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The influence of alloying additions and process parameters on the magnetic properties of PrFeB-based bonded magnets

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Abstract

The effects of Co, Zr, Nb, Ga and Dy additions upon the magnetic properties of PrFeB-based alloys have been studied. Bonded magnets have been prepared from as-cast and homogenised alloys using an optimised hydrogenation disproportionation desorption and recombination (HDDR) process. In general, the HDDR bonded magnets from homogenised alloys exhibited higher remanence (B_r), squareness factor (SF) and intrinsic coercivity (H_c). In particular, the $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Nb}_{0.1}$ HDDR magnet exhibited the best overall magnetic properties ($B_r=1032\pm 20$ mT, $H_c=793\pm 20$ kA/m and SF=0.51), indicating that Co and Nb additions, in these proportions have a beneficial effect on PrFeB-based magnets. Conversely, additions of Ga and Dy were observed to dramatically reduce the intrinsic coercivity of Pr-based HDDR magnets. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: PrFeB alloys; Bonded permanent magnets; HDDR; Alloying additions; Anisotropy

1. Introduction

Anisotropic Nd–Fe–Co–Ga–B powders and bonded permanent magnets have been produced via the hydrogenation disproportionation desorption and recombination (HDDR) process [1–3]. Recently, however, it has been shown that a $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Zr}_{0.1}$ composition achieved high anisotropy and good intrinsic coercivity following a relatively straightforward homogenising and HDDR treatment [4].

In the case of Nd-based HDDR magnets, anisotropy has been associated with additions of Co, Ga and Zr [3,5–7]. HDDR bonded magnets with the $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{Co}_{11.6}\text{B}_6\text{Ga}_x$ ($x=0.5$ and 1) composition have shown intrinsic coercivities (iH_c) in the region of 1040 kA/m [5,7]. With the further addition of Zr to these compositions (NdFeCoBZrGa-based alloys) HDDR bonded magnets produced even higher iH_c (1096 kA/m) [7]. However, until recently similar additions in praseodymium-based HDDR bonded magnets (in particular, $\text{Pr}_{13}\text{Fe}_{\text{bal}}\text{Co}_{24}\text{B}_6\text{Zr}_{0.1}\text{Ga}_1$), have induced anisotropy, but with a low coercivity (382 kA/m) [8].

In this study, a number of alloy additions and processing parameters have been investigated to assess their effect upon PrFeB-based HDDR material. The work builds upon recent studies on anisotropic PrFeB-based material [9,10], and begins with an optimisation study of the HDDR process for a general PrFeB(Ga,Co) composition. This processing trial is followed by an investigation into the effects of a homogenising treatment, degree of rare earth content and alloy additions (Zr, Co, Nb, Ga and Dy) upon the magnetic properties of PrFeB-based HDDR material.

2. Experimental procedure

The alloys investigated in this work have been supplied by Rare Earth Products (UK). Ingots were vacuum induction melted and cast into a book-mould 15 mm wide. The alloy compositions were investigated in this as-cast condition and in the homogenised condition. The homogenisation heat treatment was carried out under vacuum at 1100°C for 20 h with 40 g pieces of alloy.

For the HDDR treatment, the material being investigated was crushed into coarse lumps and 15 g batches were HDDR treated according to a typical cycle shown in Fig. 1.

The resultant HDDR powder was crushed readily in air with a mortar and pestle, such that all the material passed

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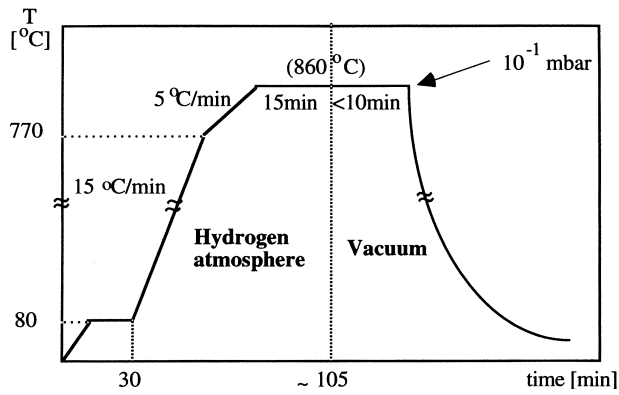


Fig. 1. Schematic diagram of the HDDR treatment cycle.

through a $<106 \mu\text{m}$ sieve. This relatively fine HDDR powder was then encapsulated in a small cylindrical rubber bag, pulsed in a magnetic field of 4.5 T and pressed isostatically at a pressure of 1200 kg/cm^2 . The compacted HDDR powder samples were then saturated with liquid wax at 100°C , such that on cooling to room temperature a cylindrical bonded magnet was formed ($\sim 13 \text{ g}$).

Magnetic characterisation of the HDDR magnets was carried out using a permeameter. Measurements were performed after saturation in a pulsed field of 4.5 T. Remanence values were normalised to assume 100% density for the HDDR samples for comparison with fully dense sintered magnets.

The first stage in the present work involved an investigation of a range of disproportionation temperatures between 800 and 900°C , with the purpose of optimising the HDDR treatment for a $\text{Pr}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_6\text{Zr}_{0.5}\text{Ga}_{1.0}$ alloy. The second stage of the work involved an in-

vestigation of a range of alloy compositions in both the as-cast and annealed conditions.

3. Results and discussion

3.1. The effect of disproportionation temperature

The initial stage of this work studied a range of disproportionation temperatures with the view to optimising magnetic properties from HDDR treated material. Fig. 2 shows the normalised remanences and intrinsic coercivities of the $\text{Pr}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_6\text{Zr}_{0.5}\text{Ga}_{1.0}$ HDDR magnets as a function of the disproportionation/recombination temperature. The optimum processing temperature is close to 860°C , as seen previously for similar batches of $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Zr}_{0.1}$ and $\text{Nd}_{16}\text{Fe}_{75.9}\text{B}_8\text{Zr}_{0.1}$ HDDR magnets [10]. Values of the intrinsic coercivities in these magnets, were similar to that reported in Ref. [8] with an alloy containing a higher amount of Co (24 at.% as opposed to 11.6 at.% in the present case). These observations indicate that the higher amounts of cobalt do not appear to influence the coercivity of the Pr-based HDDR magnets.

3.2. Effect of alloy homogenisation upon HDDR material

Table 1 compares the magnetic properties of a range of PrFeB-based magnets prepared from as-cast and homogenised alloys and subjected to the optimised HDDR process. From these data it is possible to observe the effects of different Pr contents and the influences of Co, Nb, Zr and

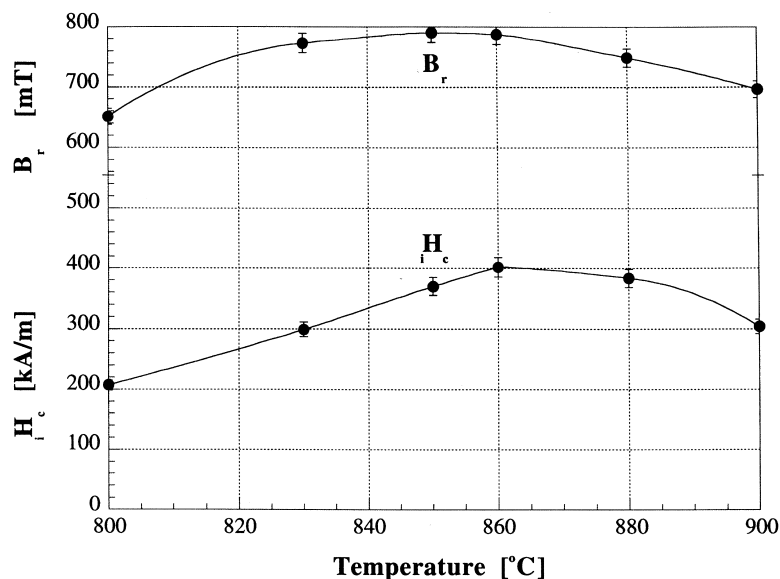


Fig. 2. Intrinsic coercivities and normalised remanences of $\text{Pr}_{12.6}\text{Fe}_{68.7}\text{Co}_{11.6}\text{B}_6\text{Zr}_{0.5}\text{Ga}_{1.0}$ magnets versus the processing temperature. The HDDR powder was prepared using the alloy in the as-cast condition.

Table 1

Normalised magnetic properties of the Pr-based HDDR magnets processed at 860°C and prepared using powder from the alloy in the as-cast state and after homogenisation (20 h at 1100°C)^a

Starting alloys	Starting condition of alloy	B_r (mT)	iH_c (kA/m)	H_c (kA/m)	$(BH)_{max}$ (kJ/m ³)	Sq. (ratio)
Pr ₁₆ Fe _{75.5} B ₈ Zr _{0.5}	As-cast	726	957	444	88	0.29
	Anneal	635	937	393	67	0.26
Pr _{13.8} Fe _{63.5} Co _{16.7} B ₆	As-cast	664	564	334	65	0.29
	Anneal	869	719	483	126	0.43
Pr _{13.7} Fe _{63.5} Co _{16.7} B ₆ Zr _{0.1}	As-cast	768	487	377	82	0.35
	Anneal	1000	732	547	168	0.49
Pr _{14.9} Fe _{63.0} Co _{16.0} B ₆ Zr _{0.1}	As-cast	728	581	368	79	0.33
	Anneal	923	762	521	141	0.43
Pr _{13.7} Fe _{63.5} Co _{16.7} B ₆ Nb _{0.1}	As-cast	727	578	359	78	0.31
	Anneal	1032	793	582	182	0.51
Pr _{12.6} Fe _{68.7} Co _{11.6} B ₆ Zr _{0.5} Ga _{1.0}	As-cast	787	403	291	73	0.28
	Anneal	1004	493	377	131	0.40
Pr _{12.7} Fe _{63.5} Co ₁₆ Dy _{1.07} B ₆ Nb _{0.1}	As-cast	–	–	–	–	–
	Anneal	498	200	137	20	0.16

^a Measurement error, $\pm 2\%$.

Dy additions on the magnetic properties of the basic PrFeB alloy. Following the HDDR treatment, the best magnetic properties were obtained from the homogenised Pr_{13.7}Fe_{63.5}Co_{16.7}B₆Nb_{0.1} alloy ($B_r=1032$ mT, $iH_c=793$ kA/m, $BH_{max}=182$ kJ/m³ and squareness ratio=0.51). Good overall magnetic properties were also exhibited by the homogenised Pr_{13.7}Fe_{63.5}Co_{16.7}B₆Zr_{0.1} HDDR powder (as reported previously [10]). It should be noted that the combined effect of homogenisation heat treatment and small additions of niobium and zirconium (0.1 at.%) significantly improve the remanence and squareness factor in these PrFeCoB-based magnets.

3.3. Effect of rare-earth content

Increasing the amount of Pr from 13.7 to 14.9 at.% results in a slight increase in iH_c , but, as expected, decreases the remanence. The homogenisation treatment does not appear to benefit the higher rare earth containing HDDR magnets (Pr₁₆Fe_{75.5}B₈Zr_{0.5}), which can be explained in terms of the excess rare earth content resulting in the removal of the detrimental free iron phase in the cast material.

3.4. Effect of zirconium additions

The effect of zirconium additions can be seen in Table 1 by comparing the properties of the Pr_{13.7}Fe_{63.5}Co_{16.7}B₆Zr_{0.1} HDDR magnet with those of the

Zr-free composition, Pr_{13.8}Fe_{63.5}Co_{16.7}B₆. The presence of 0.1at.% zirconium results in an increase in the remanence from 869 to 1000 mT and the coercivity from 719 to 732 kA/m for the homogenised material.

3.5. Effect of other additions to HDDR bonded magnets

The effects of Dy and Ga additions on the magnetic properties of the HDDR magnets, (before and after alloy homogenisation) are shown in Table 1. The Ga-containing HDDR magnet exhibited an increase in remanence as a result of homogenisation, but no significant change in the coercivity. The Pr_{12.7}Dy₁Fe_{63.5}Co_{16.7}B₆Nb_{0.1} HDDR magnet exhibited some magnetic properties but only after homogenisation. The magnetic properties of a Pr_{12.7}Dy₁Fe_{63.5}Co_{16.7}B₆Zr_{0.1} composition, on the other hand have not been included in Table 1 because the substitution of only 1 at.% of Dy for Pr caused a dramatic fall in the magnetic properties so that they were no longer discernible. Zirconium additions were seen to improve the magnetic properties of the PrFeCoB HDDR magnets and, hence, it seems that Ga alone or the combination of Ga and Zr, is responsible for the low iH_c in Pr_{12.6}Fe_{68.7}Co_{11.6}B₆Zr_{0.5}Ga₁ magnets.

Further work is being conducted to expand on this study as the results presented here represent a limited number of magnet samples, a limited variation of addition quantities and a single process mass.

4. Conclusions

1. The HDDR treatment has been optimised for a PrFeCoGaZr-based alloy, in terms of the disproportionation temperature, with the best magnetic properties being achieved from treatments at 860°C.
2. Much improved magnetic properties have been achieved for most compositions of HDDR magnets as a result of homogenising heat treatment on the cast alloy.
3. Additions of Nb and Zr have been shown to be necessary for developing optimum, anisotropic magnetic properties. The maximum remanence of 1032 mT, and squareness factor of 0.51 were achieved with a $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Nb}_{0.1}$ composition. Generally, the combination of Zr and Nb additions in homogenised and HDDR treated PrFeB-based alloys produced high remanences (>900 mT) and reasonably coercive ($H_c > 700$ kA/m) magnets.
4. Additions of Dy and Ga resulted in dramatic reductions in the coercivity of PrFeCoB-based HDDR magnets.

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