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Permeameter measurements of anisotropic PrFeCoBZr hydrogenation disproportionation desorption and recombination (HDDR) magnets

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Abstract

The magnetic properties of HDDR magnets prepared from a $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloy using an isostatic press technique have been investigated by means of permeameter measurements. It has been shown that it is possible to produce highly anisotropic HDDR material from this alloy in the annealed (1100°C for 20 h) state in a 13 g sample. Normalised (100% density) remanence in the easy direction of an aligned magnet was found to be 1000 ± 20 mT, whereas, in the hard direction it was 442 ± 10 mT. Similar studies have been performed on a $Nd_{16}Fe_{75.9}B_8Zr_{0.1}$ alloy as a comparison. The intrinsic coercivity (1050 kA/m) of the NdFeBZr HDDR magnet was much higher than that of the Pr-based HDDR permanent magnets (732 kA/m) but there was a much lower degree of anisotropy in the case of the former in the as-cast state and when subjected to an identical HDDR treatment.

Keywords: Anisotropy; Alloys; Permeameter measurements

1. Introduction

Since the discovery of the hydrogenation disproportionation desorption and recombination (HDDR) process [1,2], a decade ago, extensive research has concentrated on the study of the NdFeB-type alloys. This has been covered in detail in a recent review [3]. However, only recently have any studies been reported on the HDDR processing of praseodymium–iron–boron-based compounds [4,5]. A HDDR powder based on the alloy $Pr_{13}Fe_{bal}Co_{24}B_6Ga_1Zr_{0.1}$, was reported to have a remanence (B_r) of 980 mT with an intrinsic coercivity ($_iH_c$) of only 382 kA/m [4]. A $Pr_{13}Fe_{81}B_6$ HDDR powder [5] was reported to have a B_r of about 670 mT and an $_iH_c$ of 549 kA/m. Although a number of advantages have been attributed to PrFeB-type alloys [6,7], the most relevant with respect to the HDDR process could be the possibility of a different grain growth behaviour compared to that of Nd-based systems [7], leading to greater control of the grain growth during and after the recombination stage.

In the present work, an investigation of HDDR powders based on the alloy $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$

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has been carried out using an isostatic pressing technique [8] which avoids the detrimental influence of uniaxial pressing on the magnetic properties of the magnet [6]. A well-known Nd-alloy with a composition close to that of 'Neomax' with 0.1 at% of zirconium ($Nd_{16}Fe_{75.9}B_8Zr_{0.1}$) has been used for comparison. The magnetic properties of the HDDR powder based on this composition has been studied previously [9] in the authors laboratory. This work [9], using vibrating sample magnetometer (VSM) measurements, reported that the Nd-based alloy ($Nd_{16}Fe_{75.9}B_8Zr_{0.5}$) exhibits a high degree of anisotropy and this was confirmed to some extent by domain observations. On the other hand, it has been reported in Ref. [10] that, in the crushed state, $Nd_{16}Fe_{75.9}B_8Zr_{0.1}$ HDDR material shows no anisotropic character. The disparity between these observations could indicate the critical dependence of anisotropy on the processing conditions in this alloy. The use of a VSM could also cause differences since it employs very small and possibly atypical samples. Magnetic characterisation of a batch of Nd-based HDDR commercial powder (CP) has also been included in the present work as a standard reference.

2. Experimental

The alloys investigated in this work have been provided by Rare Earth Products Ltd. Ingots were prepared in a rectangular water-cooled copper mould and the Pr-based alloy was homogenised by heat treatment of the ingot under vacuum at 1100°C for 20 h; the Nd-based alloy was employed in the as-cast state. For the HDDR treatment, the annealed material was crushed into coarse lumps and 15 g batches placed into a HDDR reactor, which was then evacuated to backing-pump pressure ($\sim 10^{-1}$ mbar) and hydrogen introduced to a pressure of 1 bar. To allow time for the hydrogen decrepitation (HD) reaction to go to completion, the temperature was set at 80°C for half an hour. The reactor was then heated at a rate of 900°C/h up to 770°C and then at 300°C/h up to the desorption temperatures (800–900°C) with a dwell time of 15 min prior to desorption. Subsequent desorption and recombination was carried out under vacuum at the same temperature until a pressure of 10^{-1} mbar was achieved (<10 min). Subsequent rapid cooling of the material was carried out by removing the furnace and fitting a water-cooled copper coil on the Inconel reactor tube.

The resultant HDDR powder was crushed readily in air with a mortar and pestle, such that all the material passed through a $<106\,\mu m$ sieve. The relatively fine HDDR powder was then encapsulated in a small cylindrical rubber bag, pulsed at a magnetic field of 4.5 T and pressed isostatically at 1200 kg/cm^2. The consequent green compacts were then consolidated by placing wax in the bag and heating to 100°C, such that the molten wax penetrated the compacted HDDR powder sample. The mixture was then allowed to cool to room temperature and the excess wax removed to form a cylindrical magnet (~ 13 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 have been normalised to assume 100% density of the HDDR sample assuming a linear relationship between density and remanence.

3. Results and discussion

In Fig. 1 the normalised remanences of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ and $Nd_{16}Fe_{75.9}B_8Zr_{0.1}$ HDDR magnets are shown as a function of the recombination temperatures. Clearly, a high degree of alignment has been achieved in the former, whereas, in the latter, values were not far above those characteristic of the isotropic sample. Even in the isotropic condition the Pr-based magnets showed higher remanences than the Nd-based HDDR magnets and this can be attributed, partially at least, to the higher rare earth content, and hence lower proportion of Φ phase ($Nd_2Fe_{14}B$), in the Nd-based alloy. The data shown in Fig. 1 also indicates relatively wide processing conditions for the Pr-based alloy.

The present isostatic press method diminishes the adverse influence of uniaxial pressing on the magnetic properties of the magnet and employs a much larger and hence representative sample. It

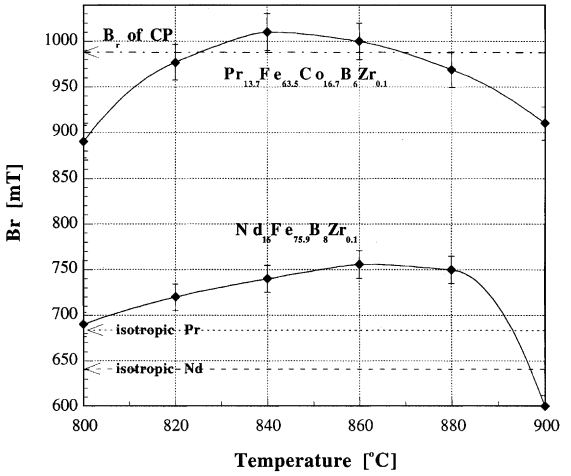

Fig. 1. Normalised remanences of HDDR magnets. Isotropic magnets were produced from powders processed at a temperature of 850°C without magnetic pulse alignment.

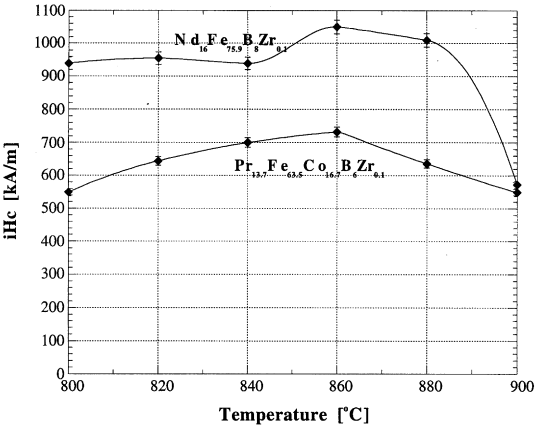

Fig. 2. Intrinsic coercivities of HDDR magnets versus the processing temperature.

can be seen (in Fig. 1), that, under the present experimental conditions, some anisotropy is present in the Nd-based powders but it is much smaller than that reported in Ref. [9]. This can be attributed, in part at least, to the non-optimisation of the experimental conditions in the present work for this particular alloy.

The remanence of the aligned magnet produced from the Nd-based alloy processed at 900°C is less than that of the isotropic magnet produced from powder processed at 850°C. This can be attributed to the large decrease in intrinsic coercivity and squareness factor of the Nd-based powder when processed at 900°C compared to that obtained on processing at 850°C, possibly due to excessive grain growth [3].

Fig. 2 shows the values of intrinsic coercivity for both the Pr and Nd-based HDDR magnets. The highest intrinsic coercivity of the Pr-based HDDR powder (732 kA/m) was much lower than that of the more rare earth-rich, Nd-based powder (1050 kA/m) and this is consistent with the much larger amount of isolating grain boundary phase in the case of the latter. The present coercivity value for the Pr-based magnets is twice that reported for a $Pr_{13}Fe_{bal}Co_{24}B_6Ga_1Zr_{0.1}$ HDDR magnet [4] and higher to that reported for anisotropic bonded magnets of $Nd_{12.6}Fe_{bal}Co_{11.5}B_6Zr_{0.1}$ HDDR powders [11].

Table 1 shows a comparison between the magnetic properties of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ HDDR magnets processed at 860°C and those of magnets produced from a standard commercial powder (CP), using the powder in the as-received condition, measured using the permeameter. The former shows better remanence, energy product, squareness factor and degree of alignment (α), whereas the latter has a higher intrinsic and inductive coercivity. Due to the higher remanence and squareness factor, a higher $(BH)_{max}$ was measured for the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ magnet compared to that of the CP magnet. The higher squareness factor for the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ magnet (0.49 compared to 0.45) indicates a greater degree of grain alignment and/or a more uniform grain size.

Compared to the magnet prepared using the CP in the as-received condition, a magnet was prepared using the CP material, crushed and sieved to <106 μm, and this showed a higher remanence (998 mT), similar intrinsic coercivity (1055 kA/m) but an inferior squareness factor (0.42).

Table 2 shows a comparison between the magnetic properties of the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ HDDR powder and those of the CP measured using a vibrating sample magnetometer (sample preparation procedure is described in Ref. [12]). These results confirm in general, the results obtained using the permeameter with some differences. Remanence values were higher in the former

Table 1
Magnetic properties of the Pr-based HDDR and CP magnets prepared using the isostatic press technique and measured in the permeameter (error: ± 2%). B_r values normalised to 100% density

Material	Direction/ condition	B_r (mT)	$_iH_c$ (kA/m)	$_bH_c$ (kA/m)	$(BH)_{max}$ (kJ/m^3)	Sq. (ratio)	α (%)
$Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$	Easy	1000	732	548	168	0.49	56
	iso	681	822	418	76	0.30	
	Hard	442	795	281	32	0.21	
CP	Easy	967	1048	620	165	0.45	45
	iso	661	1057	436	74	0.28	
	Hard	536	1103	355	48	0.20	

$\alpha = [1 - (B_r^{hard}/B_r^{easy})]100\%$; B_r^{easy} and B_r^{hard} are the remanence along the easy (parallel to powder alignment) and the hard (perpendicular to powder alignment) directions, respectively.

Table 2
Magnetic properties of the Pr-based HDDR and CP powders measured using the VSM (Error: ± 2%). No corrections were made for self-demagnetising fields

Material	Direction	B_r (mT)	$_iH_c$ (kA/m)	α (%)
$Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$	Easy	1185	680	76
	Hard	282	614	
CP	Easy	1129	916	69
	Hard	353	820	

and coercivities in the latter. It should be noted that the VSM is an open-circuit measurement, whereas the permeameter employs a closed circuit and this would give rise to lower values of remanence and the squareness factor in the case of the VSM measurement. The higher Br values, therefore, can be attributed to a significantly improved alignment in the case of the VSM sample. This could be due to some relaxation of the alignment in the pulse-aligned HDDR powder after the isostatic pressing stage.

Furthermore, density differences between the samples measured using the VSM and the permeameter could cause variations in the intrinsic coercivity due to local demagnetisation fields in the sample. Magnetic viscosity variations due to different speeds of demagnetisation in the permeameter and VSM could also affect the intrinsic coercivity values [13].

Magnetisation measurements using a pendulum magnetometer [14] on the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloy in the annealed condition indicates a Curie temperature of about 465°C, which is in agreement with the amount of Co present in this alloy (catalog specification for the CP Curie temperature is 470°C). Although the present magnets have an unsuitable density and mechanical strength for practical applications, the technique proved to be very useful for studying powders on a laboratory scale. Magnets prepared from 2/17 Sm–Fe–Co–Cu–Zr powder using an isostatic technique [8] and an epoxy resin as the binding agent, exhibited a similar percentage (70%) of the theoretical density.

As reported previously [12], HDDR powder based on $Nd_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ and processed using the present HDDR conditions showed no significant permanent magnetic properties. This could be due to the requirement for a higher quenching rate (Ar gas), after recombination, for these materials [11]. It would appear therefore, that anisotropic Pr-HDDR powders based on the present alloy are easier to produce with a relatively straightforward HDDR treatment. Microstructural investigations are underway in an attempt to explain the rather surprisingly different magnetic behaviours of the Nd- and Pr-based materials.

4. Conclusions

Anisotropic powder has been produced from a $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloy by homogenisation at 1100°C for 20 h followed by HDDR-treatments.

The highest remanence of 1010 mT (compared to 970 mT for CP) was achieved using a powder processed at 840°C. However, remanences > 970 mT were achieved using powders recombined over the temperature range from 820 to 880°C. Over the same temperature range, the intrinsic coercivity is > 637 kA/m indicating that the $Pr_{13.7}Fe_{63.5}Co_{16.7}B_6Zr_{0.1}$ alloy is relatively insensitive to processing conditions and, therefore, might be suitable for a large scale production facility. Higher coercivities were achieved for powder produced from a $Nd_{16}Fe_{75.9}B_8Zr_{0.1}$ alloy, although much lower anisotropy was found in these powders when processed under the present conditions.

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