords: NdFeB; Magnet; Anisotropic; Hydrogen; Decrepitation

1. Introduction

The effects of hydrogen gas on Nd–Fe–B alloys, particularly those with compositions close to that of the $Nd_{15}Fe_{77}B_8$ 'Neomax' composition, have been investigated by many workers (see for example Refs. [1,2]). The large quantities of hydrogen absorbed by these materials, combined with their extremely brittle nature, results in transgranular and intergranular cracking and a consequent powdering of the material. Hydrogen has been found to be readily absorbed by alloys in the cast as well as the homogenised conditions. Rapidly quenched materials produced by melt-spinning, such as MQ1 [3] have been found to be more resistant to hydrogen absorption, unless elevated temperatures of around 160°C are employed, possibly due to the presence of amorphous grain boundaries [4]. Sintered magnets too have been shown to absorb hydrogen, albeit with long activation and reaction times [5]. Recent studies [6] have shown that the absorption of hydrogen in these highly grain oriented samples occurs in an anisotropic manner, initially taking place only at the 'ends' of the magnets. This results in an easily observed anisotropic decrepitation (AHD) with the rod shaped samples gradually reducing in length as the ends of the sample decrepitate away. This work also showed that non-aligned (isotropic) samples exhibited a shorter activation time at room temperature and decrepitation occurred over the whole surface of the sample. In this paper, we report on further studies which have been undertaken in an attempt to reveal the processes which occur during this most interesting and unusual phenomenon.

2. Experimental

Cylindrical sintered magnets of composition $Nd_{16}Fe_{76}B_8$ were prepared from HD jet milled powders by isostatic pressing and vacuum sintering with subsequent heat treatment. The samples were left uncoated after centreless grinding to 10 mm diameter,

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and the ends of each sample were cut with a diamond saw at right angles to the cylinder axis to give cylinders of length approximately 30 mm. For the purposes of comparison, two types of sample were produced for this investigation: aligned samples, with the $Nd_2Fe_{14}B$ grains aligned with their [001] directions parallel to the axis of the cylinder and unaligned samples, with a random distribution of grain orientations. The aligned samples were produced by applying a large magnetic field just prior to the compaction of the powders, ensuring that the material was well aligned. As the process of sintering at around 1050°C takes the $Nd_{16}Fe_{76}B_8$ material well above its Curie temperature of 312°C, the aligned samples exhibited no remanent magnetisation after processing and appeared indistinguishable from the unoriented sample. All the experiments reported here were carried out on samples in this state. No subsequent magnetisation of the samples was undertaken.

The hydrogenation behaviours of the samples were recorded via video and 35 mm cameras. Each sintered $Nd_{16}Fe_{76}B_8$ sample was placed inside a transparent silica tube of diameter approximately 70 mm, containing purified hydrogen at a flow rate of 150 cc min^{-1} and a pressure of approximately 1 bar. Activation and reaction times, as well as the characteristic mode of decrepitation for each type of sample, were monitored.

In the electrochemical charging experiments a constant electric current density method was employed using the sintered magnet sample as the cathode and a Pd electrode as the anode, all in a 0.5 M citric acid solution with 3 g l^{-1} thiourea added as a promoter for the hydrogenation process.

Thermal stability of the hydrogenated samples was studied using differential thermal analysis (DTA) at a heating rate of 5°C min^{-1} over the temperature range 20–800°C, in a vacuum of 10^{-8} to 10^{-6} bar.

A JEOL 5200 scanning electron microscope and a Philips PW 1012/10 X-ray diffractometer (Cu Kα radiation) were used in the morphology studies and phase analysis respectively.

3. Results and discussion

3.1. Observation on the HD process

In the case of highly grain oriented, sintered samples (Fig. 1(a)), a number of reproducible features of the decrepitation process have been observed. Decrepitation of the sample began invariably from the end of the sample nearest to the incoming flow of hydrogen. The decrepitation begins with an explosive separation of a small disc, 5–7 mm in diameter, 1–2 mm thick, away from the main body of the sample, the fracture plane being parallel with, or at a small angle to, the base of the cylinder (Fig. 1(b)). The initial decrepitation at the other end of the sample took a similar form, differing only in the longer activation time.

SEM studies on this decrepitated material (Fig. 2) reveal that the fracture is predominantly intergranular in nature, little or no evidence for transgranular failure could be observed. This is in agreement with previous observations on the decrepitation behaviour of sintered Nd–Fe–B magnets [5].

Samples of this decrepitated material were desorbed in a high vacuum DTA chamber and the vacuum monitored over the temperature range room temperature to 750°C. The trace exhibited desorption peaks consistent with the decomposition of the NdH_{2+x} ($x \sim$ 0.7) hydride, without any evidence of desorption from $Nd_2Fe_{14}B$. If we combine this with the X-ray diffraction data obtained on these same decrepitated particles (Table 1), indicating no expansion of the $Nd_2Fe_{14}B$ phase, i.e. no uptake of hydrogen by this phase, then it can be concluded that decrepitation has taken place as a result of the formation of NdH_{2+x} and the consequent differential expansion which leads to grain boundary failure.

There was some evidence during the elevated temperature vacuum desorption of the hydrogen from the $Nd_{16}Fe_{76}B_8$ samples of very small but sharply defined peaks superimposed on the generally smooth trace. It is possible that these are due to the desorption of anomalously bound hydrogen. The number of these peaks was found to be considerably reduced in samples left for around 6 h after hydriding, consistent with the hydrogen having changed its state, possibly to a more stable hydride. However, these observations have yet to be confirmed by a second independent experiment and should be considered tentative at this stage.

After about 15 min from initiation of the reaction, the initial explosive, plate-like decrepitation concluded and a second, markedly different form of decrepitation began to take place. Thin layers of material were seen to peel away, still exclusively at the ends of the sample, layer by layer, eventually causing the ends of the sintered rod to "round off" (Fig. 1(c)). This slower, less dramatic form of decrepitation can be attributed to the absorption of hydrogen by the $Nd_2Fe_{14}B$ phase as well as by the Nd-rich material, probably as a result of the rise in temperature caused by the heat of the reaction. This hydriding of the $Nd_2Fe_{14}B$ phase was confirmed by subsequent X-ray diffraction studies, which showed an expansion of the unit cell consistent with the formation of $Nd_2Fe_{14}BH_{\sim 2.7}$. The "rounding off" effect results in a substantial growth of the exposed hydrogenated surface. Consequently, the rate of hydrogen absorption and the accompanying stress

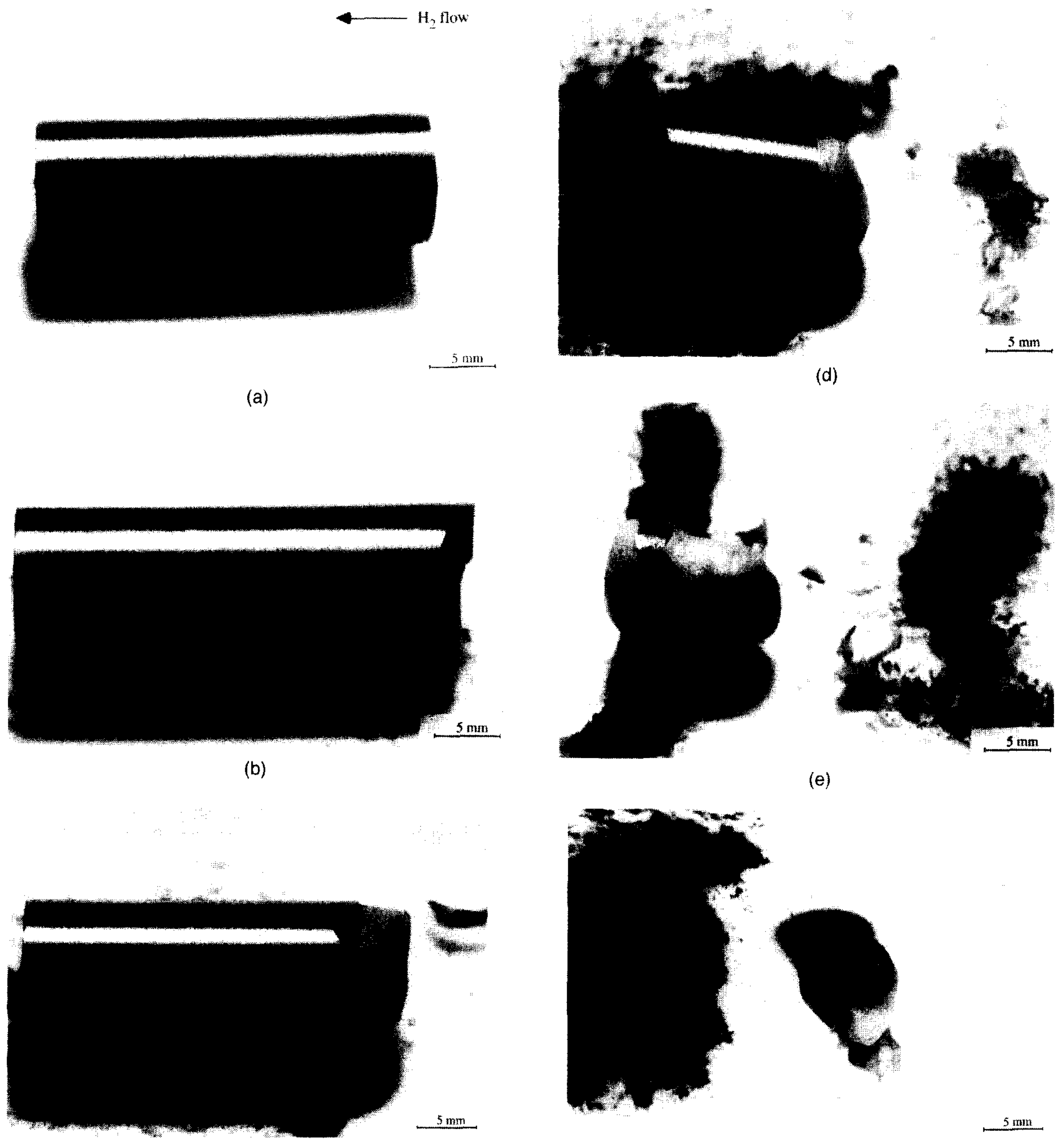

Fig. 1. Hydrogen decrepitation of the [001] aligned cylindrical sintered $Nd_{16}Fe_{76}B_8$ magnets. (a) Initial magnet. (b) "Plate-like" fracture of the magnet after the ejection of the plate from the end (stage 1). (c) Start of the ϕ-phase hydrogenation (stage 2). (d) Start of the decrepitation of the other end. (e) Movement of the hydrogenation fronts from the ends towards each other; the side part remains inactive to hydrogen. (f) The final moments of the process with the loss of the original cylindrical shape.

caused the hydrogenated end parts of the sample to break away from the non-hydrogenated central part, resulting in separate parts being formed which then decrepitated independently. In the final stages, the cylindrical shape was lost and an approximate sphere obtained (Fig. 1(d)) which reduced in size until only powder remained, with the reaction being complete after about 2 h.

In an attempt to determine how insensitive the sides of the oriented sintered sample were to hydrogen absorption, special brass endcaps were machined to cover the ends of a sample and glued in place. No decrepitation of the sample was then observed at room temperature after exposure times of 10 h. By increasing the temperature, decrepitation was finally observed at around 200°C. At these elevated temperatures the decrepitation process proceeded rapidly and particles were ejected from the sample on all sides,

Fig. 2. Surface of a plate ejected from the [001] aligned sintered $Nd_{16}Fe_{76}B_8$ magnet at the first stage of hydrogen decrepitation.

Table 1
Unit cell volumes and volume expansion of the ϕ-phase due to hydride formation

	Unit cell volume (Å^3)	$\Delta V/V$ (%)
$Nd_2Fe_{14}B$ [7]	942 ± 2	—
Plate-like particle ejected from aligned sample in the first stage of AHD	943 ± 2	0
Powder particles ejected from aligned sample in the second stage of AHD	971 ± 2	3.1 ± 0.3
Electrochemically charged non-aligned magnet	975 ± 7	3.4 ± 0.6
Electrochemically charged aligned magnet	989 ± 2	5.0 ± 0.3

resulting in a gradual decrease in the thickness of the cylinder until the sample finally broke into two pieces and then disintegrated to a powder.

3.2. Possible reasons for the AHD effect

It is likely that the anisotropic hydrogen decrepitation originates from (a) differences in the surface activation required to initiate hydrogen penetration into the material, i.e. splitting of the H_2 molecules, (b) substantially different rates of hydrogen diffusion along the *a* and *c* axis, or (c) some combination of these factors.

In order to determine whether it is activation or diffusion which is the controlling factor in AHD, two simple experiments were undertaken. If it is activation then the use of atomic instead of molecular hydrogen would reveal the influence of activation on the hydrogenation properties. In the first experiment, aligned sintered samples were saturated with hydrogen using an electrochemical charging method. In the second experiment, the samples were coated with palladium black using a Pd salt solution followed by a conventional gaseous hydrogenation procedure at 1 bar. In the former case, H^+ ions are produced directly on the surface of the sample, the quantity being proportional to the density of the electric current applied. In the latter case, the dissociation of molecular hydrogen into atomic hydrogen at the surface of the sample is catalysed by the Pd rich layer.

Electrochemical charging of the aligned sintered $Nd_{16}Fe_{76}B_8$ samples resulted in an immediate hydrogenation of the surface layers and only one minute was necessary to produce the effect. No obvious differences in the hydrogenation behaviour were observed between the end and the side part of the aligned samples and between the aligned and unaligned isotropic samples. Though no visual differences were detected between the aligned and unaligned samples in terms of their decrepitation behaviour, the results of X-ray diffraction studies indicate that the ends of the aligned samples have significantly higher hydrogen contents than those observed in the unaligned sample. A volume expansion $\Delta V/V$ of 5.0 ± 0.3% compared with 3.4 ± 0.6%. These values are very high and the former implies the formation of $Nd_2Fe_{14}BH_{>5}$, which is close to the maximum allowable approximate H content according to the available sites [8,9]. This expansion is similar to that observed by Ram and Joubert [10] as a result of washing $Nd_2Fe_{14}B$ crystallites with water.

When the Pd black coated aligned sample (which had its ends capped to prevent hydrogen being absorbed via this path) was exposed to hydrogen, an activation time of only around 10 min was observed before rapid hydrogenation took place at room temperature. This is in contrast to the stubborn resistance of the as-ground uncoated surface. Continued hydrogenation and decrepitation of the sides was observed, leading to a steady reduction in the diameter of the sample, which was finally reduced to a powder.

The observations of the HD behaviour of the electrochemically charged and Pd-coated sample indicate clearly that the critical factor in the AHD process is the activation of the surface. Once the process can be initiated, it continues until decrepitation is complete and only a powder remains.

It still has to be explained why the ends of the aligned samples are so much more active than their sides. Is the increased activity related to (a) the distribution of the grain boundary material, (b) magnetic fields at the surface, (c) the nature of the oxide layer, (d) the intrinsic activity of the atomic configuration of the basal planes of the $Nd_2Fe_{14}B$ phase, or a combination of some or all of these factors? Explanation (d) seems unlikely since it is very difficult to activate single-phase, bulk material of stoichiometric composition [2] and X-ray diffraction studies showed that the initial decrepitation of the aligned material did not involve hydrogenation of the $Nd_2Fe_{14}B$ phase.

Further experiments are underway in an attempt to answer these questions.

4. Conclusions

Two distinct stages of decrepitation can be observed when an aligned sintered rod of $Nd_{16}Fe_{76}B_8$ is exposed to a flow of hydrogen gas at room temperature. The first stage is an explosive-like fracture resulting in plates of the material being ejected from the end of the sample. X-ray diffraction studies reveal that the $Nd_2Fe_{14}B$ phase in this material remains non-hydrogenated, implying that the decrepitation is a result of the selective hydriding of the Nd-rich intergranular material.

The second stage involves hydrogenation of the $Nd_2Fe_{14}B$ phase as well as the Nd-rich intergranular material and a continuous flaking away of layers of the magnet. With the exposure of increasing amounts of fresh surface the cylindrical sample begins to break up into pieces, each of which decrepitate until, eventually, a roughly spherical shape is obtained which finally disintegrates into a powder.

Easy hydrogenation at the ends of the aligned sintered sample compared with its sides (which were inactive at room temperature) appears to be a result of their differing activation properties with regard to molecular hydrogen.

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