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Letter

Anisotropic hydrogen decrepitation and corrosion behaviour in NdFeB magnets

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Abstract

A number of $Nd_{16}Fe_{76}B_8$ sintered magnets were produced in isotropic (unaligned) and anisotropic (aligned) forms. The magnets were prepared in the conventional way via isostatic pressing and finished with a centreless grinder, no coatings were applied and the samples were left unmagnetised. These magnets were identical in every way apart from the orientation of the $Nd_2Fe_{14}B$ grains. Each magnet was exposed to hydrogen and the decrepitation behaviour observed. The anisotropic samples were found to decrepitate exclusively from the ends of the rods whereas the isotropic magnets were attacked by the hydrogen at all points on their surface. Bulk corrosion studies in steam gave comparable results, the oriented sample suffered severe corrosion at its poles and the isotropic sample was attacked over the whole surface. X-ray diffraction studies on the corrosion product indicated a greatly expanded lattice with the $Nd_2Fe_{14}B$ structure. Both the hydrogen decrepitation and the corrosion which take place in these materials can be attributed to the formation of hydrides.

1. Introduction

The effect of hydrogen on NdFeB materials has been well documented (see for example refs. 1 and 2). Hydrogen has been found to attack the $Nd_{16}Fe_{76}B_8$-type magnet alloys at room temperature due to the presence of the intergranular Nd-rich material. Without this intergranular phase, *i.e.* in the case of the $Nd_2Fe_{14}B$ single phase alloy and the MQI type melt spun material [3] with its amorphous grain boundaries, a combination of hydrogen at modest pressures and at ~160 °C is required to activate the material [4]. Sintered magnets, with approximate compositions $Nd_{16}Fe_{76}B_8$, have also been shown to be susceptible to hydrogen attack and decrepitation, although their activation and reaction times are observed to be considerably longer than with cast materials [5]. It is for this reason that NdFeB-type magnets are not suitable for use wherever they may come into contact with hydrogen gas.

In this experiment we have investigated the effect that $Nd_2Fe_{14}B$ grain orientation has on the hydrogen decrepitation and corrosion properties in the material by looking at the effect of hydrogen on anisotropic (oriented) and isotropic (unorientated) magnets.

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2. Experimental details

The hydriding of the $Nd_{16}Fe_{76}B_8$ sintered magnets was carried out in the simple apparatus shown in schematic form (Fig. 1). The system consists of a glass cylinder ~30 cm long and 2.5 cm in diameter; hydrogen gas in the form of a 10%H_2–90%Ar mixture was allowed to flow through the system at ~120 cc/min. The magnets were placed inside the cylinder in the flow of gas, and

Fig. 1. Schematic diagram illustrating apparatus used for hydriding experiments.

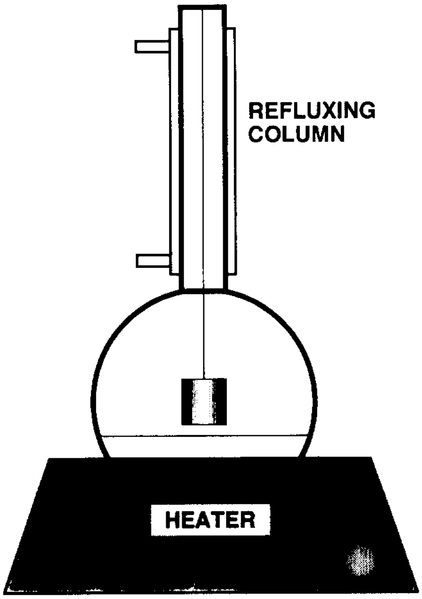

Fig. 2. Schematic diagram illustrating apparatus used for corrosion experiments.

each magnet was subjected to identical conditions, with no heat being applied. All the magnets used in this experiment were in the unmagnetised state. The decrepitation process was monitored by a video and by a 35 mm camera. The experiment was repeated eight times so as to be certain of the reproducibility of the observed events.

The corrosion experiments were carried out in the apparatus shown in schematic form (Fig. 2). Each sample was cut to ~1 cm long and suspended using a polymer coated wire a few millimetres above boiling distilled water. This kind of test is commonly referred to as a bulk corrosion (BC) test. The sample dimensions were measured prior to the experiment and daily during the course of the experiment. In addition to the dimensional changes the weight loss expressed in terms of g cm^{-3} was monitored.

3. Results

The hydrogen/argon gas was found to flow over the samples for between one and three hours before any decrepitation was observed to take place. The activation times were found to vary significantly, the activation times for each experiment along with the reaction times, (time from the first observation of the decrepitation process to the final disintegration of the sample) are listed in Table 1. The reaction times were found to be more consistent; four samples were sufficient for us to be confident that the reaction time for the isotropic (unoriented) magnet was shorter than that for the anisotropic (oriented) magnet. The average reaction time for the isotropic magnets was found to be 81

TABLE 1. Activation and reaction times for isotropic and anisotropic samples

Isotropic sample		Anisotropic sample	
Activation (mins)	Reaction (mins)	Activation (mins)	Reaction (mins)
65	75	145	105
85	85	170	115
150	85	90	105
105	80	105	100

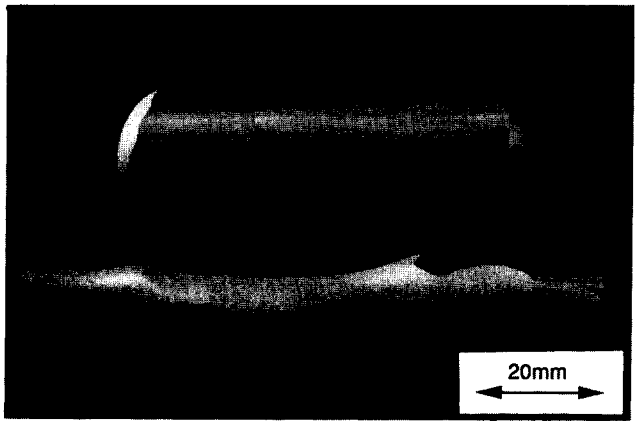

Fig. 3. Partially decrepitated anisotropic magnet (top) and isotropic magnet (bottom).

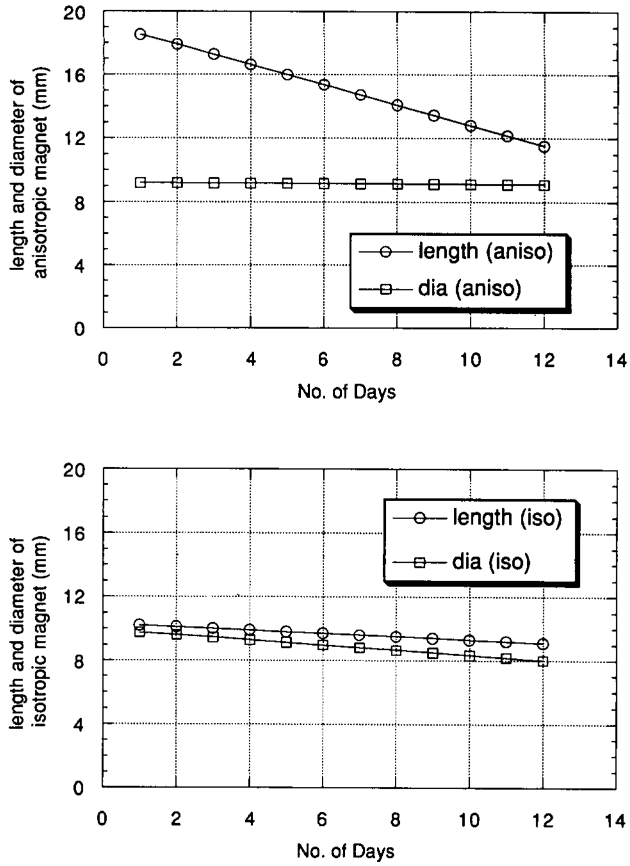

Fig. 4. Graphs illustrating dimensional changes taking place during corrosion experiment.

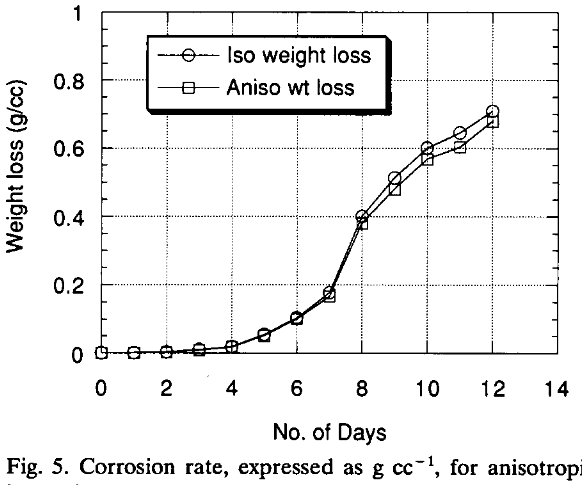

Fig. 5. Corrosion rate, expressed as g cc^{-1}, for anisotropic and isotropic magnets.

TABLE 2. Values for *a* and *c* spacings for the material before and after the corrosion test

	a-(nm)	c-(nm)	$Nd_2Fe_{14}BH_x$
$Nd_{16}Fe_{76}B_8$ magnet	0.8798	1.2171	$x=0$
$Nd_{16}Fe_{76}B_8$ magnet hydride (H_2 gas)	0.8886	1.2296	$x=2.7$
$Nd_{16}Fe_{76}B_8$ corrosion product	0.8931	1.2343	$x=5$
$Nd_2Fe_{14}B$ alloy [6]	0.879	1.218	$x=0$
$Nd_2Fe_{14}BH_{\sim 5}$ [6]	0.893	1.232	$x=5$

mins, whereas the average reaction time for the anisotropic magnet was found to be 106 mins.

The isotropic and anisotropic samples exhibited strikingly different hydrogen decrepitation behaviours. In the case of the anisotropic sample, decrepitation was found, without exception, to begin at one of the magnet poles, *i.e.* at one of the ends of the cylinder. Although the first signs of decrepitation at each end of the cylinder did not necessarily coincide, hydrogen attack at both ends was invariably observed. The process was one of gradual peeling (or breaking) away of slices of the magnet so that the overall length of the sample was reduced. There was no evidence for any attack by hydrogen at the sides of the sample. The circumferential surface of the cylinder remained unaffected. A photograph of a partially decrepitated anisotropic rod is shown in Fig. 3. In contrast the isotropic magnet began decrepitating at a number of points on its surface. The sample gradually became thinner and shorter, with material being lost from both the circumference and the ends. A photograph of a partially decrepitated sample is shown in Fig. 3.

The corrosion behaviour was found to be comparable with that observed during hydriding. Figure 4 shows the dimensional changes taking place during the 12 days of the corrosion experiment. In the case of the isotropic magnet the length and the diameter were found to decrease linearly with time and with similar rates. However, for the anisotropic magnet, the diameter was found to be almost unaffected over 12 days whereas the length was reduced dramatically, *i.e.* corrosion was taking place only at the poles of the magnet. Figure 5 shows that the overall corrosion rate for both samples was almost the same, and at the end of the experiment both samples had lost ~ 0.7 g cm^{-3}.

X-ray diffraction was used to characterise the corrosion product of the magnet suspended in steam. The $Nd_2Fe_{14}B$ structure was found to be preserved although a significant expansion of the lattice was found to have taken place. Table 2 shows the values for the *a* and *c* spacings for the material before and after the corrosion test. The values obtained for the expanded lattice were observed to be significantly larger than those obtained for the same material, hydrided using hydrogen gas. The values are almost identical to those obtained by Ram and Joubert [6] who synthesised $Nd_2Fe_{14}BH_{\sim 5}$ by washing $Nd_2Fe_{14}B$ crystallites (embedded in calcium and other by-products) with water.

4. Discussion

The susceptibility to corrosion of magnets at their poles is a particular problem since it is this part of the magnet which has the highest flux density and is often in very close proximity to the moving part of the machine or the information storage disc. Any debris falling from the magnet pole could prove catastrophic. Most NdFeB magnets are relatively "thin" and as such are exposing a proportionately larger area of their most susceptible surface to attack.

The anisotropic behaviour of hydrogen decrepitation and the similar behaviour on corrosion provide strong evidence to suggest that there is a link between the kind of corrosion occurring during the BC test and that which takes place when the magnet is left exposed to a hydrogen atmosphere. This visual observation is strongly supported by the evidence of the X-ray diffraction results which lead us to believe that the corrosion in the $Nd_{16}Fe_{76}B_8$-type magnets takes place also as a result of the material reacting with hydrogen.

5. Conclusions

There is undoubtedly anisotropic corrosion and hydrogen decrepitation behaviour in anisotropic $Nd_{16}Fe_{76}B_8$-type magnets. Experimental evidence confirms that the poles of the magnets are much more susceptible to hydrogen or humid corrosive atmospheres. The similarity in the behaviour of the magnets in the two different environments, and the evidence for the expanded $Nd_2Fe_{14}B$ lattice leads us to conclude that the two mechanisms are, in some way, linked and that the corrosion mechanism in the bulk corrosion tests involves some form of hydrogen decrepitation. Comparison with the results of Ram and Joubert [6] lead us to conclude that the corrosion product hydride has a stoichiometry of $Nd_2Fe_{14}BH_{\sim 5}$.

Studies are now underway to see if the decrepitation and corrosion behaviours can be correlated with microstructure and/or with the diffusion behaviour of the hydrogen atoms.

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